Quantum Mechanics

Angular momentum: Commutators rules, quantization of square of total angular momentum and z-component; Rigid rotator model of rotation of diatomic molecules; Schrodinger equation, transformation of spherical coordinates; separation of variables. Spherical harmonics; discussion of solution

Note: $\hbar(h-bar)$

Iran N. Levine, Quantum Chemistry, 7ed, P – 9

Angular Momentum

Consider a particle of mass "*m*" revolving around at a fixed point. The angular momentum

$L = r\times mu = r\times p$

The cross product $r\times p$ is the vector L perpendicular to the plane formed by the vectors r and p.

$L = iL_x + jL_y + kL_z$

Where "r" is the vector from the fixed point to mass point $r = ix + jy + kz$

p is the linear momentum vector $p = ip_x + jp_y + kp_z$

In classical mechanics, component of linear momentum vector are

$L_x = yp_z - zp_x \qquad L_y = zp_x - xp_z \qquad L_z = xp_y - yp_x$

$L^2 = LL = L_x^2 + L_y^2 + L_z^2$

Note: $i\times i = j\times j = k\times k = 0$ $\qquad i.i = j.j = k.k = 1$

$i\times j = k,\ j\times k = i, k\times i = j \qquad j\times i = -k,\ k\times j = -i,\ i\times k = -j \qquad i.j = j.k = k.i = 0$

Corresponding to the quantum mechanical operator $\hat{p}_x = -i\hbar\frac{\partial}{\partial x} \quad \hat{p}_y = -i\hbar\frac{\partial}{\partial y} \quad \hat{p}_z = -i\hbar\frac{\partial}{\partial z}$

$$\hat{L}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \qquad \hat{L}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \qquad \hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

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

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

$$\left[\hat{L}_z, \hat{L}_x\right] = -\left[\hat{L}_x, \hat{L}_z\right]$$

Prove

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

$$\left[\hat{L}_x, \hat{L}_y\right] = \hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x$$

Now $\hat{L}_x\hat{L}_y = \left\{-i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\right\}\left\{-i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\right\}$

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

$$= -\hbar^2\left(y\frac{\partial}{\partial x} + yz\frac{\partial^2}{\partial z\partial x} - yx\frac{\partial^2}{\partial z^2} - z^2\frac{\partial^2}{\partial y\partial x} + zx\frac{\partial^2}{\partial y\partial z}\right)$$

Similarly $\hat{L}_y\hat{L}_x = \left\{-i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\right\}\left\{-i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\right\}$

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

$$= -\hbar^2\left(zy\frac{\partial^2}{\partial x\partial z} - z^2\frac{\partial^2}{\partial x\partial y} - xy\frac{\partial^2}{\partial z^2} + x\frac{\partial}{\partial y} + xz\frac{\partial^2}{\partial z\partial y}\right)$$

Hence, $\left[\hat{L}_x, \hat{L}_y\right] = \hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x$

$$= \hbar^2\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = -i^2\hbar^2\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = i\hbar\left\{-i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\right\} = i\hbar\hat{L}_z$$

Note: L_x and L_y or L_y *and* L_z cannot be determined simultaneously and precisely, because they do not commute.

Q. L^2 and L_z can be determined simultaneously and precisely, because they commute.

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

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

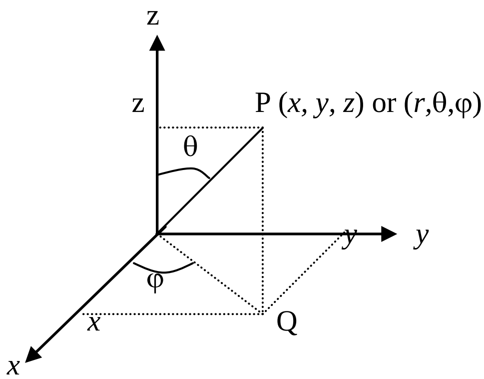
Now $\left[\hat{L}_x^2, \hat{L}_z\right] = \hat{L}_x^2, \hat{L}_z - \hat{L}_z, \hat{L}_x^2 = \hat{L}_x\hat{L}_x\hat{L}_z - \hat{L}_z\hat{L}_x\hat{L}_x$

$$= \hat{L}_x\hat{L}_x\hat{L}_z - \hat{L}_x\hat{L}_z\hat{L}_x + \hat{L}_x\hat{L}_z\hat{L}_x - \hat{L}_z\hat{L}_x\hat{L}_x = \hat{L}_x\left(\hat{L}_x\hat{L}_z - \hat{L}_z\hat{L}_x\right) + \left(\hat{L}_x\hat{L}_z - \hat{L}_z\hat{L}_x\right)\hat{L}_x$$

$$= \hat{L}_x\left[\hat{L}_{x,}\hat{L}_z\right] + \left[\hat{L}_{x,}\hat{L}_z\right]\hat{L}_x = -i\hbar\hat{L}_x\hat{L}_y - i\hbar\hat{L}_y\hat{L}_x = -i\hbar\left(\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x\right)$$

Similarly $\left[\hat{L}_y^2, \hat{L}_z\right] = i\hbar\left(\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x\right)$ and $\left[\hat{L}_z^2, \hat{L}_z\right] = 0$

Transformation of Cartesian coordinates of Laplacian operator to Spherical polar coordinates



$z = r\cos\theta$, $x = r\sin\theta\cos\varphi$ and $y = = r\sin\theta\sin\varphi$

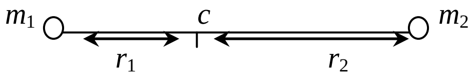
$x^2 + y^2 + z^2 = r^2$

Laplacian operator $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

$$= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}$$

Three Dimensional Rotation: ***A Rigid Rotator***

Consider diatomic molecule with mass m_1 and m_2 separated by fixed distance r and centre of mass is c. The distance from m_1 is r_1 and distance from m_2 is r_2 i.e $r_1 + r_2 = r$.



