Overview of electronic structure theories

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A first-principle computation of materials properties using quantum mechanics under the Born-Oppenheimer approximation (Finnis, 2003) involves the estimation of the electronic wave-functions by solving the time-independent Schrödinger's equation. This is an eigenvalue problem given by

$$H\psi_i = \epsilon_i \psi_i \,, \tag{1a}$$

$$H = \sum_{i=1}^{N} -\frac{1}{2}\nabla_i{}^2 + \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1 \\ j\neq i}}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^{N}\sum_{I=1}^{M} \frac{-Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \,, \tag{1b}$$

$$\psi = \psi(\mathbf{x}_1, \mathbf{x}_2, ...\mathbf{x}_N) \,, \tag{1c}$$

where H is the Hamiltonian of the system which is comprised of the kinetic energy of electrons and electrostatic interaction energy between electrons and nuclei; ψ_i denote normalized, anti-symmetric electronic wave-functions, i.e., eigenfunctions of the Hamiltonian; and ϵ_i denote the energy levels or eigenvalues of the Hamiltonian. Here, $\mathbf{x}_i = (\mathbf{r}_i, s_i)$, $\mathbf{r}_i \in \mathbb{R}^3$ denotes the spatial coordinates and s_i the spin of the i^{th} electron in the system; $\mathbf{R}_I \in \mathbb{R}^3$ represent the nuclear positions of the I^{th} nuclei in the system with a charge of Z_I; and N and M denote the total number of electrons and nuclei in the system.

Equation (1) suggests that the electronic wave-functions belong to a $3N$ dimensional space, i.e, $\psi \in \mathbb{R}^{3N}$. This translates into a computational complexity that is so huge, that it makes the computation of materials properties using quantum mechanics infeasible. To get an order of magnitude estimate of this complexity, consider a material system with 100 electrons and consider a discretization of the real line, $\mathbb{R}$, with just 100 points. A first-principle calculation of this system, which involves solving the eigenvalue problem given by equation (1), requires the computation of eigenvalues and eigenfunctions of an astronomical $100^{300} \times 100^{300}$ matrix. This problem is computationally intractable. In a landmark paper in 1929 (Dirac, 1929), Paul Dirac had remarked that "The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of quantum mechanics should be developed, which can lead to an explanation of the main features of the complex atomic systems without too much computation". These various approximate methods developed over more than 5 decades constitute the theories of electronic structure. The most popular among them are the Hartree-Fock method and density-functional theory, which are discussed below.

1 Hartree-Fock method

The Hartree-Fock method (Szabo & Ostlund, 1982) results from approximating the electronic wave-function with a Slater determinant, which respects the anti-symmetric nature of the electronic wave-function. This approximation is given by,

$$\psi(\mathbf{x}_1, \mathbf{x}_2, ...\mathbf{x}_N) = det \begin{pmatrix} \psi_1(\mathbf{x}_1) & \psi_1(\mathbf{x}_2) & ... & \psi_1(\mathbf{x}_n) \\ \psi_2(\mathbf{x}_1) & \psi_2(\mathbf{x}_2) & ... & \psi_2(\mathbf{x}_n) \\ . & . & . & . \\ . & . & . & . \\ \psi_n(\mathbf{x}_1) & \psi_n(\mathbf{x}_2) & ... & \psi_n(\mathbf{x}_n) \end{pmatrix}.$$

This approximation reduces a wave-function in $3N$ dimensional space to N wave-functions in 3 dimensional space which are computationally tractable. The approximation of the electronic wave-function by a Slater determinant is equivalent to the assumption that the electrons in the system interact with each other only through a mean field, thus effectively ignoring the electron correlations.

The ground-state energy of a material system computed from the Hartree-Fock method provides an upper bound to the actual ground-state energy of the system. In this regard, the Hartree-Fock method has a useful variational structure associated with it. Exploiting this variational structure, the Hartree-Fock method is extended to obtain a more refined electronic structure theory, which is described by multi-configuration equations. Multi-configuration equations are a generalization of the Hartree-Fock method, where a linear combination of a number of Slater determinants is used to approximate the wave-function, as against a single Slater determinant in the case of Hartree-Fock approximation. It can be shown that as the basis of the single electron wave functions is increased to span the complete Hilbert space, the multi-configuration equations reproduce the exact quantum mechanical equations (Friesecke, 2003; Lewin, 2004).

