

Black-body radiation

Black body also known as an ideal emitter is an object capable of emitting and absorbing all frequencies of radiation uniformly. A hot object emits always electromagnetic radiation and at high temperatures, an appreciable proportion of the radiation is in the visible region of the spectrum, and a higher proportion of short-wavelength blue light is generated as the temperature is raised. This behaviour is seen when a heated iron bar glowing red hot becomes white hot when heated further. The dependence is illustrated in Fig. 1, which shows how the energy output varies with wavelength at several temperatures. Energy density increases in the region of shorter wavelengths as the temperature is raised, and the peak shifts to shorter wavelengths. The total energy density (the area under the curve) increases as the temperature is increased.

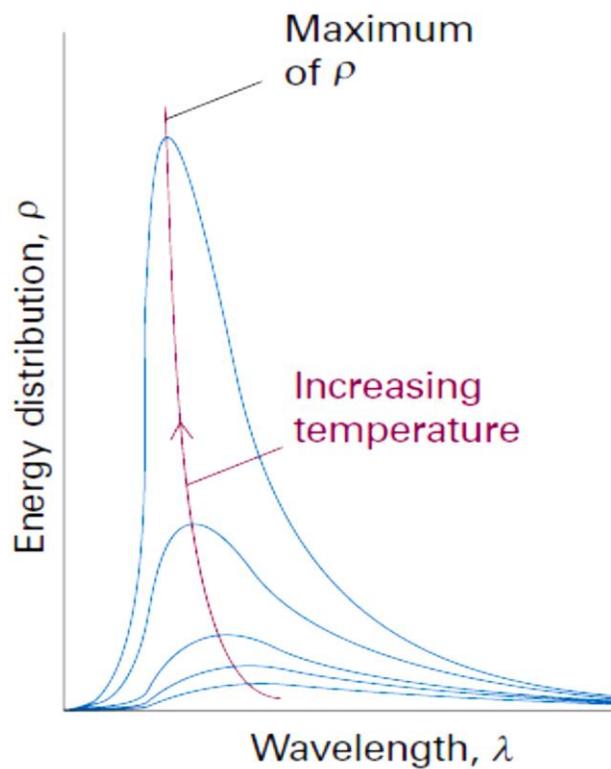


Fig. 1: The energy distribution in a blackbody cavity at several temperatures.

A good approximation to a black body is a pinhole in an empty container maintained at a constant temperature, because any radiation leaking out of the hole has been absorbed and re-emitted inside so many times that it has come to thermal equilibrium with the walls as shown in Fig. 2.

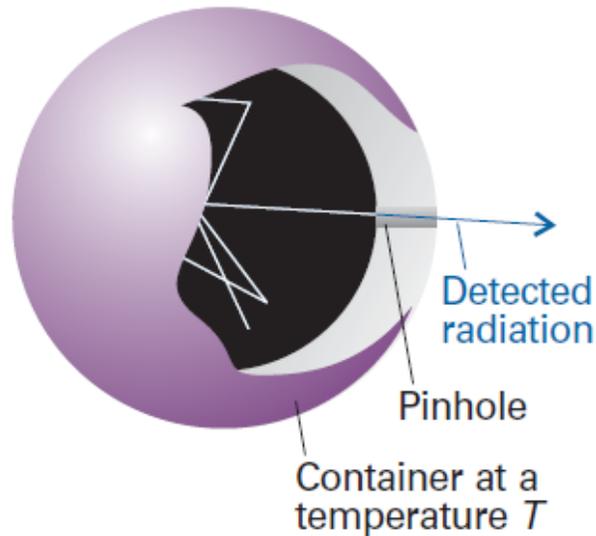


Fig. 2: An experimental representation of a black-body is a pinhole in an closed container.

The explanation of black-body radiation was theoretically given by physicist Lord Rayleigh who studied it from a classical viewpoint, and thought of the electromagnetic field as a collection of oscillators of all possible frequencies. He regarded the presence of radiation of frequency ν (and therefore of wavelength $\lambda = c/\nu$) as signifying that the electromagnetic oscillator of that frequency had been excited. Rayleigh used the equipartition principle to calculate the average energy of each oscillator as kT . Then, with minor help from James Jeans, he arrived at the Rayleigh–Jeans law as

$$dE = \rho d\lambda \quad \rho = \frac{8\pi kT}{\lambda^4}$$

where ρ (rho), the density of states, is the proportionality constant between $d\lambda$ and the energy density, dE , in the range of wavelengths between λ and $\lambda + d\lambda$, k is Boltzmann's constant ($k = 1.381 \times 10^{-23} \text{ J K}^{-1}$).

Unfortunately (for Rayleigh, Jeans, and classical physics), although the Rayleigh–Jeans law is quite successful at long wavelengths (low frequencies), it fails badly at short wavelengths (high frequencies). Thus, as λ decreases, ρ increases without going through a maximum. The equation therefore predicts that oscillators of very short wavelength (corresponding to ultraviolet radiation, X-rays, and even γ -rays) are strongly excited even at room temperature. This absurd result, which implies that a large amount of energy is radiated in the high-frequency region of the electromagnetic spectrum, is called the ultraviolet catastrophe. According to classical physics, even cool objects should radiate in the visible and ultraviolet regions, so objects should glow in the dark; there should in fact be no darkness.

The Planck distribution

The German physicist Max Planck studied black-body radiation from the viewpoint of thermodynamics. In 1900 he found that he could account for the experimental observations by proposing that the energy of each electromagnetic oscillator is limited to discrete values and cannot be varied arbitrarily. This proposal is quite contrary to the viewpoint of classical physics (on which the equipartition principle used by Rayleigh is based), in which all possible energies are allowed. The limitation of energies to discrete values is called the quantization of energy. In particular, Planck found that he could account for the observed distribution of energy if he supposed that the permitted energies of an electromagnetic oscillator of frequency ν are integer multiples of $h\nu$:

$$E = nh\nu \quad n = 0, 1, 2, \dots$$

where h is a fundamental constant now known as Planck's constant. On the basis of this assumption, Planck was able to derive the Planck distribution:

$$dE = \rho d\lambda \quad \rho = \frac{8\pi hc}{\lambda^5 (e^{hc/\lambda kT} - 1)}$$

This expression fits the experimental curve very well at all wavelengths (Fig. 1), and the value of h , which is an undetermined parameter in the theory, may be obtained by varying its value until a best fit is obtained. The currently accepted value for h is 6.626×10^{-34} J s known as Planck's constant.

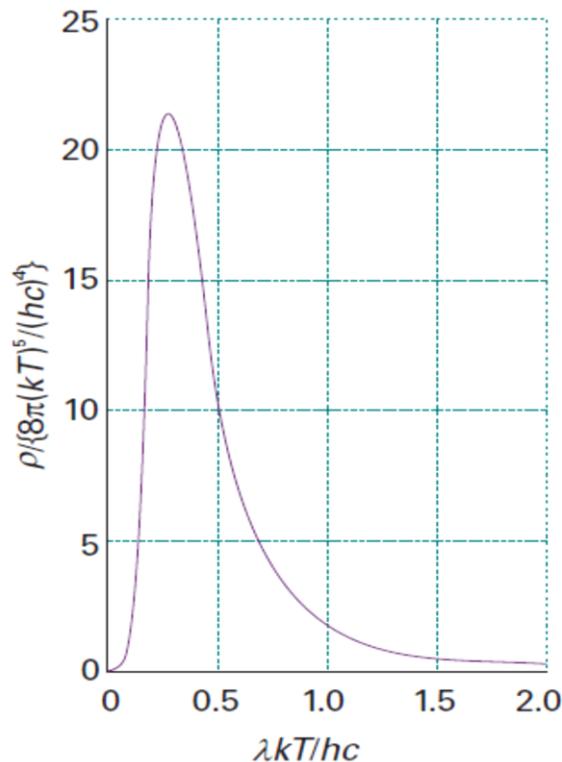


Fig. 1: The Planck distribution of black-body radiation

The Planck distribution resembles the Rayleigh–Jeans law (eqn 8.3) apart from the all-important exponential factor in the denominator. For short wavelengths, $hc/\lambda kT \gg 1$ and $e^{hc/\lambda kT} \rightarrow \infty$ faster than $\lambda^5 \rightarrow 0$; therefore $\rho \rightarrow 0$ as $\lambda \rightarrow 0$ or $\nu \rightarrow \infty$. Hence, the energy density approaches zero at high frequencies, in agreement with observation. For long wavelengths, $hc/\lambda kT \ll 1$, and the denominator in the Planck distribution can be replaced by

$$e^{hc/\lambda kT} - 1 = \left(1 + \frac{hc}{\lambda kT} + \dots \right) - 1 \approx \frac{hc}{\lambda kT}$$

When this approximation is substituted into above Planck distribution equation, it reduces to the Rayleigh–Jeans law.

It is quite easy to see why Planck’s approach was successful while Rayleigh’s was not. The thermal motion of the atoms in the walls of the black body excites the oscillators of the electromagnetic field. According to classical mechanics, all the oscillators of the field share equally in the energy supplied by the walls, so even the highest frequencies are excited. The excitation of very high frequency oscillators results in the ultraviolet catastrophe. According to Planck’s hypothesis, however, oscillators are excited only if they can acquire energy of at least $h\nu$. This energy is too large for the walls to supply in the case of the very high frequency oscillators, so the latter remain unexcited. The effect of quantization is to reduce the contribution from the high frequency oscillators, for they cannot be significantly excited with the energy available.