Now, $m_1r_1 = m_2r_2$ So, $m_1 (r - r_2) = m_2r_2$ or, $(m_1 + m_2)r_2 = m_1r$

$\therefore$ $r_2 = \dfrac{m_1 r}{m_1 + m_2}$ $r_1 = \dfrac{m_2 r}{m_1 + m_2}$

Moment of inertia $I = m_1 r_1^2 + m_2 r_2^2$ $I = \dfrac{m_1 m_2 r^2}{m_1 + m_2} = \mu r^2$

Where, reduced mass $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$

Now kinetic energy $T = \dfrac{1}{2} m_1 \mathrm{v}_1^2 + \dfrac{1}{2} m_2 \mathrm{v}_2^2 = \dfrac{1}{2}\omega^2 I = \dfrac{1}{2}\dfrac{L^2}{I} = \dfrac{1}{2}\dfrac{L^2}{\mu r^2}$

$[\mathrm{v} = \omega r,\ \ L = \omega I]$

Quantum mechanics

Hamiltonian operator $\hat{H} = \hat{T} + \hat{V}$

For rigid rotator potential energy $V = 0$

So, $\hat{H} = \hat{T} = \dfrac{\hat{L}^2}{2\mu r^2} = -\dfrac{h^2}{8\pi^2\mu}\nabla^2$

Schrodinger equation for the rigid rotator $-\dfrac{h^2}{8\pi^2\mu}\nabla^2\psi = E\psi$

The equation in terms of Spherical polar co-ordinate is

$$-\frac{h^2}{8\pi^2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\psi = E\psi$$

For the rigid rotator r is constant. So, $\dfrac{\partial\psi}{\partial r} = 0$

Therefore, $$-\frac{h^2}{8\pi^2\mu}\left[\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\psi = E\psi$$

Where, $\psi = f(\theta,\varphi)$ Let $\psi(\theta,\varphi) = \Theta(\theta)\Phi(\varphi)$

So, the equation become $$\frac{\Phi}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta + \frac{\Theta}{r^2\sin^2\theta}\frac{\partial^2\Phi}{\partial\varphi^2} + \frac{8\pi^2\mu}{h^2}E\Theta\Phi = 0$$

Dividing both sides by $\Theta\Phi$ we get

$$\frac{1}{\Theta r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta + \frac{1}{\Phi r^2\sin^2\theta}\frac{\partial^2\Phi}{\partial\varphi^2} + \frac{8\pi^2\mu}{h^2}E = 0$$

Multiplying both sides by $r^2\sin^2\theta$

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta + \frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2} + \frac{8\pi^2\mu}{h^2}r^2\sin^2\theta E = 0$$

Or, $$-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2} = \frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta + \frac{8\pi^2\mu r^2 E\sin^2\theta}{h^2}$$

Consider $$-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2} = \frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta + \frac{8\pi^2\mu r^2 E\sin^2\theta}{h^2} = m_l^2$$

So, $\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2} = -m_l^2$

Solving we get $\Phi = \frac{1}{\sqrt{2\pi}}e^{im_l\varphi}$

Again $\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta + \frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2} + \lambda\sin^2\theta = m_l^2$ $\left[\lambda = \frac{8\pi^2\mu r^2 E}{h^2} = \frac{8\pi^2 IE}{h^2}\right]$

Its solution is complicated.

Solving we get $E = l(l+1)\frac{h^2}{8\pi^2 I}$

Angular momentum component operator

The angular momentum operator L_z in spherical polar coordinate

$\hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi} = \frac{h}{2\pi i}\frac{\partial}{\partial\varphi}$

Therefore, $\hat{L}_z\Phi = \frac{h}{2\pi i}\frac{\partial}{\partial\varphi}\left(\frac{1}{\sqrt{2\pi}}e^{im_l\varphi}\right) = \frac{h}{2\pi i}\left(im_l\right)\left(\frac{1}{\sqrt{2\pi}}e^{im_l\varphi}\right) = m_l\frac{h}{2\pi}\Phi$

Eigenvalue = $m_l\frac{h}{2\pi}$ $m_l = 0, \pm 1, \pm 2$

Classically energy of rotating particle $E = \frac{1}{2}\frac{L^2}{I}$

Quantum mechanically energy of rotating particle $E = l(l+1)\frac{h^2}{8\pi^2 I}$

So, $L^2 = l(l+1)\frac{h^2}{4\pi^2}$

Therefore, the magnitude of the ***angular momentum*** $L = \sqrt{l(l+1)}\frac{h}{2\pi}$

The normalised wave function $\psi(\theta,\varphi) = \Theta(\theta)\Phi(\varphi)$ is denoted by $\Upsilon_{l,m_l}(\theta,\varphi)$. The normalised wave function $\Upsilon_{l,m_l}(\theta,\varphi)$ is known as ***spherical harmonics.***

The first few spherical harmonics

Azimuthal quantum number, l	Magnetic quantum number, m_l	Spherical harmonics, $\Upsilon_{l,m_l}(\theta,\varphi)$
0	0	$\left(\frac{1}{4\pi}\right)^{1/2}$
1	0	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
	±1	$\mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{\pm i\varphi}$
2	0	$\left(\frac{5}{16\pi}\right)^{1/2}\left(3\cos^2\theta - 1\right)$
	±1	$\mp\left(\frac{15}{8\pi}\right)^{1/2}\cos\theta.\sin\theta e^{\pm i\varphi}$

	±2	$\left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{\pm 2i\varphi}$

Qualitative treatment of hydrogen atom and hydrogen like ions: Setting up of Schrodinger equation in spherical polar coordinates, radial part, quantization of energy (only final energy expression); Average and most probable distance of electron from nucleus; setting up of Schrodinger equation for many electron atoms (He, Li)

Hydrogen like system

Hamiltonian operator $\hat{H} = \hat{T} + \hat{V}$

For hydrogen like system $V(r) = -\frac{Ze^2}{(4\pi\varepsilon_0)r}$ and $\hat{T} = -\frac{h^2}{8\pi^2\mu}\nabla^2$

Schrodinger equation for the rigid rotator $\hat{H}\psi = E\psi$

i.e $-\left[\frac{h^2}{8\pi^2\mu}\nabla^2 + \frac{Ze^2}{(4\pi\varepsilon_0)r}\right]\psi = E\psi$

The equation in terms of Spherical polar co-ordinate is

$$-\frac{h^2}{8\pi^2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]\psi(r,\theta,\varphi)$$

$$-\frac{Ze^2}{(4\pi\varepsilon_0)r}\psi(r,\theta,\varphi) - E\psi(r,\theta,\varphi) = 0$$

