Approximation Methods in Quantum Mechanics (Review)

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ABSTRACT

Approximation methods play a crucial role in quantum mechanics, enabling the study of complex systems that are analytically intractable. This paper provides an introduction to two prominent approximation methods in quantum mechanics: the Hartree-Fock approximation and atomic approximations. The Hartree-Fock approximation is a widely used method for describing the behavior of many-electron systems. It approximates the complicated many-body wavefunction by considering a single Slater determinant, where each electron occupies an independent orbital. By solving the Hartree-Fock equations, the method provides an effective mean-field description of the system, neglecting electron-electron correlations. The basic principles, mathematical formulation, and limitations of the Hartree-Fock approximation are discussed. Atomic approximations focus on modeling atomic systems, which serve as fundamental building blocks for more complex molecular structures. These approximations aim to simplify the electronic structure of atoms while retaining the essential physical characteristics. The most commonly used atomic approximations include the Thomas-Fermi model, the Thomas-Fermi-Dirac model, and the density functional theory. Each of these approximations provides valuable insights into the behavior of atoms and facilitates the calculation of various atomic properties. This paper presents a comprehensive overview of the Hartree-Fock approximation and atomic approximations, highlighting their significance and utility in quantum mechanics. The strengths and weaknesses of each method are discussed, along with their respective applications and domains of validity. Additionally, the paper addresses the relationship between these approximation methods and more advanced theories, emphasizing the need for accurate approximations to tackle the challenges posed by complex quantum systems.

Overall, this introduction serves as a foundation for further exploration and understanding of approximation methods in quantum mechanics, laying the groundwork for future research and applications in various areas of physics, chemistry, and materials science

Keywords: crucial role, quantum mechanics, Hartree-Fock and many-body and many-electron.

1. Hartree-Fock Approximation

The wave function $\Psi(r_1, r_2, r_3, \ldots r_n)$ of any system is a mathematical expression which describes the system properties as position, momentum, energy, etc. The wave function for the multi–particle is defined as [1]:

$$\Psi_{n\ell m_\ell m_s}(\bar{r}) = R_{n\ell}(r) Y_{\ell m_\ell}(\theta,\phi)\sigma(s) \qquad \text{............ (1-1)}$$

The radial part $R_{n\ell}(r)$ is related to the distance of the electron from the nucleus. It depends on the (n) "principal quantum number" and (ℓ)"angular momentum quantum number". In contrast, the angular part (spherical harmonic) $Y_{\ell m_\ell}(\theta,\phi)$ supplies an angle dependence and depends on the ℓ and m_ℓ (magnetic quantum number). The quantum numbers n, ℓ, m_ℓ and m_s take the values will be mentioned later. The analytical solutions to the Schrödinger equation for the non-relativistic Hydrogen atom are well known but cannot be obtained exact analytical solutions for a system of many electrons. The electron-electron term in the Schrodinger equation makes the solution inseparable in single-particle coordinates, except in only approximate methods. The Hartree-Fock Self-Consistent Field approximation (HF SCF) provides an excellent starting point for dealing with a many-electron system [2].

1.1. Hartree Approximation:-

In 1928, and 2 years after from propagated the Schrödinger equation, Hartree suggested a mode to resolve Schrödinger equation for multiple-electron systems based on physical standards [3]. Hartree approximation assumed that "every electron moves with average potential result from other electrons", so the wave function equal to multiplication wave function for single electron for system have N-electron [4]:

$$\Psi(1,2,3\ldots\ldots N) = \phi_1(1)\ \phi_2(2)\ \phi_3(3)\ldots\ldots\ \phi_N(N) \qquad \text{............ (1-2)}$$

$$= \phi_i(i)\ldots\ldots\phi_N(N)$$

Where $\phi_i(i)$ represents the function for the coordinates the site of the electron i , N electron number in the atom . This approximation is neglecting of the correlation [5]. Hartree gives an excellent approximation to calculate the Helium atom. He does not obey the Pauli Exclusion Principle when the electrons interchange their position, giving another error in calculating the energy because the waves function to the electrons is antisymmetric [6]. In addition, it also failed to consider the in distinguishability of the electrons. Later, Hartree and Fock used a new approximation of the wave function in which the Pauli Exclusion Principle was satisfied.