Heat capacities of solids

In the early nineteenth century, the French scientists Pierre-Louis Dulong and Alexis-Thérèse Petit determined the heat capacities of a number of monatomic solids. On the basis of some somewhat slender experimental evidence, they proposed that the molar heat capacities of all monatomic solids are the same and (in modern units) close to $25 \text{ J K}^{-1} \text{ mol}^{-1}$.

Dulong and Petit's law is easy to justify in terms of classical physics. If classical physics were valid, the equipartition principle could be used to calculate the heat capacity of a solid. According to this principle, the mean energy of an atom as it oscillates about its mean position in a solid is kT for each direction of displacement. As each atom can oscillate in three dimensions, the average energy of each atom is $3kT$; for N atoms the total energy is $3NkT$. The contribution of this motion to the molar internal energy is therefore:

$$U_m = 3N_A kT = 3RT$$

because $N_A k = R$, the gas constant. The molar constant volume heat capacity (see Comment 8.3) is then predicted to be

$$C_{V,m} = \left(\frac{\partial U_m}{\partial T} \right)_V = 3R$$

This result, with $3R = 24.9 \text{ J K}^{-1} \text{ mol}^{-1}$, is in striking accord with Dulong and Petit's value.

Unfortunately it was found that the molar heat capacities of all monatomic solids are lower than $3R$ at low temperatures, and that the values approach zero as $T \rightarrow 0$. To account for these observations, Einstein (in 1905) assumed that each atom oscillated about its equilibrium position with a single frequency ν . He then invoked Planck's hypothesis to assert that the energy of oscillation is confined to discrete values, and specifically to $n h\nu$, where n is an integer. Einstein first calculated the contribution of the oscillations of the atoms to the total molar energy of the metal and obtained

$$U_m = \frac{3N_A h\nu}{e^{h\nu/kT} - 1}$$

in place of the classical expression $3RT$. Then he found the molar heat capacity by differentiating U_m with respect to T . The resulting expression is now known as the **Einstein formula**:

$$C_{V,m} = 3Rf \quad f = \left(\frac{\theta_E}{T} \right)^2 \left(\frac{e^{\theta_E/2T}}{e^{\theta_E/T} - 1} \right)^2$$

The **Einstein temperature**, $\theta_E = h\nu/k$, is a way of expressing the frequency of oscillation of the atoms as a temperature: a high frequency corresponds to a high Einstein temperature.

At high temperatures (when $T \gg \theta_E$) the exponentials in f can be expanded as $1 + \theta_E/T + \dots$ and higher terms ignored. The result is

$$f = \left(\frac{\theta_E}{T} \right)^2 \left\{ \frac{1 + \theta_E/2T + \dots}{(1 + \theta_E/T + \dots) - 1} \right\}^2 \approx 1$$

Consequently, the classical result ($C_{v,m} = 3R$) is obtained at high temperatures. At low temperatures, when $T \ll \theta_E$,

$$f \approx \left(\frac{\theta_E}{T} \right)^2 \left(\frac{e^{\theta_E/2T}}{e^{\theta_E/T}} \right)^2 = \left(\frac{\theta_E}{T} \right)^2 e^{-\theta_E/T}$$

The strongly decaying exponential function goes to zero more rapidly than $1/T$ goes to infinity; so $f \rightarrow 0$ as $T \rightarrow 0$, and the heat capacity therefore approaches zero too. Thus we see that Einstein's formula accounts for the decrease of heat capacity at low temperatures.

Atomic spectra

The most compelling evidence for the quantization of energy comes from spectroscopy, the detection and analysis of the electromagnetic radiation absorbed, emitted, or scattered by a substance. The record of the intensity of light intensity transmitted or scattered by a molecule as a function of frequency (ν), wavelength (λ), or wavenumber ($\bar{\nu} = \nu/c$) is called its spectrum.

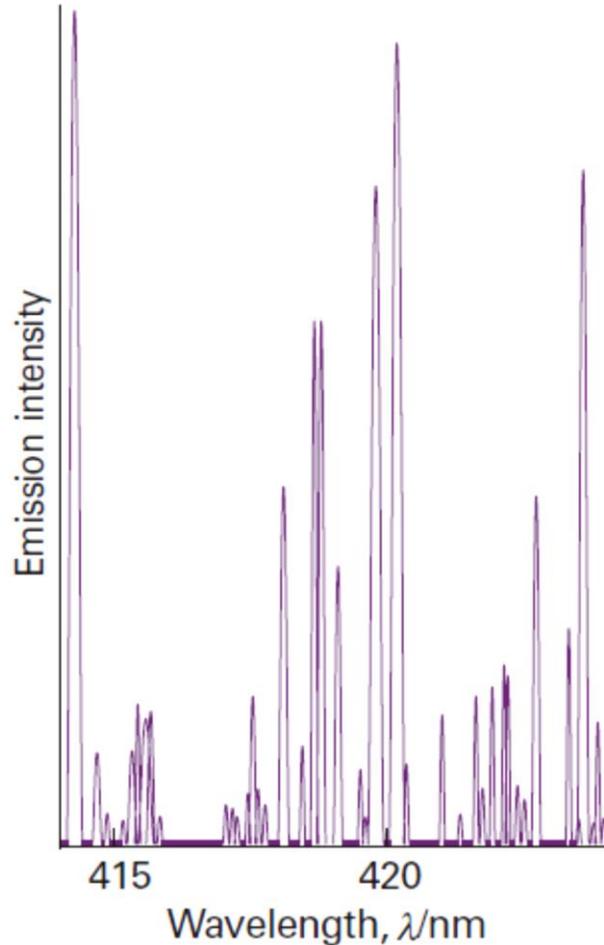


Fig. 1: A series of discrete wavelengths of the spectrum of radiation emitted by excited atoms

A typical atomic spectrum is shown in **Fig. 1** where it is observed that radiation is emitted or absorbed at a series of discrete frequencies. This observation can be understood if the energy of the atoms is also confined to discrete values, for then energy can be discarded or absorbed only in discrete amounts (**Fig. 2**). Then, if the energy of an atom decreases by ΔE , the energy is carried away as radiation of frequency ν , and an emission 'line', a sharply defined peak, appears in the spectrum. We say that an atom undergoes a spectroscopic transition, a change of state, when the Bohr frequency condition $\Delta E = h\nu$ is fulfilled.

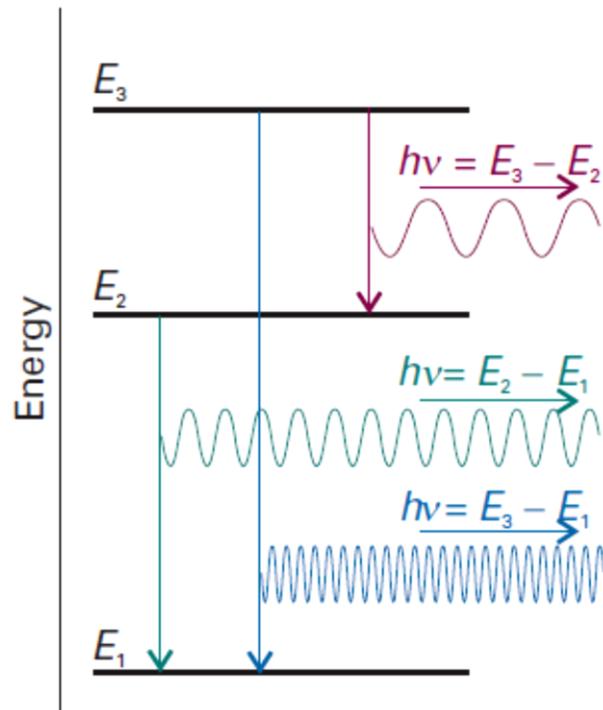


Fig. 2: Spectroscopic transitions for the atom emits a photon as it changes between discrete energy levels.

Schrödinger wave equation

Schrodinger wave equation is given by *Erwin Schrödinger* in 1926 and based on dual nature of electron. In it electron is described as a three dimensional wave in the electric field of a positively charged nucleus. The probability of finding an electron at any point around the nucleus can be determined by the help of Schrodinger wave equation which is,

$$\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2} + \frac{8\pi^2m}{h^2}(E - V)\Psi = 0$$

Where x, y and z are the 3 space co-ordinates, m = mass of electron, h = Planck's constant, E = Total energy, V = potential energy of electron, Ψ = amplitude of wave also called as wave function, ∂ = for an infinitesimal change.

The Schrodinger wave equation can also be written as,

$$\nabla^2\Psi + \frac{8\pi^2m}{h^2}(E - V)\Psi = 0$$

Where ∇ = laplacian operator.

Physical significance of Ψ and Ψ^2

The wave function may be regarded as the amplitude function expressed in terms of coordinates x, y and z . The wave function may have positive or negative values depending upon the value of coordinates. The main aim of Schrodinger equation is to give solution for probability approach. When the equation is solved, it is observed that for some regions of space the value of Ψ is negative. But the probability must be always positive and cannot be negative, it is thus, proper to use Ψ^2 in favour of Ψ .