Consider $\psi(r,\theta,\varphi) = R(r)Y(\theta,\varphi)$

So, $$-\frac{h^2}{8\pi^2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]R(r)Y(\theta,\varphi)$$

$$-\frac{Ze^2}{(4\pi\varepsilon_0)r}R(r)Y(\theta,\varphi) - ER(r)Y(\theta,\varphi) = 0$$

Multiplying by r^2 we get

$$-\frac{h^2}{8\pi^2\mu}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]R(r)Y(\theta,\varphi)$$

$$= \left[\frac{h^2}{8\pi^2\mu}\left\{\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\right\}\frac{Ze^2 r}{(4\pi\varepsilon_0)} + r^2E\right]R(r)Y(\theta,\varphi)$$

Or, $$-R\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]Y = Y\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)R + \frac{8\pi^2\mu}{h^2}\left[\frac{Ze^2 r}{(4\pi\varepsilon_0)} + r^2E\right]RY$$

Dividing this by RY

$$-\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]Y = \frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)R + \frac{8\pi^2\mu}{h^2}\left[\frac{Ze^2 r}{(4\pi\varepsilon_0)} + r^2E\right]$$

Consider $-\frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]Y$

$$= \frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)R + \frac{8\pi^2\mu}{h^2}\left[\frac{Ze^2 r}{(4\pi\varepsilon_0)} + r^2 E\right] = l(l+1)$$

Angular equation $\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]Y(\theta,\varphi) = -l(l+1)Y(\theta,\varphi)$

Radial equation $\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)R(r) + \frac{8\pi^2\mu}{h^2}\left[\frac{Ze^2 r}{(4\pi\varepsilon_0)} + r^2 E\right] = l(l+1)R(r) = l(l+1)$

Simplifying the above equations the energy eigen value

$$E = -\frac{2\pi^2 Z^2 \mu e^4}{\left(n^2 h^2\right)\left(4\pi\varepsilon_0\right)^2} \qquad n = 1, 2, 3 \ldots$$

And $\psi_{nlm_l}(r,\theta,\varphi) = R_{nl}(r)Y_{l,m_l}(\theta,\varphi)$

Values of l	0	1	2	3	4
Notation of wave function	s	p	d	f	g

Hydrogenic Radial wavefunction $R_{nl}(r)$

Orbital	n	l	$R_{nl}(r)$
1s	1	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
2s	2	0	$\frac{1}{\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}\left(1-\frac{Zr}{2a_0}\right)e^{-Zr/2a_0}$
2p	2	1	$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{5/2} re^{-Zr/2a_0}$
3s	3	0	$\frac{2}{3\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}\left(1-\frac{2Zr}{3a_0}+\frac{2Z^2r^2}{27a_0^2}\right)e^{-Zr/3a_0}$
3p	3	1	$\frac{8}{27\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}-\frac{Z^2r^2}{6a_0^2}\right)e^{-Zr/3a_0}$
3d	3	2	$\frac{1}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{7/2} r^2 e^{-Zr/3a_0}$

Many electron atoms (He, Li)

Hamiltonian operator $\hat{H} = \hat{T} + \hat{V}$

(i) Kinetic energy operator for a *n*-dynamical identical particles $\hat{T} = -\frac{h^2}{8\pi^2 m}\sum_{i=1}^{n}\nabla_i^2$

for a *n*-dynamical non-identical particles $\hat{T} = -\frac{h^2}{8\pi^2}\sum_{i=1}^{n}\frac{1}{m_i}\nabla_i^2$

For helium atom $\hat{T} = -\frac{h^2}{8\pi^2 m_e}\nabla_1^2 - \frac{h^2}{8\pi^2 m_e}\nabla_2^2 = -\frac{h^2}{8\pi^2 m_e}\left(\nabla_1^2 + \nabla_2^2\right)$

For potential energy operator have two contributions, attraction potential energy and repulsion potential energy $V = -\frac{Ze^2}{(4\pi\varepsilon_0)r_1} - \frac{Ze^2}{(4\pi\varepsilon_0)r_2} + \frac{e^2}{(4\pi\varepsilon_0)r_{12}} = \frac{1}{4\pi\varepsilon_0}\left[-\frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{Ze^2}{r_{12}}\right]$

$$\therefore \qquad \hat{H} = -\frac{h^2}{8\pi^2 m_e}(\nabla_1 + \nabla_2) - \frac{1}{4\pi\varepsilon_0}\left(\frac{Ze^2}{r_1} + \frac{Ze^2}{r_2} - \frac{Ze^2}{r_{12}}\right)$$

Schrodinger equation $\hat{H}\psi = E\psi$

Q. Calculate the expectation value of *r* for an electron in the ground state of hydrogen atom.

Ans. The normalized wave function for the ground state of hydrogen atom is

$$\psi_{1,0,0} = R_{1,0}\Theta_{0,0}\Phi_0 = \left(\frac{1}{\pi a_0^3}\right)^{3/2} e^{-r/a_0}$$

$$\langle r \rangle = \langle \psi_{1,0,0}|r|\psi_{1,0,0}\rangle = \int\left[\left(\frac{1}{\pi a_0^3}\right)^{3/2} e^{-r/a_0} r \left(\frac{1}{\pi a_0^3}\right)^{3/2} e^{-r/a_0}\right]d\tau$$

$$= \int\left[\left(\frac{1}{\pi a_0^3}\right)^{3/2} e^{-r/a_0} r \left(\frac{1}{\pi a_0^3}\right)^{3/2} e^{-r/a_0}\right]d\tau$$

$$= \left(\frac{1}{\pi a_0^3}\right)^3 \int_0^\infty r^3 e^{-2r/a_0} dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi \qquad \left[d\tau = r^2 dr \sin\theta d\theta d\phi\right]$$

$$= \left(\frac{1}{\pi a_0^3}\right)^3 \int_0^\infty r^3 e^{-2r/a_0} dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi$$

$$= \left(\frac{1}{\pi a_0^3}\right)^3 \frac{3!}{(2/a_0)^4}(2)(2\pi) = \frac{3}{2}a_0$$