The electron correlation is a generic term which depicts interactions electrons with each other's, each electron stays away from others electrons, therefore; any electron moves in multi-electrons atoms. The electrons are inside that system will alteration position to keep stability system .There are two kinds of electron correlation: Fermi and Coulomb holes [7].

1.2. Slater Determinant and Hartree-Fock Approximation

In 1926, Heisenberg and Dirac autonomously suggested that the wave function of electronic motions must be anti-symmetric (the indication of the wave function becomes inverse for the reciprocation of electrons) to apply the Pauli exclusion principle naturally, so should be represented as a determinant. The new electron–electron interaction resulting from the antisymmetrization is called the exchange interaction. Slater developed a general method for solving the Schrödinger equation based on the standardized which determinant represented the anti-symmetric wave function [8, 9, 10]. The Hartree –Fock (HF) approximation were first supposed by Fock in 1930 since then ,the HF method has taken a central role in studying the atomic and molecular electronic properties[11]. The Hartree –Fock (HF) method enables accounts not only of the ground state but also excited states of atoms and ions. Fock and Slater corrected the defects of the Hartree SCF method, they pointed out that it is necessary that the spin-orbital interaction must be taken into account and to take antisymmetric linear combinations of the products of spin-orbitals. The Hartree-Fock (HF) wave functions are independent particle-model approximations to non-relativistic Schrödinger equation, so the monocular determinant can be written as the anti-symmetrized product of all occupied Hartree-Fock spin-orbital for atoms [11, 12].

$$\Psi_{HF}(123\ldots N) = A\prod(123\ldots N) \qquad \text{............ (1-3)}$$

Where A is the anti-symmetrized operator given by [47]:

$$A = \frac{1}{\sqrt{N!}}\sum_{P}(-1)^{P}\,P \qquad \text{............ (1-4)}$$

$(-1)^P$ takes the values ± 1 for even and odd permutation, P is any permutation of the electron, and the factor $\frac{1}{\sqrt{N!}}$ introduced to ensure that the wave function is normalized. For our purpose, the wave function is written [13]

$$A_{ij}^{mn} = \phi_i(m)\phi_j(n) - \phi_j(m)\phi_i(n) \qquad \text{............ (1-5)}$$

where the pair function A_{ij}^{mn} can be defined as [30]:

$$\Psi_{HF}(123\ldots N) = \sum_{i<j}^{N} A_{ij}^{mn}(-1)^{P} A\Pi_{ij} \qquad \text{............ (1-6)}$$

And Π_{ij} Explain the product of all occupied Hartree-Fock spin orbital except $\phi_i(m)$ and $\phi_j(n)$, while i and j represent spin orbital labels, also m and n refer to electron labels.

The product $\Pi(123\ldots N)$ in equation (1-3) can be defined as:

$$\Pi(123\cdots N) = \left|\phi_1(1)\phi_2(2)\phi_3(3)\cdots\phi_N(N)\right| \qquad \text{............ (1-7)}$$

The Hartree-Fock spin-orbital ϕ are specified by the numbers 1,2,3…N begin with the bottom orbital with spin, therefore; all odd integers for α spin and all even ones for β spin. Equation (1-3) can be expressed in terms of Slater determinant as follows [12]:

$$\Psi_{HF}(123\cdots N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_1(1)\phi_1(2) & \ldots & \ldots & \phi_1(N) \\ \phi_2(1)\phi_2(2) & \ldots & \ldots & \phi_2(N) \\ \ldots\ \ldots & \ldots & \ldots & \ldots \\ \ldots\ \ldots & \ldots & \ldots & \ldots \\ \phi_N(1)\phi_N(2) & \ldots & \ldots & \phi_N(N) \end{vmatrix} \qquad \text{............ (1-8)}$$