Ψ^2 is a probability factor. It describes the probability of finding an electron within a small space. The space in which there is maximum probability of finding an electron is termed as orbital. The important point of the solution of the wave equation is that it provides a set of numbers called quantum numbers which describe energies of the electron in atoms, information about the shapes and orientations of the most probable distribution of electrons around nucleus.

Operators in Quantum Mechanics

1.1 Basic notions of operator algebra.

Position and momentum: \hat{x} and $\hat{p} = -i\hbar\nabla$

they are called “fundamental operators”.

Many operators are constructed from \hat{x} and \hat{p} ; for example the Hamiltonian for a single particle:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}(\hat{x})$$

where $\hat{p}^2/2m$ is the K.E. operator and \hat{V} is the P.E. operator. This example shows that we can **add** operators to get a new operator. So one may ask what other algebraic operations one can carry out with operators?

The product of two operators is defined by operating with them on a function.

Let the operators be \hat{A} and \hat{B} , and let us operate on a function $f(x)$ (one-dimensional for simplicity of notation). Then the expression

$$\hat{A}\hat{B}f(x)$$

is a new function. We can therefore say, by the definition of operators, that $\hat{A}\hat{B}$ is an operator which we can denote by \hat{C} :

\hat{C} is the product of operators \hat{A} and \hat{B} .

The meaning of $\hat{A}\hat{B}f(x)$ should be that \hat{B} is first operating on $f(x)$, giving a new function, and then \hat{A} is operating on that new function.

Example: $\hat{A} = \hat{x}$ and $\hat{B} = \hat{p} = -i\hbar d/dx$, then we have

$$\hat{A}\hat{B}f(x) = \hat{x}\hat{p}f(x)$$

We can of course also construct another new operator:

$$\hat{p}\hat{x}$$

Then, by definition of the operator product,

$$\hat{p}\hat{x}f(x)$$

means that \hat{x} is first operating on $f(x)$ and then \hat{p} is operating on the function $\hat{x}f(x)$.

Compare the results of operating with the products $\hat{p}\hat{x}$ and $\hat{x}\hat{p}$ on $f(x)$:

$$(\hat{x}\hat{p} - \hat{p}\hat{x})f(x) = -i\hbar \left(x \frac{df(x)}{dx} - \frac{d}{dx}(xf(x)) \right)$$

and hence by the product rule of differentiation:

$$(\hat{x}\hat{p} - \hat{p}\hat{x})f(x) = i\hbar f(x)$$

and since this must hold for any differentiable function $f(x)$, we can write this as an operator equation:

$$\hat{x}\hat{p} - \hat{p}\hat{x} = i\hbar$$

Thus we have shown that the operator product of \hat{x} and \hat{p} is non-commuting.

Because combinations of operators of the form

$$\hat{A}\hat{B} - \hat{B}\hat{A}$$

do frequently arise in QM calculations, it is customary to use a short-hand notation:

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$$

and this is called the **commutator** of \hat{A} and \hat{B} (in that order!).

If $[\hat{A}, \hat{B}] \neq 0$, then one says that \hat{A} and \hat{B} do not commute,

if $[\hat{A}, \hat{B}] = 0$, then \hat{A} and \hat{B} are said to commute with each other.

An operator equation of the form of

$$[\hat{A}, \hat{B}] = \text{something}$$

is called a **commutation relation**.

$$[\hat{x}, \hat{p}] = i\hbar$$

is the **fundamental commutation relation**.

1.2 Eigenfunctions and eigenvalues of operators.

We have repeatedly said that an operator is defined to be a mathematical symbol that applied to a function gives a new function.

Thus if we have a function $f(x)$ and an operator \hat{A} , then

$$\hat{A}f(x)$$

is a some new function, say $\phi(x)$.

Exceptionally the function $f(x)$ may be such that $\phi(x)$ is proportional to $f(x)$; then we have

$$\hat{A}f(x) = af(x)$$

where a is some constant of proportionality. In this case $f(x)$ is called an **eigenfunction** of \hat{A} and a the corresponding **eigenvalue**.

Example: Consider the function $f(x, t) = e^{i(kx - \omega t)}$.

This represents a wave travelling in x direction.

Operate on $f(x)$ with the momentum operator:

$$\begin{aligned} \hat{p}f(x) &= -i\hbar \frac{d}{dx}f(x) = (-i\hbar)(ik)e^{i(kx - \omega t)} \\ &= \hbar k f(x) \end{aligned}$$

and since by the de Broglie relation $\hbar k$ is the momentum p of the particle, we have

$$\hat{p}f(x) = pf(x)$$

Note that this explains the choice of sign in the definition of the momentum operator!

1.3 Linear operators.

An operator \hat{A} is said to be linear if

$$\begin{aligned}\hat{A}(cf(x)) &= c\hat{A}f(x) \\ \text{and} \\ \hat{A}(f(x) + g(x)) &= \hat{A}f(x) + \hat{A}g(x)\end{aligned}$$

where $f(x)$ and $g(x)$ are any two appropriate functions and c is a complex constant.

Examples: the operators \hat{x} , \hat{p} and \hat{H} are all linear operators. This can be checked by explicit calculation (Exercise!).

1.4 Hermitian operators.

The operator \hat{A}^\dagger is called the hermitian conjugate of \hat{A} if

$$\int (\hat{A}^\dagger \psi)^* \psi dx = \int \psi^* \hat{A} \psi dx$$

Note: another name for “hermitian conjugate” is “adjoint”.

The operator \hat{A} is called hermitian if

$$\int (\hat{A} \psi)^* \psi dx = \int \psi^* \hat{A} \psi dx$$

Examples:

(i) the operator \hat{x} is hermitian. Indeed:

$$\int (\hat{x} \psi)^* \psi dx = \int (x \psi)^* \psi dx = \int \psi^* x \psi dx = \int \psi^* \hat{x} \psi dx$$

(ii) the operator $\hat{p} = -i\hbar d/dx$ is hermitian:

$$\begin{aligned}\int (\hat{p} \psi)^* \psi dx &= \int \left(-i\hbar \frac{d\psi}{dx} \right)^* \psi dx \\ &= i\hbar \int \left(\frac{d\psi}{dx} \right)^* \psi dx\end{aligned}$$

and after integration by parts, and recognizing that the wfn tends to zero as $x \rightarrow \infty$, we get on the right-hand side

$$-i\hbar \int \psi^* \frac{d\psi}{dx} dx = \int \psi^* \hat{p} \psi dx$$

(iii) the K.E. operator $\hat{T} = \hat{p}^2/2m$ is hermitian:

$$\begin{aligned}\int (\hat{T} \psi)^* \psi dx &= \frac{1}{2m} \int (\hat{p}^2 \psi)^* \psi dx \\ &= \frac{1}{2m} \int (\hat{p} \psi)^* \hat{p} \psi dx \\ &= \frac{1}{2m} \int \psi^* \hat{p}^2 \psi dx \\ &= \int \psi^* \hat{T} \psi dx\end{aligned}$$

(iv) the Hamiltonian is hermitian:

$$\hat{H} = \hat{T} + \hat{V}(\hat{x})$$

here \hat{V} is a hermitian operator by virtue of being a function of the hermitian operator \hat{x} , and since \hat{T} has been shown to be hermitian, so \hat{H} is also hermitian.

Theorem: The eigenvalues of hermitian operators are real.

Proof: Let ψ be an eigenfunction of \hat{A} with eigenvalue a :

$$\hat{A}\psi = a\psi$$

then we have

$$\int (\hat{A}\psi)^* \psi dx = \int (a\psi)^* \psi dx = a^* \int \psi^* \psi dx$$

and by hermiticity of \hat{A} we also have

$$\int (\hat{A}\psi)^* \psi dx = \int \psi^* \hat{A}\psi dx = a \int \psi^* \psi dx$$

hence

$$(a^* - a) \int \psi^* \psi dx = 0$$

and since $\int \psi^* \psi dx \neq 0$, we get

$$a^* - a = 0$$

The converse theorem also holds: an operator is hermitian if its eigenvalues are real. The proof is left as an exercise.

Note: by virtue of the above theorems one can define a hermitian operator as an operator with all real eigenvalues.

Corollary: *The eigenvalues of the Hamiltonian are real.*

In fact, since by definition the Hamiltonian has the dimension of energy, therefore the eigenvalues of the Hamiltonian are the energies of the system described by the wave function.

1.5 Expectation values.

Consider a system of particles with wave function $\psi(x)$

(x can be understood to stand for all degrees of freedom of the system; so, if we have a system of two particles then x should represent

$\{x_1, y_1, z_1; x_2, y_2, z_2\}$).

