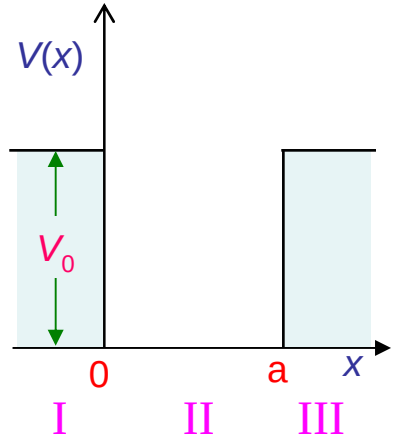
The Particle in a Rectangular Well

Consider a potential well with walls of finite height.

$V(x) = V_0 \qquad 0 > x \quad x > a$

$V(x) = 0 \qquad 0 \leqslant x \leqslant a$



How does this change affect the solution of the particle in a box problem? What are the boundary conditions?

Solve the Schrödinger Equation for the three regions:

$$\psi_I = C\exp\left\{\left[2m(V_0 - E)\right]^{1/2} x/\hbar\right\} + D\exp\left\{-\left[2m(V_0 - E)\right]^{1/2} x/\hbar\right\}$$

$$\psi_{II} = A\cos\left[(2mE)^{1/2} x/\hbar\right] + B\sin\left[(2mE)^{1/2} x/\hbar\right]$$

$$\psi_{III} = F\exp\left\{\left[2m(V_0 - E)\right]^{1/2} x/\hbar\right\} + G\exp\left\{-\left[2m(V_0 - E)\right]^{1/2} x/\hbar\right\}$$

Boundary conditions

$\psi_I \to 0$ as $x \to -\infty \Rightarrow D = 0$

$\psi_{III} \to 0$ as $x \to \infty \Rightarrow F = 0$

$\psi_I = \psi_{II}$ at $x = 0 \Rightarrow C = A$

$\psi_{II} = \psi_{III}$ at $x = a \Rightarrow G = fn(A)$

limited solutions impose quantization

$d\psi_I/dx = d\psi_{II}/dx$ at $x = 0 \Rightarrow B = (V_0 - E)^{1/2} A/E^{1/2}$

$d\psi_{II}/dx = d\psi_{III}/dx$ at $x = a \Rightarrow (2E - V_0)\sin\left[(2mE)^{1/2} a/\hbar\right] = 2\left(V_0 E - E^2\right)^{1/2}\cos\left[(2mE)^{1/2} a/\hbar\right]$

Solutions for the Particle in a Finite Box

The energy levels are given by $E = \varepsilon V_0$ where ε is a dimensionless parameter which satisfies the equation

$$(2\varepsilon - 1)\sin\left(b\varepsilon^{1/2}\right) - 2\left(\varepsilon - \varepsilon^2\right)^{1/2}\cos\left(b\varepsilon^{1/2}\right) = 0 \qquad \text{where} \qquad b = \left(2mV_0\right)^{1/2} a/\hbar$$