Though the Hartree-Fock approach has been used quite extensively, over the course of last few decades the density-functional theory (DFT) of Hohenberg, Kohn, and Sham (Parr & Yang, 1989; Finnis, 2003), which expresses the ground-state energy of the material system in terms of the electron-density, has gained popularity for its accuracy, reliability, and feasibility of electronic structure calculations on a wide range of materials.

2 Density-functional theory

Density-functional theory provides us with a framework to reformulate the problem of solving the Schrödinger's equation of a N-electron system into a problem of estimating the wave-functions and corresponding energies of an effective single-electron system. Density-functional theory is based

on a variational formulation, and is therefore very suitable for ground-state calculations, though extensions to excited states are possible (Parr & Yang, 1989). The heart of density-functional theory lies in the work by Hohenberg, Kohn, and Sham (Hohenberg & Kohn, 1964; Kohn & Sham, 1965) who prove that "*electron-density* as a basic variable is sufficient to describe the properties of a material system in its ground state". This is a remarkable and powerful statement, as it reduces the problem of solving for a quantity (electronic wave-function) in $3N$ dimensional space to solving for a quantity (electron-density) in 3 dimensional space. This very statement has revolutionized electronic structure calculations, and has put density-functional theory in the forefront of electronic structure theories. The fact that the ground-state properties of materials depend only on electron-density is not difficult to verify. We start from a variational statement: The energy of any system is always greater than or equal to its ground-state energy. Denoting the ground-state energy by E_0,

$$\langle\psi|H|\psi\rangle \geq E_0\,. \tag{2}$$

Combining equations (2) and (1), and representing the kinetic energy of electrons by T and the interaction between nuclei and electrons by $V_{ext}(\mathbf{r}_i)$, the variational statement reads as

$$\langle\psi|T + \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1\\j\neq i}}^{N}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^{N}V_{ext}(\mathbf{r}_i)|\psi\rangle \geq E_0\,. \tag{3}$$

As $\psi(\mathbf{x}_1, \mathbf{x}_2, ...\mathbf{x}_N)$ is normalized, the electron-density or the probability density of finding any of the N electrons with arbitrary spin is given by,

$$\rho(\mathbf{r}_1) = N\int ...\int |\psi(\mathbf{x}_1, \mathbf{x}_2, ...\mathbf{x}_N)|^2 ds_1 d\mathbf{x}_2..d\mathbf{x}_N\,. \tag{4}$$

Combining equations (2) and (4), and noting that $V_{ext}(\mathbf{r}_i)$ is a local operator, we get

$$\langle\psi|T + \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1\\j\neq i}}^{N}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}|\psi\rangle + \int\rho(\mathbf{r})V_{ext}(\mathbf{r})d\mathbf{r} \geq E_0\,. \tag{5}$$

The last term in equation (5), which is the interaction of the external field with the electrons in the system, is independent of the electronic wave-function and depends only on the electron-density. However, the first term, which includes the kinetic energy of electrons and the electron-electron interactions, depends on the wave-function. This dependence is dropped by defining a new functional $F(\rho)$, given by

$$F(\rho) = \min_{\psi\to\rho}\langle\psi|T + \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1\\j\neq i}}^{N}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}|\psi\rangle\,, \tag{6}$$

where $\psi \rightarrow \rho$ denotes the minimization over all possible antisymmetric ψ which give rise to a particular ρ. Thus the ground-state energy, and consequently the ground-state materials properties depend only on the electron-density. The ground-state energy is given by

$$E(\rho) = F(\rho) + \int \rho(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \sum_{I=1}^{M} \sum_{\substack{J=1 \\ J \neq I}}^{M} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}, \tag{7}$$

where the last term in equation (7) is the electrostatic repulsive energy between the nuclei.

Though it has been established that ground-state material properties depend only on electron-density, the explicit functional form of $F(\rho)$ defined in equation (6) is not known. Density-functional theory is exact in principle, but the exact evaluation of $F(\rho)$ is tantamount to solving the Schrödinger's equation. Hence, the functional $F(\rho)$ is evaluated approximately. An important step in this direction was taken by Kohn and Sham (Kohn & Sham, 1965) by using the properties of a reference system of non-interacting electrons with density ρ to write