Q. Calculate the average distance of 2s electron from nucleus of H-atom.

Ans. $$\psi_{2s} = \psi_{2,0,0} = R_{2,0}\Theta_{0,0}\Phi_0 = \left[\left(\frac{1}{2a_0}\right)^{3/2}\left(2 - \frac{r}{a_0}\right)e^{-r/2a_0}\right]\left(\frac{1}{\sqrt{2}}\right)\left(\frac{1}{\sqrt{2\pi}}\right)$$

$$= \left(\frac{1}{\sqrt{32\pi}}\right)\left(\frac{1}{a_0}\right)^{3/2}\left(2 - \frac{r}{a_0}\right)e^{-r/2a_0}$$

$$\langle r \rangle = \langle \psi_{2,0,0}|r|\psi_{2,0,0}\rangle$$

$$= \int\left[\left(\frac{1}{\sqrt{32\pi}}\right)\left(\frac{1}{a_0}\right)^{3/2}\left(2 - \frac{r}{a_0}\right)e^{-r/2a_0} r \left(\frac{1}{\sqrt{32\pi}}\right)\left(\frac{1}{a_0}\right)^{3/2}\left(2 - \frac{r}{a_0}\right)e^{-r/2a_0}\right]d\tau$$

$$= \left(\frac{1}{32\pi}\right)\left(\frac{1}{a_0^3}\right)\int r^3\left(2 - \frac{r}{a_0}\right)^2 e^{-r/a_0} dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi$$

$$= \left(\frac{1}{32\pi}\right)\left(\frac{1}{a_0^3}\right)\int\left(4r^3 + \frac{r^5}{a_0^2} - \frac{4r^4}{a_0}\right)e^{-r/a_0} dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi$$

$$= \left(\frac{1}{32\pi}\right)\left(\frac{1}{a_0^3}\right)\left[4.\frac{3!}{(1/a_0)^4} + \frac{1}{a_0^2}\frac{5!}{(1/a_0)^6} - \frac{1}{a_0}\frac{4!}{(1/a_0)^5}\right](2)(2\pi)$$

$$= 6\,a_0$$

Q. Calculate the most probable distance of electron in 1s orbital of H-atom.

Ans. $\frac{d}{dr}\left(r^2 R_{1,0}^2\right) = 0$

So, $\frac{d}{dr}\left(r^2 e^{-2r/a_0}\right) = 0$

Or, $\left[2r + r^2\left(-\frac{2}{a_0}\right)\right] e^{-2r/a_0} = 0$

Or, $r = a_0$

Q. Calculate the most probable distance of electron in 2s orbital of H-atom.

Ans. $\frac{d}{dr}\left(r^2 R_{2,0}^2\right) = 0$

So, $\frac{d}{dr}\left[r^2\left(2 - \frac{r}{a_0}\right)^2 e^{-r/a_0}\right] = 0$

Or, $\frac{d}{dr}\left[\left(4r^2 + \frac{r^4}{a_0^2} - \frac{4r^3}{a_0}\right) e^{-r/a_0}\right] = 0$

Or, $\left[\left(8r + \frac{4r^3}{a_0^2} - \frac{12r^2}{a_0}\right) + \left(4r^2 + \frac{r^4}{a_0^2} - \frac{4r^3}{a_0}\right)\left(-\frac{1}{a_0}\right)\right] e^{-r/a_0} = 0$

Or, $8r + \frac{8r^3}{a_0^2} - \frac{16r^2}{a_0} - \frac{r^4}{a_0^3} = 0$

Or, $\left(\frac{r}{a_0}\right)^3 - 8\left(\frac{r}{a_0}\right)^2 + 16\left(\frac{r}{a_0}\right) - 8 = 0$

Or, $\left[\left(\frac{r}{a_0}\right)^2 - 6\left(\frac{r}{a_0}\right) + 4\right]\left(\frac{r}{a_0} - 2\right) = 0$

$\therefore$ $\frac{r}{a_0} - 2$ or, $r = 2a_0$

Again $\frac{r}{a_0} = \frac{6 \pm \sqrt{36 - 16}}{2} = 3 \pm \sqrt{5}$

Radial distribution function F_R = (volume of spherical shell) (probability density)

= $(4\pi r^2\, dr)(R^2)$

The radial distribution function means the total probability of finding the electron in a spherical shell of thickness dr located at the distance r from the nucleus.

Note: The charge within the shell (r and r + dr) is

$$\int_r^{r+dr} R^2 r^2 dr \int_0^{\pi} \Theta^2 \sin\theta d\theta \int_0^{2\pi} \Phi^2 d\phi$$

For normalized Θ and Φ functions

$$\int_r^{r+dr} R^2 r^2 dr \int_0^{\pi} \Theta^2 \sin\theta d\theta \int_0^{2\pi} \Phi^2 d\phi \; = \; \int_r^{r+dr} R^2 r^2 dr$$

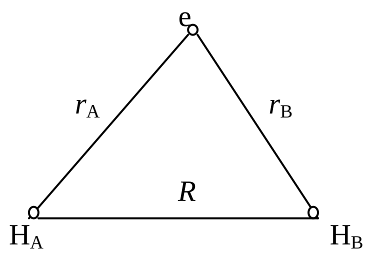
LCAO and HF-SCF: Covalent bond, valance bond and molecular orbital approaches, LCAO-MO treatment of H_2^+; bonding and antibonding orbitals; Qualitative extension to H_2; Comparisation of LCAO-MO and VB treatment of H_2 and their limitations; Hartee-Fock method development, SCF and configuration interaction (only basics)

LACO-MO of H_2^+

$$\psi_{\text{MO}} = C_1\psi_{1s(\text{A})} + C_2\psi_{1s(\text{B})}$$

The Schrodinger equation $\quad H_{\text{op}}\psi_{\text{MO}} = E\psi_{\text{MO}}$

$$H_{\text{op}} = -\frac{h^2}{8\pi^2 m}\nabla^2 - \frac{e^2}{(4\pi\varepsilon_0)r_{\text{A}}} - \frac{e^2}{(4\pi\varepsilon_0)r_{\text{B}}} + \frac{e^2}{(4\pi\varepsilon_0)R}$$



$$E = \frac{\langle\psi_{\text{MO}}|H_{\text{op}}|\psi_{\text{MO}}\rangle}{\langle\psi_{\text{MO}}|\psi_{\text{MO}}\rangle} = \frac{\langle C_1\psi_{1s(\text{A})} + C_2\psi_{1s(\text{B})}|H_{\text{op}}|C_1\psi_{1s(\text{A})} + C_2\psi_{1s(\text{B})}\rangle}{\langle C_1\psi_{1s(\text{A})} + C_2\psi_{1s(\text{B})}|C_1\psi_{1s(\text{A})} + C_2\psi_{1s(\text{B})}\rangle} =$$

