

Lecture 11 Title: Central Field Approximation

Page-1

In this lecture we will try to solve the problem of perturbation method while dealing with the electron-electron coulomb repulsion for N-electron atoms.

We will also learn the symmetric and anti-symmetric wavefunction and exchange degeneracy for identical particles.

We will know the method for incorporating Pauli exclusion for electron while evaluating the total wavefunction of the multi-electron atom.

Next we will take some examples for calculating the energy levels of He-atom

Page-2

Central Field Approximation:

→ The basic difficulty in solving the Schrödinger equation stems from the fact that the

interelectron repulsion $\sum_{i<j}^N \frac{e^2}{r_{ij}}$ is too large an effect to be treated as a perturbation.

→ It is that the inter electron repulsion contains a large spherically symmetric component. Thus it is possible to construct a potential energy function $U(r_i)$ which is a spherically symmetric.

→ One electron operator is a good approximation to the actual potential energy of the i^{th} electron in the field of the nucleus and the other $N - 1$ electrons. The Hamiltonian may be written as,

$$H = H^* + H_1$$

$$\text{where } H^* = -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N U(r_i)$$

$$\text{where } \sum_i U(r_i) = -\sum_{i=1}^N \frac{Ze^2}{r_i} + \left\langle \sum_{i<j}^N \frac{e^2}{r_{ij}} \right\rangle$$

$$\text{and } H_1 = \sum_{i<j}^N \frac{e^2}{r_{ij}} - \left\langle \sum_{i<j}^N \frac{e^2}{r_{ij}} \right\rangle \quad \text{Non-Spherical part only}$$

In which $\left\langle \sum_{i<j}^N \frac{e^2}{r_{ij}} \right\rangle$ is the average over a sphere of the electron repulsion.

It is therefore independent of the angular coordinates, then H_1 becomes the Hamiltonian which contains the non spherical part of the electron repulsions, whereas H^* contains the K.E, P.E in the field of the nucleus, and the spherical average electron repulsion energy.

This is Known as central field approximation. The advantage of this approach is that, it is assumed that H^* contains most of the inter electron repulsion, the remaining term H_1 is small enough to be treated as a perturbation.

Since $U(r_i)$ is a one electron operator, the Schrödinger equation,

$$H^* \Phi = \left\{ -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N U(r_i) \right\} \Phi = E \Phi$$

Φ is a product of single electron wave function ϕ_i . When H^* is allowed to operate on a product wave function Φ , it operates on each of the ϕ_i in turn, since the coordinates of each of electrons are independently variable. So, the equation reduced to a set of N simultaneous equation, one for each electron.

$$H_1^* \phi_1 = E_1 \phi_1 \quad ; \quad H_2^* \phi_2 = E_2 \phi_2 \quad ; \quad \dots$$

$$H^* = \sum_{i=1}^N H_i^* \quad ; \quad E = \sum_i E_i$$

Each ϕ_i is hydrogen type orbitals except radial part. These orbitals are called central field orbitals.

Exchange Degeneracy and Identical particles

In the lecture-11, we have seen that in the independent particle model the wavefunction

$\Phi(r_1, r_2) = \phi_a(r_1) \phi_b(r_2)$ is a solution of the Schrodinger equation

$$\left(-\frac{\hbar^2}{2m} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{Z e^2}{r_1} - \frac{Z e^2}{r_2} \right) \Phi(r_1, r_2) = E \Phi(r_1, r_2)$$

With the eigenvalue $E_a + E_b$

This Schrodinger equation is symmetrical, so $\phi_a(r_2) \phi_b(r_1)$ is also a solution with the same energy eigenvalue $E_a + E_b$

Here arises the degeneracy which is known as Exchange Degeneracy.

This is coming because of exchanging the two electrons

Now we take the linear combination of these

$$\Phi_S(r_1, r_2) = \frac{1}{\sqrt{2}} [\phi_a(r_1) \phi_b(r_2) + \phi_a(r_2) \phi_b(r_1)]$$

and

$$\Phi_A(r_1, r_2) = \frac{1}{\sqrt{2}} [\phi_a(r_1) \phi_b(r_2) - \phi_a(r_2) \phi_b(r_1)]$$

These are also the solutions of the same Schrodinger Equation with eigenvalue $E_a + E_b$.

The factor $\frac{1}{\sqrt{2}}$ is introduced to normalize the wavefunction.