The HF or analytic self-consistent field atomic wave function provides the un-correlated description of each atom. For any atom or ion, the Hartree-fock spatial orbital may be written as :

$$\phi = \sum_{i=1}^{j} c_i \chi_i \qquad \text{............ (1-9)}$$

Where c_i represents the constant coefficient yield from the SCF method. And χ_i is the basis function as a standard normalized Slater-type orbital (STO's), which is given by :

$$\chi_{n\ell m_\ell}(r,\theta,\phi) = R_{n\ell}(r) Y_{\ell m_\ell}(\theta,\phi) \qquad \text{............ (1-10)}$$

where $R_{n\ell}(r)$ is the wave function called the radial part of and it given as:

$$\mathrm{R}_{n\ell}(\mathrm{r}) = \mathrm{N}_{n\ell m_\ell} \mathrm{S}_{n\ell}(\mathrm{r}) \qquad \text{............ (1-11)}$$

$\mathrm{N}_{n\ell m_\ell}$ is the normalization constant given by[13]:

$$N_{n\ell m_\ell} = \frac{(2\zeta)^{n+\frac{1}{2}}}{\left[(2n)!\right]^{\frac{1}{2}}} \qquad \text{............ (1-12)}$$

and

$$S_{n\ell}(r) = r^{n-1} e^{-(\zeta r)} \qquad \text{............ (1-13)}$$

Where $S_{n\ell}(r)$ is called Slater-type orbital (STO's), ζ represents the orbital exponent and $Y_{\ell m_\ell}(\theta,\phi)$ represents the angular part of the wave function.

1.3. Pauli Principle and Quantum numbers:-

The Pauli Exclusion Principle is a quantum mechanical guideline formulated by Wolfgang Pauli in 1925, it's expresses that no two indistinguishable fermions may possess a similar quantum state at the same time. A more thorough articulation of this rule is that, for two indistinguishable fermions, the aggregate wave function is against symmetric. For electrons in a monocular atom, it expresses that no two electrons they have a similar four quantum numbers. In relativistic quantum field theory, the Pauli rule takes after from applying rotation operator in fictive time for particles of half-integer spin. [12,13].

The particles which have odd half-integer spins (1/2, 3/2 ,....), also have wave functions that are antisymmetric to an exchange of any two of them. Like protons and neutrons and electrons and applies the exclusion principle when they are in the same system, it's called Fermions particles, Fermi and Dirac discovered statistical distribution law which govern fermions. Whereas the particles which have spins are zero or an integer, also has wave functions that are symmetric to an exchange of any two of them, such as photons, alpha particles, and helium atoms, and do not applies the exclusion principle it's called bosons particles, Bose and Einstein discovered a statistical distribution law which govern bosons.

The quantum numbers represents (n) principle quantum number, this number takes integer values n=1, 2, 3…etc, it locates the main energy level of the atom. The principle quantum number denotes greater distances between the electrons and nucleus, the shells having values of n =1, 2, 3…etc, are called K, L,M,… shells, respectively. l orbital or azimuthal quantum number, it takes integral values including zero but less than the value of the corresponding n. The allowed l values are 0,1,2,3….(n-1). It decides the shapes of the subshells (circular orbits, elliptical orbits). These subshells are identified as s, p ,d,…corresponding to l =0,1,2,…respectively. (m_l) magnetic quantum number ,has integral value between l and $-l$ including zero, the value of ml is related to the orientation of the orbital in a space relative to the other orbitals in the atom. (m_s) spin quantum number, the electron spin taking values as +1/2 (upward) or -1/2 (downwards) .

1.4. Hund's Rule:-

The German physicist Friedrich Hund formulated first rule General, Hund saw that greatest stability comes if the atomic orbitals are half-filled with electrons before any of them are filled. This generalization, called Hund's rule, is sometimes stated in an alternative form, of the states associated with the ground state configuration of an atom or ion, those with greatest spin multiplicity lie most profound in energy [11,12].

2. The Atomic Properties

In this chapter, we studied some atomic properties such as the two–particle density □ *(xm,xn)*, two-particle radial density distribution function *D(r1,r2)*, one-particle radial density distribution function *D(r1)*, inter-particle distribution function $f(r_{12})$,one-particle expectation value $\langle r_1^n \rangle$, inter-particle expectation value $\langle r_{12}^n \rangle$, expectation value of the potential energy $\langle V \rangle$, expectation value of kinetic energy $\langle T \rangle$,.

