Schrödinger Equation

$$\left\{ -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V\right\}\psi(\vec{r},t) = i\hbar\frac{\partial \psi(\vec{r},t)}{dt}$$

$\hbar = h/2\pi$ V: external field ψ: wavefunction (can be complex)

For time-independent V, this is simplified to:

$$\underbrace{\left(-\frac{\hbar}{2m}\nabla^2 + V\right)}_{\mathcal{H}}\psi(\vec{r}) = E\,\psi(\vec{r}) \qquad E: \text{energy}$$

$\mathcal{H}$: Hamiltonian Operator ; $\boxed{\mathcal{H}\psi = E\psi}$ ①

The energy can be obtained by multiplying both sides of ① with the complex conjugate of ψ, ψ^*, and integrating over all space:

$$E = \frac{\int \psi^* \mathcal{H} \psi \, d\vec{r}}{\int \psi^* \psi \, d\vec{r}}$$

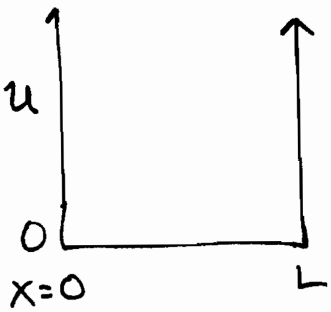
typically normalize ψ so that $\int \psi^*\psi \, d\vec{r} =$
$= \int |\psi|^2 d\vec{r} = 1$

Other operators $-\frac{\hbar^2}{2m}\nabla^2$: kinetic

$\frac{\hbar}{i}\frac{\partial}{\partial x}$: x-momentum

For electronic motion around a nucleus, the potential is $V = -\frac{ze^2}{4\pi\varepsilon_0 r}$ z: valence

For simple potentials, e.g. particle in a box, solution can be obtained analytically:



$V = 0 \quad 0 \le x \le L$

$V = \infty \quad$ elsewhere

Outside the region $x \le 0 \le L$ the solution must be $\psi = 0$.

Inside "box", we have

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = \mathcal{E}\psi \Rightarrow \frac{d^2\psi}{dx^2} = k^2\psi \qquad k = \sqrt{\frac{2m\mathcal{E}}{\hbar^2}}$$

The solutions to this second-order diff. equ. are of the form:

(Since $(\sin kx)'' = k^2 \sin kx$, $(\cos kx)'' = k^2 \cos kx$)

$$\psi = A \sin kx + B \cos kx$$

constants to be determined from boundary conditions + normalization

The boundary conditions are that

$$\left.\begin{array}{l} \psi(0) = 0 \\ \psi(L) = 0 \end{array}\right\} \Rightarrow B = 0, \quad \sin kL = 0 \Rightarrow$$

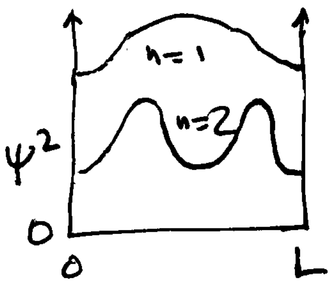
$$kL = n\pi \Rightarrow$$

$$\sqrt{\frac{2m\mathcal{E}}{\hbar}} = n\pi/L \Rightarrow$$

$$\mathcal{E}_n = \frac{\hbar^2\pi^2 n^2}{2mL^2} = \frac{h^2 n^2}{8mL^2}$$

$$\psi_n = A \sin\left(\frac{n\pi}{L} x\right)$$

Since $\int_0^L \psi_n^2(x)\,dx = 1 \Rightarrow A = \pm\sqrt{\frac{2}{L}}$



Only ψ^2 is physically meaningful, so

$$\left.\begin{aligned} \psi_n &= \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) \\ E_n &= n^2 \frac{h^2}{8mL^2} \end{aligned}\right\} \quad n = 1, 2, 3, \ldots$$

Atomic units

Charge $\quad |e| = 1.60219 \cdot 10^{-19}\,C$

Mass $\quad m_e = 9.10593 \cdot 10^{-31}\,kg$

Length (Bohr) $\quad a_0 = \dfrac{h^2 \varepsilon_0}{4\pi m_e e^2} = 5.29177 \cdot 10^{-11}\,m$

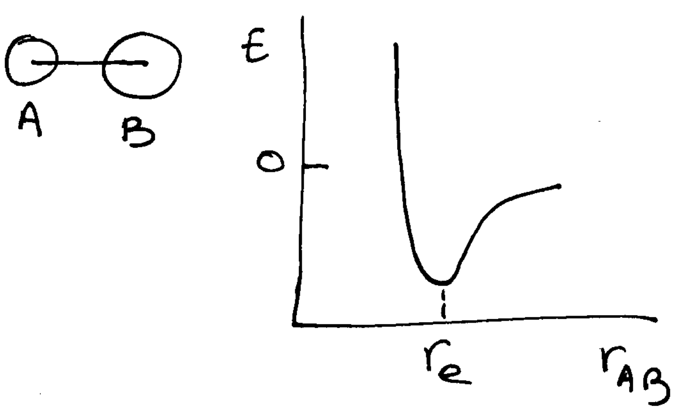
Energy (Hartree) $\quad = \dfrac{e^2}{4\pi \varepsilon_0 a_0} = 4.3598 \cdot 10^{-18}\,J$

In these units, $\hbar = 1$, $h = 2\pi$

Born-Oppenheimer approximation

Because nuclei are much heavier than electrons, they move slowly and can be treated as stationary with the electrons moving around them.