The $\Phi_S(r_1, r_2)$ and $\Phi_A(r_1, r_2)$ are known as Symmetric and AntiSymmetric wavefunctions.

Page-5

The symmetric wavefunction $\Phi_s(r_1, r_2)$ remains same even we interchange the indices 1 and 2

On the other hand antisymmetric wavefunction $\Phi_A(r_1, r_2)$ changes sign if we interchange indices 1 and 2.

This is required because of the indistinguishability of identical particles like electrons.

In Classical mechanics, identical particles are distinguishable, because it is possible to define the individual particles in terms of their space coordinate and time.

However, in Quantum mechanics, this is not possible. So, identical particles are always considered to be indistinguishable.

For two electrons system, when the two electrons are interchanged, then the wavefunctions are related with a phase factor as

$\Phi(r_1, r_2) = e^{i\varphi} \Phi(r_2, r_1)$ where φ is a real constant.

Now, we define P_{12} as the particle interchange operator.

$$P_{12} \Phi(r_1, r_2) = \Phi(r_2, r_1)$$

$$\text{So } P_{12}^2 \Phi(r_1, r_2) = P_{12} \Phi(r_2, r_1) = \Phi(r_1, r_2)$$

Again,

$$P_{12}^2 \Phi(r_1, r_2) = P_{12} \Phi(r_2, r_1) = e^{-i\phi} P_{12} \Phi(r_1, r_2)$$

$$= e^{-i\phi} \Phi(r_2, r_1) = e^{-2i\phi} \Phi(r_1, r_2)$$

$$P_{12}^2 \Phi(r_1, r_2) = e^{-2i\phi} \Phi(r_1, r_2)$$

Thus, $e^{-2i\phi} = 1$

So $e^{i\phi} = \pm 1$ and thus, $\Phi(r_1, r_2) = \pm \Phi(r_2, r_1)$

The “+” sign is for symmetric state and “-” sign is for antisymmetric state.

This shows that the wavefunction should be either symmetric or antisymmetric with respect to the interchange of the electrons.

If the two electrons are in the symmetric or antisymmetric state in a system, then these electrons remain in that state for all time unless it disturbed by external perturbation.

The Pauli Exclusion Principle

So far we discuss about the space part. For a full description of the total system, we have to consider the spin of the electrons also.

We define, $|\alpha\rangle$ as the spin up i.e. spin $s = 1/2$, and $m_s = +1/2$

And $|\beta\rangle$ as the spin down i.e. spin $s = 1/2$, and $m_s = -1/2$

For two electron system we have to take again the linear combination of these spin states.

Because of the indistinguishability of the electrons, we have to construct the linear combination in the symmetric and antisymmetric manner with respect to the interchange of the indices of the electrons.

$$\begin{aligned}\chi_s &= \alpha(1)\alpha(2) \\ &= \beta(1)\beta(2)\end{aligned}$$

$$\text{Symmetric : } = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$

$$\text{Antisymmetric } \chi_A = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

In this, the symmetric state contains three wavefunctions and antisymmetric contains one wavefunction.

According to the Pauli Exclusion principle, “No two electrons will have the same quantum numbers (n, l, m_l, s, m_s).

It means that “*the wavefunction for a system of electrons must be antisymmetric with respect to the interchange of the electrons*”

So for two electron system, the total wavefunction would be antisymmetric when we multiply the symmetric space wavefunction with antisymmetric spin wavefunction

$$\psi = \Phi_S(r_1, r_2) \chi_A$$

And when we multiply the antisymmetric space wavefunction with symmetric spin wavefunction

$$\psi = \Phi_A(r_1, r_2) \chi_S$$

For a system with N electrons, the antisymmetric total wavefunction is given by the Slater determinant

$$\psi(\lambda_1, \lambda_2, \dots, \lambda_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\lambda_1) & \psi_2(\lambda_1) & \dots & \psi_N(\lambda_1) \\ \psi_1(\lambda_2) & \psi_2(\lambda_2) & \dots & \psi_N(\lambda_2) \\ \dots & \dots & \dots & \dots \\ \psi_1(\lambda_N) & \psi_2(\lambda_N) & \dots & \psi_N(\lambda_N) \end{vmatrix}$$

Where $\psi_{n\ell m_\ell m_s} = \Phi_{n\ell m_\ell}(r) \chi(m_s)$

Note that when two would become the same the determinant would vanish.