$$\frac{C_1^2\langle\psi_{1s(\text{A})}|H_{\text{op}}|\psi_{1s(\text{A})}\rangle + C_2^2\langle\psi_{1s(\text{B})}|H_{\text{op}}|\psi_{1s(\text{B})}\rangle + C_1C_2\langle\psi_{1s(\text{A})}|H_{\text{op}}|\psi_{1s(\text{B})}\rangle + C_1C_2\langle\psi_{1s(\text{B})}|H_{\text{op}}|\psi_{1s(\text{A})}\rangle}{C_1^2\langle\psi_{1s(\text{A})}|\psi_{1s(\text{A})}\rangle + C_2^2\langle\psi_{1s(\text{B})}|\psi_{1s(\text{B})}\rangle + 2C_1C_2\langle\psi_{1s(\text{A})}|\psi_{1s(\text{B})}\rangle}$$

$$= \frac{C_1^2\langle\psi_{1s(\text{A})}|H_{\text{op}}|\psi_{1s(\text{A})}\rangle + C_2^2\langle\psi_{1s(\text{B})}|H_{\text{op}}|\psi_{1s(\text{B})}\rangle + 2C_1C_2\langle\psi_{1s(\text{A})}|H_{\text{op}}|\psi_{1s(\text{B})}\rangle}{C_1^2\langle\psi_{1s(\text{A})}|\psi_{1s(\text{A})}\rangle + C_2^2\langle\psi_{1s(\text{B})}|\psi_{1s(\text{B})}\rangle + 2C_1C_2\langle\psi_{1s(\text{A})}|\psi_{1s(\text{B})}\rangle}$$

$$= \frac{C_1^2\alpha_{\text{A}} + C_2^2\alpha_{\text{B}} + 2C_1C_2\beta_{\text{AB}}}{C_1^2 + C_2^2 + 2C_1C_2S_{\text{AB}}}$$ [β_{AB}, resonance integral; S_{AB}, overlapping integral]

Or, $\quad E\left(C_1^2 + C_2^2 + 2C_1C_2S_{\text{AB}}\right) = C_1^2\alpha_{\text{A}} + C_2^2\alpha_{\text{B}} + 2C_1C_2\beta_{\text{AB}}$ ... (1)

Differentiating w.r.t C_1 we get

$$(\partial E/\partial C_1)\left(C_1^2 + C_2^2 + 2C_1C_2S_{\text{AB}}\right) + E\left(2C_1 + 2C_2S_{\text{AB}}\right) = 2C_1\alpha_{\text{A}} + 2C_2\beta_{\text{AB}}$$

For at minima $\quad \partial E/\partial C_1 = 0$

$\therefore \quad E\left(2C_1 + 2C_2S_{\text{AB}}\right) = 2C_1\alpha_{\text{A}} + 2C_2\beta_{\text{AB}}$

Or, $\quad C_1\left(\alpha_{\text{A}} - E\right) + C_2\left(\beta_{\text{AB}} - ES_{\text{AB}}\right) = 0$

Similarly for $\partial E/\partial C_2$ we get

$$C_1\left(\beta_{\text{AB}} - ES_{\text{AB}}\right) + C_2\left(\alpha_B - E\right) = 0$$

In matrix form

$$\begin{vmatrix} \alpha_A - E & \beta_{\text{AB}} - ES_{\text{AB}} \\ \beta_{\text{AB}} - ES_{\text{AB}} & \alpha_B - E \end{vmatrix} \begin{vmatrix} C_1 \\ C_2 \end{vmatrix} = 0$$

For nontrivial solution determinant of coefficient is zero.

$$\begin{vmatrix} \alpha_A - E & \beta_{\mathrm{AB}} - ES_{\mathrm{AB}} \\ \beta_{\mathrm{AB}} - ES_{\mathrm{AB}} & \alpha_B - E \end{vmatrix} = 0$$

Here, $\alpha_A = \alpha_B = \alpha$

So, $\left(\beta_{\mathrm{AB}} - ES_{\mathrm{AB}}\right)^2 - \left(\alpha - E\right)^2 = 0$

Or, $\alpha - E = \pm\left(\beta_{\mathrm{AB}} - ES_{\mathrm{AB}}\right)$

So, the two roots are $E_+ = \dfrac{\alpha + \beta_{\mathrm{AB}}}{1 + S_{\mathrm{AB}}}$ and $E_- = \dfrac{\alpha - \beta_{\mathrm{AB}}}{1 - S_{\mathrm{AB}}}$

Using the above equation we get $C_1 = \pm C_2$

$\psi_{+\mathrm{MO}} = C_+(\psi_{1s(\mathrm{A})} + \psi_{1s(\mathrm{B})})$ and $\psi_{-\mathrm{MO}} = C_-(\psi_{1s(\mathrm{A})} - \psi_{1s(\mathrm{B})})$

$\left\langle \psi_{+\mathrm{MO}} \middle| \psi_{+\mathrm{MO}} \right\rangle = 1$

i.e $\left\langle C_+(\psi_{1s(\mathrm{A})} + \psi_{1s(\mathrm{B})} \middle| C_+(\psi_{1s(\mathrm{A})} + \psi_{1s(\mathrm{B})} \right\rangle = 1$

Or, $C_+^2 \left\{ \left\langle \psi_{1s(\mathrm{A})} \middle| \psi_{1s(\mathrm{A})} \right\rangle + \left\langle \psi_{1s(\mathrm{B})} \middle| \psi_{1s(\mathrm{B})} \right\rangle + 2\left\langle \psi_{1s(\mathrm{A})} \middle| \psi_{1s(\mathrm{B})} \right\rangle \right\} = 1$

