In this lecture we will extend the problem to more than one electron atoms. We will start with the simple one such as He atom.

The quantum mechanical calculations of the energy levels in different approximations are discussed.

From the ionization energy i.e the energy required to remove one electron from Helium atom, the ground state energy of Helium is calculated to be -79.0eV.

We use this information to check the different method approximation for calculating the Helium atom energy levels.
The emission spectra of He consists of a number of series in the visible region of the spectrum as well as in the near & far UV regions.

There are twice as many line series as for the alkalis; two principal series in the visible and near UV, as well as two diffuse, two sharp and two fundamental series.

This observation cannot be described by simple concept from hydrogen atom.

When more than one electron is present, the Hamiltonian for an atom in free space becomes

\[
H = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_i Z e_i^2 r_i + \sum_{i \neq j} e_{ij} r_{ij} \\
= T_E + V_{EN} + V_{EE}
\]

\[\text{......11.1}\]

\(V_{EN}\) is the Coulomb interaction between the nucleus and the electrons. \(V_{EE}\) is the electrostatic repulsion of the free electrons, summed over all pairs \(i\) and \(j\) at separation \(r_{ij}\). This equation (1) does not contain spin part, we assume that such effects can be treated separately.

Equation (1) contains terms \(\frac{e^2}{r_{ij}}\) for interelectronic repulsions that are not present in the Hamiltonian for hydrogen like atoms.

Because of these terms, the motion of each electron affects the motion of every other electrons, and the wave equation for polyelectronic atoms cannot be solved exactly.

Various approximate methods of solution exist. Most methods start by assuming that complex atoms can be “built up” by feeding electrons successively into atomic orbitals (AOs). That is, every electron in an atom is assigned a wave function \(\phi_i\), defined by a set of quantum numbers.

The wave function for the whole atom is written in terms of these electron wave functions \(\phi_i\). The best sets of wave functions \(\phi_i\) are those for which the residual difference between the calculated energy of the whole atom and the actual energy is as small as possible.
Independent Particle Model:

One-Electronic Wave Functions

A crude method, zeroth order approximation to the $\phi_i$ is obtained by ignoring altogether the terms $V_{EE}$ in (1), giving the Hamiltonian

$$ H = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{N} \nabla_i^2 - \sum_{i=1}^{N} \frac{Ze^2}{r_i} $$

....................11.2

Then, in the approximation in which electron spin is neglected, the eigen functions of this Hamiltonian are products of the occupied single electron orbital wave functions $\phi_i$ for the $N$ electrons,

$$ \Phi(1,2,...,N) = \phi_1(r_1, \theta_1, \varphi_1) \phi_2(r_2, \theta_2, \varphi_2) ... \phi_N(r_N, \theta_N, \varphi_N) $$

............11.3

Since interactions between the electrons are ignored, each electron moves independently of the others in the electrostatic field of the nucleus alone. The $\phi_i$ is therefore the hydrogen like wavefunctions, the eigen values of Hamiltonian are the sum or the individual energies $E_i$ for the electrons in hydrogen like orbitals:

$$ E = E_1 + E_2 + ... + E_N $$

............11.4
Let us take the example of Helium ($Z = 2$) that consists of two electrons as shown in the figure-11.1

In this approximation, Hamiltonian,

$$H = -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Z e^2}{r_i} - \frac{\hbar^2}{2m} \nabla_j^2 - \frac{Z e^2}{r_j}$$

..............11.5

Schrödinger equation,

So,

$$\left( -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{\hbar^2}{2m} \nabla_j^2 - \frac{Z e^2}{r_i} - \frac{Z e^2}{r_j} \right) \Phi(r_i, r_j) = E \Phi(r_i, r_j)$$

..............11.6

Here we take $\phi_a(r_1)$ and $\phi_b(r_2)$ are the one electron wavefunction as in hydrogen atom.

$$\Phi(r_i, r_j) = \phi_a(r_1) \phi_b(r_2)$$

$$\left( -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{Z e^2}{r_1} \right) \phi_a(r_1) = E_a \phi_a(r_1)$$

$$\left( -\frac{\hbar^2}{2m} \nabla_2^2 - \frac{Z e^2}{r_2} \right) \phi_b(r_2) = E_b \phi_b(r_2)$$

$$E = E_a + E_b$$

..............11.7
Two electrons “a” and “b” move independently of each other and the total energy of the system is simply sum of the energies of non-interacting particle.

\[
\phi_a(r_1) = R_{nl_1}(r_1) Y_{l_1m_1}(\theta_1, \phi_1) \\
\phi_b(r_2) = R_{nl_2}(r_2) Y_{l_2m_2}(\theta_2, \phi_2)
\]

\[
E_n = -\frac{Z^2}{n^2} \frac{m e^4}{2 \hbar^2} = -\frac{Z^2}{n^2} E_H \\
\text{where, } E_H = \frac{m e^4}{2 \hbar^2} = 13.605 \text{ eV}
\]

The ground state energy of Helium (when both the electrons are in 1s level)

\[
E = E_a + E_b = -\frac{4}{l^2} E_H - \frac{4}{l^2} E_H = -8E_H = -108.8 \text{ eV}
\]

The experimental value of the ionization energy i.e. the energy required to remove one electron from Helium atom = 24.63 eV

When one electron is removed then the energy of ionized Helium ion (He⁺) = -Z²×13.6 eV = -54.4 eV

So the ground state energy of Helium = -54.5 eV - 24.63 eV = -79.03 eV

Thus, Atomic energies calculated in this manner are the poor approximation to the actual eigenvalues.