Hartree's method of Self Consistent field for N-electron system

The best single electron atomic wave functions are the self consistent field (SCF) functions introduced by Hartree (1927).

To obtain these, we start with a set of N approximate single electron functions. Using of these except the i^{th} function, the average field due to their charge clouds is calculated.

This constitutes the potential field in which the i^{th} electron moves. Solution of the i^{th} equation gives an improved wave function ϕ'_i .

This is repeated for each of the N electrons, giving first improved, single electron wave functions.

These are then used to calculate a set of second improved wave functions, and so on; the process is continued until no further improvement is registered.

In other words, the electrons are supposed to move in a potential which they themselves generate. This is the reason it is known as Self Consistent

The calculated energy of the atom is the sum of the energies E_i of the individual electrons, minus the coulomb repulsion energy averaged over all pairs of electron wave functions, since this gets included twice over for each pair of electrons i & j , once in calculation E_i and once in E_j . The energy of each of the SCF/AO's, is found to be a function of n and ℓ .

When the central field orbital is multiplied by a spin function $\chi(m_s)$ which is α or β , we have a one-electron, central field spin orbital.

$\psi_{n\ell m_\ell m_s} = \Phi_{n\ell m_\ell}(r) \chi(m_s)$ Characterized by the four quantum nos. n, ℓ, m_ℓ, m_s .

Finally the spin orbitals may be organized into an antisymmetric N -electron wavefunction in order to satisfy the requirements of the Pauli principle.

$$\psi(\lambda_1, \lambda_2, \dots, \lambda_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\lambda_1) & \psi_2(\lambda_1) & \dots & \psi_N(\lambda_1) \\ \psi_1(\lambda_2) & \psi_2(\lambda_2) & \dots & \psi_N(\lambda_2) \\ \dots & \dots & \dots & \dots \\ \psi_1(\lambda_N) & \psi_2(\lambda_N) & \dots & \psi_N(\lambda_N) \end{vmatrix}$$

in which $\psi_i(\lambda_i)$ are spin orbitals.

The distribution of electrons with n and ℓ are known as configuration. Electrons in orbitals with same n and ℓ are said to be equivalent.

Example: He atom

$$\text{Hamiltonian } H = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}}$$

In zeroth order approximation; ignore $\frac{e^2}{r_{12}}$ term.

$$\begin{aligned} \text{So, } H^0 &= -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{Ze^2}{r_1} - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{r_2} \\ &= H_1 + H_2 \end{aligned}$$

Eigen functions of H_0 , $\Phi(1,2) = \phi_a(1)\phi_b(2)$

This is the product wavefunction with the electron coordinates replaced by 1 & 2 .

Eigen values, $E_0 = E_a + E_b$

Next part is to introduce the inter electronic repulsion term as a perturbation.

$$\begin{aligned} E_{ee} &= \int \Phi(1,2) \left| \frac{e^2}{r_{12}} \right| \Phi(1,2) d\tau \\ &= \int \phi_a(1)\phi_b(2) \left| \frac{e^2}{r_{12}} \right| \phi_a(1)\phi_b(2) d\tau \end{aligned}$$

So the total Energy of the system $E = (E_a + E_b) + E_{ee}$

Ground state of Helium :

In zeroth order approximation, the ground state of helium is therefore represented by

$\phi_{1s}(1)\phi_{1s}(2)$, where ϕ_{1s} is hydrogen like wavefunction

Wavefunction $\Phi(1,2) = \phi_{1s}(1)\phi_{1s}(2)$ (*Symmetric*)

Multiply it by antisymmetric spin function to make the total wavefunction antisymmetric.

$$\psi(1,2) = \Phi(1,2)\chi_A$$

So the unperturbed energy $E_0 = E_{1s} + E_{1s}$

First order perturbation energy

$$\begin{aligned} E_{ee} &= \int \Phi(1,2) \left| \frac{e^2}{r_{12}} \right| \Phi(1,2) d\tau \\ &= \int \chi_{1s}(1)\chi_{1s}(2) \left| \frac{e^2}{r_{12}} \right| \chi_{1s}(1)\chi_{1s}(2) d\tau \end{aligned}$$

So, the ground state energy $E = E_{1s} + E_{1s} + E_{ee}$

This will give slight shift from unperturbed energy level (E_0), which will be same as Central field approximation energy levels.