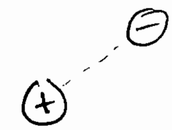
This approximation allows us to construct "molecular" potential energy curves, locate equilibrium bond distances r_e



One-electron atoms

(e.g. H, He^+) $\mathcal{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$

(in atomic units) $\mathcal{H} = -\frac{1}{2}\nabla^2 - \frac{Z}{r}$



Solve in spherical coordinates:

$$\Psi_{n\ell m} = \underbrace{R_{n\ell}(r)}_{\text{radial function}} \; \underbrace{Y_{\ell m}(\theta,\varphi)}_{\text{angular function (spherical harmonics)}}$$

orbitals

- n: principal quantum number, $1, 2, \dots$
- ℓ: azimuthal $0, 1, \dots (n-1)$
- m: magnetic $-\ell, \dots, 0, \dots, \ell$

n	ℓ	$R_{n\ell}(r)$
1	0	$2\zeta^{3/2}\exp(-\zeta r)$
2	0	$2\zeta^{3/2}(1-\zeta r)\exp(-\zeta r)$
2	1	$(4/3)^{1/2}\zeta^{5/2}\, r\exp(-\zeta r)$

ζ: orbital exponent $= Z/n$

The angular part is $Y_{\ell m}(\theta,\varphi) = \Theta_{\ell m}(\theta)\,\Phi_m(\varphi)$

where $\Phi_m(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi}$

$$\Theta_{\ell m}(\theta) = \left[\frac{(2\ell+1)(\ell-|m|)!}{2\;(\ell+|m|)!}\right]^{1/2} P_\ell^{|m|}\cos\theta$$

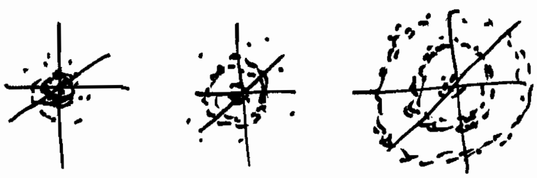
$P_\ell^{|m|}$ are "associated Legendre polynomials"

$l=0$ (s orbitals)

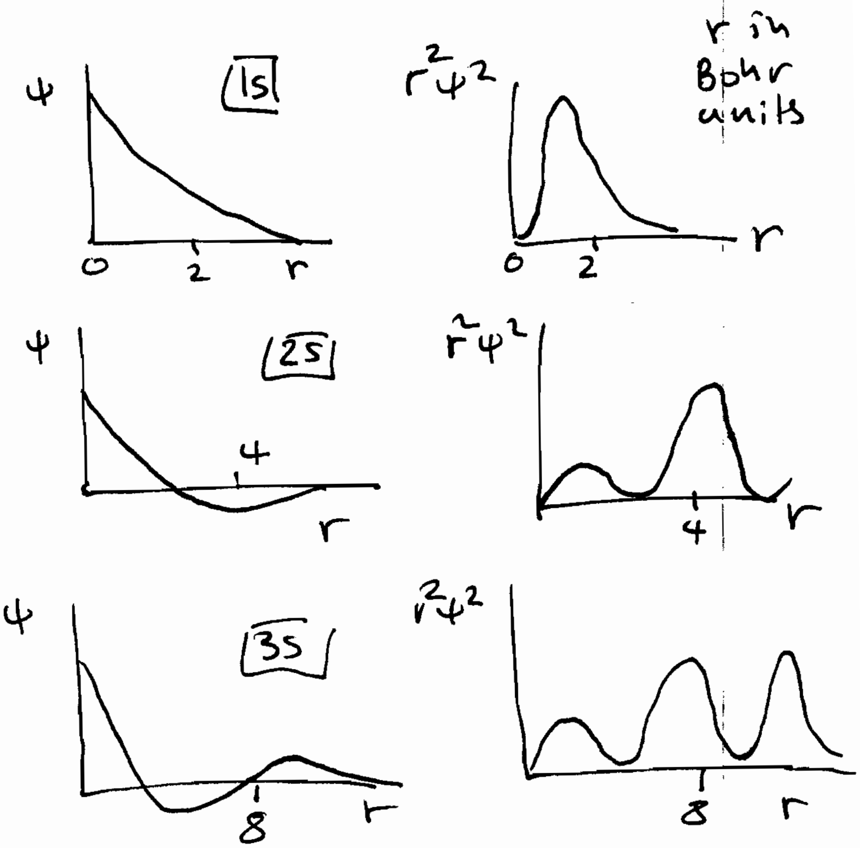
$n=1$	1s
$n=2$	2s
⋮	3s

$n \rightarrow$ shells K, L, M ...

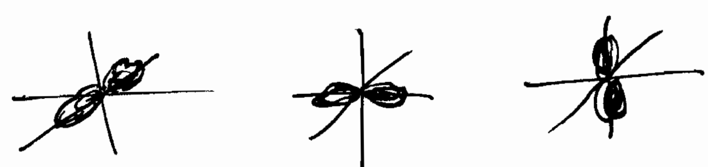
s orbitals are Spherically Symmetric:



1s 2s 3s



p orbitals look like this : (3 of them ; $l=1$, $m=-1,0,+1$)



P_x P_y P_z

d orbitals look like this (5 of them, $l=2$, $m=-2,-1,0,1,2$)