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Perspective

Perspective on "Self-consistent equations including exchange and correlation effects"

Kohn W, Sham LJ (1965) Phys Rev A 140:133–1138

E.J. Baerends

Scheikundig Laboratorium der Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

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Abstract. The paper by Kohn and Sham (KS) is important for at least two reasons. First, it is the basis for practical methods for density functional calculations. Second, it has endowed chemistry and physics with an independent particle model with very appealing features. As expressed in the title of the KS paper, correlation effects are included at the level of one-electron equations, the practical advantages of which have often been stressed. An implication that has been less widely recognized is that the KS molecular orbital model is physically well-founded and has certain advantages over the Hartree–Fock model. It provides an excellent basis for molecular orbital theoretical interpretation and prediction in chemistry.

Key words: Density functional theory – Kohn–Sham – Electron correlation – Molecular orbital theory

1 Introduction

The title paper by Kohn and Sham (KS) [1] has of course to be considered in conjunction with its predecessor, the paper by Hohenberg and Kohn (HK) [2]. The HK paper established for a many-particle system with some two-particle interaction, where all particles move in a given local potential, $v(\mathbf{r})$, and with a restriction to systems that have nondegenerate ground states, that there is a one-to-one mapping between the potential, $v(\mathbf{r})$, the particle density, $\rho(\mathbf{r})$, and the ground-state wavefunction, Ψ_0,

$$\rho(\mathbf{r}) \leftrightarrow v(\mathbf{r}) \leftrightarrow \Psi_0 \ . \tag{1}$$

If Ψ_0 is a functional of the density, then so are all properties, since any property may be determined as the expectation value of the corresponding operator, $\hat{O}$ say, $O[\rho] = \langle \Psi_0[\rho] | \hat{O} | \Psi_0[\rho] \rangle$. In particular the kinetic energy is also a functional of the density, $T[\rho]$, the electron–electron interaction energy, $W[\rho]$, and the total energy, $E[\rho]$. HK also established the existence of the total energy functional, $E_v[\rho]$, for which the ground-state energy, E_0, of the system with external potential v, is a lower bound,

$$\begin{aligned} E_v[\rho] &= \langle \Psi[\rho] | \hat{T} + \hat{V} + \hat{W} | \Psi[\rho] \rangle \\ &= T[\rho] + \int \rho v \, \mathrm{d}r + W[\rho] \geq E_0 \ . \end{aligned} \tag{2}$$

It is easy to generalize Eqs. (1) and (2) if the ground state is degenerate [3]. A particularly elegant definition of the functional $F[\rho] = T[\rho] + W[\rho]$, which automatically covers the case of ground-state degeneracy, has been provided in Levy's constrained search formulation [4]

$$F_{\mathrm{L}}[\rho] = T[\rho] + W[\rho] = \min_{\Psi \to \rho} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle \ , \tag{3}$$

where the minimum is to be searched over all possible wavefunctions that yield the given ρ as the density. There is no denying the great importance of these theorems, but it may still be argued that the step taken in the KS paper has been as important: it certainly has been for chemistry. Equation (2) holds the promise of a very efficient route to total energies of many-electron systems, from a Euler–Lagrange equation for the density, if good approximations for $T[\rho]$ and $W[\rho]$ could be found. This would effectively reduce the very high dimensional problem of the calculation of the many-particle wavefunction, Ψ_0, to the determination of just the simple function in 3D real space, $\rho(\mathbf{r})$; yet, Eq. (2) has found very little practical application. The reason is that it is very difficult to develop sufficiently accurate density functionals, in particular, for the kinetic energy. This is a problem that already plagued the Thomas–Fermi approach, and although the HK theorems give a much more theoretically sound basis to density functional theory (DFT), its practical importance might not have risen above that of the Thomas–Fermi model if it had not been for the KS one-electron model.

So it is the second step, made in the KS paper, that has been essential for DFT to become the widely applied method for electronic structure calculations that it is today. We will comment briefly on the historical context of the KS paper. Then a few remarks on practical (computational) aspects of the KS equations will be made and finally the conceptual implications of the KS one-electron or molecular orbital (MO) model and its importance for chemistry now and in the future will be commented on.