2.1. Two-Particle Density □ (x_m, x_n)

The function *Γ(1,2)* represents the probability of finding two electrons simultaneously at position 1 and 2. For any N-electron atomic system, the two-particle density $\Gamma_{HF}(x_m, x_n)$ can be written as [14,15,16]$\Gamma_{HF}(x_m, x_n) = \binom{N}{2} \int \psi(x_1, x_2, x_p, \ldots, x_q)\psi^*(x_1, x_2, x_p, \ldots, x_q)\, dx_p \ldots dx_q$

Where x_n represents the combined space and spin coordinates of electron n and $dx_p \ldots dx_q$ indicates ... (2-1)

integration summation over all N-electrons except m and n. The factor $\binom{N}{2}$ ensures that the second order density matrix is normalized to the number of electron pairs within the system:

$$\int \Gamma_{HF}(x_m, x_n) dx_m dx_n = \binom{N}{2} \quad \ldots(2\text{-}2)$$

and $\binom{N}{2}$ can be written as:

$$\binom{N}{2} = \left[\frac{N!}{2!(N-2)!}\right] \quad \ldots\ldots\ldots(2\text{-}3)$$

Where:

$$\Gamma_{\text{HF}}(x_m, x_n) = \sum_{i=1<j}^{N} \Gamma_{\text{ij}}(x_m, x_n) \quad \ldots\ldots\ldots(2\text{-}4)$$

Then for each Γ_{ij} can be expressed as[17]:

$$\Gamma_{\text{ij}}(x_m, x_n) = \frac{1}{2}\sum_{i<j}^{N} A_{ij}^{mn} (A_{ij}^{mn})^* \quad \ldots\ldots\ldots\ldots(2\text{-}5)$$

Where :

$$A_{ij}^{mn} = \phi_i(m)\phi_j(n) - \phi_j(m)\phi_i(n) \quad \ldots\ldots\ldots\ldots(2\text{-}6)$$

2.2. Two-particle radial density distribution function D(r1,r2)

The two-particle radial density distribution function *D(r1,r2)*, is the measure of probability of finding two-electrons simultaneously and their radial coordinates are in the range *r1*to *r1+dr1*,and *r2* to *r2+dr2*, or is the probability density of finding an electron at a radius *r1* and another electron at *r2*simultaneously ,in each individual electronic shell is defined by :[18]

$$D(r_1, r_2) = \binom{N}{2} r_1^2 r_2^2 \int |\psi(x_1, \ldots, x_N)|^2 dx_3, ., dx_N d\Omega_1 d\Omega_2 \quad \ldots (2\text{-}7)$$

Where($\boldsymbol{r}_i$,Ω_i)is the polar coordinate of the vector $\boldsymbol{r}$, it can be written $D(r_1, r_2)$ *as*

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$$D(r_1, r_2) = \iint □(r_1,r_2) r_1^2 r_2^2 d\Omega_1 d\Omega_2 \quad \ldots(2\text{-}8)$$

Where $d\Omega_i$ denotes that the integration is over all angular coordinates of the position vector and it is simply defined as

$\int d\Omega_i = \int_0^{\pi}\int_0^{2\pi} \sin\theta_i d\theta_i\, d\emptyset_i$ ...(2-9)

Where i =1 or 2 and the normalization condition for two-particle radial density distribution function $D(r_1, r_2)$ can define as:

$\int\int D(r_1, r_2) dr_1 dr_2 = 1$ ...(2-10)

The function $D(r_1, r_2)$ Tells us how the motion of the two-different electrons is correlated as a result of their interaction and equation (2-10) is a measure of the probability of finding two electrons simultaneously with radial coordinates enclosed between r_1 to r_1+dr_1 and r_2 to r_2+dr_2respectively.

