Undergraduate Quantum Chemistry

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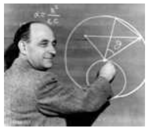
Chapter 1: Introduction to quantum mechanics

Niels Bohr (1885 - 1962; Nobel prize 1922):
"Anyone who is not shocked by quantum theory has not understood it"



Enrico Fermi (1901 - 1954; Nobel prize 1932):
"You cannot understand quantum mechanics but you can get used to it"

Richard Feynman (1918-1988; Nobel prize 1965):
"I think I can safely say that nobody understands quantum mechanics"

1.1 Classical mechanics failed to describe experiments on atomic and molecular phenomena

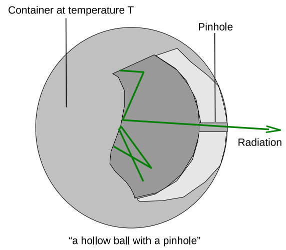
Our objective is to show that:

1. classical physics cannot describe light particles (for example, electrons)
2. a new theory is required (i.e., quantum mechanics)

Recall that classical physics:

1. allows energy to have any desired value
2. predicts a precise trajectory for particles (i.e., deterministic)

Black-body radiation:



Analogy: A heated iron bar glowing red hot becomes white hot when heated further. It emits electromagnetic radiation (e.g., photons emitted in IR/VIS; "radiation of heat"). The wavelength distribution is a function of temperature.

Note: Electromagnetic radiation is thermalized before it exits the black-body through the pinhole.

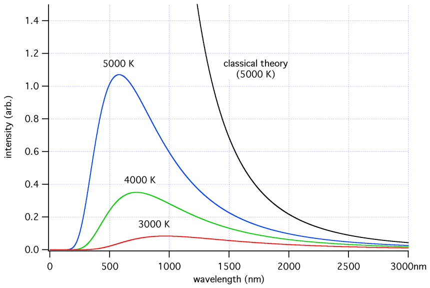
The wavelength vs. energy distribution of electromagnetic radiation from a black-body could not be explained using classical physics ("ultraviolet catastrophe"). The Rayleigh-Jeans law predicts the following energy distribution for a blackbody (radiation density):

$$\rho_\nu = \frac{8\pi\nu^2}{c^3} \times kT \text{ or } \rho_\lambda = \frac{8\pi}{\lambda^4} \times kT \tag{1.1}$$

$$d\epsilon = \rho_\nu d\nu \text{ or } d\epsilon = \rho_\nu d\lambda$$

where ν is the frequency of light (Hz), ρ_ν is the density of radiation per frequency unit (J m^{-3} Hz^{-1}), λ is the wavelength of light (m), ρ_λ is the density of radiation per wavelength unit (J m^{-3} m^{-1}), ϵ is the energy density of radiation (J m^{-3}), c is the speed of light (2.99792458×10^8 m s^{-1}), k is the Boltzmann constant (1.38066×10^{-23} J K^{-1}) and T is the temperature (K).

Breakdown of the classical Rayleigh-Jeans (R-J) equation:



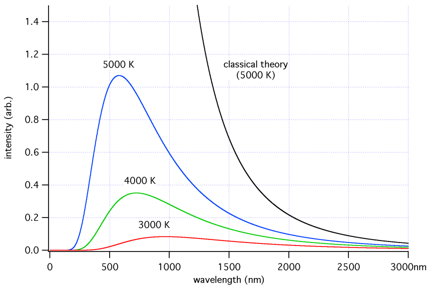
The R-J equation fails to reproduce the experimental observations at short wavelengths (or high frequencies).

Assumption of discrete energy levels in a black-body led to a model that agreed with the experimental observations (Stefan (1879), Wien (1893) and Planck (1900)). The radiation density according to Planck's law is (h is Planck's constant; 6.626076×10^{-34} J s):

$$\rho_\nu = \frac{8\pi\nu^2}{c^3} \times \frac{h\nu}{\exp\left(\frac{h\nu}{kT}\right) - 1} \text{ or } \rho_\lambda = \frac{8\pi}{\lambda^4} \times \frac{hc/\lambda}{\exp\left(\frac{hc}{\lambda kT}\right) - 1} \tag{1.2}$$

The energy density of radiation can be obtained using the differentials on the 2nd line of Eq. (1.1).

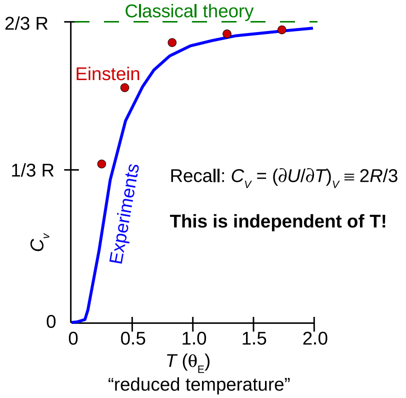
Classical physics would predict that even relatively cool objects should radiate in the UV and visible regions. In fact, classical physics predicts that there would be no darkness!



Max Planck (1858 - 1947), German physicist (Nobel prize 1918)

Heat capacities (Dulong and Petit (1819), Nernst (1905)):
Classical physics predicts a constant value (25 $\text{JK}^{-1}\text{mol}^{-1}$) for the molar heat capacity of *monoatomic solids*. Experiments at low temperatures, however, revealed that the molar heat capacity approaches zero when temperature approaches zero.

Assumption of discrete energy levels (a collection of harmonic oscillators) again led to a model that matched the experimental observations (Einstein (1905)).



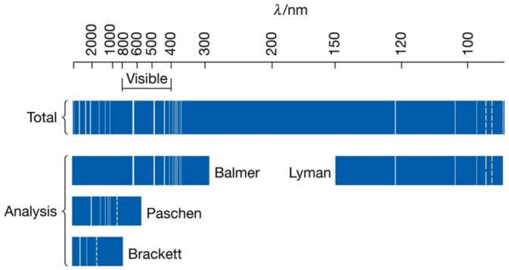
Recall: $C_v = (\partial U/\partial T)_V \equiv 2R/3$

This is independent of T!

Refined theory: Peter Debye (1912).

Atomic and molecular spectra:

Absorption and emission of electromagnetic radiation (i.e., photons) by atoms and molecules occur only at discrete energy values. Classical physics would predict absorption or emission at all energies.

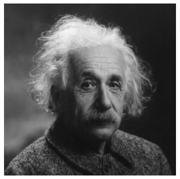


Emission spectrum of atomic hydrogen.

All the previous observations suggest that energy may take only discrete values. In other words, we say that *energy is quantized*. In classical physics energy may take any value.

What is wave-particle duality?

Classical physics treats matter as particles. However, according to quantum mechanics objects have both particle and wave character.



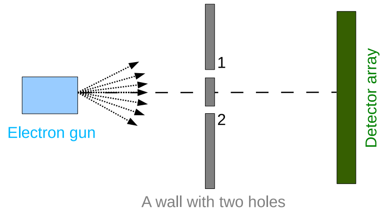
Albert Einstein, German physicist (1879 - 1955), Nobel prize 1921

1. *Particle character*: A source for electrons (or photons) can be set up for suitably low intensity that the detector will see them one by one. Since we can count them, they must be particles. In the case of photons such experiment can be made using the single photon counting technique. The concept of particle is familiar to us from classical physics. A classical particle has a well defined position and momentum.

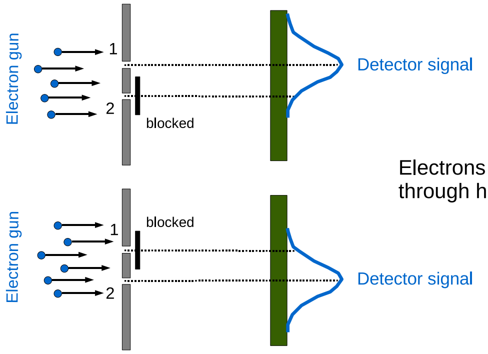
Let's consider behavior of photons as an example. Photons (i.e., light) are unusual particles with zero rest mass, which propagate at the speed of light and energy given by $E = h\nu$. Albert Einstein suggested that photons have relativistic mass m given by $E = mc^2$. Combining these equations gives (p = momentum, ν = frequency, λ = wavelength and $c = \nu\lambda$):

$$mc^2 = h\nu = \frac{hc}{\lambda} \text{ or } mc = p = \frac{h}{\lambda} \tag{1.3}$$

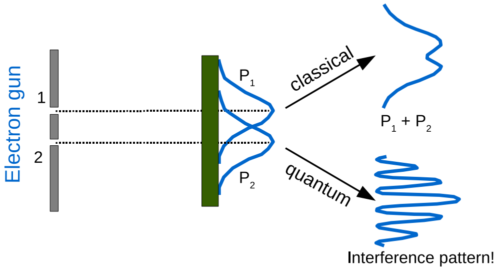
2. *Wave character*: Consider the following experiment (works with any light particle; Young's experiment):



"Young's two slit experiment"



Electrons are passing through holes 1 or 2



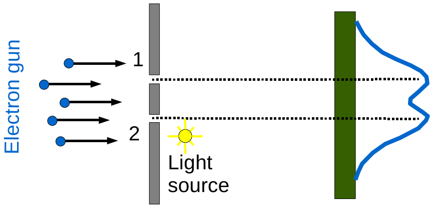
The interference pattern would arise only if we consider electrons as waves, which interfere with each other (i.e. constructive and deconstructive interference).

Notes:

- The interference pattern builds up slowly - one electron gives only one point in the above pattern.
- The same experiment would work, for example, with photons or any light particles. The heavier the particle gets, the smaller the effect will be.

When the experiment is carried out many times with only one electron going through the holes at once, we still observe the interference effect.

Which way did the electron go?



A light source is used to detect the electron at hole 2.

If we try to determine which way the electron traveled, the interference pattern disappears!

What determines the wavelength associated with a particle that has a finite rest mass?

Any particle with linear momentum has a wavelength λ (de Broglie (1924)):

$$mv = p = \frac{h}{\lambda} \text{ or } \lambda = \frac{h}{p} = \frac{h}{mv} \tag{1.4}$$

where h is the Planck's constant (6.62608×10^{-34} Js) and p is the linear momentum. λ is also called the de Broglie wavelength.

Historically relevant experiments: electron diffraction from crystalline sample (Davisson and Germer (1925)) and thin gold foil (Thomson (1925)).

Louis de Broglie, French physicist (1892 - 1987), Nobel prize 1929

Notes:

- Eq. (1.4) constitutes de Broglie's hypothesis.
- The de Broglie wavelength λ for macroscopic particles are negligibly small.
- This effect is extremely important for light particles, like electrons.
- λ determines the length scale where quantum effects are important.

Example. Estimate the wavelength of electrons that have been accelerated from rest through a potential difference of $V = 40$ kV.

Solution. In order to calculate the de Broglie wavelength, we need to calculate the linear momentum of the electrons. The potential energy difference that the electrons experience is simply $e \times V$ where e is the magnitude of electron charge. At the end of the acceleration, all the acquired energy is in the form of kinetic energy ($p^2/2m_e$).

$$\frac{p^2}{2m_e} = eV \Rightarrow p = \sqrt{2m_e eV} \tag{1.5}$$

$$\begin{aligned} \lambda &= \frac{h}{p} = \frac{h}{\sqrt{2m_e eV}} \\ &= \frac{6.626 \times 10^{-34}\ \text{Js}}{\sqrt{2 \times (9.109 \times 10^{-31}\ \text{kg}) \times (1.609 \times 10^{-19}\ \text{C}) \times (4.0 \times 10^4\ \text{V})}} \\ &= 6.1 \times 10^{-12}\ \text{m} \end{aligned}$$

The wavelength (6.1 pm) is shorter than a typical bond length in molecules (100 pm or 1 Å). This has applications in probing molecular structures using diffraction techniques.

Macroscopic objects have such high momenta (even when they move slowly) that their wavelengths are undetectably small, and the wave-like properties cannot be observed.

Exercise. If you would consider yourself as a particle moving at 4.5 mi/h (2 m/s), what would be your de Broglie wavelength? Use classical mechanics to predict your momentum (i.e., $p = mv$). Would it make sense to use quantum mechanics in this case?

According to classical physics, the total energy for a particle is given as a sum of the kinetic and potential energies:

$$E = \frac{1}{2}mv^2 + V = \frac{p^2}{2m} + V = T + V \tag{1.6}$$

If we substitute de Broglie's expression for momentum (Eq. (1.4)) into Eq. (1.6), we get:

$$\lambda = \frac{h}{\sqrt{2m(E - V)}} \tag{1.7}$$

This equation shows that the de Broglie wavelength for a particle with constant total energy E would change as it moves into a region with different potential energy.

Classical physics is *deterministic*, which means that a given cause always leads to the same result. This would predict, for example, that all observables can be determined to any accuracy, limited only by the measurement device. However, as we will see later, according to quantum mechanics this is *not correct.*

Quantum mechanics acknowledges the wave-particle duality of matter by *supposing* that, rather than traveling along a definite path, a particle is distributed through space like a wave. The wave that in quantum mechanics replaces the classical concept of particle trajectory is called a wavefunction, ψ ("psi"). The average position (i.e., the expectation value of position) of a particle can be obtained from the wavefunction $\psi(x)$ (here in one dimension for simplicity) according to:

$$\langle \hat{x} \rangle = \int\limits_{-\infty}^{\infty} \psi^*(x) x \psi(x) dx = \underbrace{\langle \psi(x) \left| \hat{x} \right| \psi(x) \rangle}_{\text{Dirac's notation}} \text{ ($\hat{x}$ is the \textit{position operator})} \quad (1.8)$$

$$\text{with } \int\limits_{-\infty}^{\infty} \underbrace{\overbrace{\left| \psi(x) \right|^2}^{=\psi^*(x)\psi(x)}}_{\text{probability at } x} dx = \langle \psi(x) \mid \psi(x) \rangle = 1 \text{ (normalization)}$$

As we will see later in more detail, every observable has its own operator that determines its value. Note that the average value for position is due to quantum mechanical behavior and has nothing to with classical distribution in positions of many particles. '*' in the above equation denotes complex conjugation. In general, ψ may have complex values but may often be taken as a real valued function.

The standard deviation for position is defined as (due to quantum mechanical uncertainty):

$$(\Delta x)^2 = \left\langle \psi \left| (x - \langle x \rangle)^2 \right| \psi \right\rangle \quad (1.9)$$

Advanced topic: The wavefunction can also be written in terms of momentum via Fourier transformation:

$$\psi(x) = \frac{1}{\sqrt{2\pi}} \int\limits_{-\infty}^{\infty} \psi(k) e^{ikx} dk \text{ (inverse transformation)} \quad (1.10)$$

$$\psi(k) = \frac{1}{\sqrt{2\pi}} \int\limits_{-\infty}^{\infty} \psi(x) e^{-ikx} dx \text{ with } p_x = \hbar k \text{ (forward transformation)} \quad (1.11)$$

$$\text{or } \psi(p_x) = \frac{1}{\sqrt{2\pi}} \int\limits_{-\infty}^{\infty} \psi(x) e^{-ip_x x/\hbar} dx \text{ and } \hbar \equiv \frac{h}{2\pi}$$

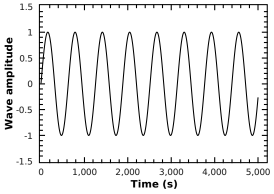
where $\psi(k)$ is the wavefunction in terms of wavevector k, which is directly related to momentum p_x (the use of k just simplifies notation). Note that:

- The functions involved in a Fourier transform may be complex valued functions.
- Fourier transformation is usually denoted by $F(\psi(x))$ and the inverse transformation by $F^{-1}(\psi(k))$. Position and momentum are called *conjugate variables.*

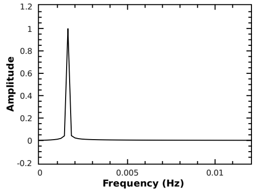
- Often, instead of carrying just Fourier transformation, a power spectrum is calculated:

$$\text{Power spectrum of } \psi = |F(\psi(x))|^2 \tag{1.12}$$

Example. Given a sound signal, Fourier transformation can be used to obtain the frequencies in the signal. It also gives information about the parity of the function transformed. When analyzing just the frequency distribution, a power spectrum is usually taken.



Sound wave at single frequency.



Power spectrum of the sound wave.

The origin of quantum mechanics is unknown. It cannot be derived without making counter intuitive assumptions!

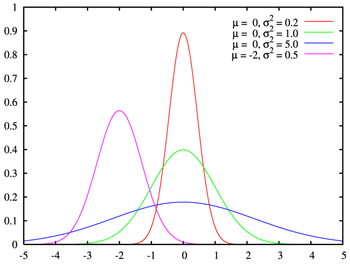
Suggested further reading:
1. R. Feynman, QED: The strange theory of light and matter.
2. A “cartoon” at `http://www.colorado.edu/physics/2000/schroedinger/`

1.2 The Heisenberg uncertainty principle

Classical mechanics: No limitations in the accuracy with which observables may be measured.

Quantum mechanics: Certain pairs of observables may not be observed with arbitrarily high precision simultaneously (Heisenberg, 1927).

Heisenberg’s uncertainty principle can be derived from the results obtained in the previous section. For simplicity, consider position ($\hat{x}$) and momentum ($\hat{p}_x$) in one dimension. Gaussian functions have the optimal properties with respect to Fourier transformation (i.e., Fourier transformation of a gaussian is another gaussian) and hence, without loss of generality, we can choose $\psi(x)$ to be a gaussian:



Localized/delocalized state

$$\psi(x) = \frac{1}{(2\pi)^{1/4}\sqrt{\sigma}} \exp\left(-\frac{(x-\mu)^2}{4\sigma^2}\right) \tag{1.13}$$

where μ is the position of the gaussian and σ^2 describes the width. The choice of μ does not affect the end result and hence we set it to zero. The standard deviation in $\hat{x}$ is equal to σ^2:

$$(\Delta x)^2 = \sigma^2 \Rightarrow \Delta x = \sigma \tag{1.14}$$

By Fourier transforming $\psi(x)$ and calculating the standard deviation for $\hat{p}_x$, we get the following result:

$$(\Delta p_x)^2 = \frac{\hbar^2}{4\sigma^2} \Rightarrow \Delta p_x = \frac{\hbar}{2\sigma} = \frac{\hbar}{2\Delta x} \Rightarrow \Delta x \Delta p_x = \frac{\hbar}{2} \tag{1.15}$$

Since gaussian functions are optimal for this property, it follows that any given function must satisfy the following inequality:

$$\Delta x \Delta p_x \geq \frac{\hbar}{2} \tag{1.16}$$

where Δx is the standard deviation in $\hat{x}$ (σ_x) and Δp_x the standard deviation in $\hat{p}_x$ (σ_{p_x}) (see Eq. (1.9) for definition of standard deviation for an operator). Eq. (1.16) is called the *Heisenberg uncertainty principle* for position and momentum. Even though time is not an observable in standard quantum mechanics, it is possible to write Eq. (1.16) for time and energy conjugate pair as well:

$$\Delta t \Delta E \geq \frac{\hbar}{2} \tag{1.17}$$

where Δt is the uncertainty in time and ΔE is the uncertainty in energy.

Exercise (advanced). Verify the expressions for Δx and Δp_x as given in Eqs. (1.14) and (1.15).

Example. The Heisenberg uncertainty principle basically states that if the wavefunction is narrow spatially, it must be wide in momentum (and vice versa). In practice, this means that if we try to localize a particle spatially, we loose information about its momentum. In classical physics, it is possible to exactly specify both position and momentum simultaneously.

Advanced topic. The Einstein-Podolsky-Rosen (EPR) paradox revised our understanding of the uncertainty principle (1935):

1. The result of a measurement performed on one part (**A**) of a quantum system has a non-local effect on the physical reality of another distant part (**B**), in the sense that quantum mechanics can predict outcomes of some measurements carried out at **B**.
2. OR Quantum mechanics is incomplete in the sense that some element of physical reality corresponding to **B** cannot be accounted for by quantum mechanics (i.e. an extra variable is needed to account for it).

This suggests that quantum behavior is inherent to the quantum system and is not a result of a perturbation from a measurement event. The EPR paradox was originally formulated to demonstrate that quantum mechanics is flawed. Einstein always considered quantum mechanics to be incomplete as he used to say “God doesn’t play dice” and Schrödinger shared the same view. Bohm later developed a non-local “hidden variable” theory that is consistent with quantum mechanics (see also the Bell inequality).

1.3 The Schrödinger equation

According to classical physics, the kinetic energy T is given by:

$$T = \frac{p^2}{2m} \tag{1.18}$$

Erwin Schrödinger, Austrian physicist (1887 - 1961), Nobel prize 1933.

Advanced topic. If we assume that the Fourier duality (Eqs. (1.10) and (1.11)) holds for position and momentum, we can derive the momentum operator in the position representation:

$$\langle \hat{p}_x \rangle = \left\langle \hbar \hat{k} \right\rangle = \hbar \left\langle \psi(k) \middle| \hat{k} \middle| \psi(k) \right\rangle = \hbar \int\limits_{-\infty}^{\infty} \psi^*(k) k \psi(k) dk \tag{1.19}$$

$$\overset{\text{Eq. (1.11)}}{\overbrace{=}} \frac{\hbar}{2\pi} \int\limits_{-\infty}^{\infty} \psi^*(x') \int\limits_{-\infty}^{\infty} e^{ikx'} k \underbrace{\int\limits_{-\infty}^{\infty} \psi(x) e^{-ikx} dx}_{\text{integration by parts}} \, dk dx'$$

$$= -\frac{i\hbar}{2\pi} \int\limits_{-\infty}^{\infty} \psi^*(x') \int\limits_{-\infty}^{\infty} e^{ikx'} \int\limits_{-\infty}^{\infty} \frac{d\psi(x)}{dx} e^{-ikx} dx dk dx'$$

Next we a result from mathematics which states that:

$$\int\limits_{-\infty}^{\infty} e^{ik(x'-x)} dk = 2\pi\delta(x'-x) \tag{1.20}$$

where δ denotes the Dirac delta measure (often incorrectly called the Dirac delta function):

$$\delta(x) = \begin{cases} \infty \text{ when } x = 0 \\ 0 \text{ when } x \neq 0 \end{cases} \text{ and } \int\limits_{-\infty}^{\infty} \delta(x) dx = 1 \tag{1.21}$$

Now we can continue working with Eq. (1.19):

$$... = -i\hbar \int\limits_{-\infty}^{\infty} \int\limits_{-\infty}^{\infty} \psi^*(x') \frac{d\psi(x)}{dx} \delta('x - x) dx dx' \tag{1.22}$$

$$= \int\limits_{-\infty}^{\infty} \psi^*(x) \left(-i\hbar \frac{d}{dx} \right) \psi(x) dx = \int\limits_{-\infty}^{\infty} \psi^*(x) \hat{p_x} \psi(x) dx$$

The above gives us the formal definition for the momentum operator:

$$\hat{p}_x = -i\hbar\frac{d}{dx} \tag{1.23}$$

If this is inserted into the classical kinetic energy expression, we have:

$$\hat{T} = \frac{\hat{p}^2}{2m} = \frac{1}{2m}\left(-i\hbar\frac{d}{dx}\right)^2 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \tag{1.24}$$

The total energy is a sum of the kinetic and potential energies:

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \tag{1.25}$$

The above expression is an operator and as such it must operate on a wavefunction:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \tag{1.26}$$

This is the *time-independent Schrödinger equation* for one particle in one dimension. For one particle in three dimensions the equation can be generalized as:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi(x,y,z)}{\partial x^2} + \frac{\partial^2\psi(x,y,z)}{\partial y^2} + \frac{\partial^2\psi(x,y,z)}{\partial z^2}\right) + V(x,y,z)\psi(x,y,z) = E\psi(x,y,z) \tag{1.27}$$

The above equation was originally written in two different forms by Schrödinger (Eq. (1.28); the differential form) and Heisenberg (the matrix form). Later Paul Dirac showed that the two forms are in fact equivalent.

The partial derivative part in Eq. (1.27) is called the Laplacian and is denoted by:

$$\Delta \equiv \nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{1.28}$$

Paul Dirac, British physicist (1902 - 1984), Nobel prize 1933

With this notation, we can rewrite Eq. (1.27) as:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + \hat{V}\psi = E\psi \tag{1.29}$$

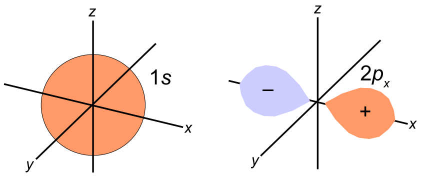
or just $\hat{H}\psi = E\psi$

Note that E is a constant and does not depend on the coordinates (x, y, z). From a mathematical point of view, this corresponds to an eigenvalue equation (E's are eigenvalues and ψ's are eigenfunctions). Operator $\hat{H}$ is usually called "Hamiltonian".

Example. Eq. (1.29) may have many different solution pairs: (E_i, ψ_i). For a hydrogen atom, which consists of an electron and a nucleus, the Schrödinger equation has the form:

$$\overbrace{-\frac{\hbar^2}{2m_e}}^{\equiv \hat{T}}\Delta\,\psi - \overbrace{\frac{e^2}{4\pi\epsilon_0}\times\frac{1}{\sqrt{x^2+y^2+z^2}}}^{\equiv \hat{V}\text{ (Coulomb potential)}}\psi = E\psi \tag{1.30}$$

where we have taken the nucleus to reside at the origin $(0,0,0)$. The values E_i give the energies of the hydrogen atom states ($1s, 2s, 2p_x$, etc.) and ψ_i give the wavefunctions for these states (orbitals). Two examples of ψ_i are plotted below:



Note that ψ_i's depend on three spatial coordinates and thus we would need to plot them in a four dimensional space! The above graphs show surfaces where the functions have some fixed value. These plots can be used to understand the shape of functions.

The wavefunction contains all the information we can have about a particle in quantum mechanics. Solutions to Eq. (1.29) are called stationary solutions (i.e., they do not depend on time).

Advanced topic. If time-dependent phenomena were to be described by quantum mechanics, the time-dependent Schrödinger equation must be used (cf. Eq. (1.29)):

$$i\hbar\frac{\partial\psi(r,t)}{\partial t} = \hat{H}\psi(r,t) \tag{1.31}$$

Interestingly, this is related to fluid dynamics via the Madelung transformation:

$$\psi(r,t) = \sqrt{\rho(r,t)}e^{iS(r,t)/\hbar} \tag{1.32}$$

where ρ is the "liquid density" and $v = \nabla S/m$ is the liquid velocity.

In Eq. (1.8) we briefly noted that square of a wavefunction is related to probability of finding the particle at a given point. To find the probability (P) for the particle to exist between x_1 and x_2, we have to integrate over this range:

$$P(x_1, x_2) = \int_{x_1}^{x_2} |\psi(x)|^2\, dx \tag{1.33}$$

When the integration is extended from minus infinity to infinity, we have the normalization condition (see Eq. (1.8)). This states that the probability for a particle to exist anywhere is one:

$$\int_{-\infty}^{\infty} |\psi(x)|^2 \, dx = \int_{-\infty}^{\infty} \psi^*(x)\psi(x)dx = 1 \tag{1.34}$$

The unit for ψ (and ψ^*) in this one-dimensional case is $\mathrm{m}^{-1/2}$. Note that probability does not have units. In three dimensions Eq. (1.34) reads:

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\psi(x,y,z)|^2 \, dxdydz = 1 \tag{1.35}$$

and the unit for ψ is now $\mathrm{m}^{-3/2}$. The probability interpretation was first proposed by Niels Bohr. From the mathematical point view, we usually make the following assumptions about ψ:

1. ψ is a function (i.e., it is single valued).
2. ψ is a continuous and differentiable function.
3. ψ is a finite valued function.
4. ψ is normalized to one (this implies square integrability; L^2).

If the volume element $dxdydz$ is denoted by $d\tau$, the normalization requirement is:

$$\int |\psi|^2 \, d\tau = \int \psi^* \psi d\tau = 1 \tag{1.36}$$

Furthermore, functions ψ_j and ψ_k are said to be orthogonal, if we have:

$$\int \psi_j^* \psi_k d\tau = 0 \tag{1.37}$$

A set of wavefunctions is said to be orthonormal, if for each member ψ_j and ψ_k:

$$\int \psi_j^* \psi_k d\tau = \delta_{jk} \tag{1.38}$$

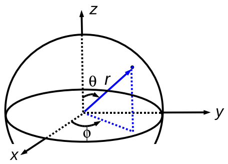
where the Kronecker delta is defined as:

$$\delta_{jk} = \begin{cases} 0, & j \neq k \\ 1, & j = k \end{cases} \tag{1.39}$$

Example. The wavefunction for hydrogen atom ground state ($1s$) in spherical coordinates is: $\psi(r) = N \times \exp(-r/a_0)$. What is the value of the normalization constant N? Here a_0 is the Bohr radius ($5.2917725 \times 10^{-11}$ m or 0.529 Å).

Solution. First we recall the spherical coordinate system:

$$\begin{aligned} x &= r\sin(\theta)\cos(\phi) \text{ where } \theta \in [0,\pi] \quad (1.40) \\ y &= r\sin(\theta)\sin(\phi) \text{ where } \phi \in [0,2\pi] \\ z &= r\cos(\theta) \text{ where } r \in [0,\infty] \\ d\tau &= r^2\sin(\theta)drd\theta d\phi \end{aligned}$$



This gives the transformation between a point the Cartesian space (x,y,z) and a point in spherical coordinates (r,θ,ϕ). Now using Eq. (1.36), we get:

$$\int |\psi|^2 \, d\tau = \int\limits_{r=0}^{\infty}\int\limits_{\theta=0}^{\pi}\int\limits_{\phi=0}^{2\pi} \underbrace{\left(Ne^{-r/a_0}\right)^2}_{=|\psi|^2} \underbrace{r^2\sin(\theta)drd\theta d\phi}_{=d\tau} \tag{1.41}$$

$$= 4\pi N^2 \underbrace{\int\limits_{r=0}^{\infty} e^{-2r/a_0} r^2 dr}_{\text{integration by parts}} = a_0^3\pi N^2 = 1 \text{ (normalization)}$$

$$\Rightarrow N = \frac{1}{\sqrt{\pi a_0^3}} \Rightarrow \psi(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

In the case of many particles, the Schrödinger equation can be written as ($3n$ dimensions, where n = number of particles):

$$-\sum_{i=1}^{n} \frac{\hbar^2}{2m_i}\Delta_i \psi(r_1,...,r_n) + V(r_1,...,r_n)\psi(r_1,...,r_n) = E\psi(r_1,...,r_n) \tag{1.42}$$

where r_i refer to coordinates of the ith particle and Δ_i refers to Laplacian for that particle. Note that:

- The dimensionality of the wavefunction increases as $3n$.
- Only for some simple potentials analytic solutions are known. In other cases approximate/numerical methods must be employed.

The following "rules" can be used to transform an expression in classical physics into an operator in quantum mechanics:

- Each Cartesian coordinate in the Hamiltonian function (i.e., classical energy) is replaced by an operator that consists of multiplication by that coordinate.
- Each Cartesian component of linear momentum p_q ($q = x, y, z$) in the Hamiltonian function is replaced by the operator shown in Eq. (1.23) for that component.

Table. Observables in classical mechanics and the corresponding quantum mechanical operators.

In one dimension:

Classical mechanics		Quantum mechanics	
Name	Symbol	Symbol	Operator
Position	x	$\hat{x}$	Multiply by x
Momentum	p_x	$\hat{p}_x$	$-i\hbar(d/dx)$
Kinetic energy	T_x	$\hat{T}_x$	$-(\hbar^2/(2m))(d^2/dx^2)$
Potential energy	$V(x)$	$\hat{V}$	Multiply by $V(x)$
Total energy	$E = T + V$	$\hat{H} = \hat{T} + \hat{V}$	Operate by $\hat{T} + \hat{V}$

In three dimensions:

Classical mechanics		Quantum mechanics	
Name	Symbol	Symbol	Operator
Position (vector)	$\vec{r}$	$\hat{\vec{r}}$	Multiply by $\vec{r}$
Momentum (vector)	$\vec{p}$	$\hat{\vec{p}}$	$-i\hbar\left(\vec{i}\frac{\partial}{\partial x}+\vec{j}\frac{\partial}{\partial y}+\vec{k}\frac{\partial}{\partial z}\right)$
Kinetic energy	T	$\hat{T}$	$-\frac{\hbar^2}{2m}\Delta$
Total energy	$E=T+V$	$\hat{H}=\hat{T}+\hat{V}$	Operate by $\hat{T}+\hat{V}$
Angular momentum	$l_x=yp_z-zp_y$	$\hat{L}_x$	$-i\hbar\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)$
	$l_y=zp_x-xp_z$	$\hat{L}_y$	$-i\hbar\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)$
	$l_z=xp_y-yp_x$	$\hat{L}_z$	$-i\hbar\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)$
	$\vec{l}=\vec{r}\times\vec{p}$	$\hat{\vec{L}}$	$-i\hbar\left(\vec{r}\times\vec{\nabla}\right)$

1.4 Operators

We have already seen examples of operators. For short, they consist of mathematical operations that can be carried out on functions. For example, the quantum mechanical momentum operator (given in Eq. (1.23)) is:

$$\hat{p}_x=-i\hbar\frac{d}{dx} \tag{1.43}$$

When this operates on a function, it does the following: (1) differentiate the function with respect to x and then (2) multiply the result from (1) by $-i\hbar$. Another example of an operator is the position operator given just by coordinate x. This would operate on a given wavefunction just by multiplying it by x. We denote operators with $\hat{}$ sign ("hat") above them.

Operators in quantum mechanics are *linear*, which means that they fulfill the following rules:

$$\hat{A}\left(\psi_1+\psi_2\right)=\hat{A}\psi_1+\hat{A}\psi_2 \tag{1.44}$$

$$\hat{A}\left(c\psi\right)=c\hat{A}\psi \text{ where } c \text{ is a constant} \tag{1.45}$$

and $\hat{A}$ is a linear operator. Operator algebra defines how operators are added, multiplied, etc. For example, adding two operators is equivalent to $\hat{A}_1+\hat{A}_2$. Multiplication corresponds to them operating one after another.

Example. Apply the following operators on the given functions:

(a) Operator $\hat{A} = d/dx$ and function x^2.
(b) Operator $\hat{A} = d^2/dx^2$ and function $4x^2$.
(c) Operator $\hat{A} = (\partial/\partial y)_x$ and function xy^2.
(d) Operator $\hat{A} = -i\hbar d/dx$ and function $\exp(-ikx)$.
(e) Operator $\hat{A} = -\hbar^2 d^2/dx^2$ and function $\exp(-ikx)$.

Solution.

(a) $\hat{A}\left(x^2\right) = \frac{d}{dx}x^2 = 2x$.
(b) $\hat{A}\left(4x^2\right) = \frac{d^2}{dx^2}\left(4x^2\right) = 8$.
(c) $\hat{A}\left(xy^2\right) = \left(\frac{\partial}{\partial y}\left(xy^2\right)\right)_x = 2xy$. Note that x is a constant.
(d) $\hat{A}\left(e^{-ikx}\right) = -i\hbar\frac{d}{dx}\left(e^{-ikx}\right) = -\hbar k e^{-ikx}$.
(e) $\hat{A}\left(e^{-ikx}\right) = -\hbar^2\frac{d^2}{dx^2}e^{-ikx} = i\hbar^2 k\frac{d}{dx}e^{-ikx} = \hbar^2 k^2 e^{-ikx}$.

Recall Eq. (1.29):

$$\hat{H}\psi_i(x, y, z) = E_i\psi_i(x, y, z) \tag{1.46}$$

This is an eigenvalue problem where one needs to determine the eigenfunctions ψ_i and the eigenvalues E_i. If ψ_i is an eigenfunction of $\hat{H}$, operating with $\hat{H}$ on it must yield a constant times ψ_i.

Example. What are the eigenfunctions and eigenvalues of operator d/dx?

Solution. Start with the eigenvalue equation:

$$\frac{d}{dx}f(x) = kf(x) \Rightarrow \frac{df(x)}{f(x)} = kdx \text{ (integrate both sides)} \tag{1.47}$$
$$\Rightarrow \ln(f(x)) = kx + c \text{ (k and c are constants)}$$
$$\Rightarrow f_k(x) = e^c e^{kx} = c' e^{kx} \text{ (c' is another constant)}$$

The eigenfunctions are $f_k(x)$ with the corresponding eigenvalue given by k. Recall Eq. (1.8), which defines the expectation value for position operator. In general, for operator $\hat{A}$, the expectation value ("quantum mechanical average") is defined as:

$$\left\langle \hat{A} \right\rangle = \int \psi^* \hat{A}\psi d\tau = \left\langle \psi \middle| \hat{A} \middle| \psi \right\rangle \tag{1.48}$$

The last "Bra - Ket" form is called the Dirac notation. Note that the Bra part always contains the complex conjugation.

If ψ is an eigenfunction of $\hat{A}$ then the expectation value is equal to the corresponding eigenvalue (a):

$$\hat{A}\psi = a\psi \Rightarrow \left\langle \hat{A} \right\rangle = \int \psi^* \underbrace{\hat{A}\psi}_{a\psi} \, d\tau = a \underbrace{\int \psi^* \psi d\tau}_{=1} = a \tag{1.49}$$

Note that operators and eigenfunctions may be complex valued; however, eigenvalues of quantum mechanical operators must be real because they correspond to values obtained from measurements. By allowing wavefunctions to be complex, it is merely possible to store more information in it (i.e., both the real and imaginary parts or "density and velocity").

Operators that yield real eigenvalues are called Hermitian operators. Operator $\hat{A}$ is Hermitian if it fulfills the following condition for *all* well-behaved functions ψ_j and ψ_k:

$$\int \psi_j^* \hat{A} \psi_k d\tau = \int \psi_k \left(\hat{A}\psi_j\right)^* d\tau \tag{1.50}$$

Note that this implies that the eigenvalues are real: Let ψ be an eigenfunction of $\hat{A}$ with eigenvalue a. Since Eq. (1.50) applies to all functions, choose $\psi_j = \psi_k = \psi$. Then $\int \psi^* \hat{A}\psi d\tau = a$ and $\int \psi \left(\hat{A}\psi\right)^* d\tau = a^*$. Now Eq. (1.50) implies that $a = a^*$, which means that a must be real.

Example. Prove that the momentum operator (in one dimension) is Hermitian.

Solution.

$$\overbrace{\int_{-\infty}^{\infty} \psi_j^*(x)\left(-i\hbar\frac{d\psi_k(x)}{dx}\right) dx}^{\text{LHS of Eq. (1.50)}} = -i\hbar \int_{-\infty}^{\infty} \psi_j^*(x)\frac{d\psi_k(x)}{dx} dx = \overbrace{\int_{-\infty}^{\infty} \psi_k(x)\left(i\hbar\frac{d\psi_j^*(x)}{dx}\right) dx}^{\text{integration by parts}}$$

$$\underbrace{= \int_{-\infty}^{\infty} \psi_k(x)\left(-i\hbar\frac{d\psi_j(x)}{dx}\right)^* dx}_{\text{RHS of Eq. (1.50)}} \Rightarrow \hat{p}_x \text{ is Hermitian.}$$

Note that the wavefunctions approach zero at infinity and thus the boundary term in the integration by parts does not contribute. In 3-D, one would have to use the Green formula.

The Hermitian property can also be used to show that the eigenfunctions (ψ_j and ψ_k), which have different eigenvalues (i.e., a_j and a_k with $a_j \neq a_k$; "non-degenerate"), are orthogonal to each other:

$$\text{LHS of Eq. (1.50):} \int \psi_j^* \hat{A} \psi_k d\tau = \int \psi_j^* a_k \psi_k d\tau = a_k \int \psi_j^* \psi_k d\tau \tag{1.51}$$

$$\text{RHS of Eq. (1.50):} \int \psi_k \left(\hat{A}\psi_j\right)^* d\tau = \int \psi_k \left(a_j \psi_j\right)^* d\tau = a_j \int \psi_j^* \psi_k d\tau \tag{1.52}$$

Here Hermiticity requires LHS = RHS. If $a_j \neq a_k$, the only way fulfill Eq. (1.50) is to have:

$$\underbrace{(a_k - a_j)}_{\neq 0} \int \psi_j^* \psi_k d\tau = 0 \tag{1.53}$$

Note that if $a_j = a_k$ ("degenerate states"), this result does not hold.

The product $\hat{A}\hat{B}$ of two operators $\hat{A}$ and $\hat{B}$ are defined as follows:

$$\hat{A}\hat{B}f = \hat{A}\left(\hat{B}f\right) \text{ (f is a function)} \tag{1.54}$$

In practice, this means that we first operate with $\hat{B}$ and then with $\hat{A}$. Note that the order of multiplication is important because they may not commute ($\hat{A}\hat{B} \neq \hat{B}\hat{A}$; just like for matrices). The commutator of two operators $\hat{A}$ and $\hat{B}$ is defined as:

$$\left[\hat{A}, \hat{B}\right] f = \left(\hat{A}\hat{B} - \hat{B}\hat{A}\right) f \tag{1.55}$$

If the commutator of $\hat{A}$ and $\hat{B}$ is zero, it means that their order in multiplication (or the operation order, in other words) may be changed. If the commutator is non-zero, the order may not be changed. Operator multiplication is associative:

$$\hat{A}\hat{B}\hat{C} = \left(\hat{A}\hat{B}\right)\hat{C} = \hat{A}\left(\hat{B}\hat{C}\right) \tag{1.56}$$

Example. Prove that operators $\hat{A} = x$ and $\hat{B} = d/dx$ do not commute (i.e., $\left[\hat{A}, \hat{B}\right] \neq 0$).

Solution. Let f be an arbitrary well-behaved function. We need to calculate both $\hat{A}\hat{B}f$ and $\hat{B}\hat{A}f$:

$$\hat{A}\hat{B}f = xf'(x) \text{ and } \hat{B}\hat{A}f = \frac{d}{dx}\left(xf(x)\right) = f(x) + xf'(x)$$

$$\left[\hat{A}, \hat{B}\right] f = \hat{A}\hat{B}f - \hat{B}\hat{A}f = -f \text{ (remove f)}$$

$$\Rightarrow \left[\hat{A}, \hat{B}\right] = -1 \text{ (this is non-zero and the operators do not commute)}$$

Simple rules for commutators:

$$[A, A] = [A, A^n] = [A^n, A] = 0 \tag{1.57}$$

$$[A, B] = -[B, A] \tag{1.58}$$

$$[B + C + ..., A] = [B, A] + [C, A] + ... \tag{1.59}$$

$$[A, B + C + ...] = [A, B] + [A, C] + ... \tag{1.60}$$

$$[A + B, C + D] = [A, C] + [A, D] + [B, C] + [B, D] \tag{1.61}$$

$$\left[A, B^2\right] = [A, B]\, B + B\, [A, B] \tag{1.62}$$

1.5 Expectation values and superposition

In most cases, we need to calculate expectation values for wavefunctions, which are not eigenfunctions of the given operator. It can be shown that for any given Hermitian operator and physically sensible boundary conditions, the eigenfunctions form a complete basis set. This means that any well-behaved function ψ can be written as a linear combination of the eigenfunctions ϕ_i ("superposition state"; the upper limit in the summation may be finite):

$$\psi(x) = \sum_{i=1}^{\infty} c_i \phi_i(x) \text{ where } \hat{A}\phi_i = a_i \phi_i \tag{1.63}$$

where c_i are constants specific to the given ψ. Since the ϕ_i are orthonormal (Eq. (1.53)) and $\psi$is normalized to one, we have:

$$1 = \int \psi^* \psi d\tau = \int \left(\sum_{i=1}^{\infty} c_i \phi_i \right)^* \left(\sum_{k=1}^{\infty} c_k \phi_k \right) d\tau = \sum_{i=1}^{\infty} c_i^* c_i \int \phi_i^* \phi_i d\tau = \sum_{i=1}^{\infty} |c_i|^2 \tag{1.64}$$

The expectation value of $\hat{A}$ is given (in terms of the eigenfunction basis; $\hat{A}$ linear):

$$\left\langle \hat{A} \right\rangle = \int \psi^* \hat{A} \psi d\tau = \int \left(\sum_{i=1}^{\infty} c_i \phi_i \right)^* \hat{A} \left(\sum_{k=1}^{\infty} c_k \phi_k \right) d\tau \tag{1.65}$$

$$= \sum_{i=1,k=1}^{\infty} c_i^* c_k \int \phi_i^* \hat{A} \phi_k d\tau = \sum_{i=1,k=1}^{\infty} c_i^* c_k \left\langle \phi_i \left| \hat{A} \right| \phi_k \right\rangle$$

Above $\left\langle \phi_i \left| \hat{A} \right| \phi_k \right\rangle$ is often called a "matrix element". Since ϕ_i's are eigenfunctions of $\hat{A}$, we get:

$$\left\langle \hat{A} \right\rangle = \sum_{i=1}^{\infty} |c_i|^2 a_i \tag{1.66}$$

Note that above ψ is not an eigenfunction of $\hat{A}$. The expectation value is a weighted average of the eigenvalues.

The coefficients $|c_i|^2$ give the probability for a measurement to give an outcome corresponding to a_i. This is often taken as one of the postulates ("assumption") for quantum mechanics (Bohr's probability interpretation). Note that the coefficients c_i may be complex but $|c_i|^2$ is always real.

Given a wavefunction ψ, it is possible to find out how much a certain eigenfunction ϕ_i contributes to it (using orthogonality of the eigenfunctions):

$$\int \phi_i^* \psi d\tau = \int \phi_i^* \left(\sum_{k=1}^{\infty} c_k \phi_k \right) d\tau = c_i \tag{1.67}$$

$$\text{OR } |c_i|^2 = \left| \int \phi_i^* \psi d\tau \right|^2 \tag{1.68}$$

Note that the discrete basis expansion does not work when the operator $\hat{A}$ has a continuous set of eigenvalues ("continuous spectrum").

The variance σ_A^2 for operator $\hat{A}$ is defined as (see Eq. (1.9)):

$$\sigma_A^2 = \left\langle \left(\hat{A} - \left\langle \hat{A} \right\rangle\right)^2 \right\rangle = \left\langle \psi \left| \left(\hat{A} - \left\langle \hat{A} \right\rangle\right)^2 \right| \psi \right\rangle = \left\langle \psi \left| \hat{A}^2 \right| \psi \right\rangle \tag{1.69}$$

$$- \underbrace{\left\langle \psi \left| 2\hat{A} \left\langle \psi \left| \hat{A} \right| \psi \right\rangle \right| \psi \right\rangle}_{=2\langle \psi | \hat{A} | \psi \rangle^2} + \left\langle \psi \left| \hat{A} \right| \psi \right\rangle^2$$

$$= \left\langle \psi \left| \hat{A}^2 \right| \psi \right\rangle - \left\langle \psi \left| \hat{A} \right| \psi \right\rangle^2 = \left\langle \hat{A}^2 \right\rangle - \left\langle \hat{A} \right\rangle^2$$

The standard deviation is given by the square root of σ_A^2.

Example. Consider a particle in a quantum state ψ that is a superposition of two eigenfunctions ϕ_1 and ϕ_2, with energy eigenvalues E_1 and E_2 of operator $\hat{H}$ ($E_1 \neq E_2$):

$$\psi = c_1\phi_1 + c_2\phi_2$$

If one attempts to measure energy of such state, what will be the outcome? What will be the average energy and the standard deviation in energy?

Solution. Since ψ is normalized and ϕ_1 and ϕ_2 are orthogonal, we have $|c_1|^2 + |c_2|^2 = 1$. The probability of measuring E_1 is $|c_1|^2$ and E_2 is $|c_2|^2$. The average energy is given by:

$$\left\langle \hat{H} \right\rangle = \left\langle \psi \left| \hat{H} \right| \psi \right\rangle = |c_1|^2 \left\langle \phi_1 \left| \hat{H} \right| \phi_1 \right\rangle + c_1^* c_2 \left\langle \phi_1 \left| \hat{H} \right| \phi_2 \right\rangle + c_2^* c_1 \left\langle \phi_2 \left| \hat{H} \right| \phi_1 \right\rangle$$

$$+ |c_2|^2 \left\langle \phi_2 \left| \hat{H} \right| \phi_2 \right\rangle = |c_1|^2 E_1 + c_1^* c_2 E_2 \underbrace{\langle \phi_1 | \phi_2 \rangle}_{=0} + c_2^* c_1 E_1 \underbrace{\langle \phi_2 | \phi_1 \rangle}_{=0} + |c_2|^2 E_2$$

$$= |c_1|^2 E_1 + |c_2|^2 E_2$$

(Exercise: write the above equation without using the Dirac notation). The standard deviation is given by (1.69): $\sigma_{\hat{H}} = \sqrt{\left\langle \hat{H}^2 \right\rangle - \left\langle \hat{H} \right\rangle^2}$. We have already calculated $\left\langle \hat{H} \right\rangle$ above and need to calculate $\left\langle \hat{H}^2 \right\rangle$ (use the eigenvalue equation and orthogonality):

$$\left\langle \hat{H}^2 \right\rangle = \left\langle \psi \left| \hat{H}^2 \right| \psi \right\rangle = \left\langle \psi \left| \hat{H} \right| E_1 c_1 \phi_1 + E_2 c_2 \phi_2 \right\rangle = \langle c_1\phi_1 + c_2\phi_2 \, | E_1^2 c_1 \phi_1 + E_2^2 c_2 \phi_2 \rangle$$

$$= |c_1|^2 E_1^2 + |c_2|^2 E_2^2 \Rightarrow \sigma_{\hat{H}} = \sqrt{|c_1|^2 E_1^2 + |c_2|^2 E_2^2 - \left(|c_1|^2 E_1 + |c_2|^2 E_2\right)^2}$$

1.6 Particle in a one-dimensional box

The simplest problem to treat in quantum mechanics is that of a particle of mass m constrained to move in a one-dimensional box of length a ("particle in a box"). The potential energy $V(x)$ is taken to be zero for $0 < x < a$ and infinite outside this region. The infinite potential can be treated as a boundary condition (i.e., the wavefunction must be zero outside $0 < x < a$). Such a bound potential will lead to quantized energy levels. In general, either a bound potential or a suitable boundary condition is required for quantization.

In the region between $0 < x < a$, the Schrödinger Eq. (1.46) can be written as:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \tag{1.70}$$

The infinite potential around the box imposes the following boundary conditions:

$$\psi(0) = 0 \text{ and } \psi(a) = 0$$

Eq. (1.70) can be rewritten as:

$$\frac{d^2\psi(x)}{dx^2} = -\frac{2mE}{\hbar^2}\psi(x) \equiv -k^2\psi(x) \text{ where } k = \sqrt{\frac{2mE}{\hbar^2}} \tag{1.71}$$

Eq. (1.71) is a second order differential equation, which has solutions of the form:

$$\psi(x) = A\cos(kx) + B\sin(kx) \tag{1.72}$$

This solution must fulfill the boundary conditions:

$$\begin{aligned} &\psi(0) = A = 0 \text{ and } \psi(a) = A\cos(ka) + B\sin(ka) = B\sin(ka) = 0 \qquad (1.73) \\ &\Rightarrow \sin(ka) = 0 \Rightarrow ka = n\pi \Rightarrow k = \frac{n\pi}{a} \text{ where } n = 1, 2, 3... \end{aligned}$$

Note that the value $n = 0$ is not allowed because it would lead to ψ being identically zero. Thus the eigenfunctions and eigenvalues are (be careful with h and $\hbar$!):

$$\psi_n(x) = B\sin\left(\frac{n\pi}{a}x\right) \text{ and } E_n = \frac{\hbar^2k^2}{2m} = \frac{\hbar^2n^2\pi^2}{2ma^2} = \frac{h^2n^2}{8ma^2} \tag{1.74}$$

This shows that the particle can only have certain energy values specified by E_n. Other energy values are forbidden (i.e., energy is said to be quantized). In the limit of large box ($a \to \infty$) or large mass ($m \to \infty$), the quantization diminishes and the particle begins to behave classically. The lowest energy level is given by $n = 1$, which implies that the energy of the particle can never reach zero ("zero-point motion"; "zero-point energy").

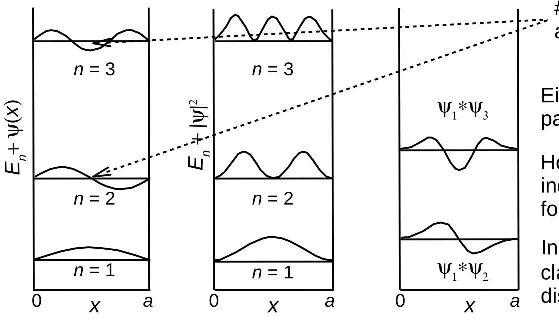
The eigenfunctions in Eq. (1.74) are not normalized (i.e., we have not specified B).

Normalization can be carried out as follows:

$$1 = \int_0^a \psi_n^*(x)\psi_n(x)dx = B^2 \underbrace{\int_0^a \sin^2\left(\frac{n\pi x}{a}\right)dx}_{=a/2 \text{ (tablebook)}} = B^2\frac{a}{2} \Rightarrow B = \pm\sqrt{\frac{2}{a}} \tag{1.75}$$

Thus the complete eigenfunctions (choosing the "+" sign) are:

$$\psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right) \tag{1.76}$$



# of nodes increases as *n* increases

Eigenfunctions for particle in 1-D box

Horizontal lines indicate positions for E_n

In the limit $n \to \infty$, classical probability distribution emerges.

As shown in the previous figure, products between different eigenfunctions ψ_i and ψ_k have equal amounts of positive and negative parts and hence integrals over these products are zero (positive and negative areas cancel). The eigenfunctions are therefore orthonormalized (normalization was carried out earlier):

$$\int_{-\infty}^{\infty} \psi_i(x)\psi_k(x)dx = \delta_{ik} \tag{1.77}$$

Note that these ψ_i's are eigenfunctions of the energy operator but not, for example, the position operator. Therefore only the average position may be calculated (i.e., the expectation value), which is $a/2$ for all states. If we carried out measurements on position of the particle in a 1-D box, we would obtain different values according to the probability distribution shown on the previous slide (with the $a/2$ average).

Example. An electron is in one-dimensional box, which is 1.0 nm in length. What is the probability of locating the electron between $x = 0$ (the left-hand edge) and $x = 0.2$ nm in its lowest energy state?

Solution. According to Eq. (1.33) the probability is given by:

$$\int_{x=0\text{ nm}}^{0.2\text{ nm}} |\psi_1(x)|^2\,dx = \overbrace{\frac{2}{1.0\text{ nm}}\int_{0\text{ nm}}^{0.2\text{ nm}} \sin^2\left(\frac{\pi x}{1.0\text{ nm}}\right)dx}^{n=1,a=1\text{ nm}}$$

$$\left(\text{Tablebook: } \int \sin^2\left(\frac{\pi}{a}x\right)dx = \frac{x}{2} - \frac{\sin\left(2\pi x/a\right)}{4\pi/a}\right)$$

$$= \frac{2}{1.0\text{ nm}}\left(\frac{0.2\text{ nm}}{2} - \frac{\sin(2\pi \times (0.2\text{ nm})/(1.0\text{ nm}))}{4\pi/(1.0\text{ nm})}\right) \approx 0.05$$

Example. Calculate $\langle p_x \rangle$ and $\langle p_x^2 \rangle$ for a particle in one-dimensional box.

Solution. The momentum operator p_x is given by Eq. (1.23).

$$\langle p_x \rangle_n = \int\limits_0^a \left[\left(\frac{2}{a}\right)^{1/2}\sin\left(\frac{n\pi x}{a}\right)\right]\left(-i\hbar\frac{d}{dx}\right)\left[\left(\frac{2}{a}\right)^{1/2}\sin\left(\frac{n\pi x}{a}\right)\right]dx$$

$$= -\frac{2i\hbar n\pi}{a^2}\underbrace{\int\limits_0^a \overbrace{\sin\left(\frac{n\pi x}{a}\right)}^{\text{even}}\overbrace{\cos\left(\frac{n\pi x}{a}\right)}^{\text{odd}}dx}_{\equiv 0} = 0$$

The value for $\langle p_x^2 \rangle$ is given by:

$$\langle p_x^2 \rangle_n = \int\limits_0^a \left[\left(\frac{2}{a}\right)^{1/2}\sin\left(\frac{n\pi x}{a}\right)\right]\left(-i\hbar\frac{d}{dx}\right)^2\left[\left(\frac{2}{a}\right)^{1/2}\sin\left(\frac{n\pi x}{a}\right)\right]dx$$

$$= -\frac{2\hbar^2}{a}\int_0^a \left[\sin\left(\frac{n\pi x}{a}\right)\right]\frac{d^2}{dx^2}\left[\sin\left(\frac{n\pi x}{a}\right)\right]dx = \frac{2\hbar^2 n^2\pi^2}{a^3}\underbrace{\int\limits_0^a \sin^2\left(\frac{n\pi x}{a}\right)dx}_{=a/2}$$

$$= \frac{\hbar^2 n^2 \pi^2}{a^2}$$

1.7 Particle in a three-dimensional box

In three dimensions the quantum mechanical Hamiltonian is written as (see Eqs. (1.29) and (1.42)):

$$-\frac{\hbar^2}{2m}\Delta\psi(x,y,z) + V(x,y,z)\psi(x,y,z) = E\psi(x,y,z) \tag{1.78}$$

OR

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + V\psi = E\psi$$

where the solutions ψ must be normalized:

$$\int\limits_{-\infty}^{\infty}\int\limits_{-\infty}^{\infty}\int\limits_{-\infty}^{\infty} |\psi(x,y,z)|^2\, dxdydz = 1 \tag{1.79}$$

Consider a particle in a box with sides of lengths a in x, b in y and c in z. The potential inside the box is zero and outside the box infinity. Again, the potential term can be treated by boundary conditions (i.e,. infinite potential implies that the wavefunction must be zero there). The above equation can be now written as:

$$-\frac{\hbar^2}{2m}\Delta\psi = E\psi \tag{1.80}$$

$$\text{with } \psi(a,y,z) = \psi(x,b,z) = \psi(x,y,c) = 0$$

$$\text{and } \psi(0,y,z) = \psi(x,0,z) = \psi(x,y,0) = 0$$

In general, when the potential term can be expressed as a sum of terms that depend separately only on x, y and z, the solutions can be written as a product:

$$\psi(x,y,z) = X(x)Y(y)Z(z) \tag{1.81}$$

By substituting (1.81) in (1.80) and dividing by $X(x)Y(y)Z(z)$, we obtain:

$$-\frac{\hbar^2}{2m}\left[\frac{1}{X(x)}\frac{d^2X(x)}{dx^2} + \frac{1}{Y(y)}\frac{d^2Y(y)}{dy^2} + \frac{1}{Z(z)}\frac{d^2Z(z)}{dz^2}\right] = E \tag{1.82}$$

The total energy E consists of a sum of three terms, which each depend separately on x, y and z. Thus we can write $E = E_x + E_y + E_z$ and separate the equation into three one-dimensional problems:

$$-\frac{\hbar^2}{2m}\left[\frac{1}{X(x)}\frac{d^2X(x)}{dx^2}\right] = E_x \text{ with } X(0) = X(a) = 0 \tag{1.83}$$

$$-\frac{\hbar^2}{2m}\left[\frac{1}{Y(y)}\frac{d^2Y(y)}{dy^2}\right] = E_y \text{ with } Y(0) = Y(b) = 0$$

$$-\frac{\hbar^2}{2m}\left[\frac{1}{Z(z)}\frac{d^2Z(z)}{dz^2}\right] = E_z \text{ with } Z(0) = Z(c) = 0$$

where the boundary conditions were obtained from Eq. (1.80).

