Chapter 10. Many-electron atoms

Spin

Elementary particles have *intrinsic* angular momentum, which is called <u>spin</u>.

Bosons (photons) have integer spin quantum numbers.

Fermions (electrons, protons) have half integer spin quantum numbers.

Electrons carry spin angular momenta ($s = 1/2$). There are two types of spins corresponding to $m_s = \pm 1/2$:

$$\alpha \rightarrow s = \frac{1}{2}, m_s = \frac{1}{2} \qquad\qquad \text{up spin}$$

$$\beta \rightarrow s = \frac{1}{2}, m_s = -\frac{1}{2} \qquad\qquad \text{down spin}$$

They are degenerate, but can split in a magnetic field (Stern-Gerlach exp.)

They are eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$

$$\hat{S}^2 \alpha = s(s+1)\hbar^2 \alpha = \frac{3}{4}\hbar^2 \alpha, \quad \hat{S}^2 \beta = \frac{3}{4}\hbar^2 \beta$$

$$\hat{S}_z \alpha = m_s \hbar \alpha = \frac{1}{2}\hbar \alpha, \qquad\qquad \hat{S}_z \beta = -\frac{1}{2}\hbar \beta$$

The spin wavefunctions are orthonormal:

$$\int \alpha^* \alpha \, d\sigma = \int \beta^* \beta \, d\sigma = 1, \quad \int \alpha^* \beta \, d\sigma = \int \beta^* \alpha \, d\sigma = 0$$

<u>Postulate 6</u>: Electronic wave functions change sign under exchange.

<u>Pauli exclusion principle</u>: Electrons in the same orbital have opposite spins.

<u>He atom</u>:

$$\hat{H} = -\frac{\hbar^2}{2\mu}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{2e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

$$= \left[-\frac{\hbar^2}{2\mu}\nabla_1^2 - \frac{2e^2}{4\pi\varepsilon_0 r_1}\right] + \left[-\frac{\hbar^2}{2\mu}\nabla_2^2 - \frac{2e^2}{4\pi\varepsilon_0 r_2}\right] + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

$$= \hat{h}_1 + \hat{h}_2 + \hat{h}_{12}$$

Intuitive approximation:

$$\Psi(1,2) = \psi(1)\psi(2)\alpha(1)\beta(2)$$

with $\psi(i)$ being the eigenfunction of single electron Hamiltonian $\hat{h}_i$. Then if $\hat{h}_{12}$ can be ignored, $\Psi(1,2)$ will be an eigenfunction of $\hat{H}$:

$$\hat{H}\Psi(1,2) = \left(\hat{h}_1 + \hat{h}_2\right)\psi(1)\psi(2)\alpha(1)\beta(2)$$

$$= \hat{h}_1\psi(1)\psi(2) + \psi(1)\hat{h}_2\psi(2)\alpha(1)\beta(2)$$

$$= [E_1\psi(1)\psi(2) + E_2\psi(1)\psi(2)]\alpha(1)\beta(2)$$

$$= (E_1 + E_2)\psi(1)\psi(2)\alpha(1)\beta(2)$$

But $\hat{h}_{12}$ can of course not be ignored, but can be taken into consideration in a mean field approximation.

General case:

$$\hat{H} = -\frac{\hbar^2}{2\mu}\sum_i \nabla_i^2 - \sum_i \frac{Ze^2}{4\pi\varepsilon_0 r_i} + \sum_i \sum_{j>i}\frac{e^2}{4\pi\varepsilon_0 r_{ij}}$$

There is no analytic solution of the Schrödinger equation, so approximation is necessary.

Hartree (orbital) approximation:

$$\Psi(1,2,\ldots,N) = \chi(1)\chi(2)\ldots\chi(N)$$

where the spin-orbital is a product of atomic orbital and spin function:

$$\chi = \phi \times \begin{cases} \alpha & \text{up spin } (s = 1/2, m_s = 1/2) \\ \beta & \text{down spin } (s = 1/2, m_s = -1/2) \end{cases}$$

Possible He ground state wavefunctions:

$$\psi_1 = 1s(1)1s(2)\alpha(1)\alpha(2) = 1s1s\alpha\alpha$$
$$\psi_2 = 1s(1)1s(2)\alpha(1)\beta(2) = 1s1s\alpha\beta$$
$$\psi_3 = 1s(1)1s(2)\beta(1)\alpha(2) = 1s1s\beta\alpha$$
$$\psi_4 = 1s(1)1s(2)\beta(1)\beta(2) = 1s1s\beta\beta$$

Exchange operator:

$$\hat{X}_{12}\phi(x_1, x_2) = \phi(x_2, x_1)$$

Here, x includes both spatial and spin coordinates.