The expectation value of an operator \hat{A} that operates on ψ is defined by

$$\langle \hat{A} \rangle \equiv \int \psi^* \hat{A}\psi dx$$

If ψ is an eigenfunction of \hat{A} with eigenvalue a , then, assuming the wave function to be normalized, we have

$$\langle \hat{A} \rangle = a$$

Now consider the rate of change of the expectation value of \hat{A} :

$$\begin{aligned}\frac{d\langle\hat{A}\rangle}{dt} &= \int \frac{\partial}{\partial t} (\psi^* \hat{A} \psi) dx \\ &= \int \left\{ \frac{\partial\psi^*}{\partial t} \hat{A} \psi + \psi^* \frac{\partial\hat{A}}{\partial t} \psi + \psi^* \hat{A} \frac{\partial\psi}{\partial t} \right\} dx \\ &= \left\langle \frac{\partial\hat{A}}{\partial t} \right\rangle + \frac{i}{\hbar} \int \left\{ (\hat{H}\psi)^* \hat{A} \psi - \psi^* \hat{A} \hat{H}\psi \right\} dx\end{aligned}$$

where we have used the Schrödinger equation

$$i\hbar \frac{\partial\psi}{\partial t} = \hat{H}\psi$$

Now by hermiticity of \hat{H} we get on the r.h.s.:

$$\begin{aligned}& \frac{i}{\hbar} \int \left\{ \psi^* \hat{H} \hat{A} \psi - \psi^* \hat{A} \hat{H} \psi \right\} dx \\ &= \frac{i}{\hbar} \int \psi^* (\hat{H} \hat{A} - \hat{A} \hat{H}) \psi dx\end{aligned}$$

hence

$$\frac{d\langle\hat{A}\rangle}{dt} = \left\langle \frac{\partial\hat{A}}{\partial t} \right\rangle + \frac{i}{\hbar} \langle [\hat{H}, \hat{A}] \rangle$$

Of particular interest in applications are linear hermitian operators that do not explicitly depend on time, *i.e.* such that

$$\partial\hat{A}/\partial t = 0$$

For this class of operators we get the following equation of motion:

$$i\hbar \frac{d\langle\hat{A}\rangle}{dt} = \langle [\hat{A}, \hat{H}] \rangle$$

Here the expectation values are taken with arbitrary square integrable functions. Therefore we can re-write this equation as an operator equation:

$$i\hbar \frac{d\hat{A}}{dt} = [\hat{A}, \hat{H}]$$

If in particular \hat{A} is an observable that commutes with \hat{H} , *i.e.* if $[\hat{A}, \hat{H}] = 0$, then

$$\frac{d\hat{A}}{dt} = 0$$

i.e. \hat{A} is a conserved observable.

We can also prove the following theorem:

if two operators \hat{A} and \hat{B} commute, then they have common eigenfunctions.

Proof: Let ψ be an eigenfunction of \hat{A} with eigenvalue a :

$$\hat{A}\psi = a\psi$$

operating on both sides with \hat{B} we get

$$\hat{B}(\hat{A}\psi) = a\hat{B}\psi$$

on the l.h.s. we can write $\hat{B}\hat{A}\psi$, and then since by assumption \hat{A} and \hat{B} commute, we get

$$\hat{A}\hat{B}\psi = a\hat{B}\psi$$

thus $\hat{B}\psi$ is an eigenfunction of \hat{A} with the same eigenvalue as ψ ; therefore $\hat{B}\psi$ can differ from ψ only by a constant factor, *i.e.* we must have

$$\hat{B}\psi = b\psi$$

i.e. ψ is also an eigenfunction of \hat{B} .

The converse theorem is also true but not as useful; I shall therefore omit the proof.

1.6 Angular momentum.

Often operators can be constructed by taking the corresponding dynamical variable of classical mechanics, which is expressed in terms of coordinates and momenta, and replacing x by \hat{x} , p by \hat{p} etc. That was in fact the way we have constructed the Hamiltonian.

Now we apply this prescription to angular momentum.

In classical mechanics one defines the angular momentum by

$$\vec{L} = \vec{r} \times \vec{p}$$

We get the angular momentum operator by replacing the vector \vec{r} by the vector operator $\hat{r} = (\hat{x}, \hat{y}, \hat{z})$ and the momentum vector by the momentum vector operator

$$\hat{p} = -i\hbar\nabla = -i\hbar(\partial_x, \partial_y, \partial_z)$$

where $\partial_x = \partial/\partial x$ etc.

The complete fundamental commutation relations of the coordinate and momentum operators are

$$[\hat{x}, \hat{p}_x] = [\hat{y}, \hat{p}_y] = [\hat{z}, \hat{p}_z] = i\hbar$$

and

$$[\hat{x}, \hat{p}_y] = [\hat{x}, \hat{p}_z] = \dots = [\hat{z}, \hat{p}_y] = 0$$

It will be convenient to use the following notation:

$$\hat{x}_1 = \hat{x}, \quad \hat{x}_2 = \hat{y}, \quad \hat{x}_3 = \hat{z}$$

and

$$\hat{p}_1 = \hat{p}_x, \quad \hat{p}_2 = \hat{p}_y, \quad \hat{p}_3 = \hat{p}_z$$

we can then summarize the fundamental commutation relations by

$$[\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij}$$

where δ_{ij} is the Kronecker symbol:

$$\delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases}$$

We can now find the commutation relations for the components of the angular momentum operator. To do this it is convenient to get at first the commutation relations with \hat{x}_i , then with \hat{p}_i , and finally the commutation relations for the components of the angular momentum operator.

Thus consider the commutator $[\hat{x}, \hat{L}_x]$: we have $\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y$, and hence by the fundamental commutation relations

$$[\hat{x}, \hat{L}_x] = 0$$

Next consider $[\hat{x}, \hat{L}_y]$: we have

$$\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z$$

hence

$$[\hat{x}, \hat{L}_y] = [\hat{x}, \hat{z}\hat{p}_x] - [\hat{x}, \hat{x}\hat{p}_z] = i\hbar\hat{z}$$

and similarly

$$[\hat{x}, \hat{L}_z] = -i\hbar\hat{y}$$

etc. We can summarize the nine commutation relations:

$$[\hat{x}_i, \hat{L}_j] = i\hbar\varepsilon_{ijk}\hat{x}_k$$

where

$$\varepsilon_{ijk} = \begin{cases} 1 & \text{if } (ijk) = (1, 2, 3) \text{ or } (2, 3, 1) \text{ or } (3, 1, 2) \\ -1 & \text{if } (ijk) = (1, 3, 2) \text{ or } (3, 2, 1) \text{ or } (2, 1, 3) \\ 0 & \text{if } i = j \text{ or } i = k \text{ or } j = k \end{cases}$$

and summation over the repeated index k is implied.

Similarly one can show

$$[\hat{p}_i, \hat{L}_j] = i\hbar\varepsilon_{ijk}\hat{p}_k$$

after which it is straight forward to deduce:

$$[\hat{L}_i, \hat{L}_j] = i\hbar\varepsilon_{ijk}\hat{L}_k$$

The important conclusion from this result is that *the components of angular momentum have no common eigenfunctions.*

Of course, we must also show that the angular momentum operators are hermitian. This is of course plausible (reasonable) since we know that the angular momentum is a dynamical variable in classical mechanics. The proof is left as an exercise.

We can construct one more operator that commutes with all components of \hat{L} : define the square of \hat{L} by

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

then

$$\begin{aligned} [\hat{L}_x, \hat{L}^2] &= [\hat{L}_x, \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2] \\ &= [\hat{L}_x, \hat{L}_y^2] + [\hat{L}_x, \hat{L}_z^2] \end{aligned}$$

Now there is a simple technique to evaluate a commutator like $[\hat{L}_x, \hat{L}_y^2]$: write down explicitly the known commutator $[\hat{L}_x, \hat{L}_y]$:

$$\hat{L}_x \hat{L}_y - \hat{L}_y \hat{L}_x = i\hbar \hat{L}_z$$

multiply this on the left by \hat{L}_y , then multiply on the right by \hat{L}_y :

$$\begin{aligned} \hat{L}_y \hat{L}_x \hat{L}_y - \hat{L}_y^2 \hat{L}_x &= i\hbar \hat{L}_y \hat{L}_z \\ \hat{L}_x \hat{L}_y^2 - \hat{L}_y \hat{L}_x \hat{L}_y &= i\hbar \hat{L}_z \hat{L}_y \end{aligned}$$

and if we add these commutation relations we get

$$\hat{L}_x \hat{L}_y^2 - \hat{L}_y^2 \hat{L}_x = i\hbar (\hat{L}_y \hat{L}_z + \hat{L}_z \hat{L}_y)$$

and similarly

$$\hat{L}_x \hat{L}_z^2 - \hat{L}_z^2 \hat{L}_x = -i\hbar (\hat{L}_y \hat{L}_z + \hat{L}_z \hat{L}_y)$$

hence

$$[\hat{L}_x, \hat{L}^2] = 0$$

and similarly

$$[\hat{L}_y, \hat{L}^2] = [\hat{L}_z, \hat{L}^2] = 0$$

Finally one can also show that the components of \hat{L} and \hat{L}^2 commute with \hat{p}^2 , and therefore also with the K.E. operator \hat{T} , and that they commute with r and hence with any function of r .

The latter statement is most easily shown by working in spherical polar coordinates (r, θ, φ) , where θ is the polar angle and φ the azimuth. If we choose the polar axis along the cartesian z direction, then we get after some tedious calculation the following expressions for the angular momentum components:

$$\begin{aligned} \hat{L}_x &= i\hbar \left(\sin \varphi \frac{\partial}{\partial \theta} + \cot \theta \cos \varphi \frac{\partial}{\partial \varphi} \right) \\ \hat{L}_y &= i\hbar \left(-\cos \varphi \frac{\partial}{\partial \theta} + \cot \theta \sin \varphi \frac{\partial}{\partial \varphi} \right) \\ \hat{L}_z &= -i\hbar \frac{\partial}{\partial \varphi} \end{aligned}$$

We can therefore conclude that the angular momentum operators commute with the Hamiltonian of a particle in a central field, for example a Coulomb field, and that implies that \hat{L}^2 and one of the components can be chosen to have common eigenfunctions with the Hamiltonian.

