

Thurs 22 Aug 2024

Today - orbital angular momentum, multi-electron atoms

Orbital angular momentum:  $\vec{L} = \vec{r} \times \vec{p}$ 

$$L^2 \equiv |\vec{L}|^2$$

$$L_z$$

$$L^2 |l\rangle = \hbar^2 l(l+1) |l\rangle, \quad l = 0, 1, 2, \dots, \quad \text{[For H-atom, max } l = n-1]$$

$$L_z |l\rangle = \hbar m |l\rangle, \quad m = -l, -(l-1), \dots, 0, 1, \dots, l-1, l$$

integers

general

For the hydrogen atom,

 $\{\hat{H}, \hat{L}^2, \hat{L}_z\}$  forms a C.S.C.O. (ignoring spin) $\Rightarrow$  label the common eigenstates by their eigenvalues or information about their eigenvalues, eg.  $|n l m\rangle$ 

$$\hat{H} |n l m\rangle = + \frac{E_1}{n^2} |n l m\rangle \quad \text{where } E_n = \frac{E_1}{n^2}$$

Eg. 1s state for H atom

$$|1 0 0\rangle \rightarrow \text{we know energy} = E_1$$

$$\langle 1 0 0 | \hat{L}^2 | 1 0 0 \rangle = 0, \quad \hat{L}^2 | 1 0 0 \rangle = 0 | 1 0 0 \rangle$$

$$\hat{L}_z | 1 0 0 \rangle = 0 | 1 0 0 \rangle$$

 $\{|n l m\rangle\}$  forms an orthonormal basis.

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

$$\frac{\hat{\vec{p}}^2}{2m} = \frac{1}{2m} \left( \hat{\vec{p}}^2 + \frac{\hat{\vec{L}}^2}{r^2} \right)$$

$$\text{Hydrogen atom } \hat{H} = \frac{\hat{\vec{p}}^2}{2m} + \underbrace{V(r)}$$

(Born-Oppenheimer approx)

 $V$  depends only on  $|\vec{r}| = r$  (central potential)

(c.f. next week's lectures).

- System has rotational symmetry  $\Rightarrow$  Angular momentum is conserved.

$$[H, L^2] = 0$$

$$[H, L_z] = 0$$

Key relation

$$[L_i, L_j] = i\hbar \epsilon_{ijk} L_k$$

Summation notation

— actually the fundamental defining property of angular momentum

- Each  $i, j, k$  appears (subscript)

either once or twice

- Free variable/index
- must appear as a free index on both LHS and RHS

Sum over all possible values

(next time, we cover other types of angular momentum, eg. spin angular momentum)

Eg.  $i \in x, j \in y$  (free variables)

$$[L_x, L_y] = i\hbar \epsilon_{xyk} L_k = i\hbar (\underbrace{\epsilon_{xyx}}_0 L_x + \underbrace{\epsilon_{xyy}}_0 L_y + \underbrace{\epsilon_{xyz}}_{+1} L_z) = i\hbar L_z$$

$i \in x, j \in x$  (free variables)

$$[L_x, L_x] = i\hbar \epsilon_{xxk} L_k = i\hbar (\underbrace{\epsilon_{xxx}}_0 L_x + \underbrace{\epsilon_{xxy}}_0 L_y + \underbrace{\epsilon_{xxz}}_0 L_z) = 0$$

$\epsilon_{ijk}$  Levi-Civita symbol

$$\epsilon_{ijk} = \begin{cases} +1 & \text{if } (i,j,k) \text{ is } (1,2,3), (2,3,1), (3,1,2) \text{ cyclic permutation} \\ -1 & \text{if } (i,j,k) \text{ is } (3,2,1), (1,3,2), (2,1,3) \text{ anticyclic} \\ 0 & \text{otherwise} \end{cases}$$

$$\delta_{ij} a_i = a_j, \quad \delta_{ik} \delta_{kj} = \delta_{ij}$$

free index  $j$   
 $i$ : sum over

$$\delta_{ij} = \begin{cases} 1 & \text{if } i=j \\ 0 & \text{otherwise} \end{cases}$$

$$\epsilon_{ijk} \epsilon_{imn} = \delta_{jm} \delta_{kn} - \delta_{jn} \delta_{km}$$

$i$ : summing over  
 $j, k, m, n$ : free

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

Definition:  $L_i = \epsilon_{ijk} r_j p_k$

Can show

$$[L_i, L_j] = i\hbar \epsilon_{ijk} L_k$$

— definition of vector cross product

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

Definition:

$$L_i = \epsilon_{ijk} r_j p_k$$

- definition of vector cross product

Consequences of  $[L_i, L_j] = i\hbar \epsilon_{ijk} L_k$

uncertainty relation (W1L2)

$$\Delta A \Delta B \geq \frac{1}{2} |\langle [A, B] \rangle|$$

So eg.

