Lecture 14

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Part I

Atomic Structure

Looking at an atom with Z protons and N neutrons, we have the following Hamiltonian:

$$H = \sum_{i=1}^{N} \left(\underbrace{\frac{\vec{p}_i^2}{2m}}_{\text{kinetic energy}} - \underbrace{\frac{Ze^2}{4\pi\varepsilon_0 |\vec{r}_i|}}_{e-\ \text{nucleus attraction}} \right) + \sum_{\substack{i,j \\ i \neq j}} \underbrace{\frac{1}{2} \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_i - \vec{r}_j|}}_{e-e\ \text{repulsion}}$$

0 Approximation

To simplify this we will ignore the electron-electron interaction (just because it is hard. You need a computer).

A hydrogen-like energy eigenstate of H_0 is:

$$|\psi_n\rangle = |n_1, l_1, m_1\rangle \otimes |n_2, l_2, m_2\rangle \otimes \cdots |n_n, l_n, m_n\rangle \otimes |m_{s_1}\rangle \otimes |m_{s_2}\rangle \otimes \cdots \otimes |m_{s_n}\rangle$$

$$H_0 |\psi_N\rangle \sum_{i=1}^{N} \frac{(-13 \text{ eV})\, Z^2}{n_i^2}$$

As n_i^2 increases, we get an absolute lower energy. To find the lowest energieigenvalues we must focus on the lower n values. As electrons are fermions, the state needs to be antisymmetric under permutation of particle labels.

$$|\psi_2\rangle = |n_1, l_1, m_1\rangle \otimes |n_2, l_2, m_2\rangle \otimes |m_{s_1}\rangle \otimes |m_{s_2}\rangle - |n_2, l_2, m_2\rangle \otimes |n_1, l_1, m_1\rangle \otimes |m_{s_2}\rangle \otimes |m_{s_1}\rangle$$

We want the ground state to be as small (negative) as possible.

$$|\psi_2\rangle = |1,0,0\rangle \otimes |1,0,0\rangle \left(|m_{s_1}\rangle \otimes |m_{s_2}\rangle - |m_{s_2}\rangle \otimes |m_{s_1}\rangle \right)$$

and so $m_{s_1} \neq m_{s_2}$ for this to not be $|NULL\rangle$ aka the singlet state.

$$|\psi_3\rangle = |1,0,0\rangle \otimes |1,0,0\rangle \otimes |1,0,0\rangle \otimes |x_3\rangle$$

$$|x_3\rangle = |m_{s_1}\rangle \otimes |m_{s_2}\rangle \otimes |m_{s_3}\rangle - |m_{s_2}\rangle \otimes |m_{s_1}\rangle \otimes |m_{s_3}\rangle \otimes |m_{s_3}\rangle + |m_{s_2}\rangle \otimes |m_{s_3}\rangle \otimes |m_{s_1}\rangle$$
$$- |m_{s_1}\rangle \otimes |m_{s_3}\rangle \otimes |m_{s_2}\rangle + |m_{s_3}\rangle \otimes |m_{s_1}\rangle \otimes |m_{s_2}\rangle - |m_{s_3}\rangle \otimes |m_{s_2}\rangle \otimes |m_{s_1}\rangle$$

No matter what spin we choose, we will always get $|NULL\rangle$. This is the Pauli exclusion principle. For $N = 3$ we need $n = 2$. When we do this, we must take into account the possible l and m values. We have the sates $|2,1,\pm 1\rangle, |2,1,0\rangle, |2,0,0\rangle$. With four states we can have 8 electrons. For each level n we have

$$2 \sum_{l=0}^{n-1} (2l + 1) = 2n^2$$

electrons with level n is a proper fermionic atomic state. Every time we were we have to increase n, the energy per particle will make a jump.

n	#	Predicted inert elements
1	2	2 (H_e)
2	8	10 (N_e)
3	18	28 (N_i) Not an element
4	32	60 (N_d) Not an element

We correct the electron-electron repulsion in an average way. When electrons are close, the potential is given by:

$$\frac{Ze^2}{2\pi\epsilon_0 r}$$

When far away the potential is given by:

$$\frac{e^2}{4\pi\epsilon_0 r}$$

We can use the shell notation to write down how many electron states we have.

$$(1s)^2(2s)^2(2p)^5$$

This shows that we have to electrons in the lowest shell, 2 in the next lowest and 5 in the third lowest. This does not tell us the m values we have to use as we have not filled out the entire 2p shell. The amount of electrons in a shell is given by $2(2l+1)$.

Shell	$n+l$
1s	1
2s 2p	2 3
3s 3p	3 4
4s 3d 4p	4 5 5
5s 4d 5p	5 6 6
6s 4f 5d 6p	6 7 7 7
7s 5f 6d 7p	7 8 8 8

Energy increase from left to right with higher n. Alternative ways to specify the groundstate:

Rotational Invariance

The groundstate can be specified by the quantum numbers for the total angular momentum $\hat{J}$, the total orbital angular momentum $\hat{L}$ and the total spin $\vec{S}$.

$$\vec{S} = \sum_{i=1}^{N} \vec{s}_i \quad , \quad \vec{L} = \sum_{i=1}^{N} \vec{l}_i \quad , \quad \vec{J} = \vec{L} + \vec{S}$$

A groundstate multiplet is denoted by:

$$^{2S+1}L_J \quad , \quad L \in \underbrace{\{S, P, D, F, G, H, \ldots\}}_{l=0,1,2,3,4,5*}$$

Example: He

He: $(1s)^2$, $n=1, l=0$. Two electrons with $n=1, l=0, s=1/2$

$$\text{total } S = \{0, 1\} \quad , \quad \text{total } L = 0 \quad , \quad \text{total } J \in \{0, 1\}$$

Only $S = L = J = 0$ is possible: $^1S_0$

Example: C

C: $(1s)^2(2s)^2(2p)^2$. In general completely filled subshells have $L = S = 0$, so here we only consider the outer $2p$-subshell. There are 2 electrons in this subshell with $n = 2$ and $l = 1$

$$L \in \{0, 1, 2\} \quad , \quad S \in \{0, 1\}$$

We now consider the symmetries and look at the Clebsch-Gordan table. The allowed values must be antisymmetric

L	Symmetry
0	+
1	-
2	+

S	Symmetries
0	-
1	0

L,S	J	
0,0	0	${}^1S_0$
1,0	1	${}^3P_0 \; {}^2P_1$
1,1	0,1,2	${}^1P_1 \; {}^3P_2 \; {}^3P_1 \; {}^3P_0 \; {}^1P_1$
2,0	2	${}^3D_2 \; {}^3D_1 \; {}^3D_0$

Hunds Rules

To find the lowest energy we use the following:

1. Highest S has the lowest energy $\rightarrow {}^3P_0 \; {}^3P_1 \; {}^3P_2$

2. Highest L has the lowest energy $\rightarrow {}^3P_0 \; {}^3P_1$

3. If the subshell has more than half filled, the

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