However, the calculated energies and wavefunctions can be improved by introducing the interelectronic repulsion terms \( V_{ee} \) as a perturbation.
Considering electron repulsion:

\[ H = -\frac{\hbar^2}{2m} \nabla^2_i - \frac{\hbar^2}{2m} \nabla^2_j - \frac{Z e^2}{r_i} - \frac{Z e^2}{r_j} + \frac{e^2}{r_{ij}} \]  

\[ \tag{11.8} \]

We will consider the first order perturbation theory. In this approximation, we take unperturbed Hamiltonian as

\[ H_0 = -\frac{\hbar^2}{2m} \nabla^2_i - \frac{\hbar^2}{2m} \nabla^2_j - \frac{Z e^2}{r_i} - \frac{Z e^2}{r_j} \]

And consider the perturbed Hamiltonian as

\[ H' = \frac{e^2}{r_{ij}} \]

Substituting in the Schrödinger Equation

\[ (H_0 + H') \phi_a (r_i) \phi_b (r_j) = E \phi_a (r_i) \phi_b (r_j) \]

We are interested to calculate the ground state energy. So both the electrons are in 1s level.

So, \( n = 1, l = 0 \) and \( m = 0 \) for both the electrons. Let us take the ground state wavefunction of the hydrogen atom for each electron.

\[ \phi_{nlm} = \phi_{l00} (r) = \frac{1}{\sqrt{4\pi}} \left( \frac{Z}{a_0} \right)^{3/2} 2 e^{-\frac{r_i}{a_0}} \]

\[ \phi_{l00} (r_i) = \frac{1}{\sqrt{4\pi}} \left( \frac{Z}{a_0} \right)^{3/2} 2 e^{-\frac{r_i}{a_0}} \]

\[ \phi_{l00} (r_j) = \frac{1}{\sqrt{4\pi}} \left( \frac{Z}{a_0} \right)^{3/2} 2 e^{-\frac{r_j}{a_0}} \]
So,

\[ \phi_{n0}(r_1)\phi_{n0}(r_2) = \frac{1}{4\pi} \left( \frac{Z}{a_0} \right)^3 4e^{-Z/a_0(\eta+\zeta)} \]

\[ = \frac{1}{\pi} \left( \frac{Z}{a_0} \right) e^{-\left( \frac{Z(\eta+\zeta)}{a_0} \right)} \]

Evaluating,

\[ \left\langle \frac{e^2}{r_{12}^2} \right\rangle = \iint \phi_{n0}^*(r_1)\phi_{n0}^*(r_2) \frac{e^2}{r_1 - r_2} \phi_{n0}(r_1)\phi_{n0}(r_2) d\tau_1 d\tau_2 \]

\[ = \frac{Z^6 e^2}{\pi^3 a_0^6} \int d\tau_1 e^{\frac{2Zr_1}{a_0}} \int d\tau_2 e^{\frac{2Zr_2}{a_0}} \frac{1}{|r_1 - r_2|} \]

\[ = \frac{1}{|r_1 - r_2|} \left[ \frac{1}{r_1} \sum_{r_2} \left( \frac{r_2}{r_1} \right)^{\ell} P_\ell(\cos \theta) \text{ for } r_1 \geq r_2 \right] \]

\[ = \frac{1}{r_2} \sum_{r_1} \left( \frac{r_1}{r_2} \right)^{\ell} P_\ell(\cos \theta) \text{ for } r_2 \geq r_1 \]

\[ \theta \Rightarrow \text{between } r_1 \& r_2 \]

\[ d\tau_2 = r_2^2 dr_2 \sin \theta d\theta d\phi \]

\[ \rho_1 = \frac{27r_1}{a_0} \quad \rho_2 = \frac{27r_2}{a_0} \]

Figure 11.2
\[
\langle \epsilon^2 \rangle = \frac{Z e^2}{32 \pi^2 a_0} \int d^4 \rho_1 \sin \theta_1 d \theta_1 d \phi_1 e^{2 \varphi} \left[ \frac{1}{\rho_1^2} \int \rho_2^2 d \rho_2 e^{-\rho_2} \times \frac{1}{\rho_2^3} \sum_r \left( \frac{\rho_2}{\rho_1} \right)^r \int \rho_1 (\cos \theta) \sin \theta d \theta d \phi \right] + \int \rho_2^2 d \rho_2 e^{2 \varphi} \times \frac{1}{\rho_2^3} \sum_r \left( \frac{\rho_2}{\rho_1} \right)^r \int \rho_1 (\cos \theta) \sin \theta d \theta d \phi
\]

\[
= \frac{Z e^2}{8 \pi^2 a_0} \int d^4 \rho_1 \sin \theta_1 d \theta_1 d \phi_1 e^{2 \varphi} \left[ \frac{1}{\rho_1^2} \int \rho_2^2 e^{2 \varphi} d \rho_2 + \int \rho_2 e^{2 \varphi} d \rho_2 \right]
\]

\[
= \frac{5}{8} \frac{Z e^2}{a_0} = \frac{5Z}{4} E_H
\]

where, \( E_H = \frac{e^2}{2a_0} = 13.605 \text{ eV} \)