Each line in Eq. (1.83) corresponds to one-dimensional particle in a box problem:

$$X(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n_x \pi x}{a}\right) \tag{1.84}$$
$$Y(y) = \sqrt{\frac{2}{b}}\sin\left(\frac{n_y \pi y}{b}\right)$$
$$Z(z) = \sqrt{\frac{2}{c}}\sin\left(\frac{n_z \pi z}{c}\right)$$

Thus the three-dimensional wavefunction (see Eq. (1.81)) is:

$$\psi(x,y,z) = X(x)Y(y)Z(z) = \sqrt{\frac{8}{abc}}\sin\left(\frac{n_x \pi x}{a}\right)\sin\left(\frac{n_y \pi y}{b}\right)\sin\left(\frac{n_z \pi z}{c}\right) \tag{1.85}$$

The total energy is given by:

$$E_{n_x,n_y,n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \tag{1.86}$$

Energy is again quantized and when $a = b = c$, we the energy levels can also be *degenerate* (i.e., the same energy with different values of n_x, n_y and n_z).

When $a = b = c$, the lowest levels have the following degeneracy factors:

$n_x n_y n_z$	111	211	221	311	222	321	322	411	331
Degen.	1	3	3	3	1	6	3	3	3

In most cases, degeneracy in quantum mechanics arises from symmetry (here $a = b = c$).

Example. Consider an electron in superfluid helium (^{4}He) where it forms a solvation cavity with a radius of 18 Å. Calculate the zero-point energy and the energy difference between the ground and first excited states by approximating the electron by a particle in a 3-dimensional box.

Solution. The zero-point energy can be obtained from the lowest state energy (e.g. $n = 1$) with $a = b = c = 36$ Å. The first excited state is triply degenerate (E_{112}, E_{121} and E_{211}). Use Eq. (1.86):

$$E_{111} = \frac{h^2}{8m_e}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

$$= \frac{(6.626076\times 10^{-34}\ \text{Js})^2}{8(9.109390\times 10^{-31}\ \text{kg})}\left(\frac{1}{(36\times 10^{-10}\ \text{m})^2} + \frac{1}{(36\times 10^{-10}\ \text{m})^2} + \frac{1}{(36\times 10^{-10}\ \text{m})^2}\right)$$

$$= 1.39\times 10^{-20}\ \text{J} = 87.0\ \text{meV}$$

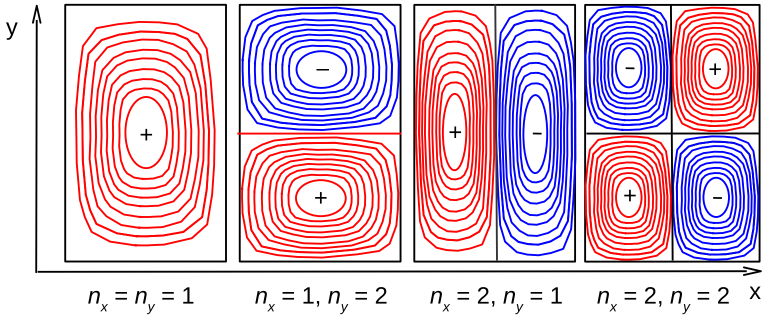
$$E_{211} = E_{121} = E_{112} = \frac{(6.626076 \times 10^{-34}\ \text{Js})^2}{8(9.109390 \times 10^{-31}\ \text{kg})}$$

$$\times \left(\frac{2^2}{(36 \times 10^{-10}\ \text{m})^2} + \frac{1^2}{(36 \times 10^{-10}\ \text{m})^2} + \frac{1^2}{(36 \times 10^{-10}\ \text{m})^2} \right)$$

$$= 2.79 \times 10^{-20}\ \text{J} = 174\ \text{meV} \Rightarrow \Delta E = 87\ \text{meV}$$

(Experimental value: 105 meV; Phys. Rev. B 41, 6366 (1990))

The solutions in three dimensions are difficult to visualize. Consider a two-dimensional particle in a box problem. In this case $\psi = \psi(x, y)$ and we can visualize the solutions:



1.8 Relation between commutability and precision of measurement

We have seen previously (Eq. (1.55)) that operators may not always commute (i.e., $[A, B] \neq 0$). An example of such operator pair is position $\hat{x}$ and momentum $\hat{p}_x$:

$$\hat{p}_x \hat{x} \psi(x) = \hat{p}_x \left(x\psi(x) \right) = \left(\frac{\hbar}{i} \frac{d}{dx} \right) \left(x\psi(x) \right) = \frac{\hbar x}{i} \frac{d\psi(x)}{dx} + \frac{\hbar}{i} \psi(x) \tag{1.87}$$

$$\hat{x} \hat{p}_x \psi(x) = x \left(\frac{\hbar}{i} \frac{d\psi(x)}{dx} \right) \tag{1.88}$$

$$\Rightarrow \left[\hat{p}_x, \hat{x} \right] \psi(x) = \left(\hat{p}_x \hat{x} - \hat{x} \hat{p}_x \right) \psi(x) = \frac{\hbar}{i} \psi(x) \tag{1.89}$$

$$\Rightarrow \left[\hat{p}_x, \hat{x} \right] = \frac{\hbar}{i} \tag{1.90}$$

In contrast, the kinetic energy operator and the momentum operators commute:

$$\left[\hat{T}, \hat{p}_x \right] = \left[\frac{\hat{p}_x^2}{2m}, \hat{p}_x \right] = \frac{p_x^3}{2m} - \frac{p_x^3}{2m} = 0 \tag{1.91}$$

In Eq. (1.16) we had the uncertainty principle for the position and momentum operators:

$$\Delta x \Delta p_x \geq \frac{\hbar}{2}$$

In general, it turns out that for operators $\hat{A}$ and $\hat{B}$ that do not commute, the <u>uncertainty principle</u> applies in the following form:

$$\Delta A \Delta B \geq \frac{1}{2}\left|\left\langle\left[\hat{A},\hat{B}\right]\right\rangle\right| \tag{1.92}$$

Example. Use Eq. (1.92) to obtain the position/momentum uncertainty principle (1.16).

Solution. Denote $\hat{A} = \hat{x}$ and $\hat{B} = \hat{p}_x$. Evaluate the right hand side of Eq. (1.92):

$$\frac{1}{2}\left|\left\langle\left[\hat{A},\hat{B}\right]\right\rangle\right| = \frac{1}{2}\left|\langle[\hat{x},\hat{p}_x]\rangle\right| = \frac{1}{2}\left|\left\langle\frac{\hbar}{i}\right\rangle\right| = \frac{1}{2}\left|\left\langle\psi\left|\frac{\hbar}{i}\right|\psi\right\rangle\right| = \frac{1}{2}\left|\frac{\hbar}{i}\underbrace{\langle\psi\,|\psi\,\rangle}_{=1}\right| = \frac{\hbar}{2}$$

$$\Rightarrow \Delta x \Delta p_x \geq \frac{\hbar}{2}$$

Example. Show that if all eigenfunctions of operators $\hat{A}$ and $\hat{B}$ are identical, $\hat{A}$ and $\hat{B}$ commute with each other.

Solution. Denote the eigenvalues of $\hat{A}$ and $\hat{B}$ by a_i and b_i and the common eigenfunctions by ψ_i. For both operators we have then:

$$\hat{A}\psi_i = a_i\psi_i \text{ and } \hat{B}\psi_i = b_i\psi_i$$

By using these two equations and expressing the general wavefunction ψ as a linear combination of the eigenfunctions, the commutator can be evaluated as:

$$\hat{A}\hat{B}\psi = \hat{A}\left(\hat{B}\psi\right) = \hat{A}\overbrace{\left(\hat{B}\sum_{i=1}^{\infty}c_i\psi_i\right)}^{\text{complete basis}} = \hat{A}\overbrace{\left(\sum_{i=1}^{\infty}c_i\hat{B}\psi_i\right)}^{\hat{B}\text{ linear}} = \hat{A}\overbrace{\left(\sum_{i=1}^{\infty}c_ib_i\psi_i\right)}^{\text{eigenfunction of }\hat{B}}$$

$$= \overbrace{\sum_{i=1}^{\infty}c_ib_i\hat{A}\psi_i}^{\hat{A}\text{ linear}} = \overbrace{\sum_{i=1}^{\infty}c_ib_ia_i\psi_i}^{\text{eigenfunction of }\hat{A}} = \overbrace{\sum_{i=1}^{\infty}c_ia_ib_i\psi_i}^{a_i\text{ and }b_i\text{ are constants}} = \sum_{i=1}^{\infty}c_ia_i\hat{B}\psi_i$$

$$= \hat{B}\sum_{i=1}^{\infty}c_ia_i\psi_i = \hat{B}\sum_{i=1}^{\infty}c_i\hat{A}\psi_i = \hat{B}\hat{A}\sum_{i=1}^{\infty}c_i\psi_i = \hat{B}\hat{A}\psi$$

$$\Rightarrow \left[\hat{A},\hat{B}\right] = 0$$

Note that the commutation relation must apply to all well-behaved functions and not just for some given subset of functions!

1.9 Quantum mechanical harmonic oscillator

In classical physics, the Hamiltonian for a harmonic oscillator is given by:

$$H = \frac{1}{2\mu}p_x^2 + \frac{1}{2}\omega^2\mu x^2 = \frac{1}{2\mu}p_x^2 + \frac{1}{2}kx^2 \text{ with } \omega = \sqrt{k/\mu} \tag{1.93}$$

where μ denotes the mass. We have chosen μ instead of m because later we will use this equation in such context where μ will refer to so called reduced mass:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \text{ (in kg; } m_1 \text{ and } m_2 \text{ are masses for two particles)} \tag{1.94}$$

The quantum mechanical harmonic oscillator is obtained by replacing the classical position and momentum by the corresponding quantum mechanical operators (Eq. (1.23)):

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2 = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + 2\pi^2\nu^2\mu x^2 \text{ where } \nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{1.95}$$

Note that the potential term may be expressed in terms of three parameters:

k	Force constant (kg s^{-2})
ω	Angular frequency ($\omega = 2\pi\nu$; Hz)
ν	Frequency (Hz; do not confuse this with quantum number v)

Depending on the context any of these constants may be used to specify the harmonic potential.

The solutions to this equation are found to be (derivations not shown):

$$E_v = \left(v + \frac{1}{2}\right)h\nu = \left(v + \frac{1}{2}\right)\hbar\omega \text{ where } v = 0, 1, 2, 3... \tag{1.96}$$

$$\psi_v = N_v \times \overbrace{H_v\left(\sqrt{\alpha}x\right)}^{\text{Hermite polynomial}} \times e^{-\alpha x^2/2} \text{ where } \alpha = \sqrt{\frac{k\mu}{\hbar^2}} \tag{1.97}$$

$$N_v = \frac{1}{\sqrt{2^v v!}}\left(\frac{\alpha}{\pi}\right)^{1/4} \tag{1.98}$$

$$H_0\left(\sqrt{\alpha}x\right) = 1, H_1\left(\sqrt{\alpha}x\right) = 2\sqrt{\alpha}x, H_2\left(\sqrt{\alpha}x\right) = 4\left(\sqrt{\alpha}x\right)^2 - 2\left(\sqrt{\alpha}x\right) \tag{1.99}$$

$$H_3\left(\sqrt{\alpha}x\right) = 8\left(\sqrt{\alpha}x\right)^3 - 12\left(\sqrt{\alpha}x\right) \tag{1.100}$$

where H_v's are Hermite polynomials. To obtain Hermite polynomials with the Maxima program, use the following commands:

```
load(orthopoly);
hermite(0, sqrt(alpha)*x);
hermite(1, sqrt(alpha)*x);
hermite(2, sqrt(alpha)*x);
hermite(3, sqrt(alpha)*x);
/* etc. */
```

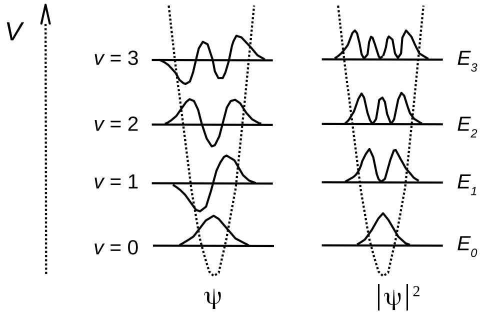
For example, the wavefunctions for the two lowest states are:

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} \tag{1.101}$$

$$\psi_1(x) = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x e^{-\alpha x^2/2} \tag{1.102}$$

Exercise. Verify that you get the same wavefunctions as in (1.101) and (1.102) by using Eqs. (1.96) - (1.100).

Some of the lowest state solutions to the harmonic oscillator (HO) problem are displayed below:



Notes:

- Solutions ψ_v with $v = 0, 2, 4, ...$ are even: $\psi_v(x) = \psi_v(-x)$.
- Solutions ψ_v with $v = 1, 3, 5, ...$ are odd: $\psi_v(x) = -\psi_v(-x)$.
- Integral of an odd function from $-a$ to a (a may be ∞) is zero.
- The tails of the wavefunctions penetrate into the potential barrier deeper than the classical physics would allow. This phenomenon is called quantum mechanical *tunneling*.

Example. Show that the lowest level of HO obeys the uncertainty principle.

Solution. To get Δx (the standard deviation), we must use Eq. (1.69):

$$\Delta x = \sigma_x = \sqrt{\langle \hat{x}^2 \rangle - \langle \hat{x} \rangle^2} \text{ and } \Delta p_x = \sigma_{p_x} = \sqrt{\langle \hat{p}_x^2 \rangle - \langle \hat{p}_x \rangle^2}$$

First we calculate $\langle \hat{x} \rangle$ (ψ_0 is an even function, x is odd, the integrand is odd overall):

$$\langle \hat{x} \rangle = \int_{-\infty}^{\infty} \psi_0(x) x \psi_0(x) dx = 0$$

For $\langle \hat{x}^2 \rangle$ we have (integration by parts or tablebook):

$$\langle \hat{x}^2 \rangle = \int_{-\infty}^{\infty} \psi_0(x) x^2 \psi_0(x) dx = \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx = \left(\frac{\alpha}{\pi}\right)^{1/2} \left[\frac{1}{2\alpha}\left(\frac{\pi}{\alpha}\right)^{1/2}\right]$$

$$= \frac{1}{2\alpha} = \frac{1}{2}\frac{\hbar}{\sqrt{\mu k}} \Rightarrow \Delta x = \sqrt{\frac{1}{2}\frac{\hbar}{\sqrt{\mu k}}}$$

For $\langle \hat{p}_x \rangle$ we have again by symmetry:

$$\langle \hat{p}_x \rangle = \int\limits_{-\infty}^{\infty} \underbrace{\psi_0(x)}_{\text{even}} \underbrace{\left(-i\hbar\frac{d}{dx}\right)\underbrace{\psi_0(x)}_{\text{even}}}_{\text{odd}} dx = 0$$

Note that derivative of an even function is an odd function. For $\langle \hat{p}_x^2 \rangle$ we have:

$$\langle \hat{p}_x^2 \rangle = \int\limits_{-\infty}^{\infty} \psi_0(x) p_x^2 \psi_0(x) dx = -\hbar^2 \left(\frac{\alpha}{\pi}\right)^{1/2} \int\limits_{-\infty}^{\infty} e^{-\alpha x^2/2} \frac{d^2}{dx^2} e^{-\alpha x^2/2} dx$$

$$= \hbar^2 \left(\frac{\alpha}{\pi}\right)^{1/2} \int\limits_{-\infty}^{\infty} (\alpha - \alpha^2 x^2) e^{-\alpha x^2} dx = \left[\hbar^2 \left(\frac{\alpha}{\pi}\right)^{1/2}\right]$$

$$\times \left(\alpha \int\limits_{-\infty}^{\infty} e^{-\alpha x^2} dx - \alpha^2 \int\limits_{-\infty}^{\infty} x^2 e^{-\alpha x^2} dx\right)$$

$$= \underbrace{\left[\hbar^2 \left(\frac{\alpha}{\pi}\right)^{1/2}\right] \times \left(\alpha\sqrt{\frac{\pi}{\alpha}} - \alpha^2 \frac{\sqrt{\pi}}{2\alpha^{3/2}}\right)}_{\underline{\text{tablebook}}}$$

$$= \left[\hbar^2 \sqrt{\frac{\alpha}{\pi}}\right] \times \left(\sqrt{\pi\alpha} - \frac{\sqrt{\pi\alpha}}{2}\right) = \frac{\hbar^2\alpha}{2} = \frac{\hbar\sqrt{\mu k}}{2} \Rightarrow \Delta p_x = \sqrt{\frac{\hbar\sqrt{\mu k}}{2}}$$

Finally, we can calculate $\Delta x \Delta p_x$:

$$\Delta x \Delta p_x = \sqrt{\frac{1}{2}\frac{\hbar}{\sqrt{\mu k}}} \times \sqrt{\frac{\hbar\sqrt{\mu k}}{2}} = \sqrt{\frac{\hbar^2}{4}} = \frac{\hbar}{2}$$

Recall that the uncertainty principle stated that: $\Delta x \Delta p_x \geq \frac{\hbar}{2}$

Thus we can conclude that ψ_0 fulfills the Heisenberg uncertainty principle.

Example. Quantization of nuclear motion ("molecular vibration") in a diatomic molecule can be approximated by the quantum mechanical harmonic oscillator model. There μ is the reduced mass as given previously and the variable x is the distance between the atoms in the molecule (or more exactly, the deviation from the equilibrium bond length R_e).

(a) Derive the expression for the standard deviation of the bond length in a diatomic molecule when it is in its ground vibrational state.
(b) What percentage of the equilibrium bond length is this standard deviation for carbon monoxide in its ground vibrational state? For $^{12}C^{16}O$, we have: $\tilde{v} = 2170$ cm^{-1} (vibrational frequency) and $R_e = 113$ pm (equilibrium bond length).

Solution. The harmonic vibration frequency is given in wavenumber units (cm^{-1}). This must be converted according to: $\nu = c\tilde{v}$. The previous example gives expression for σ_x:

$$\sigma_x = \Delta x = \sqrt{\frac{1}{2}\frac{\hbar}{\sqrt{\mu k}}}$$

In considering spectroscopic data, it is convenient to express this in terms of $\tilde{v}$:

$$k = (2\pi c\tilde{v})^2\,\mu \text{ and } \Delta x = \sigma_x = \sqrt{\frac{\hbar}{4\pi c\tilde{v}\mu}}$$

In part (b) we have to apply the above expression to find out the standard deviation for carbon monoxide bond length in its ground vibrational state. First we need the reduced mass:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(12 \times 10^{-3}\text{ kg mol}^{-1})(15.995 \times 10^{-3}\text{ kg mol}^{-1})}{((12 + 15.995) \times 10^{-3}\text{ kg mol}^{-1})\underbrace{(6.022 \times 10^{23}\text{ mol}^{-1})}_{\text{Avogadro's constant}}}$$

$$= 1.139 \times 10^{-26}\text{ kg}$$

The standard deviation is now:

$$\Delta x = \sigma_x = \left[\frac{1.055 \times 10^{-34}\text{ Js}}{4\pi\underbrace{(2.998 \times 10^{10}\text{ cm s}^{-1})}_{\text{speed of light}}(2170\text{ cm}^{-1})(1.139 \times 10^{-26}\text{ kg})}\right]^{1/2}$$

$$= 3.37\text{ pm} \Rightarrow \%\text{ of deviation} = 100\% \times \frac{3.37\text{ pm}}{113\text{ pm}} = 2.98\%$$

Finally, the following realtions are useful when working with Hermite polynomials:

$$H_v''(y) - 2yH_v'(y) + 2vH_v(y) = 0 \text{ (characteristic equation)} \tag{1.103}$$

$$H_{v+1}(y) = 2yH_v(y) - 2vH_{v-1}(y) \text{ (recursion relation)} \tag{1.104}$$

$$\int\limits_{-\infty}^{\infty} H_{v'}(y)H_v(y)e^{-y^2}dy = \begin{cases} 0, & \text{if } v' \neq v \\ \sqrt{\pi}2^v v!, & \text{if } v' = v \end{cases} \tag{1.105}$$

More results for Hermite polynomials can be found online.

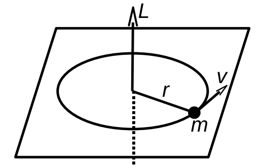
In a three-dimensional harmonic oscillator potential, $V(x,y,z) = \frac{1}{2}k_x x^2 + \frac{1}{2}k_y y^2 + \frac{1}{2}k_z z^2$, the separation technique similar to the three-dimensional particle in a box problem can be used. The resulting eigenfunctions and eigenvalues are:

$$E = \left(v_x + \frac{1}{2}\right)h\nu_x + \left(v_y + \frac{1}{2}\right)h\nu_y + \left(v_z + \frac{1}{2}\right)h\nu_z \tag{1.106}$$

$$\psi(x,y,z) = N_{v_x}H_{v_x}\left(\sqrt{\alpha_x}x\right)e^{-\alpha_x x^2/2}$$
$$\times N_{v_y}H_{v_y}\left(\sqrt{\alpha_y}y\right)e^{-\alpha_y y^2/2} \times N_{v_z}H_{v_z}\left(\sqrt{\alpha_z}z\right)e^{-\alpha_z z^2/2}$$

where the α, N, and H are defined in Eqs. (1.96) - (1.100) and the v's are the quantum numbers along the Cartesian coordinates.

1.10 Angular momentum



Rotation about a fixed point

In *classical* mechanics, the angular momentum is defined as:

$$\vec{L} = \vec{r} \times \vec{p} = \vec{r} \times (m\vec{v}) \text{ where } \vec{L} = (L_x, L_y, L_z) \tag{1.107}$$

Here $\vec{r}$ is the position and $\vec{v}$ the velocity of the mass m.

To evaluate the cross product, we write down the Cartesian components:

$$\vec{r} = (x, y, z) \tag{1.108}$$

$$\vec{p} = (p_x, p_y, p_z) \tag{1.109}$$

The cross product is convenient to write using a determinant:

$$\vec{L} = \vec{r} \times \vec{p} = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} = (yp_z - zp_y)\,\vec{i} + (zp_x - xp_z)\,\vec{j} + (xp_y - yp_x)\,\vec{k} \tag{1.110}$$

where $\vec{i}, \vec{j}$ and $\vec{k}$ denote unit vectors along the x, y and z axes.

The Cartesian components can be identified as:

$$L_x = yp_z - zp_y \tag{1.111}$$

$$L_y = zp_x - xp_z \tag{1.112}$$

$$L_z = xp_y - yp_x \tag{1.113}$$

The square of the angular momentum is given by:

$$\vec{L}^2 = \vec{L} \cdot \vec{L} = L_x^2 + L_y^2 + L_z^2 \tag{1.114}$$

In quantum mechanics, the classical angular momentum is replaced by the corresponding quantum mechanical operator (see the previous "classical - quantum" correspondence table). The Cartesian quantum mechanical angular momentum operators are:

$$\hat{L}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \tag{1.115}$$

$$\hat{L}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \tag{1.116}$$

$$\hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \tag{1.117}$$

In spherical coordinates (see Eq. (1.40)), the angular momentum operators can be written in the following form (derivations are quite tedious but just math):

$$\hat{L}_x = i\hbar\left(\sin(\phi)\frac{\partial}{\partial\theta} + \cot(\theta)\cos(\phi)\frac{\partial}{\partial\phi}\right) \tag{1.118}$$

$$\hat{L}_y = i\hbar\left(-\cos(\phi)\frac{\partial}{\partial\theta} + \cot(\theta)\sin(\phi)\frac{\partial}{\partial\phi}\right) \tag{1.119}$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi} \tag{1.120}$$

$$\hat{\vec{L}}^2 = -\hbar^2 \underbrace{\left[\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}\right]}_{\equiv\Lambda^2} \tag{1.121}$$

Note that the choice of z-axis ("quantization axis") here was arbitrary. Sometimes the physical system implies such axis naturally (for example, the direction of an external magnetic field). The following commutation relations can be shown to hold:

$$\left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}_z, \left[\hat{L}_y, \hat{L}_z\right] = i\hbar\hat{L}_x, \left[\hat{L}_z, \hat{L}_x\right] = i\hbar\hat{L}_y \tag{1.122}$$

$$\left[\hat{L}_x, \hat{\vec{L}}^2\right] = \left[\hat{L}_y, \hat{\vec{L}}^2\right] = \left[\hat{L}_z, \hat{\vec{L}}^2\right] = 0$$

Exercise. Prove that the above commutation relations hold.

Note that Eqs. (1.92) and (1.122) imply that it is not possible to measure any of the Cartesian angular momentum pairs simultaneously with an infinite precision (the Heisenberg uncertainty relation).

Based on Eq. (1.122), it is possible to find functions that are eigenfunctions of both $\hat{\vec{L}}^2$ and $\hat{L}_z$. It can be shown that for $\hat{\vec{L}}^2$ the eigenfunctions and eigenvalues are:

$$\begin{aligned}&\hat{\vec{L}}^2\psi_{l,m}(\theta,\phi) = l(l+1)\hbar^2\psi_{l,m}(\theta,\phi) \qquad (1.123)\\ &\text{where } \psi_{l,m} = Y_l^m(\theta,\phi)\\ &\text{Quantum numbers: } l = 0,1,2,3... \text{ and } |m| = 0,1,2,3,...l\end{aligned}$$

where l is the angular momentum quantum number and m is the magnetic quantum number. Note that here m has nothing to do with magnetism but the name originates from the fact that (electron or nuclear) spins follow the same laws of angular momentum. Functions Y_l^m are called spherical harmonics. Examples of spherical harmonics with various values of l and m are given below (with Condon-Shortley phase convention):

$$\begin{aligned}&Y_0^0 = \frac{1}{2\sqrt{\pi}}, , \; Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos(\theta),\; Y_1^1 = -\sqrt{\frac{3}{8\pi}}\sin(\theta)e^{i\phi} \qquad (1.124)\\ &Y_1^{-1} = \sqrt{\frac{3}{8\pi}}\sin(\theta)e^{-i\phi},\; Y_2^0 = \sqrt{\frac{5}{16\pi}}(3\cos^2(\theta)-1),\; Y_2^1 = -\sqrt{\frac{15}{8\pi}}\sin(\theta)\cos(\theta)e^{i\phi}\\ &Y_2^{-1} = \sqrt{\frac{15}{8\pi}}\sin(\theta)\cos(\theta)e^{-i\phi},\; Y_2^2 = \sqrt{\frac{15}{32\pi}}\sin^2(\theta)e^{2i\phi},\; Y_2^{-2} = \sqrt{\frac{15}{32\pi}}\sin^2(\theta)e^{-2i\phi}\end{aligned}$$

The following relations are useful when working with spherical harmonics:

$$\int\limits_0^{\pi}\int\limits_0^{2\pi} Y_{l'}^{m'*}(\theta,\phi)Y_l^m(\theta,\phi)\sin(\theta)d\theta d\phi = \delta_{l,l'}\delta_{m,m'} \qquad (1.125)$$

$$\int\limits_0^{\pi}\int\limits_0^{2\pi} Y_{l''}^{m''*}(\theta,\phi)Y_{l'}^{m'}(\theta,\phi)Y_l^m(\theta,\phi)\sin(\theta)d\theta d\phi = 0 \qquad (1.126)$$

unless $m'' = m + m'$ and a triangle with sides l, l', l'' can be formed: $l''^2 = l^2 + l'^2 - 2ll'\cos(\alpha)$ with some value of α ($|\cos(\alpha)| \le 1$)

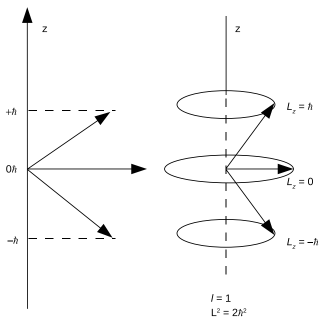
$$Y_l^{m*} = (-1)^m Y_l^{-m} \text{ (Condon-Shortley)} \qquad (1.127)$$

Operating on the eigenfunctions by L_z gives the following eigenvalues for L_z:

$$\hat{L}_z Y_l^m(\theta,\phi) = m\hbar Y_l^m(\theta,\phi) \text{ where } |m| = 0,...,l \qquad (1.128)$$

These eigenvalues are often denoted by L_z ($= m\hbar$). Note that specification of both L^2 and L_z provides all the information we can have about the system.

The vector model for angular momentum ("just a visualization tool"):



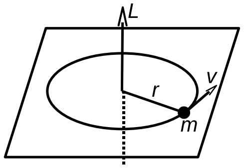
The circles represent the fact that the x & y components are unknown.

The following Maxima program can be used to evaluate spherical harmonics. Maxima follows the Condon-Shortley convention but may have a different overall sign than in the previous table.

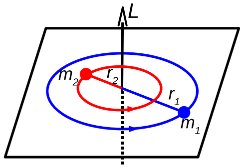
```
load(orthopoly);
/* spherical_harmonic(l, m, theta, phi) */
spherical_harmonic(0, 0, theta, phi); /* l = 0, m = 0 */
spherical_harmonic(1, 1, theta, phi);       /* l = 1, m = 1 */
```

1.11 The rigid rotor

A particle rotating around a *fixed point*, as shown below, has angular momentum and rotational kinetic energy ("rigid rotor").



Rotation about a fixed point



Rotation of diatomic molecule around the center of mass

The classical kinetic energy is given by $T = p^2/(2m) = (1/2)mv^2$. If the particle is rotating about a fixed point at radius r with a frequency ν (s^{-1} or Hz), the velocity of the particle is given by:

$$v = 2\pi r\nu = r\omega \tag{1.129}$$

where ω is the angular frequency (rad s^{-1} or rad Hz). The rotational kinetic energy can be now expressed as:

$$T = \frac{1}{2}mv^2 = \frac{1}{2}mr^2\omega^2 = \frac{1}{2}I\omega^2 \tag{1.130}$$

with $I = mr^2$ (the moment of inertia)

As I appears to play the role of mass and ω the role of linear velocity, the angular momentum can be defined as ($I = mr^2, \omega = v/r$):

$$L = \text{“mass”} \times \text{“velocity”} = I\omega = mvr = pr \tag{1.131}$$

Thus the rotational kinetic energy can be expressed in terms of L and ω:

$$T = \frac{1}{2}I\omega^2 = \frac{L^2}{2I} \tag{1.132}$$

Consider a classical rigid rotor corresponding to a diatomic molecule. Here we consider only *rotation restricted to a 2-D plane* where the two masses (i.e., the nuclei) rotate about their center of mass. First we set the origin at the center of mass and specify distances for masses 1 and 2 from it (R = distance between the nuclei, which is constant; “mass weighted coordinates”):

$$r_1 = \frac{m_2}{m_1 + m_2}R \text{ and } r_2 = \frac{m_1}{m_1 + m_2}R \tag{1.133}$$

Note that adding $r_1 + r_2$ gives R as it should. Also the moment of inertia for each nucleus is given by $I_i = m_i r_i^2$. The rotational kinetic energy is now a sum for masses 1 and 2 with the same angular frequencies (“both move simultaneously around the center of mass”):

$$T = \frac{1}{2}I_1\omega^2 + \frac{1}{2}I_2\omega^2 = \frac{1}{2}\left(I_1 + I_2\right)\omega^2 = \frac{1}{2}I\omega^2 \tag{1.134}$$

$$\text{with } I = I_1 + I_2 = m_1 r_1^2 + m_2 r_2^2 = \overbrace{\frac{m_1 m_2}{m_1 + m_2}R^2}^{(1.133)} = \overbrace{\mu R^2}^{(1.94)} \tag{1.135}$$

The rotational kinetic energy for a diatomic molecule can also be written in terms of angular momentum $L = L_1 + L_2$ (sometimes denoted by L_z where z signifies the axis of rotation):

$$T = \frac{1}{2}I\omega^2 = \overbrace{\frac{L^2}{2I}}^{(1.131)} = \overbrace{\frac{L^2}{2\mu R^2}}^{(1.135)} \tag{1.136}$$

Note that there is no potential energy involved in free rotation. In three dimensions we have to include rotation about each axis x, y and z in the kinetic energy (here vector $r = (R, \theta, \phi)$ with R fixed to the “bond length”):

$$T = T_x + T_y + T_z = \frac{L_x^2}{2\mu R^2} + \frac{L_y^2}{2\mu R^2} + \frac{L_z^2}{2\mu R^2} = \frac{\vec{L}^2}{2\mu R^2} \tag{1.137}$$

Transition from the above classical expression to quantum mechanics can be carried out by replacing the total angular momentum by the corresponding operator (Eq. (1.121)) and by noting that the external potential is zero (i.e., $V = 0$):

$$\hat{H} = \frac{\vec{\hat{L}}^2}{2I} \equiv -\frac{\hbar^2}{2I}\Lambda^2 \tag{1.138}$$

where $I = mr^2$. Note that for an asymmetric molecule, the moments of inertia may be different along each axis:

$$\hat{H} = \frac{\hat{L}_x^2}{2I_x} + \frac{\hat{L}_y^2}{2I_y} + \frac{\hat{L}_z^2}{2I_z} \tag{1.139}$$

The eigenvalues and eigenfunctions of $\hat{L}^2$ are given in Eq. (1.123). The solutions to the rigid rotor problem ($\hat{H}\psi = E\psi$) are then:

$$E_{l,m} = \frac{l(l+1)\hbar^2}{2I} \text{ where } l = 0, 1, 2, 3, ... \text{ and } |m| = 0, 1, 2, 3, ..., l \tag{1.140}$$

$$\psi_{l,m}(\theta, \phi) = Y_l^m(\theta, \phi) \tag{1.141}$$

In considering the rotational energy levels of linear molecules, the rotational quantum number l is usually denoted by J and m by m_J so that (each level is $(2J+1)$ fold degenerate):

$$E = \frac{\hbar^2}{2I}J(J+1) \tag{1.142}$$

and the total angular momentum (L^2) is given by:

$$L^2 = J(J+1)\hbar^2 \text{ where } J = 0, 1, 2, ... \tag{1.143}$$

$$\text{OR } L = \sqrt{J(J+1)}\hbar$$

Notes:

- Quantization in this equation arises from the cyclic boundary condition rather than the potential energy, which is identically zero.
- There is no rotational zero-point energy ($J = 0$ is allowed). The ground state rotational wavefunction has equal probability amplitudes for each orientation.
- The energies are independent of m_J. m_J introduces the degeneracy of a given J level.
- For non-linear molecules Eq. (1.142) becomes more complicated.

Example. What are the reduced mass and moment of inertia of H^{35}Cl? The equilibrium internuclear distance R_e is 127.5 pm (1.275 Å). What are the values of L, L_z and E for the state with $J = 1$? The atomic masses are: $m_{\mathrm{H}} = 1.673470 \times 10^{-27}$ kg and $m_{\mathrm{Cl}} = 5.806496 \times 10^{-26}$ kg.

Solution. First we calculate the reduced mass (Eq. (1.94)):

$$\mu = \frac{m_{\mathrm{H}} m_{^{35}\mathrm{Cl}}}{m_{\mathrm{H}} + m_{^{35}\mathrm{Cl}}} = \frac{(1.673470 \times 10^{-27}\text{ kg})(5.806496 \times 10^{-26}\text{ kg})}{(1.673470 \times 10^{-27}\text{ kg}) + (5.806496 \times 10^{-26}\text{ kg})}$$

$$= 1.62665 \times 10^{-27}\text{ kg}$$

Next, Eq. (1.135) gives the moment of inertia:

$$I = \mu R_e^2 = (1.626 \times 10^{-27}\ \mathrm{kg})(127.5 \times 10^{-12}\ \mathrm{m})^2 = 2.644 \times 10^{-47}\ \mathrm{kg\ m^2}$$

L is given by Eq. (1.143):

$$L = \sqrt{J(J+1)}\hbar = \sqrt{2}\left(1.054 \times 10^{-34}\ \mathrm{Js}\right) = 1.491 \times 10^{-34}\ \mathrm{Js}$$

L_z is given by Eq. (1.128):

$$L_z = -\hbar, 0, \hbar \text{ (three possible values)}$$

Energy of the $J = 1$ level is given by Eq. (1.142):

$$E = \frac{\hbar^2}{2I}J(J+1) = \frac{\hbar^2}{I} = 4.206 \times 10^{-22}\ \mathrm{J} = 21\ \mathrm{cm}^{-1}$$

This rotational spacing can be, for example, observed in gas phase infrared spectrum of HCl.

1.12 Postulates of quantum mechanics

The following set of assumptions ("postulates") lead to a consistent quantum mechanical theory:

1a: The state of quantum mechanical system is completely specified by a wavefunction $\psi(r, t)$ that is a function of the spatial coordinates of the particles and time. If the system is stationary, it can be described by $\psi(r)$ as it does not depend on time.

1b: The wavefunction ψ is a well-behaved function.

1c: The square of the wavefunction can be interpreted as a probability for a particle to exist at a given position or region in space is given by: $\psi^*(r, t)\psi(r, t)dxdydz$ ("the probability interpretation").

2: For every observable in classical mechanics there is a corresponding quantum mechanical linear operator. The operator is obtained from the classical expression by replacing the Cartesian momentum components by $-i\hbar\partial/\partial q$ where $q = x, y, z$. The spatial coordinates x, y and z are left as they are in the classical expression.

3: The possible measured values of any physical observable A correspond to the eigenvalues a_i of the equation: $\hat{A}\psi_i = a_i\psi_i$ where $\hat{A}$ is the operator corresponding to observable A.

4: If the wavefunction of the system is ψ, the probability of measuring the eigenvalue a_i (with ϕ_i being the corresponding eigenfunction) is: $|c_i|^2 = \left|\int\limits_{-\infty}^{\infty} \phi_i^* \psi d\tau\right|^2$.

5: The wavefunction of a system changes with time according to the time-dependent Schrödinger equation: $\hat{H}\psi(r,t) = i\hbar\frac{\partial\psi(r,t)}{\partial t}$.

6: The wavefunction of a system of Fermions (for example, electrons) must be anti-symmetric with respect to the interchange of any two particles (the Pauli exclusion principle). For Bosons the wavefunction must be symmetric. This applies only to systems with more than one particle (will be discussed in more detail later).

1.13 The time-dependent Schrödinger equation

- How does a quantum mechanical system evolve as a function of time?
- How does the time-independent Schrödinger equation follow from the time-dependent equation?
- What does it mean that the wavefunction is a complex valued function?

Time evolution of a quantum system is given by the time-dependent Schrödinger equation:

$$\hat{H}\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t} \tag{1.144}$$

where $\hat{H} = \hat{T} + \hat{V}$. When the potential operator $\hat{V}$ depends only on position and *not on time*, it is possible to separate Eq. (1.144) by using the following product function:

$$\Psi(x,t) = \psi(x)f(t) \tag{1.145}$$

Substitution of this into (1.144) gives:

$$\frac{1}{\psi(x)}\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi(x) = -\frac{\hbar}{i}\frac{1}{f(t)}\frac{df(t)}{dt} \tag{1.146}$$

The left hand side depends only on x and the right hand side only on t and thus both sides must be equal to a constant (denoted by E).

By substituting E into Eq. (1.146), we obtain two different equations:

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi(x) = E\psi(x) \tag{1.147}$$

$$-\frac{\hbar}{i}\frac{df(t)}{dt} = Ef(t) \tag{1.148}$$

Eq. (1.147) is the time-independent Schrödinger and the second equation can be integrated with the initial condition $\Psi(x,0) = \psi(x)$ (i.e., $f(0) = 1$) as:

$$f(t) = e^{-iEt/\hbar} \tag{1.149}$$

The time-dependent wavefunction is thus:

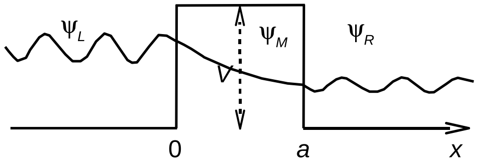
$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar} \tag{1.150}$$

where the complex phase carries information about the energy of the system.

A superposition of eigenstates can be used to construct so called wavepackets, which describe a localized system. Propagation of such wavepacket can be obtained by using the time-dependent Schrödinger equation. This is important when we are describing, for example, photodissociation of diatomic molecules using quantum mechanics.

1.14 Tunneling and reflection

Previously, we have seen that a particle may appear in regions, which are classically forbidden. For this reason, there is a non-zero probability that a particle may pass over an energy barrier, which is higher than the available kinetic energy ("tunneling"). This is demonstrated below ($V > E$).



Wavefunction for a particle with $E < V$ tunneling through a potential barrier

Consider the region left of the barrier (i.e. $x < 0$). Here the Schrödinger equation corresponds to that of a free particle ($E > 0$):

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_L(x) = E\psi_L(x) \text{ (L = "left side")} \tag{1.151}$$

The general solution to this equation is:

$$\psi_L(x) = Ae^{ikx} + Be^{-ikx} \text{ with } k^2 = \frac{2mE}{\hbar^2} \tag{1.152}$$

The term with k corresponds to an incoming wave (i.e., propagating from left to right) and $-k$ to a reflected wave (i.e., propagating from right to left).

Within the potential barrier ($0 < x < a$) the Schrödinger equation reads:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_M(x) + V\psi_M(x) = E\psi_M(x) \text{ (M = “middle”)} \tag{1.153}$$

where V is a constant (i.e., does not depend on x). When $V > E$, the general solution is:

$$\psi_M(x) = A'e^{Kx} + B'e^{-Kx} \text{ where } K^2 = \frac{2m\overbrace{(V-E)}^{>0}}{\hbar^2} \tag{1.154}$$

To the right of the potential barrier, we have a free propagating wave with only the right propagating wave component present:

$$\psi_R(x) = Fe^{ikx} \text{ (R = “right”)} \tag{1.155}$$

By requiring that the wavefunctions ψ_L, ψ_M and ψ_R, and their first derivatives are continuous, the following expression can be derived:

$$T = \frac{|F|^2}{|A|^2} = \left\{1 + \frac{\left(e^{Ka} - e^{-Ka}\right)^2}{16\epsilon(1-\epsilon)}\right\}^{-1} \text{ where } \epsilon = \frac{E}{V} \tag{1.156}$$

where T is the transmission coefficient. A value of zero means no tunneling and a value of one means complete tunneling. The corresponding reflection coefficient R can be defined using T as (conservation of probability):

$$R = 1 - T \tag{1.157}$$

Note that the above discussion **does not involve time**.

Example. Estimate the relative probabilities that a proton and a deuteron can tunnel through a rectangular potential of height 1.00 eV (1.60×10^{-19} J) and length 100 pm (1 Å) when their energy is 0.9 eV (i.e., $E - V = 0.10$ eV).

Solution. First we calculate K by using Eq. (1.154):

$$K_{\mathrm{H}} = \left\{ \frac{2\,\overbrace{(1.67\times 10^{-27}\ \mathrm{kg})}^{\text{mass of H}}\times(1.6\times 10^{-20}\ \mathrm{J})}{(1.055\times 10^{-34}\ \mathrm{Js})^2} \right\}^{1/2} = 6.9\times 10^{10}\ \mathrm{m}^{-1}$$

$$K_{\mathrm{D}} = \left\{ \frac{2\,\overbrace{(2\times 1.67\times 10^{-27}\ \mathrm{kg})}^{\text{mass of D}}\times(1.6\times 10^{-20}\ \mathrm{J})}{(1.055\times 10^{-34}\ \mathrm{Js})^2} \right\}^{1/2} = 9.8\times 10^{10}\ \mathrm{m}^{-1}$$

By using these values and Eq. (1.156), we get:

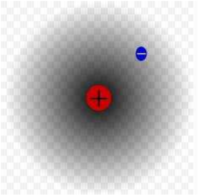
$$\epsilon = E/V = \frac{0.9\ \mathrm{eV}}{1.0\ \mathrm{eV}} = 0.9$$

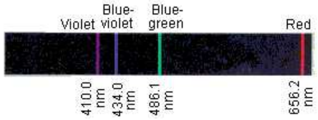
$$T_{\mathrm{H}} = \left\{1 + \frac{\left(e^{K_{\mathrm{H}}a} - e^{-K_{\mathrm{H}}a}\right)^2}{16\epsilon(1-\epsilon)}\right\}^{-1} = 1.4\times 10^{-6}$$

$$T_{\mathrm{D}} = \left\{1 + \frac{\left(e^{K_{\mathrm{D}}a} - e^{-K_{\mathrm{D}}a}\right)^2}{16\epsilon(1-\epsilon)}\right\}^{-1} = 4.4\times 10^{-9}$$

$$\frac{T_{\mathrm{H}}}{T_{\mathrm{D}}} = 310 \text{ (H tunnels more efficiently than D)}$$

Chapter 2: Quantum mechanics of atoms





Emission spectrum of hydrogen atom

2.1 Schrödinger equation for hydrogenlike atoms

Consider one electron and one nucleus with charge Ze ("hydrogenlike atom") where e is the magnitude of the electron charge ($1.6021773 \times 10^{-19}$ C) and Z is the atomic number. Examples of such systems are: H, He^{+}, Li^{2+}, etc. For these simple atomic systems, the Schrödinger equation can be solved analytically. Recall that the hydrogen atom Schrödinger equation was given in Eq. (1.30). This can be generalized for systems having nuclei with charges other than +1 as follows:

$$-\frac{\hbar^2}{2m_e}\Delta\psi_i(x,y,z) - \frac{Ze^2}{4\pi\epsilon_0\sqrt{x^2+y^2+z^2}}\psi_i(x,y,z) = E_i\psi_i(x,y,z) \tag{2.158}$$

where m_e is the electron mass, ϵ_0 is the vacuum permittivity, and subscripts for ψ and E signify the fact that there are multiple (ψ_i, E_i) combinations that satisfy Eq. (2.158). Note that we should have used the reduced mass (μ; see Eq. (1.94)) for the nucleus and electron above, but because the nucleus is much heavier then the electron, the reduced mass is very close to the electron mass.

Because of the spherical symmetry of the Coulomb potential in Eq. (2.158), it is convenient to work in spherical coordinates (see Eq. (1.40)):

$$\left[-\frac{\hbar^2}{2m_e}\Delta - \frac{Ze^2}{4\pi\epsilon_0 r}\right]\psi_i(r,\theta,\phi) = E_i\psi(r,\theta,\phi) \tag{2.159}$$

where the Laplacian (Δ) is expressed in spherical coordinates:

$$\Delta \equiv \nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2} \tag{2.160}$$

Note that the Coulomb potential term above depends only on r (and not on θ or ϕ). By using Eq. (1.121) the Laplacian can be written in terms of the angular momentum operator $\hat{L}$:

$$\Delta = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{1}{r^2}\frac{\hat{L}^2}{\hbar^2} = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{1}{r^2}\frac{\hat{L}^2}{\hbar^2} \tag{2.161}$$

By substituting this into Eq. (2.159) and multiplying both sides by $2m_er^2$, we get:

$$\left[-\hbar^2r^2\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) - \frac{m_er^2Ze^2}{2\pi\epsilon_0 r} + \hat{L}^2\right]\psi_i(r,\theta,\phi) = (2m_er^2E_i)\psi_i(r,\theta,\phi) \tag{2.162}$$

Since the operator can be split into r and angle dependent parts, the solution can be written as a product of the radial and angular parts ("separation of variables"):

$$\psi_i(r,\theta,\phi) = R_{nl}(r) Y_l^m(\theta,\phi) \tag{2.163}$$

where R_{nl} is called the radial wavefunction and Y_l^m are eigenfunctions of $\hat{L}^2$ as discussed earlier. Eq. (2.162) can now be rewritten as:

$$\begin{aligned} &-\hbar^2 Y_l^m(\theta,\phi) r^2 \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) R_{nl}(r) - Y_l^m(\theta,\phi)\frac{m_e r^2 Z e^2}{2\pi\epsilon_0 r} R_{nl}(r) \\ &+ Y_l^m(\theta,\phi) R_{nl}(r) \underbrace{l(l+1)\hbar^2}_{=\hat{L}^2} = (2m_e r^2 E_{nl}) Y_l^m(\theta,\phi) R_{nl}(r) \end{aligned} \tag{2.164}$$

Next we divide the above equation side by side by $Y_l^m \times (2m_e r^2)$:

$$\left[-\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) - \frac{Ze^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2m_e r^2}\right] R_{nl}(r) = E_{nl} R_{nl}(r) \tag{2.165}$$

Substituting $R_{nl}(r) = S_{nl}(r)/r$ and multiplying both sides by r gives a slightly simpler form:

$$-\frac{\hbar^2}{2m_e}\frac{\partial^2 S_{nl}(r)}{\partial r^2} + \underbrace{\left(-\frac{Ze^2}{4\pi\epsilon_0 r} + \overbrace{\frac{l(l+1)\hbar^2}{2m_e r^2}}^{\text{“centrifugal potential”}}\right)}_{\equiv V_{eff}(r)} S_{nl}(r) = E_{nl} S_{nl}(r) \tag{2.166}$$

with $l = 0, 1, 2, \ldots$.

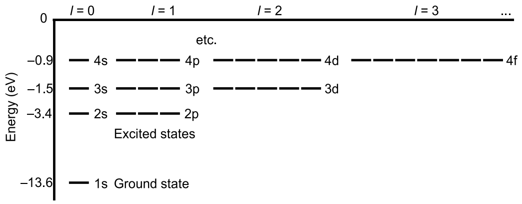
The eigenvalues E_{nl} and and the radial eigenfunctions R_{nl} can be written as (derivations are lengthy but standard math):

$$E_{nl} = -\frac{m_e e^4 Z^2}{32\pi^2\epsilon_0^2\hbar^2 n^2} \text{ with } n = 1, 2, 3\ldots \text{ (independent of } l, l < n) \tag{2.167}$$

$$R_{nl}(r) = \rho^l L_{n+l}^{2l+1}(\rho)\exp\left(-\frac{\rho}{2}\right) \text{ with } \rho = \frac{2Zr}{na_0} \text{ and } a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \tag{2.168}$$

where $L_{n+l}^{2l+1}(\rho)$ are associated Laguerre polynomials. Explicit expressions will be given later in the text. The constant a_0 is called the Bohr radius. Some of the first radial wavefunctions are listed on the next page.

To demonstrate Eq. (2.167), some of the electronic energy levels of hydrogen atom are shown below.



Energy unit Hartree:

$$E_h = \frac{e^2}{4\pi\epsilon_0 a_0} = 27.211 \text{ eV} \tag{2.169}$$

Orbital	n	l	R_{nl}
1s	1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho/2}$
2s	2	0	$\frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2} (2-\rho)e^{-\rho/2}$
2p	2	1	$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} \rho e^{-\rho/2}$
3s	3	0	$\frac{1}{9\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2} (6-6\rho-\rho^2)e^{-\rho/2}$
3p	3	1	$\frac{1}{9\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} (4-\rho)\rho e^{-\rho/2}$
3d	3	2	$\frac{1}{9\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2} \rho^2 e^{-\rho/2}$

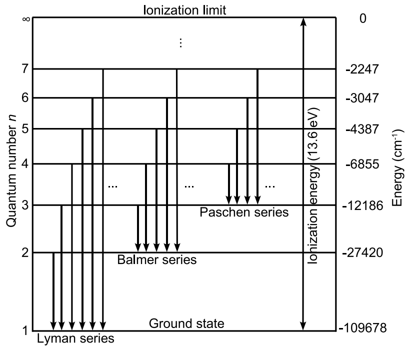
Table: Examples of the radial wavefunctions for hydrogenlike atoms.

2.2 The spectrum of hydrogenlike atoms

Eq. (2.167) can be expressed in wavenumber units (m^{-1}; usually cm^{-1} is used):

$$\tilde{E}_n = \frac{E_n}{hc} = \frac{E_n}{2\pi\hbar c} = -\overbrace{\frac{m_e e^4}{4\pi c(4\pi\epsilon_0)^2\hbar^3}}^{\equiv R} \times \frac{Z^2}{n^2} \quad (\tilde{\ }\text{for wavenumber units}) \tag{2.170}$$

where R is the Rydberg constant and we have assumed that the nucleus has an infinite mass. To be exact, the Rydberg constant depends on the nuclear mass, but this difference is very small. For example, $R_H = 1.096775856 \times 10^7$ $m^{-1} = 1.096775856 \times 10^5$ cm^{-1}, $R_D = 1.097074275 \times 10^5$ cm^{-1}, and $R_\infty = 1.0973731534 \times 10^5$ cm^{-1}. The latter value is for a nucleus with an infinite mass (i.e., $\mu = m_e$).



H atom emission lines

Eq. (2.170) can be used to calculate the differences in the energy levels:

$$\Delta\tilde{v}_{n_1,n_2} = \tilde{E}_{n_2} - \tilde{E}_{n_1} = -\frac{R_H Z^2}{n_2^2} + \frac{R_H Z^2}{n_1^2} = R_H Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \quad (2.171)$$

In the previous figure, the Lyman series is obtained with $n_1 = 1$, Balmer with $n_1 = 2$, and Paschen with $n_1 = 3$. The ionization energy (i.e., when the electron is detached from the atom; see previous figure) is given by:

$$E_i = R_H Z^2 \left(\frac{1}{1^2} - \frac{1}{\infty}\right) \quad (2.172)$$

For a ground state hydrogen atom (i.e., $n = 1$), the above equation gives a value of 109678 cm^{-1} = 13.6057 eV. Note that the larger the nuclear charge Z is, the larger the binding energy is.

Recall that the wavefunctions for hydrogenlike atoms are $R_{nl}(r)Y_l^m(\theta, \phi)$ with $l < n$. For the first shell we have only one wavefunction: $R_{10}(r)Y_0^0(\theta, \phi)$. This state is usually labeled as $1s$, where 1 indicates the shell number (n) and s corresponds to orbital angular momentum l being zero. For $n = 2$, we have several possibilities: $l = 0$ or $l = 1$. The former is labeled as $2s$. The latter is $2p$ state and consists of three degenerate states: (for example, $2p_x$, $2p_y$, $2p_z$ or $2p_{+1}$, $2p_0$, $2p_{-1}$). In the latter notation the values for m have been indicated as subscripts. Previously, we have seen that:

$$m = -l, -l+1, ..., 0, ..., l-1, l \quad (2.173)$$

For historical reasons, the following letters are used to express the value of l:

$$l = 0, 1, 2, 3, ... \quad (2.174)$$
$$\text{symbol} = s, p, d, f, ...$$

To summarize the quantum numbers in hydrogenlike atoms:

$$n = 1, 2, 3, ... \quad (2.175)$$

$$l = 0, 1, 2, ..., n-1 \quad (2.176)$$

$$m = 0, \pm 1, \pm 2, ..., \pm l \quad (2.177)$$

For a given value of n, the level is n^2 times degenerate. There is one more quantum number that has not been discussed yet: the spin quantum number. For one-electron systems this can have values $\pm\frac{1}{2}$ (will be discussed in more detail later). In absence of magnetic fields the spin levels are degenerate and therefore the total degeneracy of the levels is $2n^2$.

The total wavefunction for a hydrogenlike atom is (m is usually denoted by m_l):

$$\psi_{n,l,m_l}(r,\theta,\phi) = N_{nl} R_{nl}(r) Y_l^{m_l}(\theta,\phi) \tag{2.178}$$

$$N_{nl} = \sqrt{\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n\left[(n+l)!\right]}} \tag{2.179}$$

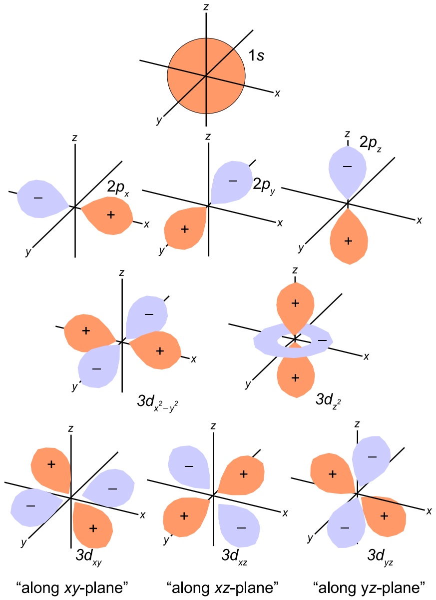
$$R_{nl}(r) = \rho^l e^{-\rho/2} \underbrace{L^{2l+1}_{n-l-1}(\rho)}_{\substack{\text{associated}\\ \text{Laguerre}\\ \text{polynomial}}},\ \rho = \frac{2Zr}{na_0}$$

n	l	m	Wavefunction
1	0	0	$\psi_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\sigma}$
2	0	0	$\psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} (2-\sigma)e^{-\sigma/2}$
2	1	0	$\psi_{2p_z} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2}\cos(\theta)$
2	1	±1	$\psi_{2p_x} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2}\sin(\theta)\cos(\phi)$
			$\psi_{2p_y} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2}\sin(\theta)\sin(\phi)$

Table: Cartesian hydrogenlike wavefunctions ($\sigma = \frac{Zr}{a_0}$).

n	l	m	Wavefunction
3	0	0	$\psi_{3s} = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \left(27 - 18\sigma + 2\sigma^2\right) e^{-\sigma/3}$
3	1	0	$\psi_{3p_z} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} (6-\sigma)\,\sigma e^{-\sigma/3}\cos(\theta)$
3	1	±1	$\psi_{3p_x} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} (6-\sigma)\,\sigma e^{-\sigma/3}\sin(\theta)\cos(\phi)$
			$\psi_{3p_y} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} (6-\sigma)\,\sigma e^{-\sigma/3}\sin(\theta)\sin(\phi)$
3	2	0	$\psi_{3d_{z^2}} = \frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3}\left(3\cos^2(\theta) - 1\right)$
3	2	±1	$\psi_{3d_{xz}} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3}\sin(\theta)\cos(\theta)\cos(\phi)$
			$\psi_{3d_{yz}} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3}\sin(\theta)\cos(\theta)\sin(\phi)$
3	2	±2	$\psi_{3d_{x^2-y^2}} = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3}\sin^2(\theta)\cos(2\phi)$
			$\psi_{3d_{xy}} = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3}\sin^2(\theta)\sin(2\phi)$

Table: Cartesian hydrogenlike wavefunctions (continued).



Plots demonstrating the shapes of different hydrogenlike atomic orbitals.