best solved numerically

The number of bound states is given by $N - 1 < b/\pi \leqslant N$

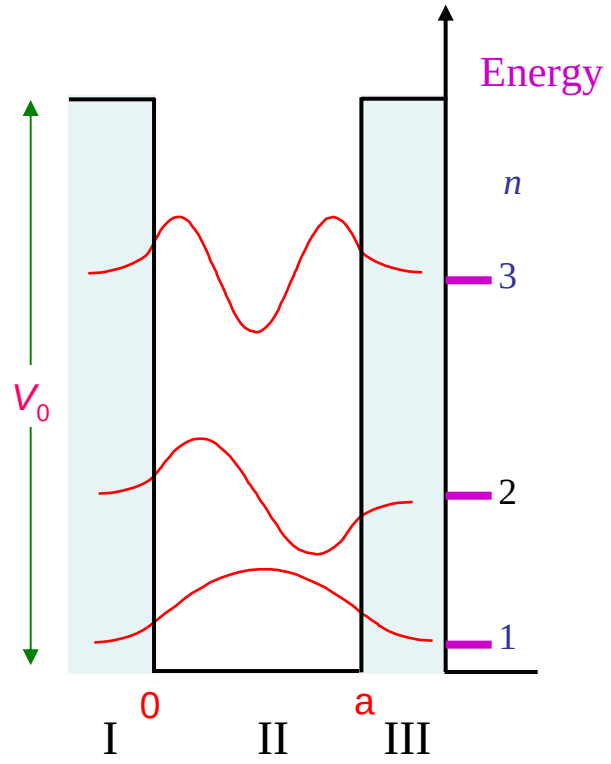
The wave functions are

$$\psi_{\mathrm{I}} = A\exp\{\kappa x\} \qquad \kappa = \left[2m(V_0 - E)/\hbar^2\right]^{1/2} \qquad x < 0$$

$$\psi_{\mathrm{II}} = A\cos\left[\left(2mE\right)^{1/2} x/\hbar\right] + B\sin\left[\left(2mE\right)^{1/2} x/\hbar\right]$$

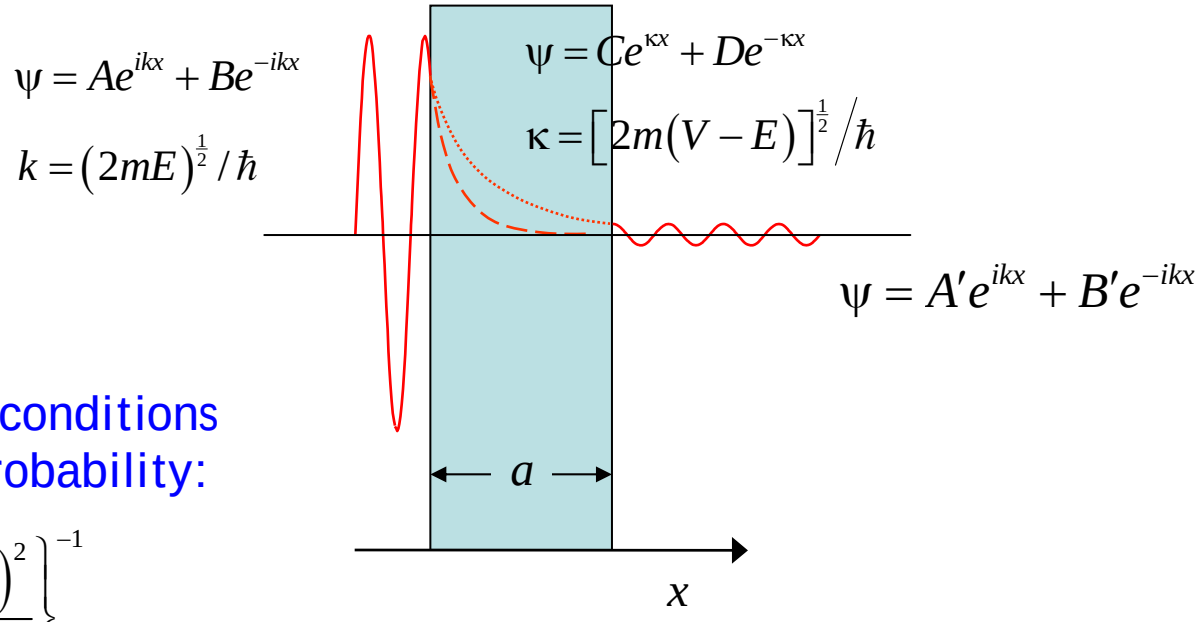
$$\psi_{\mathrm{III}} = G\exp\{-\kappa x\} \qquad \kappa = \left[2m(V_0 - E)/\hbar^2\right]^{1/2} \qquad x > 0$$

- Inside the box the functions look like those of the infinite well.
- The wave functions penetrate the walls and decay exponentially.



Tunnelling

Consider a particle of energy *E* striking a potential barrier of height *V*.