2 Historical context

In the many years that have passed since the publication of the KS paper, the way that their results are usually presented, and where the emphasis is put, has of course shifted. It is now customary to stress from the outset that the KS theory introduces a system of noninteracting electrons, moving in a local potential, $v_s(\mathbf{r})$. The ground-state wavefunction of the KS system – a single Slater determinant of the lowest N orbitals – will yield precisely the same electron density as the exact interacting electron system with potential $v(\mathbf{r})$. So the KS Hamiltonian, $\hat{H}_s$, is just a sum of one-electron Hamiltonians, $\hat{h}_s$, and the wavefunction of the KS system is a simple one-determinantal wavefunction,

$$\begin{aligned}
\hat{H}_s &= \sum_i \hat{h}_s(i) = \sum_i \left(-\frac{1}{2}\nabla^2(i) + v_s(\mathbf{r}_i)\right)\\
\hat{h}_s(1)\phi_i(1) &= \varepsilon_i\phi_i(1)\\
\Psi_s &= |\phi_1(1),\phi_2(2),\ldots,\phi_N(N)|\\
\rho_s(\mathbf{r}) &= \sum_{i=1}^{N}\sum_{s}|\phi_i(\mathbf{r},s)|^2 = \rho^{\mathrm{exact}}(\mathbf{r})
\end{aligned} \tag{4}$$

The KS paper does not even mention Ψ_s, but it concentrates on the orbital equations and right away specializes on systems with slowly varying density. It uses the local density approximation (LDA) from the outset. Considerable attention is given to corrections to be introduced, dependent on the gradient of the density, to take variation of the density into account. It is historically understandable, in view of the importance at the time (and for some 10–15 years after the publication date) of Slater's exchange approximation [5], that extensive comparison is made to this exchange approximation, which led to a potential proportional to $\rho(\mathbf{r})^{1/3}$. It is pointed out that the variation procedure that is inherent to the KS approach leads to an exchange potential that is two-thirds of Slater's, a point that had been shown earlier by Gáspár [6]. Slater next introduced a constant α in his exchange potential; this could be determined according to various criteria. There has been considerable debate over this constant, which has now long subsided, the KS treatment with its explicit inclusion of a correlation functional and potential having been generally adopted. In their paper KS also discuss the possibility that one could use a nonlocal exchange potential, and add only a local correlation potential. Although they stress (in the title of the paper) that they introduce self-consistent equations that include correlation effects, it is, with hindsight, interesting to observe that KS only mentioned in a note added in proof that the paper has actually achieved the possible replacement of the many-electron problem with an exactly equivalent set of self-consistent one-electron equations. In this note they introduce the local exchange–correlation potential $v_{xc}(\mathbf{r}) = \delta E_{xc}[\rho]/\delta\rho(\mathbf{r})$ which features in the exact v_s,

$$v_s(\mathbf{r}) = v(\mathbf{r}) + v_{\mathrm{Coul}}(\mathbf{r}) + v_{xc}(\mathbf{r}) \ , \tag{5}$$

where $v_{\mathrm{Coul}} = \int\rho(\mathbf{r}_2)/r_{12}\,\mathrm{d}\mathbf{r}_2$. The exchange–correlation energy, E_{xc}, which is a crucial quantity in DFT, is defined only within the context of the KS one-electron model. We will comment later on E_{xc} more extensively, but note at this point that it is exactly this feature, of treating the complicated many-electron system in principle exactly with only the computational expense of a self-consistent-field calculation, which has been so appealing in KS theory. However enticing the promise of computational simplicity and efficiency is, the possibility to treat correlation at the one-electron level has been hard to accept for a quantum chemistry community that was steeped in the belief that correlation was by definition everything that could not be covered at the one-electron level.

3 Computational considerations

The KS equation shares with Slater's Xα method the replacement of the nonlocal exchange operator of Hartree–Fock (HF) theory by a local potential. This particular feature of Slater's exchange approximation had been extensively exploited in solid-state physics, and initially the interest in quantum chemistry almost exclusively focussed on the efficiency of the scattered-wave technique borrowed from physics for solving the Xα and LDA one-electron equations [7]. The required muffin-tin approximation of the potential, however, proved to be too severe in molecules, prohibiting reliable bond energy and structure determinations. The obvious alternative is to use basis sets [8, 9], as was common in quantum chemistry, and evaluate the matrix elements of v_{xc} by numerical integration. The approximate Diophantine method was introduced by Ellis for this purpose [10]. Although this method was sufficiently precise to calculate bond energies and structures, it was not capable of high numerical precision. In the mid 1980s the problem of 3D numerical integration of molecular integrands, with their characteristic singularities at the nuclear sites, was solved simultaneously, in somewhat different ways, by Becke [11] and by Boerrigter et al. [12].