Particle in a 1D Box

First we will consider a free particle moving in 1D so $V(x) = 0$. The TDSE now reads

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

which is solved by the function

$$\psi = Ae^{ikx}$$

where

$$k = \pm \frac{\sqrt{2mE}}{\hbar}$$

A general solution of this equation is

$$\psi(x) = Ae^{ikx} + Be^{-ikx}$$

where A and B are arbitrary constants. It can also be written in terms of sines and cosines as

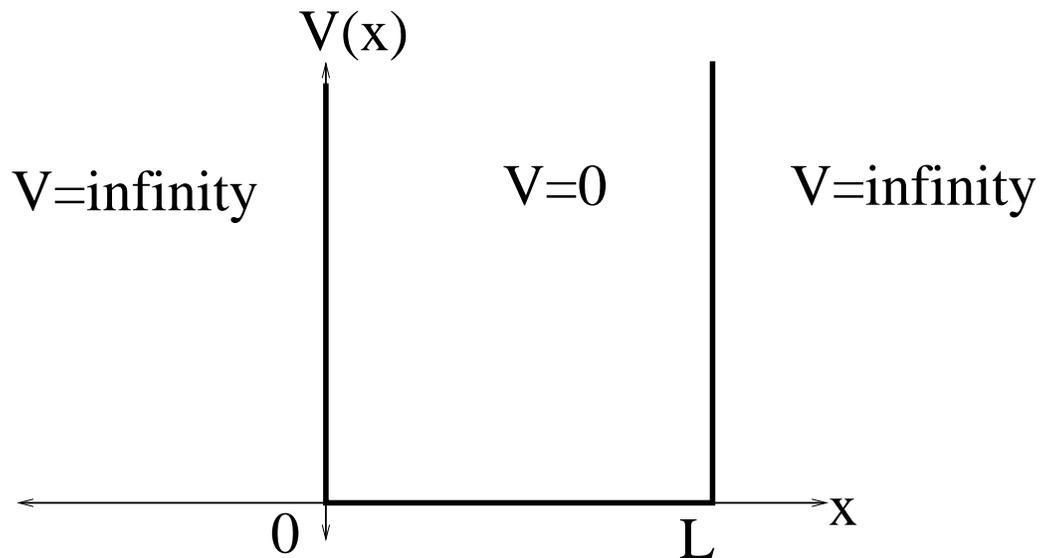
$$\psi(x) = C \sin(kx) + D \cos(kx)$$

The constants appearing in the solution are determined by the boundary conditions. For a free particle that can be anywhere, there is no boundary conditions, so k and thus $E = \hbar^2 k^2 / 2m$ can take any values. The solution of the form e^{ikx} corresponds to a wave travelling in the +x direction and similarly e^{-ikx} corresponds to a wave travelling in the -x direction. These are eigenfunctions of the momentum operator. Since the particle is free, it is equally likely to be anywhere so $\psi^*(x)\psi(x)$ is independent of x . Incidentally, it cannot be normalized because the particle can be found anywhere with equal probability.

Now, let us confine the particle to a region between $x = 0$ and $x = L$. To do this, we choose our interaction potential $V(x)$ as follows

$$\begin{aligned} V(x) &= 0 & \text{for } 0 \leq x \leq L \\ &= \infty & \text{otherwise} \end{aligned}$$

It is always a good idea to plot the potential energy, when it is a function of a single variable, as shown in Fig.1. The TISE is now given by



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

First consider the region outside the box where $V(x) = \infty$. Since $V(x)\psi(x)$ has to be finite for finite energy, we insist that $\psi(x) = 0$. In other words, the particle cannot go outside the box.

In the box, we have the TISE given by the free particle term

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

now subjected to the boundary conditions given by

$$\psi(0) = \psi(L) = 0$$

Thus, we take the general solution

$$\psi(x) = A \sin(kx) + B \cos(kx)$$

If we put $x = 0$, we get $\psi(0) = B = 0$. If we now put $\psi(L) = 0$, we get

$$A \sin(kL) = 0 \quad \text{or } k = \frac{n\pi}{L}$$

where n is any integer. Clearly $n = 0$ is not valid as the wavefunction vanishes. Also, we see that changing the sign of n simply changes the sign of the wavefunction and as we said before, it does not produce a new wavefunction.

Thus the solution of the TISE that satisfies the boundary condition is written as

$$\psi_n(x) = A \sin\left(\frac{n\pi x}{L}\right) \quad \text{where } n = 1, 2, 3, \dots$$

The constant A is determined by the normalization condition to be $\sqrt{2/L}$. The corresponding energy is given by

$$E_n = \frac{\hbar^2 k^2}{2m} = \frac{n^2 \hbar^2}{8mL^2}$$

so we have quantization of energy with

$$E_1 = \frac{\hbar^2 k^2}{2m} \quad E_2 = \frac{4\hbar^2 k^2}{2m}$$

and so on. Notice that the lowest possible energy is not zero. This is referred to as zero point energy. The first few wavefunctions are plotted schematically as shown below. Notice that as the quantum number increases, the wavefunction becomes more oscillatory. For $n = 2$, the wavefunction is zero at the midpoint of the box $x = L/2$. This point is a node of this wavefunction. A node refers to a point (other than boundary points) where the wavefunction goes to zero. For the particle in a 1D box, we see that the number of nodes is equal to $n - 1$.

Though the particle in a 1D box is a simple model system, it illustrates the important features of a quantum mechanical description. It is a very useful first approximation to the behavior of π electrons in conjugated alkenes.

Molecular orbital theory

Valence bond theory gave us a qualitative picture of chemical bonding.

Useful for predicting shapes of molecules, bond strengths, etc.

It fails to describe some bonding situations accurately because it ignores the wave nature of the electrons.

Molecular orbital (MO) theory has the potential to be more quantitative.

Usually we settle for simplified models here too. These simple models do not give very accurate orbital and bond energies, but they do explain concepts such as resonance (e.g., in the ferrocene molecule) that are hard to represent otherwise. We can get accurate energies from MO theory by computational "number crunching."

While MO theory is more "correct" than VB theory and can be very accurate in predicting the properties of molecules, it is also rather complicated even for fairly simple molecules. For example, you should have no trouble drawing the VB pictures for CO, NH₃, and benzene, but we will find that these are increasingly challenging with MO theory.

Constructing the molecular orbitals for a molecule:

We use atomic orbitals (AO) as a basis for constructing MO's.

LCAO-MO = linear combination of atomic orbitals

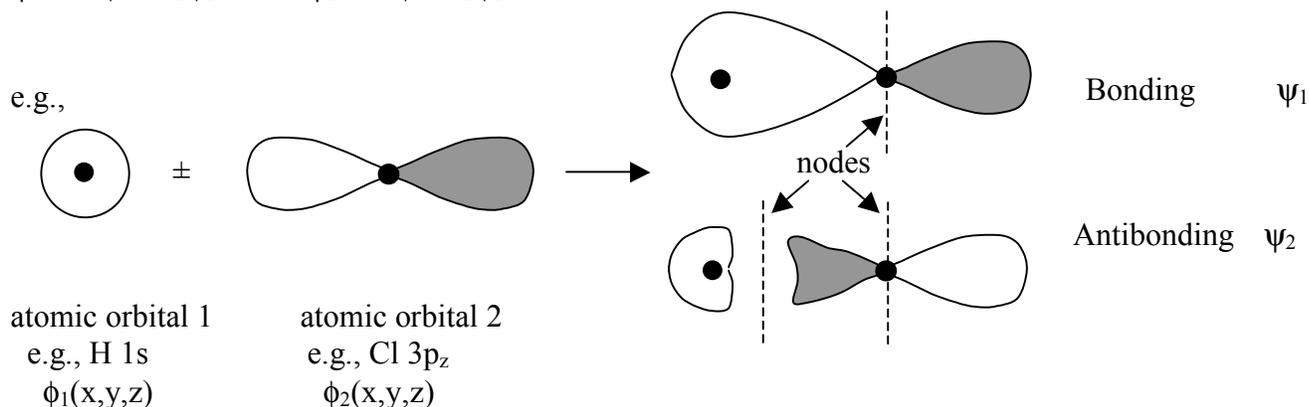
Physicists call this the "tight binding approximation."

The molecular orbitals, also called wavefunctions (ψ), are obtained by adding and subtracting atomic orbitals (ϕ). The ϕ 's are multiplied by scalar coefficients (c) to give normalized linear combinations.

For example, to make MO's from two AO's ϕ_1 and ϕ_2 , we write:

$$\psi_{\pm} = c_1\phi_1 \pm c_2\phi_2, \text{ or}$$

$$\psi_1 = c_1\phi_1 + c_2\phi_2 \quad \text{and} \quad \psi_2 = c_1\phi_1 - c_2\phi_2$$



Nodes. The wavefunctions ϕ and ψ are probability *amplitudes*. They have lobes with (+) or (-) signs, which we indicate by shading or color. Wherever the wavefunction changes sign we have a node. As you can see in the picture above, nodes in MOs result from destructive interference of (+) and (-) wavefunctions. Generally, the more nodes, the higher the energy of the orbital.