$D(r_1, r_2) = R_{1S}^2(1)R_{1S}^2(2)r_1^2r_2^2$...(2-11)

2.3. One-particle radial density distribution function D(r1)

The One Particle Radial Density Distribution D(r1) is essential for studying the electrons in an atom, the probability density function of finding an electron at a distance *r* from the coordinate origin, i.e., the nucleus, which means the probability of finding electrons in each shell is obtained from integration over two–electron radial density function D(r_1, r_2) and defined as

$D(r_1) = \int_0^{\infty} D(r_1, r_2)dr_2$ ...(2-12)

One-particle expectation value $\langle r_1^m \rangle$

The one-electron expectation value $\langle r_1{}^m \rangle$is determined by the expression as:

$\langle r_1^m \rangle = \int_0^{\infty} D(r_1)r_1^m\, dr_1$ ...(2-13)

where $(-2 \le m \le 2)$ in this research

In the case Where $m = 0$ the expectation valule $\langle r_1^m \rangle$ must be equal to one, this means :

$\langle r_1^m \rangle = \int_0^{\infty} D(r_1)r_1^0\, dr_1$=$\int_0^{\infty} D(r_1)\, dr_1 = 1$ ...(2-14)

In the case (*m*= -1)the expectation value for one-electron $\langle \frac{1}{r_1} \rangle$ leads to the electron-nuclear potential energy and Nuclear magnetic Shielding constant, *(m* = 1) required to the position ; *m* = +2 the one-particle expectation value $\langle r_1^2 \rangle$ can be used in calculation of the evaluate the diamagnetic susceptibility The radial expectation value for one electron $\langle r_1^m \rangle$ for K-shell could be found by substituting equation (2-12) in equation(2-13) as,

$\langle r_1^m \rangle_K = \int_0^{\infty} R_{1S}^2(r_1)r_1^2r_1^m\, dr_1$ ...(2-15)

2.4. Standard deviation Δr_1

The standard deviation $\Delta r_1$is a square root of the variance; which it is especially useful for representing the diffuseness of each radial density distribution, because it has the unit of ***r*** and it is defined by

$\Delta r_1 = [\langle r_1^2 \rangle - \langle r_1 \rangle^2]^{1/2}$ ...(2-16)

2.5. inter-particle distribution function f(r12)

Cousin and Neilson proposed a distribution function for inter-electronic separation of *f(r12)* of s-states associated with spin - orbital pair (i,j)

$f_{ij}(r_{12})dr_{12} = \int \Gamma_{ij}(r_1, r_2)dr_1dr_2$ ...(2-17)

Where the function $f_{ij}(r_{12})$ is the probability distribution distance between electron l and electron 2 ; this function also can use to fined **–two-particle expectation value** as The normalize condition for the inter-particle distribution function is defined as[17]

$\int_0^{\infty} f(r_{12})\, dr_{12} = 1$ ...(2-18)

2.6. Interparticle expectation value $\langle r_{12}^m \rangle$

The inter-particle (interelectronic separation) expectation values $\langle r_{12}^m \rangle$can be determined from the formula

$\langle r_{12}^m \rangle = \int_0^{\infty} f(r_{12})r_{12}^m\, dr_{12}$ ...(2-19)

where r_{12} represents the distance between two-electrons when $m = -1$, that $\langle \frac{1}{r_{12}} \rangle$represents the repulsion energy between two-electrons V_{ee}

where;

$\langle E \rangle = \langle T \rangle + \langle V_{en} \rangle + \langle V_{ee} \rangle$ ...(2-20)

Where $\langle T\rangle$ is the expectation value of kinetic energy ,$\langle V_{ee}\rangle$ is the Coulomb repulsion between electron-electron, and $\langle V_{en}\rangle$ is an attraction energy between electron-nucleus, we can write

$$\langle T\rangle = {}^{-1}/_{2}\int \psi^{*}\left[\sum_{i=1}^{N}\nabla_{i}^{2}\right]\psi d\tau \quad ...(2\text{-}21)$$

$$\langle V_{en}\rangle = -\int \psi^{*}\left[\sum_{i=1}^{N}\quad \frac{Z}{r_{i}}\right]\psi d\tau \quad ...(2\text{-}22)$$

$$\langle V_{ee}\rangle = \int \psi^{*}\left[\sum_{j>i}^{N}\frac{1}{r_{ij}}\right]\psi d\tau \quad ..(2\text{-}23)$$