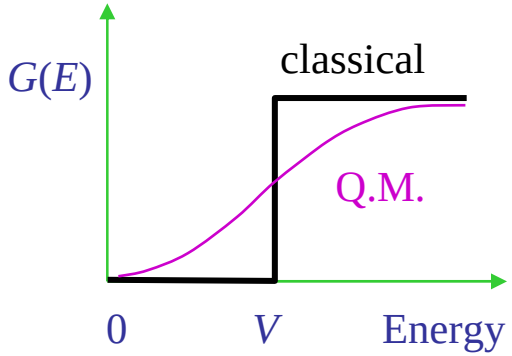


Application of boundary conditions gives the transmission probability:

$$G = \frac{A'^2}{A^2} = \left\{ 1 + \frac{\left(e^{\kappa a} - e^{-\kappa a}\right)^2}{16\frac{E}{V}\left(1-\frac{E}{V}\right)} \right\}^{-1}$$

Tunnelling depends on:

- the mass of the particle
- its energy (compared to the barrier)
- the width of the barrier



Internal Coordinates and Reduced Mass

If the potential energy of a system depends only on the internal coordinates of the system, then the motion of the centre of mass can always be separated from the internal motion.

Consider two point masses m_1 and m_2, both in motion and interacting with each other.

$$E = \tfrac{1}{2} m_1 (\dot{x}_1^{\,2} + \dot{y}_1^{\,2} + \dot{z}_1^{\,2}) + \tfrac{1}{2} m_2 (\dot{x}_2^{\,2} + \dot{y}_2^{\,2} + \dot{z}_2^{\,2}) + V(x_1, y_1, z_1, x_2, y_2, z_2)$$

Define centre of mass coordinates: $X = \dfrac{m_1 x_1 + m_2 x_2}{m_1 + m_2}$ $Y = \dfrac{m_1 y_1 + m_2 y_2}{m_1 + m_2}$ $Z = \dfrac{m_1 z_1 + m_2 z_2}{m_1 + m_2}$

and internal coordinates: $x = x_1 - x_2$ $y = y_1 - y_2$ $z = z_1 - z_2$

then $$E = \underbrace{\tfrac{1}{2}(m_1 + m_2)(\dot{X}^2 + \dot{Y}^2 + \dot{Z}^2)}_{\text{translational energy}} + \underbrace{\tfrac{1}{2}\mu(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)}_{\text{internal energy}} + V(x, y, z)$$

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

Internal Coordinates – 2 Dimensional Case

Consider two point masses m_1 and m_2, both in motion and interacting with each other.

$$T = \tfrac{1}{2} m_1 (\dot{x}_1^{\,2} + \dot{y}_1^{\,2}) + \tfrac{1}{2} m_2 (\dot{x}_2^{\,2} + \dot{y}_2^{\,2})$$

Define centre of mass coordinates: $X = \dfrac{m_1 x_1 + m_2 x_2}{m_1 + m_2}$ $Y = \dfrac{m_1 y_1 + m_2 y_2}{m_1 + m_2}$

and internal coordinates: $x = x_1 - x_2$ $y = y_1 - y_2$

$$(m_1 + m_2)\dot{X} = m_1 \dot{x}_1 + m_2 \dot{x}_2 \qquad (m_1 + m_2)\dot{Y} = m_1 \dot{y}_1 + m_2 \dot{y}_2$$

$$(m_1 + m_2)^2 \dot{X}^2 = m_1^2 \dot{x}_1^2 + m_2^2 \dot{x}_2^2 + 2 m_1 m_2 \dot{x}_1 \dot{x}_2 \qquad (m_1 + m_2)^2 \dot{Y}^2 = m_1^2 \dot{y}_1^2 + m_2^2 \dot{y}_2^2 + 2 m_1 m_2 \dot{y}_1 \dot{y}_2$$