A function is antisymmetry if:

$$\hat{X}_{12}\phi(x_1, x_2) = \phi(x_2, x_1) = -\phi(x_1, x_2)$$

We note that

$$\hat{X}_{12}\psi_1 = \psi_1, \qquad \hat{X}_{12}\psi_4 = \psi_4$$

so they violate Pauli principle and are not allowed.

To construct allowed wavefunctions, we use the <u>projection operator</u> $(1 - \hat{X}_{12})/\sqrt{2}$ to antisymmetrize:

$$\psi_1' = \frac{1}{\sqrt{2}}(1 - \hat{X}_{12})\psi_1 = 0$$

$$\psi_2' = \frac{1}{\sqrt{2}}(1 - \hat{X}_{12})\psi_2 = \frac{1}{\sqrt{2}}(\psi_2 - \psi_3)$$

$$= \frac{1}{\sqrt{2}}1s1s(\alpha\beta - \beta\alpha)$$

$$\psi_3' = \frac{1}{\sqrt{2}}1s1s(\beta\alpha - \alpha\beta) = -\psi_2$$

$$\psi_4' = 0$$

Indeed, the antisymmetrized wavefunctions satisfy the Pauli principle:

$$\hat{X}_{12}\frac{1}{\sqrt{2}}1s1s(\alpha\beta - \beta\alpha) = \frac{1}{\sqrt{2}}1s1s(\beta\alpha - \alpha\beta)$$

$$= -\frac{1}{\sqrt{2}}1s1s(\alpha\beta - \beta\alpha)$$

There are two electrons in the 1s orbital with opposite spins!

Hartree+antisymmetrization = Hartree-Fock approximation.

The self-consistent field (SCF):

The central idea of SCF is to follow individual electrons. Each electron has its kinetic energy and Coulomb interaction with the nucleus. However, its interactions with other electrons are treated as a mean field (i.e. electron cloud).

The Schrödinger equations for individual electrons are solved by iteration until the orbitals are self consistent (converged).

It is an approximation.

<u>Shielding and penetration</u>

When there is more than 1 e⁻, subshell orbitals are no longer degenerate.

2s has lower E than 2p, because Ψ_{2s} is closer to nucleus (penetration).

In other words, 2p electrons experience less nuclear charge. This effect can be approximated by the shielding constant:

$$Z_{\text{eff}} = Z - \sigma, \qquad\qquad s < p < d.$$

<u>Building-up (Aufbau) principle:</u>

Electronic configuration of an atom can be determined by the following rules:

i. <u>Orbital ordering</u>:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, ...

Fill the orbitals from the lowest one.

The <u>electronic configuration</u> of Ti is $[Ar]4s^2 3d^2$

ii. <u>Pauli exclusion principle:</u> 2 e⁻ may occupy one orbital with opposite spins (α and β).

iii. <u>Double occupancy rule</u>: Electrons occupy different orbitals of a given subshell before doubly occupying any one of them.

Carbon atom (6 e⁻): $[He]2s^2 \, 2p^1 2p^1$ (an open shell atom).

<u>Valence electrons</u>: outmost shell e⁻, 2s, 2p for C
<u>Core electrons</u>: inner shell e⁻.

Chemistry typically involves only valence electrons.

iv. <u>Hund's rule</u> (spin)

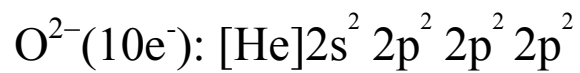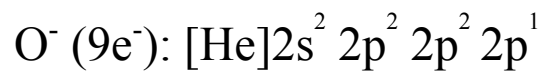Unpaired electrons tend to have parallel spins. (spin correlation)

The 2 p e⁻ in C have parallel spins $\alpha\alpha$ ($\beta\beta$).

Oxygen atom (8 e⁻)

$\quad$ $[He]2s^2 \, 2p^2 \, 2p^1 \, 2p^1$ $\qquad\qquad$ $\alpha\alpha$ $\quad$ or $\quad$ $\beta\beta$

<u>Electronic configuration of ions</u> can be obtained by removing or adding outer electrons from neutrals.

Ca: $[Ar]4s^2$, $\quad$ Ca^{2+}: $[Ar]$

O⁻ (9e⁻): $[He]2s^2\,2p^2\,2p^2\,2p^1$

O²⁻(10e⁻): $[He]2s^2\,2p^2\,2p^2\,2p^2$

Periodicity

Ionization energy: minimal E for removing an e⁻.

Electron affinity: E release when an e⁻ attaches to an atom.