$L_0^k(x)$	1
$L_1^k(x)$	$k - x + 1$
$L_2^k(x)$	$\frac{1}{2}\left(k^2 + 3k + x^2 - 2(k+2)x + 2\right)$
$L_3^k(x)$	$\frac{1}{6}\left(k^3 + 6k^2 + 11k - x^3 + 3(k+3)x^2 - 3(k+2)(k+3)x + 6\right)$
$L_4^k(x)$	$\frac{1}{24}(x^4 - 4(k+4)x^3 + 6(k+3)(k+4)x^2 - 4k(k(k+9)+26)x$ $-96x + k(k+5)(k(k+5)+10) + 24)$

Table: Examples of associated Laguerre polynomials.

Advanced topic. The following Maxima program generates the associated Laguerre polynomial $L_5^k(x)$:

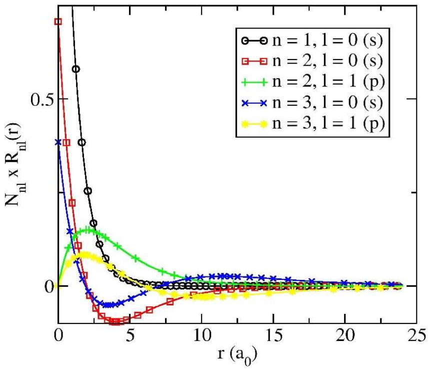
```
/* Evaluate associate Laguerre polynomial */

/* Load orthopoly package */
load(orthopoly);
/* Generate the polynomial using gen_laguerre() function and simplify
 * the result using ratsimp() function. */
ratsimp(gen_laguerre(5,k,x));
```

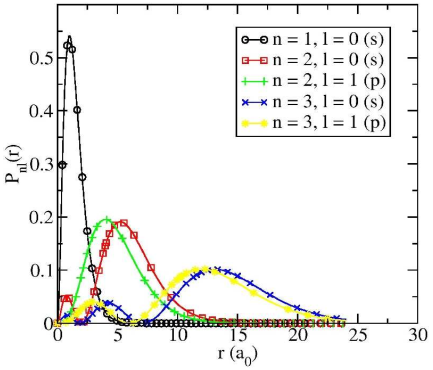
2.3 Eigenfunctions and probability densities for hydrogenlike atoms

A wavefunction for a one-electron system is called an orbital. For an atomic system such as H (hydrogen atom), it is called an atomic orbital.

The orbital plots on the previous slide demonstrated the shapes of the orbitals but this does not tell us anything about the radial extent (i.e., how far the orbital reaches).



Radial wavefunctions $N_{nl} \times R_{nl}(r)$.



Radial probabilities $P_{nl}(r)$.

Advanced topic. The following Maxima program can be used to plot the radial wavefunctions on the previous page (if wxMaxima is used, replace plot2d with wxplot2d):

```
/* Plot normalized radial wavefunctions for hydrogen atom */
load(orthopoly);
Z:1; /* Nuclear charge 1 (hydrogen) */
a0:1;/* Output in the units of Bohr */
/* Definition of the radial wavefunction */
R(r,n,l):= (
  rho:2*Z*r/(n*a0),  /* definition of rho */
  norm:sqrt((2*Z/(n*a0))^3 * (n - l - 1)! / (2*n*((n + l)!))),
  norm * rho^l * exp(-rho/2) * gen_laguerre(n-l-1,2*l+1,rho)
  );
/* Plot the radial wavefunction (range from 0 to 24) */
plot2d(
  [R(r,1,0),R(r,2,0),R(r,2,1),R(r,3,0),R(r,3,1)],
  [r,0,24],
  [
    legend,"n = 1, l = 0(s)", "n = 2, l = 0(s)",
    "n = 2, l = 1(p)", "n = 3, l = 0(s)", "n = 3, l = 1(p)"
  ],
  [xlabel,"r(a0)"],
  [ylabel,"Nnl x Rnl(r)"]
  );
```

Note that:

- As the value of Z is increased, the radial extent decreases. This indicates that for higher nuclear charge, the electrons will reside closer to the nucleus.
- The radial functions have $n - l - 1$ zero values ("nodes") between distances from zero to infinity.
- The existence of the nodes makes the wavefunctions orthogonal. For example, ψ_{1s} and ψ_{2s} in hydrogenlike atoms are orthogonal.

When visualizing the radial probabilities, it is possible to do directly plot the square of the radial wavefunction (R_{nl}^2) or the radial probability density (P_{nl}):

$$P_{nl}(r) = r^2 N_{nl}^2 R_{nl}^2(r) \tag{2.180}$$

According to this expression, the most probable radius for an electron on hydrogen atom $1s$ orbital is a_0 (the Bohr radius). Previous figures showed examples of R_{nl} and P_{nl}. Probability densities are useful, for example, in understanding charge distributions in atoms and molecules.

As the principal quantum number n increases, the electron moves out to greater distances from the nucleus. The average distance for an electron in a given orbital (with quantum numbers n and l) is given by (this is *not* the expectation value):

$$\begin{aligned}\langle r \rangle_{nl} &= \int_0^\infty r \times P_{nl}(r)dr \qquad (2.181)\\ &= \frac{n^2 a_0}{Z}\{1 + \frac{1}{2}[1 - \frac{l(l+1)}{n^2}]\}\end{aligned}$$

Note that the expectation value of r and the most probable value for r are not equal. The expectation value can be thought of like "an average" and the most probable value like a "maximum value".

The probability density (including the angular variables) for the electron in a hydrogenlike atom is given by:

$$\psi_{nlm}^*(r,\theta,\phi)\psi_{nlm}(r,\theta,\phi) = |N_{nl}R_{nl}(r)Y_l^m(\theta,\phi)|^2 \tag{2.182}$$

This function depends on three variables and is difficult to plot directly. Previously, we have seen that it is convenient to plot contour levels, which contain the electron with, for example, 90% probability.

For degenerate states with $l > 0$, we have an additional degree of freedom in choosing how to represent the orbitals. In fact, any linear combination of given $3l$ orthogonal eigenfunctions corresponding to a degenerate set with orbital angular momentum l, is also a solution to the Schrödinger equation.

Two commonly used representations are the Cartesian form, which are real valued functions and have been, in the case of $l = 1$, denoted by p_x, p_y and p_z, and the eigenfunctions of the angular momentum (L^2 and L_z), which are complex valued and are denoted by p_{-1}, p_0 and p_{+1}. The relation between the representations is:

$$\begin{aligned} p_x &= -\frac{1}{\sqrt{2}}\left(p_{+1} - p_{-1}\right) \propto \sin(\theta)\cos(\phi) \propto x \qquad (2.183) \\ p_y &= \frac{i}{\sqrt{2}}\left(p_{+1} + p_{-1}\right) \propto \sin(\theta)\sin(\phi) \propto y \\ p_z &= p_0 \end{aligned}$$

Note by combining p_x, p_y and p_z, the lobe of the orbital can be made to point at any direction. For d-orbitals, we have five degenerate levels:

$$\begin{aligned} d_{x^2-y^2} &= \frac{1}{\sqrt{2}}\left(d_{+2} + d_{-2}\right), \; d_{xy} = -\frac{i}{\sqrt{2}}\left(d_{+2} - d_{-2}\right) \qquad (2.184) \\ d_{xz} &= -\frac{1}{\sqrt{2}}\left(d_{+1} - d_{-1}\right), \; d_{yz} = \frac{i}{\sqrt{2}}\left(d_{+1} + d_{-1}\right) \\ d_{z^2} &= d_0 \end{aligned}$$

2.4 Orbital angular momentum of the hydrogen atom

In hydrogenlike atoms degeneracy implies that the angular momentum is non-zero. If the quantum numbers l and m are known, it is possible to calculate L^2 and L_z directly based on Eqs. (1.123) and (1.128):

$$L^2 = l(l+1)\hbar^2 \text{ (or formally } L = \sqrt{l(l+1)}\hbar) \qquad (2.185)$$

$$L_z = m\hbar \text{ where } m = -l, ..., 0, ..., +l \qquad (2.186)$$

Without external electric or magnetic fields and electron spin, the energy of hydrogen atom is independent of quantum number m. The Lorentz force law (see your physics course lecture notes) gives the interaction of a charged particle with an electromagnetic field (for a classical particle):

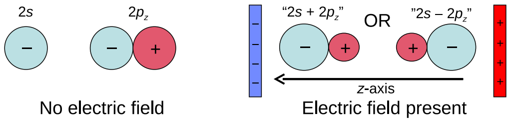
$$\vec{F} = q\left(\vec{E} + \vec{v} \times \vec{B}\right) \qquad (2.187)$$

where vector $\vec{F}$ is the force experienced by the charged particle, q is the particle charge, $\vec{E}$ is the electric field vector, $\vec{v}$ is the particle velocity vector and $\vec{B}$ is the magnetic field vector. Even though the above expression strictly applies to the classical case, it suggests that the presence of external magnetic or electric fields should somehow affect the electron orbit in hydrogenlike atoms.

The effect of electric field. The effect of electric field is to mix the orbitals of the same symmetry along the direction of the applied field. This is called the Stark effect. By assuming that the electric field is time-independent, the quantum mechanical operator is proportional to position vector $\vec{r}$ that is in the direction of the applied field. Thus the Hamiltonian, including the hydrogenlike atomic part and the external field, is (direction chosen along the z-axis below):

$$\hat{H}_{tot} = \hat{H}_{atom} + e\epsilon\hat{z} \text{ (the general form: } e\vec{\epsilon}\cdot\vec{r}\text{)} \tag{2.188}$$

where ϵ is the electric field strength (N C^{-1} or V m^{-1}) and e is the electron charge. Consider, for example, $2s$ and three degenerate $2p$ orbitals. The p_x and p_y orbitals are unaffected by the field but the $2s$ and $2p_z$ orbitals are mixed by the field:



The low energy state has the electron wavefunction distorted towards the positively charged pole above.

Johannes Stark (1874 – 1957), German physicist, Nobel prize (1919).

Because $2p_x$ and $2p_y$ are not affected by the field, this means that the degeneracy of the $2p$ orbitals is broken. Also $2s$ and $2p_z$ are no longer pure states and experience shift in energy. This shift can be observed by spectroscopic measurements.

The effect of magnetic field. As shown in Eq. (2.187), a moving charge will also interact with an external magnetic field. When an electron is in a state with $l > 0$, it can be thought to be in quantum mechanical circular motion around the nucleus and generate its own magnetic field. Note that this motion is not classical but here we are just trying to obtain a wire frame model based on classical interpretation. The electron has now a magnetic moment given by (see your physics lecture notes):

$$\vec{\mu} = \gamma_e\vec{L} \tag{2.189}$$

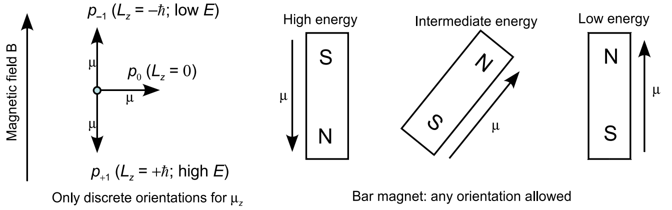
where γ_e is the magnetogyric ratio of the electron ($-\frac{e}{2m_e}$). We choose the external magnetic field to lie along the z-axis and therefore it is important to consider the z component of $\vec{\mu}$:

$$\mu_z = -\left(\frac{e}{2m_e}\right)L_z = -\left(\frac{e\hbar}{2m_e}\right)m \equiv -\mu_B m \tag{2.190}$$

where μ_B is the Bohr magneton as defined above. The interaction between a magnetic moment and an external magnetic field is given by (classical expression):

$$E = -\vec{\mu}\cdot\vec{B} = -|\vec{\mu}||\vec{B}|\cos(\alpha) \tag{2.191}$$

where α is the angle between the two magnetic field vectors. This gives the energy for a bar magnet in presence of an external magnetic field:



In quantum mechanics, a magnetic moment (here corresponding to a p-electron) may only take specific orientations. In classical mechanics any orientation is allowed. When the external magnetic field is oriented along z-axis, Eq. (2.191) reads:

$$E = -\mu_z B = \frac{eB}{2m_e} L_z \tag{2.192}$$

where the z-axis is often called the quantization axis. The eigenvalues of $\hat{L}_z$ essentially give the possible orientations of the magnetic moment with respect to the external field. For example, consider an electron on $2p$ orbital in a hydrogenlike atom. The electron may reside on any of $2p_{+1}$, $2p_0$ or $2p_{-1}$ orbitals (degenerate without the field). For these orbitals L_z may take the following values $(+\hbar, 0, -\hbar)$:

$$\hat{L}_z|p_{+1}\rangle = +1 \times \hbar|p_{+1}\rangle,\ \hat{L}_z|p_0\rangle = 0 \times \hbar|p_0\rangle,\ \hat{L}_z|p_{-1}\rangle = -1 \times \hbar|p_{-1}\rangle \tag{2.193}$$

The relative orientations with respect to the external magnetic field are shown on the left side of the figure.

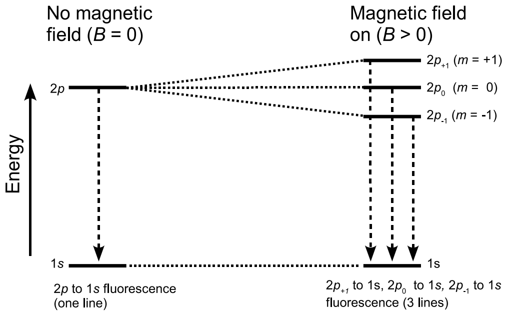
The total quantum mechanical Hamiltonian for a hydrogenlike atom in a magnetic field can now be written as:

$$\hat{H} = \hat{H}_0 + \frac{eB}{2m_e}\hat{L}_z \tag{2.194}$$

where $\hat{H}_0$ denotes the Hamiltonian in absence of the magnetic field. The eigenvalues for Eq. (2.194) are (derivation not shown):

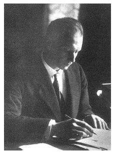
$$E_{nlm} = -\frac{m_e e^4 Z^2}{2(4\pi\epsilon_0)^2 n^2 \hbar^2} + \mu_B m B \tag{2.195}$$

where $n = 1, 2, ...$; $l = 0, 1, ..., n-1$; and $m = -l, ..., 0, ..., +l$. In the presence of magnetic field, the $(2l+1)$ degenerate levels have been split (i.e., the degeneracy is lifted). This is called the orbital Zeeman effect.



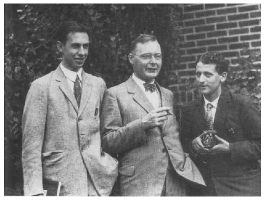
Splitting of the p-states in presence of magnetic field.

2.5 Electron spin



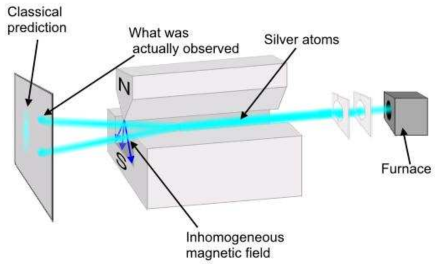
Walter Gerlach (1889 - 1979)

Otto Stern (1888 - 1969), Nobel prize 1943



L: George Uhlenbeck (1900 - 1988),
M: Hendrik Kramers (1894 - 1952),
R: Samuel Goudsmit (1902 - 1978).

Stern-Gerlach experiment:



Note that silver atoms have one unpaired electron.

The electron appears to have an intrinsic magnetic moment, which originates from electron spin.

The Schrödinger equation does not account for electron spin. The concept of electron spin originates from Dirac's relativistic equation. However, it can be included in the Schrödinger equation as an extra quantum number (s). Furthermore, it appears to follow the general laws of angular momentum.

The spin angular momentum vector $\vec{S}$ has a magnitude: $|\vec{S}| = S = \sqrt{s(s+1)}\hbar$ where s is the spin quantum number ($\frac{1}{2}$). A crude way of thinking about the origin of the spin angular momentum is to consider the magnetic moment to arise from the internal spinning motion of the electron about its own axis. However, this is not exactly true because electrons have internal structure that we have ignored here.

To summarize the behavior of electron spin angular momentum:

$$S^2 = s(s+1)\hbar^2 = \frac{3}{4}\hbar^2 \text{ (since } s = \frac{1}{2}) \tag{2.196}$$

$$S_z = m_s\hbar \text{ with } m_s = \pm\frac{1}{2} \;\; (+\frac{1}{2} = \text{“spin up”};\; -\frac{1}{2} = \text{“spin down”}) \tag{2.197}$$

The corresponding operators are denoted by $\hat{S}_z$ and $\hat{S}^2$. How about the eigenfunctions?

The eigenfunctions are denoted by α and β and we don't write down their specific forms. The following relations apply for these eigenfunctions:

$$\hat{S}^2\alpha \equiv \hat{S}^2|\alpha\rangle = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2\alpha = \frac{3}{4}\hbar^2\alpha \equiv \frac{3}{4}\hbar^2|\alpha\rangle \tag{2.198}$$

$$\hat{S}^2\beta \equiv \hat{S}^2|\beta\rangle = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2\beta = \frac{3}{4}\hbar^2\beta \equiv \frac{3}{4}\hbar^2|\beta\rangle \tag{2.199}$$

$$\hat{S}_z\alpha \equiv \hat{S}_z|\alpha\rangle = +\frac{1}{2}\hbar\alpha \equiv +\frac{1}{2}\hbar|\alpha\rangle \tag{2.200}$$

$$\hat{S}_z\beta \equiv \hat{S}_z|\beta\rangle = -\frac{1}{2}\hbar\beta \equiv -\frac{1}{2}\hbar|\beta\rangle \tag{2.201}$$

Note that all the following operators commute: $\hat{H}$, $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$, and $\hat{S}_z$. This means that they all can be specified simultaneously. The spin eigenfunctions are taken to be orthonormal:

$$\int \alpha^*\alpha d\sigma \equiv \langle\alpha|\alpha\rangle = \int \beta^*\beta d\sigma \equiv \langle\beta|\beta\rangle = 1 \tag{2.202}$$

$$\int \alpha^*\beta d\sigma \equiv \langle\alpha|\beta\rangle = \int \beta^*\alpha d\sigma \equiv \langle\beta|\alpha\rangle = 0 \tag{2.203}$$

where the integrations are over variables that the spin eigenfunctions depend on. Note that we have not specified the actual forms these eigenfunctions. We have only stated that they follow from the rules of angular momentum. A complete wavefunction for a hydrogen like atom must specify also the spin part. The total wavefunction is then a product of the spatial wavefunction and the spin part.

Note that analogously, the $\hat{S}_x$ and $\hat{S}_y$ operators can be defined. These do not commute with $\hat{S}_z$. Because electrons have spin angular momentum, the unpaired electrons in silver atoms (Stern-Gerlach experiment) produce an overall magnetic moment (“the two two spots of silver atoms”). The spin magnetic moment is proportional to its spin angular momentum (compare with Eq. (2.189)):

$$\vec{\hat{\mu}}_S = -\frac{g_e e}{2m_e}\vec{\hat{S}} \tag{2.204}$$

where g_e is the free electron g-factor (2.002322 from quantum electrodynamics). The z-component of the spin magnetic moment is (z is the quantiziation axis):

$$\hat{\mu}_z = -\frac{g_e e}{2m_e}\hat{S}_z \tag{2.205}$$

Since S_z is given by 2.197, we have:

$$\mu_z = -\frac{g_e e\hbar}{2m_e}m_s = -g_e\mu_B m_s \tag{2.206}$$

Thus the total energy for a spin in an external magnetic field is:

$$E = g_e\mu_B m_s B \tag{2.207}$$

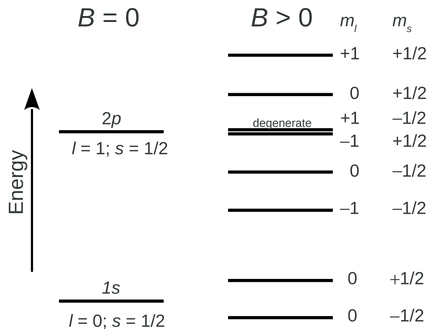
where B is the magnetic field strength (in Tesla).

By combining the contributions from the hydrogenlike atom Hamiltonian and the orbital and electron Zeeman terms, we have the total Hamiltonian:

$$\hat{H} = \hat{H}_0 + \frac{eB}{2m_e}\hat{L}_z + \frac{g_e eB}{2m_e}\hat{S}_z = \hat{H}_0 + \frac{eB}{2m_e}\left(\hat{L}_z + g_e\hat{S}_z\right) \tag{2.208}$$

The eigenvalues of this operator are (derivation not shown):

$$E_{n,m_l,m_s} = -\frac{m_e e^4 Z^2}{2(2\pi\epsilon_0)^2\hbar n^2} + \frac{eB\hbar}{2m_e}\left(m_l + g_e m_s\right) \tag{2.209}$$



Splitting of hydrogenlike atom energy levels in external magnetic field

2.6 Variational method

The Schrödinger equation can only be solved analytically for simple systems, which consist of just one particle. When many particles interact through physically meaningful potentials, analytic solution is not possible. For example, no analytic solution to Schrödinger equation describing helium atom (two electrons) has been found. Thus it is important to develop approximate methods for finding the solutions and to be able to evaluate how close the approximate solution is to the correct one.

The variational method states, that for any "trial" wavefunction ψ_t, the following inequality holds:

$$\begin{aligned}\frac{\int \psi_t^*\hat{H}\psi_t d\tau}{\int \psi_t^*\psi_t d\tau} &\equiv \frac{\langle\psi_t|\hat{H}|\psi_t\rangle}{\langle\psi_t|\psi_t\rangle} \geq E_1 \\ \int \psi_t^*\hat{H}\psi_t d\tau &\equiv \langle\psi_t|\hat{H}|\psi_t\rangle \geq E_1 \text{ (only when } \psi_t \text{ normalized!)}\end{aligned} \tag{2.210}$$

where $\hat{H}$ is the Hamiltonian and E_1 is the true ground-state energy. If the true ground-state wavefunction ψ_1 is inserted in place of ψ_t, the equality is reached. For all other wavefunctions (often called trial wavefunctions) the energy expectation value (i.e. the left side) will always be larger. The ratio on the first line is also called the "Rayleigh ratio".

Proof. The proof is as follows:

First we express a given trial solution ψ_t as a linear combination of the eigenfunctions of $\hat{H}$. The eigenfunctions are said to form a complete set of basis functions and hence any well behaved function can be expressed as a linear combination of these basis functions.

$$\psi_t = \sum_{i=1}^{\infty} c_i \psi_i \text{ where } \hat{H}\psi_i = E_i \psi_i \tag{2.211}$$

Next, consider the following integral (assume that ψ_t is normalized):

$$\int \psi_t^* \left(\hat{H} - E_1\right) \psi_t d\tau \overbrace{=}^{(2.211)} \sum_{i,j=1}^{\infty} c_i^* c_j \int \psi_i^* \left(\hat{H} - E_1\right) \psi_j d\tau \tag{2.212}$$

$$= \sum_{i,j=1}^{\infty} c_i^* c_j \left(E_j - E_1\right) \underbrace{\int \psi_i^* \psi_j d\tau}_{\text{orthogonality}} = \sum_{j=1}^{\infty} \underbrace{c_j^* c_j}_{\equiv |c_j|^2 \geq 0} \underbrace{\left(E_j - E_1\right)}_{\geq 0} \geq 0$$

$$\Rightarrow \int \psi_t^* \left(\hat{H} - E_1\right) \psi_t d\tau \geq 0 \Rightarrow \int \psi_t^* \hat{H} \psi_t d\tau \geq E_1$$

Note that we have exchanged (infinite) summation and integration orders above and this requires that the series is uniformly convergent (not shown above).

Example. Consider a particle in a one-dimensional box problem (boundaries at 0 and a). Use the variational theorem to obtain an upper bound for the ground state energy by using the following normalized wavefunction:

$$\psi_t(x) = \frac{\sqrt{30}}{a^{5/2}} x(a - x)$$

Solution. Clearly, this is not the correct ground state wavefunction (see 1.76). Next, we check that this wavefunction satisfies the boundary conditions: $\psi_t(0) = 0$ and $\psi_t(a) = 0$ (OK). The Hamiltonian for this problem is:

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \ (0 \leq x \leq a)$$

Plugging in both the Hamiltonian and ψ_t into 2.210 gives:

$$\int_0^a \psi_t^* \hat{H} \psi_t d\tau = -\frac{30\hbar^2}{2a^5 m} \int_0^a \left(ax - x^2\right) \frac{d^2}{dx^2} \left(ax - x^2\right) dx$$

$$= \frac{30\hbar^2}{a^5 m} \int_0^a \left(ax - x^2\right) dx = \frac{5\hbar^2}{a^2 m} \overbrace{\geq}^{(1.74)} E_1$$

As indicated above, this gives an upper limit for the ground state energy E_1.

2.7 Helium atom

The Schrödinger equation for helium atom is already extremely complicated from the mathematical point of view. No analytic solutions to this equation has been found. However, with certain approximations, useful results can be obtained. The Hamiltonian for He atom can be written as:

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m_e}\left(\Delta_1 + \Delta_2\right)}_{\text{Kinetic energy}} \underbrace{-\frac{1}{4\pi\epsilon_0}\left(\frac{Ze^2}{r_1} + \frac{Ze^2}{r_2} \overbrace{-\frac{e^2}{r_{12}}}^{\text{Tough!!}}\right)}_{\text{Potential energy}} \tag{2.213}$$

where Δ_1 is the Laplacian for the coordinates of electron 1, Δ_2 for electron 2, r_1 is the distance of electron 1 from the nucleus, r_2 is the distance of electron 2 from the nucleus and r_{12} is the distance between electrons 1 and 2. For He atom $Z = 2$.

1. Approximation: Ignore the "Tough" term containing r_{12}. In this case the Hamiltonian consists of a sum of two hydrogenlike atoms:

$$\hat{H} = \hat{H}_1 + \hat{H}_2 \tag{2.214}$$

$$\hat{H}_1 = -\frac{\hbar^2}{2m_e}\Delta_1 - \frac{Ze^2}{4\pi\epsilon_0 r_1} \tag{2.215}$$

$$\hat{H}_2 = -\frac{\hbar^2}{2m_e}\Delta_2 - \frac{Ze^2}{4\pi\epsilon_0 r_2} \tag{2.216}$$

Because the Hamiltonian is a sum of two independent parts, the Schrödinger equation separates into two (each hydrogelike atom equation):

$$\hat{H}_1\psi(r_1) = E_1\psi(r_1) \tag{2.217}$$

$$\hat{H}_2\psi(r_2) = E_2\psi(r_2) \tag{2.218}$$

The total energy is a sum of E_1 and E_2 and the total wavefunction is a product of $\psi(r_1)$ and $\psi(r_2)$. Based on our previous wavefunction table for hydrogenlike atoms, we have:

$$E = E_1 + E_2 \overbrace{=}^{(2.192)} -RZ^2\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right) \tag{2.219}$$

$$\psi(r_1)\psi(r_2) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr_1/a_0}\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr_2/a_0} = \frac{1}{\pi}\left(\frac{Z}{a_0}\right)^{3} e^{-Z(r_1+r_2)/a_0} \tag{2.220}$$

For a ground state He atom both electron reside on the lowest energy orbital and therefore the total wavefunction is $\psi(r_1, r_2) = \psi(r_1)\psi(r_2) = \psi(1)\psi(2) = 1s(1)1s(2)$. The energy obtained from this approximation is not sufficiently accurate (missing electron – electron repulsion) but the wavefunction can be used for qualitative analysis. The variational principle Eq. (2.210) gives a systematic way to asses how good our approximation is. The exact ground state energy has been found (very extensive analytic & numerical calculations) as -79.0 eV. By using the approximate wavefunction, we can calculate the expectation value for energy. This yields -74.8 eV and thus the error in energy for this wavefunction is -5.2 eV. Note that the approximate value is, in accordance with the variational principle, higher than the true energy.

2. A better approximation: We can take the wavefunction from the previous step and use the nuclear charge Z as a variational parameter. The variational principle states that minimization of the energy expectation value with respect to Z should approach the true value from above (but obviously will not reach it). By judging the energy, we can say that this new wavefunction is better than the previous wavefunction. The obtained value of Z is less than the true Z (= 2). This can be understood in terms of electrons shielding the nucleus from each other and hence giving a reduced nuclear charge. If the wavefunction in Eq. (2.220) is used in calculating the energy expectation value, we get:

$$E = \langle\psi|\hat{H}|\psi\rangle = ... = \left[Z^2 - \frac{27Z}{8}\right]\frac{e^2}{4\pi\epsilon_0 a_0} \tag{2.221}$$

In order to minimize Eq. (2.221), we should differentiate it with respect to Z and set it to zero (extremum point; here it is clear that this point is a minimum):

$$\frac{dE}{dZ} = \left(2Z - \frac{27}{8}\right)\frac{e^2}{4\pi\epsilon_0 a_0} = 0 \tag{2.222}$$

The above equation gives $Z = 27/16 \approx 1.7$ and $E \approx -77.5$ eV (previous -74.8 eV and exact -79.0 eV). This result could be improved by adding more terms and variables into the trial wavefunction. For example, higher hydrogenlike atom orbitals with appropriate variational coefficients would yield a much better result.

Another type of approximate method is based on perturbation theory, which would typically assume that the electron – electron repulsion is treated as an additional (small) perturbation to case 1) above.

2.8 Pauli exclusion principle

Our previous wavefunction for He atom did not include electron spin. For two electrons, the spin functions can be written as products:

$$\alpha(1)\alpha(2),\ \beta(1)\alpha(2),\ \alpha(1)\beta(2) \text{ or } \beta(1)\beta(2) \tag{2.223}$$

where, for example, $\alpha(1)$ indicates that electron 1 has spin α. Electrons are indistinguishable and therefore it makes no sense to try to use the two middle terms alone but combine them as:

Wolfgang Pauli (1900 - 1958), Austrian physicist, Nobel prize 1945.

$$\alpha(1)\alpha(2) \text{ (symmetric if 1 and 2 are exchanged)} \tag{2.224}$$

$$\beta(1)\beta(2) \text{ (symmetric)} \tag{2.225}$$

$$\frac{1}{\sqrt{2}}\left(\alpha(1)\beta(2)+\alpha(2)\beta(1)\right) \text{ (symmetric)} \tag{2.226}$$

$$\frac{1}{\sqrt{2}}\left(\alpha(1)\beta(2)-\alpha(2)\beta(1)\right) \text{ (antisymmetric)} \tag{2.227}$$

In 1926 Pauli showed that the wavefunction must be antisymmetric with respect to exchange of the electron indices. This applies also for systems with more than two electrons. An outcome of this principle is that no two electrons can have exactly the same quantum numbers: n, l, m_l, s, m_s. In non-relativistic quantum mechanics this is a postulate.

In order to construct a complete wavefunction for He atom, we need to tag on the spin part to the wavefunction in Eq. (2.220):

$$\psi = 1s(1)1s(2) \times \frac{1}{\sqrt{2}}\left(\alpha(1)\beta(2)-\alpha(2)\beta(1)\right) \tag{2.228}$$

John Slater (1900 - 1976), American physicist

A generalization of this result for many-electron systems was proposed by Slater in 1929:

$$\psi(r_1,...,r_n) = \frac{1}{\sqrt{n!}}\begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1) & ... \\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2) & ... \\ 1s(3)\alpha(3) & ... & ... & ... \\ ... & ... & ... & ... \end{vmatrix} \tag{2.229}$$

For a ground state He atom this can be written:

$$\psi(r_1,r_2) = \frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1)\alpha(1) & 1s(1)\beta(1) \\ 1s(2)\alpha(2) & 1s(2)\beta(2) \end{vmatrix} \tag{2.230}$$

The Slater determinant automatically ensures that the total wavefunction is antisymmetric. Note that from the mathematical point of view the antisymmetry requirement restricts the allowed solutions to the Schrödinger equation. The lowest energy solutions are typically symmetric and the antisymmetric states correspond to higher energy. However, one must be careful with terminology here because only the antisymmetric states exist for electrons (Fermions) and as such they are the lowest energy (ground state) solutions for them. Particles that have symmetric wavefunctions are called Bosons (for example, ^{4}He atoms).

In general, particles with half-integral spin ($s = \frac{1}{2}, \frac{3}{2}, ...$) are Fermions (Fermi-Dirac statistics) and particles with integral spin ($s = 0, 1, 2, ...$) are Bosons (Bose-Einstein statistics). Note that electron spin enters the Hamiltonian only when external fields are present or when spin-orbit interaction is included (will be discussed later).

Example. Show that the Slater determinant in Eq. (2.229) for the ground state helium atom is an eigenfunction of the total spin operator $\hat{S}_{z,tot} = \hat{S}_{z_1} + \hat{S}_{z_2}$, where 1 and 2 refer to the two electrons.

Solution. First we recall how $\hat{S}_z$ operates on electron spin as follows (Eqs. (2.200) and (2.201)):

$$\hat{S}_z|\alpha\rangle = +\frac{\hbar}{2}|\alpha\rangle \text{ and } \hat{S}_z|\beta\rangle = -\frac{\hbar}{2}|\beta\rangle$$

Next, we expand the Slater determinant in Eq. (2.229):

$$\psi = \overbrace{1s(1)1s(2)}^{\text{symmetric}} \times \overbrace{\frac{1}{\sqrt{2}}\left(\alpha(1)\beta(2) - \alpha(2)\beta(1)\right)}^{\text{antisymmetric}}$$

Operate on this by $\hat{S}_{z_1}$ and $\hat{S}_{z_2}$. They operate only on the spin-part and on the corresponding electron only:

$$\hat{S}_{z_1}|\psi\rangle = |1s(1)1s(2)\rangle \times \frac{1}{\sqrt{2}}\left(\frac{\hbar}{2}|\alpha(1)\beta(2)\rangle + \frac{\hbar}{2}|\beta(1)\alpha(2)\rangle\right)$$

$$\hat{S}_{z_2}|\psi\rangle = |1s(1)1s(2)\rangle \times \frac{1}{\sqrt{2}}\left(-\frac{\hbar}{2}|\alpha(1)\beta(2)\rangle - \frac{\hbar}{2}|\beta(1)\alpha(2)\rangle\right)$$

$$\Rightarrow\ \hat{S}_{z,tot}|\psi\rangle = \left(\hat{S}_{z_1} + \hat{S}_{z_2}\right)|\psi\rangle = \hat{S}_{z_1}|\psi\rangle + \hat{S}_{z_2}|\psi\rangle = 0$$

Note that the two terms are equal in magnitude but have opposite signs and they cancel. Thus the eigenvalue of the z-component of the total spin is zero. It can also be shown that $S^2 = 0$. This kind of electronic configuration is called a *singlet state* (i.e. the two electrons have opposite spins).

Previously we had both electrons on $1s$ orbital with opposite spins. If the electrons reside on two different orbitals, for example, $1s$ and $2s$, we would have an excited helium atom. Such state can be created experimentally by a suitable high-energy process (laser induced break-down etc.). The spatial part of the wavefunction is $\psi = 1s(1)2s(2)$. It could as well be $\psi = 2s(1)1s(2)$ as we cannot distinguish the electrons from each other. Obviously we must form a linear combination of these so that both electrons appear identical (two possibilities):

$$\psi_{sym} = \frac{1}{\sqrt{2}}\left(1s(1)2s(2) + 1s(2)2s(1)\right) \text{ (symmetric)} \tag{2.231}$$

$$\psi_{asym} = \frac{1}{\sqrt{2}}\left(1s(1)2s(2) - 1s(2)2s(1)\right) \text{ (antisymmetric)} \tag{2.232}$$

Note that these two states may have different energies.

Next, we consider adding the spin part to these wavefunctions. Because the electrons are on two different orbitals, we have the following four possibilities:

$$\left.\begin{array}{r}\phi_1 = \alpha(1)\alpha(2) \text{ (symmetric)}\\ \phi_2 = \beta(1)\beta(2) \text{ (symmetric)}\\ \phi_3 = \frac{1}{\sqrt{2}}\left(\alpha(1)\beta(2) + \beta(1)\alpha(2)\right) \text{ (symmetric)}\end{array}\right\} \text{Triplet state}$$

$$\left.\phi_4 = \frac{1}{\sqrt{2}}\left(\alpha(1)\beta(2) - \beta(1)\alpha(2)\right)\right\} \text{Singlet state}$$

Before we can combine the spatial and spin wavefunctions, we must consider the symmetries of these functions. Remember that the total wavefunction must be antisymmetric. Thus the allowed combinations are: symmetric (spatial) × antisymmetric (spin) or antisymmetric (spatial) × symmetric (spin). The total wavefunction for the triplet state is therefore:

$$\psi_1 = \frac{1}{\sqrt{2}}\left(1s(1)2s(2) - 2s(1)1s(2)\right)\alpha(1)\alpha(2) \tag{2.233}$$

$$\psi_2 = \frac{1}{2}\left(1s(1)2s(2) - 2s(1)1s(2)\right)\left(\alpha(1)\beta(2) + \beta(1)\alpha(2)\right) \tag{2.234}$$

$$\psi_3 = \frac{1}{\sqrt{2}}\left(1s(1)2s(2) - 2s(1)1s(2)\right)\beta(1)\beta(2) \tag{2.235}$$

For the singlet state we have:

$$\psi_4 = \frac{1}{2}\left(1s(1)2s(2) + 2s(1)1s(2)\right)\left(\alpha(1)\beta(2) - \alpha(2)\beta(1)\right) \tag{2.236}$$

Singlet and triplet states have been named after the number of spin degenerate levels they posses. The total spin $\hat{S}^2$ and $\hat{S}_z$ operators for these states yield:

$$\text{Triplet: } \begin{cases}\hat{S}_z|\psi_1\rangle = +\hbar|\psi_1\rangle,\ \hat{S}_z|\psi_2\rangle = 0|\psi_2\rangle,\ \hat{S}_z|\psi_3\rangle = -\hbar|\psi_3\rangle\\ \hat{S}^2|\psi_i\rangle = 2\hbar^2|\psi_i\rangle \text{ where } i = 1, 2, 3.\end{cases} \tag{2.237}$$

$$\text{Singlet: } \begin{cases}\hat{S}_z|\psi_4\rangle = 0|\psi_4\rangle\\ \hat{S}^2|\psi_4\rangle = 0|\psi_4\rangle\end{cases}$$

For helium atom the singlet/triplet consideration is only relevant for the excited states but for atoms with more electrons this may have to be considered in order to determine the ground state. When more electrons are added, the wavefunction becomes more complicated. For example, the Slater determinant for Li can be written as:

$$\psi = \frac{1}{\sqrt{6}}\begin{vmatrix}1s(1)\alpha(1) & 1s(1)\beta(1) & 2s(1)\alpha(1)\\ 1s(2)\alpha(2) & 1s(2)\beta(2) & 2s(2)\alpha(2)\\ 1s(3)\alpha(3) & 1s(3)\beta(3) & 2s(3)\alpha(3)\end{vmatrix} \tag{2.238}$$

Note that the last column could have been labeled as β as well (degeneracy).

2.9 Hartree-Fock self-consistent field method

Even approximate methods for many-electron atoms become very complicated to treat with a pen and paper. Fortunately modern computers can be programmed to solve this type of problems efficiently. Such approach relies heavily on the methods of numerical analysis.

In 1928 Douglas Hartree introduced the self-consistent field (SCF) method. This method can be used to calculate an approximate wavefunction and energy for any ground-state atom (or molecule).

If the inter-electron repulsion terms in the Schrödinger equation are ignored, the n-electron equation can be separated into n one-electron equations (just like was done for He). The approximate wavefunction is then a product of the one-electron wavefunctions (orbitals).

Douglas Hartree
(1897 - 1958)
English physicist

Hartree used a symmetric variational wavefunction corresponding to a product of the orbital functions ϕ_i:

$$\psi = \phi_1\phi_2...\phi_n \tag{2.239}$$

where each orbital satisfies the hydrogenlike Schrödinger equation (i.e. just one electron):

$$-\frac{\hbar^2}{2m_e}\Delta\phi_i(x,y,z) + V_i(x,y,z)\phi_i(x,y,z) = \epsilon_i\phi_i \tag{2.240}$$

where ϵ_i is the energy of the orbital i. There are n such equations for each electron in the atom (or molecule). The effective potential V_i depends on other orbitals and hence the n equations are coupled and must be solved iteratively. For the exact form of the potential, see Molecular Quantum Mechanics (3rd ed.) by Atkins and Friedman. The SCF process is continued until the orbitals and their energies no longer change during the iteration. Note that the Hartree approach is missing two important effects: antisymmetry of the wavefuinction and so called electron correlation (not discussed further here). The antisymmetry is required by the Pauli principle.

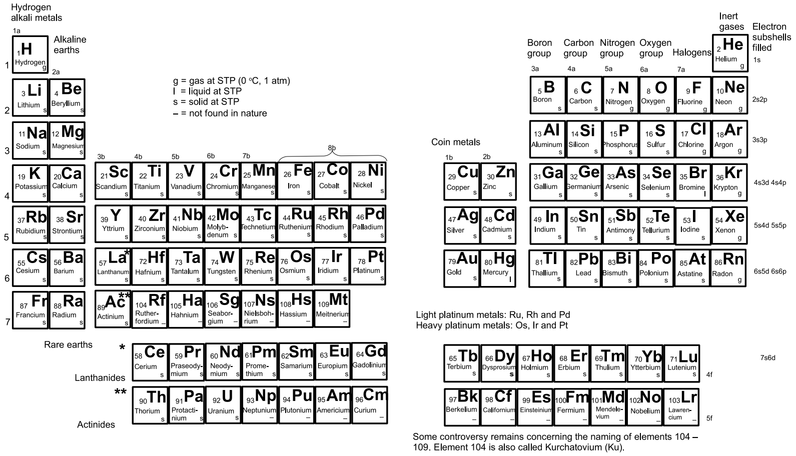
In 1930 Fock and Slater concluded that the wavefunction must be antisymmetric and the Hartree method should employ the Slater determinant form (Eq. (2.229)), which includes spin orbitals. This method is referred to as the Hartree-Fock (HF) method. Note that we have skipped all the details of the model as well as its derivation (see the previously mentioned reference for more information). There are number of methods (computationally very demanding) that can include electron correlation on top of the HF model (configuration interaction (CI) and coupled clusters (CC); see Introduction to Computational Chemistry by Jensen). Computational methods typically employ a set of Gaussian functions for describing the orbitals ("basis set"). The larger the basis set, the better results it gives but at the expense of computer time. These basis sets are typically expressed with various acronyms like STO-3G, 3-21G, 6-311G*, etc.

2.10 The periodic table and the aufbau principle

The quantum theory of atoms provides an explanation of the structure of the periodic table. The electron subshells in atoms are designated as $1s$, $2s$, $2p$, $3s$, ..., where the number denotes the quantum number n and the letter gives the orbital angular momentum quantum number l. According to the Pauli exclusion principle, all s subshells may contain 2 electrons (with α and β spins), p subshells 6, and d subshells 10. Thus each subshell may have a maximum of $2(2l+1)$ electrons.

To find the ground-state electron configuration of an atom, we add electrons to the subshells (i.e., orbitals) beginning with the lowest energy orbital and remember that two electrons (with opposite spins) go on each orbital. Note that this approach is approximate since it relies on the one-electron hydrogenlike atom orbitals. For this reason, it is often difficult to predict the energy order of orbitals. The symbols He, Ne, Ar, ... (or sometimes in brackets) are used to represent closed-shell electron configurations. With this notation it is not necessary to explicitly list the inner shell electron configuration.

Quantum mechanics explains the logic behind the periodic table of elements: along the columns the number of outer shell electrons varies and along the rows the number of inner shell orbitals increases.



g = gas at STP (0 °C, 1 atm)
l = liquid at STP
s = solid at STP
– = not found in nature

Light platinum metals: Ru, Rh and Pd
Heavy platinum metals: Os, Ir and Pt

Some controversy remains concerning the naming of elements 104 – 109. Element 104 is also called Kurchatovium (Ku).

The periodic table of elements.

- Within a row in the periodic table, the atomic radius tends to decrease with the atomic number.
- Within a column in the table, the atomic radius tends to increase with the atomic number.

Element	Symbol	Atomic number	Relative atomic mass (AMU)	Atom radius (pm)	Electron config.	Term symbol	Ionization energy (eV) I / II	Electron affinity (eV)	Electron negativity
Actinium	Ac	89	(227)	245	Rn 6d^1 7s^2	$^2D_{3/2}$	6.9 / 12.1	–	1.1
Aluminum	Al	13	26.98154	202	Ne 3s^2 3p^1	$^2P_{1/2}$	6.0 / 18.8	0.5	1.5
Americium	Am	95	(243)	242	Rn 5f^7 7s^2	$^8S_{7/2}$	– / –	–	1.3
Antimony	Sb	51	121.75	168	Kr 4d^{10} 5s^2 5p^3	$^4S_{3/2}$	8.6 / 16.5	–	1.9
Argon	Ar	18	39.948	89	Ne 3s^2 3p^6	$^1S_0$	15.8 / 27.6	–	–
Arsenic	As	33	74.9216	141	Ar 3d^{10} 4s^2 4p^3	$^4S_{3/2}$	9.8 / 18.6	–	2.0
Astatine	At	85	(210)	132	Xe 4f^{14} 5d^{10} 6s^2 6p^5	$^2P_{3/2}$	– / –	–	2.2
Barium	Ba	56	137.327	248	Xe 6s^2	$^1S_0$	5.2 / 10.0	–	0.9
Berkelium	Bk	97	(247)	226	Rn 5f^9 7s^2	$^8H_{17/2}$	– / –	–	–
Beryllium	Be	4	9.0122	149	1s^2 2s^2	$^1S_0$	9.3 / 18.2	–	1.5
Bishmuth	Bi	83	208.980	188	Xe 4f^{14} 5d^{10} 6s^2 6p^3	$^4S_{3/2}$	7.3 / 16.7	–	1.9
Boron	B	5	10.811	134	1s^2 2s^2 2p^1	$^2P_{1/2}$	8.3 / 25.1	0.3	2.0
Bromine	Br	35	79.904	114	Ar 3d^{10} 4s^2 4p^5	$^2P_{3/2}$	11.8 / 21.6	3.4	2.8
Cadmium	Cd	48	112.412	152	Kr 4d^{10} 5s^2	$^1S_0$	9.0 / 16.9	–	1.7
Calcium	Ca	20	40.078	225	Ar 4s^2	$^1S_0$	6.1 / 11.9	–	1.0
Californium	Cf	98	(251)	224	Rn 5f^{10} 7s^2	$^5I_8$	– / –	–	–
Carbon	C	6	12.01115	100	1s^2 2s^2 2p^2	$^3P_0$	11.3 / 24.4	1.2	2.5
Cerium	Ce	58	140.12	241	Xe 4f^1 5d^1 6s^2	$^1G_4$	6.6 / 12.3	–	1.1
Cesium	Cs	55	132.9054	322	Xe 6s^1	$^2S_{1/2}$	3.9 / 25.1	–	0.7
Chlorine	Cl	17	35.4527	90	Ne 3s^2 3p^5	$^2P_{3/2}$	13.0 / 23.8	3.7	3.0
Chromium	Cr	24	51.9961	197	Ar 3d^5 4s^1	$^7S_3$	6.8 / 16.5	–	1.6
Cobalt	Co	27	58.9332	162	Ar 3d^7 4s^2	$^4F_{9/2}$	7.9 / 17.1	–	1.8
Copper	Cu	29	63.546	163	Ar 3d^{10} 4s^1	$^2S_{1/2}$	7.7 / 20.3	2.4	1.9
Curium	Cm	96	(247)	228	Rn 5f^7 6d^1 7s^2	$^8S_{7/2}$	– / –	–	–
Dysprosium	Dy	66	162.50	236	Xe 4f^{10} 6s^2	$^5I_8$	6.8 / –	–	–
Einsteinium	Es	99	(252)	222	Rn 5f^{11} 7s^2	$^5I_{15/2}$	– / –	–	–
Erbium	Er	68	167.26	230	Xe 4f^{12} 6s^2	$^3H_6$	6.1 / –	–	1.2
Europium	Eu	63	151.96	245	Xe 4f^7 6s^2	$^8S_{7/2}$	5.7 / 11.2	–	–
Fermium	Fm	100	(257)	221	Rn 5f^{12} 7s^2	$^3H_6$	– / –	–	–
Fluorine	F	9	18.998403	60	1s^2 2s^2 2p^5	$^2P_{3/2}$	17.4 / 35.0	3.5	4.0
Francium	Fr	87	(223)	313	Rn 7s^1	$^2S_{1/2}$	4.0 / –	–	0.7
Gadolinium	Gd	64	157.25	226	Xe 4f^7 5d^1 6s^2	$^9D_2$	6.2 / 12	–	1.1
Gallium	Ga	31	69.723	196	Ar 3d^{10} 4s^2 4p^1	$^2P_{1/2}$	6.0 / 20.6	–	1.6
Germanium	Ge	32	72.59	160	Ar 3d^{10} 4s^2 4p^2	$^3P_0$	7.9 / 15.9	–	1.8

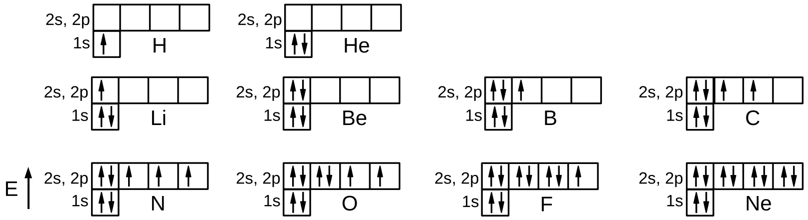
Table: Atomic data (part 1).

Element	Symbol	Atomic number	Relative atomic mass	Atom radius (pm)	Electron config.	Term symbol	Ionization energy (eV) I / II	Electron affinity (eV)	Electron negativity
Gold	Au	79	196.9665	162	Xe 4f^{14} 5d^{10} 6s^1	$^2S_{1/2}$	9.2 / 25.1	–	2.4
Hafnium	Hf	72	178.49	191	Xe 4f^{14} 5d^2 6s^2	$^3F_2$	7.0 / 14.9	–	1.3
Helium	He	2	4.002602	54	1s^2	$^1S_0$	24.6 / 54.4	0.2	–
Holmium	Ho	67	164.930	233	Xe 4f^{11} 6s^2	$^4I_{15/2}$	– / –	–	1.2
Hydrogen	H	1	1.00798	79	1s^1	$^2S_{1/2}$	13 / –	0.8	2.1
Indium	In	49	114.82	216	Kr 4d^{10} 5s^2 5p^1	$^2P_{1/2}$	5.8 / 18.9	–	1.7
Iodine	I	53	126.9044	138	Kr 4d^{10} 5s^2 5p^5	$^2P_{3/2}$	10.5 / 19.1	3.1	2.5
Iridium	Ir	77	192.22	165	Xe 4f^{14} 5d^7 6s^2	$^4F_{9/2}$	9.2 / –	–	2.2
Iron	Fe	26	55.844	168	Ar 3d^6 4s^2	$^5D_4$	7.9 / 16.2	–	1.8
Kyrpton	Kr	36	83.80	103	Ar 3d^{10} 4s^2 4p^6	$^1S_0$	14.0 / 24.6	–	–
Lanthanum	La	57	138.91	232	Xe 5d^1 6s^2	$^2D_{3/2}$	5.6 / 11.4	–	1.1
Lawrencium	Lr	103	(261)	216	Rn 5f^{14} 6d^1 7s^2	$^2P_{1/2}$	– / –	–	–
Lead	Pb	82	207.19	169	Xe 4f^{14} 5d^{10} 6s^2 6p^2	$^3P_0$	7.4 / 15.0	–	1.8
Lithium	Li	3	6.941	205	1s^2 2s^1	$^2S_{1/2}$	5.4 / 75.6	0.6	1.0
Lutetium	Lu	71	174.97	200	Xe 4f^{14} 5d^1 6s^2	$^2D_{3/2}$	6.2 / 14.7	–	1.2
Magnesium	Mg	12	24.3051	178	Ne 3s^2	$^1S_0$	7.6 / 15.0	–	1.2
Manganese	Mn	25	54.9380	173	Ar 3d^5 4s^2	$^6S_{5/2}$	7.4 / 15.6	–	1.5
Mendelevium	Md	101	(258)	219	Rn 5f^{13} 7s^2	$^2F_{7/2}$	– / –	–	–
Mercury	Hg	80	200.59	156	Xe 4f^{14} 5d^{10} 6s^2	$^1S_0$	10.4 / 18.8	1.5	1.9
Molybdenum	Mo	42	95.93	194	Kr 4d^5 5s^1	$^7S_3$	7.1 / 16.2	–	1.8
Neodymium	Nd	60	144.24	255	Xe 4f^4 6s^2	$^5I_4$	6.3 / –	–	–
Neon	Ne	10	20.180	53	1s^2 2s^2 2p^6	$^1S_0$	21.6 / 41.1	–	–
Neptunium	Np	93	(237)	234	Rn 5f^4 6d^1 7s^2	$^4L_{11/2}$	– / –	–	1.3
Nickel	Ni	28	58.69	157	Ar 3d^8 4s^2	$^3F_4$	7.6 / 18.2	–	1.8
Niobium	Nb	41	92.906	100	Kr 4d^4 5s^1	$^6D_{1/2}$	6.9 / 14.3	–	1.6
Nitrogen	N	7	14.00672	81	1s^2 2s^2 2p^3	$^4S_{3/2}$	14.5 / 29.6	0.05	3.0
Nobelium	No	102	(259)	218	Rn 5f^{14} 7s^2	$^1S_0$	– / –	–	–
Osmium	Os	76	190.2	169	Xe 4f^{14} 5d^6 6s^2	$^5D_4$	8.7 / 17	–	2.2
Oxygen	O	8	15.9994	70	1s^2 2s^2 2p^4	$^3P_2$	13.6 / 35.1	1.5	3.5
Palladium	Pd	46	106.42	76	Kr 4d^{10}	$^1S_0$	8.3 / 19.4	–	2.2
Phosphorus	P	15	30.97376	130	Ne 3s^2 3p^3	$^4S_{3/2}$	11.0 / 19.7	1.1	2.1
Platinum	Pt	78	195.08	175	Xe 4f^{14} 5d^9 6s^1	$^3D_3$	9.0 / 18.6	–	2.2
Plutonium	Pu	94	(244)	244	Rn 5f^6 7s^2	$^3F_0$	5.8 / –	–	–
Polonium	Po	84	(209)	170	Xe 4f^{14} 5d^{10} 6s^2 6p^4	$^3P_2$	8.4 / –	–	–
Potassium	K	19	39.0983	280	Ar 4s^1	$^2S_{1/2}$	4.3 / 31.8	0.8	0.8

Table: Atomic data (part 2).

Element	Symbol	Atomic number	Relative atomic mass	Atom radius (pm)	Electron config.	Term symbol	Ionization energy (eV) I / II	Electron affinity (eV)	Electron negativity
Praseodymium	Pr	59	140.9076	258	Xe $4f^3\ 6s^2$	$^4I_{9/2}$	5.8 / –	–	1.1
Prometium	Pm	61	(145)	251	Xe $4f^5\ 6s^2$	$^6H_{5/2}$	– / –	–	–
Protactinium	Pa	91	(231)	239	Rn $5f^2\ 6d^1\ 7s^2$	$^4K_{11/2}$	– / –	–	1.5
Radium	Ra	88	(226)	262	Rn $7s^2$	$^1S_0$	5.3 / 10.1	–	0.9
Radon	Rn	86	(222)	124	Xe $4f^{14}\ 5d^{10}\ 6s^2\ 6p^6$	$^1S_0$	10.7 / –	–	–
Rhenium	Re	75	186.207	173	Xe $4f^{14}\ 5d^5\ 6s^2$	$^6S_{5/2}$	7.9 / 16.6	–	1.9
Rhodium	Rh	45	102.9055	179	Kr $4d^8\ 5s^1$	$^4F_{9/2}$	7.5 / 18.1	–	2.2
Rubidium	Rb	37	85.4678	268	Kr $5s^1$	$^2S_{1/2}$	4.2 / 27.5	–	0.8
Ruthenium	Ru	44	101.07	183	Kr $4d^7\ 5s^1$	$^5F_5$	7.4 / 16.8	–	2.2
Samarium	Sm	62	150.36	248	Xe $4f^6\ 6s^2$	$^7F_0$	5.6 / 11.2	–	1.2
Scandium	Sc	21	44.95591	212	Ar $3d^1\ 4s^2$	$^2D_{3/2}$	6.6 / 12.8	–	1.3
Selenium	Se	34	78.96	126	Ar $3d^{10}\ 4s^2\ 4p^4$	$^3P_2$	9.8 / 21.5	1.7	2.4
Silicon	Si	14	28.0855	157	Ne $3s^2\ 3p^2$	$^3P_0$	8.1 / 16.3	–	1.8
Silver	Ag	47	107.868	172	Kr $4d^{10}\ 5s^1$	$^2S_{1/2}$	7.6 / 21.5	2.5	1.9
Sodium	Na	11	22.989767	221	Ne $3s^1$	$^2S_{1/2}$	5.1 / 47.3	0.8	0.9
Strontium	Sr	38	87.62	220	Kr $5s^2$	$^1S_0$	5.7 / 11.0	–	1.0
Sulphur	S	16	32.064	101	Ne $3s^2\ 3p^4$	$^3P_2$	10.4 / 23.4	2.1	2.5
Tantalum	Ta	73	180.948	184	Xe $4f^{14}\ 5d^3\ 6s^2$	$^4F_{3/2}$	7.9 / 16.2	–	1.5
Thallium	Tl	81	204.383	205	Xe $4f^{14}\ 5d^{10}\ 6s^2\ 6p^1$	$^2P_{1/2}$	6.1 / 20.4	–	1.8
Technetium	Tc	43	(98)	172	Kr $4d^5\ 5s^2$	$^6S_{5/2}$	7.3 / 15.3	–	1.9
Tellurium	Te	52	127.60	157	Kr $4d^{10}\ 5s^2\ 5p^4$	$^3P_2$	9.0 / 18.6	3.6	2.1
Terbium	Tb	65	158.9253	224	Xe $4f^9\ 6s^2$	$^6H_{15/2}$	6.7 / –	–	1.2
Thorium	Th	90	232.0381	233	Rn $6d^2\ 7s^2$	$^3F_2$	7.0 / 11.5	–	1.3
Thulium	Tm	69	168.9342	227	Xe $4f^{13}\ 6s^2$	$^2F_{7/2}$	6.8 / 12.1	–	1.2
Tin	Sn	50	118.710	161	Kr $4d^{10}\ 5s^2\ 5p^2$	$^3P_0$	7.3 / 14.6	–	1.8
Titanium	Ti	22	47.88	197	Ar $3d^2\ 4s^2$	$^3F_2$	6.8 / 13.6	–	1.5
Tungsten	W	74	183.85	178	Xe $4f^{14}\ 5d^4\ 6s^2$	$^4D_0$	8.0 / 17.7	–	1.7
Uranium	U	92	238.0289	234	Rn $5f^3\ 6d^1\ 7s^2$	$^5L_4$	6.1 / –	–	1.7
Vanadium	V	23	50.9415	188	Ar $3d^3\ 4s^2$	$^4F_{3/2}$	6.7 / 14.7	–	1.6
Xenon	Xe	54	131.29	127	Kr $4d^{10}\ 5s^2\ 5p^6$	$^1S_0$	12.1 / 21.2	–	–
Ytterbium	Yb	70	173.03	215	Xe $4f^{14}\ 6s^2$	$^1S_0$	6.3 / 12.1	–	1.1
Yttrium	Y	39	88.9058	204	Kr $4d^1\ 5s^2$	$^2D_{3/2}$	6.4 / 12.2	–	1.3
Zinc	Zn	30	65.40	148	Ar $3d^{10}\ 4s^2$	$^1S_0$	9.4 / 18.0	–	1.6
Zirconium	Zr	40	91.224	193	Kr $4d^2\ 5s^2$	$^3F_2$	6.8 / 13.1	–	1.4

Table: Atomic data (part 3).



