

CH107: Week 5

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16th January 2023

1 Hamiltonian in Multielectron Systems

We studied the Hamiltonian in helium atom. Here the Hamiltonian contained 6 terms. We then performed separation of electronic and nuclear parts just like in case of hydrogen atom. The nuclear Hamiltonian remains the same. The electronic Hamiltonian can be written as:

$$\hat{H}_e = \hat{H}_1 + \hat{H}_2 + \frac{Qe^2}{r_{12}} \quad (1)$$

The first two terms are similar as hydrogen and the third term represents e-e PE. We then performed the **orbital approximation** which assumes that the total wave function can be written as a product of the wavefunction for the two electrons. $\psi_e(r_1, \theta_1, \phi_1, r_2, \theta_2, \phi_2) = \psi_{1e}(r_1, \theta_1, \phi_1, r_2) \psi_{2e}(r_1, \theta_1, \phi_1, r_2)$. This can be used to write the eigen equation and find energies of two electrons.

We then studied the general expression of Hamiltonian in multielectron systems. These eqns can only be solved numerically. They cannot be solved using analytical methods.

Effective Nuclear Charge Electrons in addition of attraction from nucleus also faces repulsion from the other electrons therefore effective charge is decreased. The third term of electronic Hamiltonian when summed over many electrons cannot be ignored. $Z_{eff} = Z - \sigma$. For Helium atom $Z_{eff} = 1.69$. In the Hamiltonian, we replace the Z_N to Z_{eff} . The total energy also changes by a factor of $\left(\frac{Z-\sigma}{Z}\right)^2$.

2 Spin Orbital Momentum

The spin of the electrons were predicted due to the **Stern-Gerlach Experiment** where a beam of Ag atoms passed through an inhomogeneous magnetic field split into two lines representing the two spin states. Later in 1925 it was proven that **spin** was a property **intrinsic** to electrons and not due to actual spinning of electrons.

The spin angular momentum $|S| = \hbar\sqrt{s(s+1)}$ where s is the spin quantum number. For electron $s = 1/2$ and $S_z = \pm\frac{1}{2}\hbar$. The spin is a **completely quantum mechanical property** and has **no classical analogy**. Basically "spin up" (or α) and "spin down" (or β) are two eigen functions of the spin operator having same eigen values but with opposite sign. The spin is not result of actual spinning of electron as that will cause $v > c$.

Spin Orbital Wavefunction: Total wavefunction has both spatial part and spin part; $\Psi(r, \theta, \phi, \omega) = \Psi(r, \theta, \phi) \cdot \alpha(\omega)$ or $\Psi(r, \theta, \phi) \cdot \beta(\omega)$. **Spin Orbital:** One electron wavefunction containing spatial as well as spin parts.

3 Slater Determinant and Linear Combinations

Wavefunctions must reflect indistinguishability of electrons. no known experiments can differentiate between two electrons: **No observable** change if co-ords of 2 electrons are interchanged.

In two electron system (electron label 1 and 2): there are 4 wavefunctions: $\alpha(1)\alpha(2), \beta(1)\beta(2), \alpha(1)\beta(2), \beta(1)\alpha(2)$. Out of this The first two are indistinguishable and the other two, we have to take a linear combination as **Symmetric:** $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$ and **Anti-symmetric:** $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$. Its antisymmetric as $\Psi(1, 2) = -\Psi(2, 1)$. Note: Here we take the **Linear Combination** of these two orbitals because given two electrons in opposite spin, we can't decide whether one is spin down and other is spin up or vice-versa.

6th Postulate of QM: The complete wavefunction of a system of identical fermions (e.g. electrons) must be anti-symmetric with respect to interchange of all their coordinates (spatial and spin) of any two particles. This is similar to **Pauli's Exclusion Principle** which was derived independently

$$\Psi(1, 2) = -\Psi(2, 1)$$

He atom wavefunction:

$$\begin{aligned}\Psi_{He} &= \Psi_{1s}(1) \cdot \Psi_{1s}(2) \cdot \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \\ &= \frac{1}{\sqrt{2}} \begin{vmatrix} \Psi_{1s}(1)\alpha(1) & \Psi_{1s}(1)\beta(1) \\ \Psi_{1s}(2)\alpha(2) & \Psi_{1s}(2)\beta(2) \end{vmatrix}\end{aligned}\quad (2)$$

In General,

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(1)\beta(1) & \cdots & \phi_m(1)\beta(1) \\ \phi_1(2)\alpha(2) & \phi_1(2)\beta(2) & \cdots & \phi_m(2)\beta(2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(n)\alpha(n) & \phi_1(n)\beta(n) & \cdots & \phi_m(n)\beta(n) \end{vmatrix}\quad (3)$$

This determinant is known as **Slater Determinant**. The following points are to be noted from Slater determinant:

- If any two rows/columns are **same** then the determinant becomes zero. hence no two electrons can occupy the same spin orbital. **Pauli's Exclusion Principle**
- **Exchange** of two rows/columns: Changes the sign of the determinant: **Antisymmetric**.

4 Helium Atom: Excited States

If the second electron in the **2s** orbital then it could have same spin or the opposite spin.

The spatial part of the wave function can be formed with the linear combination of $1s(1) \cdot 2s(2)$ and $1s(2) \cdot 2s(1)$. If spatial part is symmetric then the spin part is antisymmetric and vice-versa, since the total wave function needs to be symmetric. For + its symmetric and for - , antisymmetric. There can be two types of excited states: **Singlet & Triplet**.

- **Singlet $1s^1 \cdot 2s^2$** Here $S = 0$ and $M_s = 0$. The wave function is $\Psi^{1,0}$.

$$\begin{aligned}\Psi^{1,0} &= \frac{1}{\sqrt{2}}[1s(2) \cdot 2s(2) + 1s(2) \cdot 2s(1)] \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \\ &= \frac{1}{2} \begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\beta(1) \\ 1s(2)\alpha(2) & 2s(2)\beta(2) \end{vmatrix} - \frac{1}{2} \begin{vmatrix} 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\beta(2) & 2s(2)\alpha(2) \end{vmatrix}\end{aligned}\quad (4)$$

- **Triplet $1s^1 \cdot 2s^2$** Here $S = 1$ and $M_s = -1, 0, 1$. There are three possible wavefunctions:

$$\Psi = \frac{1}{\sqrt{2}}[1s(2) \cdot 2s(2) - 1s(2) \cdot 2s(1)] \begin{cases} \alpha(1)\alpha(2) & (S = 1, M_S = 1) \\ \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)] & (S = 1, M_S = 0) \\ \beta(1)\beta(2) & (S = 1, M_S = -1) \end{cases}$$

$$\begin{aligned}\Psi^{3,1} &= \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\alpha(1) \\ 1s(2)\alpha(2) & 2s(2)\alpha(2) \end{vmatrix} & \Psi^{3,-1} &= \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1)\beta(1) & 2s(1)\beta(1) \\ 1s(2)\beta(2) & 2s(2)\beta(2) \end{vmatrix} \\ \Psi^{3,0} &= \frac{1}{2} \begin{vmatrix} 1s(1)\alpha(1) & 2s(1)\beta(1) \\ 1s(2)\alpha(2) & 2s(2)\beta(2) \end{vmatrix} + \frac{1}{2} \begin{vmatrix} 1s(1)\beta(1) & 2s(1)\alpha(1) \\ 1s(2)\beta(2) & 2s(2)\alpha(2) \end{vmatrix}\end{aligned}\quad (5)$$

So basically, **Spin-orbital wavefunctions are represented as Slater Determinants or their sums**. Further, note that triplet are usually stable than singlet.