Or, $C_+^2\left(1 + 1 + 2S_{AB}\right) = 1$

$\therefore$ $C_+ = \dfrac{1}{\sqrt{2\left(1 + S_{AB}\right)}}$

Similarly $C_- = \dfrac{1}{\sqrt{2\left(1 - S_{AB}\right)}}$

Now $\alpha_A = \left\langle \psi_{1s(\mathrm{A})} \middle| H_{\mathrm{op}} \middle| \psi_{1s(\mathrm{A})} \right\rangle$ and

$$H_{\mathrm{op}} = -\frac{h^2}{8\pi^2 m}\nabla^2 - \frac{e^2}{(4\pi\varepsilon_0)r_{\mathrm{A}}} - \frac{e^2}{(4\pi\varepsilon_0)r_{\mathrm{B}}} + \frac{e^2}{(4\pi\varepsilon_0)R}$$

So, $\alpha_A = \left\langle \psi_{1s(\mathrm{A})} \middle| -\dfrac{h^2}{8\pi^2 m}\nabla^2 - \dfrac{e^2}{(4\pi\varepsilon_0)r_{\mathrm{A}}} - \dfrac{e^2}{(4\pi\varepsilon_0)r_{\mathrm{B}}} + \dfrac{e^2}{(4\pi\varepsilon_0)R} \middle| \psi_{1s(\mathrm{A})} \right\rangle$

$= \left\langle \psi_{1s(\mathrm{A})} \middle| -\dfrac{h^2}{8\pi^2 m}\nabla^2 - \dfrac{e^2}{(4\pi\varepsilon_0)r_{\mathrm{A}}} \middle| \psi_{1s(\mathrm{A})} \right\rangle + \left\langle \psi_{1s(\mathrm{A})} \middle| -\dfrac{e^2}{(4\pi\varepsilon_0)r_{\mathrm{B}}} \middle| \psi_{1s(\mathrm{A})} \right\rangle +$

$\left\langle \psi_{1s(\mathrm{A})} \middle| \dfrac{e^2}{(4\pi\varepsilon_0)R} \middle| \psi_{1s(\mathrm{A})} \right\rangle$

$= E_{1s(\mathrm{H})} + J + \dfrac{e^2}{(4\pi\varepsilon_0)R}$

[J = Coulomb integral, electrostatic attraction between proton B and an electron in a 1s orbital centred on proton A]

$\beta_{\mathrm{AB}} = \left\langle \psi_{1s(\mathrm{A})} \middle| -\dfrac{h^2}{8\pi^2 m}\nabla^2 - \dfrac{e^2}{(4\pi\varepsilon_0)r_{\mathrm{A}}} - \dfrac{e^2}{(4\pi\varepsilon_0)r_{\mathrm{B}}} + \dfrac{e^2}{(4\pi\varepsilon_0)R} \middle| \psi_{1s(\mathrm{B})} \right\rangle$

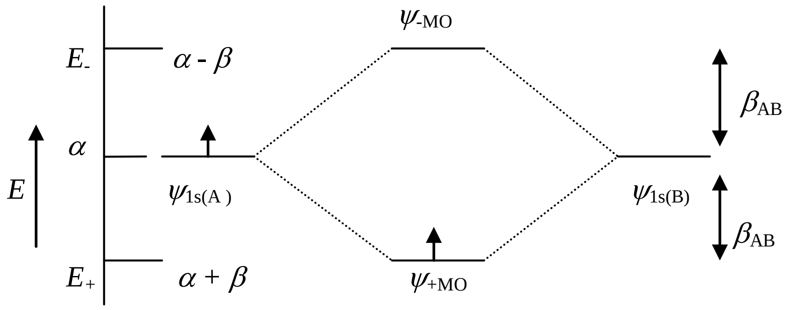
$= \left\langle \psi_{1s(\mathrm{A})} \middle| -\dfrac{h^2}{8\pi^2 m}\nabla^2 - \dfrac{e^2}{(4\pi\varepsilon_0)r_{\mathrm{B}}} \middle| \psi_{1s(\mathrm{B})} \right\rangle + \left\langle \psi_{1s(\mathrm{A})} \middle| -\dfrac{e^2}{(4\pi\varepsilon_0)r_{\mathrm{A}}} \middle| \psi_{1s(\mathrm{B})} \right\rangle +$

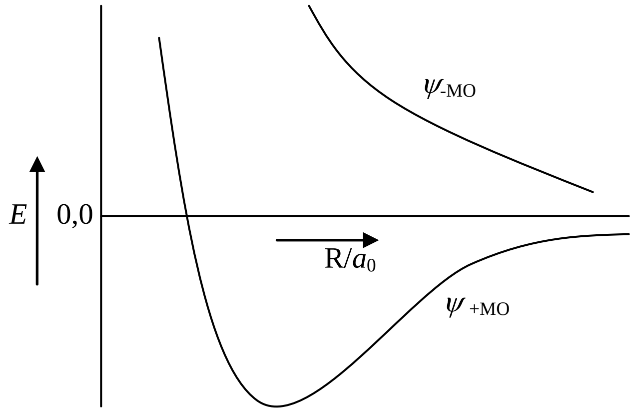
$\left\langle \psi_{1s(\mathrm{A})} \middle| \dfrac{e^2}{(4\pi\varepsilon_0)R} \middle| \psi_{1s(\mathrm{B})} \right\rangle$

$$= E_{1s(\mathrm{H})}S_{\mathrm{AB}} + K + \left(\frac{e^2}{(4\pi\varepsilon_0)R}\right)S_{\mathrm{AB}}$$

Now the exchange integral $K = \left\langle \psi_{1s(\mathrm{A})} \middle| -\frac{e^2}{(4\pi\varepsilon_0)r_{\mathrm{A}}} \middle| \psi_{1s(\mathrm{B})} \right\rangle$

[Exchange of electron between A and B]

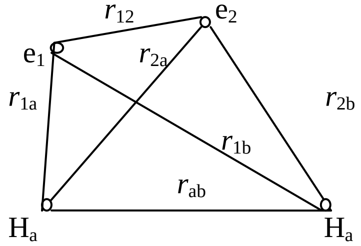




Hydrogen molecule **H_2**

MO

$$H_{\mathrm{op}} = -\frac{h^2}{8\pi^2 m}\nabla_1^2 - \frac{h^2}{8\pi^2 m}\nabla_2^2 - \frac{e^2}{(4\pi\varepsilon_0)r_{1a}} - \frac{e^2}{(4\pi\varepsilon_0)r_{2a}}$$
$$- \frac{e^2}{(4\pi\varepsilon_0)r_{1b}} - \frac{e^2}{(4\pi\varepsilon_0)r_{2b}} + \frac{e^2}{(4\pi\varepsilon_0)r_{ab}} + \frac{e^2}{(4\pi\varepsilon_0)r_{12}}$$



$$\psi = \psi_{\text{spatial}}\psi_{\text{spin}}$$

$$\psi_{\text{spatial}} = \psi_{+}(1)\psi_{+}(2)$$

$$\psi_{\text{spin}} = \frac{1}{\sqrt{2}}\{\alpha(1)\beta(2) - \alpha(1)\beta(2)\}$$