The total expectation value of potential energy is

$$\langle V\rangle = \langle V_{en}\rangle + \langle V_{ee}\rangle \quad ....(2\text{-}24)$$

Hartree-Fock method satisfied the virial theorem . The viral theorem is a necessary condition for the stationary state, the condition of the viral theorem is:

$$\langle E\rangle = \langle T\rangle + \langle V\rangle \quad ...(2\text{-}25)$$

$$\langle E\rangle = -\langle T\rangle = {}^{\langle V\rangle}/_{2} \quad ...(2\text{-}26)$$

Expectation value of potential energy proportional to the expectation values of $\langle r_{1}^{-1}\rangle$ and $\langle r_{12}^{-1}\rangle$, respectively. Where

$$\langle V_{en}\rangle = -Z.\langle r_{1}^{-1}\rangle \quad ...(2\text{-}27)$$

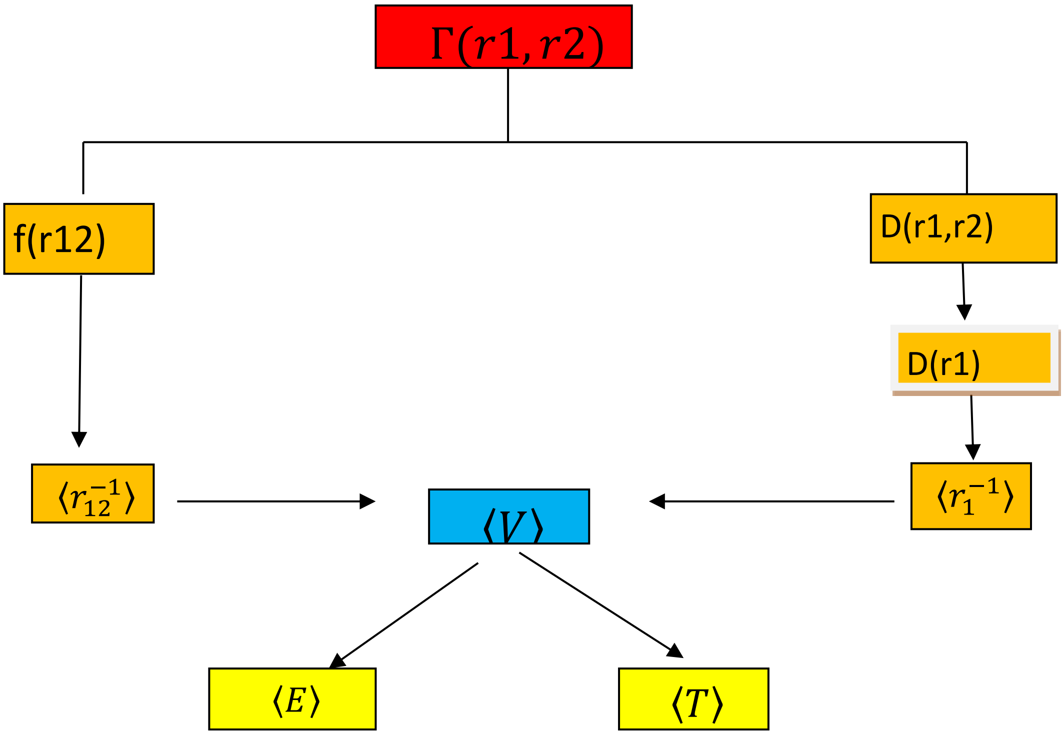
and

$$\langle V_{ee}\rangle = \langle r_{12}^{-1}\rangle \quad ...(2\text{-}28)$$

So , we can write potential energy according to equation (2-24) as

$$\langle V\rangle = -Z\langle r_{1}^{-1}\rangle + \langle r_{12}^{-1}\rangle \quad ...(2\text{-}29)$$

Where the expectation values in equation (2-29) are related to the electron density distribution function $D(r_{1})$ and the distribution function of the interelectronic distance $f(r_{12})$, respectively.



Fig(1).Scheme illustrates the use of the particle density $\Gamma(r1, r2)$ in the calculation of some atomic properties in the position space

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