Demonstration of the aufbau principle.

2.11 Ionization energy and electron affinity

Ionization energy: The energy required to remove an electron completely from an atom in the gas phase.

The first ionization energy E_1 corresponds to: $\mathrm{A} + E_1 \rightarrow \mathrm{A}^+ + e^-$.

The second ionization energy E_2 corresponds to: $\mathrm{A}^+ + E_2 \rightarrow \mathrm{A}^{2+} + e^-$.

Ionization energies can be determined by irradiating atoms with short wavelength light. Ionization energies of atoms can be found from the previous table of atomic data. As an example, ionization energies of some atoms are given below:

Element	First	Second	Third	Fourth	Fifth	Sixth	Seventh
Na	496	4,560					
Mg	738	1,450	7,730				
Al	577	1,816	2,881	11,600			
Si	786	1,577	3,228	4,354	16,100		
P	1,060	1,890	2,905	4,950	6,270	21,200	
S	999.6	2,260	3,375	4,565	6,950	8,490	27,107
Cl	1,256	2,295	3,850	5,160	6,560	9,360	11,000
Ar	1,520	2,665	3,945	5,770	7,230	8,780	12,000

Table: Ionization energies of selected atoms (kJ mol^{-1}).

Electron affinity: This is the energy released in the process of adding an electron to the atom (or molecule). It is usually denoted by E_a.

An example of such process is: $\mathrm{Cl(g)} + e^- \rightarrow \mathrm{Cl^-(g)}$.

Electron affinities of atoms are listed in the previous table. Note that a negative value means that the energy is lowered when the atom accepts an electron and a positive value means that the energy is increased. In practice, the more negative the value is, the more eager the atom is to accept an electron.

Note: The Koopmans' theorem states that the first ionization energy of an atom or a molecule can be approximated by the energy of the highest occupied orbital (from the Hartree-Fock method). This allows for a simple estimation of the ionization energy by using computational methods.

2.12 Angular momentum of many-electron atoms

In many-electron atoms, each electron has both orbital and spin angular momenta. First, for simplicity, consider only the *total* orbital angular momentum operator:

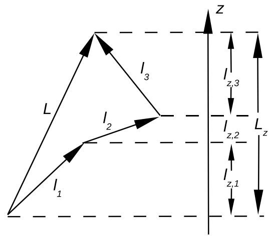
$$\hat{L} = \sum_{i=1}^{N} \hat{l}_i \tag{2.241}$$

where N is the number of electrons and $\hat{l}_i$ is the angular momentum operator for electron i. The projection operator along the z-axis is then given by:

$$\hat{L}_z = \sum_{i=1}^{N} \hat{l}_{z,i} \tag{2.242}$$

By combining this with Eq. (2.186), we get:

$$M_L = \sum_{i=1}^{N} m_i \tag{2.243}$$



Vector model for adding 3 angular momenta:
$\vec{L}$ = Total orbital angular momentum.
$\vec{l_1}, \vec{l_2}, \vec{l_3}$ = individual angular momenta.

Notes:

- $\hat{L}, \hat{l}_i$ are operators; L, l_i are the corresponding quantum numbers.
- We assume a light atom and thus neglect the spin-orbit coupling.

1. Total orbital angular momentum in a many-electron atom.

Consider an atom with two electrons each with orbital angular momentum l_1 and l_2, respectively. The maximum total angular momentum is obtained when the two angular momenta vectors are parallel: $L = l_1 + l_2$. When they point in opposite directions, we have: $L = l_1 - l_2$.

Hence the total angular momentum quantum number L can take values ("Glebsch-Gordan series"):

$$L = l_1 + l_2, l_1 + l_2 - 1, ..., |l_1 - l_2| \tag{2.244}$$

where l_1 and l_2 are the angular momentum quantum numbers for electrons 1 and 2, respectively. For example, if we have two electrons on p-orbitals, the above gives: $L = 2, 1$ or 0. Furthermore, for $L = 2$, we can have $M_L = +2, +1, 0, -1, -2$; for $L = 1$, $M_L = +1, 0, -1$; and $L = 0$, $M_L = 0$. It is instructive to check that we actually have the same number of states in both representations (i.e., the uncoupled vs. the coupled representation). In the uncoupled representation: $3^2 = 9$ states (3 p-orbitals and 2 electrons) and in the coupled $5 + 3 + 1 = 9$.

Note: Usually closed shell inner core electrons are not included in the consideration as they don't contribute to the end result.

2. Total spin angular momentum in many-electron atom.

The total spin angular momentum operator for a many-electron atom is given by:

$$\hat{S} = \sum_{i=1}^{N} \hat{s}_i \tag{2.245}$$

and the z-component of the total spin angular momentum operator is defined as:

$$\hat{S}_z = \sum_{i=1}^{N} \hat{s}_{z,i} \tag{2.246}$$

Here $\hat{s}_i$ and $\hat{s}_{z,i}$ refer to spin angular momenta of the individual electrons. In similar fashion to (2.243), total quantum number M_S can be written:

$$M_S = \sum_{i=1}^{N} m_{s,i} \tag{2.247}$$

This value can range from $-S$ to S and the total quantum number S is given by:

$$S = s_1 + s_2, s_1 + s_2 - 1, ..., |s_1 - s_2| \tag{2.248}$$

For example, for two electrons, $S = 1$ ("triplet state") or $S = 0$ ("singlet state").

3. The total angular momentum (combined orbital and spin).

The total angular momentum operator$\hat{J}$, is as a vector sum of $\hat{L}$ and $\hat{S}$:

$$\vec{\hat{J}} = \vec{\hat{L}} + \vec{\hat{S}} \tag{2.249}$$

$$\hat{J}_z = \hat{L}_z + \hat{S}_z \tag{2.250}$$

The total quantum number J is given by:

$$J = L + S, L + S - 1, ..., |L - S| \tag{2.251}$$

with the corresponding total magnetic quantum number M_J as:

$$M_J = M_L + M_S \tag{2.252}$$

The previous coupling scheme is called the LS coupling or Russell-Saunders coupling. This approach is only approximate when spin-orbit coupling is included in the Hamiltonian. Spin-orbit interaction arises from relativistic effects and its origin is not considered here. Instead, it should be simply thought to couple the orbital and spin angular momenta to each other with some given magnitude ("spin-orbit coupling constant"). Note that the spin-orbit effect is larger for heavier atoms. For these atoms the LS coupling scheme begins to break down and only J remains a good quantum number. This means that, for example, one can no longer speak about singlet and triplet electronic states. The LS coupling scheme works reasonably well for the first two rows in the periodic table.

2.13 Atomic term symbols

In the previous table, column #7 (“level”) denotes a term symbol for the given atom. This term symbol contains information about the total orbital and spin angular momenta as well as the total angular momentum (i.e., $J = L + S$). This is expressed as follows:

$$^{2S+1}L_J \tag{2.253}$$

where S is the total spin defined in Eq. (2.248), L is the total angular momentum of Eq. (2.244), and J is the total angular momentum Eq. (2.251). Both $2S + 1$ and J are expressed as numbers and for L we use a letter: S for $L = 0$, P for $L = 1$, D for $L = 2$, etc. $2S + 1$ is referred to as spin multiplicity (1 = singlet, 2 = doublet, 3 = triplet, ...). The term symbol specifies the ground state electronic configuration exactly. Note that column #6 (“electron configuration”) in the table, is much longer and it ignores the exact configuration of electron spins. Note that only the valence electrons contribute to the term symbol.

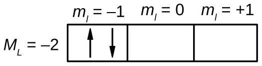
Example. What is the atomic term symbol for He atom in its ground state?

Solution. The electron configuration in He is $1s^2$ (i.e., two electrons on 1s orbital with opposite spins). First we use Eq. (2.248) to obtain S. We have two possibilities: $S = 1$ (triplet) or $S = 0$ (singlet). However, since we are interested in the ground state, both electrons are on 1s orbital and hence they must have opposite spins giving a singlet state. Thus $S = 0$ and $2S + 1 = 1$. Since both electrons reside on s-orbital, $l_1 = l_2 = 0$ and $L = 0$ by Eq. (2.244). Eq. (2.249) now gives $J = L + S = 0 + 0 = 0$. The term symbol is therefore $^1S_0$.

Example. What are the lowest lying state term symbols for a carbon atom?

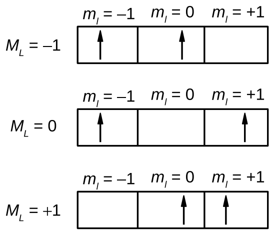
Solution. The electronic configuration for ground state C is $1s^2 2s^2 2p^2$. To get the possible lowest lying states, we only consider the two p-electrons. From Eq. (2.248) we get: $S = \frac{1}{2} + \frac{1}{2} = 1$ or $S = 0$. The first case corresponds to triplet and the last singlet state. The total orbital angular momentum quantum numbers are given by Eq. (2.244): $L = 2, 1, 0$, which correspond to D, P and S terms, respectively. Again, because the electrons must have opposite spins when the go on the same orbital, some S and L combinations are not possible. Consider the following scenarios:

1. $L = 2$ (D term): One of the states ($M_L = -2$) must correspond to configuration, where both electrons occupy a p-orbital having $m_l = -1$. Note that the electrons must go on the above orbital with opposite spins and therefore the triplet state, where the electrons could be parallel, is not allowed:



Thus we conclude that for $L = 2$, only the singlet state (i.e., ^1D) is possible.

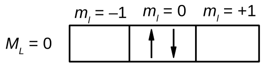
2. $L = 1$ (P term): The three eigen states correspond to:



(triplet state shown)

In principle, all these configurations could also be written for the singlet state but it requires a more complicated consideration to see that this is *not allowed* (see below).

3. $L = 0$ (S term): For this term we can only have $M_L = 0$, which corresponds to:



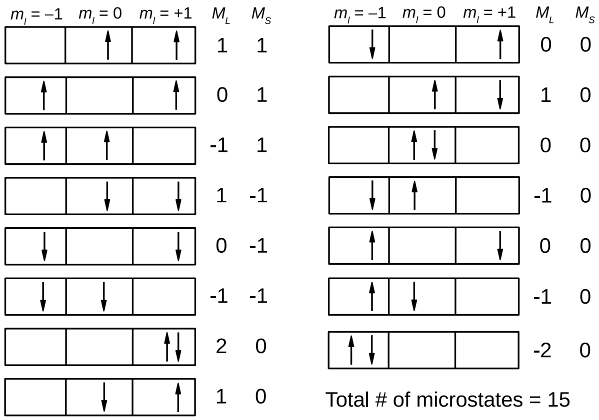
Again, it is not possible to have triplet state because the spins would have to be parallel on the same orbital. Hence only ^{1}S exists.

We conclude that the following terms are possible: ^{1}D, ^{3}P and ^{1}S. As we will see below, the Hund's rules predict that the ^{3}P term will be the ground state (i.e., the lowest energy). The total angular momentum quantum number J for this state may have the following values: $J = L + S = 2, 1$, or 0. Due to spin-orbit coupling, these states have different energies and the Hund's rules predict that the $J = 0$ state lies lowest in energy. Therefore the $^3\mathrm{P}_0$ state is the ground state of C atom.

The above method is fast and convenient but does not always work and is not able to show that ^{1}P does not exist. In the following (for carbon) we will list each possible electron configuration (microstate), label them according to their M_L and M_S numbers, count how many times each (M_L,M_S) combination appears and decompose this information into term symbols. The total number of possible microstates N is given by:

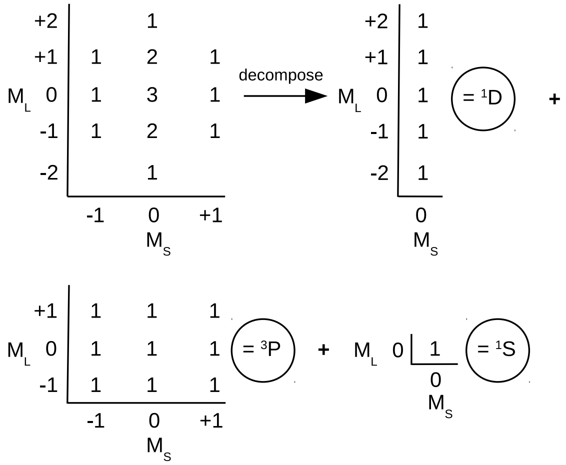
$$N = \frac{(2(2l+1))!}{n!(2(2l+1)-n)!} \tag{2.254}$$

where n is the number of electrons and l is the orbital angular momentum quantum number (e.g., 1 for p orbitals, 2 for d, etc.). Next we need to count how many states of each M_L and M_S we have:



Total # of microstates = 15

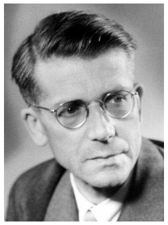
The total number of (M_L,M_S) combinations appearing above are counted in the following table and its decomposition into term symbols is demonstrated (note that ^{1}P does not exist).



$$\begin{array}{c|ccc} +2 & & 1 & \\ +1 & 1 & 2 & 1 \\ 0 & 1 & 3 & 1 \\ -1 & 1 & 2 & 1 \\ -2 & & 1 & \\ \hline M_L \backslash M_S & -1 & 0 & +1 \end{array} \xrightarrow{\text{decompose}} \begin{array}{c|c} +2 & 1 \\ +1 & 1 \\ 0 & 1 \\ -1 & 1 \\ -2 & 1 \\ \hline M_L \backslash M_S & 0 \end{array} = {}^1D \; +$$

$$\begin{array}{c|ccc} +1 & 1 & 1 & 1 \\ 0 & 1 & 1 & 1 \\ -1 & 1 & 1 & 1 \\ \hline M_L \backslash M_S & -1 & 0 & +1 \end{array} = {}^3P \; + \; \begin{array}{c|c} 0 & 1 \\ \hline M_L \backslash M_S & 0 \end{array} = {}^1S$$

Excercise. Carry out the above procedure for oxygen atom (4 electrons distributed on $2p$ orbitals). What are resulting the atomic term symbols?



Friedrich Hund (1896 - 1997), German Physicist

Hund's (partly empirical) rules are:

1. The term arising from the ground configuration with the maximum multiplicity $(2S+1)$ lies lowest in energy.
2. For levels with the same multiplicity, the one with the maximum value of L lies lowest in energy.
3. For levels with the same S and L (but different J), the lowest energy state depends on the extent to which the subshell is filled:

- If the subshell is less than half-filled, the state with the smallest value of J is the lowest in energy.
- If the subshell is more than half-filled, the state with the largest value of J is the lowest in energy.

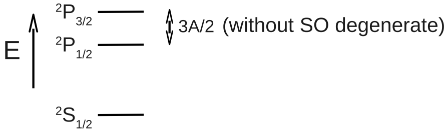
Spin-orbit interaction (very briefly): This relativistic effect can be incorporated into non-relativistic quantum mechanics by including the following term into the Hamiltonian:

$$\hat{H}_{SO} = A\hat{\vec{L}} \cdot \hat{\vec{S}} \tag{2.255}$$

where A is the spin-orbit coupling constant and L and S are the orbital and spin angular momentum operators, respectively. The total angular momentum J commutes with both $\hat{H}$ and $\hat{H}_{SO}$ and therefore it can be specified simultaneously with energy. We say that the corresponding quantum number J remains good even when spin-orbit interaction is included whereas L and S do not. The operator dot product $\hat{L} \cdot \hat{S}$ can be evaluated and expressed in terms of the corresponding quantum numbers:

$$\hat{\vec{L}} \cdot \hat{\vec{S}} \left|\psi_{L,S,J}\right\rangle = \frac{1}{2}\left[J(J+1) - L(L+1) - S(S+1)\right]\left|\psi_{L,S,J}\right\rangle \tag{2.256}$$

For example in alkali atoms $(S = 1/2, L = 1)$, the spin-orbit interaction breaks the degeneracy of the excited ^{2}P state (^{2}S$_{1/2}$ is the ground state):



2.14 Atomic spectra and selection rules

The following selection rules for photon absorption or emission in one-electron atoms can be derived by considering the symmetries of the initial and final state wavefunctions (orbitals):

$$\Delta n = \text{unrestricted}, \Delta l = \pm 1, \Delta m_l = +1, 0, -1 \tag{2.257}$$

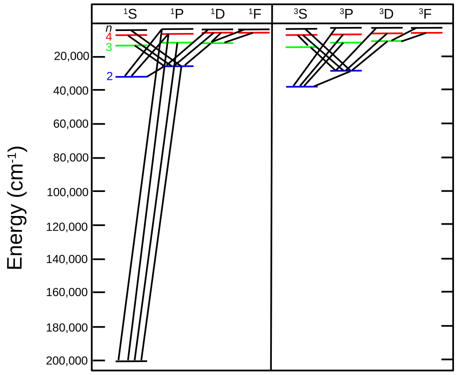
where Δn is the change in the principal quantum number, Δl is the change in orbital angular momentum quantum number and Δm_l is the change in projection of l. For derivation, see Molecular Quantum Mechanics by Atkins and Friedman. Qualitatively, the selection rules can be understood by conservation of angular momentum. Photons are spin 1 particles with $m_l = +1$ (left-circularly polarized light) or $m_l = -1$ (right-circularly polarized light). When a photon interacts with an atom, the angular momentum in it may chance only by $+1$ or -1; just like in the selection rules above.

Note that light is electromagnetic radiation and, as such, it has both electric and magnetic components. The oscillating electric field component is used in driving transitions in optical spectroscopy (UV/VIS, fluorescence, IR) whereas the magnetic component is used in magnetic resonance spectroscopy (NMR, EPR/ESR). Photon emission from an atom (e.g., fluorescence) is rather difficult to understand with the quantum mechanical machinery that we have developed so far. The plain Schrödinger equation would predict that excited states in atoms would have infinite lifetime in vacuum. However, this is not observed in practice and atoms/molecules return to ground state by emitting a photon. This transition is caused by fluctuations of electric field in vacuum (see your physics lecture notes).

In many-electron atoms the selection rules can be written as follows:

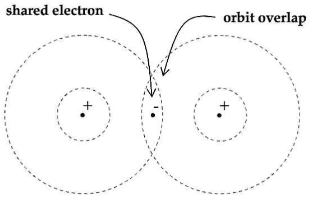
1. $\Delta L = 0, \pm 1$ except that transition from $L = 0$ to $L = 0$ does not occur.
2. $\Delta l = \pm 1$ for the electron that is being excited (or is responsible for fluorescence).
3. $\Delta J = 0, \pm 1$ except that transition from $J = 0$ to $J = 0$ does not occur.
4. $\Delta S = 0$. The electron spin does not change in optical transition. The exact opposite holds for magnetic resonance spectroscopy, which deals with changes in spin states.

In some exceptional cases, these rules may be violated but the resulting transitions will be extremely weak ("forbidden transitions"). Because of the last rule, some excited triplet states may have very long lifetime because the transition to the ground singlet state is forbidden (metastable states).



Grotrian diagram of He atom.

Chapter 3: Quantum mechanics of molecules



Lewis-type Chemical bond

G. N. Lewis: “An electron may form a part of the shell of two different atoms and cannot be said to belong to either one exclusively.”

3.1 Molecules and the Born-Oppenheimer approximation

Because nuclei are much heavier than electrons, the Schrödinger equation can be approximately separated into the nuclear and the electron parts. Thus the electronic Schrödinger equation for a molecule can be solved separately at each fixed nuclear configuration. This is called the Born-Oppenheimer approximation.

In the following, we will consider the simplest molecule H_2^+, which contains only one electron. This simple system will demonstrate the basic concepts in chemical bonding. The Schrödinger equation for H_2^+ is:

$$H\psi(\vec{r}_1, \vec{R}_A, \vec{R}_B) = E\psi(\vec{r}_1, \vec{R}_A, \vec{R}_B) \tag{3.258}$$

where $\vec{r}_1$ is the vector locating the (only) electron and $\vec{R}_A$ and $\vec{R}_B$ are the positions of the two protons. The Hamiltonian for H_2^+ is:

$$\hat{H} = -\frac{\hbar^2}{2M}(\Delta_A + \Delta_B) - \frac{\hbar^2}{2m_e}\Delta_e + \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{R} - \frac{1}{r_{1A}} - \frac{1}{r_{1B}}\right) \tag{3.259}$$

where M is the proton mass, m_e is the electron mass, r_{1A} is the distance between the electron and nucleus A, r_{1B} is the distance between the electron and nucleus B and R is the A - B distance.

Max Born (1882 - 1970), German physicist and Mathematician, Nobel Prize 1954.

Robert Oppenheimer (1904 - 1967) American theoretical physicist, “the father of atomic bomb”

Note that the Hamiltonian includes also the quantum mechanical kinetic energy for the protons. As such the wavefunction depends on $\vec{r}_1$, $\vec{R}_A$ and $\vec{R}_B$. Because the nuclear mass M is much larger than the electron mass m_e, the wavefunction can be separated (Born-Oppenheimer approximation):

$$\psi(\vec{r}_1, \vec{R}_A, \vec{R}_B) = \psi_e(\vec{r}_1, R)\psi_n(\vec{R}_A, \vec{R}_B) \tag{3.260}$$

where ψ_e is the electronic wavefunction that depends on the distance R between the nuclei and ψ_n is the nuclear wavefunction depending on $\vec{R}_A$ and $\vec{R}_B$. It can be shown that the nuclear part can be often be separated into vibrational, rotational and translational parts. The electronic Schrödinger equation can now be written as:

$$\hat{H}_e\psi_e = E_e\psi_e \tag{3.261}$$

Note that Eq. (3.261) depends parametrically on R ("one equation for each value of R"). The *electronic Hamiltonian* is:

$$\hat{H}_e = -\frac{\hbar^2}{2m_e}\Delta_e + \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{R} - \frac{1}{|r_1 - R_A|} - \frac{1}{|r_1 - R_B|}\right) \tag{3.262}$$

Because R is a parameter, both E_e and ψ_e are functions of R.

3.2 The hydrogen molecule ion

The electronic Schrödinger equation for H_2^+ (Eqs. (3.261) and (3.262)) can be solved exactly because the equation contains only one particle. However, the involved math is very complicated and here we take another simpler but approximate approach ("*molecular orbital theory*"). This method will reveal all the important features of chemical bond. An approximate (trial) wavefunction is written as (real functions):

$$\psi_\pm(\vec{r}_1) = c_1 1s_A(\vec{r}_1) \pm c_2 1s_B(\vec{r}_1) \tag{3.263}$$

where $1s_A$ and $1s_B$ are hydrogen atom wavefunctions centered at nucleus A and B, respectively, and c_1 and c_2 are constants. This function is essentially a linear combination of the atomic orbitals (LCAO molecular orbitals). Because the two protons are identical, we must have $c_1 = c_2 \equiv c$ (also $c > 0$). The ± notation in Eq. (3.263) indicates that two different wavefunctions can be constructed, one with "+" sign and the other with "−" sign. Normalization of the wavefunction requires:

$$\int \psi_\pm^* \psi_\pm d\tau = 1 \tag{3.264}$$

In the following, we consider the wavefunction with a "+" sign and evaluate the normalization integral (S = overlap integral, which depends on R):

$$1 = c^2\int(1s_A + 1s_B)(1s_A + 1s_B)d\tau = c^2\underbrace{\int 1s_A^2 d\tau}_{=1} + c^2\underbrace{\int 1s_B^2 d\tau}_{=1} \tag{3.265}$$

$$+c^2\underbrace{\int 1s_A 1s_B d\tau}_{=S} + c^2\underbrace{\int 1s_B 1s_A d\tau}_{=S} = c^2(2 + 2S)$$

This can be rewritten as:

$$1 = c^2(2 + 2S) \Rightarrow c = \frac{1}{\sqrt{2 + 2S}} \tag{3.266}$$

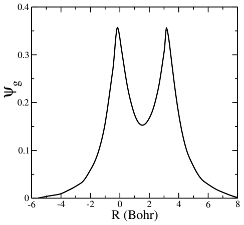
and the complete "+" wavefunction is then:

$$\psi_+ \equiv \psi_g = \frac{1}{\sqrt{2(1+S)}}(1s_A + 1s_B) \tag{3.267}$$

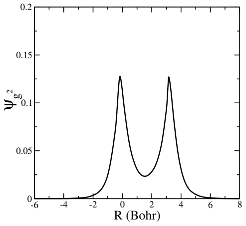
In exactly the same way, we can get the "−" wavefunction:

$$\psi_- \equiv \psi_u = \frac{1}{\sqrt{2(1-S)}}(1s_A - 1s_B) \tag{3.268}$$

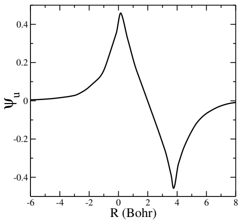
Walter Heitler, Ava Helen Pauling and Fritz London (1926). Heitler and London invented the valence bond method for describing H_2 molecule in 1927.



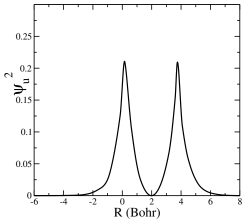
Bonding orbital (ψ_g)



Bonding orbital (ψ_g^2)



Antibonding orbital (ψ_u)



Antibonding orbital (ψ_u^2)

Note that the antibonding orbital has zero electron density between the nuclei.

Recall that the square of the wavefunction gives the electron density. In the left hand side figure (the "+" wavefunction), the electron density is amplified between the nuclei whereas in the "−" wavefunction the opposite happens. *The main feature of a chemical bond is the increased electron density between the nuclei.* This identifies the "+" wavefunction as a bonding orbital and "−" as an antibonding orbital.

When a molecule has a center of symmetry (here at the half-way between the nuclei), the wavefunction may or may not change sign when it is inverted through the center of symmetry. If the origin is placed at the center of symmetry then we can assign symmetry labels g and u to the wavefunctions. If $\psi(x, y, z) = \psi(-x, -y, -z)$ then the symmetry label is g (even parity) and for $\psi(x, y, z) = -\psi(-x, -y, -z)$ we have u label (odd parity). This notation was already used in Eqs. (3.267) and (3.268). According to this notation the g symmetry orbital is the bonding orbital and the u symmetry corresponds to the antibonding orbital. Later we will see that this is reversed for π-orbitals!

The overlap integral $S(R)$ can be evaluated analytically (derivation not shown):

$$S(R) = e^{-R}\left(1 + R + \frac{R^3}{3}\right) \tag{3.269}$$

Note that when $R = 0$ (i.e. the nuclei overlap), $S(0) = 1$ (just a check to see that the expression is reasonable).

3.3 Energy of the hydrogen molecule ion

Using a linear combination of atomic orbitals, it is possible to calculate the best values, in terms of energy, for the coefficients c_1 and c_2. Remember that this linear combination can only provide an approximate solution to the H_2^+ Schrödinger equation. The variational principle (see Eq. (2.210)) provides a systematic way to calculate the energy when R (the distance between the nuclei) is fixed:

$$\begin{aligned} E &= \frac{\int \psi_g^* \hat{H}_e \psi_g d\tau}{\int \psi_g^* \psi_g d\tau} = \frac{\int (c_1 1s_A + c_2 1s_B) \hat{H}_e (c_1 1s_A + c_2 1s_B) d\tau}{\int (c_1 1s_A + c_2 1s_B)^2 d\tau} \\ &= \frac{c_1^2 H_{AA} + 2c_1c_2 H_{AB} + c_2^2 H_{BB}}{c_1^2 \underbrace{S_{AA}}_{=1} + 2c_1c_2 \underbrace{S_{AB}}_{=S} + c_2^2 \underbrace{S_{BB}}_{=1}} \end{aligned} \tag{3.270}$$

where H_{AA}, H_{AB}, H_{BB}, S_{AA}, S_{AB} and S_{BB} have been used to denote the integrals occurring in Eq. (3.270). The integrals H_{AA} and H_{BB} are called the *Coulomb integrals* (sometimes generally termed as matrix elements). This interaction is attractive and therefore its numerical value must be negative. Note that by symmetry $H_{AA} = H_{BB}$. The integral H_{AB} is called the *resonance integral* and also by symmetry $H_{AB} = H_{BA}$.

To minimize the energy expectation value in Eq. (3.270) with respect to c_1 and c_2, we have to calculate the partial derivatives of energy with respect to these parameters:

$$E \times (c_1^2 + 2c_1c_2S + c_2^2) = c_1^2 H_{AA} + 2c_1c_2 H_{AB} + c_2^2 H_{BB} \tag{3.271}$$

Both sides can be differentiated with respect to c_1 to give:

$$E \times (2c_1 + 2c_2S) + \frac{\partial E}{\partial c_1} \times (c_1^2 + 2c_1c_2S + c_2^2) = 2c_1 H_{AA} + 2c_2 H_{AB} \tag{3.272}$$

In similar way, differentiation with respect to c_2 gives:

$$E \times (2c_2 + 2c_1S) + \frac{\partial E}{\partial c_2} \times (c_1^2 + 2c_1c_2S + c_2^2) = 2c_2 H_{BB} + 2c_1 H_{AB} \tag{3.273}$$

At the minimum energy (for c_1 and c_2), the partial derivatives must be zero:

$$c_1(H_{AA} - E) + c_2(H_{AB} - SE) = 0 \tag{3.274}$$

$$c_2(H_{BB} - E) + c_1(H_{AB} - SE) = 0 \tag{3.275}$$

In matrix notation this is (a generalized matrix eigenvalue problem):

$$\begin{pmatrix} H_{AA} - E & H_{AB} - SE \\ H_{AB} - SE & H_{BB} - E \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0 \tag{3.276}$$

From linear algebra, we know that a non-trivial solution exists only if:

$$\begin{vmatrix} H_{AA} - E & H_{AB} - SE \\ H_{AB} - SE & H_{BB} - E \end{vmatrix} = 0 \tag{3.277}$$

It can be shown that $H_{AA} = H_{BB} = E_{1s} + J(R)$, where E_{1s} is the energy of a single hydrogen atom and $J(R)$ is a function of internuclear distance R:

$$J(R) = e^{-2R}\left(1 + \frac{1}{R}\right) \tag{3.278}$$

Furthermore, $H_{AB} = H_{BA} = E_{1s}S(R) + K(R)$, where $K(R)$ is also a function of R:

$$K(R) = \frac{S(R)}{R} - e^{-R}(1 + R) \tag{3.279}$$

If these expressions are substituted into the previous secular determinant, we get:

$$\begin{vmatrix} E_{1s} + J - E & E_{1s}S + K - SE \\ E_{1s}S + K - SE & E_{1s} + J - E \end{vmatrix} = (E_{1s} + J - E)^2 - (E_{1s}S + K - SE)^2 = 0 \tag{3.280}$$

This equation has two roots:

$$E_g(R) = E_{1s} + \frac{J(R) + K(R)}{1 + S(R)} \tag{3.281}$$

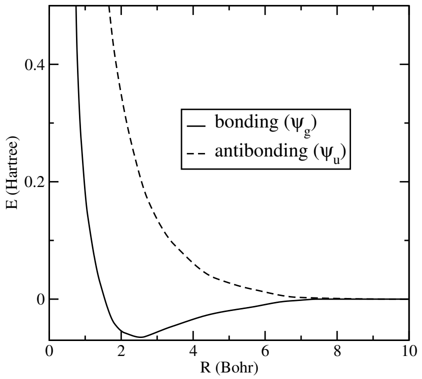
$$E_u(R) = E_{1s} + \frac{J(R) - K(R)}{1 - S(R)} \tag{3.282}$$

Since energy is a relative quantity, it can be expressed relative to separated nuclei:

$$\Delta E_g(R) = E_g(R) - E_{1s} = \frac{J(R) + K(R)}{1 + S(R)} \tag{3.283}$$

$$\Delta E_u(R) = E_u(R) - E_{1s} = \frac{J(R) - K(R)}{1 - S(R)} \tag{3.284}$$

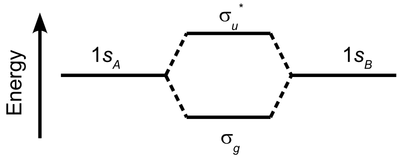
The energies of these states are plotted in the figure below.



Energies of the bonding and antibonding states in H_2^+.

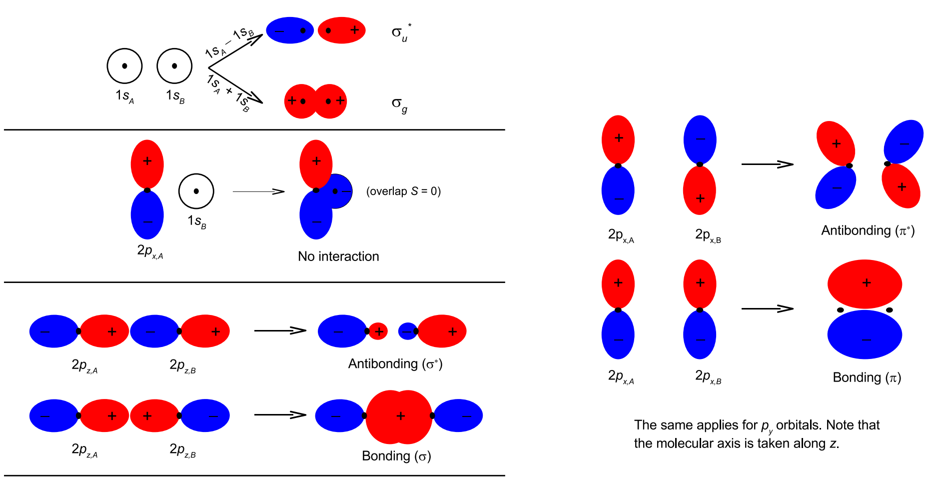
These values can be compared with experimental results. The calculated ground state equilibrium bond length is 132 pm whereas the experimental value is 106 pm. The binding energy is 170 kJ mol^{-1} whereas the experimental value is 258 kJ mol^{-1}. The excited state (labeled with u) leads to repulsive behavior at all bond lengths R (i.e. antibonding). Because the u state lies higher in energy than the g state, the u state is an excited state of H_2^+. This calculation can be made more accurate by adding more than two terms to the linear combination. This procedure would also yield more excited state solutions. These would correspond u/g combinations of $2s$, $2p_x$, $2p_y$, $2p_z$ etc. orbitals.

It is a common practice to represent the molecular orbitals by molecular orbital (MO) diagrams:



MO diagram showing the σ_g and σ_u molecular orbitals.

The formation of bonding and antibonding orbitals can be visualized as follows:

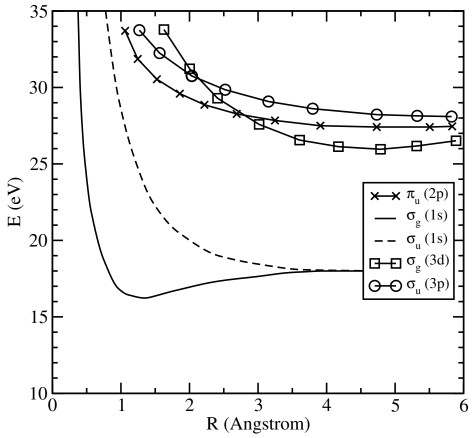


The same applies for p_y orbitals. Note that the molecular axis is taken along z.

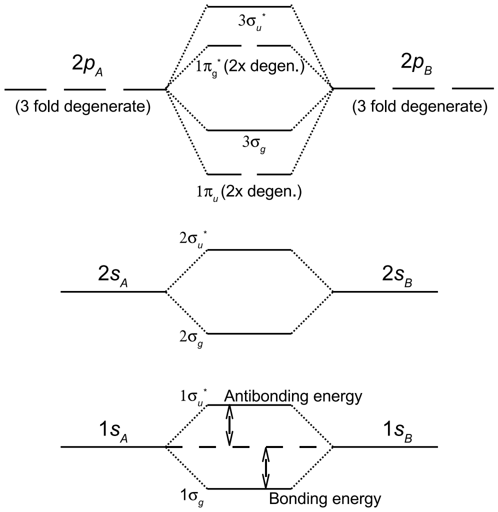
1. σ orbitals. When two s or p_z orbitals interact, a σ molecular orbital is formed. The notation σ specifies the amount of angular momentum about the molecular axis (for σ, $\lambda = 0$ with $L_z = \pm\lambda\hbar$). In many-electron systems, both bonding and antibonding σ orbitals can each hold a maximum of two electrons. Antibonding orbitals are often denoted by *.

2. π orbitals. When two $p_{x,y}$ orbitals interact, a π molecular orbital forms. π-orbitals are doubly degenerate: π_{+1} and π_{-1} (or alternatively π_x and π_y), where the $+1/-1$ refer to the eigenvalue of the L_z operator ($\lambda = \pm 1$). In many-electron systems a bonding π-orbital can therefore hold a maximum of 4 electrons (i.e. both π_{+1} and π_{-1} each can hold two electrons). The same holds for the antibonding π orbitals. Note that only the atomic orbitals of the same symmetry mix to form molecular orbitals (for example, $p_z - p_z$, $p_x - p_x$ and $p_y - p_y$). When atomic d orbitals mix to form molecular orbitals, $\sigma(\lambda = 0)$, $\pi(\lambda = \pm 1)$ and $\delta(\lambda = \pm 2)$ MOs form.

Excited state energies of H_2^+ resulting from a calculation employing an extended basis set (e.g. more terms in the LCAO) are shown on the left below. The MO energy diagram, which includes the higher energy molecular orbitals, is shown on the right hand side. Note that the energy order of the MOs depends on the molecule.



The lowest excited states of H_2^+.



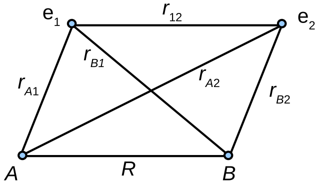
MO diagram for homonuclear diatomic molecules.

3.4 Molecular orbital description of hydrogen molecule

Using the Born-Oppenheimer approximation, the electronic Hamiltonian for H_2 molecule can be written as:

$$H = -\frac{\hbar^2}{2m_e}\left(\Delta_1 + \Delta_2\right) + \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{R} + \frac{1}{r_{12}} - \frac{1}{r_{A1}} - \frac{1}{r_{A2}} - \frac{1}{r_{B1}} - \frac{1}{r_{B2}}\right) \quad (3.285)$$

The distances between the electrons and the nuclei are indicated below.



The main difficulty in the Hamiltonian of Eq. (3.285) is the $1/r_{12}$ term, which connects the two electrons to each other. This means that a simple product wavefunction is not sufficient. No known analytic solutions have been found to the electronic Schrödinger equation of H_2. For this reason, we will attempt to solve the problem approximately by using the LCAO-MO approach that we used previously. For example, the ground state for H_2 is obtained by placing two electrons with opposite spins on the $1\sigma_g$ orbital. This assumes that the wavefunction is expressed as antisymmetrized product (e.g. a Slater determinant).

According to the Pauli principle, two electrons with opposite spins can be assigned to a given spatial orbital. As a first approximation, we assume that the molecular orbitals in H_2 remain the same as in H_2^+. Hence we can say that both electrons occupy the $1\sigma_g$ orbital (the ground state) and the electronic configuration is denoted by $(1\sigma_g)^2$. This is a similar notation that we used previously for atoms (for example, He atom is $(1s)^2$).

The molecular orbital for electron 1 in $1\sigma_g$ molecular orbital is (see Eq. (3.267)):

$$1\sigma_g(1) = \frac{1}{\sqrt{2(1+S)}}\left(1s_A(1) + 1s_B(1)\right) \quad (3.286)$$

In Eq. (2.229) we found that the total wavefunction must be antisymmetric with respect to change in electron indices. This can be achieved by using the Slater determinant:

$$\psi_{MO}^{(1\sigma_g)^2} = \frac{1}{\sqrt{2}}\begin{vmatrix} 1\sigma_g(1)\alpha(1) & 1\sigma_g(1)\beta(1) \\ 1\sigma_g(2)\alpha(2) & 1\sigma_g(2)\beta(2) \end{vmatrix} \quad (3.287)$$

where α and β denote the electron spin. The Slater determinant can be expanded as follows:

$$\psi_{MO}^{(1\sigma_g)^2} = \frac{1}{\sqrt{2}}(1\sigma_g(1)1\sigma_g(2)\alpha(1)\beta(2) - 1\sigma_g(1)1\sigma_g(2)\beta(1)\alpha(2)) \tag{3.288}$$
$$= \frac{1}{2\sqrt{2}(1+S_{AB})}(1s_A(1)+1s_B(1))(1s_A(2)+1s_B(2))(\alpha(1)\beta(2)-\alpha(2)\beta(1))$$

Note that this wavefunction is only approximate and is definitely not an eigenfunction of the H_2 electronic Hamiltonian. Thus we must calculate the electronic energy by taking an expectation value of this wavefunction with the Hamiltonian given in Eq. (3.285) (the actual calculation not shown):

$$E(R) = 2E_{1s} + \frac{e^2}{4\pi\epsilon_0 R} - \text{“integrals”} \tag{3.289}$$

where E_{1s} is the electronic energy of one hydrogen atom. The second term represents the Coulomb repulsion between the two positively charged nuclei and the last term (“integrals”) contains a series of integrals describing the interactions of various charge distributions with one another (see P. W. Atkins, Molecular Quantum Mechanics, Oxford University Press). With this approach, the minimum energy is reached at $R = 84$ pm (experimental 74.1 pm) and dissociation energy $D_e = 255$ kJ mol^{-1} (experimental 458 kJ mol^{-1}).

This simple approach is not very accurate but it demonstrates that the method works. To improve the accuracy, ionic and covalent terms should be considered separately:

$$\underbrace{1s_A(1)1s_A(2)}_{\text{Ionic (H}^- + \text{H}^+)} + \underbrace{1s_A(1)1s_B(2) + 1s_A(2)1s_B(1)}_{\text{Covalent (H + H)}} + \underbrace{1s_B(1)1s_B(2)}_{\text{Ionic (H}^+ + \text{H}^-)} \tag{3.290}$$

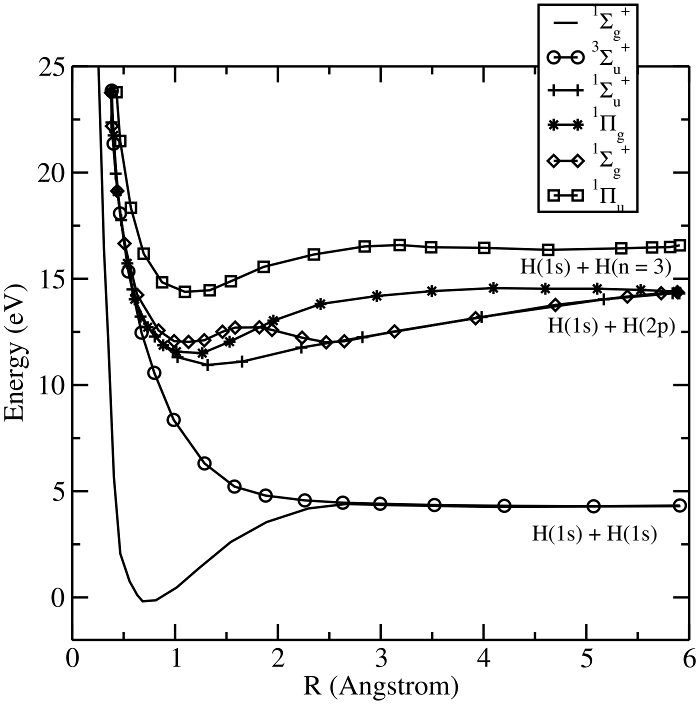
Both covalent and ionic terms can be introduced into the wavefunction with their own variational parameters c_1 and c_2:

$$\psi = c_1\psi_{\text{covalent}} + c_2\psi_{\text{ionic}} \tag{3.291}$$

$$\psi_{\text{covalent}} = 1s_A(1)1s_B(2) + 1s_A(2)1s_B(1) \tag{3.292}$$

$$\psi_{\text{ionic}} = 1s_A(1)1s_A(2) + 1s_B(1)1s_B(2) \tag{3.293}$$

Note that the variational constants c_1 and c_2 depend on the internuclear distance R. Minimization of the energy expectation value with respect to these constants gives $R_e = 74.9$ pm (experiment 74.1 pm) and $D_e = 386$ kJ mol^{-1} (experiment 458 kJ mol^{-1}). Further improvement could be achieved by adding higher atomic orbitals into the wavefunction. The previously discussed Hartree-Fock method provides an efficient way for solving the problem. Recall that this method is only approximate as it ignores the electron-electron correlation effects completely. The full treatment requires use of configuration interaction methods, which can yield essentially exact results: $D_e = 36117.8$ cm^{-1} (CI) vs. 36117.3 ± 1.0 cm^{-1} (exp) and $R_e = 74.140$ pm vs. 74.139 pm (exp).



Some of the lowest lying excited states of H_2.

In diatomic (and linear) molecules, the quantization axis is chosen along the molecule. When spin-orbit interaction is negligible, this allows us to define the total orbital and spin angular momenta about the molecular axis:

$$\Lambda = |\lambda_1 + \lambda_2 + ...| \tag{3.294}$$

where $\lambda_i = 0$ for a σ orbital, $\lambda_i = \pm 1$ for a π orbital, $\lambda_i = \pm 2$ for a δ orbital, etc. The value of Λ is expressed using the following capital Greek letters (just like we had s, p, d for atoms):

Λ	=	0	1	2	3	...
Symbol	=	Σ	Π	Δ	Φ	...

The state multiplicity is given by $2S + 1$ where S is the sum of the electron spins in the molecule. The term symbol for a diatomic molecule is represented by:

$$^{2S+1}\Lambda \tag{3.295}$$

Example. What is the term symbol for ground state H_2?

Solution. Both electrons are on a σ orbital and hence $\lambda_1 = \lambda_2 = 0$. This gives $\Lambda = 0$, which corresponds to Σ. The electrons occupy the same molecular orbital with opposite spins and hence $2S + 1 = 1$. This gives the term symbol as $^1\Sigma$.

For Σ terms superscripts "+" and "−" are used to express the parity of the wavefunction with respect to reflection in the plane containing the internuclear axis. For example, for ground state H_2, we would have a "+" symbol. As we have seen before, orbitals in diatomic molecules may be characterized by the g/u labels. These labels are often added to term symbols as subscripts. If only one unpaired electron is present, the u/g label reflects the symmetry of the unpaired electron orbital. Closed shell molecules have always g. With more than one unpaired electron, the overall parity should be calculated using the following rules: $g \times g = g$, $g \times u = u$, $u \times g = u$ and $u \times u = g$.

Example. What is the term symbol for ground state O_2?

Solution. Ground state O_2 has two electrons with parallel spins on the π_{+1} and π_{-1} orbitals. Thus this is a triplet state molecule with the orbital angular momentum from the two π-electrons being cancelled. This gives a $^3\Sigma$ term. The two π's are anti-bonding and as such they are desginated as g and further $g \times g = g$ (remember that for π orbigals the g/u vs. bonding/anti-bonding is reversed from that of σ orbitals). To see the $+/-$ symmetry, it is convenient to think about π_x and π_y Cartesian orbitals (draw a picture!) and see that one of them is + and the other is − (they are perpendicular to each other). Again $+ \times - = -$ and we have the complete term symbol as $^3\Sigma_g^-$.

Notes:

- When spin-orbit interaction is small, the above term symbols are adequate ("Hund's case (a)").
- When spin-orbit interaction is large, S and Λ can no longer be specified but their sum $J = |S + \Lambda|$ is a good quantum number.

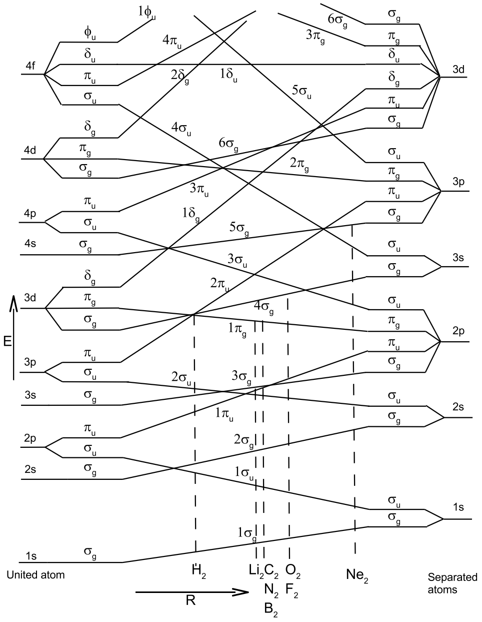
3.5 Electron configurations of homonuclear diatomic molecules

Which atomic orbitals mix to form molecular orbitals and what are their relative energies? The graph on the left can be used to obtain the energy order of molecular orbitals and indicates the atomic orbital limits.

The non-crossing rule: States with the same symmetry never cross.

Bonding orbitals:	$1\sigma_g$, $2\sigma_g$, $1\pi_u$, etc.
Antibonding orbitals:	$1\sigma_u^*$, $2\sigma_u^*$, $1\pi_g^*$, etc.

Note that the u/g labels are reversed for bonding/antibonding π orbitals!



The orbitals should be filled with electrons in the order of increasing energy. Note that π, δ, etc. orbitals can hold a total of 4 electrons. If only one bond is formed, we say that the bond order (BO) is 1. If two bonds form (for example, one σ and one π), we say that the bond order is 2 (double bond). Molecular orbitals always come in pairs: bonding and antibonding.

Molecule	# of els.	El. Conf.	Term sym.	BO	R_e (Å)	D_e (eV)
H_2^+	1	$(1\sigma_g)$	$^2\Sigma_g$	0.5	1.060	2.793
H_2	2	$(1\sigma_g)^2$	$^1\Sigma_g$	1.0	0.741	4.783
He_2^+	3	$(1\sigma_g)^2(1\sigma_u)$	$^2\Sigma_u$	0.5	1.080	2.5
He_2	4	$(1\sigma_g)^2(1\sigma_u)^2$	$^1\Sigma_g$	0.0	Not bound	
Li_2	6	$He_2(2\sigma_g)^2$	$^1\Sigma_g$	1.0	2.673	1.14
Be_2	8	$He_2(2\sigma_g)^2(2\sigma_u)^2$	$^1\Sigma_g$	0.0	Not bound	
B_2	10	$Be_2(1\pi_u)^2$	$^3\Sigma_g$	1.0	1.589	≈3.0
C_2	12	$Be_2(1\pi_u)^4$	$^1\Sigma_g$	2.0	1.242	6.36
N_2^+	13	$Be_2(1\pi_u)^4(3\sigma_g)$	$^2\Sigma_g$	2.5	1.116	8.86
N_2	14	$Be_2(1\pi_u)^4(3\sigma_g)^2$	$^1\Sigma_g$	3.0	1.094	9.902
O_2^+	15	$N_2(1\pi_g)$	$^2\Pi_g$	2.5	1.123	6.77
O_2	16	$N_2(1\pi_g)^2$	$^3\Sigma_g$	2.0	1.207	5.213
F_2	18	$N_2(1\pi_g)^4$	$^1\Sigma_g$	1.0	1.435	1.34
Ne_2	20	$N_2(1\pi_g)^4(3\sigma_u)^2$	$^1\Sigma_g$	0.0	Not bound	

Note that the Hund's rules predict that the electron configuration with the largest multiplicity lies the lowest in energy when the highest occupied MOs are degenerate.

3.6 Electronic structure of polyatomic molecules: the valece bond method

The valence bond method is an approximate approach, which can be used in understanding formation of chemical bonding. In particular, concepts like hybrid orbitals follow directly from it.

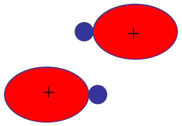
The valence bond method is based on the idea that a chemical bond is formed when there is non-zero overlap between the atomic orbitals of the participating atoms. Note that the the atomic orbitals must therefore have the same symmetry in order to gain overlap.

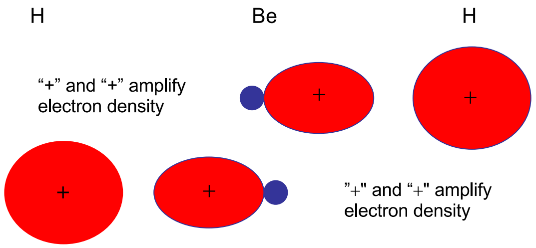
Hybrid orbitals are essentially linear combinations of atomic orbitals that belong to a single atom. Note that hybrid orbitals are not meaningful for free atoms as they only start to form when other atoms approach. The idea is best illustrated through the following examples.

1.BeH_2 molecule. Be atoms have atomic electron configuration of He$2s^2$. The two approaching hydrogen perturb the atomic orbitals and the two outer shell electrons reside on the two hybrid orbitals formed (z-axis is along the molecular axis):

$$\psi_{sp}^1 = \frac{1}{\sqrt{2}}(2s + 2p_z) \quad (3.296)$$

$$\psi_{sp}^2 = \frac{1}{\sqrt{2}}(2s - 2p_z) \quad (3.297)$$



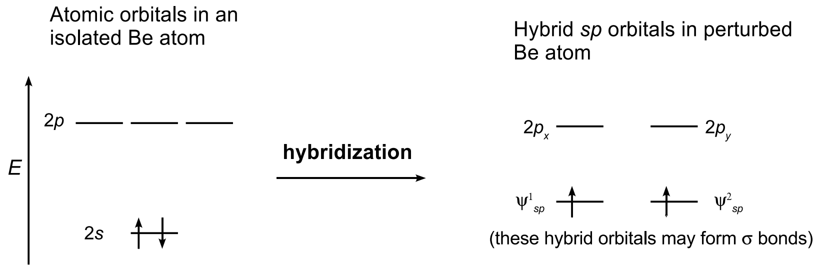


The hybrid orbitals further form two molecular σ orbitals:

$$\psi = c_1 1s_A + c_2 \psi_{sp}^1 \quad (3.298)$$

$$\psi' = c_1' 1s_B + c_2 \psi_{sp}^2 \quad (3.299)$$

This form of hybridization is called *sp*. This states that one s and one p orbital participate in forming the hybrid orbitals. For *sp* hybrids, linear geometries are favored and here H–Be–H is indeed linear. Here each MO between Be and H contain two shared electrons. Note that the number of initial atomic orbitals and the number of hybrid orbitals formed must be identical. Here s and p atomic orbitals give two *sp* hybrid orbitals. Note that hybrid orbitals should be orthonormalized.



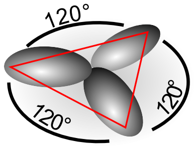
2. BH$_3$ molecule. All the atoms lie in a plane (i.e. planar structure) and the angles between the H atoms is 120°. The boron atom has electron configuration $1s^2 2s^2 2p$. Now three atomic orbitals ($2s$, $2p_z$, $2p_x$) participate in forming three hybrid orbitals:

$$\psi^1_{sp^2} = \frac{1}{\sqrt{3}}2s + \sqrt{\frac{2}{3}}2p_z \tag{3.300}$$

$$\psi^2_{sp^2} = \frac{1}{\sqrt{3}}2s - \frac{1}{\sqrt{6}}2p_z + \frac{1}{\sqrt{2}}2p_x \tag{3.301}$$

$$\psi^3_{sp^2} = \frac{1}{\sqrt{3}}2s - \frac{1}{\sqrt{6}}2p_z - \frac{1}{\sqrt{2}}2p_x \tag{3.302}$$

The three orbitals can have the following spatial orientations:



sp^2 hybrid orbitals.

Each of these hybrid orbitals bind form σ bonds with H atoms. This is called sp^2 hybridization because two p orbitals and one s orbital participate in the hybrid.

3a. CH$_4$ molecule. The electron configuration of carbon atom is $1s^2 2s^2 2p^2$. The outer four valence electrons should be placed on four sp^3 hybrid orbitals:

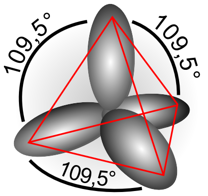
$$\psi^1_{sp^3} = \frac{1}{2}(2s + 2p_x + 2p_y + 2p_z) \tag{3.303}$$

$$\psi^2_{sp^3} = \frac{1}{2}(2s - 2p_x - 2p_y + 2p_z) \tag{3.304}$$

$$\psi^3_{sp^3} = \frac{1}{2}(2s + 2p_x - 2p_y - 2p_z) \tag{3.305}$$

$$\psi^4_{sp^3} = \frac{1}{2}(2s - 2p_x + 2p_y - 2p_z) \tag{3.306}$$

These four hybrid orbitals form σ bonds with the four hydrogen atoms.

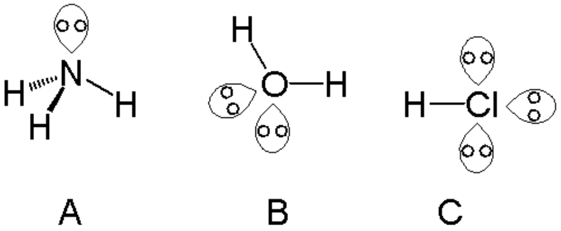


sp^3 hybrid orbitals.

The sp^3 hybridization is directly responsible for the geometry of CH_4 molecule. Note that for other elements with d-orbitals, one can also get bipyramidal (coordination 5) and octahedral (coordination 6) structures.

<u>3b. NH_3 molecule.</u> In this molecule, nitrogen is also sp^3 hybridized. The N atom electron configuration is $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$. Thus a total of 5 electrons should be placed on the four hybrid orbitals. One of the hybrid orbitals becomes doubly occupied ("lone-pair electrons") and the three remaining singly occupied hybrid orbitals form three sigma bonds to H atoms. Because of the lone-pair electrons, the geometry of NH_3 is tetrahedral with a bond angle of 109°(experimental value 107°).

<u>3c. H_2O molecule.</u> The oxygen is sp^3 hybridized with O atom electron configuration: $1s^2 2s^2 2p^4$. Now two of the four hybrid orbitals are doubly occupied with the electrons from oxygen atom and the remaining two hybrid orbitals can participate in σ bonding with two H atoms. This predicts the bond angle H–O–H as 109°(experimental value 104°). Thus H_2O has two lone-pair electrons.



Lone electron pairs in A: NH_3, B: H_2O and C: HCl.

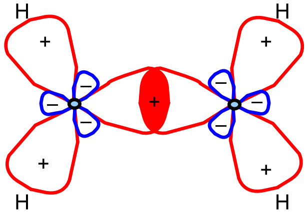
<u>Note:</u>

In numerical quantum chemical calculations, basis sets that resemble linear combinations of atomic orbitals are typically used (LCAO-MO-SCF). The atomic orbitals are approximated by a group of Gaussian functions, which allow analytic integration of the integrals, for example, appearing in the Hartree-Fock (SCF; HF) method. Note that hydrogenlike atom orbitals differ from Gaussian functions by the power of r in the exponent. A useful rule for Gaussians: A product of two Gaussian functions is another Gaussian function.