For excited states, Φ should be linear combinations of $\phi_a(1)\phi_b(2)$ & $\phi_a(2)\phi_b(1)$.

$$\Phi_s(r_1, r_2) = \frac{1}{\sqrt{2}} [\phi_a(r_1) \phi_b(r_2) + \phi_a(r_2) \phi_b(r_1)]$$

$$\Phi_A(r_1, r_2) = \frac{1}{\sqrt{2}} [\phi_a(r_1) \phi_b(r_2) - \phi_a(r_2) \phi_b(r_1)]$$

First order interelectron repulsion perturbation,

$$H'_{\phi_s\phi_s} = \int \Phi_s \left| \frac{e^2}{r_{12}} \right| \Phi_s d\tau = C_1 + A_1$$

$$H'_{\phi_s\phi_a} = \int \Phi_a \left| \frac{e^2}{r_{12}} \right| \Phi_s d\tau = C_1 - A_1$$

$$\text{where, } C_1 = \int \phi_a(1)\phi_b(2) \left| \frac{e^2}{r_{12}} \right| \phi_a(1)\phi_b(2)$$

$$A_1 = \int \phi_a(1)\phi_b(2) \left| \frac{e^2}{r_{12}} \right| \phi_a(2)\phi_b(1)$$

C_1 represents the **Coulombic Interaction** of the electron charge clouds $\phi_a^2(1)$ & $\phi_b^2(2)$.

A_1 is called **Exchange Integral**.

Next is to include spin to get spin orbital. So,

$$\text{Singlet } \frac{1}{\sqrt{2}} [\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

$$\text{Triplet } \frac{1}{\sqrt{2}} [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] \alpha(1)\alpha(2)$$

$$\frac{1}{\sqrt{2}} [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] \beta(1)\beta(2)$$

$$\frac{1}{\sqrt{2}} [\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

First excited state :

Case: 2 1s 2s

$\phi_{1s}(1) \phi_{2s}(2)$
 $\phi_{2s}(1) \phi_{1s}(2)$ product wavefunction

Symmetric wavefunction $\Phi_s(1,2) = \frac{1}{\sqrt{2}} [\phi_{1s}(1)\phi_{2s}(2) + \phi_{2s}(1)\phi_{1s}(2)]$

And the antisymmetric wavefunction $\Phi_A(1,2) = \frac{1}{\sqrt{2}} [\phi_{1s}(1)\phi_{2s}(2) - \phi_{2s}(1)\phi_{1s}(2)]$

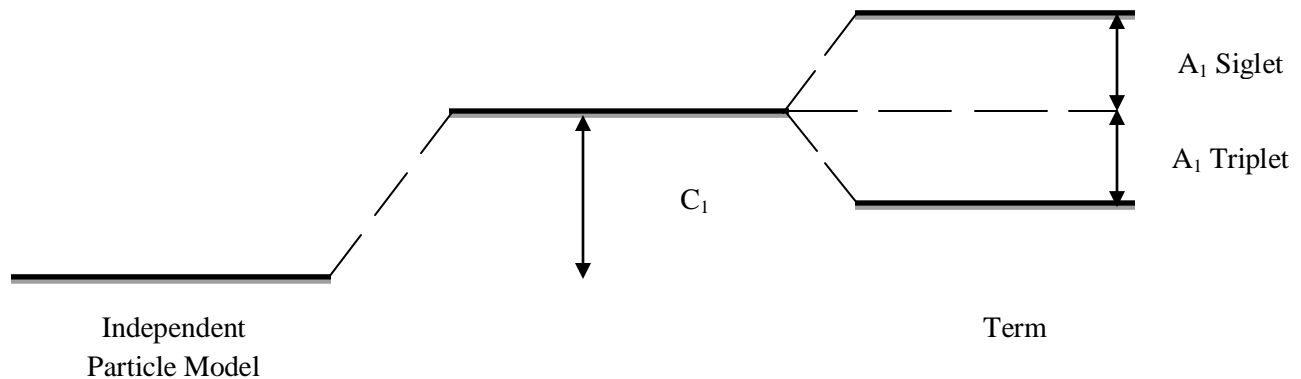
We have to multiply it with corresponding symmetric and antisymmetric spin wavefunction.

