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## Density Functionals beyond the Local Approximation [and Discussion]

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# Density functionals beyond the local approximation

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A review of the current effort in improvement over the local density approximation is given. Within the density functional theory, the exchange-correlation energy and potential may be unambiguously defined. Based on the field theoretical expressions for them, approximations for classes of systems and approximate evaluations for specific solids are critically reviewed. Further lines of development are discussed. Relation to the quasi-particle energies is explored.

## 1. Introduction

The density functional theory (Hohenberg & Kohn 1964; Kohn & Sham 1965) in the local density approximation gives a simple way of utilizing the knowledge of the exchange-correlation effects of the electron gas in real atoms, molecules and solids. Through the effort of many workers in this field, the theory has been thoroughly tested in a wide range of systems including atoms, molecules, solids and nuclei and found particularly useful for ground-state properties (Schlüter & Sham 1982; Lundqvist & March 1983; Parr & Yang 1989). There is of course room for improvement. There are two separate aspects. One is the improvement of the energy functionals for the ground-state properties. The other is how the energies of low-lying excited states may be found within the context of the density functional theory.

In §2 the definitions of the exchange and correlation energy functionals and potentials are given in the context of the density functional theory and the motivation of the particular definitions is shown to be the transformation of a many-particle problem to an effective one-particle one. This does not eliminate the interacting particle physics but only moves it to the construction of the effective potential. Section 3 reviews a formal expression for the exchange-correlation energy. Section 4 explains the difference between the density functional exchange and the Fock exchange in the Hartree–Fock approximation. Section 5 explores a number of approaches that go beyond the local density approximation (LDA).

The low-lying excited state energies may be viewed as quasi-particle energies. The density functional equation for constructing the ground-state density naturally has a set of single-particle energies. Whether they can represent the quasi-particle energies has been investigated. In general the two sets are not related. None the less, the density functional theory is shown to be a useful framework to construct the self-energy. The insulator or semiconductor band gap is a special case in which it is related to the ground-state energies of the system and of the system with the addition or removal of an electron. The discontinuity of the exchange-correlation

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potential on adding an electron in an insulator plays a prominent role in the determination of the band gap (§6). The Fermi surface is formally not given by the density functional eigenvalues but is in practice remarkably well approximated by the LDA in a disparate range of metals (§7). The reason remains to be explored. The final section summarizes the situation that improvement over the LDA involves considerations of specific systems with the loss of the simplicity and universality of the LDA.

## 2. Definition of the exchange-correlation energy functional

The density functional theory has three key features: (1) any property of a many-electron system is a functional of the ground state density; (2) for a given external potential, the ground state energy is a variational minimum at the correct density; (3) the density is determined by a one-particle Schrödinger equation with an effective potential.

In the consideration of the class of all many-electron systems, which share the common attributes of the electron mass, Fermi statistics, and the same Coulomb interaction between a pair of electrons, the position-dependent external potential  $v(r)$ , i.e. the potential experienced by each electron due to the fixed nuclei, characterizes a particular system. A property of the system is said to be a functional of  $v(r)$ . In particular, the density  $n(r)$  is a functional of  $v(r)$ , it being understood that either the total number of electrons or the chemical potential is given. The theorem of Hohenberg & Kohn (1964) asserts that the external potential is a functional of the ground-state density, apart from a trivial constant.

It follows that the ground-state energy is a functional of the density. It may be separated into two terms:

$$E = T_s[n] + U[n], \quad (2.1)$$

where  $T_s[n]$  is the kinetic energy functional of a non-interacting electron system with the same density distribution. By comparing the variational equation

$$\delta T_s / \delta n + \delta U / \delta n = \mu, \quad (2.2)$$

$\mu$  being the chemical potential, with the corresponding one for the non-interacting system, one arrives at the one-electron Schrödinger equation

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{eff}}(r)\right]\psi_j(r) = \epsilon_j \psi_j(r), \quad (2.3)$$

which determines the density

$$n(r) = \sum_j \theta(\mu - \epsilon_j) |\psi_j(r)|^2. \quad (2.4)$$

The effective one-electron potential is given by

$$v_{\text{eff}}(r) = \delta U / \delta n. \quad (2.5)$$

Formally, the density functional theory has reduced the many-body problem to the solution of a one-particle Schrödinger equation. The many-body problem now consists in the construction of the energy functional  $U[n]$  or its functional derivative  $v_{\text{eff}}(r)$ . The procedure necessitates no explicit construction of the single-particle kinetic energy functional  $T_s[n]$ , although such constructions have been considered (Herring 1986).

Again, in  $U[n]$  we may separate out the terms which we know, namely the potential energy due to  $v(r)$  and the electrostatic energy due to the electron charge distribution

$$U[n] = \int dr v(r) n(r) + \frac{1}{2} \int dr \int dr' n(r) \frac{e^2}{|r-r'|} n(r') + E_{xc}[n], \quad (2.6)$$

and name the remainder the exchange-correlation energy  $E_{xc}[n]$ . The corresponding effective potential is composed of:

$$v_{\text{eff}}(r) = v(r) + \int dr' \frac{e^2}{|r-r'|} n(r') + v_{xc}(r), \quad (2.7)$$

i.e. the external potential, the electrostatic potential due to the electronic charge distribution, and the exchange-correlation potential

$$v_{xc}(r) = \delta E_{xc} / \delta n(r). \quad (2.8)$$

In this way, the exchange-correlation term is unambiguously defined and at the same time the motivation of the separation, to isolate the single-particle kinetic energy, is made clear. However, without a more explicit expression for the exchange-correlation potential or energy, the term is given a certain mysterious shroud. We discuss next a formal construction.