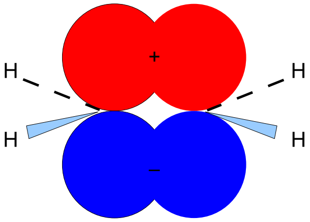
3.7 Hückel molecular orbital theory

Erich Hückel (1896 - 1980), German physical chemist.

Molecules with extensive π bonding systems, such as benzene, are not described very well by the valence bond theory because the π electrons are delocalized over the whole molecule. σ and π bonds are demonstrated below for ethylene (C_2H_4 with sp^2 carbons):



Formation of σ bonds from hybrid orbitals.



Formation of π bond from the non-hybrid p-orbitals.

Note that we have chosen z-axis along the internuclear axis. Because both σ and π bonding occurs between the two carbon atoms, we say that this is a double bond. Note that the hybrid orbitals here also explain the geometry. For triple bonds, one σ and two π bonds are formed.

Hückel molecular orbital theory assumes that the π electrons, which are responsible for the special properties of conjugated and aromatic hydrocarbons, do not interact with one another and the total wavefunction is just a product of the one-electron molecular orbitals. The π molecular orbital of the two carbons in C_2H_4 can be written approximately as:

$$\psi = c_1\phi_1 + c_2\phi_2 \tag{3.307}$$

where ϕ_1 and ϕ_2 are the $2p_y$ atomic orbitals for carbon 1 and 2, respectively. By using the variational principle (see Eq. (3.277)) gives the following secular determinant:

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0 \text{ with } H_{ij} = \int \phi_i^* H \phi_j d\tau \text{ and } S_{ij} = \int \phi_i^* \phi_j d\tau \tag{3.308}$$

In Hückel theory, the secular equation is simplified by assuming:
1. All the overlap integrals S_{ij} are set to zero unless $i = j$, when $S_{ii} = 1$.
2. All diagonal matrix elements H_{ii} are set to a constant denoted by α.
3. The resonance integrals H_{ij} $(i \neq j)$ are set to zero except for those on the neighboring atoms, which are set equal to a constant (β). Note that the indices here also identify atoms because the atomic orbitals are centered on atoms.

Now Eq. (3.308) becomes:

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0 \tag{3.309}$$

In Hückel theory, the Coulomb integral α and the resonance integral β are regarded as empirical parameters. They can be obtained, for example, from experimental data. Thus, in the Hückel theory it is not necessary to specify the Hamiltonian operator! Expansion of the determinant in Eq. (3.309) leads to a quadratic equation for E. The solutions are found to be $E = \alpha \pm \beta$. In general, it can be shown that $\beta < 0$, which implies that the lowest orbital energy is $E_1 = \alpha + \beta$. There are two π electrons and therefore the total energy is $E_{tot} = 2E_1 = 2\alpha + 2\beta$. Do not confuse α and β here with electron spin.

The wavefunctions (i.e. the coefficients c_1 and c_2 in Eq. (3.307)) can be obtained by substituting the two values of E into the original linear equations (cf. Eqs. (3.274) and (3.275)):

$$c_1(\alpha - E) + c_2\beta = 0 \tag{3.310}$$

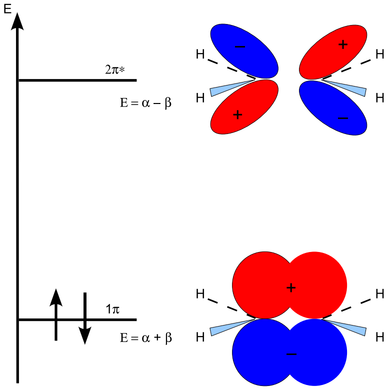
$$c_1\beta + c_2(\alpha - E) = 0 \tag{3.311}$$

For the lowest energy orbital ($E_1 = \alpha + \beta$), we get (including normalization):

$$\psi_1 = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2) \qquad \text{(i.e. } c_1 = c_2 = \frac{1}{\sqrt{2}}\text{)} \tag{3.312}$$

and for the highest energy orbital ($E_2 = \alpha - \beta$) (including normalization):

$$\psi_2 = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2) \qquad \text{(i.e. } c_1 = \frac{1}{\sqrt{2}}, c_2 = -\frac{1}{\sqrt{2}}\text{)} \tag{3.313}$$



Energy level diagram showing the low energy (bonding) and high energy (antibonding) orbitals.

These orbitals resemble the H_2^+ LCAO MOs discussed previously. This also gives us an estimate for one of the excited states where one electron is promoted from the bonding to the antibonding orbital. The excitation energy is found to be $2|\beta|$, which allows for, for example, estimation of β from UV/VIS absorption spectroscopy.

HOMO orbital = The highest occupied molecular orbital.
LUMO orbital = The lowest unoccupied molcular orbital.

Example. Calculate the π electronic energy for 1,3-butadiene ($CH_2{=}CHCH{=}CH_2$) by using the Hückel theory.

Solution. First we have to write the secular determinant using the rules given earlier. In order to do this, it is convenient to number the carbon atoms in the molecule:

$$\overset{1}{CH_2} = \overset{2}{CH} - \overset{3}{CH} = \overset{4}{CH_2}$$

In this case there are two scenarios that should be considered:

1. A localized solution where the π electrons are shared either with atoms 1 and 2 or 3 and 4. This would imply that the β parameter should not be written between nuclei 2 and 3.
2. A delocalized solution where the π electrons are delocalized over all four carbons. This would imply that the β parameters should be written between nuclei 2 and 3.

Here it turns out that scenario 2) gives a lower energy solution and we will study that in more detail. In general, however, both cases should be considered. The energy difference between 1) and 2) is called the *resonance stabilization energy*. The secular determinant is:

$$\begin{array}{c|cccc|} & 1 & 2 & 3 & 4 \\ 1 & \alpha - E & \beta & 0 & 0 \\ 2 & \beta & \alpha - E & \beta & 0 \\ 3 & 0 & \beta & \alpha - E & \beta \\ 4 & 0 & 0 & \beta & \alpha - E \end{array} = 0 \quad (3.314)$$

The numbers outside the determinant are just guides to see which atoms each row/column correspond to.

To simplify notation, we divide each row by β and denote $x = (\alpha - E)/\beta$:

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0 \quad (3.315)$$

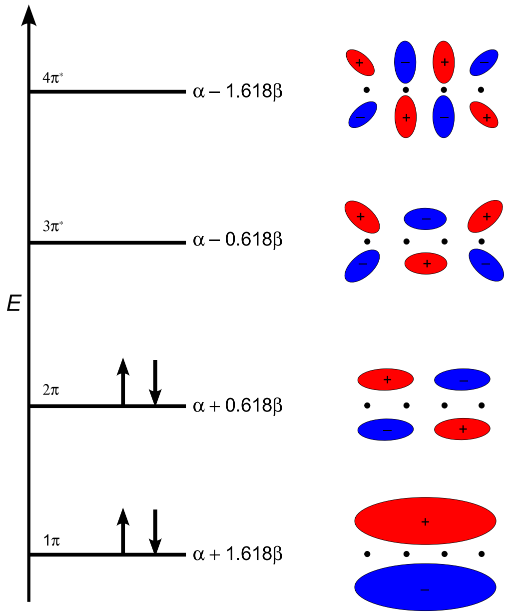
Expansion of this determinant gives $x^4 - 3x^2 + 1 = 0$. There are four solutions $x = \pm 0.618$ and $x = \pm 1.618$. Thus there are four possible orbital energy levels:

$$\begin{aligned} E_1 &= \alpha + 1.618\beta \qquad \text{(lowest energy)} \\ E_2 &= \alpha + 0.618\beta \\ E_3 &= \alpha - 0.618\beta \\ E_4 &= \alpha - 1.618\beta \qquad \text{(highest energy)} \end{aligned} \quad (3.316)$$

There are four π electrons, which occupy the two lowest energy orbitals. This gives the total π electronic energy for the molecule:

$$E_\pi = 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta) = 4\alpha + 4.472\beta \quad (3.317)$$

and the lowest excitation energy is $1.236|\beta|$.



Note especially the delocalization of the orbitals over the whole molecule.

The four Hückel MO wavefunctions are (calculations not shown):

$$\begin{aligned}\psi_1 &= 0.372\phi_1 + 0.602\phi_2 + 0.602\phi_3 + 0.372\phi_4 \\ \psi_2 &= 0.602\phi_1 + 0.372\phi_2 - 0.372\phi_3 - 0.602\phi_4 \\ \psi_3 &= 0.602\phi_1 - 0.372\phi_2 - 0.372\phi_3 + 0.602\phi_4 \\ \psi_4 &= 0.372\phi_1 - 0.602\phi_2 + 0.602\phi_3 - 0.372\phi_4\end{aligned} \tag{3.318}$$

Example. Apply the Hückel method for benzene molecule.

Solution. The secular determinant for benzene is (electrons delocalized):

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha - E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha - E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha - E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha - E & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0 \tag{3.319}$$

The solutions are (where the six π electrons should be placed):

$$\begin{aligned} E_1 &= \alpha + 2\beta \quad \text{(lowest energy)} \\ E_2 &= E_3 = \alpha + \beta \\ E_4 &= E_5 = \alpha - \beta \\ E_6 &= \alpha - 2\beta \quad \text{(highest energy)} \end{aligned} \tag{3.320}$$

3.8 Dipole moments and ionic bonding

The *classical* electric dipole moment μ with charges Q_i is defined:

$$\vec{\mu} = \sum_{i=1}^{N} Q_i \vec{r_i} \tag{3.321}$$

where N is the number of charges, Q_i are the charge magnitudes and $\vec{r_i}$ are their position vectors. Note that both the dipole moment $\vec{\mu}$ and $\vec{r_i}$ are vectors. Often only the magnitude of the dipole moment is used. Dipole moment has SI units of C m ("Coulomb × meter").

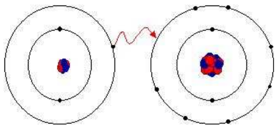
To calculate the dipole moment of a molecule, we must calculate the expectation value for the electric dipole moment operator:

$$\begin{aligned} &\hat{\vec{\mu}} = (\hat{\mu}_x, \hat{\mu}_y, \hat{\mu}_z) \\ &\hat{\mu}_x = \sum_{i=1}^{N} Q_i x_i, \quad \hat{\mu}_y = \sum_{i=1}^{N} Q_i y_i, \quad \hat{\mu}_z = \sum_{i=1}^{N} Q_i z_i \\ &\left\langle \hat{\vec{\mu}} \right\rangle = \int \psi^* \hat{\vec{\mu}} \psi d\tau \end{aligned} \tag{3.322}$$

Here x_i, y_i and z_i represent the coordinates of particle i and integrations are over the $3N$ dimensional space with a volume element denoted by $d\tau$.

When atoms with nearly the same electronegativity form bonds, the molecular orbitals are distributed evenly over the two atoms and a covalent bond forms. If the atoms have somewhat different electronegativities, the molecular orbitals are unevenly distributed and an ionic bond forms. In a pure ionic bond, atomic orbitals do not exhibit any overlap and the stabilization is only due to the electrostatic attraction between the charges. Note that neither pure ionic or covalent bonds exist.

Example. Lithium fluoride (LiF). The ionization energy of Li is 5.4 eV and the electron affinity of F is 3.5 eV (difference 1.9 eV). These two values are sufficiently close to each other and therefore we expect ionic bonding to occur.



The bonding orbitals have more electron density on the more electronegative atom.

This can be compared, for example, with C–H bond, where the difference between electron affinities and ionization energies are greater than 10 eV. Alternatively, one can compare the electronegativities of the atoms to see, if ionic or covalent bonding is expected to dominate.

At long distances, the two charges in an ionic compound (i.e. $\mathrm{A}^+ - \mathrm{B}^-$) are bound by the Coulomb attraction (Q_i are the total charges of the ions):

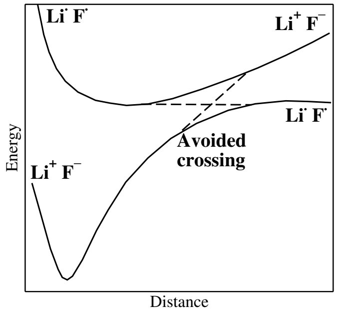
$$E(R) = \frac{Q_1 Q_2}{4\pi\epsilon_0 R} \tag{3.323}$$

When the ions approach close enough so that the doubly filled atomic orbitals begin to overlap, strong repulsion occurs because molecular orbitals form with both bonding and antibonding orbitals filled ("antibonding orbitals are more repulsive than the bonding orbitals are attractive"). This is also called the *Pauli repulsion.* To account for this repulsive behavior at the short distances, an empirical exponential repulsion term is usually added to Eq. (3.323):

$$E(R) = \frac{Q_1 Q_2}{4\pi\epsilon_0 R} + be^{-aR} \tag{3.324}$$

where the energy is expressed relative to the dissociated ions. Note that the repulsive term is important only at short distances and even at the equilibrium distance R_e the Coulomb term gives a good approximation for the binding energy. Further refinement of this expression can be obtained by including terms representing attraction between the induced dipoles and "instantaneous charge fluctuations" (van der Waals).

Eq. (3.324) applies to dissociation into separated ions. However, due to an avoided crossing between the ionic and covalent states, the dissociation occurs into separated neutral atoms. An example of this behavior is shown below.



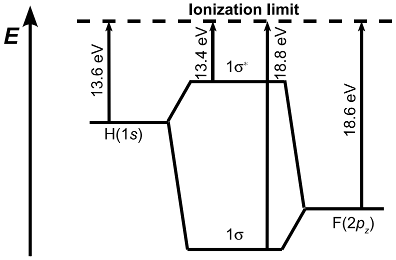
A schematic graph of avoided crossing between covalent and ionic states in LiF molecule.

The dissociation energy into neutral atoms from an ionic state is given by:

$$D_e(\mathrm{MX} \to \mathrm{M} + \mathrm{X}) = D_e(\mathrm{MX} \to \mathrm{M}^+ + \mathrm{X}^-) - E_{ea}(\mathrm{X}) \tag{3.325}$$

where M denotes metal and X non-metal, $D_e(\mathrm{MX} \to \mathrm{M} + \mathrm{X})$ is the dissociation energy into atoms, $D_e(\mathrm{MX} \to \mathrm{M}^+ + \mathrm{X}^-)$ is the dissociation energy into ions, $E_i(\mathrm{M})$ is the ionization energy of metal atom, and $E_{ea}(\mathrm{X})$ is the electron affinity of the non-metal atom.

Note that for heteronuclear diatomic molecules, the molecular orbitals form with non-equivalent atomic orbitals. For example, in HF molecule the H($1s$) and F($2p_z$) form bonding and antibonding orbitals:



Bonding and antibonding orbitals fromed from H($1s$) and F($2p_z$) atomic orbitals.

By using the variational principle, it is possible to obtain the orbitals as:

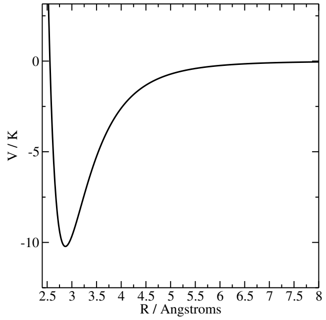
$$E = -18.8\text{eV: } 1\sigma_g = 0.19 \times 1s(\text{H}) + 0.98 \times 2p_z(\text{F}) \tag{3.326}$$

$$E^* = -13.4\text{eV: } 1\sigma_u^* = 0.98 \times 1s(\text{H}) - 0.19 \times 2p_z(\text{F}) \tag{3.327}$$

The symmetry and energetics of the atomic orbitals determine which atomic orbitals mix to form molecular orbitals. Note that u/g labels cannot be used anymore.

3.9 Intermolecular forces

Consider two atoms or molecules that do not form chemical bonds. When they approach each other, a small binding (van der Waals; vdW) occurs first and after that strong repulsion (Pauli repulsion). The repulsion follows from the overlap of the doubly occupied orbitals as discussed earlier. The small vdW binding contributes to physical processes like freezing and boiling. At large distances, the interaction energy approaches zero. For example, a "pair potential" might look like:



Pair potential between two helium atoms.

Note that the energy unit above is K (Kelvin; i.e. multiplication by the Boltzmann constant gives energy). Very often Ångströms (Å) or Bohr (atomic units; a.u.) are used for units of distance.

1. Dipole - dipole interaction. The dipole – dipole interaction between two freely rotating dipoles (i.e., molecules with dipole moments) is zero. However, because their mutual potential energy depends on their relative orientation, the molecules do not in fact rotate completely freely, even in gas phase. The lower energy orientations are marginally favored, so there is a nonzero average interaction between the dipoles. It can be shown that this interaction has the form (*the Keesom interaction*):

$$\langle V(R)\rangle_{dd} = -\frac{2}{3kT}\left(\frac{\mu_A\mu_B}{4\pi\epsilon_0}\right)^2 \times \frac{1}{R^6} \tag{3.328}$$

where k is the Boltzmann constant, T is the temperature (K), μ_A and μ_B are dipole moments of the molecules, ϵ_0 is the vacuum permittivity and R is the distance between the molecules. The angular brackets denote thermal averaging (statistical mechanics). Note that as the temperature increases, this interaction becomes less important and that the interaction is negative (attractive).

2. Dipole - induced dipole interaction. If molecule A has a permanent dipole moment μ_A, it creates an electric field that polarizes the electron cloud on molecule B. This creates an induced dipole moment proportional to $\alpha_B\mu_A$, where α_B is called the (averaged) polarizability of molecule B. The dipole - induced dipole attractive energy can be shown to be (including the effect both ways):

$$\langle V(R)\rangle_{ind} = -4\frac{\alpha_B\mu_A^2 + \alpha_A\mu_B^2}{(4\pi\epsilon_0)^2}\frac{1}{R^6} \tag{3.329}$$

3. London force (or dispersion force). This attractive force has its origins in the concept of electron correlation. A simple model ("Drude oscillator") considers correlated displacements of electrons in the two atoms / molecules, which generate instantaneous dipoles and attractive interaction. Of course, this is model not entirely correct because this process does not involve real time (i.e. only quantum mechanical motion). This interaction occurs even between molecules with no permanent dipole or charge.

Fritz London (1900 - 1954), German-American physicist.

The exact form for the expression is very complicated, but to a good approximation:

$$\left\langle V(R)_{disp}\right\rangle = -\frac{3}{2}\left(\frac{E_AE_B}{E_A+E_B}\right)\frac{\alpha_A\alpha_B}{(4\pi\epsilon_0)^2}\frac{1}{R^6} \tag{3.330}$$

The above three terms add to give the total attractive energy between molecules A and B. This interaction depends strongly on the interacting atoms/molecules but it is typically few meV around 5 Å separation.

It is common to express the interaction energy between two atoms / molecules by using the Lennard-Jones form (or "6-12 form"):

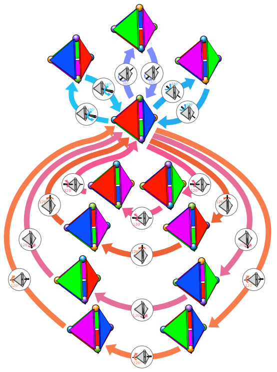
$$V(R) = 4\epsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right] \tag{3.331}$$

The first term (left) represents the Pauli repulsion and the second term (right) represents the van der Waals binding discussed previously. Note that the interaction energy is often called the potential energy because in molecular dynamics simulations (nuclear dynamics), this represents the potential energy. The magnitude of binding in this potential is ϵ, which occurs at distance $R_e = 2^{1/6}\sigma$. These parameters may be obtained from experiments or theory. Typical values for ϵ and σ in different atom / molecule pairs are given below (rotationally averaged).

	ϵ [K]	σ [Å]	Freezing pt.[K]	Boiling pt. [K]
Ar	120	3.41	84.0	87.3
Xe	221	4.10	161.3	165.1
H_2	37	2.93	13.8	20.3
N_2	95.1	3.70	63.3	77.4
O_2	118	3.58	54.8	90.2
Cl_2	256	4.40	172.2	239.1
CO_2	197	4.30	216.6	194.7
CH_4	148	3.82	89	111.7
C_6H_6	243	8.60	278.7	353.2

Note the loose correlation between ϵ and the freezing/boiling temperatures.

Chapter 4: Symmetry



4.1 Symmetry elements and symmetry operations

Molecules in their equilibrium geometries often exhibit a certain degree of symmetry. For example, a benzene molecule is symmetric with respect to rotations around the axis perpendicular to the molecular plane. The concept of symmetry can be applied in quantum mechanics to simplify the underlying calculations. For example, in chemistry, symmetry can be used to predict optical activities of molecules as well as their dipole moments. Especially, in spectroscopy symmetry is a powerful tool for predicting optically allowed transitions.

Symmetry element: A symmetry element is a geometrical entity, which acts as a center of symmetry. It can be a plane, a line or a point.

Symmetry operation: Action that leaves an object looking the same after it has been carried out is called a symmetry operation. Typical symmetry operations include rotations, reflections and inversions. The corresponding symmetry element defines the reference point for the symmetry operation. In quantum mechanics symmetry operations appear as operators, which can operate on a given wavefunction.

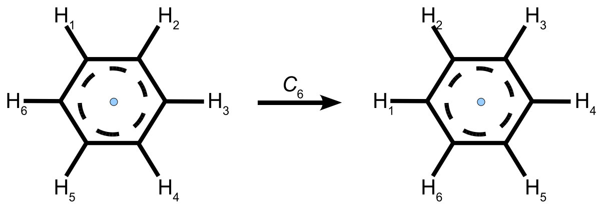
Point group: A collection of symmetry operations defines the overall symmetry for the molecule. When these operations form a mathematical group, they are called a point group. As we will see later, molecules can be classified in terms of point groups.

Symmetry operation	Symmetry element	Operation
i	Center of symmetry (point)	Projection through the center of symmetry to the equal distance on the opposite side.
C_n	Proper rotation axis (line)	Counterclockwise rotation about the axis by $2\pi/n$, where n is an integer.
σ	Mirror plane (plane)	Reflection across the plane of symmetry.
S_n	Improper rotation axis (line)	Counterclockwise rotation about the axis by $2\pi/n$ followed by a reflection across the plane perpendicular to the rotation axis.
E	Identity element	This operation leaves the object unchanged.

4.2 The rotation operation

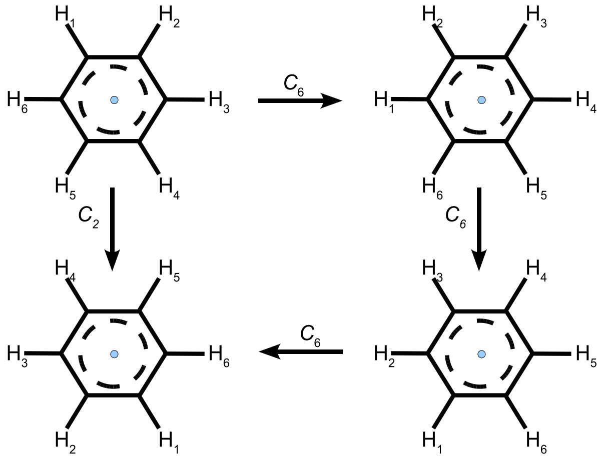
The rotation operation is denoted by C_n, where the (counterclockwise) rotation angle is given by $2\pi/n$ in radians. Thus a C_1 operation rotates a given object by 360°, which effectively does nothing to the object. Here n is called the **order of rotation** and the corresponding symmetry element is called an n-fold rotation axis. Often notation C_n^+ is used to denote clockwise and C_n^- counterclockwise rotations.

Consider a planar benzene molecule as an example (note that both C and H nuclei are transformed):



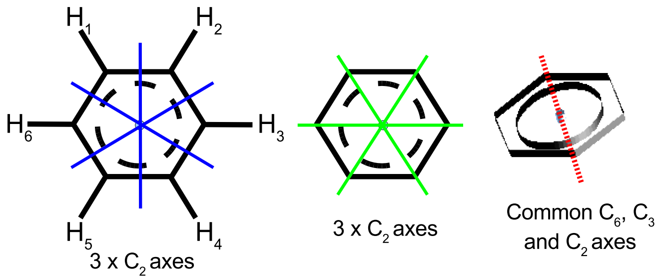
The symmetry element is indicated in the middle (line pointing out of plane).

Rotations can be combined to yield other rotation operations. For example, for benzene $C_6^3 = C_2$:



Demonstration of $C_6^3 = C_2$.

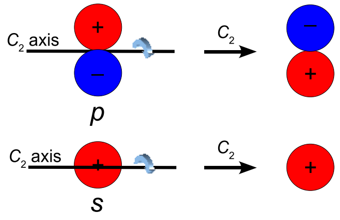
A molecule may have many different rotation symmetry axes. For example, benzene has a number of different possible C_n with various symmetry elements. Consider the C_6 symmetry element going through the center of the molecule and being perpendicular to the plane of the molecule. As shown previously, both C_6 and C_2 have collinear symmetry axes. In addition, C_3 also has the same symmetry axis. Furthermore, there are six other C_2 symmetry axes. These axes are indicated below.



Various C_6, C_3 and C_2 symmetry axes in benzene.

Note that there are three different kinds of C_2 axes and in this case we distinguish between them by adding primes to them (e.g. C_2, C_2', C_2''). The **principal axis** of rotation is the C_n axis with the highest n. For benzene this is C_6.

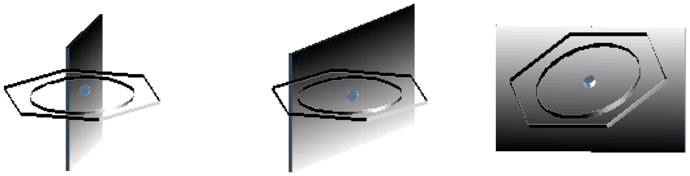
Symmetry operations can be performed on any object defined over the molecule. For example, a C_2 operation on a s and p orbitals can visualized as follows:



Operation of C_2 on s and p orbitals.

4.3 The reflection operation

The reflection operation is denoted by σ and the corresponding symmetry element is called a mirror plane. Given a symmetry plane, the σ operation reflects each point to the opposite side of the plane. For example, some of the σ symmetry elements in benzene are shown below.



One of the σ_d planes going through only the center of symmetry

One of the σ_v planes going through the center and the two carbons

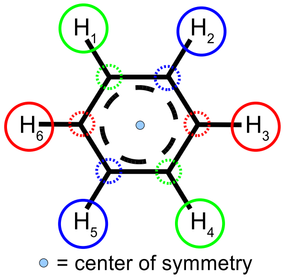
The only σ_h plane containing all the carbon atoms

Some of the σ symmetry elements in benzene.

σ_d denotes a plane, which bisects the angle between the two C_2 axes and lies parallel to the principal axis. The σ_v plane includes the protons and the principal axis. The σ_h is perpendicular to the principal axis. Note that two successive reflections $\sigma\sigma$ bring the molecule back to its original configuration (corresponding to an E operation).

4.4 The inversion operation

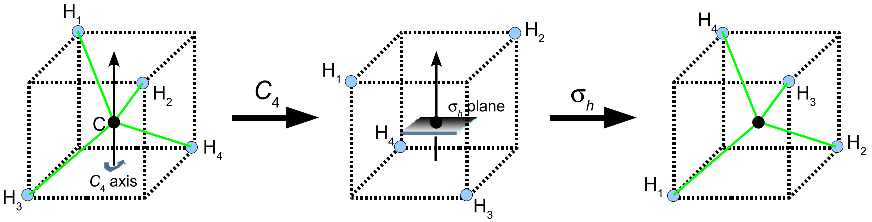
The inversion operation is denoted by i and it is expressed relative to the central point (i.e. the symmetry element) in the molecule through which all the symmetry elements pass. This point is also called the **center of symmetry**. If the center point is located at origin $(0,0,0)$, the inversion operation changes coordinates as $(x,y,z) \rightarrow (-x,-y,-z)$. Molecules with inversion symmetry are called **centrosymmetric**. Note that there are obviously molecules which do not fulfill this requirement. Application of i operation twice (e.g. $i^2 = ii$) corresponds to the identity operation E.



Atoms related to each other via the inversion symmetry in benzene.

4.5 Rotation-reflection operation

Rotation-reflection operation is denoted by S_n. It consists of two different operations: C_n and σ_h, which are executed in sequence. Note that a molecule may not necessary possess a proper symmetry with respect to these individual operations but may still have the overall S_n symmetry. For example, benzene has S_6 symmetry as well as C_6 and σ_h whereas a tetrahedral CH_4 has S_4 but not C_4 or σ_h alone:



S_4 symmetry operation in methane. Note that the symmetry is temporarily lost after C_4.

It can be shown that $(S_4)^2 = C_2$ and $(S_4)^4 = E$.

4.6 Identification of point groups of molecules

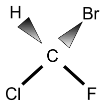
A given molecule may have a number of possible symmetry operations. These symmetry operations form a mathematical group if they satisfy the following requirements:

1. If two symmetry operations are "multiplied" together (i.e. they are applied in sequence), the resulting overall symmetry operation must also belong to the group.
2. The group must always contain the identity operation (E).
3. The symmetry operations in a group must be associative: $(AB)C = A(BC)$. Note that they do not have to commute (e.g. it may be that $AB \neq BA$).
4. Each symmetry operation must have an inverse operation: for symmetry operation A there must be another symmetry operation A^{-1} for which $AA^{-1} = E$.

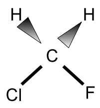
A group is called **Abelian** if the multiplication operation is commutative (i.e. $AB = BA$). If this does not hold, the group is **non-Abelian**.

Niels Henrik Abel (1802 - 1829)
Norwegian mathematician.

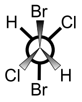
The groups of symmetry operations for molecules are called **point groups** because one spatial point is left unchanged by every symmetry operation. Note that this point is not necessarily occupied by any nucleus. The **Schoenflies notation** is typically used in quantum mechanics and spectroscopy whereas the **Hermann-Mauguin notation** is used in crystallography. In the following, we will concentrate on the Schoenflies notation. A list of point groups and the corresponding symmetry operations are given below.



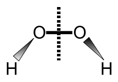
C_1: E



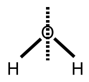
C_s: E, σ



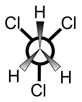
C_i: E, i



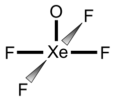
C_2: E, C_2



C_{2v}: E, C_2, $\sigma_v(xz)$, $\sigma_v'(yz)$

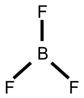


C_{3v}: E, $2C_3$, $3\sigma_v$

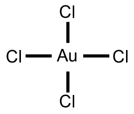


C_{4v}: E, $2C_4$, C_2, $2\sigma_v$, $2\sigma_d$

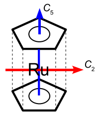
$C_{\infty v}$: E, $2C_\infty$, $\infty\sigma_v$



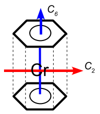
D_{3h}: E, $2C_3$, $3C_2$, σ_h, $2S_3$, $3\sigma_v$



D_{4h}: E, $2C_4$, C_2, $2C_2'$, $2C_2''$, i, $2S_4$, σ_h, $2\sigma_v$, $2\sigma_d$

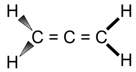


D_{5h}: E, $2C_5$, $2C_5^2$, $5C_2$, σ_h, $2S_5$, $2S_5^2$, $5\sigma_v$

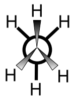


D_{6h}: E, $2C_6$, $2C_3$, C_2, $3C_2'$, $3C_2''$, i, $2S_3$, $2S_6$, σ_h, $3\sigma_d$, $3\sigma_v$

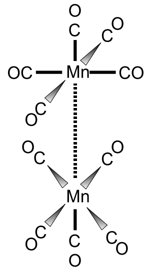
$D_{\infty h}$: E, $2C_\infty$, $\infty\sigma_v$, i, $2S_\infty$, ∞C_2



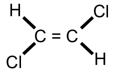
D_{2d}: E, $2S_4$, C_2, $2C_2'$, $2\sigma_d$



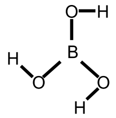
D_{3d}: E, $2C_3$, $3C_2$, i, $2S_6$, $3\sigma_d$



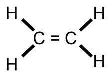
D_{4d}: E, $2S_8$, $2C_4$, $2S_8^3$, C_2, $4C_2'$, $4\sigma_d$



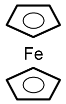
C_{2h}: E, C_2, i, σ_h



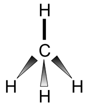
C_{3h}: E, C_3, C_3^2, σ_h, S_3, S_3^5



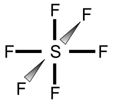
D_{2h}: E, $C_2(z)$, $C_2(y)$, $C_2(x)$, i, σ_{xy}, σ_{xz}, σ_{yz}



D_{5d}: E, $2C_5$, $2C_5^2$, $5C_2$, i, $2S_{10}^3$, $2S_{10}$, $5\sigma_d$



T_d: E, $8C_3$, $3C_2$, $6S_4$, $6\sigma_d$

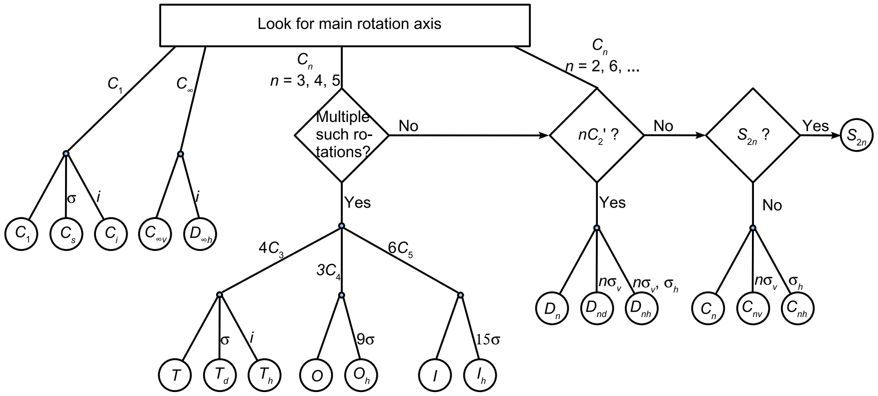


O_h: E, $8C_3$, $6C_2$, $6C_4$, $3C_2$, i, $6S_4$, $8S_6$, $3\sigma_h$, $6\sigma_d$

Notes:

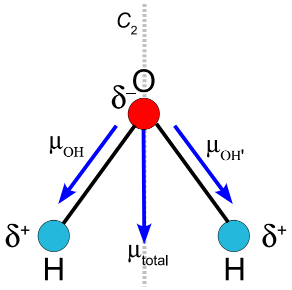
- Linear molecules are always either $C_{\infty v}$ or $D_{\infty h}$.
- Point groups $C_{\infty v}$, $D_{\infty h}$, T_d and O_h are sometimes called **special groups**.
- Short notation, for example: $2C_3$ indicates that there are two "similar" C_3 operations (for example, the $+/-$ pairs).

Determination of the point group for a given molecule can be a tedious task. Therefore it is helpful to use the following flowchart for determining the point group:



4.7 Symmetry, polarity and chirality

A **polar molecule** has a permanent dipole moment. Examples of polar molecules are HCl, O_3 and NH_3. If a molecule belongs to C_n group with $n > 1$, it cannot possess a charge distribution with a dipole moment perpendicular to the symmetry axis. Any dipole that exists in one direction perpendicular to the axis is cancelled by an opposing dipole from the other side. For example, in H_2O the perpendicular component of the dipole associated with one OH bond is cancelled by an equal but opposite component of the dipole of the second OH bond. Thus the dipole moment must be oriented along the C_2 axis of water:



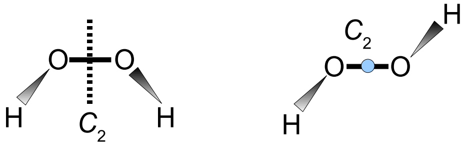
The total dipole moment in water is a vector sum from the polar bonds.

The same reasoning applies to molecules having C_{nv} symmetry and they may be polar. In all other groups, such as C_{3h}, D, etc., there are symmetry operations that take one end of the molecule into the other. Therefore these molecules may not have permanent dipole moment along any axis. In general, only molecules belonging to the groups C_n, C_{nv} and C_s may have a permanent dipole moment. For C_n and C_{nv} the dipole moment lies along the symmetry axis. For example, O_3 (ozone), which is nonlinear and belongs to C_{2v}, may be polar (and is). On the other hand, CO_2, which is linear and belongs to $D_{\infty h}$, is not polar.

A **chiral molecule** is a molecule that cannot be superimposed on its mirror image. Chiral molecules are optically active in the sense that they rotate the plane of polarized light. A chiral molecule and its mirror-image partner constitute an **enantiomeric pair** of isomers and rotate the plane of polarization in equal amounts but in opposite directions.

According to the theory of optical activity, a molecule may be chiral only if it does not possess an axis of improper rotation (S_n; "converts a left-handed molecule into a right-handed molecule"). Note that such an axis may be present implicitly as, for example, C_{nh} has an S_n axis (combined C_n and σ_h). Also, any molecule that has a center of inversion (i) has an S_2 axis (combined C_2 and σ_h). Thus any molecule with centers of inversion are **achiral** (not chiral). Because $S_1 = \sigma$ any molecule with a mirror plane is achiral. Note that a molecule may be achiral eventhough it does not have a center of inversion. Thermal motion may also result in fast conversion between the isomers quenching the optical activity.

Example. Is H_2O_2 chiral?
Solution. H_2O_2 has two isomers:



Two isomers of H_2O_2 with the C_2 symmetry axes (along the plane and out of plane) are shown.

This molecule has no explicit or implicit S_n axes and therefore it may be chiral. In fact, it is known to be chiral at low temperatures where the interconversion between the two isomers is forbidden. Equal populations of the isomers give a solution that is achiral overall (*rasemic*).

4.8 Matrix representation of symmetry operations

Symmetry operations can be written as matrices, which transform the object accordingly in space. In case of rotation, these are called **rotation matrices**. Consider first the inversion (i) operation, which we have seen to map coordinates (x_1, y_1, z_1) to (x_2, y_2, z_2) where $x_1 = -x_2, y_1 = -y_2, z_1 = -z_2$. This can be written in matrix form as follows:

$$\begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix} = \begin{pmatrix} -x_1 \\ -y_1 \\ -z_1 \end{pmatrix} \tag{4.332}$$

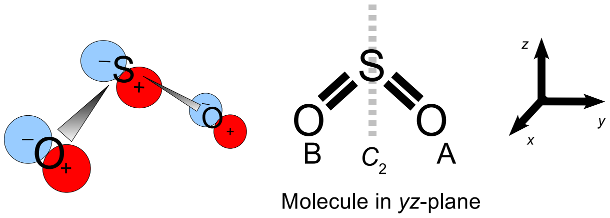
Now we can identify the matrix that corresponds to i as:

$$D(i) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \tag{4.333}$$

The identity operation (E) is clearly then:

$$D(E) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{4.334}$$

In general, **the matrix representation depends on the basis set and the choice of coordinate system**. In the following, we consider three atomic p_x orbitals in SO_2 molecule:



Atomic p_x orbitals in SO_2 (C_{2v}). Consider the orbitals as free atomic orbitals in this example.

Denote the p_x orbitals on O atoms labeled as A and B by p_A and p_B, respectively. The p_x orbital of S atom is denoted by p_S. Consider first a σ_v operation, which transforms $(p_S, p_A, p_B) \rightarrow (p_S, p_B, p_A)$. This can be written in matrix form as follows:

$$\begin{pmatrix} p_S \\ p_B \\ p_A \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} p_S \\ p_A \\ p_B \end{pmatrix} \tag{4.335}$$

Thus the **matrix representative** of $\sigma_v(xz)$ in this case is:

$$D(\sigma_v) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \tag{4.336}$$

The same method can be used to find matrix representatives for the other symmetry operations in C_{2v}. The effect of C_2 is to map $(p_S, p_A, p_B) \rightarrow (-p_S, -p_B, -p_A)$ and its representative is:

$$D(C_2) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix} \tag{4.337}$$

The effect of $\sigma_v'(yz)$ is $(p_S, p_A, p_B) \rightarrow (-p_S, -p_A, -p_B)$ and the representative is:

$$D(\sigma_v') = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \tag{4.338}$$

The identity operation (E) has no effect on the p orbitals and therefore it corresponds to a unit matrix:

$$D(E) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{4.339}$$

The set of matrices that represents all the operations of the group is called a **matrix representation** (denoted by Γ). The dimension of the basis set (above 3 - the three p_x orbitals) is denoted by a superscript, $\Gamma^{(3)}$.

The **character** of an operation in a given representation (χ) is the sum of the diagonal elements of its matrix representative (matrix trace denoted by Tr()). The character of an operation depends on the basis set used. For example, the characters of previously found matrix representations are:

$$\begin{aligned}
&\chi(E) \equiv \mathrm{Tr}(E) = 1+1+1 = 3 \\
&\chi(C_2) \equiv \mathrm{Tr}(C_2) = -1+0+0 = -1 \\
&\chi(\sigma_v(xz)) \equiv \mathrm{Tr}(\sigma_v(xz)) = 1+0+0 = 1 \\
&\chi(\sigma_v'(yz)) \equiv \mathrm{Tr}(\sigma_v'(yz)) = -1-1-1 = -3
\end{aligned} \tag{4.340}$$

The previous matrix representatives appear to be in **block diagonal form**:

$$D = \begin{pmatrix} X & 0 & 0 \\ 0 & X & X \\ 0 & X & X \end{pmatrix} \tag{4.341}$$

Thus the symmetry operations in C_{2v} do not mix p_S with p_A and p_B basis functions. This suggests that the matrix representation $\Gamma^{(3)}$ can be decomposed into two independent matrix representations (one for p_S and one for p_A and p_B).

For p_S we get (parentheses signify that these are matrices in general):

$$\begin{aligned}
&D(E) = (1) \\
&D(C_2) = (-1) \\
&D(\sigma_v) = (1) \\
&D(\sigma_v') = (-1)
\end{aligned} \tag{4.342}$$

This one dimensional matrix representation is now denoted by $\Gamma^{(1)}$. For the p_A and p_B, the matrix representation is found to be:

$$\begin{aligned}
&D(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \\
&D(\sigma_v) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\
&D(C_2) = \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix} \\
&D(\sigma_v') = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}
\end{aligned} \tag{4.343}$$

This is denoted by $\Gamma^{(2)}$.

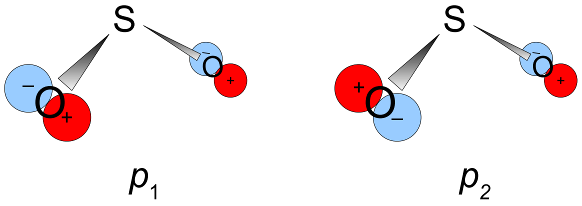
The relationship between the original matrix representation and the above two reduced representations is written symbolically as:

$$\Gamma^{(3)} = \Gamma^{(1)} + \Gamma^{(2)} \tag{4.344}$$

Clearly the one-dimensional matrix representation $\Gamma^{(1)}$ cannot be reduced any further. A matrix representation that cannot reduced any further is called an **irreducible representation** (or irrep for short).

How about the two-dimensional $\Gamma^{(2)}$? The matrices are not in block diagonal form and no further reduction is possible in this basis set. However, if we would choose our basis set slightly differently:

$$\begin{aligned} p_1 &= p_A + p_B \\ p_2 &= p_A - p_B \end{aligned} \tag{4.345}$$



p_1 and p_2 basis functions in SO$_2$.

In this new basis set the matrix representations in $\Gamma^{(2)}$ can be written as ("how does (p_1, p_2) transform?"):

$$\begin{aligned} D(E) &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \\ D(\sigma_v) &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \\ D(C_2) &= \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \\ D(\sigma_v') &= \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} \end{aligned} \tag{4.346}$$

These matrices are in block diagonal form and therefore we can break the above representation into two one-dimensional representations. p_1 spans (identical to $\Gamma^{(1)}$ for p_S):

$$\begin{aligned} D(E) &= (1) \\ D(C_2) &= (-1) \\ D(\sigma_v) &= (1) \\ D(\sigma_v') &= (-1) \end{aligned} \tag{4.347}$$

and p_2 spans (denoted by $\Gamma^{(1)'}$):

$$\begin{aligned} D(E) &= (1) \\ D(C_2) &= (1) \\ D(\sigma_v) &= (-1) \\ D(\sigma_v') &= (-1) \end{aligned} \tag{4.348}$$

In C_{2v} the irreducible representation (irrep) corresponding to $\Gamma^{(1)}$ above is denoted by B_1 and $\Gamma^{(1)'}$ is denoted by A_2. What irreps would arise from an oxygen s-atom orbital basis?

In general, C_{2v} can can have four kinds of irreps each with its own unique set of characters (ignore the Modes and Operators columns for now) as shown in the C_{2v} character table.

Table: Character table for C_1 point group (Abelian, possibly chiral).

C_1	E	Modes	Operators
A	1	$R_x, R_y, R_z, T_x, T_y, T_z$	$x, y, z, \ldots$

Table: Character table for $C_s = C_h$ point group (Abelian, achiral).

C_s	E	σ_h	Modes	Operators
A'	1	1	R_z, T_x, T_y	x, y, x^2, y^2, z^2, xy
A''	1	-1	R_x, R_y, T_z	z, yz, xz

Table: Character table for $C_i = S_2$ point group (Abelian, achiral).

C_i	E	i	Modes	Operators
A_g	1	1	R_x, R_y, R_z	$x^2, y^2, z^2, xy, xz, yz$
A_u	1	-1	T_x, T_y, T_z	x, y, z

Table: Character table for C_{2v} point group (Abelian, achiral).

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	Modes	Operators
A_1	1	1	1	1	T_z	z, x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	T_x, R_y	x, xz
B_2	1	-1	-1	1	T_y, R_x	y, yz

Table: Character table for C_{3v} point group (non-Abelian, achiral).

C_{3v}	E	$2C_3$	$3\sigma_v$	Modes	Operators
A_1	1	1	1	T_z	z, x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	T_x, T_y, R_x, R_y	$x, y, x^2-y^2, xy, xz, yz$

Table: Character table for C_{4v} point group (non-Abelian, achiral).

C_{4v}	E	C_2	$2C_4$	$2\sigma_v$	$2\sigma_d$	Modes	Operators
A_1	1	1	1	1	1	T_z	z, x^2+y^2, z^2
A_2	1	1	1	-1	-1	R_z	
B_1	1	1	-1	1	-1		x^2-y^2
B_2	1	1	-1	-1	1		xy
E	2	-2	0	0	0	T_x, T_y, R_x, R_y	x, y, xz, yz

Table: Character table for C_{5v} point group (non-Abelian, achiral, $\alpha = 2\pi/5$).

C_{5v}	E	$2C_5$	$2C_5^2$	$5\sigma_v$	Modes	Operators
A_1	1	1	1	1	T_z	z, x^2+y^2, z^2
A_2	1	1	1	-1	R_z	
E_1	2	$2\cos(\alpha)$	$2\cos(2\alpha)$	0	R_x, R_y, T_x, T_y	x, y, xz, yz
E_2	2	$2\cos(2\alpha)$	$2\cos(\alpha)$	0		xy, x^2-y^2

Table: Character table for C_{6v} point group (non-Abelian, achiral).

C_{6v}	E	C_2	$2C_3$	$2C_6$	$3\sigma_d$	$3\sigma_v$	Modes	Operators
A_1	1	1	1	1	1	1	T_z	z, x^2+y^2, z^2
A_2	1	1	1	1	-1	-1	R_z	
B_1	1	-1	1	-1	-1	1		
B_2	1	-1	1	-1	1	-1		
E_1	2	-2	-1	1	0	0	R_x, R_y, T_x, T_y	x, y, xz, yz
E_2	2	2	-1	-1	0	0		xy, x^2-y^2

Table: Character table for $C_{\infty v}$ point group (non-Abelian, achiral). When $\phi = \pi$ only one member in C_ϕ.

$C_{\infty v}$	E	$2C_\phi$	...	$\infty\sigma_v$	Modes	Operators
$A_1 = \Sigma^+$	1	1	...	1	T_z	z, x^2+y^2, z^2
$A_2 = \Sigma^-$	1	1	...	-1	R_z	
$E_1 = \Pi$	2	2cos(ϕ)	...	0	T_x, T_y, R_x, R_y	x, y, xz, yz
$E_2 = \Delta$	2	2cos(2ϕ)	...	0		x^2-y^2, xy
$E_3 = \Phi$	2	2cos(3ϕ)	...	0		
...	...	...	...	...		

Table: Character table for D_2 point group (Abelian, possibly chiral).

D_2	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	Modes	Operators
A_1	1	1	1	1		x^2, y^2, z^2
B_1	1	1	-1	-1	R_z, T_z	z, xy
B_2	1	-1	1	-1	R_y, T_y	y, xz
B_3	1	-1	-1	1	R_x, T_x	x, yz

Table: Character table for D_{2h} point group (Abelian, achiral).

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	Modes	Operators
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	T_z	z
B_{2u}	1	-1	1	-1	-1	1	-1	1	T_y	y
B_{3u}	1	-1	-1	1	-1	1	1	-1	T_x	x

Table: Character table for D_{2d} point group (non-Abelian, achiral).

D_{2d}	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$	Modes	Operators
A_1	1	1	1	1	1		x^2+y^2, z^2
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		x^2-y^2
B_2	1	-1	1	-1	1	T_z	z, xy
E	2	0	-2	0	0	T_x, T_y, R_x, R_y	x, y, xz, yz

Table: Character table for D_3 point group (non-Abelian, possibly chiral).

D_3	E	$2C_3$	$3C_2'$	Modes	Operators
A_1	1	1	1		z^2, x^2+y^2
A_2	1	1	-1	R_z, T_z	z
E	2	-1	0	R_x, R_y, T_x, T_y	$x, y, xz, yz, xy, x^2-y^2$

Table: Character table for D_{3h} point group (non-Abelian, achiral).

D_{3h}	E	σ_h	$2C_3$	$2S_3$	$3C_2'$	$3\sigma_v$	Modes	Operators
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	1	1	-1	-1	R_z	
A_1''	1	-1	1	-1	1	-1		
A_2''	1	-1	1	-1	-1	1	T_z	z
E'	2	2	-1	-1	0	0	T_x, T_y	x, y, x^2-y^2, xy
E''	2	-2	-1	1	0	0	R_x, R_y	xz, yz

Table: Character table for D_4 point group (non-Abelian, possibly chiral).

D_4	E	C_2	$2C_4$	$2C_2'$	$2C_2''$	Modes	Operators
A_1	1	1	1	1	1		z^2, x^2+y^2
A_2	1	1	1	-1	-1	R_z, T_z	z
B_1	1	1	-1	1	-1		x^2-y^2
B_2	1	1	-1	-1	1		xy
E	2	-2	0	0	0	R_x, R_y, T_x, T_y	x, y, xz, yz

Table: Character table for D_{6h} point group (non-Abelian, achiral).

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$	Modes	Operators
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	1	-1	-1	1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1		
B_{2g}	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1		
E_{1g}	2	1	-1	-2	0	0	2	1	-1	-2	0	0	R_x, R_y	xz, yz
E_{2g}	2	-1	-1	2	0	0	2	-1	-1	2	0	0		x^2-y^2, xy
A_{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	T_z	z
B_{1u}	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1		
B_{2u}	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1		
E_{1u}	2	1	-1	-2	0	0	-2	-1	1	2	0	0	T_x, T_y	x, y
E_{2u}	2	-1	-1	2	0	0	-2	1	1	-2	0	0		

Table: Character table for $D_{\infty h}$ point group (non-Abelian, achiral).

$D_{\infty h}$	E	$2C_\phi$	...	$\infty\sigma_v$	i	$2S_\phi$	...	$\infty C_2'$	Modes	Operators
$A_{1g} = \Sigma_g^+$	1	1	...	1	1	1	...	1		$x^2 + y^2, z^2$
$A_{1u} = \Sigma_u^+$	1	1	...	1	−1	−1	...	−1	T_z	z
$A_{2g} = \Sigma_g^-$	1	1	...	−1	1	1	...	−1	R_z	
$A_{2u} = \Sigma_u^-$	1	1	...	−1	−1	−1	...	1		
$E_{1g} = \Pi_g$	2	$2\cos(\phi)$	...	0	2	$-2\cos(\phi)$	...	0	R_x, R_y	xz, yz
$E_{1u} = \Pi_u$	2	$2\cos(\phi)$	...	0	−2	$2\cos(\phi)$	...	0	T_x, T_y	x, y
$E_{2g} = \Delta_g$	2	$2\cos(2\phi)$	...	0	2	$2\cos(2\phi)$	...	0		$x^2 - y^2, xy$
$E_{2u} = \Delta_u$	2	$2\cos(2\phi)$	...	0	−2	$-2\cos(2\phi)$	...	0		

Table: Character table for T_d point group (non-Abelian, achiral).

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	Modes	Operators
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	−1	−1		
E	2	−1	2	0	0		$2z^2 - x^2 - y^2, x^2 - y^2$
T_1	3	0	−1	1	−1	R_x, R_y, R_z	
T_2	3	0	−1	−1	1	T_x, T_y, T_z	x, y, z, xy, xz, yz

Table: Character table for O_h point group (non-Abelian, achiral).

O_h	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$	i	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$	Modes	Operators
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1		
E_g	2	−1	2	0	0	2	−1	2	0	0		$2z^2 - x^2 - y^2, x^2 - y^2$
T_{1g}	3	0	−1	1	−1	3	0	−1	1	−1	R_x, R_y, R_z	
T_{2g}	3	0	−1	−1	1	3	0	−1	−1	1		xy, xz, yz
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1		
E_u	2	−1	2	0	0	−2	1	−2	0	0		
T_{1u}	3	0	−1	1	−1	−3	0	1	−1	1	T_x, T_y, T_z	x, y, z
T_{2u}	3	0	−1	−1	1	−3	0	1	1	−1		

Table: Character table for I point group (non-Abelian, possibly chiral, $\alpha = 2\pi/5$).

I	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	Modes	Operators
A	1	1	1	1	1		$x^2 + y^2 + z^2$
T_1	3	$-2\cos(2\alpha)$	$-2\cos(\alpha)$	0	−1	$R_x, R_y, R_z, T_x, T_y, T_z$	x, y, z
T_2	3	$-2\cos(\alpha)$	$-2\cos(2\alpha)$	0	−1		
G	4	−1	−1	1	0		
H	5	0	0	−1	1		$2z^2 - x^2 - y^2, x^2 - y^2,$ xy, yz, xz

Labels A and B are used to denote one-dimensional representations (there are no higher dimensional irreps in C_{2v}). If the character under the principal rotation is $+1$ it is labeled A and if the character is -1 it is labeled B. When higher dimensional irreps occur in a group, they are denoted by E (two-dimensional), T (three-dimensional), G (four-dimensional) and H (five-dimensional) labels. Note that there is an unfortunate use of notation as E may represent a label for irreps and the identity operation. The number of irreps is always the same as the number of symmetry operations in a group. Some of the the higher dimensional irreps may have characters equal to zero. For example, for E the two degenerate states may behave differently with respect to a symmetry operation. One of them might change sign whereas the other one might not and the character would be a sum of these: $\chi = 1 - 1 = 0$. In general, χ consists of a sum of characters for all degenerate states.

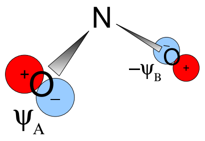
The characters of identity operation (E) reveal the degeneracy of the orbitals (or whatever entities we are dealing with). For example, any orbital that has symmetry A_1 or A_2 in a C_{3v} molecule may not be degenerate. Any doubly degenerate pair of orbitals must belong to E irreducible representation. Often symmetries of orbitals are denoted by lower case letters (for example, a_1) whereas the overall symmetries of electronic wavefunctions are denoted with capital letters (for example, A_1). Note that, for example, it is not possible to have triply degenerate orbitals in C_{3v} because the maximum value for the identity operation E is 2. The symmetry classifications also apply for wavefunctions constructed from linear combinations of some basis functions (such as atomic orbitals).

Example. Can a triagonal BF_3 molecule have triply degenerate orbitals? What is the minimum number of atoms from which a molecule can be built that does exhibit triple degeneracy?

Solution. First we identify the point group of the molecule as D_{3h} by using the previous flowchart. The D_{3h} character table shows that the highest degree of degeneracy that can occur is 2 (i.e. E terms). Therefore there cannot be any triply degenerate molecular orbitals in BF_3 (this would require a T term to occur in the character table). The minimum number of atoms required to build a molecule that can have triply degenerate is four (for example, tetrahedral P_4 molecule, which belongs to T_d).

Example. What are the symmetry species of orbital $\psi = \psi_A - \psi_B$ in NO_2 molecule (C_{2v}). ψ_A is an $O2p_x$ orbital on one of the O atoms and ψ_B that on the other O atom.

Solution. The orbitals ψ_A and $-\psi_B$ are centered on the O atoms:



One must consider each symmetry operation in C_{2v} and calculate the characters:

1. E. This operation does nothing and leaves the wavefunction (ψ) unchanged. Thus $\chi(E) = 1$.
2. C_2. This operation rotates ψ by 180°. This does not change ψ and $\chi(C_2) = 1$.
3. σ_v. This operation swaps the $+$ and $-$ sections in ψ. Thus $\chi(\sigma_v) = -1$.
4. σ_v'. This operation also swaps the $+$ and $-$ sections in ψ. Thus $\chi(\sigma_v') = -1$.

By reference to the C_{2v} character table, it can be seen that this corresponds to A_2 symmetry species. Thus ψ (linear combination) orbital is labeled as a_2.

4.9 Symmetry and vanishing integrals

Suppose you would like to evaluate an integral of the following form:

$$I = \int f_1 f_2 d\tau \tag{4.349}$$

where f_1 and f_2 are some functions. They could, for example, be atomic orbitals centered at two different nuclei. In this case I would be the same as the overlap integral S. Recall that if $S = 0$, the two atomic orbitals do not interact with each other to form molecular orbitals. It turns out that the symmetries of f_1 and f_2 can be used in deciding if the above integral is zero.

Recall how we used the u/g symmetry labels (i.e. odd/even functions) to determine if integration over some function would give a value of zero. A generalization of this result says that if the function has symmetry other than A_1, its integral will be zero. Note that this result cannot be reversed: if a function has A_1 symmetry, this does not guarantee that the corresponding integral is non-zero. In Eq. (4.349) we consider a product of two functions and we should somehow determine the symmetry the product $f_1 \times f_2$ based on the individual symmetries of f_1 and f_2. This can be done my "multiplying" the symmetries of f_1 and f_2 according to the **direct product table** of the point group in question. For u/g symmetry labels, we used previously simple product rules: $g \times g = g$, $u \times g = u$, $g \times u = u$ and $u \times u = g$, which represents a simple example of symmetry multiplication operations. Direct product tables for some common point groups are given below.