In LCAO-MO $\quad \psi_{+} = C_1\psi_{1s(\text{H}_\text{a})} + C_1\psi_{1s(\text{H}_b)}$

$$C_1 = C_2 = \frac{1}{\sqrt{2(1+S)}}$$

$$E = \frac{\langle \psi_{+}(1)\psi_{+}(2)|H_{\text{op}}|\psi_{+}(1)\psi_{+}(2)\rangle}{\langle \psi_{+}(1)\psi_{+}(2)|\psi_{+}(1)\psi_{+}(2)\rangle}$$

Calculated value – 30.68 eV (– 2.96 MJmol^{-1}) at internuclear distance 73 pm
Observed value – 31.95 eV (– 3.08 MJ mol^{-1}) at internuclear distance 74.1 pm

VB

$$\psi = \psi_{1s(\text{H}_\text{a})}(1)\psi_{1s(\text{H}_\text{b})}(2)$$

$$H_{\text{op}} = H_\text{a} + H_\text{b} + H'$$

$$H_\text{a} = -\frac{h^2}{8\pi^2 m}\nabla_1^2 - \frac{e^2}{(4\pi\varepsilon_0)r_{1a}} = -\frac{h^2}{8\pi^2 m}\nabla_2^2 - \frac{e^2}{(4\pi\varepsilon_0)r_{2a}}$$

$$H_\text{a} = -\frac{h^2}{8\pi^2 m}\nabla_2^2 - \frac{e^2}{(4\pi\varepsilon_0)r_{2\text{b}}} = -\frac{h^2}{8\pi^2 m}\nabla_1^2 - \frac{e^2}{(4\pi\varepsilon_0)r_{1\text{b}}}$$

$$H' = -\frac{e^2}{(4\pi\varepsilon_0)r_{2\text{a}}} - \frac{e^2}{(4\pi\varepsilon_0)r_{1\text{b}}} + \frac{e^2}{(4\pi\varepsilon_0)r_{12}} + \frac{e^2}{(4\pi\varepsilon_0)r_{\text{ab}}}$$

$$= -\frac{e^2}{(4\pi\varepsilon_0)r_{1\text{a}}} - \frac{e^2}{(4\pi\varepsilon_0)r_{2\text{b}}} + \frac{e^2}{(4\pi\varepsilon_0)r_{12}} + \frac{e^2}{(4\pi\varepsilon_0)r_{\text{ab}}}$$

$$E = \langle \psi|H|\psi\rangle$$

$$E = \left\langle \psi_{1s(\text{H}_\text{a})}(1)\psi_{1s(\text{H}_\text{b})}(2)\middle|H_\text{a} + H_\text{b} + H'\middle|\psi_{1s(\text{H}_\text{a})}(1)\psi_{1s(\text{H}_\text{b})}(2)\right\rangle$$

$$= \left\langle \psi_{1s(\text{H}_\text{a})}(1)\middle|H_\text{a}\middle|\psi_{1s(\text{H}_\text{a})}(1)\right\rangle\left\langle \psi_{1s(\text{H}_\text{b})}(2)\middle|\psi_{1s(\text{H}_\text{b})}(2)\right\rangle$$

$$+ \left\langle \psi_{1s(\text{H}_\text{b})}(2)\middle|H_\text{b}\middle|\psi_{1s(\text{H}_\text{b})}(2)\right\rangle\left\langle \psi_{1s(\text{H}_\text{a})}(1)\middle|\psi_{1s(\text{H}_\text{a})}(1)\right\rangle$$

$$+ E = \left\langle \psi_{1s(\text{H}_\text{a})}(1)\psi_{1s(\text{H}_\text{b})}(2)\middle|H'\middle|\psi_{1s(\text{H}_\text{a})}(1)\psi_{1s(\text{H}_\text{b})}(2)\right\rangle$$

$$E = E_{1s(\text{H}_\text{a})} + E_{1s(\text{H}_\text{b})} + Q$$

$$E_{binding} = E(H_2) - 2E(H) = Q$$

At 90 pm (r_{ab}) binding energy = 24 kJmol^{-1}
Heitler and London wave function

$$\psi_{\text{VB}} = C_1\psi_{1s(\text{H}_\text{a})}(1)\psi_{1s(\text{H}_\text{b})}(2) + C_2\psi_{1s(\text{H}_\text{a})}(2)\psi_{1s(\text{H}_\text{b})}(1)$$

$$\psi_{\text{VB}} = C_1\psi_1 + C_2\psi_2$$

Where, $\psi_1 = \psi_{1s(\text{H}_\text{a})}(1)\psi_{1s(\text{H}_\text{b})}(2)$ and $\psi_2 = \psi_{1s(\text{H}_\text{a})}(2)\psi_{1s(\text{H}_\text{b})}(1)$

$$E = \frac{\langle \psi_{\mathrm{VB}} | H_{\mathrm{op}} | \psi_{\mathrm{VB}} \rangle}{\langle \psi_{\mathrm{VB}} | \psi_{\mathrm{VB}} \rangle}$$

Minimizing E w.r.t C_1 and C_2 ($\partial E/\partial C_1 = 0$, $\partial E/\partial C_2 = 0$), we get

In matrix form

$$\begin{vmatrix} \alpha_1 - E & \beta_{12} - ES^2 \\ \beta_{12} - ES^2 & \alpha_1 - E \end{vmatrix} \begin{vmatrix} C_1 \\ C_2 \end{vmatrix} = 0$$

For nontrivial solution determinant of coefficient is zero.

$$\begin{vmatrix} \alpha_1 - E & \beta_{12} - ES^2 \\ \beta_{12} - ES^2 & \alpha_1 - E \end{vmatrix} = 0$$