### 3. A formal construction of exchange and correlation energy

It is possible to construct a perturbation series in powers of the Coulomb interaction. In the density functional theory, the unperturbed state is the non-interacting electron state which produces the same ground-state density as the exact one. The same effective potential  $v_{\text{eff}}(r)$  holds for the unperturbed and exact states. Then a coupling constant integral for the exchange-correlation energy functional can be derived (Harris & Jones 1974). An alternative of making the density at every intermediate coupling constant value equal to the exact density (Gunnarsson & Lundqvist 1976) simplifies the expression sufficiently to see the physical picture of an exchange-correlation hole. In actual practice of an approximate evaluation, the unknown coupling constant dependence is difficult to account for and is generally neglected without justification.

From the Harris–Jones choice of the unperturbed state, the coupling constant integral can be formally evaluated into a perturbation series (Sham 1985):

$$E_{xc}[n] = i\text{Tr} [\ln (1 - \Sigma G_0) + \Sigma G] + Y, \quad (3.1)$$

where  $G_0$  and  $G$  are the unperturbed and exact one-electron Green's functions,  $\Sigma$  is the exchange-correlation part of the self-energy, trace  $\text{Tr}$  is taken over position and energy, and  $Y$  is the sum of all skeleton diagrams for the exchange-correlation energy in terms of  $G$ . Functional differentiation yields an integral equation for the exchange-correlation potential:

$$\begin{aligned} \int dr' v_{xc}(r') \left[ \int d\omega G_0(r, r'; \omega) G(r', r; \omega) \right] \\ = \int dr_1 \int dr_2 \int d\omega G_0(r, r_1; \omega) \Sigma(r_1, r_2; \omega) G(r_2, r; \omega). \end{aligned} \quad (3.2)$$

Thus the exchange-correlation potential is expressed in terms of the one-particle Green's function and self-energy. To treat the magnetic systems, the density has to

be extended to two spin components. The extension of the expression for  $v_{xc}$  to the spin case has been given by Ng (1989).

For a confined system, the solution of the integral equation has the correct asymptotic behaviour (Sham 1985). It is interesting that the dominant contributions for the asymptotic behaviour for an atom and for a metal surface are different. At a large distance  $r$  from an atom, the limit

$$v_{xc}(r) \sim e^2/r \quad (3.3)$$

is dominated by the exchange term (defined in the next section). At a large normal distance  $z$  outside the metal surface, the limit

$$v_{xc}(z) \sim -e^2/4z \quad (3.4)$$

comes entirely from the correlation term, specifically the surface plasmon contribution to the correlation energy.

#### 4. Density functional exchange

To first order in the Coulomb interaction, the exchange energy is from equation (3.1)

$$E_x[n] = -\frac{1}{4} \int dr \int dr' \frac{e^2}{|r-r'|} n(r, r') n(r', r), \quad (4.1)$$

where the one-particle density matrix is given in terms of the density functional orbitals of equation (2.3):

$$n(r, r') = \sum_j \theta(\mu - \epsilon_j) \psi_j(r) \psi_j^*(r'), \quad (4.2)$$

summing over both spin states.

The corresponding equation of the exchange potential  $v_x(r)$  is exactly the same as the local potential yielding orbitals which minimize the Hartree–Fock energy (Sharp & Horton 1953). Thus  $E_x[n]$  is close to the Hartree–Fock exchange energy but is not identical to it. In the density functional theory, the exchange potential  $v_x(r)$  exists on its own right rather than is a local approximation to the non-local Fock potential. Consequently, the density functional correlation energy  $E_c[n]$  is not the same as the correlation energy defined as the difference between the total energy and the Hartree–Fock energy.

#### 5. Approximations for the exchange-correlation

The approximation (Kohn & Sham 1965) which makes the density functional theory widely used is the LDA:

$$E_{xc}^{\text{LDA}} = \int dr \epsilon_{xc}(n(r)) n(r), \quad (5.1)$$

i.e. in a small neighbourhood the exchange-correlation energy density is given by the corresponding term  $\epsilon_{xc}(n)$  of the homogeneous electrons gas at the local density. The LDA potential is given by

$$v_{xc}^{\text{LDA}}(r) = \mu_{xc}(n(r)), \quad (5.2)$$

the exchange-correlation part of the chemical potential of the homogeneous electron gas. The guiding principle is clearly that of the Thomas–Fermi approximation. The

difference lies in that the LDA does not approximate the kinetic energy term  $T_s[n]$ , which gives the advantage of retaining the major quantum features such as the density oscillations. In the exchange-correlation part, the LDA suffers from the same disadvantages as the Thomas–Fermi approximation, such as the lack of the gradient correction and the incorrect treatment in the decaying region where the energy is lower than the potential. The latter is largely responsible for the incorrect asymptotic behaviour of LDA in a confined system.

