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Perspective

Perspective on "Inhomogeneous electron gas"

Hohenberg P, Kohn W (1964) Phys Rev 136: B864

Matthias Ernzerhof, Gustavo E. Scuseria

Department of Chemistry, Rice University, P.O. Box 1892, Houston, TX 77005, USA

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Abstract. The Hohenberg–Kohn theorems in "Inhomogeneous electron gas" established a whole new perspective for the study of electronic structure theory and marked the birth of modern density functional theory (DFT). In our view, DFT and wavefunction theories complement each other. Starting with the invention of the Kohn–Sham method a fruitful synthesis of DFT and wavefunction theories took place and the most powerful computational tools currently available are combinations of both methods. The Hohenberg–Kohn theorems inspire the quest for simple density functionals of increased accuracy. We believe that the synthesis of accurate density functionals and computationally efficient wavefunction methods will continue to dominate electronic structure theory.

Key words: Density functional theory – Hohenberg–Kohn theorems

1 Introduction

The electronic structure of molecules and atoms has long been at the focus of chemists' interests. Soon after the electron was discovered in 1897, electron theories of valence were developed [1, 2]. However, at that time, nothing was known about the driving force behind the formation of a chemical bond or an ion. The discovery of quantum mechanics in 1925 made it possible to address the fundamental questions of chemistry. Schrödinger's equation [3] became the central point in electronic structure theory. In 1927, Condon [4] gave a quantum mechanical explanation of the bond in H_2 and initiated molecular orbital theory. In the same year, Heitler and London [5] developed the valence-bond description of H_2.

With the development of computers and efficient algorithms, remarkable advances have been made in the calculation of wavefunctions. The starting point in conventional wave-mechanical treatments of electronic structure is the Hartree–Fock approximation, which is a molecular orbital type of approximation. In Hartree–Fock theory, the exchange energy is calculated exactly, but electron correlation is completely neglected. We understand now that this treatment often leads to an unbalanced description. A typical example is the rupture of a covalent bond. The correlation energy is larger in magnitude in the molecule compared to the atoms, and neglecting it introduces significant errors in the dissociation energy. Unfortunately, accurate calculations of the correlation energy using wavefunction techniques are still severely limited because of the steep scaling of the computational effort with molecular size.

Modern density functional theory (DFT) was born with the title paper and was developed in parallel with wavefunction methods. The Kohn–Sham method [6] is an example of a unification between pure DFT methods and wavefunction theory, a synthesis that has lead to some of the most powerful tools in computational quantum chemistry.

2 Early work in DFT

Shortly after the Schrödinger equation had been formulated it became obvious that finding its solution for the most simple atoms and molecules is a challenging problem. Back in the early days of quantum mechanics even the independent-particle problem posed to be a difficult task. In 1927, Thomas [7] and Fermi [8] independently introduced an approximation which avoids the calculation of single-particle orbitals. In the Thomas–Fermi approach, the electron density appears as the variational degree of freedom in an equation for the ground-state energy. For a given external potential $v(\mathbf{r})$, Thomas and Fermi introduced the minimization problem

$$E_v = \min_\rho \left[\frac{3}{10}(3\pi^2)^{2/3} \int d^3r \rho^{5/3}(\mathbf{r}). + \int d^3r v(\mathbf{r})\rho(\mathbf{r}) + U[\rho] - \mu\left(\int d^3r \rho(\mathbf{r}) - N \right) \right] . \quad (1)$$

Correspondence to: G. E. Scuseria

μ denotes the chemical potential which is adjusted such that the electron density ρ integrates to the desired number of electrons (N).

$$U[\rho] = \frac{1}{2}\int \mathrm{d}^3r\mathrm{d}^3r'\rho(\mathbf{r})\rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'| \tag{2}$$

approximates the electron–electron interaction energy V_{ee}. The remarkable step taken by Thomas and Fermi was to approximate the kinetic energy of a Slater determinant (T_{S}) by a functional of the electron density, i.e.,

$$T_{\mathrm{S}}[\rho] = \frac{3}{10}(3\pi^2)^{2/3}\int \mathrm{d}^3r\rho^{5/3}(\mathbf{r}) \ . \tag{3}$$

This expression gives the exact kinetic energy for a homogeneous electron gas of noninteracting electrons.

In 1930, Dirac [9] proposed that a density functional for exchange be added to the Thomas–Fermi energy expression (Eq. 1). Dirac's exchange functional

$$E_{\mathrm{X}} = \frac{-3}{4}\left(\frac{3}{\pi}\right)^{1/3}\int \mathrm{d}^3r\rho^{4/3}(\mathbf{r}) \tag{4}$$

is identical to the local density approximation (LDA) [6] for exchange.