$$\begin{aligned}(m_1 + m_2)^2 (\dot{X}^2 + \dot{Y}^2) &= (m_1 + m_2)(m_1 \dot{x}_1^2 + m_2 \dot{x}_2^2 + m_1 \dot{y}_1^2 + m_2 \dot{y}_2^2) \\ &\quad - m_1 m_2 (\dot{x}_1^2 + \dot{x}_2^2 + \dot{y}_1^2 + \dot{y}_2^2) + 2 m_1 m_2 (\dot{x}_1 \dot{x}_2 + \dot{y}_1 \dot{y}_2) \\ &= (m_1 + m_2)(m_1 \dot{x}_1^2 + m_2 \dot{x}_2^2 + m_1 \dot{y}_1^2 + m_2 \dot{y}_2^2) - m_1 m_2 (\dot{x}_1 - \dot{x}_2)^2 - m_1 m_2 (\dot{y}_1 - \dot{y}_2)^2\end{aligned}$$

$$\tfrac{1}{2}(m_1 + m_2)(\dot{X}^2 + \dot{Y}^2) = \tfrac{1}{2}(m_1 \dot{x}_1^2 + m_2 \dot{x}_2^2 + m_1 \dot{y}_1^2 + m_2 \dot{y}_2^2) - \tfrac{1}{2} \frac{m_1 m_2}{(m_1 + m_2)} (\dot{x}^2 + \dot{y}^2)$$

$$\tfrac{1}{2}(m_1 + m_2)(\dot{X}^2 + \dot{Y}^2) + \tfrac{1}{2}\mu(\dot{x}^2 + \dot{y}^2) = \tfrac{1}{2}(m_1 \dot{x}_1^2 + m_2 \dot{x}_2^2 + m_1 \dot{y}_1^2 + m_2 \dot{y}_2^2) = T \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

translation internal total kinetic energy

Vectors in Quantum Mechanics

Generalize concept of classical vector in Euclidean space into *n* dimensions (hyperspace)

$$\underset{\sim}{a} = (a_1, a_2, a_3, \ldots, a_n) = a_1 \mathrm{e}_1 + a_2 \mathrm{e}_2 + a_3 \mathrm{e}_3 + \ldots + a_n \mathrm{e}_n$$

The unit vectors form an orthonormal basis:

$$\mathrm{e}_1 = (1,0,0,\ldots)$$
$$\mathrm{e}_2 = (0,1,0,\ldots)$$
$$\mathrm{e}_3 = (0,0,1,\ldots)$$
$$\mathrm{e}_n = (0,0,\ldots,1)$$

The magnitude of the vector $= |a| = \left(a_1^2 + a_2^2 + a_3^2 + \ldots + a_n^2\right)^{1/2}$

A wave function can be represented by a vector:

$$\psi_a = |a\rangle = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \end{pmatrix} \quad \text{with} \quad \langle a| = \left(a_1^* \, a_2^* \ldots a_n^*\right)$$

The inner product ≡ scalar product $= \langle \psi_a | \psi_b \rangle = a_1^* b_1 + a_2^* b_2 + \ldots + a_n^* b_n$

Vectors are normalized if $|a| = 1$, i.e. $\langle a | a \rangle = 1$ and orthogonal if $\langle a | b \rangle = 0$

A state function is typically expressed in a basis set of eigenfunctions.

$$\Psi = \sum_k c_k |k\rangle \quad \text{where} \quad \hat{\mathrm{A}} |k\rangle = \alpha_k |k\rangle$$

The coefficient c_j is the component in the direction of the base vector $|j\rangle$

$$\langle j | \Psi \rangle = \sum_k c_k \langle j | k \rangle = c_j$$

Orbital Angular Momentum Operators

Classical: $$\underset{\sim}{L} = \underset{\sim}{r} \times \underset{\sim}{p} = \begin{vmatrix} \underset{\sim}{\mathrm{i}} & \underset{\sim}{\mathrm{j}} & \underset{\sim}{\mathrm{k}} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} = \left(yp_z - xp_y, zp_x - xp_z, xp_y - yp_z \right)$$

