Many-Electron Atoms

The Hamiltonian operator for electrons in many-electron atoms can be written as

$$H_{op} = -\frac{h^2}{8\pi^2 m}\sum_{i=1}^{n}\nabla_i^2 - Ze'^2\sum_{i=1}^{n}\frac{1}{r_i} + \sum_{i=1}^{n}\sum_{j=i+1}^{n}\frac{e'^2}{r_{ij}} \qquad \dots\dots\dots(1)$$

The first term represent the total kinetic energy of all the n electrons, the second term represents the nuclear-electronic attractions and the last term represents the electronic -electronic repulsions. The Schrodinger equation a usual can be written as

$$H_{op}\,\Psi = E\Psi \qquad \dots\dots\dots\dots\dots\dots (2)$$

where the function Ψ is a function of 3n independent variables.

Unfortunately, it has not possible to solve Eq. 2 accurately and one has to resort to the approximate methods. The major difficulty in solving Eq. 2 comes from the electronic - electronic repulsion terms. In absence of these terms, Schrodinger equation can be solved by writing the wave function Ψ as the product of one electron wave functions (represented hereafter as Ψ^0). The latter can be chosen from the hydrogen like wav functions. When this product function is substituted in Eq.2 , the latter splits into a number of equations , each involving the coordinates of the individual electron. The form of the resultant equations is identical to those of the hydrogen - like ions. The total energy is equal to the sum of the individual energies of various electrons.

The above results are very approximate and do not represent the quantitative behaviour of electrons in the atom.

SELF- CONSISTENT METHOD (Hartree - Fock method):

The above procedure of solving the Schrodinger equation cannot be extended if the atom contains larger number of electrons. Another method, which is a more practical one, was suggested by Hartree in 1928 and is known as the **Self-Consistent Field (SCF)** method. Later it was developed by Scientist Fock and so the method is renamed as **Hartree - Fock method.**

The method:

1. The total wave function of the system can be written as the product of one -electron wave function, i.e.,

$$\psi = \varphi_1(1)\ \varphi_2(2)\ \varphi_3(3)..... \varphi_n(n)$$

where $\varphi_1(1)$ is wave function of the electron 1 , and so on . These one electron wave functions can be trial functions.

2. Each electron is supposed to be moving in an average spherically symmetric potential energy function V_i arises because of the nuclear attraction and the repulsion from all other electrons .In order to evaluate the function V_i for the ith electron, which is usually done by numerically integration, we require the knowledge of the wave functions of all electrons except the one under steady.

3. Once the function V_i is available is available, we can write the one electron Schrodinger equation as

$$-\sum_{i=1}^{n} \nabla_i^2 \varphi_i + V_i \varphi_i = E_i \varphi_i$$

.... (2)

solving this questions , we get the improved wave function φ_i and he corresponding energy E_i.

Now, we can summarize the procedural part of the SCF-method. Suppose, we start with the electron-1. First of all V_1 is evaluated by employing the trial functions $\varphi_2(2)$, $\varphi_3(3)$, ..., $\varphi_n(n)$. This is substituted in Eq. 2 and is solved for the first-improved wave function $\varphi'_1(1)$ and the corresponding energy E'_1. We now shift to the electron 2 and evaluate the function V_2 by employing the first improved wave function $\varphi'_1(1)$ and the starting trial -functions $\varphi_3(3)$, $\varphi_4(4)$,... $\varphi_n(n)$. This is substituted in Eq. 2 and is solved for the first improved wave function

$\varphi'_2(2)$ and the corresponding energy E'_2. This process is repeated one by one for all the electrons and thus we get the first improved wave functions and the corresponding first improved energies. Now, we start once again from the electron 1. Its modified potential V_1 is evaluated by employing the first improved wave functions of all other electrons , viz $\varphi_2(2)$, $\varphi_3(3)$, ...On substituting V_1 in eq 1 and subsequently solving, we get the second improved wave function $\varphi''_1(1)$ and the corresponding energy E''_1. Similarly, the second improved wave functions for all the n -electrons are obtained. We then again repeat the process a third time, this time using the second improved φ functions and thus obtained the third improved wave functions and third improve energies. This iterative process is repeated until the nth improved wave functions agree

within the limit with the (n-1)th improved wave functions, i.e, they become self consistent. The energy of the atom is then given by

$$E = \sum_{i=1}^{n} E_i$$

....(3)

The Schrodinger equation as give by the eq 2 for the multi-electron atom is identical to that of a single electron in the hydrogen like ions, with the only difference of the form of the sphericaly symmetric potential energy term V_t. Thus, the mechanism of solution of eq 2 is very similar to that employed for the hydrogen like ions. Since V_1 appears only in the radical equations, the solutions for the angular dependence $\Theta(\theta_t)$ and $\Phi(\varphi_t)$ are exactly the same as those of hydrogen like ion. This means that the angular shapes and probability distributions in the multi electron atoms are exactly identical to those for the single electron in the hydrogen like ion. Thus, the various orbitals may be designated as usual by the symbol s, p, d and f and so on.

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