These early steps in DFT (for a review see Ref. [10]) were too crude for chemical applications since, as later shown (see Ref. [11] and references therein), no chemical binding can be obtained within Thomas–Fermi theory. In 1951, Slater [12] derived a local approximation to the nonlocal exchange operator in the Hartree–Fock equations. His single-particle equations, in which the kinetic energy is evaluated exactly, are precursors of the Kohn–Sham equations [6]. A method which has an even greater similarity with the widely used Kohn–Sham scheme was proposed by Gáspár [13]. Gáspár used the LDA for the exchange energy in the Hartree–Fock approach and derived the corresponding self-consistent equation.

3 The paper on the inhomogeneous electron gas

The early density functional approximations were not deduced from Schrödinger's equation by a series of well-understood approximations. Rather they were based on an intuitive physical picture of electronic systems. As such, these approximations cannot be systematically improved, and it was not clear at the time if density functionals could in principle be exact.

The lack of a theoretical framework certainly did not promote the development of density functionals. This situation changed radically in 1964 with the paper of Pierre Hohenberg and Walter Kohn. Hohenberg and Kohn established a one-to-one correspondence between electron densities of nondegenerate ground states and external local potentials, $v(\mathbf{r})$, which differ by more than a constant. All physical properties obtainable with v can therefore be expressed in terms of the electron density. It was thus established that, for example, the Thomas–Fermi approximation to the kinetic energy can in principle be refined to yield arbitrary precision. Hohenberg and Kohn defined the density functional $F[\rho]$

$$F[\rho] = \langle\psi[\rho]|\hat{T}+\hat{V}_{\mathrm{ee}}|\psi[\rho]\rangle \ , \tag{5}$$

where ψ denotes the nondegenerate ground-state wavefunction which yields ρ, and $\hat{V}_{\mathrm{ee}}$ is the electron repulsion operator. Having introduced the functional $F[\rho]$, Hohenberg and Kohn showed that for a given external potential, v, the ground-state density minimizes the energy functional

$$E_v[\tilde{\rho}] = \int \mathrm{d}^3r\tilde{\rho}(\mathbf{r})v(\mathbf{r}) + F[\tilde{\rho}] \ . \tag{6}$$

$\tilde{\rho}$ denotes an appropriate trial density which integrates to the correct particle number. The problem of finding the ground-state energy for a given external potential has hereby been completely reformulated in terms of the electron density which is a function of three variables regardless of the number of electrons. There is, however, no systematic way of generating practical approximations to $F[\rho]$. Nevertheless, the knowledge that such a functional exists has greatly motivated physicists and chemists ever since.

For certain limiting cases, Hohenberg and Kohn were able to construct the functional $F[\rho]$. They showed that $F[\rho]$ can be expressed in terms of the electronic polarizability for densities of the form $\rho(\mathbf{r}) = \rho_0 + \tilde{\rho}(\mathbf{r})$ with $\tilde{\rho}(\mathbf{r})/\rho_0 \ll 1$. Furthermore, they formulated the gradient expansion, valid in the slowly varying limit, and presented a scheme by which the gradient coefficient can be obtained from the nth-order ($n = 1, 2, \ldots, \infty$) polarizabilities of the system. These two construction schemes for $F[\rho]$ have inspired subsequent approaches to developing approximate density functionals.

An important extension of the original Hohenberg–Kohn approach has been proposed by Levy [14, 15] based on earlier work by Percus [16]. The functional $F[\rho]$ of Hohenberg and Kohn is defined only for densities which are obtained from a nondegenerate ground-state wavefunction corresponding to an external local potential. Levy introduced a functional $\mathscr{F}$

$$\mathscr{F}[\rho] = \min_{\psi\rightarrow\rho}\langle\psi|\hat{T}+\hat{V}_{\mathrm{ee}}|\psi\rangle \ , \tag{7}$$

where $\psi \rightarrow \rho$ means that the search extends over all antisymmetric wavefunctions yielding ρ. Obviously, this functional is defined for any density which can be obtained from an antisymmetric wavefunction. $\mathscr{F}$ can then be used in Eq. (6) to obtain the ground-state energy even if the ground state is degenerate.

4 The Kohn–Sham equations: a synthesis of wavefunction theory and DFT

Following the Hohenberg–Kohn paper, a successful synthesis was made between DFT and wavefunction theory. Useful approximations to the kinetic energy as a functional of the electron density are difficult to obtain. The kinetic energy is of the same order of magnitude as the total energy, and even small errors in the absolute value of the kinetic energy can lead to unacceptably large energy errors upon reactions or other chemical transformations.