QM: $$\hat{L} = -i\hbar\left(\underset{\sim}{r} \times \nabla\right) = -i\hbar \begin{vmatrix} \underset{\sim}{\mathrm{i}} & \underset{\sim}{\mathrm{j}} & \underset{\sim}{\mathrm{k}} \\ x & y & z \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \end{vmatrix}$$

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

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

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

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

In spherical polar coordinates

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

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

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

$$\hat{L}^2 = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \right)$$

Orbital Angular Momentum Operators – 2

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

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

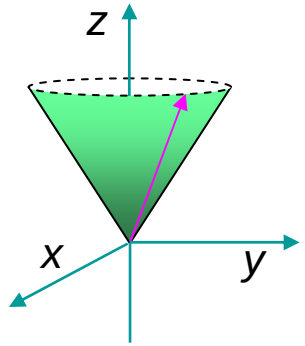
It is not possible to determine precise values of L_x and L_y simultaneously…

…but it is possible to determine precise values of L^2 and one component.

$$\hat{L}^2\,\mathrm{Y}_{l,m}(\theta,\phi)=\hbar^2 l(l+1)\,\mathrm{Y}_{l,m}(\theta,\phi)$$

$$\hat{L}_z\Phi_m(\phi)=m\hbar\,\Phi_m(\phi)$$

$$\hat{L}_z\,\mathrm{Y}_{l,m}(\theta,\phi)=m\hbar\,\mathrm{Y}_{l,m}(\theta,\phi)$$



Since $\left(\hat{L}^2-\hat{L}_z{}^2\right)\mathrm{Y}_{l,m}(\theta,\phi)=\left(\hat{L}_x{}^2+\hat{L}_y{}^2\right)\mathrm{Y}_{l,m}(\theta,\phi)=\left[l(l+1)-m^2\right]\mathrm{Y}_{l,m}(\theta,\phi)$

and the sum of the square components of angular momentum cannot be negative,

$\left[l(l+1)-m^2\right]\geqslant 0$ or $|m|\leqslant l$ i.e. $m=0,\pm1,\pm2,\ldots,\pm l$

Ladder Operators

Define raising and lowering operators

$$\hat{L}_+ = \hat{L}_x + i\hat{L}_y \qquad \hat{L}_x = \tfrac{1}{2}\left(\hat{L}_+ + \hat{L}_-\right)$$
$$\hat{L}_- = \hat{L}_x - i\hat{L}_y \qquad \hat{L}_y = \tfrac{1}{2i}\left(\hat{L}_+ - \hat{L}_-\right)$$

In spherical polar coordinates

$$\hat{L}_+ = \hbar e^{i\phi}\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right)$$
$$\hat{L}_- = \hbar e^{-i\phi}\left(-\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right)$$

$$\left[\hat{L}^2, \hat{L}_+\right] = \left[\hat{L}^2, \hat{L}_-\right] = 0$$

$$\left[\hat{L}_z, \hat{L}_+\right] = \hbar\hat{L}_+ \quad \text{and} \quad \left[\hat{L}_z, \hat{L}_-\right] = -\hbar\hat{L}_-$$

$$\left[\hat{L}_+, \hat{L}_-\right] = 2\hbar\hat{L}_z$$

$$\hat{L}_z\hat{L}_+|m\rangle = \hat{L}_+\hat{L}_z|m\rangle + \hbar\hat{L}_+|m\rangle = m\hbar\hat{L}_+|m\rangle + \hbar\hat{L}_+|m\rangle$$
$$= (m+1)\hbar\hat{L}_+|m\rangle$$

$$\hat{L}_z\left(\hat{L}_+|m\rangle\right) = (m+1)\hbar\left(\hat{L}_+|m\rangle\right)$$
$$\hat{L}_z\left(\hat{L}_-|m\rangle\right) = (m-1)\hbar\left(\hat{L}_-|m\rangle\right)$$