In this example we have drawn a simplified picture of the Cl $3p_z$ orbital and the resulting MOs, leaving out the radial node. Recall that 2p orbitals have no radial nodes, 3p orbitals have one, 4p have two, etc. The MOs we make by combining the AOs have these nodes too.



Normalization. We square the wave functions to get probabilities, which are always positive or zero. So if an electron is in orbital ϕ_1 , the probability of finding it at point xyz is the square of $\phi_1(x,y,z)$. The total probability does not change when we combine AOs to make MOs, so for the simple case of combining ϕ_1 and ϕ_2 to make ψ_1 and ψ_2 ,

$$\psi_1^2 + \psi_2^2 = \phi_1^2 + \phi_2^2$$

Overlap integral and c values. The spatial overlap between two atomic orbitals ϕ_1 and ϕ_2 is described by the overlap integral S,

$$S = \int \phi_1 \phi_2 d\tau \text{ where the integration is over all space (} d\tau = dx dy dz \text{).}$$

From the normalization criterion we get:

$$\Psi_1 = \frac{1}{\sqrt{2}} \left(\frac{1}{1+S} \right) (\phi_1 + \phi_2) \text{ (bonding orbital)}$$

and

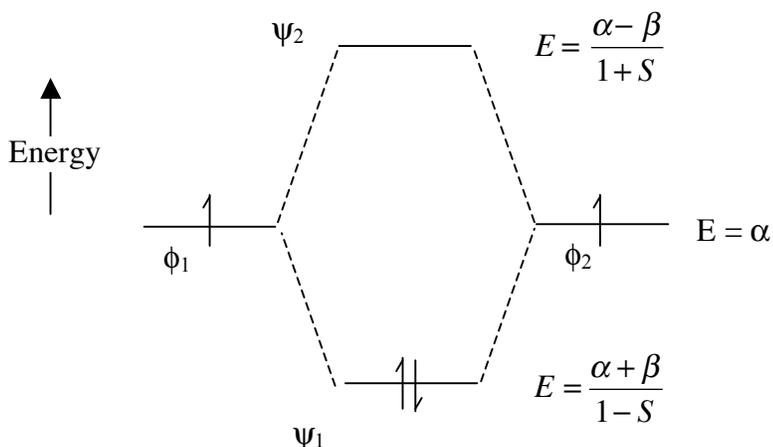
$$\Psi_2 = \frac{1}{\sqrt{2}} \left(\frac{1}{1-S} \right) (\phi_1 - \phi_2) \text{ (antibonding orbital)}$$

In the case where $S=0$, this simplifies to $c_1 = c_2 = \frac{1}{\sqrt{2}}$.

Energies of bonding and antibonding MOs:

The energies of the bonding and antibonding molecular orbitals (ψ_1 , ψ_2) are lower and higher, respectively, than the energies of the atomic basis orbitals ϕ_1 and ϕ_2 .

For the simple case where ϕ_1 and ϕ_2 have the same energy (e.g., the two H 1s orbitals that combine to make the MO's of the H₂ molecule) we have the following picture:



The energy of an electron in one of the atomic orbitals is α , the *Coulomb integral*.

$\alpha = \int \phi_1 H \phi_1 d\tau = \int \phi_2 H \phi_2 d\tau$, where H is the *Hamiltonian operator*. Essentially, α represents the ionization energy of an electron in atomic orbital ϕ_1 or ϕ_2 .

The energy difference between an electron in the AO's and the MO's is determined by the *exchange integral* β ,

$$\beta = \int \phi_1 H \phi_2 d\tau$$

Note that the bonding orbital is stabilized by an energy $\frac{\beta}{1 + S}$ and the antibonding orbital is destabilized by $\frac{\beta}{1 - S}$. That is, the antibonding orbital goes up in energy more than the bonding orbital goes down. This means that H₂ ($\psi_1^2 \psi_2^0$) is energetically more stable than two H atoms, but He₂ with four electrons ($\psi_1^2 \psi_2^2$) is unstable relative to two He atoms.

LCAO-MO Correlation Diagrams

(Linear Combination of Atomic Orbitals to yield Molecular Orbitals)

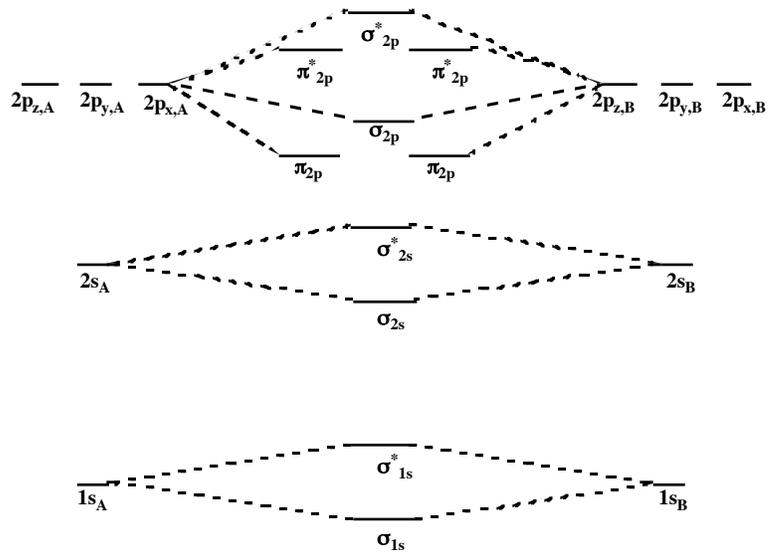
- For (Second Row) Homonuclear Diatomic Molecules (X_2) - the following

LCAO-MO's are generated:

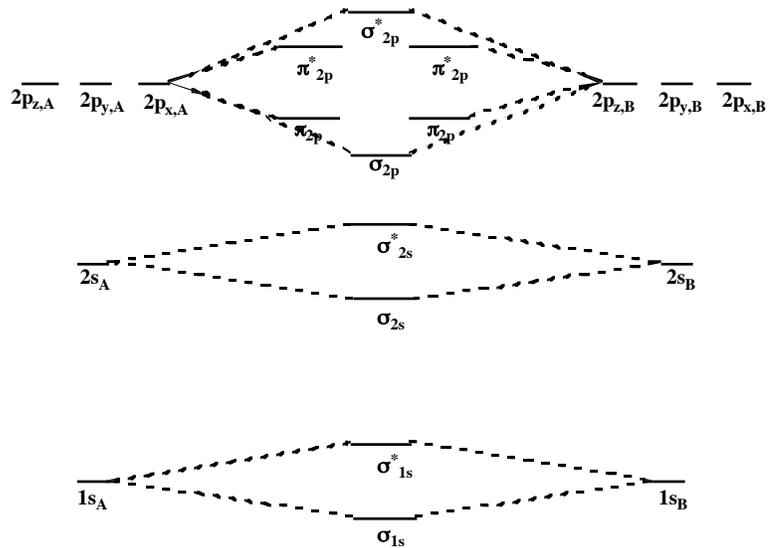
LCAO	MO symbol
$1s_A + 1s_B$	σ_{1s}
$1s_A - 1s_B$	σ_{1s}^*
$2s_A + 2s_B$	σ_{2s}
$2s_A - 2s_B$	σ_{2s}^*
$2p_{x,A} + 2p_{x,B}$	π_{2p}
$2p_{x,A} - 2p_{x,B}$	π_{2p}^*
$2p_{y,A} + 2p_{y,B}$	π_{2p}
$2p_{y,A} - 2p_{y,B}$	π_{2p}^*
$2p_{z,A} + 2p_{z,B}$	σ_{2p}
$2p_{z,A} - 2p_{z,B}$	σ_{2p}^*

For the above LCAO-MO combinations, the coordinate system is chosen such that the “z” axis is along the horizontal direction and is considered the **internuclear** (“bond”) axis. Here, the y-axis is considered to be along the vertical direction and the x-axis is considered to be perpendicular to the plane of the page. **This choice is, of course, arbitrary.** The correlation diagrams showing the energy ordering and relationship between the Atomic Orbitals (AO's) and resultant Molecular Orbitals (MO's) for several situations are listed below. Each MO can maximally contain two (2) electrons - with opposite spins ($\uparrow\downarrow$) - as required by the Pauli Exclusion Principle (PEP). Also, degenerate MO's - when occupied - will follow Hund's Rule in order to achieve a ground state (energy-preferred) electron configuration. There are two schemes - I and II below. Scheme I applies for Li through N (and their ions), inclusive and Scheme II applies for O through Ne (and their ions), inclusive. As can be seen, the difference lies in the relative energy ordering of the π_{2p} MO's versus the σ_{2p} MO's. For $Z \leq 7$ atoms, the (degenerate) π_{2p} MO's are lower in energy than σ_{2p} MO. For $Z \geq 8$ atoms, the (degenerate) π_{2p} MO's are greater in energy than σ_{2p} MO. The reason has to do with energy stabilization by attenuation of electron-electron repulsion. In Scheme I, the π_{2p} MO's are filled before the σ_{2p} MO because the electron density in the π_{2p} MO's are concentrated (between the atoms) away from (i.e., above and below) the internuclear axis. This leads to a reduction in the electron-electron repulsions. This is particularly important since the electrons in the already - occupied $\sigma_{2s} - \sigma_{2s}^*$ MO's will interact less strongly with electrons in the π_{2p} MO's than those in the σ_{2p} MO's (electron density also directed along the internuclear axis). In Scheme II - followed by atoms toward the end of the second row - the already occupied $\sigma_{2s} - \sigma_{2s}^*$ MO's are drawn closer (“tighter”) due to the greater nuclear charge (Z). For $Z \geq 8$, this is enough so that the σ_{2p} MO's will interact less strongly with the $\sigma_{2s} - \sigma_{2s}^*$ MO's. Hence, the σ_{2p} MO will be lower in energy than the π_{2p} MO's. [After discussing Scheme II, your text sometimes follows Scheme I - for simplicity - for all second row diatomics (and their ions) in some of the homework problems.] By paying attention to the PEP and Hund's Rule - as mentioned above - we fill the MO's from “bottom - up” in an “Aufbau” manner for our chosen MO scheme. This will give us **ground state (MO) electron configurations.**

