4/9/01

Lecture 33 Atoms

Pauli exclusion principle

Wave function of many fermion system must be antisymmetric under interchange of space <u>and</u> spin coordinates of any two fermions.

Example two electrons

$$\psi_1(\vec{r}_1, m_{s_1}) = \psi_a(\vec{r}_1)\,\chi_{m_{s_1}}$$

$$\psi_2(\vec{r}_2, m_{s_2}) = \psi_b(\vec{r}_2)\,\chi_{m_{s_2}}$$

Combine spins

$$|10\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow)$$

symmetric under $1 \Rightarrow 2$

$$|00\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$$

spin 0 is antisym.

Legal wave functions

$$\left[\psi_a(\vec{r}_1)\,\psi_b(\vec{r}_2) + \psi_a(\vec{r}_2)\,\psi_b(r_1)\right]|00\rangle$$

or

$$\left[\psi_a(\vec{r}_1)\,\psi_b(\vec{r}_2) - \psi_a(\vec{r}_2)\,\psi_b(r_2)\right]|10\rangle$$

Wave function is ether symmetric in space times antisym. in spin or

Symmetric in spin $(S=1)$ times antisym. in space.

He Atom $Z=2$

$$H = \left(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1}\right) + \left(-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0 r_2}\right)$$

$$+ \frac{e^2}{4\pi\epsilon_0}\frac{1}{|\vec{r}_1-\vec{r}_2|}$$

If ignore last term

$$\psi(\vec{r}_1,\vec{r}_2) \simeq \psi_{nlm}(\vec{r}_1)\,\psi_{n'l'm'}(\vec{r}_2)$$

Energy of H like ion

$$H(Z) = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1}$$

$$H(Z)\,\psi_{nlm} = E(Z)\,\psi_{nlm}$$

$$E(Z) = -\frac{mc^2}{2}\frac{(Z\alpha)^2}{n^2} = -\frac{13.6\,eV}{n^2}Z^2$$

Note replace $e^2 \rightarrow Ze^2$ and $E_n \propto e^4$
thus $E_n \propto Z^2$

Ground state place both electrons in $n=1$ $l=m=0$ state.

In this case need antisym. spin state

$$\psi(r_1, m_{s_1}, r_2, m_2) = \psi_{100}(r_1,\theta_1,\phi_1)\,\psi_{100}(r_2,\theta_2,\phi_2)\,|00\rangle$$

$$|00\rangle = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow)$$

$E_0 = 2(-13.6\ eV)\,4 = -8(13.6)\ eV$

$E_0 = -109\ eV$

Observed $E_0 = -79\ eV$

Difference comes from neglected e-e repulsion

Periodic table Neglect e-e repulsion as a first guess for many electron atoms

Fill up R_{nl} orbitals. Each orbital holds $2l+1$ different m values times 2 spins

Z	Element	
1	H	$1s$
2	He	$(1s)^2$
3	Li	$(He)\ 2s$ $\quad E \approx 2E(n=1) + E(n=2)$
4	Be	$He\ (2s)^2$
5	B	$He\ (2s)^2\ 2p$
6	C	$He\ (2s)^2\ (2p)^2$
7	N	$(He)\ (2s)^2\ (2p)^3$
⋮		
10	Ne	$(He)\ (2s)^2\ (2p)^6$

We see that He is a closed shell all $n=1$ orbitals are filled

Likewise Ne $Z = 10$ is a closed shell all $n=1$ and $n=2$ orbitals are filled

$n=1$ has $l = m = 0$ $\qquad 2$

$n=2$ has $l = m = 0$ $\quad 2s \qquad 2$

has $l=1$ $\quad m = \left.\begin{matrix}1\\0\\-1\end{matrix}\right\}\ 2p$ $\qquad$ 3 states × 2

$\overline{\quad 10 \quad}$

Notation $\ell = 0$ are called s states

$\ell = 1$ are p states

$\ell = 2$ d

3 f

4 g

5 h

6 i

...

sharp, principle, diffuse, fundamental