What we know so far...

1D motion in a real space

"Main" operators $\hat{x}, \hat{p}_x$

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

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

Usually operate in x-basis

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

$\hat{H}|E_n\rangle = E_n|E_n\rangle$

"3D" spin space

Spin angular momentum $\hat{\vec{S}}$

$\hat{S}^2$ "total spin"

$\hat{S}_x, \hat{S}_y, \hat{S}_z$ – spin components

$[\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z$, $[\hat{S}_y, \hat{S}_z] = i\hbar\hat{S}_y$

$[\hat{S}_z, \hat{S}_x] = i\hbar\hat{S}_y$

$[\hat{S}^2, \hat{S}_i] = 0$ ← common eigenstates

$\hat{S}^2|s,m\rangle = \hbar^2 s(s+1)|s,m\rangle$

$\hat{S}_z|s,m\rangle = \hbar m|s,m\rangle$

3D motion in a real space

$x \to \vec{r}$: $\hat{x}, \hat{y}, \hat{z}$, $\hat{\vec{r}} = \hat{x}\vec{i} + \hat{y}\vec{j} + \hat{z}\cdot\vec{k}$

$p_x \to \vec{p}$: $\hat{p}_x, \hat{p}_y, \hat{p}_z$, $\hat{\vec{p}} = \hat{p}_x\vec{i} + \hat{p}_y\vec{j} + \hat{p}_z\cdot\vec{k}$

Motion along each direction is independent, thus different coordinates and momenta commute!

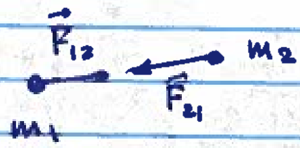
$[\hat{x}, \hat{p}_x] = i\hbar$ $\quad [\hat{y}, \hat{p}_x] = [\hat{z}, \hat{p}_x] = 0$

Common notation

$x, y, z \to x_1, x_2, x_3 \quad \to \quad [\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij}$ $\quad \delta_{ij} = \begin{cases} 1 & i=j \\ 0 & i\neq j \end{cases}$

1D	3D
$\hat{p}_x\psi(x) = \left(-i\hbar\frac{d}{dx}\right)\psi(x)$	$\hat{\vec{p}}\,\psi(\vec{r}) = (-i\hbar\nabla)\psi(\vec{r})$
$\langle\hat{x}\|\hat{p}_x\rangle = \frac{1}{\sqrt{2\pi\hbar}}e^{ip_x\cdot x/\hbar}$	$\langle\vec{r}\|\vec{p}\rangle = \frac{1}{(2\pi\hbar)^{3/2}}e^{i\vec{p}\cdot\vec{r}/\hbar}$
$\hat{H}\psi(x) = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi(x)$	$\hat{H}\psi(\vec{r}) = -\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + V(\vec{r})\psi(\vec{r})$

Let's talk about a molecule (the simplest one)



$$\hat{H} = \hat{K}_1 + \hat{K}_2 + V(\hat{\vec{r}}_1, \hat{\vec{r}}_2) =$$

$$= \frac{\hat{p}_1^2}{2m_1} + \frac{\hat{p}_2^2}{2m_2} + V(\hat{\vec{r}}_1, \hat{\vec{r}}_2)$$

Two-body interaction $V(\vec{r}_1, \vec{r}_2) = V(|\vec{r}_1 - \vec{r}_2|)$

Possible kinds of motions

1. Motion of the molecule as a whole (center-of-mass motion)
2. Rotation of each atom around these center of mass
3. Vibration of each atom around their equilibrium position.

① Basically a motion of a free particle, just as we studied before.

$$\hat{\vec{R}} = \frac{m_1\hat{\vec{r}}_1 + m_2\hat{\vec{r}}_2}{m_1 + m_2}$$ center of mass coordinate

$$\hat{\vec{P}} = \hat{\vec{p}}_1 + \hat{\vec{p}}_2$$ c-o-m momentum

- - - -

$$\hat{\vec{r}} = \hat{\vec{r}}_1 - \hat{\vec{r}}_2$$ relative coordinate

$$\hat{\vec{p}} = \frac{m_2\hat{\vec{p}}_1 - m_1\hat{\vec{p}}_2}{m_1 + m_2}$$ — " — momentum

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

$$[\hat{x}_i, \hat{P}_j] = 0 \ \& \ [\hat{X}_i, \hat{p}_j] = 0$$

C-o-m motion and relative motion are independent!

$$\hat{H} = \frac{\hat{p}_1^2}{2m_1} + \frac{\hat{p}_2^2}{2m_2} + V(|\vec{r}_1 - \vec{r}_2|) = \underbrace{\frac{\hat{P}^2}{2(m_1+m_2)}}_{\hat{H}_{cm}} + \underbrace{\frac{\hat{p}^2}{2\mu} + V(|\vec{r}|)}_{\hat{H}_{rel}}$$

$$\boxed{\mu = \frac{m_1 m_2}{m_1 + m_2} \text{ reduced mass}}$$

If E_{CM} is the energy of CM motion and E_{rel} — " — relative — " —

$$\hat{H}|E_{CM}, E_{rel}\rangle = \hat{H}_{cm}|E_{cm}, E_{rel}\rangle + \hat{H}_{rel}|E_{CM}, E_{rel}\rangle =$$

$$= E_{CM}|E_{CM}, E_{rel}\rangle + E_{rel}|E_{CM}, E_{rel}\rangle = E_{tot}|E_{CM}, E_{rel}\rangle$$

$$|E_{CM}, E_{rel}\rangle = |E_{CM}\rangle \otimes |E_{rel}\rangle = \frac{1}{(2\pi\hbar)^{3/2}} e^{i\vec{P}\cdot\vec{R}/\hbar} |E_{rel}\rangle$$

$$\underbrace{\hat{H}_{CM}|E_{CM}\rangle \otimes |E_{rel}\rangle} + \underbrace{\hat{H}_{rel}}|E_{CM}\rangle \otimes |E_{rel}\rangle =$$

$$= E_{CM}|E_{CM}\rangle \otimes |E_{rel}\rangle + |E_{CM}\rangle \otimes \hat{H}_{rel}|E_{rel}\rangle =$$

$$= (E_{CM} + E_{rel})|E_{CM}\rangle \otimes |E_{rel}\rangle =$$

$$= E_{CM}|E_{CM}\rangle \otimes |E_{rel}\rangle + |E_{CM}\rangle \otimes (E_{rel}|E_{rel}\rangle)$$

$$\hat{H}_{rel}|E_{rel}\rangle = E_{rel}|E_{rel}\rangle$$

$$\hat{H} = \frac{\hat{p}^2}{2\mu} + V(\hat{r})$$ — can consider only relative motion now

This Hamiltonian is rotationally-invariant!

That means the orbital angular momentum is conserved.

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