Advertisement: CAP prize exam Feb 4 @ 2pm.

commuting operators

$[A, B] = 0 \Rightarrow$ can diagonalise simultaneously (procedure below)

Example: SP $A = \begin{pmatrix} 1 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 1 \end{pmatrix}$; $B = \begin{pmatrix} 2 & 1 & 1 \\ 1 & 0 & -1 \\ 1 & -1 & 2 \end{pmatrix}$

$\Rightarrow AB = BA = \begin{pmatrix} 3 & 0 & 3 \\ 0 & 0 & 0 \\ 3 & 0 & 3 \end{pmatrix}$

eigen- (vectors) (values)

diagonalising A gives: $v_1 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$ for $a_1 = 0$

$v_2 = \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix}$ for $a_2 = 2$ degenerate

$v_3 = \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}$ for $a_3 = 0$

$B v_1 = v_3$

$B v_3 = v_3 + 2 v_1$

degeneracy $\Rightarrow$ v_1 and v_3 not eigenvectors of B, but v_2 is.

Why? $B \cdot v_2 = \cdots = 3 v_2 \Rightarrow B$ has eigenvector v_2 corresp. to eigenvalue $b_2 = 3$.

Find eigenvectors $\tilde{v}_1$ and $\tilde{v}_3$ in terms of v_1 and v_2:

$$\tilde{B} = \begin{pmatrix} \langle v_1 | B | v_1 \rangle & \langle v_1 | B | v_3 \rangle \\ \langle v_3 | B | v_1 \rangle & \langle v_3 | B | v_3 \rangle \end{pmatrix} = \begin{pmatrix} \langle v_1 | v_3 \rangle = 0 & 2 \\ 1 & 1 \end{pmatrix}$$

diagonalize B in subspace spanned by v_1 and v_3.

$\Rightarrow \tilde{b}_1 = 2, \quad \tilde{b}_2 = -1, \quad \tilde{v}_1 = v_1 + v_3, \quad \tilde{v}_3 = v_1 - \frac{1}{2} v_3$

Last time.

$$\frac{1}{2\mu}\langle r|\hat{p}^2|\psi\rangle = \frac{1}{2\mu r^2}\left[\langle r|\hat{L}^2|\psi\rangle - \hbar^2 r\frac{\partial}{\partial r} r\frac{\partial}{\partial r}\langle r|\psi\rangle - \hbar^2 r\frac{\partial}{\partial r}\langle r|\psi\rangle\right]$$

Recall: $\langle r|\psi\rangle = \psi(r)$.

Now,

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{\hat{L}^2}{2\mu r^2} + V(r)\right)\psi(r) = E\psi(r) \quad \cdots \quad (1)$$

indep of angles => can seperate ψ into angles and radius

can actually seperate the two angles since $[L_z, L^2] = 0$

pick the z-axis.

$$\Rightarrow \quad \psi(r) = R(r)\cdot\underbrace{\Theta(\theta)\cdot\Phi(\varphi)}_{|l,m\rangle}$$

rotation about the z-axis.

=> get $\quad H|R(r), l, m\rangle = E|R(r), l, m\rangle$

Note: in eq^n (1), can replace $\hat{L}^2$ by its eigenvalues $\hbar^2 l(l+1)$

- change variables: $\frac{u(r)}{r} := R(r) \quad \cdots (2)$

So we're seperating variables in the dif eq (1). Let's just look at the R(r) stuff, replaced by the change of variables (2).

$$\Rightarrow \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right)\frac{u(r)}{r} = \frac{\partial^2 u}{\partial r^2}\cdot\frac{1}{r} + 2\frac{\partial u}{\partial r}\cdot\frac{\partial}{\partial r}\left(\frac{1}{r}\right) + u\frac{\partial^2}{\partial r^2}\left(\frac{1}{r}\right) + \frac{2}{r^2}\frac{\partial u}{\partial r} + \frac{2}{r}u\frac{\partial}{\partial r}\left(\frac{1}{r}\right)$$

$$= \frac{1}{r}\frac{\partial^2 u}{\partial r^2}$$

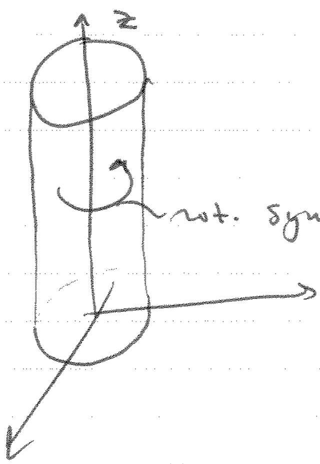
21-01-14 Quantum

⇒ multidimensional problem reduced to 1D problem in $u(r)$:

$$\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + \underbrace{\frac{\hbar^2}{2\mu r^2}\,l(l+1) + V(r)}_{V_{eff}(r)}\right] u(r) = E\,(r) \quad \cdots \quad (3)$$

