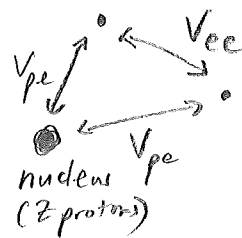


Multiparticle states

System of N electrons near a nucleus at origin.

$\vec{r}_i, \vec{p}_i$ = position, momentum of i th electron



(Neglect fine structure)

$$H = H^0 + H^1$$

$$H^0 = \sum_i \frac{p_i^2}{2m} + \sum_i V_{pe}(\vec{r}_i), \quad H^1 = \sum_{i < j} V_{ee}(\vec{r}_i - \vec{r}_j)$$

$$V_{pe} = -\frac{KZe^2}{r} = -\frac{Z\alpha\hbar c}{r}$$

$$V_{ee} = +\frac{Ke^2}{r} = \frac{\alpha\hbar c}{r}$$

System described by single state $|\psi\rangle$, not states for each particle

Multiparticle wavefunction $\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$

Prob. density = $|\psi(\vec{r}_1, \dots)|^2$ = prob of finding an electron at $\vec{r}_1$, one at $\vec{r}_2$, one at $\vec{r}_3$ etc.

Identical particles $\Rightarrow |\psi(\vec{r}_1, \vec{r}_2, \dots)|^2$ invariant under exchange of arguments

$$\Rightarrow \psi(\dots, \vec{r}_i, \dots, \vec{r}_j, \dots) = \pm \psi(\dots, \vec{r}_j, \dots, \vec{r}_i, \dots) \quad \text{for } \begin{cases} \text{bosons} \\ \text{fermions} \end{cases}$$

First, solve unperturbed Schrodinger eqn
(neglect interelectron repulsion)

$$H^0 u(\vec{r}_1, \vec{r}_2, \dots) = E u(\vec{r}_1, \vec{r}_2, \dots)$$

$$\sum_i \left(-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Z\alpha mc^2}{r_i} \right) u = E u$$

Separable ansatz: $u(\vec{r}_1, \vec{r}_2, \dots) = \prod u^{(i)}(\vec{r}_i)$

$$\Rightarrow \sum \underbrace{\frac{1}{u^{(i)}(\vec{r}_i)} \left(-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Z\alpha mc^2}{r_i} \right) u^{(i)}(\vec{r}_i)}_{\text{const, } E^{(i)}} = E$$

$$\left(-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Z\alpha mc^2}{r_i} \right) u^{(i)}(\vec{r}_i) = E^{(i)} u^{(i)}(\vec{r}_i)$$

"one particle Schrodinger eqn"

$\Rightarrow$ solutions: hydrogen atom $\forall \alpha \rightarrow Z\alpha$

$$E_n = -\frac{1}{2} \frac{Z^2 \alpha^2 mc^2}{n^2} = -\frac{Z^2 (Ryd)}{n^2}$$

$$U_{nlm}(\vec{r}) = U_A(\vec{r}) \quad a_0 \rightarrow \frac{\hbar}{mc Z \alpha} = \frac{a_0}{Z}$$

For each i , choose a set of quantum #s $(n, l, m_l, m_s) \equiv A$

$$\text{then } \begin{cases} u(\vec{r}_1, \vec{r}_2, \dots) = \prod_i U_{A_i}(\vec{r}_i) = U_{A_1}(\vec{r}_1) U_{A_2}(\vec{r}_2) \dots U_{A_n}(\vec{r}_n) \\ E = \sum_i E_{A_i} \end{cases}$$

If all labels A_i are distinct, then

$\prod U_{A_i}(\vec{r})$ is $n!$ fold degenerate

(permuting labels)

so linear combinations of these are also energy eigenstates

Because electrons are fermions, must choose
coupling antisymmetric combination

$$U_{A_1}(\vec{r}_1)U_{A_2}(\vec{r}_2)U_{A_3}(\vec{r}_3) - U_{A_2}(\vec{r}_1)U_{A_1}(\vec{r}_2)U_{A_3}(\vec{r}_3) \pm (4 \text{ others})$$

$$U(\vec{r}_1, \dots) = \frac{1}{\sqrt{n!}} \begin{vmatrix} U_{A_1}(\vec{r}_1) & U_{A_1}(\vec{r}_2) & U_{A_1}(\vec{r}_3) & \dots \\ U_{A_2}(\vec{r}_1) & U_{A_2}(\vec{r}_2) & U_{A_2}(\vec{r}_3) & \dots \\ U_{A_3}(\vec{r}_1) & U_{A_3}(\vec{r}_2) & U_{A_3}(\vec{r}_3) & \dots \\ \vdots & \vdots & \vdots & \ddots \end{vmatrix} = \text{Slater determinant}$$

A_i must be distinct, else $U = 0$ (Pauli exclusion)

Also, prob. of finding 2 electrons in same location = 0