$\left(\hat{L}_+|m\rangle\right)$ and $\left(\hat{L}_-|m\rangle\right)$ are eigenfunctions of $\hat{L}_z$

$\hat{L}_+$ raises m and $\hat{L}_-$ lowers it.

$$\hat{L}_+|l,m\rangle = \left\{l(l+1) - m(m+1)\right\}^{1/2}|l,m+1\rangle \qquad = 0 \text{ for } m = l$$

$$\hat{L}_-|l,m\rangle = \left\{l(l+1) - m(m-1)\right\}^{1/2}|l,m-1\rangle \qquad = 0 \text{ for } m = -l$$

laddering is confined to

$$m = 0, \pm 1, \pm 2, \ldots, \pm l$$

How to Generate Orthonormal Functions

Suppose you have a set of functions $\phi_1, \phi_2, \phi_3, \ldots$ which are not orthogonal.

The Gram-Schmidt procedure generates an orthonormal basis set $\psi_1, \psi_2, \psi_3, \ldots$

1. Normalize the first function $$|\psi_1\rangle = \frac{1}{\langle\phi_1|\phi_1\rangle^{1/2}}|\phi_1\rangle$$

2. Subtract from the second vector its projection along the first. $$|\psi_2'\rangle = |\phi_2\rangle - \langle\psi_1|\phi_2\rangle|\psi_1\rangle$$

3. Normalize $|\psi_2'\rangle$ $$|\psi_2\rangle = \frac{1}{\langle\psi_2'|\psi_2'\rangle^{1/2}}|\psi_2'\rangle$$

4. Subtract from the next vector its projections along the earlier ones. $$|\psi_3'\rangle = |\phi_3\rangle - \langle\psi_1|\phi_3\rangle|\psi_1\rangle - \langle\psi_2|\phi_3\rangle|\psi_2\rangle$$

5. Normalize and continue.

Generation of Orthonormal Functions – Example

Suppose you have a set of functions ϕ_1, ϕ_2, ϕ_3, which satisfy the conditions:

$$\langle \phi_j | \phi_k \rangle = 2 \quad \text{for } j = k \quad \text{and} \quad \langle \phi_j | \phi_k \rangle = 1 \quad \text{for } j \neq k$$

Generate an orthonormal basis set.

$$|\psi_1\rangle = \frac{1}{\langle \phi_1 | \phi_1 \rangle^{1/2}} |\phi_1\rangle = \frac{1}{\sqrt{2}} |\phi_1\rangle$$

$$|\psi_2'\rangle = |\phi_2\rangle - \langle \psi_1 | \phi_2 \rangle |\psi_1\rangle = |\phi_2\rangle - \tfrac{1}{2}\langle \phi_1 | \phi_2 \rangle |\phi_1\rangle = |\phi_2\rangle - \tfrac{1}{2}|\phi_1\rangle$$

$$\langle \psi_2' | \psi_2' \rangle = \langle \phi_2 | \phi_2 \rangle - \tfrac{1}{2}\langle \phi_2 | \phi_1 \rangle - \tfrac{1}{2}\langle \phi_1 | \phi_2 \rangle + \tfrac{1}{4}\langle \phi_1 | \phi_1 \rangle = 2 - 1 + \tfrac{1}{2} = \tfrac{3}{2}$$

$$|\psi_2\rangle = \sqrt{\tfrac{2}{3}} |\phi_2\rangle - \sqrt{\tfrac{1}{6}} |\phi_1\rangle$$

$$\begin{aligned} |\psi_3'\rangle &= |\phi_3\rangle - \langle \psi_1 | \phi_3 \rangle |\psi_1\rangle - \langle \psi_2 | \phi_3 \rangle |\psi_2\rangle \\ &= |\phi_3\rangle - \tfrac{1}{2}\langle \phi_1 | \phi_3 \rangle |\phi_1\rangle - \tfrac{2}{3}\langle \phi_2 - \tfrac{1}{2}\phi_1 | \phi_3 \rangle |\phi_2 - \tfrac{1}{2}\phi_1\rangle \\ &= |\phi_3\rangle - \tfrac{1}{2}|\phi_1\rangle - \tfrac{2}{3}\cdot\tfrac{1}{2}|\phi_2 - \tfrac{1}{2}\phi_1\rangle \\ &= |\phi_3\rangle - \tfrac{1}{3}|\phi_2\rangle - \tfrac{1}{3}|\phi_1\rangle \end{aligned}$$