Table: Direct product table for C_1.

C_1	A
A	A

Table: Direct product table for C_s.

C_s	A'	A''
A'	A'	A''
A''	A''	A'

Table: Direct product table for C_i.

C_i	A_g	A_u
A_g	A_g	A_u
A_u	A_u	A_g

Table: Direct product table for C_{2v}.

C_{2v}	A_1	A_2	B_1	B_2
A_1	A_1	A_2	B_1	B_2
A_2	A_2	A_1	B_2	B_1
B_1	B_1	B_2	A_1	A_2
B_2	B_2	B_1	A_2	A_1

Table: Direct product table for C_{3v} and D_3.

C_{3v}	A_1	A_2	E
A_1	A_1	A_2	E
A_2	A_2	A_1	E
E	E	E	$A_1 + A_2 + E$

Table: Direct product table for C_{4v}, D_{2d} and D_4.

C_{4v}	A_1	A_2	B_1	B_2	E
A_1	A_1	A_2	B_1	B_2	E
A_2	A_2	A_1	B_2	B_1	E
B_1	B_1	B_2	A_1	A_2	E
B_2	B_2	B_1	A_2	A_1	E
E	E	E	E	E	$A_1 + A_2 + B_1 + B_2$

Table: Direct product table for C_{5v}.

C_{5v}	A_1	A_2	E_1	E_2
A_1	A_1	A_2	E_1	E_2
A_2	A_2	A_1	E_2	E_1
E_1	E_1	E_1	$A_1 + A_2 + E_2$	$E_1 + E_2$
E_2	E_2	E_2	$E_1 + E_2$	$A_1 + A_2 + E_2$

Table: Direct product table for C_{6v} and D_{6h}. For D_{6h}: $g \times g = g$, $g \times u = u$, $u \times g = u$, $u \times u = g$.

C_{6v}	A_1	A_2	B_1	B_2	E_1	E_2
A_1	A_1	A_2	B_1	B_2	E_1	E_2
A_2	A_2	A_1	B_2	B_1	E_1	E_2
B_1	B_1	B_2	A_1	A_2	E_2	E_1
B_2	B_2	B_1	A_2	A_1	E_2	E_1
E_1	E_1	E_1	E_2	E_2	$A_1 + A_2 + E_2$	$B_1 + B_2 + E_1$
E_2	E_2	E_2	E_1	E_1	$B_1 + B_2 + E_1$	$A_1 + A_2 + E_2$

Table: Direct product table for D_2 and D_{2h}. For D_{2h}: $g \times g = g$, $g \times u = u$, $u \times g = u$, $u \times u = g$.

D_2	A	B_1	B_2	B_3
A	A	B_1	B_2	B_3
B_1	B_1	A	B_3	B_2
B_2	B_2	B_3	A	B_1
B_3	B_3	B_2	B_1	A

Table: Direct product table for D_{3h}.

C_{3h}	A_1'	A_2'	E'	A_1''	A_2''	E''
A_1'	A_1'	A_2'	E'	A_1''	A_2''	E''
A_2'	A_2'	A_1'	E'	A_2''	A_1''	E''
E'	E'	E'	$A_1' + A_2' + E'$	E''	E''	$A_1'' + A_2'' + E''$
A_1''	A_1''	A_2''	E''	A_1'	A_2'	E'
A_2''	A_2''	A_1''	E''	A_2'	A_1'	E'
E''	E''	E''	$A_1'' + A_2'' + E''$	E'	E'	$A_1' + A_2' + E'$

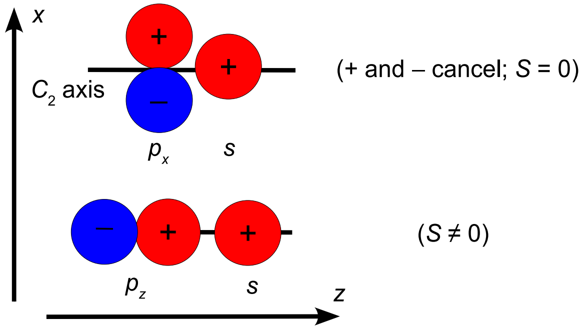
Table: Direct product table for T_d and O_h. For O_h: $g \times g = g$, $g \times u = u$, $u \times g = u$, $u \times u = g$.

T_d	A_1	A_2	E	T_1	T_2
A_1	A_1	A_2	E	T_1	T_2
A_2	A_2	A_1	E	T_2	T_1
E	E	E	$A_1 + A_2 + E$	$T_1 + T_2$	$T_1 + T_2$
T_1	T_1	T_2	$T_1 + T_2$	$A_1 + E + T_1 + T_2$	$A_2 + E + T_1 + T_2$
T_2	T_2	T_1	$T_1 + T_2$	$A_2 + E + T_1 + T_2$	$A_1 + E + T_1 + T_2$

Table: Direct product table for I_h with $g \times g = g$, $g \times u = u$, $u \times g = u$, $u \times u = g$.

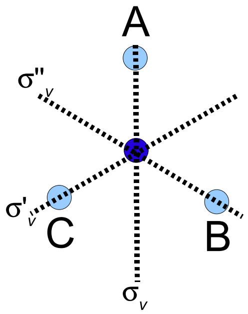
I_h	A	T_1	T_2	G	H
A	A	T_1	T_2	G	H
T_1	T_1	$A + T_1 + H$	$G + H$	$T_2 + G + H$	$T_1 + T_2 + G + H$
T_2	T_2	$G + H$	$A + T_2 + H$	$T_1 + G + H$	$T_1 + T_2 + G + H$
G	G	$T_2 + G + H$	$T_1 + G + H$	$A + T_1 + T_2 + G + H$	$T_1 + T_2 + G + 2H$
H	H	$T_1 + T_2 + G + H$	$T_1 + T_2 + G + H$	$T_1 + T_2 + G + 2H$	$A + T_1 + T_2 + 2G + 2H$

Example. Consider $(s,\, p_x)$ and $(s,\, p_z)$ orbital pairs within C_{2v} symmetry:



By using the C_{2v} character table, we can assign these orbitals the following symmetries: s and p_z span A_1 and p_x spans B_1. To see if s and p_x overlap (i.e. to see if the overlap integral is possibly non-zero), we have to multiply A_1 (for s) and B_1 (for p_x) according to the C_{2v} direct product table. This gives $A_1 \times B_1 = B_1$ as the result, which means that the overlap integral is zero. On the other hand, both s and p_z are A_1 and multiplying $A_1 \times A_1 = A_1$, which means that the overlap integral between these two orbitals may be non-zero. This was just a simple demonstration of the method and often the end result is not as clear as in this example.

Example. Consider NH_3 molecule (C_{3v}) with just the atomic s orbitals on the hydrogens as a basis set. Note that we do not consider any functions on the nitrogen as we will try to see which of its atomic orbitals would have the right symmetry to form MOs with the hydrogen atom orbitals (AO). The hydrogen AOs should be combined to have the proper symmetry within C_{3v}. Such orbitals are called symmetry adapted linear combinations (SALCs). Label the hydrogen AOs as s_A, s_B, s_C.



The C_{3v} axis is perpendicular to the plane of the paper and goes through the nitrogen atom.

First we construct the matrix representations for the symmetry operations in C_{3v}. The symmetry operations have the following effect on the hydrogen AOs:

	s_A	s_B	s_C
E	s_A	s_B	s_C
C_3^-	s_C	s_A	s_B
C_3^+	s_B	s_C	s_A
σ_v	s_A	s_C	s_B
σ_v'	s_B	s_A	s_C
σ_v''	s_C	s_B	s_A

Thus the matrix representatives can be written:

$$(A, B, C) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} A \\ B \\ C \end{pmatrix} \Rightarrow D(E) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \text{(with Tr = 3)}$$

$$(C, A, B) = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} A \\ B \\ C \end{pmatrix} \Rightarrow D(C_3^-) = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \text{(with Tr = 0)}$$

$$(B, C, A) = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} A \\ B \\ C \end{pmatrix} \Rightarrow D(C_3^+) = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} \text{(with Tr} = 0)$$

$$(A, C, B) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} A \\ B \\ C \end{pmatrix} \Rightarrow D(\sigma_v) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \text{(with Tr} = 1)$$

$$(B, A, C) = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} A \\ B \\ C \end{pmatrix} \Rightarrow D(\sigma_v') = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \text{(with Tr} = 1)$$

$$(C, B, A) = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} A \\ B \\ C \end{pmatrix} \Rightarrow D(\sigma_v'') = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \text{(with Tr} = 1)$$

Note that the matrix trace operation is invariant under similarity transformations (i.e., multiplication by rotation matrices). Thus if we "rotate" our basis set in such a way that we choose it to be some linear combination of our present basis functions, the matrix character is unaffected by this choice.

To summarize the matrix characters:

E	C_3	σ_v
3	0	1

Next we could proceed in finding the irreps for the matrix representatives but there is a shortcut we can take. Since the matrix character is invariant with respect to basis set rotations, we can just find the irreps that sum up to give the above characters. If we sum A_1 ((1, 1, 1) from the character table) and E ((2, −1, 0) from the character table) we get:

$$A_1 + E = (1, 1, 1) + (2, -1, 0) = (3, 0, 1).$$

This means that the three s orbitals may form SALCs with A_1 and E symmetries within C_{3v}. Note that E is doubly degenerate and that we have a consistent number of orbitals (three AOs giving three SALCs). This approach tells us only the symmetries of the orbitals but does not give explicit expressions for them. The expressions could be obtained by finding the diagonal matrix representations but this would involve essentially diagonalization of matrices which can be rather laborous. Instead we use the following rules for constructing the SALCs:

1. Construct a table showing the effect of each operation on each orbital of the original basis (this was done already on page 241).
2. To generate the combination of a specified symmetry species, take each column in turn and:
   - i Multiply each member of the column by the character of the corresponding operation.
   - ii Add together all the orbitals in each column with the factors determined in (i).
   - iii Divide the sum by the order of the group. The order of the group is the total number of characters; for C_{3v} this is 6.

The first SALC with A_1 symmetry can now found to be (the s_A column multiplied by A_1 characters (1, 1, 1, 1, 1, 1); the total number of symmetry operations is 6 in C_{3v}) (dimension = 1):

$$\psi_{A_1} = \frac{1}{6}\left(s_A + s_B + s_C + s_A + s_B + s_C\right) = \frac{1}{3}\left(s_A + s_B + s_C\right)$$

From our previous consideration we know that we are still missing two orbitals, which belong to degenerate E. The same method with each column of the table (page 241) and E characters (2, −1, −1, 0, 0, 0) gives (dimension = 2):

$$\psi_E = \tfrac{1}{6}\left(2s_A - s_B - s_C\right),\ \psi'_E = \tfrac{1}{6}\left(2s_B - s_A - s_C\right),\ \psi''_E = \tfrac{1}{6}\left(2s_C - s_B - s_A\right)$$

We know that we should only have two orbitals in E but the above gives us three orbitals. It turns out that any one of these three expressions can be written as a sum of the other two (i.e., they are linearly dependent). The difference of the second and third equations gives:

$$\psi'''_E = \frac{1}{2}\left(s_B - s_C\right)$$

which is orthogonal to the first equation. Thus the required two orthogonal SALCs are:

$$\psi'''_E = \frac{1}{2}\left(s_B - s_C\right) \text{ and } \psi_E = \frac{1}{6}\left(2s_A - s_B - s_C\right)$$

The remaining question is that which of these SALCs may have non-zero overlap with the AOs of the nitrogen atom? Recall that a non-zero overlap leads to formation of MOs. The nitrogen atom has s, p_x, p_y and p_z valence AOs, which may overlap with the SALCs. The s orbital is clearly A_1 since it is spherically symmetric. By inspecting the character table, one can see labels x, y and z in the "Operator" column. In addition to just operators, it also tells us the symmetries of the p orbitals. Thus both p_x and p_y belong to E and p_z belongs to A_1. Recall that for overlap to occur, the multiplication of orbital symmetries must give A_1. To check for this:

SALC	N AO	N AO symmetry	Overlap integral
ψ_{A_1}	s	A_1	$A_1 \times A_1 = A_1$ (**overlap**)
ψ_{A_1}	p_x	E	$A_1 \times E = E$ (no overlap)
ψ_{A_1}	p_y	E	$A_1 \times E = E$ (no overlap)
ψ_{A_1}	p_z	A_1	$A_1 \times A_1 = A_1$ (**overlap**)
ψ_E	s	A_1	$E \times A_1 = E$ (no overlap)
ψ_E	p_x	E	$E \times E = A_1$ (**overlap**)
ψ_E	p_y	E	$E \times E = A_1$ (**overlap**)
ψ_E	p_z	A_1	$E \times A_1 = E$ (no overlap)
ψ_E'''	s	A_1	$E \times A_1 = E$ (no overlap)
ψ_E'''	p_x	E	$E \times E = A_1$ (**overlap**)
ψ_E'''	p_y	E	$E \times E = A_1$ (**overlap**)
ψ_E'''	p_z	A_1	$E \times A_1 = E$ (no overlap)

Following the LCAO method, we would therefore construct three linear combinations, which form the final molecular orbitals:

LC1: $c_1\psi_{A_1} + c_2 s + c_3 p_z$ (with overall symmetry A_1)
LC2: $c_4\psi_E + c_5 p_x + c_6 p_y$ (with overall symmetry E)
LC3: $c_7\psi_E''' + c_8 p_x + c_9 p_y$ (with overall symmetry E)

Integrals of the form:

$$I = \int f_1 f_2 f_3 d\tau \tag{4.350}$$

are also common in quantum mechanics. For example, such integrals occur in calculation of allowed transitions in optical spectroscopy (i.e., transition dipole moment). In similar way to Eq. (4.349), the direct products of symmetries of the three functions must span A_1 where the multiplication is carried out by using the direct product table for the group in question.

Example. It can be shown that the intensity of an optical transition I between states ψ_i and ψ_f is proportional to the square of the transition dipole matrix element:

$$I \propto |\vec{\mu}_{fi}|^2 = \mu_x^2 + \mu_y^2 + \mu_z^2 \tag{4.351}$$

where the Cartesian components ($k = x, y, z$) of the transition dipole matrix element are defined:

$$\mu_{k,fi} = \langle \psi_f | \hat{\mu}_k | \psi_i \rangle = -e \int \psi_f^* k \psi_i \, d\tau \tag{4.352}$$

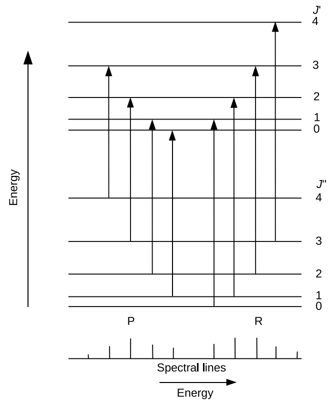
The Cartesian component k defines the propagation axis of linearly polarized light. If the above integral is zero, the transition is optically forbidden (and cannot be seen in optical absorption or emission spectra).

For example, to see if an electron in hydrogen atom can be excited optically from $1s$ to $2s$ orbital, we would have to calculate the following integral (due to spherical symmetry, all the Cartesian components are the same – here we chose z):

$$\int \psi_{2s} z \psi_{1s} d\tau$$

The center of symmetry is located at the nucleus and the symmetry operations operate on the hydrogen atom orbitals. For our present purposes, we can treat H atom as a D_{2h} object. Both $1s$ and $2s$ are A_g (spherically symmetric). The transition dipole operator z spans B_{1u} (see the Operator column the character table). According to D_{2h} direct product table the result is B_{1u}. Since this is different from A_g, the integral is zero. This means that it is not possible to introduce the $1s \to 2s$ transition optically (i.e., it is forbidden). Note that in general one needs to also consider the x and y components (which are also zero here).

Chapter 5: Optical spectroscopy

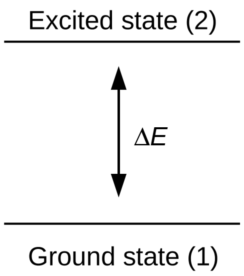


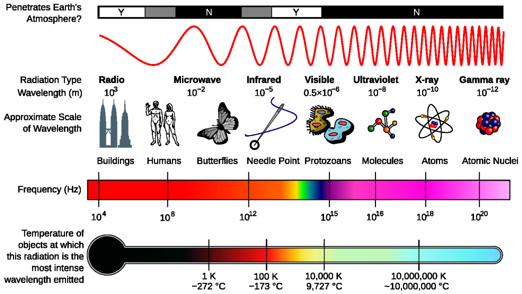
5.1 The basic ideas of spectroscopy

An atom or a molecule may be photoexcited from one quantized energy level E_1 to some other level corresponding to E_2. Very often E_1 would correspond to the ground state energy and E_2 would then be one of the excited states of the system. The energy of the incident photons (i.e. light with wavelength λ) must then match the energy difference $\Delta E = E_2 - E_1$ (also $\lambda = c/\nu$ and $\tilde{\nu} = \nu/c$):

$$h\nu \equiv hc\tilde{\nu} = |E_2 - E_1| = \Delta E \qquad (5.353)$$

where $\tilde{\nu}$ is the energy in wavenumber units $(1/\lambda)$. Usually wavenumbers are expressed in cm^{-1} rather than in m^{-1}. c denotes the speed of light (2.99792458×10^8 m/s in vacuum). If $E_2 > E_1$ the process corresponds to *absorption* and when $E_2 < E_1$ to *emission*.





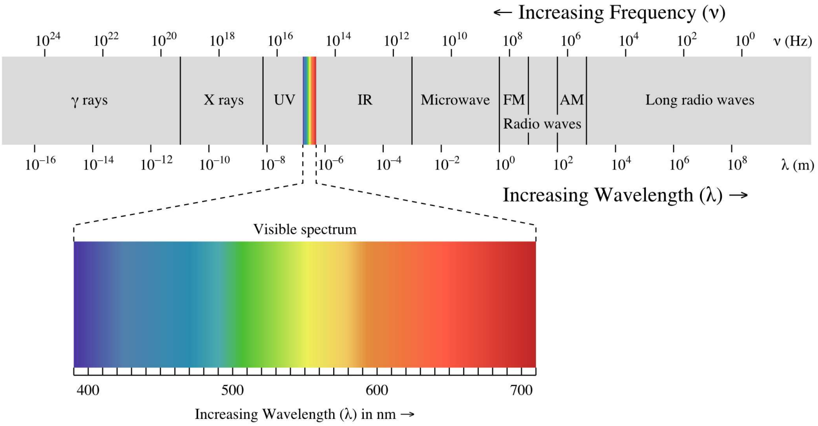
The energy of the photon being absorbed or emitted often tells us to what kind of process it corresponds to in atoms and molecules. Also depending on the process, either the electric or magnetic field may be responsible for inducing the transition between two levels. Recall that photons (i.e., light) have both oscillating electric and magnetic components (Maxwell's equations – see your physics notes).

Transition type	Absorption / emission energy	Component
Molecular rotation	Microwave radiation	Electric field
Molecular vibration	Infrared radiation	Electric field
Electronic transition	Visible and ultraviolet (somtimes infrared)	Electric field
Electron spin ($\approx$ 300 mT)	Microwaves	Magnetic field
Nuclear spin ($\approx$ 2 T)	Radiowaves	Magnetic field

Based on the interaction, we divide spectroscopy into two categories: 1) *optical spectroscopy* (using the electric field component of photons) and 2) *magnetic resonance spectroscopy* (using the magnetic field component of photons). Examples of optical spectroscopy based methods: UV/Vis absorption spectroscopy, IR spectroscopy, Raman spectroscopy. Examples of magnetic resonance spectroscopy: nuclear magnetic resonance (NMR), electron spin resonance (ESR or EPR), electron - nuclear double resonance (ENDOR). Since the energetics for electronic, vibronic, rotational and spin transitions are often very different magnitudes, we will be able to separate our hamiltonian to treat each part separately.

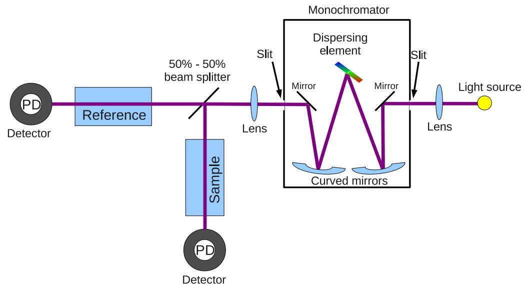
5.2 Experimental techniques

In *emission spectroscopy*, a molecule undergoes a transition from a state of high energy E_2 to a state of lower energy E_1 and emits the excess energy as a photon. In *absorption spectroscopy*, the total amount of absorption of incident light is monitored as the frequency of the light is varied. This implies that the light must be nearly monochromatic (i.e., contains a very narrow range of wavelengths). In chemical applications photons with the following energies are often applied:



Both emission and absorption spectroscopy provide similar information, i.e. differences between the energy levels in atoms/molecules. Absorption experiments are more commonly applied than emission but in some cases emission experiments can be made more sensitive than absorption measurement. For systems with many degrees of freedom (i.e., molecules or atoms trapped in solids), absorption measurement probes the system when it is in its equilibrium geometry with respect to the ground state whereas the emission measurement probes the system *often* after it has relaxed into its excited state equilibrium geometry.

A schematic for a typical UV/VIS absorption experiment is shown below.

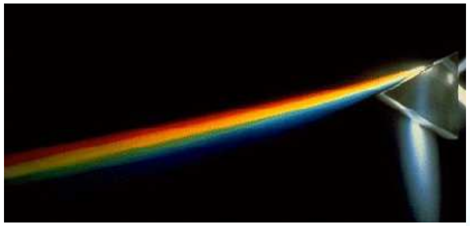


Note that very often the monochromator is after the sample, which means that the sample is being irradiated with all frequencies that originate from the light source.

Source of radiation: The source generally produces radiation over a range of frequencies (i.e., wavelengths), and a dispersing element (see below) is used to extract the wanted frequency from it. Typical light sources are listed below.

Region	Source	Remarks
far infrared	mercury arc	radiation from hot quartz housing
near infrared	Nernst filament	a heated ceramic filament rare-earth oxides
visible	tungsten/iodine lamp	emits intense white light
UV	D_2 or Xe discharge	also pulsed applications
IR, Vis, UV	Various lasers	High intensity, continuous and pulsed (also tunable: dye lasers, OPO etc.)
microwaves	Klystron	tunable monochromatic source
radiowaves	RF oscillators	tunable monochromatic source
UV - X-rays	Synchrotron	tunable monochromatic source

The dispersing element: Unless the light source is already monochromatic, absorption spectrometers include a dispersing element that can spatially separate the different frequencies of light that the light source is emitting. This allows for the monitoring of a desired frequency. Examples of dispersing elements are glass or quartz *prism* and *diffraction grating*.



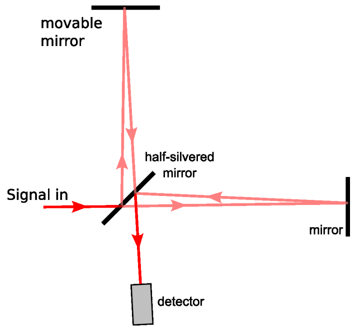
Prism demonstration

Grating demonstration

Prism utilizes the variation of refractive index with the frequency of the incident radiation. Materials typically have a higher refractive index for high-frequency radiation than low-frequency radiation. Therefore high-frequency radiation undergoes a greater deflection when passing through a prism.

Diffraction grating consists of a glass or ceramic plate, which has fine grooves cut into it (about 1000 nm apart; separation comparable to visible light) and covered with a reflective aluminum coating. The grating causes interference between waves reflected from its surface, and constructive interference occurs at specific angles that depend on the wavelength of radiation. Note that the above example is not from a real diffraction grating but from a CDROM disk, which has similar grooves and demonstrates the separation of the colors in white light.

Fourier transform techniques: Modern optical spectrometers, particularly those operating in infrared, mostly use Fourier transform techniques of spectral detection and analysis. The heart of a Fourier transform spectrometer is a *Michelson interferometer*, a device that analyzes the frequencies present in a signal. A Michelson interferometer works by splitting the beam from the sample into two and introducing a varying path length difference (ΔL) into one of the beams.



Michelson interferometer.

When the two components recombine, there is a phase difference between them, and they interfere either constructively or destructively depending on the difference in path lengths. The detected signal oscillates as the two components alternately come into and out of phase as the path length difference is varied. If the radiation has wavenumber $\tilde{\nu}$, the intensity of the detected signal due to radiation in the range of wavenumbers from $\tilde{\nu}$ to $\tilde{\nu}+d\tilde{\nu}$, which we denote $I\left(\Delta L, \tilde{\nu}\right)$, varies as a function of ΔL as:

$$I\left(\Delta L, \tilde{\nu}\right) d\tilde{\nu} = I\left(\tilde{\nu}\right)\left(1 + 2\cos\left(2\pi\tilde{\nu}\Delta L\right)\right) \tag{5.354}$$

Hence, the interferometer converts the presence of a particular wavenumber component in the signal into a variation in intensity of the radiation reaching the detector. An actual signal does not usually consist of just one wavenumber component but it spans a large number of different wavenumbers. The total signal at the detector is a sum of all these components and hence we integrate over $\tilde{\nu}$:

$$I\left(\Delta L\right) = \int\limits_0^\infty I\left(\Delta L, \tilde{\nu}\right) d\tilde{\nu} = \int\limits_0^\infty I\left(\tilde{\nu}\right)\left(1 + \cos\left(2\pi\tilde{\nu}\Delta L\right)\right) d\tilde{\nu} \tag{5.355}$$

To separate the wavenumber components from the sum, we can use the Fourier transform (actually a cosine transform here) to determine the components:

$$I(\tilde{\nu}) \propto \mathrm{Re}\left(\frac{1}{\sqrt{2\pi}}\int\limits_{-\infty}^{\infty} I(\Delta L)e^{-i2\pi\tilde{\nu}\Delta L}d\Delta L\right) \tag{5.356}$$

$$= \sqrt{\frac{2}{\pi}}\int\limits_0^\infty I(\Delta L)\cos\left(2\pi\tilde{\nu}\Delta L\right) d\Delta L$$

This should be compared to the original spectrum of the light source and then one can obtain the wavenumber components that were absorbed by the sample.

A major advantage of the Fourier transform method is that all the radiation emitted by the light source is monitored continuously. A traditional spectrometer monitors only one wavenumber (or frequency) at a time. Fourier transform based spectrometers have typically higher sensitivity (through fast spectral accumulation), measure spectrum faster and are cheaper to construct than conventional spectrometers. The highest resolution achieved by Fourier based spectrometer, $\Delta\tilde{\nu}_{min}$, is determined by the maximum possible path length difference in the Michelson interferometer, ΔL_{max}:

$$\Delta\tilde{\nu}_{min} = \frac{1}{2\Delta L_{max}} \tag{5.357}$$

To achieve a resolution of 0.1 cm^{-1} requires a maximum path lenght difference of 5 cm.

Detectors: Detector is a device that converts the incident radiation into an electric current. This electrical signal can then be recorded by a computer for further processing or plotted directly on the screen. For infrared the following sensors are often used:

Type	Spectral range (μm)
InGaAs photodiodes	0.7 - 2.6
Germanium photodiodes	0.8 - 1.7
PbS photoconductive detectors	1 - 3.2
PbSe photoconductive detectors	1.5-5.2
InAs photovoltaic detectors	1 - 3.8
PtSi photovoltaic detectors	1 - 5
InSb photoconductive detectors	1 - 6.7
InSb photodiode detectors	1 - 5.5
HgCdTe (MCT) photoconductive detectors	0.8 - 25

For visible and UV light photodiodes and photomultiplier tubes can be used. The detectors can also be constructed as an array, for example an array of photodiodes is called a *diode array detector*. Radiation-sensitive semiconductor devices, such as a charge-coupled device (CCD), are increasingly dominating the detector market. These are typically also detector arrays which are employed, for example, in modern digital cameras. A major advantage of array detectors is that, when combined with a monochromator, it can record a spectrum containing many frequencies at once. A single detector is able to see only one frequency at a time and recording a spectrum involves turning of the diffractive element inside the spectrometer (slow). The sensitivity range of most UV detectors can be extended to even higher energies (VUV; vacuum UV) by using *scintillators*.

A common technique used in continuous wave experiments is to modulate the light intensity. The signal from the detector can then be amplified in such a way that only the frequency component corresponding to the modulated light is picked up. This is called *phase sensitive detection* and it can be used to significantly reduce noise present in the signal. This arrangement requires the use of a *light chopper* and a *lock-in amplifier*.

For microwaves a *microwave detector diodes* and for radio frequencies *detection coils* can be used.

The sample: The highest resolution is obtained when the sample is gaseous and at such low pressure that collisions between the molecules are infrequent. Gaseous samples are essential for rotational (microwave) spectroscopy because under these conditions molecules can rotate freely. To achieve sufficient absorption, the path lengths through gaseous samples must be very long, of the order of meters. This can also be achieved by having multiple passage of the beam between parallel mirrors at each end of the sample cavity.

The most common range for infrared spectroscopy if from 4000 cm^{-1} to 625 cm^{-1}. Ordinary glass and quartz absorb over most of this range and hence some other materials must be used. The sample could be placed between salt windows, for example NaCl or KBr, which are transparent down to 625 cm^{-1} and 400 cm^{-1}, respectively. For solid samples, one can prepare a pellet with a pellet press. For UV/Vis, NMR, ESR experiments quartz cuvettes can be employed. Remember that all optical components (e.g., windows, mirrors, prisms, gratings, beam splitters) used in the experiment must be compatible with the frequency of the light being used!

5.3 Einstein coefficients and selection rules

The overall spectrum of an atom or a molecule consists of series of lines, which correspond to the different types of transitions discussed previously. The strength of a given transition depends on the number of absorbing molecules per unit volume and the probability that the transition will take place. The latter can be evaluated using quantum mechanics. Einstein proposed that the rate of absorption of photons is proportional to the density of the electromagnetic radiation with the frequency matching the energy difference ΔE. The *rate of absorption* of photons is given by the equation:

$$\left(\frac{dN_1}{dt}\right)_{\text{abs}} = -B_{12}\rho_\nu(\nu_{12})N_1 \tag{5.358}$$

where B_{12} is the *Einstein coefficient for stimulated absorption* (m kg^{-1}). The minus sign signifies that the number of molecules in state 1 is decreasing when electromagnetic radiation is absorbed. We also need to have balance between the transfer rates: $dN_1/dt = -dN_2/dt$.

Due to (random) fluctuations in the electromagnetic field ("zero-point for electromagnetic field" – see your physics notes), atoms/molecules do not stay in the excited state indefinitely. The return process from the excited state to back to the initial state (*spontaneous emission*) is described by adding a decay term for the excited state popoulation N_2:

$$\left(\frac{dN_2}{dt}\right)_{\text{spont}} = -A_{21}N_2 \tag{5.359}$$

where A_{21} is the *Einstein coefficient for spontaneous emission* (s^{-1}). The since the field causing the emission is random, the emitted light will also have random direction and phase.

There is another possible way an atom/molecule can return from state 2 to state 1. It turns out that photons can both be absorbed or they can induce emission (*stimulated emission*). The emitted photon will have the same direction and phase as the other photon that caused the emission. The rate of simulated emission can be included in the rate equation by:

$$\left(\frac{N_2}{dt}\right)_{\text{stim}} = -B_{21}\rho_\nu(\nu_{12})N_2 \tag{5.360}$$

where B_{21} is the *Einstein coefficient for stimulated emission.* It is interesting to note that this leads to amplification of the incident photons. This the fundamental process behind lasers ("light amplification by stimulated emission of radiation").

Overall the resulting equations look like the ones you have seen in chemical kinetics. To summarize all the terms:

$$\frac{dN_1}{dt} = -\frac{dN_2}{dt} = -B_{12}\rho_\nu(\nu_{12})N_1 + A_{21}N_2 + B_{21}\rho_\nu(\nu_{12})N_2 \tag{5.361}$$

The three Einstein coefficients are related to each other as can be seen by setting $dN_1/dt = 0$ (or $dN_2/dt = 0$):

$$\rho_\nu(\nu_{12}) = \frac{A_{21}}{(N_1/N_2)\,B_{12} - B_{21}} \tag{5.362}$$

When the system is in thermal equilibrium, the ratio between the populations is given by the *Boltzmann distribution*:

$$\frac{N_2}{N_1} = e^{-(E_2-E_1)/(k_BT)} \tag{5.363}$$

Since $E_2 > E_1$, most atoms/molecules will be in the lower energy level at thermal equilibrium. If the system is exposed to electromagnetic radiation at frequency ν_{12}, which matches the energy gap $E_2 - E_1$, the final equilibrium that will be reached is given by:

$$\frac{N_2}{N_1} = e^{-h\nu_{12}/(k_BT)} \tag{5.364}$$

Replacing N_1/N_2 in Eq. (5.362) by the above expression gives:

$$\rho_\nu(\nu_{12}) = \frac{A_{21}}{B_{12}e^{h\nu_{12}/(k_BT)} - B_{21}} \tag{5.365}$$

This must be in agreement with *Planck's blackbody distribution law* (see Ch. 1):

$$\rho_\nu(\nu_{12}) = \frac{8\pi h\left(\nu_{12}/c\right)^3}{e^{h\nu_{12}/(k_BT)} - 1} \tag{5.366}$$

Comparison of Eqs. (5.365) and (5.366) term by term leads us to conclude:

$$B_{12} = B_{21} \tag{5.367}$$

$$A_{21} = \frac{8h\pi\nu_{12}^3}{c^3}B_{21} \tag{5.368}$$

Thus if we know one of the Einstein coefficients, the above two relations will give the other two. Furthermore, since $B_{12} = B_{21}$ we can just denote these by B. For A_{21} we can also use just A since there is no A_{12} (i.e. no spontaneous absorption). Integration of Eq. (5.361) along with replacing N_1 with $N_{total} - N_2$ where $N_{total} = N_1 + N_2$:

$$\frac{N_2}{N_{total}} = \frac{B\rho_\nu\left(\nu_{12}\right)}{A + 2B\rho_\nu\left(\nu_{12}\right)}\left(1 - \exp\left(-\left[A + 2B\rho_\nu\left(\nu_{12}\right)\right]t\right)\right) \tag{5.369}$$

At $t = 0$ there are no atoms/molecules in the excited state. If the radiation density is held constant, N_2/N_{total} rises to an asymptotic value of $B\rho_\nu\left(\nu_{12}\right)/\left(A + 2B\rho_\nu\left(\nu_{12}\right)\right)$ as time progresses. Since $A > 0$ the previous expression is necessarily less than 1/2. Thus *irradiation of a two-level system can never put more atoms/molecules in the higher level than in the lower level.* This result will explain why a two-level system cannot be used to make a laser. In order to obtain laser action, stimulated emission must be greater than the rate of absorption so that amplification of radiation can be achieved. This requires that:

$$B_{21}\rho_\nu\left(\nu_{12}\right)N_2 > B_{12}\rho_\nu\left(\nu_{12}\right)N_1 \tag{5.370}$$

Since $B_{12} = B_{21}$, laser action can only be obtained when $N_2 > N_1$. This situation is referred to as a *population inversion*.

Quantum mechanics can be used to calculate the Einstein coefficients. To calculate the coefficients A and B between levels n and m, we need to evaluate the *transition dipole moment*:

$$\vec{\mu}_{mn} = \int \psi_n^*\vec{\mu}\psi_m d\tau = \langle\psi_n|\,\vec{\mu}\,|\psi_m\rangle \tag{5.371}$$

where $\vec{\mu}$ is the quantum mechanical transition dipole operator for the atom/molecule:

$$\vec{\mu} = \sum_i q_i\vec{r}_i \tag{5.372}$$

where the sum is over all the electrons and nuclei of the atom/molecule, q_i is the charge, and $\vec{r}_i$ is the position of the particle.

If the transition diple moment vanishes, the spectral line has no intensity (i.e. no absorption occurs). The group theory and symmetry arguments can be used to derive *selection rules* that helps us decide which transitions can occur (see Sec. 4).

If the initial state has sufficient population and the transition dipole moment is non-zero, the corresponding spectral (absorption) line can be observed. It can be shown (derivation not shown) that the relation ship between the quantum mechanical transition dipole moment and the Einstein coefficients A and B are given by:

$$A = \frac{12\pi^3\nu^3 g_1}{3\epsilon_0 hc^3 g_2}\left|\mu_{12}\right|^2 \tag{5.373}$$

$$B = \frac{2\pi 2 g_1}{3h^2\epsilon_0 g_2}\left|\mu_{12}\right|^2 \tag{5.374}$$

where g_1 and g_2 are the degeneracy factors for the initial and the final states, respectively, c is the speed of light, h is the Planck's constant, and ϵ_0 is the vacuum permittivity. Eq. (5.373) indicates that the rate of spontaneous emission ($A_{12}N_2$) increases rapidly with frequency (i.e., decreasing wavelength). The spontaneous emission process is less significant for microwave and infrared regions whereas it is more important in the visible and UV regions.

If the rate of spontaneous emission is negligible (i.e. A is small), the net rate of absorption $R_{1\leftarrow 2}$ is given simply by:

$$R_{2\leftarrow 1} = B_{21}N_1\rho_\nu\left(\nu_{12}\right) - B_{12}N_2\rho_\nu\left(\nu_{12}\right) = \left(N_1 - N_2\right)B\rho_\nu\left(\nu_{12}\right) \tag{5.375}$$

The above result shows that if the populations of the two states are equal, there will be no net absorption of radiation. The system is said to be *saturated*.

The coefficient A_{12} can also be thought as a measure of the lifetime of state 2. You can think about the analogy between the current rate equations and the ones you have seen in chemical kinetics. Consider molecules in state 2 (i.e. excited state) with no radiation present and no stimulated emission. The molecules will make transition to state 1, emitting a photon having frequency ν_{12} with probability $A_{12}N_2$. This process is called *fluorescence*. After a time t, the number of molecules per unit volume in state 2 is given by:

$$N_2(t) = N_2(0)e^{-A_{12}t} = N_2(0)e^{-t/\tau} \tag{5.376}$$

where $\tau = \frac{1}{A_{12}}$ is called the *radiative lifetime*. In general, the atom/molecule may be able to fluoresce to many different states (labelled as 2, 3, ...) giving emission at multiple wavelengths. In this case the *total radiative lifetime* is given by:

$$\frac{1}{\tau} = \sum_i A_{2i} \tag{5.377}$$

Note that there are other possibilities for energy dissipation than just radiation of photons. In some cases the energy is transferred to nuclear motion and the system may not fluoresce at all provided that the rate is faster than the radiative process. Such transitions are called *non-radiative transitions*. To account for non-radiative transitions, one must add the appropriate decay terms into Eq. (5.377).

5.4 Schrödinger equation for nuclear motion

The Born-Oppenheimer equation (see Eq. (3.260)) allows us to separate the nuclear and electronic degrees of freedom. The nuclear hamiltonian for N nuclei can be now written in such a way that the electronic part appears as a potential term:

$$\hat{H} = \sum_{i=1}^{N} -\frac{\hbar^2}{2m_i}\nabla^2_{R_i} + E(R_1, R_2, ..., R_N) \tag{5.378}$$

In the absence of external electric or magnetic fields, the potential term E depends only on the relative positions of the nuclei, as shown above, and not on the overall position of the molecule or its orientation in space. The above hamiltonian H can often be approximately written as a sum of the following terms:

$$\hat{H} = \hat{H}_{tr} + \hat{H}_{rot} + \hat{H}_{vib} \tag{5.379}$$

where H_{tr} is the translational, H_{rot} the rotational, and H_{vib} the vibrational hamiltonian. The translational and rotational terms have no potential part but the vibrational part contains the potential E, which depends on the distances between the nuclei. In some cases the terms in Eq. (5.379) become coupled and one cannot use the following separation technique. Separation of H means that we can write the wavefunction as a product:

$$\psi = \psi_{tr}\psi_{rot}\psi_{vib} \tag{5.380}$$

The resulting three Schrödinger equations are then:

$$\hat{H}_{tr}\psi_{tr} = E_{tr}\psi_{tr} \tag{5.381}$$

$$\hat{H}_{rot}\psi_{rot} = E_{rot}\psi_{rot} \tag{5.382}$$

$$\hat{H}_{vib}\psi_{vib} = E_{vib}\psi_{vib} \tag{5.383}$$

The translational part is not interesting since there is no external potential or boundary conditions that could lead to quantization (i.e., it produces a continuous spectrum). On the other hand, the rotational part is subject to cyclic boundary condition and the vibrational part to potential E, hence we expect these to produce quantization, which can be probed by spectroscopic methods.

The original number of variables in the hamiltonian is given by $3 \times N$ (i.e. the x, y, z coordinates for each nuclei). We can neglect the translational motion and we are left with $3N - 3$ coordinates. To account for molecular rotation, three variables are required or if we have a linear molecule, only two variables. Therefore the vibration part must have either $3N - 6$ variables for a non-linear molecule or $3N - 5$ variables for a linear molecule. These are referred to as *vibrational degrees of freedom* or *internal coordinates.*

5.5 Rotational spectra of diatomic molecules

We assume that the molecule is a rigid rotor, which means that the molecular geometry does not change during molecular rotation. We have solved this problem already (Eqs. (1.140) and (1.141)):

$$E_r = \frac{\hbar^2}{2I} J(J+1) \text{ with } J = 0, 1, 2... \text{ and } M = -J, ..., 0, ...J \tag{5.384}$$

where I is the moment of inertia for the molecule (see Eq. (1.130)). Since the energy does not depend on M, each rotational level is $2J+1$ fold degenerate.

Energies are typically expressed in wavenumber units (cm^{-1} although the basic SI unit is m^{-1}) by dividing E by hc. The use of wavenumber units is denoted by including a tilde sign above the variable (e.g., $\tilde{\nu}$). The rotational energies expressed in wavenumbers are given by:

$$\tilde{E}_r(J) = \frac{E_r}{hc} = \frac{J(J+1)h}{8\pi^2 Ic} = J(J+1)\tilde{B} \tag{5.385}$$

where the *rotational constant* is given by:

$$\tilde{B} = \frac{h}{8\pi^2 Ic} \tag{5.386}$$

where c is the speed of light. The rotational constant defines the rotational energy levels for a rigid diatomic molecule.

When the molecule is in electronic state e and vibrational state v, the total wavefunction is written as $\psi = \psi_e \psi_v \psi_{J,M}$. The *transition moment* between two different rotational levels J, M and J', M':

$$\int\int\int \psi_e^* \psi_v^* \psi_{J',M'} \hat{\mu} \psi_e \psi_v \psi_{J,M} d\tau_e d\tau_{rot} d\tau_{vib} \tag{5.387}$$

where $\hat{\mu}$ is the transition dipole operator (see Eq. (3.322)) and only the rotational wavefunction has change. The electronic part gives the permanent dipole moment:

$$\mu_0^{(e)} = \int \psi_e^* \hat{\mu} \psi_e d\tau_e \tag{5.388}$$

Therefore we can reduce Eq. (5.387) to:

$$\int\int \psi_v^* \psi_{J',M'}^* \mu_0^{(e)} \psi_v \psi_{J,M} d\tau_{rot} d\tau_{vib} \tag{5.389}$$

The vibrational part just gives the dipole moment for the molecule in vibrational state v and we can write:

$$\int \psi_{J',M'}^* \mu_0 \psi_{J,M} d\tau_{rot} \tag{5.390}$$

The rotational transition can only occur if this integral has a non-zero value. Clearly μ_0 must be non-zero for the transition to occur, which means that the molecule must have a permanent dipole moment for the rotational transition to occur. For example, homonuclear diatomic molecules like H_2 and O_2 will not show pure rotational spectra. Heteronuclear molecules show pure rotational spectra.

Using the known properties for spherical harmonics, one can show the following selection rule:

$$\Delta J = J' - J = \pm 1 \text{ and } \Delta M = M' - M = 0, \pm 1 \tag{5.391}$$

Since photons have one unit of angular momentum, the above rule can be understood in terms of angular momentum transfer. The transition frequencies between the rotational levels are given by ($J = 0, 1, 2, ...$):

$$\tilde{\nu} = \tilde{E}_r(J+1) - \tilde{E}_r(J) = ((J+1)(J+2) - J(J+1))\,\tilde{B} = 2\tilde{B}(J+1) \tag{5.392}$$

The successive line positions in the rotational spectrum are given by $2\tilde{B}, 4\tilde{B}, 6\tilde{B}, ...$ Note that molecules with different atomic isotopes have different moments of inertia and hence different positions for the rotational lines.

In reality molecules are not rigid rotors and one must consider the coupling between H_{rot} and H_{vib}. Classically thinking, with increasing rotational motion, the chemical bond stretches due to centrifugal forces, which increases the moment of inertia, and consequently, the rotational energy levels come closer together. It can be shown that this can be accounted for by including an additional term in Eq. (5.385):

$$\tilde{E}_r(J) = \tilde{B}J(J+1) - \tilde{D}J^2(J+1)^2 \tag{5.393}$$

where $\tilde{D}$ is the *centrifugal distortion constant* (cm^{-1}). Note that both $\tilde{B}$ and $\tilde{D}$ are positive.

When the centrifugal distortion is taken into account, the rotational transition frequencies are given by:

$$\tilde{\nu} = \tilde{E}_r(J+1) - \tilde{E}_r(J) = 2\tilde{B}(J+1) - 4\tilde{D}(J+1)^3 \text{ where } J = 0, 1, 2, ... \tag{5.394}$$

Example. Measurement of pure rotational spectrum of H^{35}Cl molecule gave the following positions for the absorption lines:

$$\tilde{\nu} = \left(20.794\text{cm}^{-1}\right)(J+1) - \left(0.000164\text{cm}^{-1}\right)(J+1)^3$$

What is the equilibrium bond length and what is the value of the centrifugal distortion constant?

Solution. We first write the expression for $\tilde{B}$ and then use the definition of the moment of inertia I:

$$\tilde{B} = \frac{h}{8\pi^2 cI} = \frac{h}{8\pi^2 c\mu R_0^2}$$

where μ is the reduced mass for the molecule and R_0 is the equilibrium bond length. Solving for R_0 gives:

$$R_0 = \sqrt{\frac{h}{8\pi^2 c\mu\tilde{B}}} = 129 \text{ pm}$$

The centrifugal distortion constant can obtained by comparing the above equation with Eq. (5.392):

$$\tilde{D} = 4.1 \times 10^{-5}\ \mathrm{cm}^{-1}$$

Another factor that affects the line intensities in a rotational spectrum is related to the thermal population of the rotational levels. Thermal populations of the rotational levels is given by the Boltzmann distribution (for a collection of molecules):

$$f_J = \frac{g_J e^{-hc\tilde{E}_r(J)/(k_BT)}}{\sum\limits_{J'} g_{J'} e^{-hc\tilde{E}_r(J')/(k_BT)}} = \frac{g_J e^{-hc\tilde{E}_r(J)/(k_BT)}}{q} \tag{5.395}$$

where q is called the *partition function* and $g_J = 2J + 1$ corresponds to the degeneracy count of state J. A useful comparison of thermal energy is given by kT and if the energy of a state is much higher than this, it will not be thermally populated. Based on Eq. (5.395) one expects the intensities to first increase as a function of the initial state J, reach a maximum, and then decrease because the thermal populations decrease. In an absorption experiment, one can see the thermal populations of the initial rotational levels.

Note: For systems, where the rotational degrees of freedom may exchange identical nuclei, an additional complication arises from the symmetry requirement for the nuclear wavefunction. Recall that bosons must have symmetric wavefunctions and fermions antisymmetric. We will not discuss this in more detail here.

5.6 Rotational spectra of polyatomic molecules

In the following we assume that the polyatomic molecule is a rigid rotor (i.e., the centrifugal distortion is ignored). The center of mass for a molecule is defined as:

$$\vec{R}_{cm} = \frac{\sum\limits_i m_i \vec{R'}_i}{\sum\limits_i m_i} \tag{5.396}$$

where the summation is over the nuclei in the molecule. The *moment of inertia* is defined as:

$$I = \sum_i m_i \left|\vec{R}'_i - \vec{R}_{cm}\right|^2 = \sum_i m_i \left|\vec{R}_i\right|^2 \tag{5.397}$$

where R'_i denotes the coordinates for nucleus i with mass m_i. To simplify notation we used $\vec{R}_i = \vec{R}'_i - \vec{R}_{cm} = (x_i, y_i, z_i)$ where x_i, y_i, z_i refer to the Cartesian components for the position of nulceus i with respect to the center of mass. The moments of inertia about x, y, and z axes can be written as:

$$I_x = \sum_i m_i \left(y_i^2 + z_i^2\right),\ I_y = \sum_i m_i \left(x_i^2 + z_i^2\right),\ I_z = \sum_i m_i \left(x_i^2 + y_i^2\right) \tag{5.398}$$

Products of inertia are defined (other combinations in a similar way):

$$I_{xy} = I_{yx} = \sum_i m_i x_i y_i \tag{5.399}$$

Principal axes are perpendicular axes chosen in such way that they all pass through the center of mass and all products of intertia vanish (see Eq. (5.399)). The moments of inertia with respect to these axes are called *principal moments of inertia* and denoted by I_a, I_b, and I_c. The axes a, b, and c are expressed in the *molecular frame* (as opposed to the *laboratory frame*), which means that they rotate with the molecule. The principal axes are labeled such that $I_a \leq I_b \leq I_c$. The principal axes can often be assigned by inspecting the symmetry of the molecule.

The principal moments of inertia are used to classify molecules:

Moments of inertia	Type of rotor	Examples
$I_b = I_c, I_a = 0$	Linear	HCN
$I_a = I_b = I_c$	Spherical top	CH_4, SH_6, UF_6
$I_a < I_b = I_c$	Prolate symmetric top	CH_3Cl
$I_a = I_b < I_c$	Oblate symmetric top	C_6H_6
$I_a \neq I_b \neq I_c$	Asymmetric top	CH_2Cl_2, H_2O

The next task is to come up with a quantum mechanical hamiltonian for the molecular rotation. We will do it as follows:

1. Write the classical expression for molecular rotation in terms of classical angular momentum
2. Replace the classical angular momentum with the corresponding quantum mechanical operators
3. Solve the resulting Schrödinger equation

According to classical mechanics kinetic energy for rotation around one axis is given by:

$$E_r = \frac{1}{2}I\omega^2 = \frac{(I\omega)^2}{2I} = \frac{L^2}{2I} \tag{5.400}$$

where ω is the angular velocity (rad/s), I is the moment of inertia (Eq. (5.397)) and L is the angular momentum. For an object that can rotate in 3-D, we have to account for rotation about each axis:

$$E_r = \frac{1}{2}I_a\omega_a^2 + \frac{1}{2}I_b\omega_b^2 + \frac{1}{2}I_c\omega_c^2 \tag{5.401}$$

This can be written in terms of angular momentum about the corresponding axes (see Eq. (5.400)):

$$E_r = \frac{L_a^2}{2I_a} + \frac{L_b^2}{2I_b} + \frac{L_c^2}{2I_c} \tag{5.402}$$

with the total angular momentum given by $L^2 = L_a^2 + L_b^2 + L_c^2$.

Spherical top: For a spherical top we have $I = I_a = I_b = I_c$ and therefore we can rewrite Eq. (5.402) as:

$$E_r = \frac{L^2}{2I} \tag{5.403}$$

To make the transition to quantum mechanics, we need to replace L^2 with the quantum mechanical operator (Eqs. (1.114), (1.115), (1.116), and (1.117)). We have already found the eigenfunctions and eigenvalues of the L^2 operator (Eqs. (1.121) and (1.123)) and therefore we can just write down the solution:

$$E_r = \frac{J(J+1)\hbar^2}{2I} = BJ(J+1) \text{ where } J = 0, 1, 2, ... \tag{5.404}$$

where $B = \hbar^2/(2I)$ is the rotational constant. When studying molecular rotation, it is customary to use the wavenumber units for rotational constants:

$$\tilde{B} = \frac{\hbar}{4\pi c I} \tag{5.405}$$

The rotational energy is often also expressed in wavenumber units:

$$\tilde{E}_r = \tilde{B}J(J+1) \tag{5.406}$$

The energy separation between two adjacent levels is then given by:

$$\tilde{E}_r(J) - \tilde{E}_r(J-1) = 2\tilde{B}J \tag{5.407}$$

Spherical top molecules cannot have permanent dipole moment (based on symmetry as discussed earlier) and therefore they do not have pure rotational spectra. They may exhibit rotational fine structure in their vibrational or electronic spectra.
The moment of inertia for a symmetrical tetrahedral molecule, such as CH_4, is given by:

$$I = \frac{8}{3}mR^2 \tag{5.408}$$

where R is the bond length and m is the mass of hydrogen.

Linear molecule: For a linear molecule, $I_b = I_c$ with $I_a = 0$. Eq. (5.401) shows that the rotational energy about the a axis is zero. Therefore we can write the rotational energy as ($L_a^2 = 0$):

$$E_r = \frac{L_b^2}{2I_b} + \frac{L_c^2}{2I_c} = \frac{L_b^2 + L_c^2}{2I_b} = \frac{L^2}{2I_b} \tag{5.409}$$

The rotational energies are therefore at (see Eq. (5.404)):

$$\tilde{E}_r = \tilde{B}J(J+1) \tag{5.410}$$

Symmetric top: This covers both prolate symmetric top ($I_a < I_b = I_c$) and oblate symmetric top ($I_a = I_b < I_c$) cases. To account for both cases, we will just denote the moments of inertia as perpendicular $I_\perp$ (with the angular momenta L_x and L_y) and parallel $I_{||}$ (with angular momentum L_z). The classical expression for rotation is now:

$$E_r = \frac{L_x^2 + L_y^2}{2I_\perp} + \frac{L_z^2}{2I_{||}} \tag{5.411}$$

By noting that the total amount of angular momentum is $L^2 = L_x^2 + L_y^2 + L_z^2$, we can rewrite the above as:

$$\begin{aligned} E_r &= \frac{1}{2I_\perp}\left(L_x^2 + L_y^2 + L_z^2\right) - \frac{1}{2I_\perp}L_z^2 + \frac{1}{2I_{||}}L_z^2 \qquad (5.412) \\ &= \frac{1}{2I_\perp}L^2 + \left(\frac{1}{2I_{||}} - \frac{1}{2I_\perp}\right)L_z^2 \end{aligned}$$

Transition to quantum mechanics can be carried out by replacing $L^2 = J(J+1)\hbar^2$ (see Eq. (1.123)) and $L_z^2 = K^2\hbar^2$ (see Eq. (1.128)). Here J describes the total amount of angular momentum whereas K is related to the projection of angular momentum on the rotation axis ($K = 0$ angular momentum perpendicular or $K = \pm J$ parallel). K cannot exceed the total amount of angular momentum: $K = 0, \pm 1, ..., \pm J$. Now we can write the quantum mechanical rotational energy:

$$E_r = \frac{1}{2I_\perp}J(J+1)\hbar^2 + \left(\frac{1}{2I_{||}} - \frac{1}{2I_\perp}\right)K^2\hbar^2 \qquad (5.413)$$

with $J = 0, 1, 2, ...$ and $K = 0, \pm 1, \pm 2, ..., \pm J$. Converting to wavenumber units and introducing rotational constants $\tilde{B}$ and $\tilde{A}$ we arrive at:

$$\tilde{E}_r = \tilde{B}J(J+1) + (\tilde{A} - \tilde{B})K^2 \qquad (5.414)$$

with

$$\tilde{B} = \frac{\hbar}{4\pi c I_\perp} \text{ and } A = \frac{\hbar}{4\pi c I_{||}} \qquad (5.415)$$

The rotational selection rule for symmetric top molecules are $\Delta J = \pm 1$ and $\Delta K = 0$. The latter restriction arises from the fact that the permanent dipole moment, which is oriented along the principal axis (i.e., J), can interact with electromagnetic radiation. The perpendicular component to the principal axis (i.e., K) cannot as the dipole moment has no component in this direction.

- Pure rotational spectroscopy has enabled the most precise evaluations of bond lengths and bond angles. However, for polyatomic molecules there is usually no unique way to extract this information. In these cases at least the three moments of inertia can be evaluated.
- Additional information can be obtained by studying different isotopic combinations of molecules. This provides additional restrictions when information on the molecular geometry is sought based on the experimental measurements.
- To avoid collisional broadening, very dilute gas phase samples are required (≈ 10 Pa).
- Permanent dipole moments can be studied by introducing an external electric field (Stark effect). This results in splitting of the rotational levels that is proportional to the dipole moment.

5.7 Vibrational spectra of diatomic molecules (harmonic oscillator)

Earlier when we have discussed the harmonic oscillator problem and we briefly mentioned that it can be used to approximate atom - atom interaction energy ("potential energy curve") near the equilibrium bond length. Harmonic potential would not allow for molecular dissociation and therefore it is clear that it would not be a realistic model when we are far away from the equilibrium geometry. The harmonic potential is given by:

$$E(R) = \frac{1}{2}k(R - R_e)^2 \tag{5.416}$$

where k is called the *force constant*, R_e is the *equilibrium bond length*, and R is the distance between the two atoms. The actual potential energy curve can be obtained from theoretical calculations or to some degree from spectroscopic experiments. This curve has usually complicated form and hence it is difficult to solve the nuclear Schrödinger equation exactly for this potential. One way to see the emergence of the harmonic approximation is to look at *Taylor series expansion*:

$$E(R) = E(R_e) + \left(\frac{dE}{dR}\right)_{R=R_e}(R - R_e) + \frac{1}{2}\left(\frac{d^2E}{dR^2}\right)_{R=R_e}(R - R_e)^2 + ... \tag{5.417}$$

Note that at the minimum we get $E(R) = E(R_e)$.

The quantitized energy levels of harmonic oscillator are given by (see Eq. (1.96)):

$$E_v = \left(v + \frac{1}{2}\right)h\nu \text{ with } v = 0, 1, 2, ... \tag{5.418}$$

where v is the vibrational quantum number, the vibrational frequency $\nu = \frac{1}{2\pi}\sqrt{k/\mu}$ and μ is the reduced mass of the diatomic molecule (see Eq. (1.94)). Note that v and ν look very similar but have different meaning! This can be expressed in wavenumber units as:

$$\tilde{E}_v = \frac{E_v}{hc} = \tilde{\nu}\left(v + \frac{1}{2}\right) \tag{5.419}$$

A typical value for vibrational frequency would be around 500 - 4000 cm^{-1}. Small values are associated with weak bonds whereas strong bonds have larger vibrational frequencies.