Here we've been working w/ spherical symmetry.

What if we worked w/ a <u>reduced</u> <u>symmetry</u>. e.g. cylindrical sym.



rot. symmetry ⇒ $[\hat{H}, \hat{L}_z] = 0$

So, complete basis: $|m, p_z, \rho\rangle$

momentum out of plane.

could also use z

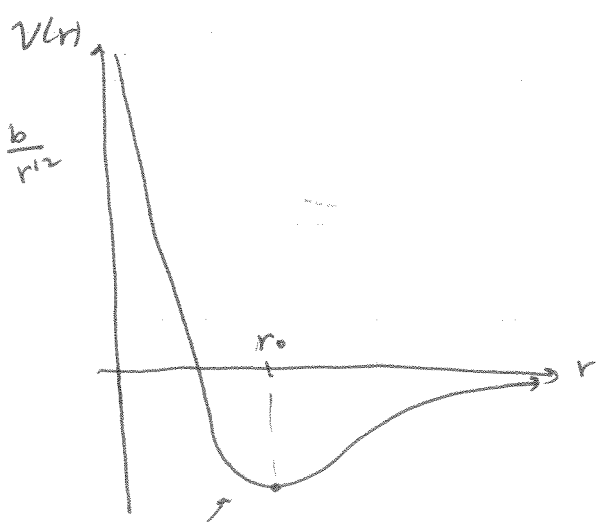
radius in the plane

| Aside: <u>REDUCED</u> <u>SYMMETRY</u> |

Diatomic Molecule

- Van der Waals potential
- yukawa potential: $V_y(r) = \frac{a}{r^6} - \frac{b}{r^{12}}$
- how can we "solve" this?

→ Harmonic Approx
  ↳ Taylor expand about the stable point $= r_0$



want some stable point (<u>bound</u> <u>state</u>)

Harmonic Approx:

$$V(r) \approx V(r_0) + \cancel{(r-r_0)V'(r)\big|_{r_0}}^{\;0} + \underbrace{\tfrac{1}{2}(r-r_0)^2 V''(r)\big|_{r_0}}_{:= \frac{1}{2}(r-r_0) K_{eff} \,=\, V(r)} + \cdots$$

since r_0 min.

$\Rightarrow$ we have a harmonic oscillator:

$$E_n = (n + \tfrac{1}{2})\hbar\omega$$

Recall: $^*\ \omega = \sqrt{k/m}$, where $k = k_{eff} = V''(r)\big|_{r_0}$

$m = \mu =$ reduced mass

$$\Rightarrow \omega = \sqrt{\frac{k}{m}} = \sqrt{\frac{V''}{\mu}} = \sqrt{\frac{k_{eff}}{\mu}}$$

$\rightarrow$ How to evaluate ω:

- assume length scale where $V(r) \approx e^2/a$

$\Rightarrow k = V'' \approx e^2/a^3$ $\Big\}$ $a = \dfrac{\hbar^2}{m_e e^2}$, from experiment.

$$\Rightarrow \hbar\omega = \hbar e\, m_e^{3/2} e^3 / \hbar^3 M^{1/2}$$

M — typical atom mass

$$= \sqrt{\frac{m_e}{M_N}}\ \underbrace{\left(\frac{m_e e^4}{\hbar^2}\right)}_{E \text{ scale of atom}}, \quad \sqrt{\frac{m_e}{M_N}} \sim \frac{1}{40}$$

M_N: nuclear mass

$\Rightarrow \hbar\omega \approx 0.4\,eV$

$\Rightarrow \dfrac{\hbar\omega}{\hbar} \approx 10^{14}\,Hz.$

$\Rightarrow$ transition energy: $\Delta E = E_{n+1} - E_n$.