The Virial Theorem

If the potential energy has a r^n dependence, then $\langle T \rangle = \frac{1}{2} n \langle V \rangle$

e.g. (1) the H atom $V \propto r^{-1}$

$$\langle E \rangle = \langle T \rangle + \langle V \rangle$$
$$= -\tfrac{1}{2}\langle V \rangle + \langle V \rangle = \tfrac{1}{2}\langle V \rangle = -\langle T \rangle$$

e.g. (2) the harmonic oscillator $V \propto r^2$

$$\langle T \rangle = \langle V \rangle = \tfrac{1}{2}\langle E \rangle$$

A more general version of the Quantum Mechanical Virial Theorem is

$$\langle T \rangle = \tfrac{1}{2}\left\langle \sum_j q_j \frac{\partial V}{\partial q_j} \right\rangle$$

Harmonic Oscillator Ladder Operators

Transform the Schrödinger Equation $-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}+\frac{1}{2}k\,x^2=E\psi$ into dimensionless form

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}y^2}-y^2\right)\psi_\lambda=-\lambda\psi_\lambda$$ with substitutions $\omega_0=\sqrt{\frac{k}{\mu}}$, $\lambda=\frac{2E}{\hbar\omega_0}$, $y=\sqrt{\frac{\mu\omega_0}{\hbar}}\cdot x$

Define $\hat{a}=\left(\frac{\mathrm{d}}{\mathrm{d}y}+y\right)$ and $\hat{a}^+=\left(\frac{\mathrm{d}}{\mathrm{d}y}-y\right)$

so that

$$\hat{a}\hat{a}^+=\frac{\mathrm{d}^2}{\mathrm{d}y^2}-y^2-1$$

$$\hat{a}^+\hat{a}=\frac{\mathrm{d}^2}{\mathrm{d}y^2}-y^2+1$$

and

$$\hat{a}\,\hat{a}^+\psi_\lambda=-(\lambda+1)\psi_\lambda$$

$$\hat{a}^+\hat{a}\,\psi_\lambda=-(\lambda-1)\psi_\lambda$$

$$\left[\hat{a}^+,\hat{a}\right]=2$$

alternative forms of the Schrödinger eqn.

premultiply $\hat{a}\,\hat{a}^+\hat{a}\,\psi_\lambda=-(\lambda-1)\hat{a}\,\psi_\lambda$

apply commutator $\left(\hat{a}^+\hat{a}-2\right)(\hat{a}\,\psi_\lambda)=-(\lambda-1)(\hat{a}\,\psi_\lambda)$

$$\left(\hat{a}^+\hat{a}\right)(\hat{a}\,\psi_\lambda)=-(\lambda-3)(\hat{a}\,\psi_\lambda)$$

But $\hat{a}^+\hat{a}\,\psi_{\lambda-2}=-(\lambda-3)\psi_{\lambda-2}$

$\therefore\ \psi_{\lambda-2}\propto\hat{a}\,\psi_\lambda$

$\hat{a}$ transforms the wave function to one of lower energy.

Similarly $\hat{a}^+$ generates a higher energy function.

Harmonic Oscillator Ladder Operators – 2

Successive operations of $\hat{a}$ give wave functions labeled with $\lambda-2,\ \lambda-4,\ \lambda-6,\ \ldots$

Successive operations of $\hat{a}^{+}$ give wave functions labeled with $\lambda+2,\ \lambda+4,\ \lambda+6,\ \ldots$

But how far?