- Homonuclear (Second Row) Diatomic Molecules (X_2) - or their ions**
Scheme I - $X = \text{Li, Be, B, C, N}$; i.e., Atomic # $Z \leq 7$
 (Energy increases vertically up the page)



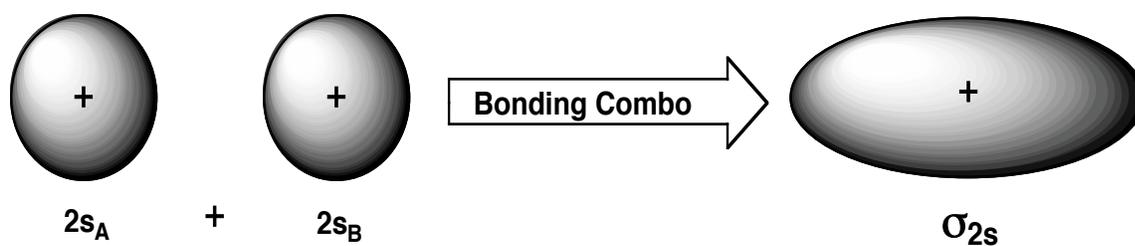
- Homonuclear (Second Row) Diatomic Molecules (X_2) - or their ions**
Scheme II - $X = \text{O, F, Ne}$; i.e., Atomic # $Z \geq 8$
 (Energy increases vertically up the page)



Boundary Surface Diagrams (BSD) for the LCAO-MO's formed from $2s$, $2p_x$, $2p_y$, & $2p_z$ AO's of second row homonuclear diatomic molecules.

- **2s Atomic Orbital (Bonding & Antibonding) Combinations:**

2s Bonding:

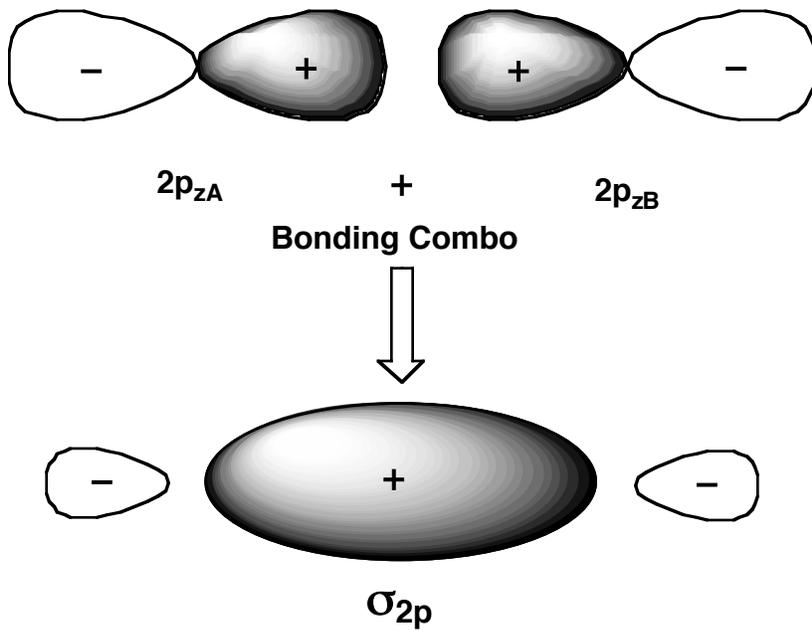


2s Antibonding:

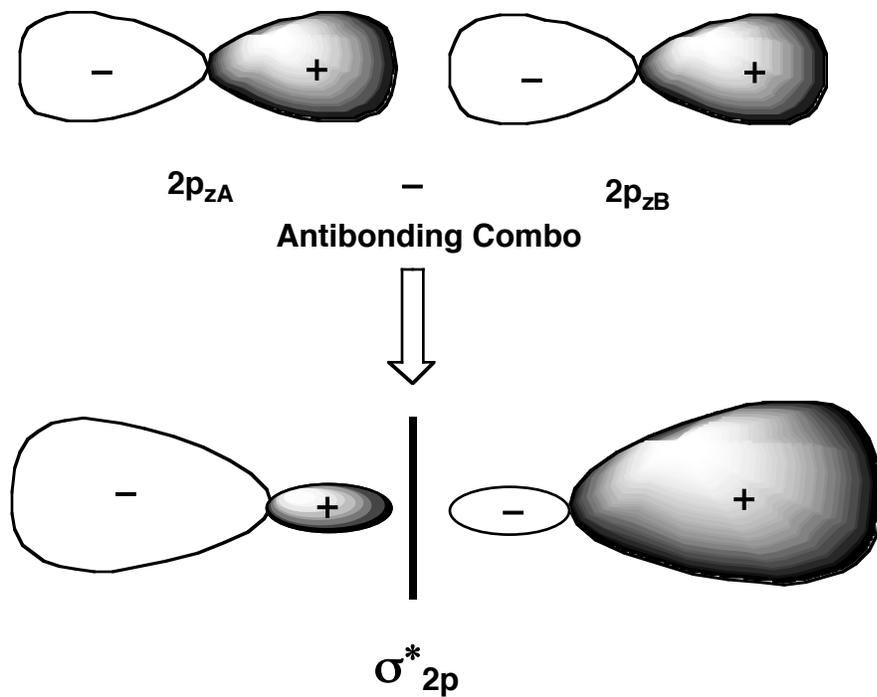


• 2p Atomic Orbital Combinations along BOND AXIS:

2p Bonding (Along Bond Axis):

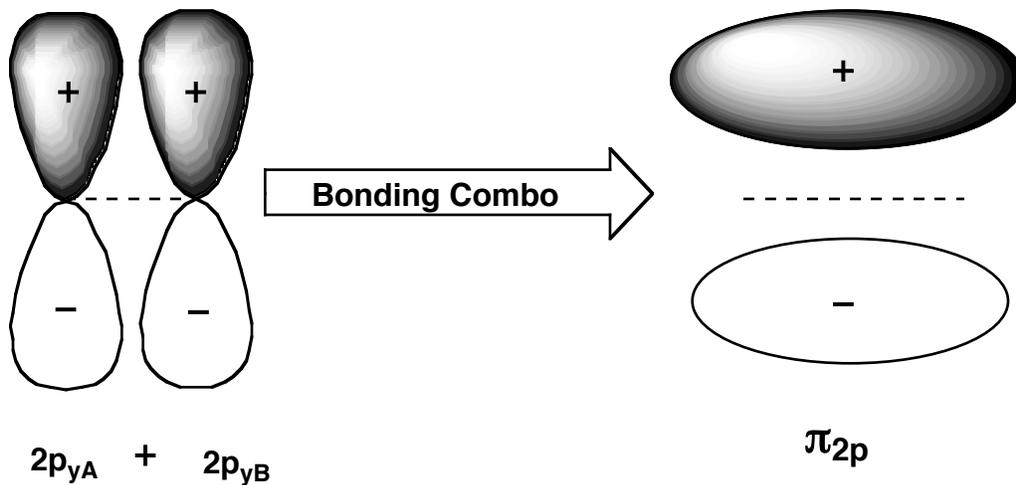


2p Antibonding (Along Bond Axis):

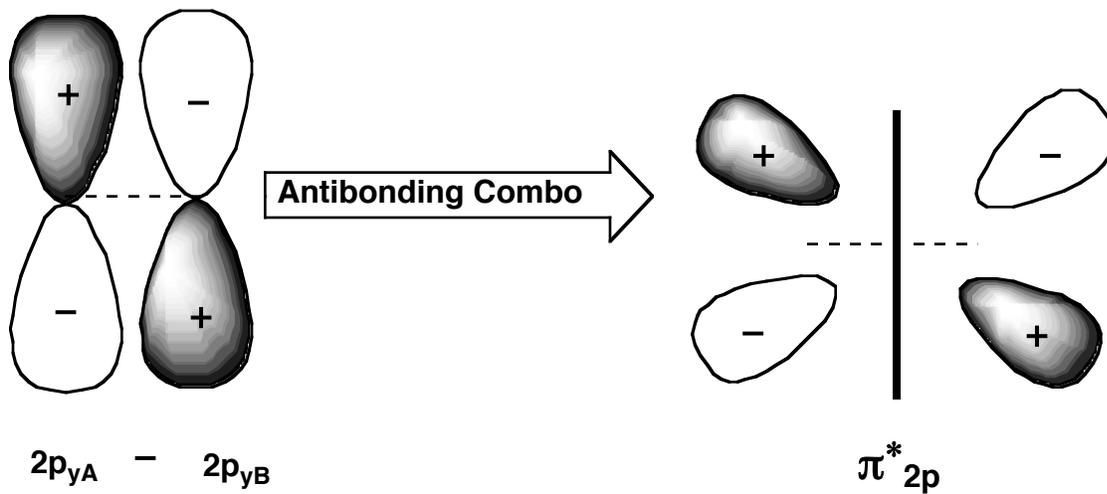


- 2p Atomic Orbital Combinations PERPENDICULAR TO Bond Axis:

2p Bonding (Perpendicular to Bond Axis):



2p Antibonding (Perpendicular to Bond Axis):



& SIMILARLY for $2p_{xA}$ & $2p_{xB}$ - Bonding & Antibonding M.O.'s

(These M.O.'s will be perpendicular to the plane of the paper.)