$$F(\rho) = T_s(\rho) + E_H(\rho) + E_{xc}(\rho), \tag{8}$$

where T_s is the kinetic energy of non-interacting electrons, E_H is the classical electrostatic interaction energy (also referred to as Hartree energy), and E_{xc} denotes the exchange and correlation energy. Though the exact form of E_{xc} is not known, good approximations of the exchange and correlation functionals are available using local density approximations (LDA) and generalized gradient approximations (GGA) (Koch & Holthausen, 2001; Ceperley & Alder, 1980; Perdew & Zunger, 1981). In the Kohn-Sham scheme of things (KS-DFT), $T_s(\rho)$ is computed in an indirect approach by observing that the the Euler-Lagrange equations corresponding to $E(\rho)$ under the constraint $\int \rho(\mathbf{r}) d\mathbf{r} = N$ are identical to that of a single-electron Schrödinger's equation in an effective mean-field. Thus, the problem of computing T_s reduces to solving an eigenvalue problem given by,

$$\Big(-\frac{1}{2}\nabla^2 + V_{eff}(\rho; \mathbf{R}) \Big) \psi_i = \epsilon_i \psi_i, \quad i = 1, 2, \ldots, N \tag{9a}$$

$$\rho = \sum_{i=1}^{N} |\psi_i|^2, \qquad V_{eff} = \frac{\partial (E_{xc} + E_H + E_{ext})}{\partial \rho}, \tag{9b}$$

where ψ_is denote the wave-functions or orbitals of a material system with N electrons. Upon solving equation (9), the kinetic energy term is computed to be $T_s(\rho) = \sum_{i=1}^{N} \frac{1}{2} \int |\nabla \psi_i(\mathbf{r})|^2 d\mathbf{r}$. Traditionally equation (9) is solved in a self-consistent manner, since V_{eff} is a functional of ρ, which in turn is determined from the solution, ψ_is. The computational complexity involved in this self-consistent calculation is huge and restricts tractable system sizes to a few hundred atoms. This limitation has inspired studies on orbital-free forms of kinetic energy functionals, where $T_s(\rho)$ is modeled.

Numerous efforts have been made to come up with explicit forms of $T_s(\rho)$ without the need

to compute electronic wave functions; these are called *orbital-free* kinetic energy functionals. The version of density-functional theory where $T_s(\rho)$ is modelled using orbital-free kinetic energy functionals is commonly referred to as *Orbital-Free Density-Functional Theory* (OFDFT). The earliest of the works in this direction date back to the Thomas-Fermi model proposed in 1927 (Thomas, 1927; Fermi, 1927). Thomas and Fermi derived an explicit representation of the kinetic energy using a local density approximation. The Thomas-Fermi model approximates the kinetic energy of a system of non-interacting electrons with that of a homogeneous electron gas and is given by

$$T_s(\rho) = C_F \int \rho^{5/3}(\mathbf{r}) d\mathbf{r}\,, \tag{10}$$

where $C_F = \frac{3}{10}(3\pi^2)^{2/3}$. A major setback to the Thomas-Fermi approach was the Teller non-bonding theorem for this class of functionals (Parr & Yang, 1989), which showed that the Thomas-Fermi model does not predict binding in materials. This deficiency was corrected by including in the kinetic energy functionals a term depending on the gradient of the electron density. This correction led to a family of kinetic energy functionals called the Thomas-Fermi-Weizsacker functionals (Parr & Yang, 1989), which are given by the expression

$$T_s(\rho) = C_F \int \rho^{5/3}(\mathbf{r}) d\mathbf{r} + \frac{\lambda}{8} \int \frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})} d\mathbf{r}\,, \tag{11}$$

where λ is a parameter. Different values of λ are found to work better in different cases (Parr & Yang, 1989); $\lambda = 1$ and $\lambda = 1/9$ are the most commonly used values. There have been considerable efforts (Wang et al., 1998, 1999; Choly & Kaxiras, 2002; Smargiassi & Madden, 1994; Wang & Teter, 1992) to improve these orbital-free kinetic energy functionals by introducing an additional non-local term called the kernel energy. These kinetic energy functionals have a functional form given by

$$T_s(\rho) = C_F \int \rho^{5/3}(\mathbf{r}) d\mathbf{r} + \frac{1}{8} \int \frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})} d\mathbf{r} + \int\int f(\rho(\mathbf{r})) K(|\mathbf{r} - \mathbf{r}'|) g(\rho(\mathbf{r}')) d\mathbf{r} d\mathbf{r}'\,, \tag{12}$$

where f, g, and K are chosen to satisfy known limits of exact $T_s(\rho)$, and such that the total kinetic energy functional exhibits correct linear response.

To end this overview, I wish to note that KS-DFT is the most accepted electronic structure theory in the community. Any deviations from KS-DFT, which include the use of OFDFT must first be tested carefully before using them for quantitative prediction of materials properties.

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