Now $\alpha_1 = \alpha_2$

So, $(\alpha_1 - E)^2 - (\beta - ES^2)^2 = 0$

Therefore, $E_+ = \dfrac{\alpha + \beta}{1 + S^2}$ and $E_- = \dfrac{\alpha + \beta}{1 - S^2}$

So, $C_1 = \pm C_2$ $C_1 = C_2$

Many Electron Atoms

Hamiltonian operator for many electron system

$$H_{\mathrm{op}} = -\frac{h^2}{8\pi^2 m}\sum_{i=1}^{n}\nabla_i^2 - \sum_{i=1}^{n}\frac{Ze^2}{(4\pi\varepsilon_0)r_i} + \sum_{i=1}^{n}\sum_{j=i+1}^{n}\frac{e^2}{(4\pi\varepsilon_0)r_{ij}}$$

Schorindger equation

$$H_{\mathrm{op}}\psi = E\psi$$

The Perturbation Method

In perturbation method electronic repulsion terms are consider as small perturbation on Hamiltonian operator

$$H_{op}^0 = -\frac{h^2}{8\pi^2 m}\sum_{i=1}^{n}\nabla_i^2 - \sum_{i=1}^{n}\frac{Ze^2}{(4\pi\varepsilon_0)r_i}$$

$$H_{\mathrm{op}} = H_{op}^0 + \sum_{i=1}^{n}\sum_{j=i+1}^{n}\frac{e^2}{(4\pi\varepsilon_0)r_{ij}}$$

$$E = \frac{\int \psi^{0*} H_{op} \psi^0 d\tau}{\int \psi^{0*}\psi^0 d\tau}$$

Note: ψ^0 is not eigenfunction of H_{op}. So, not obtain exact energy eigenvalue.

$$\tilde{E} = \frac{\int \psi^{0*} H_{op}^0 \psi^0 d\tau + \int \psi^{0*}\left(\sum_{i=1}^{n}\sum_{j=i+1}^{n}\frac{e^2}{(4\pi\varepsilon_0)r_{ij}}\right)\psi^0 d\tau}{\int \psi^{0*}\psi^0 d\tau}$$

$$\tilde{E} = E^0 + \frac{\int \psi^{0*}\left(\sum_{i=1}^{n}\sum_{j=i+1}^{n}\frac{e^2}{(4\pi\varepsilon_0)r_{ij}}\right)\psi^0 d\tau}{\int \psi^{0*}\psi^0 d\tau}$$

For He atom, Z = 2. The second term is $\frac{5e^2}{(4\pi\varepsilon_0)(4a_0)} = -\frac{5}{2}E_H =$ –108.8 eV

Where $E_H = -\frac{5e^2}{(4\pi\varepsilon_0)(4a_0)}$ = –13.6 eV

Now $E^0 = E_1^0 + E_2^0 = \frac{Z^2}{n_1^2}E_H + \frac{Z^2}{n_2^2}E_H = 8E_H$ = 8(–13.6 eV) = –108.8 eV

Where, $Z = 2$, $n_1 = n_2 = 1$

∴ E = –108.8 eV + 34.0 eV = – 74.8 eV

The experimental value is – 79.0 eV.

The Variational method

In variational method wavefunction is written with few adjustable parameters.

The choice of best orbital is ***Slater orbital***. In Slater orbital angular part is same as Hydrogen like orbital but radial part is different.

$$R_{slater} = \left(\frac{2\zeta}{a_0}\right)^{n+1/2}\left[\frac{1}{(2n)!}\right]r^{n-1}e^{-\zeta r/a_0}$$

The parameter ζ is called orbital exponent.

$$\tilde{E} = \frac{\int \psi^* H_{op}\psi\, d\tau}{\int \psi^* \psi\, d\tau}$$

ψ is the approximate wave function.

Now $\tilde{E} \geq E^0$

Where, E^0 is the true value.

Minimizing the $\tilde{E}$ with respect to adjustable parameter.

Consider He atom, in hydrogen like orbital Z is replace by Z'.

$$\psi = \left(\frac{1}{\pi}\right)\left(\frac{Z'}{a_0}\right)^3 \exp(-Z'r_1/a_0)\exp(-Z'r_2/a_0)$$

$$H_{\text{op}} = -\frac{h^2}{8\pi^2 m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{Ze^2}{(4\pi\varepsilon_0)r_1} - \frac{Ze^2}{(4\pi\varepsilon_0)r_2} + \frac{e^2}{(4\pi\varepsilon_0)r_{12}}$$

and $\tilde{E} = \int \psi^* H_{op}\psi\, d\tau = \left[-2Z'^2 + \frac{27}{4}Z'\right]E_H$

Now $\left(\frac{\partial E}{\partial Z'}\right) = \left(-4Z' + \frac{27}{4}\right)E_H = 0$

∴ $Z' = \frac{27}{16}$

$$\left[-2\left(\frac{27}{16}\right)^2 + \left(\frac{27}{4}\right)\left(\frac{27}{16}\right)\right]\left(-13.6 \text{ ev}\right) = -77.5 \text{ ev}$$

SCF (Self-Consistent Field) Method (Hartree – 1928)

(i) Total wave function of a system is a product of one-electron wave function.

$$\psi = \varphi(1)\varphi(2)......\varphi(n)$$

One electron wave function is written as trial function.

(ii) Each electron is moving in an average spherically symmetric potential energy V_i. The potential energy arises due to nuclear attraction and repulsion from all other electrons. V_i obtain numerically using electrons wave function.

(iii) Write one electron Schrodinger equation

$$-\frac{h^2}{8\pi^2 m}\nabla_i^2\varphi_i + V_i\varphi_i = E_i\varphi_i \qquad \tilde{E} = \sum_{i=1}^{n}\tilde{E}_i$$

$$H_{\text{op}}\psi_{\text{MO}} = E\psi_{\text{MO}}$$

Or, $$\left[2r + r^2\left(-\frac{2}{a_0}\right)\right]e^{-2r/a_0} = 0$$

hree(i) Vector addition $\vec{a}+\vec{b}=\vec{b}+\vec{a}$ $(\vec{a}+\vec{b})+\vec{c}=\vec{a}+(\vec{b}+\vec{c})$

(ii) Multiplication of vector by a scalar $|\lambda\vec{a}|=|\lambda||\vec{a}|$

(iii) Components of vector $\vec{r}=x\hat{i}+y\hat{j}+z\hat{k}$