First order energy

$$\begin{aligned}
 E_{1s,2s}^{ee}(\text{Singlet}) &= \int \Phi_s(1,2) \left| \frac{e^2}{r_{12}} \right| \Phi_s(1,2) d\tau \\
 &= \int \frac{1}{\sqrt{2}} \{ \phi_{1s}(1)\phi_{2s}(2) + \phi_{2s}(1)\phi_{1s}(2) \} \left| \frac{e^2}{r_{12}} \right| \frac{1}{\sqrt{2}} \{ \phi_{1s}(1)\phi_{2s}(2) + \phi_{2s}(1)\phi_{1s}(2) \} d\tau \\
 &= \frac{1}{2} 2 \int \phi_{1s}(1)\phi_{2s}(2) \left| \frac{e^2}{r_{12}} \right| \phi_{1s}(1)\phi_{2s}(2) d\tau + \frac{1}{2} 2 \int \phi_{1s}(1)\phi_{2s}(2) \left| \frac{e^2}{r_{12}} \right| \phi_{2s}(1)\phi_{1s}(2) d\tau \\
 &= C_{1s,2s} + A_{1s,2s}
 \end{aligned}$$

$$E_{1s,2s}^{ee}(\text{triplet}) = C_{1s,2s} - A_{1s,2s} \quad A_1 \text{ exchange integrals}$$

The spin wavefunctions are normalized and integrations give values 1

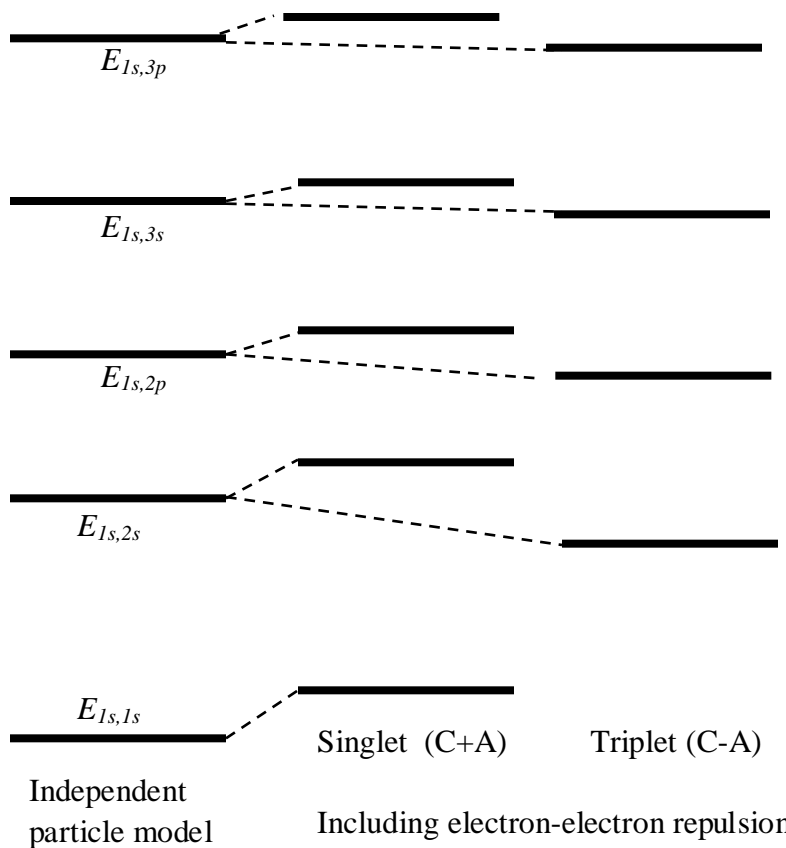


So the energy difference: $2A_1$

Note that

- 1) For closed shell, such as $1s^2$, this exchange integral is not present. So there is no splitting. Even for other closed shell, the exchange integral is present.
- 2) For closed shell i.e. both coulomb and exchange potential are spherically symmetric.
- 3) For all excited states of Helium, the energy levels split into two, Singlet and Triplet
- 4) Splitting comes from exchange integrals so this is non central part of the electrostatic repulsion.
- 5) Before that it is just central field approximation

The Helium atom energy levels



Page-14

Recap

Here we discussed the method for handling the large coulomb repulsion part in the perturbation method.

The saving feature of the problem is that the large part of the electron repulsion contains a large spherically symmetric component.

This spherically symmetric part can be treated with one electron operator and is a good approximation to make a potential of i th electron in the field of nucleus and $(N-1)$ electrons.

The asymmetric part causes the splitting of energy levels and for helium this produces singlet and triplet states. The splitting energy is the value of the exchange integrals.