According to first order perturbation theory the ground state energy of He,

\[
E_{ground} = -8E_H + \frac{5Z}{4} E_H = -8E_H + \frac{10}{4} E_H
\]

\[
= -108.84 + 34.01 = -74.83 \text{ eV}
\]

**Experimental** = \(-79.0 \text{ eV}\)

**Error** = 4.2 eV
The effect of the repulsive term $\frac{e^2}{r_{12}}$ is to reduce the nuclear charge on each electron. One way to accommodate this is to assume hydrogen like wavefunction corresponding to effective nuclear charge $Z'$, which will be assumed to be the variable parameter. We assume the (trial) normalized wavefunction,

$$\Phi(r_1, r_2) = \phi_a(r_1) \phi_b(r_2)$$

$$= \left( \frac{Z'^3}{\pi a_0^3} \right) e^{-Z_{1}/a_0} e^{-Z_{2}/a_0}$$

$Z = 2$;

$\phi$ is normalized, so we have to minimize the integral

$$E(Z') = \iint \phi^* H \phi d\tau_1 d\tau_2$$

$$= \iint \phi^* \left[ -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - Z e^2 \left( \frac{1}{r_1} + \frac{1}{r_2} \right) + e^2 \frac{1}{r_{12}} \right] \phi d\tau_1 d\tau_2$$
Since $\Phi (r_1, r_2)$ is the solution of

$$\left[ -\frac{h^2}{2m} \nabla^2 + \frac{Z' e^2}{r_1} \right] \Phi (r_1, r_2) = -Z'^2 E_H \Phi (r_1, r_2)$$

$$E (Z') = \iint \phi' \left[ -Z'^2 E_H - Z'^2 E_H + \frac{Z'^2 e^2}{r_1} + \frac{Z'^2 e^2}{r_2} - \frac{Z e^2}{r_1} - \frac{Z e^2}{r_2} + \frac{e^2}{r_{12}} \right] \phi \, d\tau_1 \, d\tau_2$$

$$= \iint \phi' \left[ -2Z'^2 E_H + (Z' - Z) e^2 \left( \frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{e^2}{r_{12}} \right] \phi \, d\tau_1 \, d\tau_2$$

$\ldots \ldots 11.9$

1st integration:

$$\iint \phi' (-2Z'^2 E_H) \phi \, d\tau_1 \, d\tau_2 = -2Z'^2 E_H$$

2nd integration:

$$\iint \phi' (Z' - Z) e^2 \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \phi \, d\tau_1 \, d\tau_2$$

$$= (Z' - Z) e^2 \iint \phi' \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \phi \, d\tau_1 \, d\tau_2$$

$$= (Z' - Z) e^2 2 \iint \phi' \phi \, d\tau_1 \, d\tau_2$$

$$= (Z' - Z) e^2 \frac{2Z'}{a_0} = 4Z' (Z' - Z) E_H$$

where, $E_H = \frac{e^2}{2a_0}$

3rd Integration:

$$\iint \phi' \frac{e^2}{r_{12}} \phi \, d\tau_1 \, d\tau_2 = \frac{5}{4} Z' E_H$$
Substituting in equation-11.9,

\[ E(Z') = -2Z'^2E_H + 4Z'(Z' - Z)E_H + \frac{5}{4}Z'E_H \]

\[ \Rightarrow \frac{\partial E(Z')}{\partial Z'} = 0 = -4Z'E_H + 8Z'E_H - 4ZE_H + \frac{5}{4}E_H \]

\[ \Rightarrow \left(-4Z' + 8Z' - 4Z + \frac{5}{4}\right)E_H = 0 \]

\[ \Rightarrow 4Z' - 4Z + \frac{5}{4} = 0 \]

\[ \Rightarrow Z' = Z - \frac{5}{16} \]

So, the ground state energy,

\[ E = -2Z'^2E_H \]

\[ = -2\left(Z - \frac{5}{16}\right)^2E_H \]

\[ = -2\left(Z - \frac{5}{16}\right)^213.605 \]

\[ = -77.48 \text{eV} \]

*Experimental* = -79.0 eV

*Error* = 0.02%

Other trial function yield values within 0.01% of the observed one.
Recap

What we observed is that the perturbation method fails to calculate the ground state energy of Helium. The basic difficulty in solving the Schrödinger equation with this Hamiltonian stems from the fact that the $\frac{e^2}{r_{12}}$ is too large an effect to be treated as a perturbation. On the other hand the variational principle is an effective approximation and is able to produce the experimental observation.

Now the question is that,

“In this Helium problem can we use perturbation method?.”

The answer is : Yes, but we have to use “Central Field Approximation. In the next lecture, we elaborate the central field approximation.