Precise 3D numerical integration affords solution of the KS equations with a basis-set-expansion method. It would, however, make a KS calculation more expensive than a HF calculation, simply adding the burden of numerical integration of the v_{xc} matrix elements to the two-electron integral evaluation still required for the Coulomb potential matrix elements. The latter would cause an n^4 scaling of DFT calculations just as they did for HF calculations (ignoring distance cut-offs). KS DFT has often inappropriately been quoted as being relatively efficient, and in particular as scaling better than HF theory. As a matter of fact, the reputation of "local-density methods" was initially (1970s first half of 1980s) largely based on computational efficiency, the often higher accuracy than HF methods, in particular for transition-metal systems (complexes, cluster compounds) being considered a nice advantage, but not a decisive one since it was ill-understood. However, efficiency compared to the standard HF calculations of the day was achieved by the introduction of auxiliary basis sets for the expansion of the density [8]. This density-fitting, which has been employed in most DFT codes, having later been adopted by Sambe and Felton [13] and improved by Dunlap et al. [14], can also be formulated as an insertion of a resolution of the identity and is sometimes denoted as such (RI-*J*[15]). Auxiliary basis sets can just as well be used to provide better scaling (as n^3) of the Coulomb operator matrix elements in HF calculations. The KS equations do not, with basis-set methods, inherently scale better than the HF equations. The real virtue of the KS method is the possibility to deal with effects of electron correlation, in particular the calculation of the correlation energy, with the computational expense of a one-electron method, while post-HF methods become very expensive indeed. The success of the KS method therefore hinges on the availability of good approximations to E_{xc}, which have been much improved by the introduction of the generalized gradient approximations (GGA) [16, 17].

4 Electron correlation in a one-electron method

The great appeal of the KS scheme is, as previously mentioned, that it offers the promise of correlated energies with a one-electron method, which scales much more favourably than traditional correlation calculations. The definition of the crucial quantity, the exchange–correlation energy, $E_{xc}[\rho]$, has been somewhat confusing for quantum chemists, who have all been trained with the "standard model" where the "best" one-electron model is HF, the exchange energy is defined within that model, and the correlation energy is by definition the difference between the HF energy and the exact energy. KS introduced $E_{xc}[\rho]$, which they said is "by our definition" the exchange and correlation energy. Until rather recently [18–20], it had almost never been emphasized that KS's definition was not the standard one. The KS definition is straightforward once one puts aside the reservation that has long existed, certainly in the quantum chemistry community, against using the one-determinantal wavefunction of KS orbitals, Ψ_s. The general feeling has been for a long time that the KS orbitals were only mathematical constructs that one could use to build the total density, but that these orbitals were deprived of physical meaning. They should therefore not be used to build a wavefunction like Ψ_s. It was considered to be against the spirit of DFT anyway to go back to a wavefunction. I believe that this conviction has considerably delayed a full appreciation of the meaning and status of the KS orbitals. They are much more useful and physically meaningful than they were held to be, and they can play a significant role in interpretation and prediction in chemistry, combining the elegance and transparency of the qualitative MO theory with the high accuracy that modern density functionals afford. We return to this point later.

KS did not stress a point which received more attention later: their basic ansatz is that for every interacting electron system with a given external local potential, $v(\mathbf{r})$, there actually exists a corresponding noninteracting system, i.e. there exists a local potential, $v_s(\mathbf{r})$, such that a noninteracting system of electrons moving in that potential will have the same density as the interacting one. In spite of occasional assertions to the contrary, it has not been proven that for every interacting system the KS potential $v_s(\mathbf{r})$ exists. What has been proven is the following. Consider an interacting electron system with potential $v(\mathbf{r})$. To this system belongs a ground-state density (nondegenerate case) or a set of pure state and ensemble representable densities in the case of degeneracy. The HK functional, $F[\rho] = T[\rho] + W[\rho]$, can be extended by Levy's constrained-search approach [4] to a functional $F_L[\rho]$ (see Eq. 3) that can be proven to have a functional derivative $\delta F_L[\rho]/\delta\rho(\mathbf{r})$, with the potential $v(\mathbf{r})$ as a tangent functional, at those densities and nowhere else [21–23]. Similarly, for noninteracting electrons the analogous constrained-search functional, $T_L[\rho]$ (only the kinetic energy remains when $\hat{W} = 0$), can be defined. Again, when the noninteracting system is characterized by a local potential $v_s(\mathbf{r})$, the differentiability of $T_L[\rho]$ has been established at its pure state or ensemble representable densities, with $v_s(\mathbf{r})$ as its functional derivative. However, these results, although sometimes quoted as such, do not constitute the desired proof, which requires the demonstration that the set of interacting densities is contained in the set of noninteracting ground-state densities. It is a sobering thought that after such a long time this proof has not been found. In practice this has not been a drawback: a breakdown of the KS ansatz has not been observed so far. Nevertheless, one should not naively expect that for every nondegenerate interacting ground-state density a nondegenerate (one-determinantal) KS system actually exists. It was pointed out by Levy [24] that there are many densities (for instance, convex combinations of densities belonging to a set of degenerate ground states) that are not pure-state representable. Given an interacting ground-state density, one therefore has to consider the possibility that this density is not representable by a pure state of a noninteracting KS system, but that it is ensemble-representable in the noninteracting case. Cases have been identified where a nondegenerate ground-state density of an interacting system was ensemble-representable by degenerate KS ground-state densities [25].