Not all diatomic molecules have vibrational absorption spectrum. To see this, we have to calculate the electric dipole transition moment (see Eq. (5.387)). In Eqs. (5.388) and (5.389) we found that the dipole moment depends on the internuclear distance. To proceed, we expand $\mu_0^{(e)}$ in a Taylor series about $R = R_e$:

$$\mu_0^{(e)}(R) = \mu_e + \left(\frac{\partial\mu}{\partial R}\right)_{R=R_e}(R - R_e) + \frac{1}{2}\left(\frac{\partial^2\mu}{\partial R^2}\right)_{R=R_e}(R - R_e)^2 + ... \tag{5.420}$$

Next we integrate over the vibrational degrees of freedom (see Eq. (5.388)):

$$\int \psi_{v''}^* \mu_0 \psi_{v'} dR = \mu_e \int \psi_{v''}^* \psi_{v'} dR + \left(\frac{\partial \mu}{\partial R}\right)_{R=R_e} \int \psi_{v''}^* (R - R_e) \psi_{v'} dR \quad (5.421)$$
$$+\frac{1}{2}\left(\frac{\partial^2 \mu}{\partial R^2}\right)_{R=R_e} \int \psi_{v''}^* (R - R_e)^2 \psi_{v'} dR + ...$$

The first term above is zero since the vibrational eigenfunctions are orthogonal. The second term is nonzero if the dipole moment depends on the internuclear distance R. Therefore we conclude that the selection rule for pure vibrational transition is that the dipole moment must change as a function of R. For example, all homonuclear diatomic molecules (e.g., H_2, O_2, etc.) have zero dipole moment, which cannot change as a function of R. Hence these molecules do not show vibrational spectra. In general, all molecules that have dipole moment have vibrational spectra as change in R also results in change of dipole moment. We still have the integral present in the second term. For harmonic oscillator wavefunctions, this integral is zero unless $v'' = v' \pm 1$ (Eqs. (1.103), (1.104), and (1.105)). This provides an additional selection rule, which says that the vibrational quantum number may either decrease or increase by one.

The higher order terms in Eq. (5.421) are small but they give rise to *overtone transitions* with $\Delta v = \pm 2, \pm 3, ...$ with rapidly decreasing intensities.

For harmonic oscillator, the Boltzmann distribution (see Eqs. (5.394) and (5.395)) gives the statistical weight for the vth level:

$$f_v = \frac{e^{-(v+1/2)h\nu/(k_BT)}}{\sum\limits_{v=0}^{\infty} e^{-(v+1/2)h\nu/(k_BT)}} \quad (5.422)$$
$$= \frac{e^{-vh\nu/(k_BT)}}{\sum\limits_{v=0}^{\infty} e^{-vh\nu/(k_BT)}}$$

Note that the degeneracy factor is identically one because there is no degeneracy in one dimensional harmonic oscillator. To proceed, we recall geometric series:

$$\sum_{v=0}^{\infty} x^v = \frac{1}{1-x} \text{ with } x < 1 \quad (5.423)$$

The denominator in Eq. (5.422) now gives:

$$\sum_{v=0}^{\infty} e^{-vh\nu/(k_BT)} = \frac{1}{1 - e^{-h\nu/(k_BT)}} \quad (5.424)$$

Now we can simplify Eq. (5.422):

$$f_v = \left(1 - e^{-h\nu/(k_BT)}\right) e^{-vh\nu/(k_BT)} \tag{5.425}$$

For example, for $H^{35}Cl$ the thermal population of the first vibrational level $v = 1$ is very small (9×10^{-7}) and therefore the excited vibrational levels do not contribute to the (IR) spectrum.

5.8 Vibrational spectra of diatomic molecules (Morse potential)

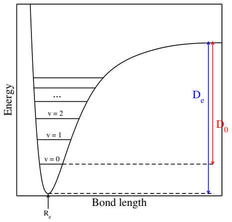
As discussed previously, the harmonic oscillator model is expected to work well near the equilibrium bond length and does not allow for dissociation of molecules. As the potential function is usually unknown, we attempt to account for the deviation from the harmonic behavior by adding higher order polynomial terms $\tilde{E}_v$:

$$\tilde{E}_v = \tilde{\nu}_e(v + \frac{1}{2}) - \tilde{\nu}_e x_e(v + \frac{1}{2})^2 + \tilde{\nu}_e y_e(v + \frac{1}{2})^3 \tag{5.426}$$

where $\tilde{\nu}_e$ is the vibrational wavenumber, x_e and y_e are anharmonicity constants, and v is the vibrational quantum number. Usually the third term is ignored and we can write the vibrational transition frequencies as ($v \to v + 1$):

$$\tilde{\nu}(v) = \tilde{E}_{v+1} - \tilde{E}_v = \tilde{\nu}_e - 2\tilde{\nu}_e x_e(v + 1) \tag{5.427}$$

As we will see soon that by adding the 2nd order polynomial term to the eigenvalues, we actually imply the use of a potential function that allows for dissociation. One has to distinguish between two kinds of dissociation energies: *equilibrium dissociation energy* D_e and *spectroscopic dissociation energy* D_0. D_e is measured from the bottom of the potential to the dissociation limit whereas D_0 is measured from the lowest vibrational level to the dissociation limit. The meaning of these two quantities is demonstrated below.



Definitions of D_e and D_0.

The ground vibrational level energy is given by:

$$\tilde{E}_0 = \frac{\tilde{\nu}_e}{2} - \frac{\tilde{\nu}_e x_e}{4} + \frac{\tilde{\nu}_e y_e}{8} \tag{5.428}$$

And therefore the difference between D_0 and D_e is:

$$\tilde{D}_e - \tilde{D}_0 = \tilde{E}_0 \tag{5.429}$$

When starting from the lowest vibrational level ($v = 0$), the observed absorption frequencies for $v' = 1, 2, 3...$ are given by:

$$\tilde{\nu}(v') = \tilde{E}_{v'} - \tilde{E}_0 = \tilde{\nu}_e v' - \tilde{\nu}_e x_e v'(v' + 1) \tag{5.430}$$

Note that sometimes the frequency ν may be expressed as angular frequency ω. The relationship between the two is just a constant factor: $\omega = 2\pi\nu$. To convert these to energy, one must use either $E = h\nu$ or $E = \hbar\omega$.

We added a second order term (3rd order ignored) to the expression for $\tilde{E}_v$ in Eq. (5.426) but what kind of potential would this correspond to? It can be shown that this potential is the *Morse potential*:

$$V(R) = \tilde{D}_e \left(1 - \exp\left(-\alpha(R - R_e)\right)\right)^2 \tag{5.431}$$

where D_e is the equilibrium dissociation energy and α is a parameter related to the anharmonicity in the potential.

This allows for a diatomic molecule to dissociate and therefore it is more realistic than the harmonic function. Solution of the Schrödinger equation using the Morse function gives the following expression for the vibrational energy levels:

$$\tilde{E}_v = \alpha\sqrt{\frac{\hbar\tilde{D}_e}{\pi c\mu}}\left(v + \frac{1}{2}\right) - \frac{\hbar\alpha^2}{4\pi c\mu}\left(v + \frac{1}{2}\right)^2 \tag{5.432}$$

By comparing this with Eq. (5.426) we can identify:

$$\tilde{\nu}_e = \alpha\sqrt{\frac{\hbar\tilde{D}_e}{\pi c\mu}} \tag{5.433}$$

$$\tilde{\nu}_e x_e = \frac{\hbar\alpha^2}{4\pi c\mu} \tag{5.434}$$

Solving for $\tilde{D}_e$ gives:

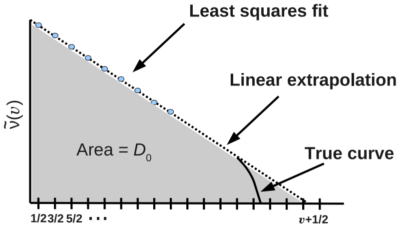
$$\tilde{D}_e = \frac{\tilde{\nu}_e}{4x_e} \tag{5.435}$$

Note that the actual potential energy curve most likely deviates from the Morse potential and therefore the above expressions are only approximate.

The Birge-Sponer plot can be used to estimate the dissociation energy D_0 by using the following sum:

$$D_0 = \sum_{v=0} \tilde{\nu}(v) \approx \int \tilde{\nu}(v) dv \tag{5.436}$$

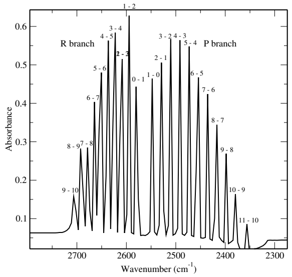
D_0 therefore represents the area under linear function $\tilde{\nu}(v)$. By using the mid-point numerical integration scheme, one should prepare the x-axis as $v + 1/2$ and the y-axis as $\tilde{\nu}(v)$. The integration can be carried out with a pen and paper or a computer as demonstrated below.



Example of Birge-Sponer plot.

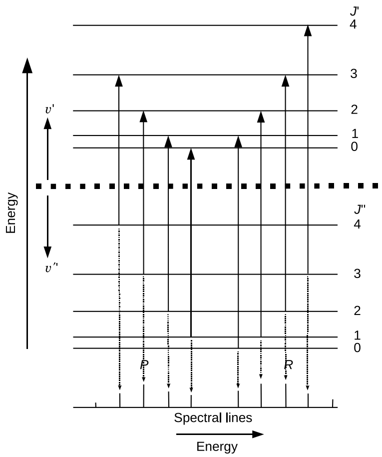
5.9 Vibration-rotation spectra of diatomic molecules

Rotational structure can often be observed to accompany vibronic transitions when using sufficiently high spectral resolution. Spectral lines in such spectrum correspond to simultaneous change in both vibrational and rotational quantum numbers. For example, for HCl molecule one can observe the vibrational quantum number to change $v' = v'' \pm 1$ and $J' = J'' \pm 1$. The vibration-rotation spectrum of HBr is shown below. Note that the rotational structure can usually only be observed in dilute gas phase samples as molecular rotations tend to be quenched in liquids and solids.



Vibration-rotation spectrum of HBr molecule in the gas phase. The peaks are labeled according to their initial (first) and final (last) rotational states.

Because the ground vibrational level ($v'' = 0$) is predominantly populated up to room temperatures, transitions from the excited vibrational states do not contribute to the spectrum at these temperatures. They can contribute when temperature is increased, however. For rotational states many states are thermally populated and therefore the excited rotational states contribute to the spectrum. Note that at close to 0 K one could only observe one rotational transition ($J'' = 0 \to J' = 1$). Transitions where the rotational quantum number increases by one ($\Delta J = +1$) are said to belong to the R branch and transitions where the rotational quantum number decreases by belong to the P branch ($\Delta J = -1$). The intensities of the spectral lines reflect the thermal populations on the initial rotational states. The Q branch corresponds to $\Delta J = 0$ but is only allowed in when the molecule has orbital angular momentum (e.g., NO).



Both v and J change in transitions.

The energies of the vibration-rotation levels are approximately given by (in wavenumbers; see Eqs. (5.385) and (5.426)):

$$\tilde{E}_{vr} = \tilde{E}_v + \tilde{E}_r = \tilde{\nu}_e\left(v + 1\right) - \tilde{v}_e x_e \left(v + \frac{1}{2}\right)^2 + \tilde{B}_v J(J+1) \qquad (5.437)$$

where we have included separate rotational constant B_v for each vibrational level v. Usually $B_1 < B_0$ etc. The dependence of the rotational constant on the vibrational quantum number can be expressed as:

$$\tilde{B}_v = \tilde{B}_e - \tilde{\alpha}_e\left(v + \frac{1}{2}\right) \qquad (5.438)$$

where $\tilde{\alpha}_e$ is the *vibration-rotation constant*.

Next we consider a fairly common case where the vibrational transition occurs from $v = 0$ to $v = 1$ and consider only rotational transitions that fulfill the selection rule $\Delta J = \pm 1$. In the ground vibrational level the rotational level energies are given by:

$$\tilde{E_{vr}}(v = 0, J) = \tilde{\nu}_e/2 - \tilde{v}_e x_e/4 + \tilde{B}_0 J(J+1) \qquad (5.439)$$

When a molecule absorbs light, the vibrational quantum number increases by one. For the R branch the rotational quantum number J also increases by one. Thus we need the energy for this level:

$$\tilde{E}_{vr}(v = 1, J+1) = \frac{3}{2}\tilde{\nu} - \tilde{\nu}_e x_e \left(\frac{3}{2}\right)^2 + \tilde{B}_1(J+1)(J+2) \qquad (5.440)$$

The energy differences give the positions of the spectral lines for the R branch:

$$\begin{aligned}\tilde{\nu}_R &= \tilde{E}_{vr}(v=1,J+1) - \tilde{E}_{vr}(v=0,J) \qquad (5.441)\\ &= \tilde{\nu}_0 + \tilde{B}_1(J+1)(J+2) - \tilde{B}_0 J(J+1)\\ &= \tilde{\nu}_0 + 2\tilde{B}_1 + \left(3\tilde{B}_1 - \tilde{B}_0\right) J + \left(\tilde{B}_1 - \tilde{B}_0\right) J^2\\ &= \tilde{\nu}_0 + \left(\tilde{B}_0 + \tilde{B}_1\right)(J+1) + \left(\tilde{B}_1 - \tilde{B}_0\right)(J+1)^2\end{aligned}$$

$$\tilde{\nu}_0 = \tilde{\nu}_e - 2\tilde{\nu}_e x_e \qquad (5.442)$$

where $\tilde{\nu}_0$ is the center of the vibration-rotation band. There will be no absorption at $\tilde{\nu}_0$ unless the molecule has a Q branch. If $B_1 = B_0$ these lines are equally spaced.

For the P branch $J \to J-1$ and the excite state energy level is given by:

$$\tilde{E}_{vr}(v=1,J-1) = \frac{3}{2}\tilde{\nu}_e - \tilde{\nu}_e x_e \left(\frac{3}{2}\right)^2 + \tilde{B}_1(J-1)J \qquad (5.443)$$

The corresponding transitions occur at:

$$\begin{aligned}\tilde{\nu}_P &= \tilde{E}_{vr}(v=1,J-1) - \tilde{E}_{vr}(v=0,J) \qquad (5.444)\\ &= \tilde{\nu}_0 + \tilde{B}_1(J-1)J - \tilde{B}_0 J(J+1)\\ &= \tilde{\nu}_0 - \left(\tilde{B}_1 + \tilde{B}_0\right) J + \left(\tilde{B}_1 - \tilde{B}_0\right) J^2\end{aligned}$$

To extract B_0 and B_1 from an experimental spectrum, the following expressions are useful:

$$\begin{aligned}\tilde{\nu}_R(J-1) - \tilde{\nu}_P(J+1) &= 4\tilde{B}_0\left(J + \frac{1}{2}\right) \qquad (5.445)\\ \tilde{\nu}_R(J) - \tilde{\nu}_P(J) &= 4\tilde{B}_1\left(J + \frac{1}{2}\right)\end{aligned}$$

where J is the initial state rotational quantum number. To apply these equations one must label the rotational lines according to their J and record the peak positions in wavenumbers. This should be applied to many peak pairs and then obtain the averaged values for $\tilde{B}_0$ and $\tilde{B}_1$.

Example. Calculate the relative populations of the first five rotational levels of the ground vibrational state of $H^{35}Cl$ at 300 K. The ground vibrational state rotational constant $B_0 = 10.44$ cm^{-1}.

Solution. The level populations are given by the Boltzmann distribution (Eq. (5.394)):

$$\frac{N_J}{N_0} = (2J+1)\, e^{-hcJ(J+1)\tilde{B}_0/(k_B T)}$$

where N_0 is the number of molecules in the rotational ground state. First we calculate the factor appearing in the exponent:

$$\frac{hc\tilde{B}_0}{k_BT} = \frac{(6.626\times10^{-34}\ \text{Js})(2.998\times10^{8}\ \text{m/s})(10.44\ \text{cm}^{-1})(10^{2}\ \text{cm/m})}{(1.3806\times10^{-23}\ \text{J K}^{-1})(300\ \text{K})}$$

$$= 5.007\times10^{-2}$$

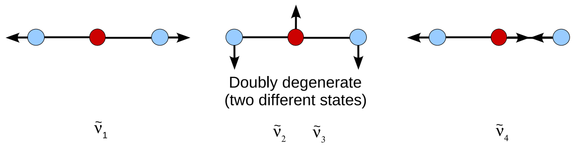
Then, for example, for $J = 1$ we get:

$$\frac{N_1}{N_0} = 3e^{-2(5.007\times10^{-2})} = 2.71$$

The same way one can get the relative populations as: 1.00, 2.71, 3.70, 3.84, 3.31, and 2.45 for $J = 0, 1, 2, 3, 4, 5$. Note that these are relative populations since we did not calculate the partition function q.

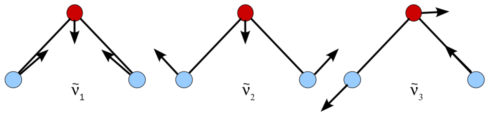
5.10 Vibrational spectra of polyatomic molecules

Recall that $3N - 6$ coordinates are required to describe the internal motions in a molecule with N nuclei (or $3N - 5$ for a linear molecule). The different types of possible vibrational motion can be described in terms of *normal modes of vibration*. For a diatomic molecule, $N = 2$ and $3N - 5 = 1$ and there can only be one normal mode in such molecule (the bond vibration). For a linear CO_2 molecule we can have $3N - 5 = 4$ normal modes as shown below:



Normal modes of CO_2

For a nonlinear H_2O, $3N - 6 = 3$ and these normal modes are shown below:



Normal modes of H_2O

First we consider classical vibration of a polyatomic molecule and transition to quantum mechanics later. The kinetic energy of a polyatomic molecule is given by:

$$T = \frac{1}{2}\sum_{k=1}^{N} m_k \left[\left(\frac{dx_k}{dt}\right)^2 + \left(\frac{dy_k}{dt}\right)^2 + \left(\frac{dz_k}{dt}\right)^2\right] \tag{5.446}$$

This can be simplified by choosing mass-weighted Cartesian coordinates:

$$\begin{aligned} &q_1 = \sqrt{m_1}\,(x_1 - x_{1e})\,,\ q_2 = \sqrt{m_1}\,(y_1 - y_{1e})\,,\ q_3 = \sqrt{m_1}\,(z_1 - z_{1e}) \quad (5.447)\\ &q_4 = \sqrt{m_2}\,(x_2 - x_{2e})\,,\ ...,\ q_{3N} = \sqrt{m_N}\,(z_N - z_{Ne}) \end{aligned}$$

where x_{ie} correspond to the equilibrium geometry of the molecule. The equilibrium geometry is independent of time and therefore the kinetic energy is:

$$T = \frac{1}{2}\sum_{i=1}^{3N}\left(\frac{dq_i}{dt}\right)^2 \tag{5.448}$$

The potential energy V is a function of the nuclear coordinates and therefore it is also a function of the mass-weighted coordinates. It is convenient to expand V in Taylor series about the equilibrium geometry:

$$V = V_e + \sum_{i=1}^{3N}\left(\frac{\partial V}{\partial q_i}\right)_e q_i + \frac{1}{2}\sum_{i=1}^{3N}\sum_{j=1}^{3N}\left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_e q_i q_j + ... \tag{5.449}$$

where V_e is the potential energy at the equilibrium and subscript e refers to the equilibrium geometry. Since V_e is a constant it does not affect the potential shape and therefore we can set it to zero when considering molecular vibration. Also the first derivative term is zero at the equilibrium geometry and hence we are left with the 2nd derivative term. If we ignore the higher order terms, we can write the potential function as:

$$V = \frac{1}{2}\sum_{i=1}^{3N}\sum_{j=1}^{3N} K_{ij} q_i q_j \tag{5.450}$$

where K is a second derivative matrix with elements given by $K_{ij} = (\partial^2 V)/(\partial q_i \partial q_j)$. The total energy is now given by:

$$E = T + V = \frac{1}{2}\sum_{i=1}^{3N}\left(\frac{dq_i}{dt}\right)^2 + \frac{1}{2}\sum_{i=1}^{3N}\sum_{j=1}^{3N} K_{ij} q_i q_j \tag{5.451}$$

The main problem with this expression is the off-diagonal terms appearing in K. However, it is possible to find a linear transformation that converts the mass-weighted coordinates q into new coordinates Q in such way that K is transformed into diagonal form. In practice, one should construct K, diagonalize it using similarity transformations R (i.e., RKR^{-1}), and use R to transform q to Q. After eliminating the off-diagonal terms, we can write Eq. (5.451):

$$E = \frac{1}{2}\sum_{i=1}^{3N}\left(\frac{dQ_i}{dt}\right)^2 + \frac{1}{2}\sum_{i=1}^{N'}\kappa_i Q_i^2 \tag{5.452}$$

where $N' = 3N - 6$ for a nonlinear molecule or $N' = 3N - 5$ for a linear molecule. Coordinates Q_i are referred to as *normal coordinates*. Note that it usually the diagonalization step is carried out numerically using computers. In a normal mode, the center of mass for the molecule does not move and the molecule does not rotate. Each normal mode has its characteristic *vibration frequency*. Sometimes two or more normal modes may have the same energy, in which case they are said to be *degenerate*. It can be shown that any vibrational motion of a polyatomic molecule can be expressed as a linear combination of normal mode vibrations.

Next we carry out the quantum mechanical treatment of the normal mode problem. Since Eq. (5.452) is a sum of terms, which depend on different coordinates, we can separate the equation. This means that we can solve the problem separately for each normal mode. The equation corresponds to the harmonic oscillator problem along each normal mode and the energies are given by:

$$E = \sum_{i=1}^{N'}\left(v_i + \frac{1}{2}\right)hc\tilde{\nu}_i \tag{5.453}$$

---

where the frequency $\tilde{\nu}_i = \sqrt{\kappa_i/\mu_{Q_i}}/(2\pi)$. The eigenfunctions are then given by taking a product of the normal mode functions.

For a given normal mode to be IR active, the displacement introduced by the normal mode must cause a change in dipole moment. This is a similar selection rule that we had for diatomic molecules. For example, the symmetric stretch of CO_2 is not IR active whereas all the other normal modes in this molecule produce a change in dipole moment. This can be also derived by using group theory. Note that the molecule in its equilibrium geometry does not have a dipole but when distorted, it can acquire dipole moment. Another restriction is that we can change the quantum number by ±1 for each mode. This selection rule is the same as we obtained for one harmonic oscillator earlier. Note that it is possible to have *combination bands*, which means that two or more different modes are excited simultaneously. However, each of them just by ±1. This selection rule does not always hold rigorously, which means that it is possible to see overtone as we have already discussed for diatomic molecules. Furthermore, we have made the harmonic approximation, which may not hold for all molecules.

IR spectroscopy of polyatomic molecules is often used for identifying certain groups based on their characteristic frequencies ("fingerprints"). Below some common characteristic frequencies are given.

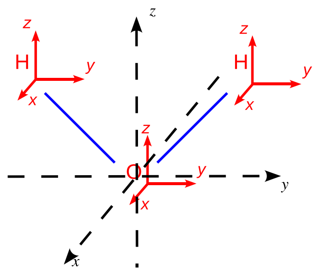
- Hydrogen stretching vibrations, 3700 – 2500 cm^{-1}. These vibrations occur at high frequencies because of the low mass of the hydrogen atom. If an OH group is not involved in hydrogen bonding, it usually has a frequency around 3600 – 3700 cm^{-1}. Hydrogen bonding can cause the frequency to drop by 300 – 1000 cm^{-1}. Other groups: NH (3300 – 3400 cm^{-1}), CH (2850 – 3000 cm^{-1}), SiH ($\approx$ 2200 cm^{-1}), PH ($\approx$ 2400 cm^{-1}), and SH ($\approx$ 2500 cm^{-1}).
- Triple-bond region, 2500 – 2000 cm^{-1}. Triple bonds have typically high frequencies because of the large force constants ("strong bonds"). For example, C≡C is typically 2050 – 2300 cm^{-1} (possibly weak) and C≡N 2200 – 2300 cm^{-1}.
- Double-bond region, 2000 – 1600 cm^{-1}. Carbonyl groups, C=O of ketones, aldehydes, etc. show strong bands near 1700 cm^{-1}. Also C=C appears near 1650 cm^{-1}. Note that C-N-H bending may appear in this region as well.
- Single-bond region (stretch & bend), 500 – 1700 cm^{-1}. This region is not useful for identifying specific groups but it can be used as a "fingerprint" region since it can show even small differences between similar molecules. Organic molecules usually show peaks in the region between 1300 and 1475 cm^{-1} (hydrogen bending). Out-of-plane bending of olefinic and aromatic CH groups usually occur between 700 – 1000 cm^{-1}.

Symmetry species of normal modes and allowed transitions:

A powerful way of dealing with normal modes, especially of complex molecules, is to classify them according to their symmetries. Each normal mode must belong to one of the symmetry species ("irrep") of the molecular point group. This will also allow us to use Eq. (4.350) in calculating the allowed transitions. To see how normal modes are labeled, consider the following example.

Example. Establish the symmetry species of the normal modes of H_2O as shown at the beginning of this section. Water belongs to C_{2v} point group. Which normal modes are IR allowed?

Solution. First we draw "local coordinates axes" on each at atom as shown below.



The total number of coordinates to describe H_2O is $3N - 6 = 3$ ($N = 3$). The corresponding three normal modes were shown earlier. Next we have to find out which irreps span the normal modes in water. We will use the following rules to determine this:

1. If a local coordinate axis is unchanged in the symmetry operation, a value of 1 is added to the character.
2. If a local coordinate axis changed direction in the symmetry operation, a value of -1 is added to the character.
3. If any other displacement of the axis follows, no value is added to the character.

The outcome of these operations is:

$$\begin{aligned}
\chi(E) &= 1+1+1+1+1+1+1+1+1 = 9 \\
\chi(C_2) &= \overbrace{-1-1+1}^{\text{oxygen}}\overbrace{+0+0+0}^{\text{hydrogen}}\overbrace{+0+0+0}^{\text{hydrogen}} = -1 \\
\chi(\sigma_v(xz)) &= 1+1-1+0+0+0+0+0+0 = 1 \\
\chi(\sigma_v'(yz)) &= 1+1-1+1+1-1+1+1-1 = 3
\end{aligned} \tag{5.454}$$

Recall that we have carried out similar task for molecular orbitals earlier (Ch. 4).

Next we need to find the combination of irreps that add up to this character. First we have to remember that our current treatment still includes translation and rotation (a total of 6 irreps), which give (see the C_{2v} character table): A_1, A_2, $2 \times B_1$, and $2 \times B_2$. If these are added up, we get:

$$\chi(E) = 6, \chi(C_2) = -2, \chi(\sigma_v(xz)) = 0 \text{ and } \chi(\sigma_v'(yz)) = 0$$

As we are still missing the three molecular vibrational normal modes, this does not add up to $(9, -1, 1, 3)$ but $(6, -2, 0, 0)$. To make the two characters match, we have to include $2 \times A_1$ and B_2, which add up to the following character:

$$\chi(E) = 3, \chi(C_2) = 1, \chi(\sigma_v(xz)) = 1 \text{ and } \chi(\sigma_v'(yz)) = 3$$

Adding the two characters above, matches what we had on the previous slide. Thus we conclude that water will have two A_1 and one B_2 symmetry normal modes. By carrying out symmetry operations on the normal modes of water (see the figure at the beginning of the section), we conclude that $\tilde{\nu}_1$ belongs to A_1, $\tilde{\nu}_2$ to A_1, and $\tilde{\nu}_3$ to B_2. When doing this, one should be observing how the directions of the arrows change and then comparing this with the numbers given in the character table (verify that you get the same result as given here!).

To see if a given transition is IR active, one should consider the following integral, which gives the intensity I of the transition (see also Eq. (4.352)):

$$I_l \propto \left|\left\langle \psi_i \left|\vec{\mu}\right| \psi_f \right\rangle\right|^2 = \left|\int \psi_i^* \vec{\mu} \psi_f d\tau\right|^2 \tag{5.455}$$

where $\vec{\mu}$ is the dipole moment operator. The above relation is also know as Fermi's golden rule (with the proportionality constants omitted). Here i refers to the initial (ground) vibrational state, which is always totally symmetric (i.e. A_1, A_g, etc.). The symmetry of the dipole moment operator (components μ_x, μ_y, and μ_z) are proportional to the corresponding coordinates x, y, and z. The symmetries of these operators (i.e., x, y, and z in the C_{2v} character table) are, respectively, B_1, B_2, and A_1. Based on Eq. (4.350), the above integral can be nonzero only if the direct product of the three components in the integral yield the totally symmetric irrep. As molecules tend to be either randomly oriented in solid samples or rotating freely in liquid/gas samples, it is sufficient that one of the components x, y, z gives a nonzero result. For the B_2 normal mode we get:

$$A_1 \times B_1 \times B_2 = (A_1 \times B_1) \times B_2 = B_1 \times B_2 = A_2 \neq A_1 (\text{no contribution})$$
$$A_1 \times B_2 \times B_2 = (A_1 \times B_2) \times B_2 = B_2 \times B_2 = A_1 (\text{contributes})$$
$$A_1 \times A_1 \times B_2 = (A_1 \times A_1) \times B_1 = B_1 \times B_2 = B_2 \neq A_1 (\text{no contribution})$$

For the two A_1 normal modes we get:

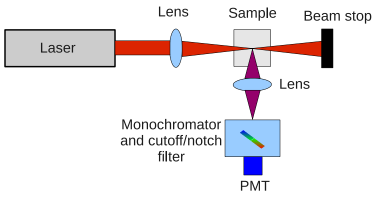
$$A_1 \times B_1 \times A_1 = (A_1 \times B_1) \times A_1 = B_1 \times A_1 = B_1 \neq A_1 (\text{no contribution})$$
$$A_1 \times B_2 \times A_1 = (A_1 \times B_2) \times A_1 = B_2 \times A_1 = B_2 \neq A_1 (\text{no contribution})$$
$$A_1 \times A_1 \times A_1 = (A_1 \times A_1) \times A_1 = A_1 \times A_1 = A_1 (\text{contributes})$$

Thus we conclude that all three normal modes are IR active.

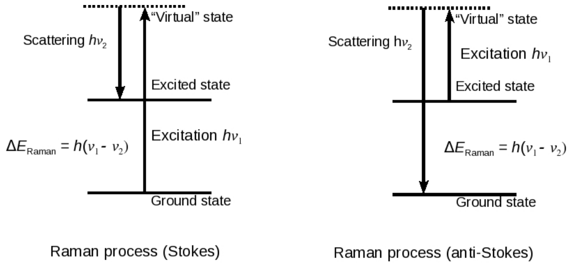
5.11 Raman spectroscopy

When a sample is irradiated with monochromatic light, the incident radiation may be absorbed, may stimulate emission, or may be scattered. There are several types of scattering processes: *Rayleigh scattering*, *Mie scattering*, and *Raman scattering*. Rayleigh scattering is the elastic scattering of light by particles that are much smaller than the wavelength of the light. For example, Rayleigh scattering makes the sky look blue because short wavelengths (blue) are scattered more than long wavelengths (red) in the atmosphere. Mie scattering occurs when the particles are about the same size as the wavelength of light. This can be important, for example, in atmosphere where small soot and dust can scatter light.

In this section we are interested in Raman scattering where the incident light exchanges energy with the sample as it scatters. If the incident photons loose energy in the process, the spectral lines of the scattered light are called *Stokes lines*. If the opposite happens, the lines are called *anti-Stokes lines*. The spectral line from scattered light that is at the exactly at the excitation wavelength is called the *Rayleigh line*. If the incident monochromatic light is resonant with some electronic state, the process is called *resonance Raman*. Resonance Raman process is much more efficient than non-resonant Raman. Most often the amount of (non-resonant) Raman scattering is very small (less than 1 part in 10^6) and therefore the method is not very sensitive. Furthermore, the Raman frequency shifts may sometimes be small and the strong Rayleigh line may overlap with the Raman lines. Lasers produce intense monochromatic light and therefore they are ideal for Raman experiments.



Typical Raman experiment setup.



Raman process (Stokes)

Raman process (anti-Stokes)

Stokes and anti-Stokes Raman transitions.

Energy is conserved in a Raman process and therefore we must have:

$$h\nu + E_i = h\nu' + E_f \tag{5.456}$$

where ν is the frequency of the incoming light, ν' is the frequency of the Raman scattered light, E_i is the initial energy of the molecule, and E_f is the final energy of the molecule. This can be arranged into the following resonance condition:

$$h(\nu' - \nu) = E_i - E_f = h\Delta\nu_R = hc\Delta\tilde{\nu}_R \tag{5.457}$$

where $\Delta\tilde{\nu}_R$ is the Raman shift in wavenumber units. The Raman shifts observed correspond to vibrational and rotational level spacings and hence it can be used to obtain information about molecular vibration and rotation. Thus it obtains similar information that IR spectroscopy does but, as we will see later, it will have different selection rules. It is important from the experimental point of view that the Raman effect can be observed with monochromatic light source operating at any wavelength. This offers an important advantage over IR spectroscopy. Consider, for example, a water based sample, which would obviously absorb all incident IR light making any IR measurement impossible. Raman, on the other hand, can employ a wavelength that is not absorbed by water and therefore it is possible to measure these samples.

The Raman effect arises from the induced polarization of scattering molecules that is caused by the electric field component of light. By polarization we refer to the shift in the electron density in an atom/molecule. In the following, we will carry out classical treatment of Raman scattering. The full quantum treatment is out of the scope of this course.

We start by considering an isotropic molecule, which has the same optical properties in all directions. This could be, for example, CH_4. A dipole moment $\vec{\mu}$ is induced in the molecule by an electric field $\vec{E}$:

$$\vec{\mu} = \alpha\vec{E} \tag{5.458}$$

where α is the *polarizability tensor* with elements $\alpha_{xx}, \alpha_{xy}, \ldots.$ The elements of this tensor α_{ij} tell us how easy it is to polarize the electronic cloud int direction i when the field is oriented along j. The unit for polarizability is $\mathrm{Cm/Vm^{-1}} = \mathrm{C^2m^2/J}$. The isotropic part of the polarizability is given by $(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$. If we consider molecular rotation, the molecule must have anisotropy in α or in case of molecular vibration α must change along the vibration. When this molecule rotations (or vibrates) at frequency ν_k, we can write the change in polarizability as a function of the frequency:

$$\alpha = \alpha_0 + (\Delta\alpha)\cos(2\pi\nu_k t) \tag{5.459}$$

where α_0 is the equilibrium polarizability and $\Delta\alpha$ is its variation. The electric field in electromagnetic radiation varies with time as:

$$E = E^0\cos(2\pi\nu_0 t) \tag{5.460}$$

Now we can calculate the induced dipole moment as a function of time:

$$\begin{aligned}\mu(t) &= \left(\alpha_0 + \Delta\alpha \times \cos(2\pi\nu_k t)\right) E^0 \cos(2\pi\nu_0 t) \qquad (5.461)\\ &= \alpha_0 E^0 \cos(2\pi\nu_0 t) + \frac{1}{2}\Delta\alpha E^0 \left(\cos(2\pi(\nu_0 + \nu_k)t) + \cos(2\pi(\nu_0 - \nu_k)t)\right)\end{aligned}$$

where the last form has been obtained by $\cos(a)\cos(b) = (\cos(a+b) + \cos(a-b))/2$. The three terms that emerged represent the Rayleigh scattering (at ν_0), anti-Stokes ($\nu_0 + \nu_k$), and Stokes ($\nu_0 - \nu_k$). This treatment does not account for the fact that anti-Stokes lines originate from excited levels (see the the previous transition diagram), which have lower thermal population than the ground state. Thus anti-Stokes lines are weaker than Stokes lines. At very low temperatures, only Stoke lines would be observed.

For a molecular motion to be Raman active, we must clearly have $\Delta\alpha \neq 0$. This means that the polarizability of the molecule must change along the coordinate of the motion (i.e. vibration or rotation). For both heteronuclear and homonuclear diatomic molecules polarizability changes as a function of bond length because the electronic structure changes. Also, for molecular rotation, it is fairly easy to see that the spatial orientation of molecules should also change the polarizability (note: does not apply to spherical rotors). This means that it is possible to study these molecules by using the Raman technique except spherical top molecules which do not show the rotational Raman effect.

Just like we predicted IR activity in the previous section, one can use symmetry to predict Raman activity. The transition operator in Eq. (5.455) consist now of terms such as $x^2, xy, y^2, ...$ (see character tables), which highlights the fact that two photons are acting on the sample. Again, one would have to show that the direct products of irreps gives the totally symmetry representation. For example, all modes in CH_4 molecule (normal mode symmetries A_1, E, and T_2 in T_d) are Raman active because the Raman operators span the same symmetry elements. This leads to a general rule that states: *if the symmetry species of a normal mode is the same as the symmetry species of a quadratic form for the operator, then the mode may be Raman active.*

Since Raman is a two-photon process, it is more difficult treat than simple absorption or emission. We just summarize the rotational Raman selection rules:

$$\begin{aligned}&\text{Linear molecules: } \Delta J = 0, \pm 2 \qquad (5.462)\\ &\text{Symmetric top: } \Delta J = 0, \pm 2,\ \Delta K = 0 \text{ when } K = 0\\ &\qquad\qquad\qquad \Delta J = 0, \pm 1, \pm 2,\ \Delta K = 0 \text{ when } K \neq 0\end{aligned}$$

When molecular vibration is involved, the selection rule is $\Delta v = \pm 1$. When vibrational Raman transitions are accompanied by rotational transitions, $\Delta J = 0, \pm 2$. These selection rules can be derived by using group theory.

The frequencies of the Stokes lines ($\Delta J = 2$) in the rotational Raman spectrum of a linear molecule are given by:

$$\Delta\tilde{\nu}_R = \tilde{B}J'(J'+1) - \tilde{B}J''(J''+1) \tag{5.463}$$

where J'' refers to the initial state rotational quantum number. These lines appear at lower frequencies than the exciting light and are referred to as the S branch. The line intensities depend on the initial state thermal populations. The anti-Stokes lines ($\Delta J = -2$) are given by:

$$\Delta\tilde{\nu}_R = -2\tilde{B}(2J''-1) \text{ where } J'' \geq 2 \tag{5.464}$$

These lines are referred to as the O branch. It is also possible to observe the Q branch for which $\Delta J = 0$.

For vibrational Raman, the selection rule is basically $\Delta v = \pm 1$ but one should use group theory to see more accurately which modes can be active. *If the molecule has a center of symmetry, then no mode can be both IR and Raman active.* The *technique of depolarization* can be used to determine if a particular Raman line belongs to a totally symmetric normal mode. The depolarization ratio, ρ, of a line is the ratio of the intensities, I, of the scattered light with light polarizations perpendicular and parallel to the plane of polarization of incident light:

$$\rho = \frac{I_\perp}{I_{||}} \tag{5.465}$$

To measure ρ, the intensity of a Raman line is measured with a polarizing filter first parallel and then perpendicular to the polarization of the incident light. If the scattered light is not polarized, then both intensities in Eq. (5.465) are the same and $\rho \approx 1$. If the light retains its initial polarization, then $I_\perp \approx 0$ and also $\rho \approx 0$. A line is classified as *depolarized* if $\rho \geq 0.75$ and *polarized* if $\rho < 0.75$. It can be shown that only totally symmetric vibrations give rise to polarized lines (i.e. the light polarization is largely preserved).

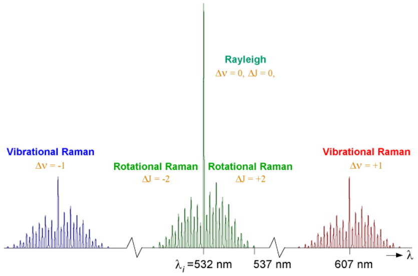
The intensity of Raman transitions can be enhanced by *coherent anti-Stokes Raman spectroscopy* (CARS). In this technique two laser beams with frequencies ν_1 and ν_2 are mixed together in the sample so that they give rise to coherent radiation at several different frequencies. One of the frequencies is:

$$\nu' = 2\nu_1 - \nu_2 \tag{5.466}$$

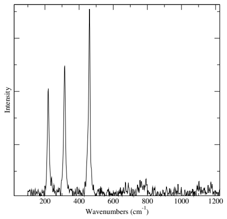
Suppose that frequency ν_2 is varied until it matches one of the Stokes lines of the sample. If this is $\nu_1 - \Delta\nu$ then the coherent emission will have frequency:

$$\nu' = 2\nu_1 - (\nu_1 - \Delta\nu) = \nu_1 - \Delta\nu \tag{5.467}$$

which is the frequency of the corresponding anti-Stokes line. This coherent radiation forms a spatially narrow beam of high intensity. CARS is a four wave mixing process (i.e., four photons are involved).



Example of rotation-vibration Raman spectrum (N_2 gas)



Example of vibration Raman spectrum (CCl_4 liquid)

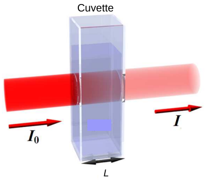
5.12 The Lambert-Beer law

Consider an experiment where monochromatic light is passing through a sample of known concentration and thickness. The *transmittance* of light at a particular wavelength can be determined by measuring the transmitted light intensity I (W m^{-2}; $I = c \times \rho_\nu$) relative to the incident light intensity I_0 (W m^{-2}):

$$T = \frac{I}{I_0} \tag{5.468}$$

Note that in most cases I_0 must include the possible effect of absorption by the solvent (and the sample cuvette), in which case I_0 refers to the intensity of light passing through the sample with the cuvette and solvent but not the compound being studied. Transmittance can be mapped at different wavelengths, and the absorption spectrum can be determined.

To consider the absorption of light within the sample, we will derive the *Lambert-Beer* law. The light beam is passed through the sample cuvette as shown below:



The probability that a photon will be absorbed is usually proportional to the concentration of absorbing molecules, to the intensity of light, and to the thickness of the sample for a very thin sample. This can be expressed as:

$$dI = -\kappa c dx I \Rightarrow \frac{dI}{I} = -\kappa c dx \tag{5.469}$$

where I is the light intensity (W m^{-2}), dI is the change in light intensity by a sample layer with thickness dx (dm), c is the concentration (mol L^{-1}), and κ is the e-base molar absorption coefficient (dm^2 mol^{-1}). The distance x is measured along the path of light propagation through the sample. This differential equation can be integrated:

$$\int\limits_{I_0}^{I} \frac{dI}{I} = -\kappa c \int\limits_{0}^{L} dx \tag{5.470}$$

$$\Rightarrow \ln\left(\frac{I}{I_0}\right) = 2.303 \log\left(\frac{I}{I_0}\right) = -\kappa c L$$

Usually the 10-base logarithm is used (the *Lambert-Beer law*):

$$\log\left(\frac{I_0}{I}\right) \equiv A = \epsilon c L \tag{5.471}$$

---

where A is the absorbance (dimensionless), L is the length of the sample (dm), and ϵ is the *molar absorption coefficient* (dm^2 mol^{-1}). If the sample length is given in cm, the molar absorption coefficient has units L mol^{-1} cm^{-1}. ϵ is characteristic to a given absorbing species and it depends on wavelength, solvent, and temperature. Clearly, the absorbance A also depends on the same conditions. Note that the Lambert-Beer law may not be obeyed if the incident light is not monochromatic, the compound photoassociates or photodissociates, or the sample is optically thick.

For mixtures of independently absorbing substances the absorbance is given by:

$$A = \log\left(\frac{I_0}{I}\right) = \left(\epsilon_1 c_1 + \epsilon_2 c_2 + ...\right) L \tag{5.472}$$

The Lambert-Beer law can also be written in alternative ways:

$$\begin{aligned} I &= I_0 10^{-\epsilon c L} \\ I &= I_0 e^{-\kappa c' L'} \\ I &= I_0 e^{-\sigma N x} \end{aligned} \tag{5.473}$$

The difference between the first and second equations is just the use of different base for the logarithm. In the third equation N is the number density of molecules (m^{-3}), x is the length of the sample (m), and σ is the *absorption cross section* (m^2). For broad peaks, the molar absorption coefficient is recorded at the maximum absorbance (ϵ_{max}).

5.13 Molar absorption coefficient and the transition dipole moment

The relationship between the transition dipole moment and the molar absorption coefficient ϵ (m^2 mol^{-1}) is given by:

$$\int_{band} \epsilon d\nu = \frac{2\pi^2 N_A \nu_{12}}{2.303 \times 3hc\epsilon_0} |\vec{\mu}|^2 \tag{5.474}$$

where N_A is the Avogadro's number (mol^{-1}), ν_{12} is the excitation frequency (Hz), h is the Planck's constant, c the speed of light and ϵ_0 the vacuum permittivity.

Derivation. We will first establish the relationship between κ ($\kappa = 2.303\epsilon$) and the Einstein coefficient B. After this we will insert the expression for B and convert to using ϵ rather than κ.

Starting from the stimulated absorption expression (Eq. (5.358)):

$$\left(\frac{dN_1}{dt}\right)_{abs} = -\underbrace{B\rho_\nu(\nu_{12})}_{\text{"rate; 1/s"}} N_1 \tag{5.475}$$

with B expressed in m kg^{-1}, ρ_ν in J s m^{-3}, we can write this in terms of concentration:

$$\left(\frac{d[A]}{dt}\right)_{abs} = -B_{12}\rho_\nu(\nu_{12})[A] \tag{5.476}$$

where $[A]$ denotes the ground state concentration of the absorbing molecule A. The LHS in Eq. (5.476) is equal to the number of moles of photons (ph) absorbed per unit time (note the change in sign):

$$\left(\frac{d[ph]}{dt}\right)_{abs} = B\rho_\nu(\nu_{12})[A] \tag{5.477}$$

The LHS in this equation is related to the intensity of light absorbed, which is usually expressed in terms of number of photons rather than moles of photons. This is given by (in units of W m^{-2}):

$$dI_{abs} = h\nu_{12} \times \left(\frac{d[ph]}{dt}\right) \times N_A \times dx \tag{5.478}$$

where dx represens a depth over which the absorption occurs. Using this result we can write Eq. (5.477) as:

$$dI_{abs} = B\rho_\nu(\nu_{12})[A] N_A h\nu_{12} dx \tag{5.479}$$

The light intensity I (W m^{-2}) passing through the sample is:

$$I = I_0 - I_{abs} \tag{5.480}$$

where I_0 is the incident light intensity on the sample. In terms of differentials this becomes:

$$dI = -dI_{abs} \tag{5.481}$$

The above result combined with Eq. (5.479) gives:

$$dI = -B\rho_\nu(\nu_{12})\left[A\right]h\nu_{12}dx \tag{5.482}$$

ρ_ν can be related to the light intensity per frequency (Hz):

$$dE = I(\nu_{12}) \times A \times \Delta t \times d\nu_{12}/\Delta\nu_{12} \tag{5.483}$$

where A is the area of the incident light over time period Δt and $\Delta\nu_{12}$ is the frequency range of radiation. This can be used to write ρ_ν as (V volume in which the radiation is contained):

$$\rho_\nu(\nu_{12})d\nu_{12} = \frac{dE}{V} = \frac{I(\nu_{12})A\Delta t d\nu_{12}}{\Delta\nu_{12}Ac\Delta t} = \frac{I(\nu_{12})}{\Delta\nu_{12}c}d\nu_{12} \tag{5.484}$$

This gives directly:

$$\rho_\nu(\nu_{12}) = \frac{I(\nu_{12})}{\Delta\nu_{12}c} \tag{5.485}$$

Combining this with Eq. (5.482) gives:

$$dI = -\frac{BN_A h\nu_{12}}{c\Delta\nu_{12}}\left[A\right]dxI \tag{5.486}$$

This can be compared with Eq. (5.469) to identify:

$$\kappa = \frac{BN_A h\nu_{12}}{c\Delta\nu_{12}} \tag{5.487}$$

---

where κ is in units of $\mathrm{m}^2\ \mathrm{mol}^{-1}$. We eliminate $\Delta\nu_{12}$ by assuming that:

$$\kappa\Delta\nu_{12} \approx \int_{band}\kappa d\nu_{12} \tag{5.488}$$

which allows us to writen Eq. (5.487) as:

$$\int_{band}\kappa d\nu = \frac{BN_A h\nu_{12}}{c} \tag{5.489}$$

with B given by Eq. (5.374). By also noting that $\kappa \approx 2.303\epsilon$ we can finally write:

$$\int_{band}\epsilon d\nu = \frac{2\pi^2 N_A\nu_{12}}{2.303 \times 3hc\epsilon_0}\left|\vec{\mu}\right|^2 \tag{5.490}$$

5.14 Linewidths

In the following we will consider two common sources of line broadening present in spectroscopic experiments.

Doppler broadening: The *Doppler effect* results in line broadening because the radiation is shifted in frequency when the source is moving towards or away from the observer. When a source emitting electromagnetic radiation of frequency ν moves with a speed s relative to the observer, the observer detects radiation frequency:

$$\nu_{rec} = \nu\sqrt{\frac{1-s/c}{1+s/c}} \text{ and } \nu_{appr} = \nu\sqrt{\frac{1+s/c}{1-s/c}} \tag{5.491}$$

where c is the speed of light. For non-relativistic speeds ($s << c$), these expressions simplify to:

$$\nu_{rec} \approx \frac{\nu}{1+s/c} \text{ and } v_{appr} \approx \frac{\nu}{1-s/c} \tag{5.492}$$

Molecule have high speeds in all directions in a gas, and a stationary observer detects the corresponding Doppler-shifted range of frequencies. The detected absorption or emission line will have contributions from all the Doppler-shifted frequencies. It can be shown that the Doppler-shifted distribution width is given by the following expressions:

$$\delta\nu = \frac{2\nu}{c}\sqrt{\frac{2kT\ln(2)}{m}} \tag{5.493}$$

For a molecule (e.g., N_2) at room temperature ($T \approx 300$ K), $\delta\nu/\nu \approx 2.3 \times 10^{-6}$. To minimize the Doppler broadening one should work at low temperatures.

Lifetime broadening: It is found that spectroscopic lines from gas-phase samples are not infinitely sharp even when Doppler broadening has been eliminated by working at low temperature. The residual linewidth is due to a quantum mechanical effect, which is related to the uncertainty between energy and time. For example, if an excited state has short lifetime, its uncertainty in terms of energy increases. The Fourier duality between energy and time can be used to rationalize the situation. Recall that there was a similar duality between position and momentum. Formally, an uncertainty principle cannot be formulated between energy and time because in the non-relativistic quantum mechanics time is not an observable but a parameter. Nevertheless we can write the following approximate relation between the state lifetime τ and its energy E:

$$\delta E \approx \frac{\hbar}{\tau} \tag{5.494}$$

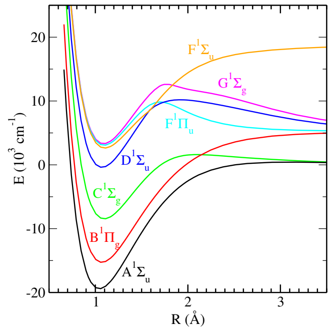
This is called *lifetime broadening*. It can be written in more common units for spectroscopy as:

$$\delta\tilde{\nu} \approx \frac{5.3 \text{ cm}^{-1}}{\tau/\text{ps}} \tag{5.495}$$

The reduction in the state lifetime can be caused by collisions between molecules in the gas phase (*collisional broadening*; $\tau = \tau_{col}$ in Eq. (5.494)) or by internal changes in molecular geometry (or even dissociation). To obtain high resolution, one should work with dilute gas samples.

As the rate of spontaneous emission (Einstein coefficient A) cannot be changed, there is a natural limit to the lifetime of an excited state. The resulting broadening is called the *natural linewidth*. This broadening effect becomes more and more important at high frequencies and less so at low frequencies. For example, in the microwave region, the collisional and Doppler broadening are larger than the natural linewidth.

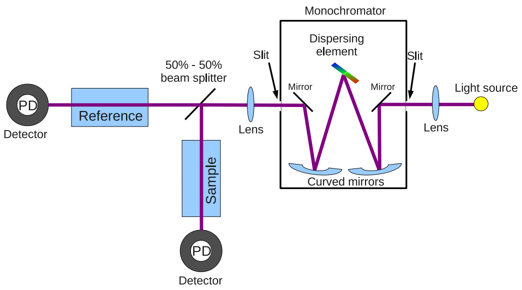
Chapter 6: Electronic spectroscopy



He$_2^*$

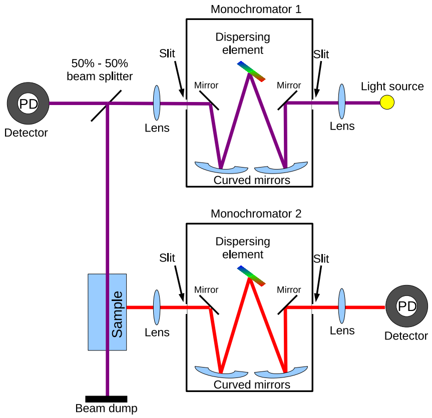
6.1 Absorption and fluorescence experiments

Earlier we briefly discussed the instrumentation used in absorption measurements.



The absorbance is obtained from $A = \log(I_0/I)$ where I_0 is the light intensity at the reference detector and I is the light intensity at the sample detector (see Eq. (5.472)). The monochromator and the lamp in this setup can be replaced with a tunable laser, which typically have the advantage of having a high power and narrow linewidth (in wavelength). Examples of tunable lasers are dye lasers, optical parametric oscillators (OPO) and its variants. Most laser sources, however, have a fixed wavelength and can only be used to determine absorption at one wavelength. If an additional excitation source is included, absorption spectra of transient species may also be obtained (fast response instrumentation typically needed).

Fluorescence (or phosphoresence) can be measured with a similar experimental arrangement but now two monochromators are needed: one for selecting the excitation wavelength and the other to select the monitored emission wavelength. Scanning the excitation wavelength allows one to record *excitation spectrum*, which closely resembles the absorption spectrum (observed through fluorescence; high sensitivity).



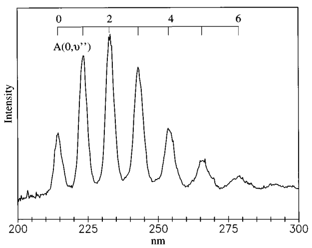
Monochromator 1 and the light source can be replaced with a laser (*laser induced fluorescence*). The high power provided by lasers increases the sensitivity of the measurement greatly (even single molecule level). With a pulsed laser and fast response detector (both in ns timescale), excited state lifetimes may be obtained. Note that the normalized fluorescence intensity is obtained as the ratio between the sample fluorescence intensity and the reference intensity. When a high sensitivity is needed, it is possible to replace monochromator 2 with a long-pass filter, which cuts off the excitation but allows the fluorescence to pass through.

6.2 Electronic energy levels and selection rules

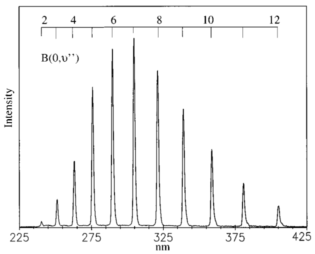
In electronic spectroscopy the electric field component of photons (i.e., light) is used to introduces transitions between the stationary electronic energy levels in atoms or molecules. Electronic spectroscopy therefore belongs to the broad class of optical spectroscopy. The energies required to change the electronic state are typically much larger than is required for molecular vibrations and rotations. Hence, electronic transitions occur mostly in the visible and UV ranges (< 1000 nm) and extend down to vacuum UV (< 200 nm). For molecules the electronic transitions are also accompanied by vibrational and rotational transitions giving additional structure around each electronic transition absorption or emission (i.e., fluorescence or phosphoresence) line.

Under most experimental conditions only the ground electronic and vibrational state is thermally populated whereas this usually does not hold for rotational states. Absorption and fluorescence measurements can be used to determine transition energies, vibrational frequencies, rotational constants and dissociation energies for gound state (emission) or excited states (absorption). If the excited state is purely repulsive, excitation to such state can lead to *phtodissociation*. Furthermore, the chemical properties of excited state species are most often different from the ground state and hence it is possible to use light to affect chemical reactivity.

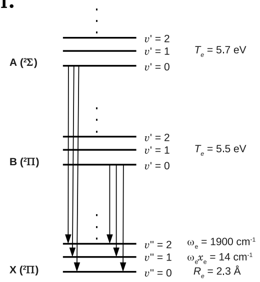
Example. Laser induced fluorescence from NO radical.



A to X fluorescence ($\Sigma - \Pi$; τ = 216 ns).



B to X fluorescence ($\Pi - \Pi$; τ = 3 μs).



Energy levels in NO radical.

Note: The rotational structure is not resolved in the above spectra.

Experimental procedure:

1. Excite the sample containing NO with light (perhaps a laser) that covers the X - A/B absorption band.
2. Use a detector (e.g., PMT or CCD camera) equipped with a monochromator to observe the wavelength resolved fluorescence spectrum.

Usually the vibrational/rotational lines can only be resolved in the gas phase. For large molecules, the rotational constants are very small and this leads to high density of rotational states and high spectral congestion.

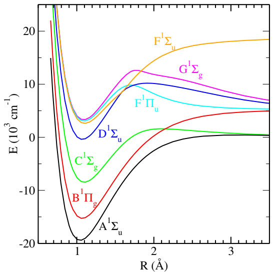
The following selection rules for the electric dipole allowed transitions can be derived by using group theory:

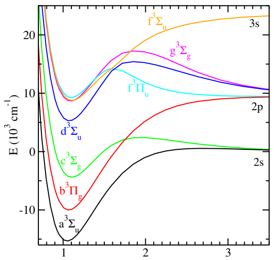
1. $\Delta\Lambda = 0, \pm 1$ where Λ is the orbital angular momentum along the diatomic (or linear) molecular axis. Λ can be 0 (Σ), 1 (Π), 2 (Δ), 3 (Φ), etc. For example, the following transitions are allowed $\Sigma - \Sigma$ ($\Delta\Lambda = 0$), $\Sigma - \Pi$ ($\Delta\Lambda = \pm 1$), $\Pi - \Delta$ ($\Delta\Lambda = \pm 1$) but $\Sigma - \Delta$ ($\Delta\Lambda = \pm 2$) is not. This rule holds for LS coupling where Λ is a good quantum number (i.e., spin-orbit coupling negligible).
2. $\Delta\Omega = 0, \pm 1$ where $\Omega\hbar$ is the projection of the total angular momentum, $J = |\Lambda + \Sigma|$, along the molecular axis. Note that this selection rule holds even when the LS coupling scheme is not applicable.
3. The $\Sigma^+ - \Sigma^+$ and $\Sigma^- - \Sigma^-$ transitions are allowed but $\Sigma^+ - \Sigma^-$ are not.
4. The parity rule: $g - u$ is allowed but $g - g$ and $u - u$ are not.
5. The multiplicity cannot change in an electronic transition: $\Delta S = 0$. For example, singlet – singlet and triplet – triplet transitions are allowed but singlet – triplet are not. This selection rule holds when LS coupling is appropriate (i.e., when spin-orbit coupling is small). Note that in heavy atoms this may not be the case.
6. $\Delta\Sigma = 0$ where $\Sigma = -S, -S+1, ..., S-1, S$. This is only relevant when the spin degenracy is broken by an external magnetic field.

Forbidden transitions may occur under some circumstances but at rates that are typically many orders of magnitude slower than for allowed transitions (unless spin-orbit coupling is very large).

