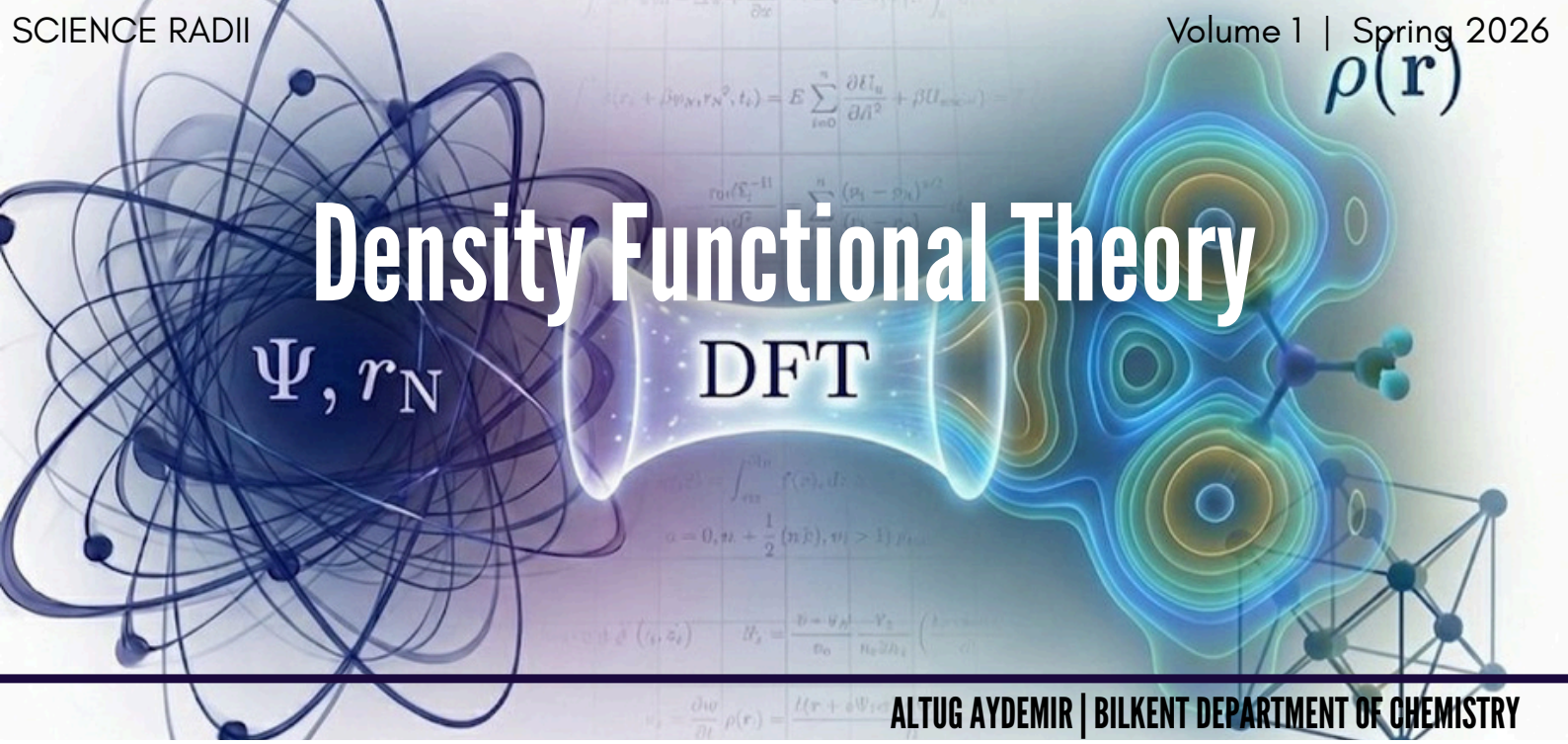

Density Functional Theory

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Density Functional Theory (DFT) is a cornerstone of modern computational chemistry and solid-state physics. In quantum mechanics, the wavefunction must be determined to obtain information about the electronic structure of the system. However, for many-particle systems, the exact wavefunction cannot be found, and an approximate wavefunction must be used. Generally, finding an approximate wavefunction is computationally expensive and time-consuming. However, DFT provides an alternative way to describe the electronic structure of the system by using electron density instead of its wavefunction[1]. This makes it significantly more efficient than Hartree-Fock and post-Hartree-Fock methods, which require solving the complex 3N-body problem (N: number of electrons) to formally reduce to a single body problem. Therefore, Hartree-Fock methods are computationally inefficient. DFT has proven itself as an accurate method that can be used to find molecular geometries, electronic band structures, etc.

From Many-Electron Wavefunctions to Electron Density

The central problem of quantum chemistry is solving the Schrödinger equation for many-electron systems:

$$H\Psi\left(r_1, r_2, \ldots, r_N\right) = E\Psi\left(r_1, r_2, \ldots, r_N\right) (1)$$

where Ψ is the many-electron wavefunction that is a function of electronic coordinates, and Hˆ is the Hamiltonian that gives the energy of the system[1]. However, this equation cannot be solved exactly, since the complexity of the equation increases quickly with the number of electrons [2], and the Coulombic interactions between the electrons prevent an exact solution from being found. [3].

