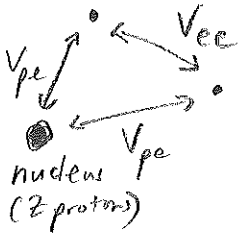
Multiparticle states

System of N electrons near a nucleus at origin

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



(Neglect fine structure)

$$H = H^0 + H'$$

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

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

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

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

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

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

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

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

First, solve unperturbed Schrödinger eqn
(neglect interelectron repulsion)

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

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

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

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

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

"one particle Schrödinger eqn"

$\Rightarrow$ solutions: hydrogen atom w/ $\alpha \to Z\alpha$

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

$$u_{nlm_l m_s}(\vec{r}) = u_A(\vec{r}) \qquad a_0 \to \frac{\hbar}{mcZ\alpha} = \frac{a_0}{Z}$$

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

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

If all labels A_i are distinct, then

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

(permuting labels)

so linear combinations of these are also energy eigenstates

Because electrons are fermions, must choose coupling antisymmetric combination

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

$$u(\vec{r}_1 \cdots) = \frac{1}{\sqrt{n!}} \begin{vmatrix} u_{A_1}(\vec{r}_1) & u_{A_1}(\vec{r}_2) & u_{A_1}(\vec{r}_3) & \cdots \\ u_{A_2}(\vec{r}_1) & u_{A_2}(\vec{r}_2) & u_{A_2}(\vec{r}_3) & \cdots \\ u_{A_3}(\vec{r}_1) & u_{A_3}(\vec{r}_2) & u_{A_3}(\vec{r}_3) & \cdots \\ & & & \end{vmatrix} = \text{Slater determinant}$$

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

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