Assuming that v_s exists, and therefore the KS orbitals can be calculated, the quantity E_{xc} is defined as the remaining unknown part of the exact total energy, E, the kinetic energy, the nuclear attraction energy, and the classical electron–electron repulsion energy following straightforwardly from the knowledge of the density and orbitals

$$E = T_s[\rho] + \int v(\mathbf{r})d\mathbf{r} + \frac{1}{2}\iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}' + E_{xc}[\rho] \ . \tag{6}$$

E_{xc} is different from the corresponding HF quantities. Its meaning becomes very simple when we consider the energy of the single-determinantal wavefunction of KS orbitals, Ψ_s,

$$\begin{aligned} E^{KS} &= \langle \Psi_s | \hat{H} | \Psi_s \rangle \\ &= T_s + \int v(\mathbf{r})d\mathbf{r} + \frac{1}{2}\iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}' + W_x \ , \end{aligned} \tag{7}$$

where the exchange energy, W_x has the same form as in the HF case but is to be evaluated with the KS orbitals. Defining the correlation energy, E_c in DFT as the difference between the energy of the determinant with the exact KS orbitals and the exact energy, one obtains

$$\begin{aligned} E_c &= E - E^{KS} = E_{xc} - W_x \\ E_c^{HF} &= E - E^{HF} \end{aligned} \tag{8}$$

where E^{HF} is the traditional HF energy. So the DFT definitions of exchange and correlation are natural when one recognizes that KS introduced a one-electron model that may be considered an alternative to the long-established HF model, with the KS determinant taking the place of the HF determinant. The difference between the DFT and standard definitions of exchange and correlation energies was only given attention a long time after the KS paper appeared (see Ref. [26] for a review). The KS noninteracting electron system and its determinantal wavefunction have a somewhat different status than the HF model, being related to exact properties (notably the density) of the real system. A clear advantage of the HF model from an operational point of view, and therefore of the related definition of the correlation energy, is the possibility to obtain very accurate HF wavefunctions, no knowledge of the exact solution being required. Since the HF determinant minimizes the expectation value of the Hamiltonian, the DFT correlation energy will always be larger in an absolute sense, i.e. more negative, than the HF-based correlation energy,

$$\begin{aligned} \langle \Psi^{HF} | \hat{H} | \Psi^{HF} \rangle &\le \langle \Psi_s | \hat{H} | \Psi_s \rangle \\ E_c &\le E_c^{HF} \end{aligned} \tag{9}$$

The reservation against the use of Ψ_s was caused by the suspicion that the KS orbitals might not be "normal" orbitals, and should not be used in the same way as HF or extended Hückel orbitals for qualitative rationalization of experimental trends. On the other hand, the orbitals of Xα (i.e. exchange-only LDA) or LDA and later GGA calculations have always been used as such. It has been argued [20, 26, 27] that this is actually perfectly in order. It has emerged from detailed comparisons between HF and KS orbitals, and between components of the energy (kinetic energy, electron–nuclear attraction, classical electron–electron repulsion, exchange energy) in the two models, that the KS orbitals and determinantal wavefunction are not very different from their HF counterparts, and to the extent that they are, one might argue that they have some advantages. This may best be understood from an analysis of the KS potential $v_s(\mathbf{r})$, which may be written as the sum of a number of physically meaningful terms,

$$\begin{aligned} v_s(\mathbf{r}) = v(\mathbf{r}) + v_{Coul}(\mathbf{r}) + v_x^{hole}(\mathbf{r})r + v_c^{hole}(\mathbf{r}) \\ + v_{c,kin}(\mathbf{r}) + v^{resp}(\mathbf{r}) \ . \end{aligned} \tag{10}$$