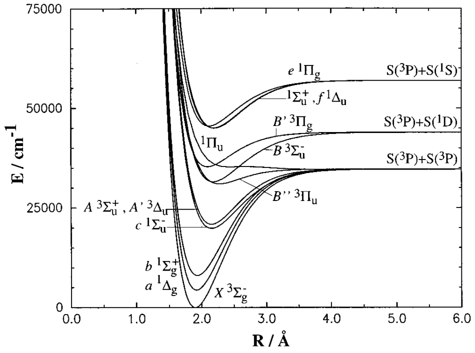
In addition to term symbols, which are not unique labels, additional letters are also assigned to electronic states. The letter X denotes the ground state, A the first excited state, B the second excited state etc. States with higher multiplicity than the ground state are typically labelled with lower case letters using the same logic. Note, however, that the labels were initially given based on experimental observations where some states might have not been observed due to the lack of suitable allowed transitions. This may cause the order of the letters to get mixed up and often a prime (') is used to add more states (e.g., a, a' etc.). Star is sometimes used to denote a metastable state (e.g., He_2^*).

Example. Excited states of He_2 in the singlet and triplet electronic manifolds.





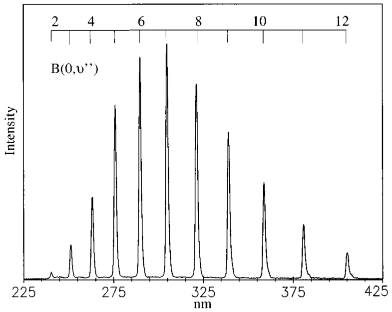
Example. Low lying electronic states of S_2.



Excercise. What transitions of molecular S_2 are electric dipole allowed? How about at the atomic asymptotes (i.e., atomic transitions)?

6.3 Franck-Condon principle

What determines the line intensities in vibronic progressions?



NO radical B → X.

The lines belong to the same electronic transition but to different vibrational states. There must clearly be a factor that dictates the relative line intensities in the fluorescence spectrum. In the above example the initial state corresponds to $v' = 0$ with the final states $v'' = 0, 1, 2, 3...$, which clearly indicates that the final state determines both the line position and intensity.

The *Franck-Condon principle* (FC) states that the degree of overalp between the vibronic wavefunctions between the ground and excited electronic states determines the line intensity. This assumes that the electronic transition is much faster than the nuclear motion and hence the transitions are said to be "vertical". The FC principle can be derived by calculating the transition dipole moment (g = ground state, e = excited state):

$$\langle\vec{\mu}\rangle = \int \Psi_g^* \vec{\hat{\mu}} \Psi_e d\tau \tag{6.496}$$

where Ψ_g and Ψ_e are the full wavefunctions (i.e., electronic, vibrational, rotational degrees included) for the ground and excited states, respectively, and $\vec{\hat{\mu}} = (\hat{\mu}_x, \hat{\mu}_y, \hat{\mu}_z)$ is the transition dipole vector operator with the indicated Cartesian components.

When the electronic, rotation and vibration degrees of freedom are not coupled, we can write the total wavefunction as a product:

$$\begin{aligned}\Psi_g &= \psi_{g,el} \times \psi_{g,vib}^{v} \times \psi_{g,rot}^{J,M} \qquad (6.497)\\ \Psi_e &= \psi_{e,el} \times \psi_{e,vib}^{v} \times \psi_{e,rot}^{J,M}\end{aligned}$$

Inserting Eq. (6.497) into Eq. (6.496), we get:

$$\langle\vec{\mu}\rangle = \int \psi_{g,el}^* \psi_{g,vib}^{v*} \psi_{g,rot}^{J,M*} \vec{\mu} \psi_{e,el} \psi_{e,vib}^{v'} \psi_{e,rot}^{J',M'} d\tau_e d\tau_{vib} \tau_{rot} \tag{6.498}$$

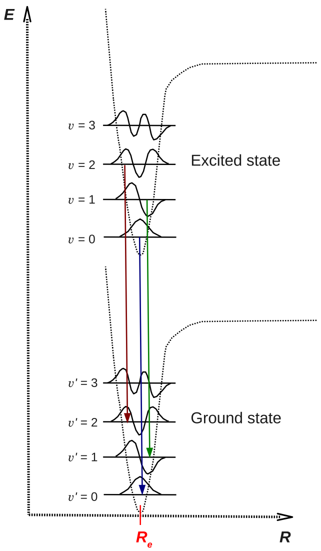
Note that $\vec{\mu}$ depends only on the electronic coordinate r_e (i.e., $\vec{\mu} = \vec{\mu}(r_e)$). Assuming that the electronic transition dipole integral does not depend on the nuclear coordinates, we can write Eq. (6.498) as:

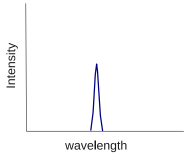
$$\begin{aligned}\langle\vec{\mu}\rangle &= \int \psi_{g,el}^* \vec{\mu} \psi_{e,el} d\tau_{el} \times \int \psi_{g,vib}^{v*} \psi_{g,rot}^{J,M*} \psi_{e,vib}^{v'} \psi_{e,rot}^{J',M'} d\tau_{vib} \tau_{rot} \qquad (6.499)\\ &= \int \psi_{g,el}^* \vec{\mu} \psi_{e,el} d\tau_{el} \times \int \psi_{g,vib}^{v*} \psi_{e,vib}^{v'} d\tau_{vib} \times \int \psi_{e,rot}^{J,M*} \psi_{e,rot}^{J',M'} d\tau_{rot}\end{aligned}$$

For an allowed transition, all the three integrals above must be non-zero. The first term basically gives the selection rules for electronic transitions in molecules (through group theory). The second term is the overlap integral between the vibronic wavefunctions in the ground and excited states ("FC overlap") and the last term gives the rotational selection rule: $\Delta J = \pm 1$ and $\Delta M_J = 0, \pm 1$. The latter is the same selection rule as we had found previously for pure rotational spectra.

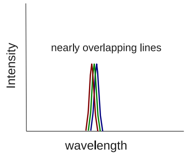
To summarize: The relative line intensities in a vibrational progression are determined by the FC overlap integral.

Equal R_e in both states



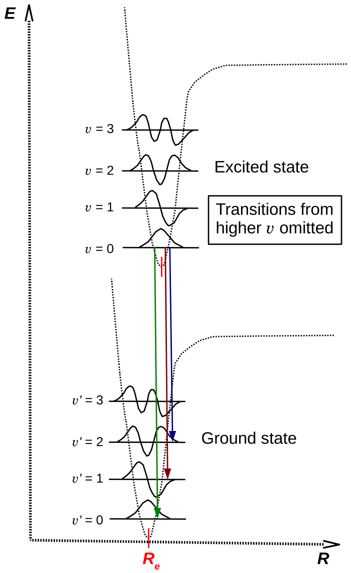


If only v = 0 populated



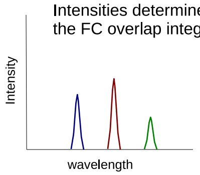
If many v are populated

Excited state R_e larger than the ground state R_e



Transitions from higher v omitted

Intensities determined by the FC overlap integral.



If only v = 0 populated

Many v populated: The above spectrum for each initial v with shift in wavelength.

Remember that most often the equilibrium bond length (R_e) is different in ground and excited states and in practive the situation shown on the previous slide is most common. A good approximation for the diatomic molecular potentials is the Morse potential (see Eq. (5.431)).

Recall that the transition probabilities are related to the square of the transition dipole moment and hence the relative intensities $I(v', v)$ in a vibrational progression are given by:

$$I(v', v) \propto \left| \int \psi_{g,vib}^{v*} \psi_{g,vib}^{v'} d\tau_{vib} \right|^2 \tag{6.500}$$

1. If the transition occurs from the excited state ($v = 0$) to the ground state (i.e., fluorescence), the vibrational progression will yield the vibrational energy spacings for the ground state.
2. If the transition occurs from the ground state ($v' = 0$) to the excited state (i.e., absorption), the vibrational progression will yield the vibrational energy levels for the excited state.
3. If the excited state is purely repulsive, only a broad line in absorption is seen. This can be understood in the presence of continuum vibrational states in the excited electronic state.

6.4 Oscillator strength

The *oscillator strength* f of a transition is defined as:

$$f = \frac{|\vec{\mu}|^2}{|\vec{\mu}_{osc}|^2} \tag{6.501}$$

where $\vec{\mu}$ is the eletric tramsition dipole moment for the electronic transition and $\vec{\mu}_{osc}$ is the same quantity for an electron confined in a three-dimensional harmonic potential (see Eq. (1.106)). Strongly allowed transitions have values close to one and forbidden transitions close to zero. For example, typical singlet-triplet transitions have $f \approx 10^{-5}$.

In Eq. (5.474) we established the connection between transition dipole moment $|\vec{\mu}|^2$ and the integrated molar absorption coefficient. Solving for $|\vec{\mu}|^2$ gives:

$$|\vec{\mu}|^2 = \frac{2.303 \times 3hc\epsilon_0}{2\pi^2 N_A \nu_{12}} \int_{band} \epsilon(\nu) d\nu \tag{6.502}$$

For an harmonic oscillator the transition dipole between two levels is:

$$|\vec{\mu}_{osc}|^2 = \frac{3he^2}{8\pi^2 m_e \nu_{12}} \tag{6.503}$$

When Eqs. (6.502) and (6.503) are inserted into Eq. (6.501) we get:

$$f = \frac{|\vec{\mu}|^2}{|\vec{\mu}_{osc}|^2} = \frac{2.303 \times 4m_e c\epsilon_0}{N_A e^2} \int_{band} \epsilon(\nu) d\nu \tag{6.504}$$

If the electron can be promoted to many different excited levels, the total oscillator strength is normalized to unity:

$$\sum_{states} f_i = 1 \tag{6.505}$$

Excercise. What conversion factors need to be included for f if ϵ is expressed in units L mol^{-1} cm^{-2} rather than the basic SI units?

Note that when fluorescence is considered, both $|\vec{\mu}|^2$ and f are related to the radiative lifetime of the excited state as discussed previously in the context of the Einstein model.

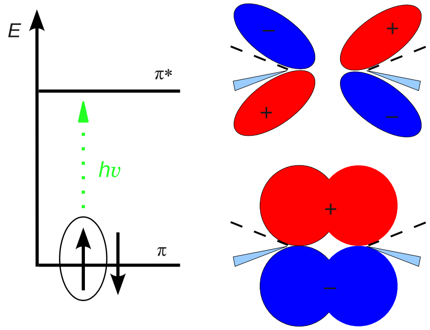
6.5 Electronic spectra of polyatomic molecules

Just like in diatomic molecules electronic transitions in polyatomic molecules occur between the electronic ground and the excited states. The orbitals involved in the electronic excitation can be localized to certain group of atoms ("chromophore") or they can be delocalized over the whole molecule. In the former case the following chromophores have fairly consistent energy ranges of absorption:

Group	$\tilde{\nu}$ (cm^{-1})	λ_{max} (nm)	ϵ_{max} (L mol^{-1} cm^{-1})
C=O ($\pi^* \leftarrow \pi$)	61,000	163	15,000
	57,300	174	5,500
C=O ($\pi^* \leftarrow n$)	37,000	270	10
	35,000	290	20
−N=N−	29,000	350	15
	>39,000	<260	Strong
$-NO_2$	36,000	280	10
	48,000	210	10,000
C_6H_5-	39,000	255	200
	50,000	200	6,300
	55,000	180	100,000
$\left[Cu\,(OH_2)_6\right]^{2+}$(aq)	12,000	810	10
$\left[Cu\,(NH_3)_4\right]^{2+}$(aq)	17,000	600	50
H_2O ($\pi^* \leftarrow n$)	60,000	167	7,000

$\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$ transitions:

When an electron residing on a bonding π-orbital is excited to the corresponding anti-bonding orbital, we have a $\pi^* \leftarrow \pi$ transition. For example in a $-$C=C$-$ fragment we can construct the following MO diagram:

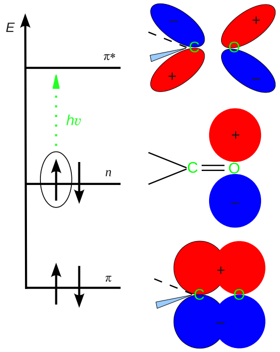


This particular $\pi^* \leftarrow \pi$ transition is at around 7 eV in the vacuum UV ($\approx$ 180 nm). When the double bond is part of a conjugated system, the $\pi^* \leftarrow \pi$ transition moves towards longer wavelengths ("redshift") and may even reach the visible region of the spectrum.

Example. The retina of the eye contains 'visual purple', which is a protein in combination with 11-cis-retinal. The 11-cis-retinal acts as a chromophore, and it is the primary receptor for photons entering the eye. The transition in this system is of $\pi^* \leftarrow \pi$ -type. The chromophore absorbs around 380 nm but in combination with the protein the absorption maximum shifts to about 500 nm with tails to the blue (i.e., towards shorter wavelengths).

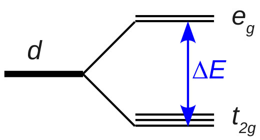
$\pi^* \leftarrow n$ transitions:

If the chromophore has lone pair of electrons, it can show $\pi^* \leftarrow n$ type transition. One of the lone pair electrons is promoted to the anti-bonding π^* orbital. The MO diagram is shown below.



$d - d$ transitions in metal complexes:

For a d-metal complex the surrounding *crystal field* (or *ligand field*) can introduce a non-spherical potential, which can break the degeneracy in the d orbitals. In an octahedral complex, such as $\left[\mathrm{Ti}\left(\mathrm{OH}_2\right)_6\right]^{3+}$, the five degenerate d orbitals are split as shown below.



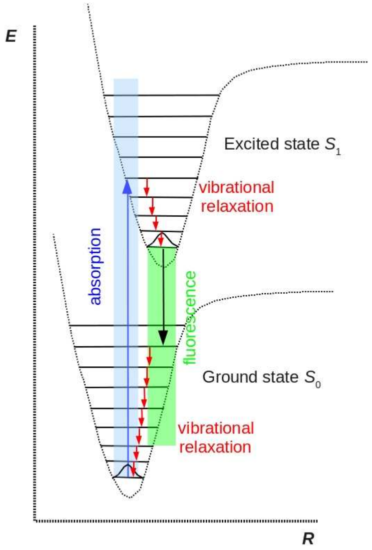
The energy difference ΔE is the *crystal field splitting*. The order of the orbitals depends on the symmetry of the crystal field. For example, in a tetrahedral complex the order of the e_g and t_{2g} states is reversed. The crystal field splittings are typically rather small and hence these absorptions appear mainly in the visible region of the spectrum. For $\left[\mathrm{Ti}\left(\mathrm{OH}_2\right)_6\right]^{3+}$ the splitting is about 20,000 cm^{-1} (500 nm) corresponding to about 2.5 eV.

Note that the above $e_g \leftarrow t_{2g}$ transition is forbidden by the parity rule ($u - g$ is allowed whereas $u - u$ and $g - g$ are not). The transition may become allowed if the central atom is displaced asymmetrically by vibrational motion.

Charge-transfer transitions:

In charge-transfer transitions electrons are displaced from one atom to the other. Such transitions are usually very strong because of the relatively large distance for electron transfer (i.e., large transition dipole moment). In d-metals this may involve transfer of an electron to/from the central metal to the surrounding ligands. For example, in MnO_4^- the intense violet color (420 - 700 nm) is due to a charge-transfer process where the electron moves from oxygen to manganese. When an electron is transferred from the ligands to the central metal atom, this is called *ligand-to-metal charge-transfer transition* and in the opposite case *metal-to-ligand charge-transfer transition*. Another example of charge-transfer transition is Xe - Cl where one of the excited states corresponds to Xe^+ - Cl^-. This used in excimer lasers to produce 308 nm laser light.

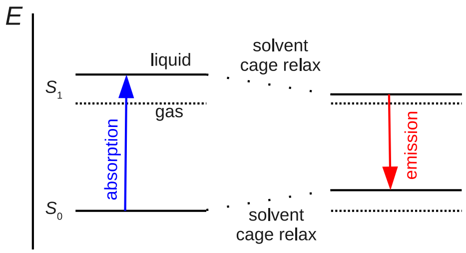
6.6 Fluorescence and phosphoresence



Both fluorescence and phosphoresence correspond to emission of photons from molecules when they return from an excited state to a lower electronic state (often the ground state). Fluorescence occurs between the electronic states of the same spin multiplicity whereas a change in the electron spin orientation occurs in phosphoresence. Recall that one of the selection rules for optical transitions is $\Delta S = 0$ (i.e., no change in multiplicity), which implies that phosphoresence is a much slower process than fluorescence. The radiative lifetime of fluorescence is typically less than 1 μs (most often ns) whereas for phosphoresence this may extend up to seconds. The electronic singlet states are often denoted by S_0 (singlet ground), S_1, ... and triplet T_0 (triplet ground), T_1, ... written in the order of energy.

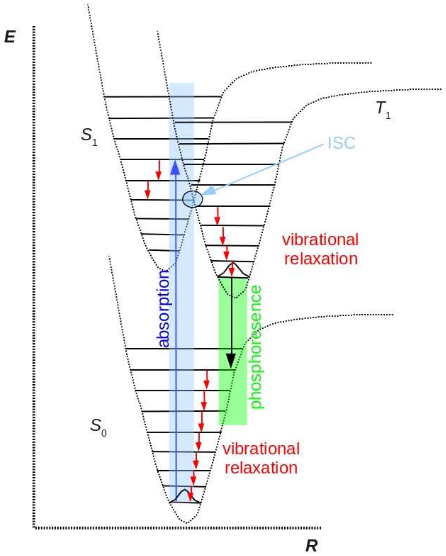
Nonradiative transitions (*internal conversion*; IC) between the vibrational levels (*vibrational relaxation*) may allow the molecule to relax to the ground vibrational state in the excited state before emitting provided that the IC is faster than the readiative lifetime. Note that the fluorescence always appears at longer wavelengths than the excitation. IC is caused by collisions with other molecules in gas, liquid or solid states. If there is a change in the electronic state or even a chemical reaction in the excited state, the strength of the fluorescence signal decreases or disappears completely (*fluorescence quenching*).

The surrounding solvent, solid or buffer gas ("bath") usually also causes shifting and broadening of both absorption and fluorescence lines. The bath usually causes the absorption to blueshift whereas the fluorescence is redshifted. The blueshift can be understood in terms of larger electronic extent of the excited state which couples to the bath more than the ground state whereas in the latter case the solvation of the excited state molecule is responsible for the redshift.



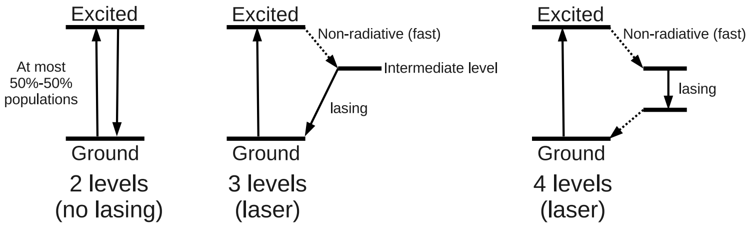
To observe phosphoresence, one must be able to create an excited state that has different multiplicity than the ground state. However, this cannot be done efficiently directly because such transition is spin forbidden. What is the mechanism for the change in multilpicity?

At the point where the two potential energy curves cross (*intersystem crossing*; ISC), spin-orbit coupling may induce transitions between the states of different spin multiplicty. Remember that spin-orbit coupling is responsible for mixing the states of different multiplicity (e.g., singlet - triplet mixing). Note that ISC is usually much slower than IC. ISC can sometimes be triggered by molecular collisions, which manifests as the disappearance of fluorescence and appearance of phosphoresence (e.g., glyoxal S_1/T_0).



6.7 Lasers

The Einstein model identified three processes: stimulated absorption, spontaneous emission and stimulated emission. If an active medium can be produced where more than half of the molecules are in the excited states (i.e., *population inversion*), a single seed photon can cause an avalanche (stimulated emission) such that all the molecules emit at the same time with the same photon characteristics. However, accodring to the Einstein model this is not possible for a two-level system. With three or more levels this is possible and this constitutes the basic idea behind lasers (*light amplification by stimulated emission of radiation*).



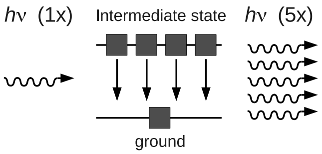
To see that the population inversion leads to light amplification, consider the Einstein model for the excited state:

$$\frac{dN_2}{dt} = BN_1\rho_\nu(\nu_{12}) - A_{21}N_2 - BN_2\rho_\nu(\nu_{12}) \tag{6.506}$$
$$= B\rho_\nu(\nu_{12})\left(N_1 - N_2\right) - A_{21}N_2 \approx B\rho_\nu(\nu_{12})\left(N_1 - N_2\right)$$

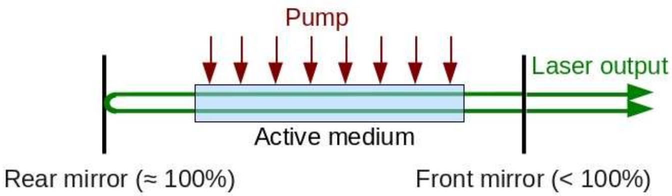
where A_{21} was assumed to be negligible. Consider three different cases:

1. $N_1 > N_2$: Irradiation of the sample with light leads to absorption.
2. $N_1 = N_2$: Light not absorbed or emitted (saturation).
3. $N_1 < N_2$: Irradiation of the sample with light leads to emission (i.e., light amplification).

The third case corresponds to population inversion that is responsible for lasing. Under the condition of population inversion, one photon entering the sample can cause an avalanche of photons to be generated.



A laser consists of an active medium that is placed between two mirrors:



The active medium must have the three or four -level structure. The active medium must be excited to generate the population inversion. Typically a flash lamp or electrical discharge is used for this purpose. The *gain* of the laser cavity is defined as amplification per round trip in the laser cavity. The gain must be high enough to overcome the losses within the cavity (e.g., light scattering). The distance between the two mirrors must be fixed such that (*resonant modes*):

$$\lambda = \frac{2d}{n} \text{ or } \nu = \frac{nc}{2d} \tag{6.507}$$

where the frequency $\nu = c/\lambda$, λ is the wavelength of the laser light and $n = 1, 2, 3, ...$ This condition is needed to obtain constructive interference within the cavity.

Laser radiation is *coherent* in the sense that all photons are identical. *Spatial coherence* is defined as the coherence across the cross-section of the laser beam and *temporal coherence* as the coherence as a function of time. The spatial coherence is usually defined in terms of *coherence length* (d_C), which is related to the range of wavelengths ($\Delta\lambda$) present in the beam:

$$d_C = \frac{\lambda^2}{2\Delta\lambda} \tag{6.508}$$

For a light bulb the coherence length is in the micrometer scale whereas for a He-Ne laser this is typically about 100 m.

In general, there are two types of lasers: continuous wave (CW) and pulsed lasers. Excitation of the active medium in CW lasers must occur continuously. Disadvantages of CW excitation can be the generation of excessive amount of heat and hence the low overall intensity. A laser can generate output for as long as the population inversion is maintained. Sometimes it is advantageous to use pulsed lasers to carry out fast kinetic measurements.

Q-switching: For producing nanosecond (≈ 10 ns) width laser pulses, the Q-switching technique can be applied. The idea is to produce an enhanced population inverse in the absence of resonant laser cavity (low Q factor). Once the enhanced population inversion is achieved, the Q-switch can be activated such that the resonant condition of the cavity is restored (high Q factor) and the laser pulse can emerge. Example implementations of Q-switching are *saturable dyes* (a dye which becomes transparent after sufficient excitation) and *Pockels cell* (switching of light polarization).

Mode locking: This technique can be used to produce pulses with temporal widths of picoseconds and even femtoseconds. As predicted by Eq. (6.507), a laser cavity may be able to support multiple modes, which differ in frequency by multiples of $\frac{c}{2d}$. These modes have normally random phases relative to each other. The mode locking process involves synchronizing the relative phases to each other. If there are sufficiently many modes sustained in the cavity, the constructive/destructive interference will occur such that a train of pulses will form. The more modes the cavity can support, the narrower the temporal width of the pulse will be. Note that the repetition frequency of the system is defined by the cavity characteristics. Mode locking is achieved by varying the Q factor of the cavity periodically at the frequency $\frac{c}{2L}$. The two main techniques are *passive mode locking* (e.g., saturable absorber) and *active mode locking* (e.g., acousto-optic modulator).

Examples of lasers:

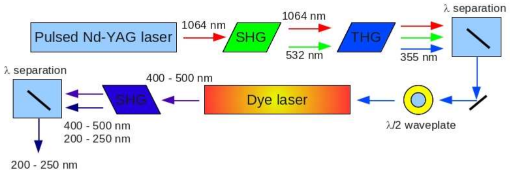
- *Solid state lasers.* The active medium consists of a single crystal or glass. The first laser was the Ruby laser (Al_2O_3 with a small amount of Cr^{3+} ions) at 694 nm. Rb lasers are typically pulsed lasers. Another popular laser in this class is the Nd-YAG laser (a small amount of Nd^{3+} ions in yttrium aluminum garnet) at 1064 nm.

- *Gas lasers.* Since the active medium (gas) can be cooled down by a rapid flow of gas through the cavity, these lasers can be used to generate high powers. The pumping is achieved through a gas that is different from the gas reponsible for lasing. For example, in He-Ne laser the initial step of excitation by high voltage discharge is to generate excited state He atoms ($1s^1 2s^1$), which then transfer energy through collisions to Ne atoms. The excited state Ne atoms are then responsible for the laser emission at 633 nm. Exceptions to this arrangement are, for example, the Argon ion (488 nm and 512 nm), CO_2 (main line at 10.6 μm), and N_2 laser (337 nm).
- *Chemical lasers.* Chemical reactions may also be used to generate population inversion condition. For example, photolysis of Cl_2 leads to the formation of excited state Cl atoms, which may further react with H_2 to produce HCl and H. The hydrogen atom can then react with Cl_2 to produce vibrationally excited HCl molecules. The system may lase when returning to the ground vibrational ground state. Another class of chemical lasers are *excimer* (or *exciplex*) lasers. For example, consider a mixture of Xe and Cl_2 subject to high-voltage discharge ($\approx$ 20 kV; buffer gas, neon for example). The discharge process produceses excited state Cl^* atoms, which may form a bound exciplex Cl^*-Xe with a radiative lifetime of about 10 ns. This is sufficiently stable to produce population inversion and the lasing occurs between the bound Cl^*-Xe and repulsive Cl-Xe ground state (308 nm in UV). Other common excimer lasers are Ar-F (193 nm), Kr-F (248 nm) and F_2 (157 nm).

- *Dye lasers.* Most lasers can only operate at fixed wavelengths (i.e., the wavelength cannot be scanned continuously). In a dye laser a dye (e.g., rhodamine 6G) mixed in a solvent (e.g., methanol) is placed inside the laser cavity. The dye solution has a broad absorption and emission spectra, which means that an excitation in the absorption band will yield a broad fluorescence spectrum. By placing a grating (i.e., selects a given wavelength) inside the laser cavity, any wavelength can be selected from the fluorescence band and the cavity can be made to lase at this wavelength. As long as the selected wavelength is within the dye emission band, laser output is obtained. Scanning the grating will change the output wavelength. Dye lasers are very useful for high-resolution spectroscopy where narrow linewidth is required. Additional reduction in the linewidth can be obtained by using an intracavity etalon.
- *Diode lasers.* Semiconductors often have suitable bands that can be made to lase. An electronic current can be applied to drive the electrons to excited levels, which can emit laser light when used as an active medium. An example is of this phenomenom is a light emitting diode (which just by itself does not lase). For example, most laser pointers employ this principle.

Note: Non-linear crystals can be used to combine multiple photons to produce one photon with a higher energy. A common application is to mix two photons of the same wavelength to produce one photon at half of the initial wavelength (*Frequency doubling* or *second harmonic generation*; twice the initial photon energy). Such crystals must be oriented appropriately with respect to the incident laser beam (*phase matching*).

Example. An Nd-YAG pumped dye laser system that can produce laser light between 200 - 250 nm wavelength range. Note that the wavelength can be scanned continuously.



SHG denotes second harmonic generation, THG third harmonic generator, λ separation removes unwanted wavelenghts and $\lambda/2$ waveplate rotates the light polarization such that it is suitable for the dye laser. Note that high peak powers (i.e., lasers) are needed for the non-linear SHG and THG processes.

6.8 Photoelectron spectroscopy

In photoelectron spectroscopy (PES) electrons are detached from atoms or molecules by ultraviolet (UPS) or X-ray (XPS) photons. The photon energy at which an electron is detached is related to the orbital energy for that electron. The ejected electrons are called *photoelectrons*. In UPS experiment the electrons are typically detached from the valence orbitals whereas in the XPS from core orbitals. The photoionization process is:

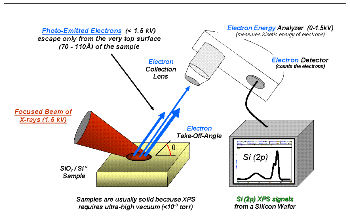
$$M + h\nu \rightarrow M^+ + e^- \tag{6.509}$$

where M denotes the molecule and $h\nu$ denotes the photon. In this process some of the energy of the photon may also excite molecular vibrations of M^+. The kinetic energy T of the ejected electron is given by:

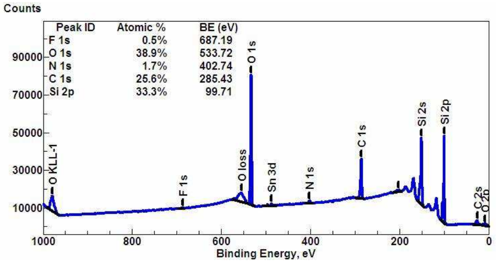
$$T = h\nu + E(M) - E(M^+) \tag{6.510}$$

where $E(M)$ is the energy of M, $E(M^+)$ the energy of M^+, and $E(M) - E(M^+)$ represents the ionization energy of M. Note that $E(M^+)$ depends on the vibrational state of M^+, which means that the kinetic energy T depends on the vibrational state of M^+ and thus vibronic structure can be often observed in UPS spectra. Note that both UPS and XPS can be used to determine surface electronic structure of a solid. XPS is mainly sensitive to the individual elements whereas UPS gives information about the valence orbitals, which is more specific to the molecular structure.

A schematic diagram of an XPS instrument is shown below.



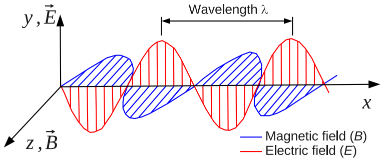
Example. A survey XPS spectrum of elements along with the orbital energetics.



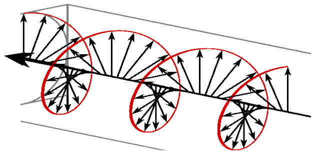
6.9 Optical activity

Terminology for light polarization:

- *Linearly polarized light*: The direction of the oscillating electric field vector about a given axis does not change as the wave propagates. Depending on the experimental arrangement, two perpendicular components are usually identified as horizontal and vertical.
- *Circularly polarized light*: The direction of the oscillating electric field vector rotates as the wave propagates. If the direction of the vector rotates clockwise (observed facing from the light source) it is *right-hand circularly polarized light* and in the opposite case *left-hand circularly polarized light*. Linearly polarized light can be though to be formed of equal amounts of left and right -hand polarized light.

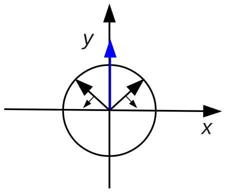


E is oscillating about the y-axis and *B* about the z axis.

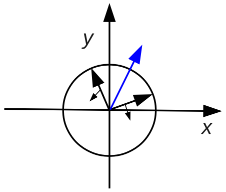


E and *B* are rotating but perpendicular with respect to each other at all times.

Chiral molecules exist as two nonsuperimposable structures that are mirror images of each other. These stereoisomers are called *enantiomers*. Such molecules are *optically active*, which means that they interact with right (R) and left (L) circularly polarized light differently. As a consequence, L and R light propagates at different velocities in the bulk sample (*circular birefringence*) and their absorption properties may be different as well (*circular dichroism*; circular dichroism (CD) absorption spectrum). As linearly polarized light can be thought to form from R and L components, a change in their propagation velocities will result in rotation of polarization:



Polarization along y-axis (in)



Polarization off y-axis (out)

Rotation of polarization can be measured with a *polarimeter*, which consists of a polarized light source and a polarizer that can be rotated to determine the rotation angle. *Specific rotation* $[\alpha]$ is defined as:

$$[\alpha] = \frac{\alpha}{cL} \tag{6.511}$$

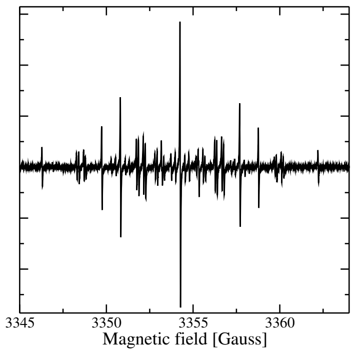
where L is the path length of the sample, c is the concentration in mass per unit volume and α is the rotation angle. α is negative for L (*levorotary*; counterclockwise) and positive for R (*dextrotary*; clockwise).

If either R or L component is being absorbed more than the other by the sample, this will result in *elliptic polarization*.

Notes:

- We will not attempt to explain here why R and L circularly polarized light interact with the material in different ways. See, for example, P. Atkins and R. Friedman, Molecular Quantum Mechanics.
- Useful optical components: light polarizer (filters only certain polarization out), quarter-wave plate (rotate polarization between linear and circular), half-wave plate (rotate polarization by 90 degrees).

Chapter 7: Magnetic Resonance Spectroscopy



EPR spectrum of hydroquinone cation radical

7.1 Electron and nuclear magnetism

Electrons, protons and neutrons are Fermions that have spin 1/2 (i.e., spin angular momentum of $\hbar/2$). In a nucleus, the spin angular momenta of protons and neutrons add (recall the rules for adding multiple source of angular momenta) up to give the total nuclear angular momentum. If a nucleus has an even number of protons and neutrons, all the spins are paired and the total nuclear angular momentum is zero. The quantum number corresponding to the total nuclear spin is denoted by I and the z-axis projection by m_I. Note that the z-axis direction is usually taken to be the direction of the external magnetic field. Quantum numbers I and m_I are both related to the eigenvalues of the angular momentum operator $\hat{I}^2$ and $\hat{I}_z$ (see Sec. 2.5):

$$\begin{aligned} \hat{I}^2\phi &= I(I+1)\hbar^2\phi \qquad (7.512) \\ \hat{I}_z\phi &= m_I\hbar\phi \end{aligned}$$

where ϕ represents the eigenfunction. Without external magnetic field, each state is $2I+1$ times degenerate. For example, for $I = 1$ (e.g., D or ^{14}N), there are three degenerate levels: $m_I = +1, 0, -1$.

Note: Spin is a relativistic phenomenom but it can be included in non-relativistic quantum mechanics as an angular momentum degree of freedom.

The magnetic dipole moment for an electron is (see Sec. 2.5):

$$\hat{\mu}_S = -\frac{g_e \times e}{2m_e}\hat{S} = -\frac{g_e \mu_B}{\hbar}\hat{S} \tag{7.513}$$

with μ_B being the Bohr magneton (see Eq. (2.190)). For a magnetic nucleus:

$$\hat{\mu}_I = \frac{g_N \times e}{2m_P}\hat{I} = \frac{g_N \mu_N}{\hbar}\hat{I} \tag{7.514}$$

where the nuclear magneton is defined as $\mu_N = \frac{e\hbar}{2m_P} = 5.050787 \times 10^{-27}$ J/T. If an external magnetic field is oriented along the z-axis, the projections are given by:

$$\begin{aligned} \hat{\mu}_{S,z} &= -\frac{g_e \times e}{2m_e}\hat{S}_z \Rightarrow \mu_{S,z} = -g_e \mu_B m_S \\ \hat{\mu}_{I,z} &= \frac{g_N \times e}{2m_P}\hat{I}_z \Rightarrow \mu_{I,z} = g_N \mu_N m_I \end{aligned} \tag{7.515}$$

where $g_e \approx 2.002322$ is the free electron g-value, $m_e = 9.109390 \times 10^{-31}$ kg is the electron mass and $m_P = 1.672623 \times 10^{-27}$ kg is the proton mass.

To simplify the notation, sometimes the *magnetogyric ratio* γ for both nucleus and electron (see Eq. (2.189)) is used:

$$\begin{aligned} \gamma_N &= g_N \mu_N / \hbar \\ \gamma_e &= g_e \mu_S / \hbar \end{aligned} \tag{7.516}$$

The magnetic moment operators can be written as:

$$\hat{\mu}_N = \gamma_N \hbar \hat{I} \text{ and } \hat{\mu}_S = \gamma_e \hbar \hat{S} \tag{7.517}$$

with the corresponding eigenvalues for the z-components:

$$\mu_{N,z} = \gamma_N \hbar m_I \text{ and } \mu_{S,z} = \gamma_e \hbar m_S \tag{7.518}$$

7.2 Energy level structure

A magnetic dipole interacts with an external magnetic field (see Eq. (2.191)):

$$\hat{H} = -\vec{\hat{\mu}} \cdot \vec{B} = -\hat{\mu}_z B_z \tag{7.519}$$

where the magnetic field is along the z-axis $\vec{B} = (0, 0, B_z)$ and $\vec{\mu}$ is the magnetic moment of the dipole. For an electron spin (see Eq. (7.515)) this gives:

$$\hat{H} = -\hat{\mu}_{S,z} B_z = \frac{g_e \mu_B}{\hbar} \hat{S}_z B_z \tag{7.520}$$

and for a nuclear spin:

$$\hat{H} = -\hat{\mu}_{I,z} B_z = -\frac{g_N \mu_N}{\hbar} \hat{I}_z B_z \tag{7.521}$$

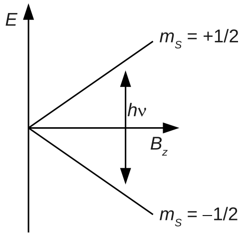
By using Eq. (7.512) we get the energies of the spin levels:

$$\begin{aligned} E_S &= g_e \mu_B m_S B_z \text{ with } m_S = +S, ..., 0, ..., -S \\ E_I &= -g_N \mu_N m_I B_z \text{ with } m_I = +I, ..., 0, ... - I \end{aligned} \tag{7.522}$$

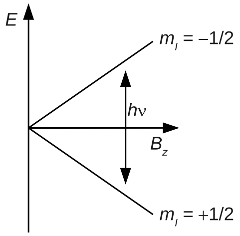
For a spin 1/2 particle, the energy difference between the levels is ($g = g_e$ or g_N and $\mu = \mu_B$ or μ_N):

$$\Delta E(B_z) = \left| E\left(m = +\frac{1}{2}\right) - E\left(m = -\frac{1}{2}\right) \right| = g\mu B_z \tag{7.523}$$

For electron spin the splitting of the levels is called the *electron Zeeman effect* and for nuclear spins the *nuclear Zeeman effect*. Energy as a function of the external magnetic field are shown below.



Electron spin



Nuclear spin

The resonance frequency can now be identified as:

$$\nu = \frac{\Delta E}{h} = \frac{g\mu B_z}{h} = \frac{\gamma B_z}{2\pi} \tag{7.524}$$

where γ is either γ_e or γ_N. ν is called the *Larmor frequency*. Sometimes Larmor frequency is expressed in terms of angular frequency $\omega = \gamma B_z$.

Both *nuclear magnetic resonance* (NMR) and *electron paramagnetic resonance* (EPR; also called *electron spin resonance*; ESR) classify as magnetic resonance spectroscopy. They employ the oscillating magnetic field component of the electromagnetic field to induce transitions. In NMR the electromagnetic radiation lies in the radio frequency range (RF; 50 - 800 MHz) whereas in EPR it is typically in the microwave region (MW; 9 GHz, X-band). The transitions occur between the m_S or m_I levels, for which the energies are given by Eq. (7.524). The general selection rule for NMR is $\Delta I = 0$ and $\Delta m_I = \pm 1$, and for EPR $\Delta S = 0$ and $\Delta m_S = \pm 1$.

As discussed in the context of the Einstein model for stimulated absorption (see Sec. 5.3), it is necessary to have a population difference between the spin levels for absorption to occur. In magnetic resonance spectroscopy the energy levels are typically so close to each other that they have significant thermal populations. The Boltzmann distribution between two such levels gives:

$$\frac{P_2}{P_1} = e^{-\Delta E/(kT)} \tag{7.525}$$

where P_1 and P_2 are the populations of the lower and upper spin levels, respectively. For an electron spin this gives:

$$\frac{P_2}{P_1} = e^{-g_e \mu_B B_z/(kT)} \approx 1 - \frac{g_e \mu_B B_z}{kT} \tag{7.526}$$

For a nuclear spin the population difference is:

$$\frac{P_2}{P_1} = e^{-g_N \mu_N B_z/(kT)} \approx 1 - \frac{g_N \mu_N B_z}{kT} \tag{7.527}$$

For absorption to occur, we must have $P_2/P_1 < 1$. If $P_1 \approx P_2$ the sample is said to be *saturated* and no absorption occurs.

Example. What is the resonance frequency for ^{19}F nucleus in 1 T magnetic field? For ^{19}F nucleus $g_N = 5.256$.

Solution. Eq. (7.523) gives:

$$\Delta E = g_N \mu_N B_z = (5.256) \times (5.051 \times 10^{-27}\ \text{J T}^{-1}) \times (1\ \text{T}) = 2.655 \times 10^{-26}\ \text{J}$$

The resonance frequency can be then obtained from Eq. (7.524):

$$\nu = \frac{\Delta E}{h} = \frac{2.655 \times 10^{-26}\ \text{J}}{6.626 \times 10^{-34}\ \text{J s}} = 40.07 \times 10^{6}\ \text{s}^{-1} = 40.07\ \text{MHz}$$

Example. What magnetic field strength is required to generate a 220 MHz Larmor frequency for a proton, which has $g_N = 5.585$?

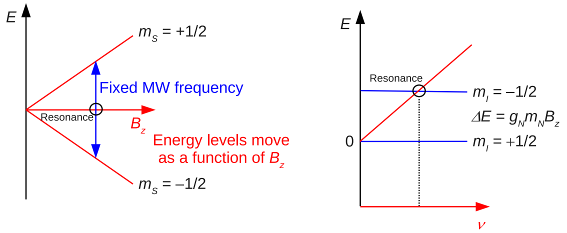
Solution. Combining both Eqs. (7.523) and (7.524) we get:

$$B_z = \frac{h\nu}{g_N \mu_N} = \frac{(6.626 \times 10^{-34}\ \text{J s}) \times (220 \times 10^{6}\ \text{s}^{-1})}{(5.585)(5.051 \times 10^{-27}\ \text{J T}^{-1})} = 5.167\ \text{T}$$

7.3 NMR and EPR experiments

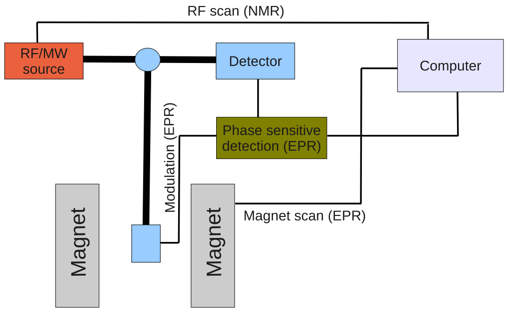
Two different approaches can be employed to record an EPR or NMR spectrum 1) continuous wave (CW) excitation or 2) pulsed excitation employing the Fourier technique. The pulsed method is nowadays the most common approach for NMR whereas the CW method is typically used in EPR experiments. Due to the large difference in the nuclear and electron magnetic moments, NMR experiments require larger magnetic fields than EPR.

CW excitation: In a CW experiment both external magnetic and RF/microwave excitation fields are kept on constantly. In most NMR experiments the magnetic field is kept constant and the RF field frequency is varied to record the spectrum (i.e., to locate the resonant frequencies of the spins). Due to instrumental factors, in EPR experiments the microwave frequency is held constant while sweeping the external magnetic field. In NMR spectra the x-axis corresponds to frequency and in EPR to magnetic field value (in Tesla or Gauss). Note that the resonant frequencies and fields are related to each other through the resonance condition (see Eqs. (7.523) (7.524)). Most CW experiments employ so called *phase sensitive detection* technique (i.e., lock-in amplifier), which greatly enhances the sensitivity of the instrument but usually provides the y-axis as the first derivative of the absorption signal.



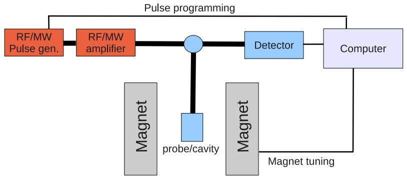
Resonance (EPR) Resonance (NMR)

NMR/EPR resonance condition.



NMR/EPR block diagram (CW).

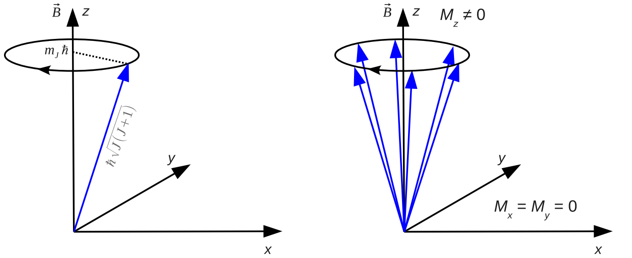
Pulsed excitation: The pulsed technique, which is also called the *Fourier transform spectroscopy*, uses short RF/MW pulses to excite the spins in a static external magnetic field (i.e., the field is not swept). This approach attempts to excite all the spins at the same time and collect the spectrum from a single execution of the experiment, which typically takes less than a second. Typical pulse lengths for NMR are in the microsecond timescale whereas in EPR they are in nanoseconds.



EPR magnet: electric magnet (room temperature coils)
NMR magnet: superconducting magnet (liquid helium)

NMR/EPR block diagram (pulsed instrument).

To understand the pulsed magnetic resonance experiment, it is helpful to consider the time-dependent behavior of the spins and employ the vector model for spin angular momentum to represent their orientation with respect to the external magnetic field. A particle with spin 1/2 can have two orientations with respect to the external magnetic field ($m = 1/2$ or $m = -1/2$), which precess about the z axis at the Larmor frequency:

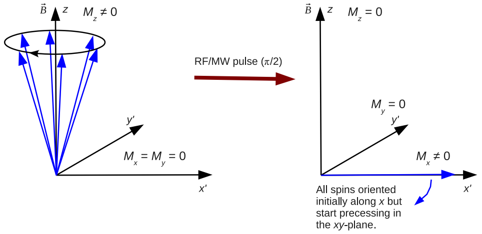


Single spin Larmor precession about z An ensemble of spins precessing about z

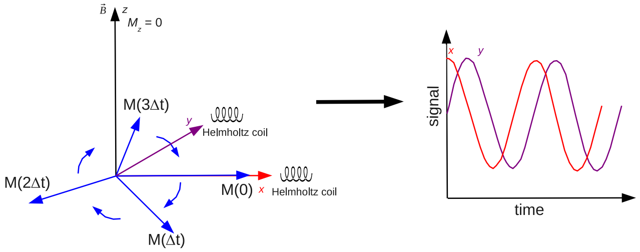
For an ensemble of spins (on the right) the total magenization $\vec{M}$ is oriented along the z-axis. As the spins are randomly distributed around z, there is no net magnetization along x or y (vector sum). In this case the spins are said to be *out of phase* with respect to each other.

Recall from Sec. 6.9 that linearly polarized electromagnetic field can be thought to consist of both clockwise and counter clockwise rotating components. If one of these components precesses at the same frequency as the spins (i.e., the Larmor frequency), it appears that it follows the spins in the xy-plane. From the point of view of the spins, it appears that the RF/MW field is stationary and we can use this *rotating frame coordinate system* (denoted by a prime below). The RF/MW component rotating in the opposite direction does not induce any transitions.

If a sufficiently high intensity RF/MW pulse is applied along the x' axis (rotating frame), the magnetization M can be rotated along the x' axis:



Because all the spins precess in the xy plane the same way (*phase coherence*), the total magnetization will begin to oscillate in the xy plane as well and this can be picked up by a Helmholtz coil (for NMR):



Whenever the magnetization vector M in the xy-plane passes a Holmholtz coil, a current is picked up by the coil. The two coils placed at x and y axes pick up a signal that is 90° out of phase with respect to each other.

Interaction of the spins with the surroundings (e.g., solvent, solid matrix) will eventually result in decay in the magnetization in the xy-plane. Two general mechanisms are responsible for this decay:

1. Spin-lattice relaxation (T_1): The magnetization in the xy-plane is formed from an equal population of spins on the two spin states. If there are external oscillating magnetic fields present near the spins (from the surroundings; solvent, solid matrix etc.), they may return back to the original thermal distribution as a result of this interaction. This decreases the magnetization in the xy-plane. T_1 is also called *longitudal relaxation time*.
2. Spin-spin relaxation (T_2): If the individual spins in the xy-plane start to fan-out because their Larmor frequencies are slightly different, the total magnetization will be reduced as there will be a partial cancellation of the magnetic moments of the individual spins in xy ("out of phase"). The spins are said to loose their coherence the xy-plane. T_2 is also called the *transverse relaxation time*.

Both processes result in an exponential decay of the magnetization:

$$M_z(t) - M_0 \propto e^{-t/T_1} \tag{7.528}$$
$$M_{x,y}(t) - M_0 \propto e^{-t/T_2}$$

In fluid liquids, T_1 may have a similar magnitude to T_2 whereas in solids T_1 is often much longer than T_2. In liquids, T_1 is typically in the range of 0.5 - 50 seconds but in solids it can be up to 1000 seconds. Since most often $T_2 << T_1$, T_2 determines the NMR/ESR linewidth $\Delta\nu_{1/2}$ (half-width at half-height):

$$\Delta\nu_{1/2} = \frac{1}{\pi T_2} \tag{7.529}$$

In addition to T_1 and T_2 processes, the linewidhts can be affected by the sample inhomogeneity where each spin experiences a slightly different envronment (static; trapping sites in solids etc.). The overall spectrum appears as a sum of different NMR/EPR lines and gives *inhomogeneous broadening*. For homogeneous lines the lineshape is Lorentzian (derivation from the Bloch equations) whereas for inhomoheneously broadened lines a Gaussian lineshape is obtained (statistical distribution). Note that in the presence of inhomogeneous broadening, Eqn. (7.529) does not apply. If inhomogeneous effects are included, this is usually denoted by T_2^*.

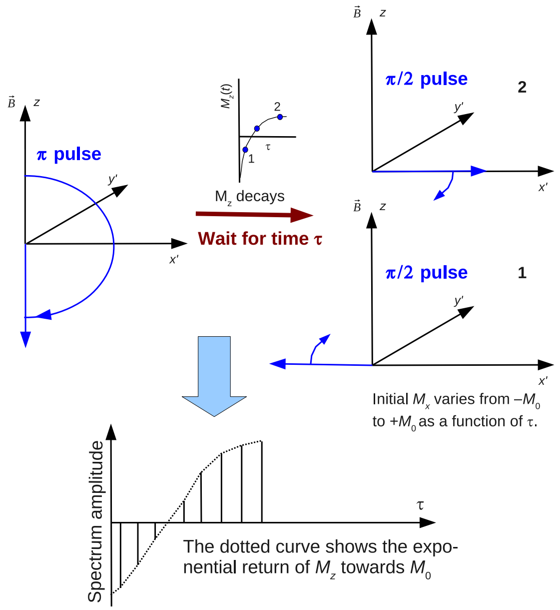
After pulsed excitation of the spins, the signal recorded by the Helmholtz coils is called the *free induction decay* (FID). The FID contains an oscillating signal for each Larmor frequency present in the sample, which can be analyzed through the Fourier technique. Thus a Fourier transformation of the FID will yield the frequency domain NMR/EPR spectrum. Note that the FID decays in time by T_1 and T_2 processes, which contribute to the increased linewidth in the frequency domain spectrum. There are also other dynamic effects such as conformational changes, ion pair formation, etc. that may contribute to linewidhts (*dynamical NMR/EPR*).

How can a single pulse excite many different Larmor frequencies at once in the sample?

Remember that time (s) and frequency (1/s or Hz) are Fourier pairs. A short pulse in time will then correspond to a wide pulse in frequency. The shorter the pulse is, the more frequencies it will cover. However, a short pulse must be relatively more intense than a long pulse to produce the 90° rotation of the magnetization ("$\pi/2$ pulse"). Therefore for both NMR and EPR it is advantageous to have as short and intense pulses as possible. Such pulses have one disadvantage, which is related to the deposition of large amount of power into the probe/cavity. The detector system will pick up an extremely strong signal from the excitation pulse and this will cover part of the FID. This condition is called *ringing* and its effect on the spectrum can be partially overcome by *windowing* the FID appropriately (for more information, see windowing and Fourier transformation). Typical pulse lengths are in μs - ms range for NMR and in ns for EPR.

7.4 Pulse sequences and the measurement of T_1 and T_2

Measurement of T_1:

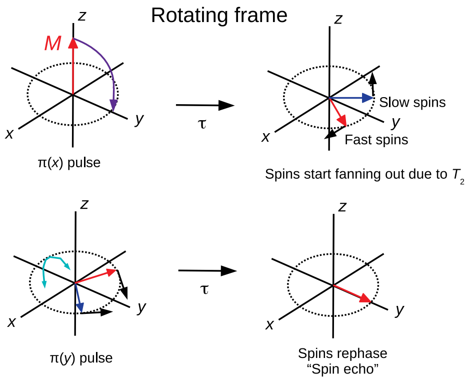


Initial M_x varies from $-M_0$ to $+M_0$ as a function of τ.

The dotted curve shows the exponential return of M_z towards M_0

The first π pulse rotates the magnetization from $+z$ to $-z$. After this the magnetization begins to relax back towards the initial value (along $+z$) due to the spin-lattice relaxation. This can be viewed as individual spins falling back from the higher spin energy level back to the lower level. At the point where there is equal population of spin up and down, the magnetization along the z-axis is zero. The magnetization along z after time τ can be probed by a $\pi/2$ pulse, which takes the remaining M_z to the xy-plane where the spectrum can be recorded by the coils. The overall intensity of the spectrum is proportional to $M_z(\tau)$. T_1 can be determined by fitting Eq. (7.528) to the intensity vs. delay time (τ) data.

Measurement of T_2:



Pulse sequence: $\pi/2(x) - \tau - \pi(y) - \tau -$ <spin echo>

The first $\pi/2$ pulse rotates the magnetization from z to y. Because the spins are in different environments, they will have slightly different Larmor frequencies. In the rotating frame coordinate system, this corresponds to the slow spins rotating counter clockwise and the fast spins clockwise. After the spins have fanned out (delay time τ), a π pulse is applied to flip the spins about the x-axis. This will flip the spins to the other side while preserving their direction of rotation. After time τ, they will now refocus on the y-axis producing the *spin echo* signal. Note that the magnetization is in the xy-plane can then be picked up by the coils. By recording the spin echo amplitude as a function of τ, one can fit a decaying exponential, $\exp(-2\tau/T_2^*)$, to this data and obtain T_2^*. Note that T_2^* is equal to T_2 only if there is no inhomogeneous broadening.

7.5 The chemical shift (NMR)

The nuclear magnetic moments interact with the *local magnetic field*, which may be different from the applied external field. The difference between the two originates from the spin-orbit coupling that induces quantum mechanical currents in the electronic cloud. The local field can either augment the external field or oppose it. We denote the deviation of the local magnetic from the external field by δB, which is usually written in terms of the *shielding constant* σ ($B \equiv B_z$):

$$\delta B = -\sigma B \tag{7.530}$$

where B is the strength of the external magnetic field. The shielding constant is usually positive but may sometimes also be negative. The ability of the applied external field to induce an electronic current in the molecule, and after the strength of the resulting local magnetic field at the nucleus, depends on the details of the electronic structure near the magnetic nucleus. This means that nuclei in different chemical environments usually have different shielding constants.

According to Eq. (7.530) the local magnetic field at nucleus is given by:

$$B_{loc} = B + \delta B = (1 - \sigma)B \tag{7.531}$$

with the Larmor frequency given by (see Eq. (7.524)):

$$\nu = \frac{\gamma B_{loc}}{2\pi} = (1 - \sigma)\frac{\gamma B}{2\pi} \tag{7.532}$$

Thus the Larmor frequency may be different for each magnetic nucleus depending on their chemical environment.

The resonance frequencies are usually expressed in terms of *chemical shift*, which is related to the difference between the resonance frequency ν and that of a standard ν°:

$$\delta = \frac{\nu - \nu^\circ}{\nu^\circ} \times 10^6 \tag{7.533}$$

where δ is expressed in PPM (parts per million) as dictated by the 10^6 factor above. The standard used for proton NMR is usually the proton resonance in tetramethylsilane ($Si(CH_3)_4$ or TMS). For ^{13}C the TMS carbon-13 resonance is often used and for ^{31}P $H_3PO_4(aq)$. Note that the chemical shift scale is independent of the applied magnetic field whereas the resonance frequency expressed in Hz depends on the strength of the external magnetic field.

The relationship between the chemical shift and the shielding constant can be obtanined from Eqs. (7.531) and (7.533):

$$\delta = \frac{(1-\sigma)B - (1-\sigma^\circ)B}{(1-\sigma^\circ)B} \times 10^6 = \frac{\sigma^\circ - \sigma}{1-\sigma^\circ} \times 10^6 \approx (\sigma^\circ - \sigma) \times 10^6 \tag{7.534}$$

Note that as shielding σ decrases, δ increases. Thus nuclei with large chemical shift are said to be *deshielded*. An NMR spectrum is typically displayed with δ icreasing from right to left. A list of typical chemical shifts in a given group are listed on the next slide.

Table. Chemical shifts observed for protons in different molecular environments. X denotes a halogen atom.

Shift (ppm)	Group	Shift (ppm)	Group
-0.5 – 0.5	Cyclopropyl protons	2.0 – 4.0	CH_2–N
0.5 – 1.5	CH_3–C	2.0 – 4.5	CH_2–X
0.5 – 1.5	CH–C	2.5 – 3.5	CH–C_6H_4R
0.5 – 4.5	R_2NH	2.5 – 4.5	CH–N
0.5 – 10.0	R–OH, alcohols	3.0 – 4.0	CH_3–O
1.0 – 2.0	CH_2–C	3.0 – 4.0	CH_2–O
1.0 – 2.5	CH_3–C=C	3.5 – 5.5	CH–O
1.5 – 2.5	CH_2–C=C	4.0 – 6.0	CH–X
1.5 – 3.0	CH_3C=O	4.5 – 6.5	Alkenes, nonconj.
2.0 – 3.0	CH_3–C_6H_4R	5.5 – 7.5	Alkenes, conjugated
2.0 – 3.0	CH_2–C=O	6.0 – 9.0	Heteroaromatics
2.0 – 3.0	CH–C=O	6.5 – 8.5	Aromatics
2.0 – 3.0	RNH_2	9.0 – 10.5	H–C=O, aldehydes
2.0 – 4.0	CH_3–N	10.0 – 13.0	RCOOH, acids