Molecular Orbital Theory for Hydrogen Molecule Ion

We have seen that the Schrödinger equation cannot be solved for many electron systems. The H_2^+ molecule ion is a molecule that has only one electron. However, there are 2 nuclei so it becomes a 3-particle problem. To solve this problem, we invoke an approximation that is known as the Born-Oppenheimer approximation wherein we assume that the electronic and nuclear degrees of freedom can be solved independently. Further, assuming that the kinetic energy of the nuclei are very small, we can solve the electronic problem at fixed internuclear separation as illustrated below.

$$\hat{H}(R_A, R_B, r) = -\frac{\hbar^2}{2m_p}(\nabla_A^2 + \nabla_B^2) - \frac{\hbar^2}{2m_e}\nabla_r^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_A} + \frac{1}{r_B} - \frac{1}{R}\right)$$

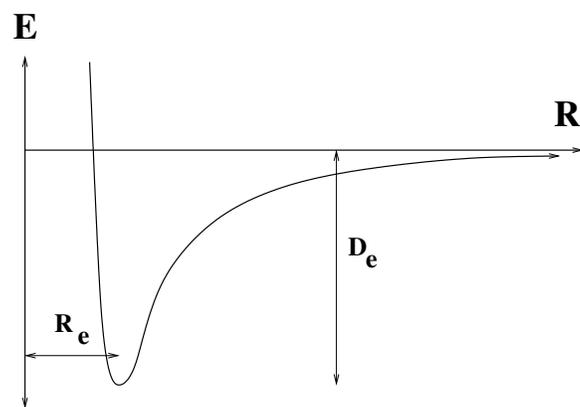
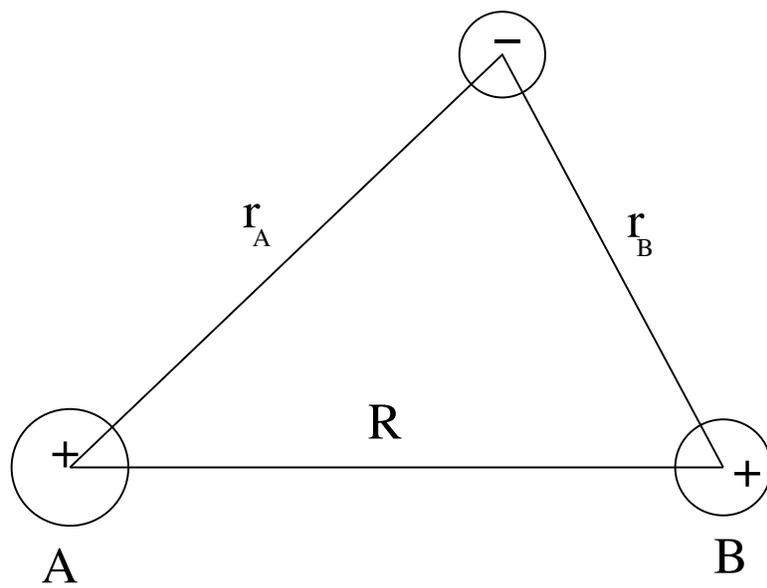
Under the BO approximation, we have

$$\hat{H}_{el}(r; R) = -\frac{\hbar^2}{2m_e}\nabla_r^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_A} + \frac{1}{r_B} - \frac{1}{R}\right)$$

The electronic wavefunction is to be treated as a function of the electronic coordinate r for fixed internuclear separation R . Thus the Schrödinger equation is given by

$$\hat{H}_{el}\psi(r; R) = E(R)\psi(r; R)$$

We can imagine solving this for different R . If there is a bond, then this energy should be minimum for some value of R as shown in the figure. This gives the equilibrium bond length R_e and the dissociation energy D_e of the



molecule. We will briefly describe this physical picture of the bond using Molecular Orbital theory.

According to MO theory, the electron in a molecule is located in orbitals (single-electron functions) called molecular orbitals. The molecular orbitals are different from the atomic orbitals since they are not centered at atomic nuclei. One way to construct the functions corresponding to molecular orbitals is to use linear combination of atomic orbitals (LCAO). For example, we can consider the linear combination of the 1s wavefunctions centered on both atoms.

$$\psi_{MO}(\vec{r}) = N(\psi_{1sA}(\vec{r}) \pm \psi_{1sB}(\vec{r}))$$

Note that ψ_{1sA} is a function centered at nucleus A. Thus we have

$$\psi_{1sA}(\vec{r}) = N_1 e^{-r_A/a_0}$$

and similarly for ψ_{1sB} . Assuming that the wavefunctions for ψ_{1sA} and ψ_{1sB} are normalized, we can calculate the value of N as follows

$$1 = \int \psi_{MO}^*(\vec{r}) \psi_{MO}(\vec{r}) d\vec{r} = N^2 \int \psi_{1sA}^*(\vec{r}) \psi_{1sA}(\vec{r}) d\vec{r} + 3 \text{more terms}$$

We can easily show for real orbitals that the terms lead to

$$1 = N^2(2 \pm 2 \int \psi_{1sA}^*(\vec{r}) \psi_{1sB}(\vec{r}) d\vec{r})$$

The last term is denoted by S , so we can write

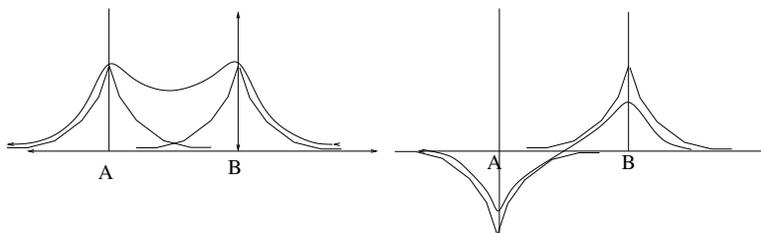
$$N = \frac{1}{\sqrt{2(1 \pm S)}}$$

where S denotes the overlap between the orbitals.

Of the two orbitals, the one with the positive sign turns out to have lower energy than the 1s orbital and is called the bonding MO and the one with negative sign has higher energy than 1s orbital and is called the antibonding MO.

$$\psi_{MO-Bonding} = \frac{1}{\sqrt{2(1+S)}}(\psi_{1sA}(\vec{r}) + \psi_{1sB}(\vec{r}))$$

Thus we can say that for a given R , the two 1s orbitals combine to give one bonding and one antibonding MO. The bonding MO turns out to have lower energy, but you could only know this if you could calculate the energies which



is difficult. The bonding MO has higher electron density in the internuclear axis, unlike in the case of the antibonding MO. The $1s$ bonding orbital is symmetric to inversion about the center and is referred to as *gerade* or simply *g* for short.

In fact we will write the previous equation in short form as

$$1\sigma_g \propto (1s_A + 1s_B)$$

The convention for naming this orbital is $1\sigma_g$. The antibonding orbital is labelled as $1\sigma_u^*$.

We could also combine the two $2s$ orbitals to form a $2\sigma_g$ and $2\sigma_u^*$ MOs. With p orbitals things get a little more complicated because the phase of the orbitals matters. Consider $2p_z$ orbital. This has opposite signs in the different halves. Now, when combining wavefunctions, we have to see the sign. For example, the bonding orbital is denoted as $3\sigma_u$ is given by

$$3\sigma_g \propto 2pz_A - 2pz_B$$

where we assume that the Z -axis is along the internuclear axis. The antibonding MO is given by

$$3\sigma_u^* \propto 2pz_A + 2pz_B$$

The sigma orbitals are spherically symmetric about the internuclear axis. We can also have orbitals which do not satisfy this condition. For example, if we take a linear combination of $2px$ orbitals located on the two atoms, we will see that

$$1\pi_u \propto 2px_A + 2px_B$$

and similarly for the $2py$ orbitals. These two MOs are degenerate. The antibonding MO is denoted by

$$1\pi_g^* \propto 2px_A - 2px_B$$

In the Hydrogen molecule ion, there is only one electron. The ground state corresponds to the electron in the $1\sigma_g$ orbital so this orbital is referred to as the Highest Occupied Molecular Orbital(HOMO). The lowest unoccupied MO(LUMO) is the $1\sigma_u^*$. These MOs were calculated at fixed internuclear separation. We can qualitatively see what happens when the internuclear separation is changed and define R_e and D_e as we had before for the $1\sigma_g$ MO. The antibonding MO does not show a minimum energy at some separation. This qualitative picture is borne out by numerical calculations.