The leading terms in v_s are the attractive nuclear field, $v(\mathbf{r})$, and the repulsive Coulomb potential of the electronic charge density, $v_{Coul}(\mathbf{r})$. The next important term is the exchange hole potential. It is local and therefore different from the HF exchange operator, but it also represents an exchange hole comprising one electronic charge, and taken together the first three terms make the KS potential rather similar to the HF operator. These terms determine the rough features of the spectrum of orbital energies and the shape of the MOs. KS orbitals are therefore most of the time very similar to HF orbitals. The difference is in the last three terms of v_s. In particular, it is interesting to note that the potential of the Coulomb hole, v_c^{hole}, is present in v_s. It has been stressed [26, 27] that in situations of strong left–right correlation, such as in dissociating bonds, this potential makes an important difference. While in that case the HF orbitals and the electron density become much too diffuse, the Coulomb hole potential causes the KS orbitals not to suffer from this deficiency. As a consequence, the correlation error in individual energy terms such as the kinetic energy or the electron–nuclear energy, is much smaller in the KS case. This illustrates in what sense and with what effect electron correlation is embodied in the one-electron KS model. It is interesting to observe that the incorporation of the potential of both the exchange and correlation holes, i.e. neglecting $v_{c,kin}$ and v^{resp} in Eq. (10), gives precisely the potential advocated by Slater for use in one-electron equations just 2 years after his introduction of the exchange approximation [28]. Slater conjectured that this potential, based on the conditional probability to find other electrons around a given position of the reference electron, might give optimal orbitals for a configuration interaction. Speculating that the Xα potential might actually incorporate part of the correlation effects led Slater to denote the Xα potential as an exchange–correlation potential (this has been corroborated by the finding that the current exchange approximations of DFT, which are still predominantly the Slater exchange, actually incorporate the nondynamical correlation effects in chemical bonds [27]). Löwdin [29] was inspired by Slater's proposal to investigate the equations for optimal orbitals in a configuration interaction. These natural orbitals obey an equation in which the physics of the exchange–correlation hole potential, v_{xc}^{hole} (sometimes referred to as the Slater–Löwdin potential), can indeed be recognized; however, the application of only v_{xc}^{hole} in one-electron equations leads to too contracted orbitals and density, and the remaining potentials, $v_{c,kin}$ and v^{resp} in the KS potential play an important role to build precisely the right shape of the total density. It is possible to relate special features in the potentials $v_{c,kin}$ (peak behaviour around the bond midpoint) and v^{resp} (repulsive steps in atomic shells) to specific electron correlation effects [26].

It is worth noting that not just the occupied KS orbitals but also the virtual KS orbitals and orbital energies can be used for qualitative interpretation. They surely are not devoid of physical meaning, but they are directly related to excitation energies and to the electronic nature of excited states. This has become evident very recently from the development of time-dependent DFT methods for response properties, in particular excitation energies [30–32]. (see also the results in Ref. [33]).

The properties of the KS orbitals recommend them strongly for use in the qualitative MO theories of chemistry. It would be hard to find a better MO theoretical context in which to apply concepts such as "charge control" and "orbital control" than the KS one-electron model. In view of the good quality of several energy components (those directly following from the electron density are in fact exact) the KS one-electron model can be used reliably for interpretation using analysis along the lines delineated by Morokuma [34] within the HF model. Energy contributions such as classical electrostatic interaction, Pauli repulsion, and donor–acceptor interaction (orbital interaction energy) can be calculated and used for interpretation in the KS model [35–38]. We refer to Ref. [39] for a recent review with more complete discussion and examples. It is thought provoking that KS MO theory is actually related to exact energetics by way of the exchange–correlation functional, E_{xc}. The implication is that the concepts mentioned above, that traditionally were used only qualitatively since they were defined in a one-electron model (HF) that did not yield the exact energy, can now be used with accurate energies. Within the KS model, the MO-type analysis constitutes a complete conceptual framework. Since qualitative understanding and interpretation is the primary objective of this type of analysis, this may in practice not be such a huge advantage over MO theory based on semiempirical methods as it may seem at first sight, but it doubtless recommends the KS one-electron model as the preferred basis for MO theory.

We conclude that the 1965 paper by KS has had a singular influence in the electronic structure theory of physics in the last part of the century. Its impact in chemistry has enormously increased in the last decade. Its implications are only gradually being understood and its full depth may not yet have been fathomed. There can be no doubt that it will exert a large influence well into the next century.

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