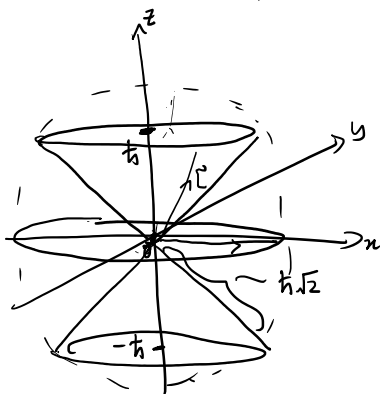
$$i \equiv x, j \equiv y, [L_x, L_y] = i\hbar L_z \text{ from above}$$

$$\hat{L}_{10,00} \quad \Delta L_x \Delta L_y \geq \frac{1}{2} |i\hbar \langle L_z \rangle| = \frac{\hbar}{2} |\langle L_z \rangle|$$

= 0

For  $l=0$ , we know  $\hat{L} = (0, 0, 0)$

otherwise, it is not possible to simultaneously determine  $L_x, L_y, L_z$ .



$l=1$

$$L^2 |nlm\rangle = \hbar^2 l(l+1) |nlm\rangle \Rightarrow |L|$$

eg  $l=1$ ,  
 $|L|$  for  $|nlm\rangle$   
 is  $\hbar\sqrt{2}$ .

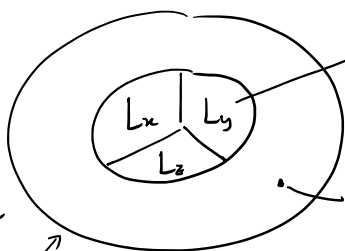
$$L_z |nlm\rangle = m\hbar |nlm\rangle$$

Eg  $l=1$ ,

$m = -1, 0, 1$

An eigenstate of  $L_z$  is an eigenstate of  $L^2$ .

but not an eigenstate of  $L_x$  or  $L_y$ .



eigenstate of both  $L^2$  and  $L_y$

eigenstate of  $L^2$

but not an eigenstate of  $L_x, L_y, L_z$ .

$$\text{Eg. } |4\rangle = \frac{1}{\sqrt{2}} (\underbrace{|1\ 0\rangle}_{|lm\rangle} + i \underbrace{|1\ 1\rangle}_{|lm'\rangle})$$

Multi-electron atoms

Before :  $|\psi\rangle$  described a single particle

wavefunction  $\langle \vec{r} | \psi \rangle = \psi(\vec{r})$

↑ one real-space coordinate

Now  $|\psi\rangle$  describes more than one particle in a multi-electron system.

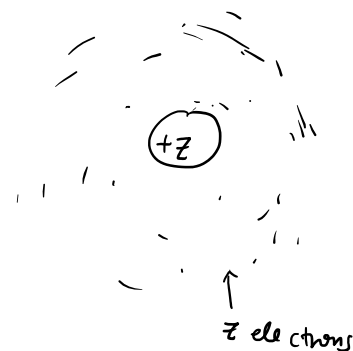
many-electron wavefunction  $\langle \vec{r}_1, \vec{r}_2, \dots, \vec{r}_N | \psi \rangle = \psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$

$|\psi(\vec{r}_1^0, \vec{r}_2^0, \dots, \vec{r}_N^0)|^2 \Delta V_1 \Delta V_2 \dots \Delta V_N$  ——— probability of finding  
 particle 1 in a volume  $\Delta V_1$  about  $\vec{r}_1^0$ ,  
 " 2 ——— " —  $\Delta V_2$  "  $\vec{r}_2^0$ ,  
 and  
 " N ——— "  $\Delta V_N$  "  $\vec{r}_N^0$ .

For a multi-electron atom,  
 in the Born-Oppenheimer approx.

$$\hat{H} = \underbrace{\sum_{i=1}^Z \frac{p_i^2}{2m_e}}_{\text{KE of } e^-} - \underbrace{\sum_{i=1}^Z \frac{Ze^2}{r_i}}_{\text{attractive potential energy}} + \underbrace{\sum_{i < j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}}_{\text{repulsive potential energy between } e^-}$$

makes the Hamiltonian  
 challenging to solve.



All terms are 'huge'.

Interestingly, in the periodic table, multi-electron atoms  
 are described quite simply in terms of s, p, d, f orbitals, (orbital angular momentum  
 eigenstates)

relevant for  
 central potentials.

Here, we introduce the single particle approximation / quasiparticle approximation

where instead of considering  $\psi(r_1, \dots, r_Z)$ , we consider

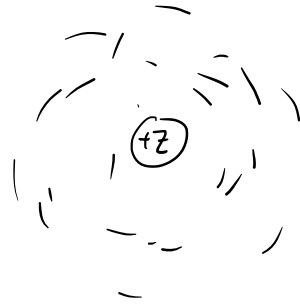
effective single particle wavefunctions  $\psi^{\text{eff}}(r_1)$   
 $\psi^{\text{eff}}(r_2)$   
 $\vdots$   
 $\psi^{\text{eff}}(r_Z)$

We need an effective single particle Hamiltonian

$H^{\text{eff}}$  for  $\psi^{\text{eff}}(r)$ , that captures the essential physics of the many-e system.

Today, we will learn <sup>about</sup> one such  $H^{\text{eff}}$ ,  
called the central potential approximation.

$$H^{\text{eff}} = \frac{\vec{p}_i^2}{2m_i} + V_c(r) \quad (r = |\vec{r}|)$$



Let's just consider limiting cases.

$r \rightarrow 0$  close to nucleus  $V_c(r) \sim -\frac{Ze^2}{r}$

$r \gg 0$  far from nucleus.  $V_c(r) \sim -\frac{e^2}{r}$  (shielding / screening)

Central potential

- Solutions approx. as 1s, 2s, 2p, etc.  
(see above)