The Hohenberg–Kohn theorems find a very important application in the derivation of the Kohn–Sham equations, in which the problem of approximating the noninteracting kinetic energy (T_S) is eliminated by introducing single-particle orbitals φ_i. The exact electron density is written as the electron density of a Slater determinant,

$$\rho(\mathbf{r}) = \sum_i^{\mathrm{occ}} \varphi_i(\mathbf{r}) \varphi_i(\mathbf{r}) \ . \tag{8}$$

The ground-state energy is split up according to

$$E = T_S + \int \mathrm{d}^3 r \, v(\mathbf{r}) \rho(\mathbf{r}) + U[\rho] + E_{XC}[\rho] \ , \tag{9}$$

where $E_{XC} = T - T_S + V_{ee} - U$ is the exchange–correlation energy, and T_S is the kinetic energy of the determinant formed from the orbitals φ_i, i.e., $T_S = -1/2 \sum_i^{\mathrm{occ}} \langle \varphi_i | \Delta | \varphi_i \rangle$. The variational equation (Eq. 6) is then simply solved by requiring that

$$\frac{\delta E}{\delta \varphi_i(\mathbf{r})} = 0 \quad \text{and} \quad \langle \varphi_i | \varphi_j \rangle = \delta_{ij} \ . \tag{10}$$

The resulting single-particle eigenvalue equations are the Kohn–Sham equations. The Hohenberg–Kohn theorems ensure that the exchange–correlation energy in Eq. (9) is a functional of the electron density.

5 Some developments in quantum chemistry initiated by the Hohenberg–Kohn paper

It is not practical to give a complete account of the impact of the Hohenberg–Kohn paper on quantum chemistry. Therefore, in this section, we mostly focus on a few aspects which influenced our own research. For a general overview we refer to Refs. [11, 17–19].

After the computational resources became available and reliable algorithms for the solution of the Kohn–Sham equations were in place, the LDA for exchange and correlation employed in the Kohn–Sham scheme turned out to be a powerful tool for electronic structure calculations [18]. Consequently, a large fraction of the early work in DFT focused on the question why LDA works so well even for very inhomogeneous systems. The exchange–correlation hole, which surrounds an electron, became the key in understanding the success of the LDA to E_{XC}. It turned out that many important constraints satisfied by the exact exchange correlation hole are also satisfied by its LDA (for an overview we refer to Refs. [11, 17, 18, 20–24]. Based on the understanding of the LDA improved approximations for exchange and correlation, known as generalized gradient approximations (GGAs) [25–31], were developed. GGAs reached a level of accuracy which made the Kohn–Sham method the most effective tool in quantum chemistry. An additional boost in accuracy was obtained with hybrid methods [32–39] in which a fraction of exact exchange (calculated from the Kohn–Sham wavefunction) is added to density functional approximations for exchange and correlation. This ensures that the long-range part of the exchange–correlation hole is accounted for. Recently, a new generation of kinetic energy density dependent functionals appeared in the literature [40–46]. In these methods, the kinetic energy density of the Kohn–Sham determinant and the electron density are employed to model E_{XC}. These functionals challenge the accuracy of hybrid schemes but avoid the computationally unfavorable evaluation of exact exchange.

In chemistry, excited states and time-dependent phenomena are often of interest. Although the Hohenberg–Kohn variational principle applies only to ground states, various extensions of DFT have been developed over the years which successfully model excitation energies and time-dependent phenomena (for an overview see Refs. [47–49]).

For us, a very exciting development initiated by the Hohenberg and Kohn paper is that insight into the problem of exchange and correlation became the essential ingredient in the development of approximations. Exchange and correlation effects are condensed into the relatively simple expressions of present days functionals and can sometimes be explained by a few general conditions for E_{XC} [30, 46]. This is a significant advance in our understanding of electronic structure provided by DFT.

It is often said that the lack of a systematic procedure to improve the accuracy of an approximate density functional is a disadvantage of DFT; however, at a high level of accuracy probably any systematic approximation scheme for the correlation energy produces a considerable amount of information which is not relevant for the problem at hand. The lack of a systematic procedure to construct density functionals and the knowledge of its existence motivates us to uncover the essentials of electronic structure. Often it turns out that difficult problems in wavefunction theory can be solved with simple density functionals and, in other cases, computationally inexpensive wavefunction methods increase the accuracy of approximate density functionals. We expect that in the foreseeable future electronic structure theory will benefit from new ideas emerging from the synthesis of DFT and wavefunction theory.

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