There must be a minimum value of λ corresponding to the lowest possible energy. $E \geqslant 0$

Then $\hat{a}\,\psi_{\lambda_{\min}} = 0$

$$\hat{a}^{+}\hat{a}\,\psi_{\lambda_{\min}} = 0 = -(\lambda-1)\psi_{\lambda_{\min}} \quad \text{i.e.} \quad \lambda_{\min} = 1 \qquad \lambda = 1,3,5,\ldots(2n+1) \qquad n = 0,1,2,\ldots$$

Quantized energy levels: $E = \frac{1}{2}\hbar\omega_0\lambda = \frac{1}{2}\hbar\omega_0(2n+1) = \hbar\omega_0\left(n+\frac{1}{2}\right)$

The wave functions can be generated from the ground state

$$\hat{a}\,\psi_0 = \left(\frac{\mathrm{d}}{\mathrm{d}y} + y\right)\psi_0 = 0 \quad \Rightarrow \quad \psi_0 = c_0\, e^{-\frac{1}{2}y^2}$$

and successive operations of $\hat{a}^{+}$ $\quad \psi_n = c_n\left(\hat{a}^{+}\right)^n \psi_0$

$$= c_n H_n(y) e^{-\frac{1}{2}y^2}$$

Hermite Polynomials

$$H_n(y) = (-1)^n\, \mathrm{e}^{y^2}\, \frac{\mathrm{d}^n}{\mathrm{d}y^n}\mathrm{e}^{-y^2}$$

$$H_0 = 1$$

$$H_1 = 2y$$

$$H_2 = 4y^2 - 2$$

$$H_3 = 8y^3 - 12y$$

Nuclear Spin Statistics

Pauli Principle — The total wave function must be antisymmetric with respect to interchange of fermions and symmetric for exchange of bosons.

Consider the H_2 molecule $\quad \Psi_{\text{Total}} = \psi_{\text{el}}\psi_{\text{vib}}\psi_{\text{rot}}\psi_{\text{nucl. spin}}$

ψ_{el} is symmetric for the ground state.

ψ_{vib} is symmetric for the ground state.

$\psi_{\text{rot}} \rightarrow (-1)^J \psi_{\text{rot}}$ i.e. the symmetry alternates with J, the rotational quantum number

look at the spherical harmonics

$$\psi_{\text{nucl. spin}} = \begin{cases} \alpha(1)\alpha(2) \\ \left[\alpha(1)\beta(2)+\beta(1)\alpha(2)\right]/\sqrt{2} \\ \beta(1)\beta(2) \end{cases} \quad \text{symmetric} \quad \text{ortho hydrogen}$$

$$\left[\alpha(1)\beta(2)-\beta(1)\alpha(2)\right]/\sqrt{2} \quad -\text{ antisymmetric} \quad \text{para hydrogen}$$

Para hydrogen only has odd J rotational states. Ortho only has even J states.

Slater Determinants

Pauli Principle The total wave function must be antisymmetric

Consider the Li atom, which has three indistinguishable electrons.

The ground state has two electrons in 1s and one in 2s.

An acceptable wave function is

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

often written as

$$\psi = \frac{1}{\sqrt{6}} \begin{vmatrix} 1s(1) & \overline{1s}(1) & 2s(1) \\ 1s(2) & \overline{1s}(2) & 2s(2) \\ 1s(3) & \overline{1s}(3) & 2s(3) \end{vmatrix} = \left|1\bar{1}2\right\rangle - \left|12\bar{1}\right\rangle + \left|\bar{1}21\right\rangle - \left|\bar{1}\bar{1}2\right\rangle + \left|2\bar{1}\bar{1}\right\rangle - \left|2\bar{1}\bar{1}\right\rangle$$

in shorthand $\psi = \left|1s\,\overline{1s}\,2s\right|$

In general $\psi = \left|1s\,\overline{1s}\,2s\,\overline{2s}\,2p\,\overline{2p}\,2p...\right|$

with implied normalization constant $\frac{1}{\sqrt{n!}}$