So, instead of using a complicated wavefunction, can we use a physical observable to calculate the properties of a system [4]. DFT is founded on using the electron density in place of the wavefunction. As such[1]:

$$\rho\left(r\right) = N \int \left|\Psi\left(r_1, r_2, \ldots, r_N\right)\right|^2 dr_2 \ldots dr_N (2)$$

Where ρ is the electron density, which only depends on the spatial coordinates of the electrons.

$\left|\Psi\left(r_1, r_2, \ldots, r_N\right)\right|^2$ is the probability density that allows us to find the probabilities of a measurement.

When the integral given previously is evaluated, the total number of electrons in a system can be found,

$$\int \rho(r)dr = N \quad (3)$$

In DFT, the main parameter is electron density, or ρ(r), which greatly reduces the complexity and allows for the calculation of physical properties such as energy[1].

The Hohenberg-Kohn Theorems

There are two theorems that are essential for DFT, and they were developed by Pierre Hohenberg and Walter Kohn in 1964. The Hohenberg-Kohn Existence Theorem: This theorem states that the ground-state energy and the properties of the system at the ground-state are uniquely determined by the electron density [4]. Meaning that, the ground-state energy can be formulated as a functional of the ground-state electron density.

$$E[\rho] = T[\rho] + V_e[\rho] + \int \rho(r)V(r)dr \quad (4)$$

Where E(ρ) is the energy functional, $V_e[\rho]$ is the potential energy that comes from electron-electron repulsion, and ∫ρ(r)v(r)dr is the external potential energy term [1]. The Hohenberg-Kohn Variational Theorem: This theorem states that there is a true ground-state energy functional and a corresponding electron density, where the value of the energy functional with a trial density function cannot be lower than the true ground-state energy functional [5].

$$E_O = min_\rho E[\rho] \quad (5)$$

: and,

$$E[\rho] = F[\rho] + \int \rho(r)V(r)dr \quad (6)$$

Where F [ρ] is the functional that includes both kinetic and electron-electron interaction energies [1].

Moreover, the variations in the ground-state electron density subjected to the constraint [1,5]:

$$\delta[E[\rho] - \mu \int \rho(r)dr] \quad (7)$$

Thus, the ground-state electron density must satisfy the equation 5:

$$\mu = V(r) + \frac{\delta E[\rho]}{\delta \rho} \quad (8)$$

These theorems mathematically establish expressions for quantum mechanical energy in terms of electron densities [1]. But, they do not provide a way to find a functional that can be used to do these calculations [5]. In a way, they are only proofs of existence for an energy functional.

The Kohn-Sham Equations:

In 1965, Walter Kohn and Lu Jeu Sham formulated a method to approximate the unknown functional, F [ρ]. In their method, the interacting many-electron system was approximated by an idealized system where there is no electron-electron interaction that has the same electron density as the original system [5]. The total energy functional in the Kohn-Sham method is formulated as:

$$E[\rho] = T_S[\rho] + \int V_{ext}(r)\rho(r)dr + \frac{1}{2}\int \frac{\rho(r)p(r')}{|r-r'|}drdr' + E_{XC}[\rho] \quad (9)$$

where T [ρ] is the kinetic energy of the non-interacting particles, the second term corresponds to the external potential energy, the third term is the potential energy that comes from electron-electron interaction, and Exc[ρ] is the exchange-correlation energy functional [1]. The last term accounts for the difference between true kinetic energy and T [ρ], and quantum mechanical effects such as exchange and correlation. [6].

When the Hohenberg-Kohn Variational Theorem is applied to equation 9, and energy is minimized with respect to ρ, the Kohn-Sham equations can be derived:

$$\left[\frac{-1}{2}\nabla^2 + V_{eff}(r)\right]\psi_i(r) = \varepsilon_i\psi_i(r) \quad (10)$$

where the effective potential is given by

$$V_{eff}(r) = V_{ext}(r) + \int \frac{\rho\left(r'\right)}{|r-r'|}dr' + V_{XC} \quad (11)$$

the solutions of the KS equation give KS orbitals [1].

$$\rho(r) = \sum_{i}^{occ} |\psi_i(r)|^2 \quad (12)$$

Taking the square of KS orbitals and taking a sum over all occupied KS orbitals will give the electron density of the system[1]. Moreover, KS equations are self-consistent, and by starting from an initial guess for ρ(r), one can solve the KS equation and calculate the new density of the system according to this initial solution. Then, by using this new density, the equation can be solved iteratively until the change of density decreases below a certain threshold.

Applications of DFT:

Following the publication of these seminal works on the theoretical formulation of DFT and the development of exchange and correlation functionals, such as the BP86 functional, it gained popularity in computational chemistry and solid-state physics. In quantum chemistry, DFT can be used to predict molecular geometries, electronic charge densities, and molecular orbitals. In spectroscopy, DFT can be used to calculate vibrational frequencies of molecules, electronic excitation energies [7].

In material science, DFT can be used to calculate the band structure and density of states for materials. DFT has a crucial role in nanoscience, and it can be used to study structures such as graphene, nanotubes, and quantum dots. DFT can also be used in biochemistry and molecular biology. For example, it can be used in drug design and modeling active sites in enzymes.

Conclusion:

By reformulating the wavefunction approach to quantum mechanics by using electron densities, DFT provides an elegant, accurate, and efficient way to calculate the electronic structure of molecules or condensed-matter systems. Despite its mathematically rigorous theory, it became a workhorse for computational and theoretical chemistry.

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