Because LDA is shown to account for much of the exchange-correlation effect in a wide range of inhomogeneous systems, any improvement should keep the advantage of LDA. The non-local correction to LDA proposed by Langreth & Mehl (1983) retains the LDA and adds a gradient term based on an analysis of the small wave-vector behaviour of the exchange-correlation energy. The correction appears to improve the surface energy of the jellium. In tests for small atoms where the exact results are known (Pedroza 1986), the correction improves over LDA on total energy and density. For larger atoms, Langreth & Mehl (1983) have found the density functional eigenvalues of equation (2.3) far from the exact values, but the energy differences to be in good agreement, from which they inferred that the error in the exchange-correlation potential is almost constant over the atom. For bulk silicon, the theory gives improved values for the ground-state properties, such as cohesive energy, equilibrium volume, and bulk modulus but essentially the same band gap as LDA (U. von Barth & R. Car 1987, personal communication). The band gap problem arises because the gradient correction does not yield the essential discontinuity in  $v_{xc}$ . (See the next section.)

A different approach (Gunnarsson & Jones 1980) is to construct a better exchange-correlation hole in the pair correlation function than that which reproduces the LDA for the energy functional. The pair correlation appears in the coupling constant integral for the exchange-correlation energy. The construction of the so-called weighted density approximation is made to satisfy the sum rules. In atoms, it yields better total energy than LDA but not better density nor density functional eigenvalues (Pedroza 1986). It gives much too large a surface energy for the semi-infinite jellium.

A third approach is to construct approximations based on the field theoretic expression for  $v_{xc}$ , equation (3.3). Use of the LDA for the self-energy and Green's function (Sham & Kohn 1966) recovers LDA for  $v_{xc}$ . The equation with exchange only has been solved for atoms (Aashamar *et al.* 1978). A simple form of  $v_{xc}$  which was suggested by Sharp & Horton (1953) follows from putting the electron energy  $\epsilon_k$  in one of the pair of Green's functions on each side of equation (3.3) to a constant. The advantage over LDA is the correct asymptotic behaviour. The disadvantage is that it does not reduce to LDA in the slowly varying density limit which means that it does not have the well-tested aspects of LDA. A form suggested by Sham (1985) is to average the self-energy over the Fermi surface for a metal and over the highest occupied density functional orbitals in an insulator. It would reduce to LDA in the slowly varying density limit and would have the correct asymptotic limit away from the surface of a confined system. It has, however, not been numerically tested.

Solution of equation (3.3) for  $v_{xc}$  depends on the construction of a self-energy. This has been done for diamond, silicon, GaAs and AlAs (Godby *et al.* 1988). The self-energy is evaluated in the random phase approximation (RPA) in a self-consistent procedure starting with orbitals in LDA. The resultant  $v_{xc}$  is quite close to the LDA potential if the corresponding RPA is used for the homogeneous electron gas. We

expect that if the self-energy were evaluated beyond RPA the resultant  $v_{xc}$  would be still close to the LDA with the accurate  $\mu_{xc}$  in the electron gas given by Ceperley & Alder (1980). Why would one need the density functional theory if one has to construct the self-energy? The RPA work on  $v_{xc}$  shows that it is advantageous to start with the LDA orbitals. Hartree–Fock orbitals, for example, in general would be a poor starting approximation in solids and would in addition be much more difficult to obtain.

## 6. The band gap problem and discontinuity in $v_{xc}$

Against the wide-ranging success of LDA in ground-state properties, the uniform lack of agreement between LDA and experiment on the band gaps in semiconductors and insulators is striking. LDA values are always smaller than experiment, roughly different by a factor of two. Two possible sources of error are the LDA for  $v_{xc}$  and the use of the eigenvalues of the density functional equation (2.3) for the energies of the excited states.

In semiconductors, the  $v_{xc}$  calculated beyond LDA using RPA for the self-energy as described in the last section (Godby *et al.* 1988) yields a band gap only slightly bigger than the LDA gap. The LDA potential is sufficiently accurate that the large discrepancy in band gaps cannot come from this approximation.

In general, the eigenvalues  $\epsilon_j$  from the effective one-particle equation (2.3) with the exact exchange–correlation potential  $v_{xc}$  do not represent the energies of the excited states. Although the band gap may be expressed in terms of excited state energies, it does have a special relation to the lowest energy states of  $N \pm 1$  particles in the same insulator with an  $N$ -particle ground state. The highest occupied density functional eigenenergy does represent the valence band edge in the insulator or semiconductor case. The band gap of an insulator or a semiconductor can be defined precisely in terms of the ground-state energy as a function  $E_M$  of the number of particles  $M$ . If the insulating ground state has  $N$  particles, the conduction band edge is the change of the total ground-state energy when an electron is added and the valence band edge is given by the change when an electron is removed:

$$E_c = E_{N+1} - E_N, \quad (6.1)$$

$$E_v = E_N - E_{N-1}. \quad (6.2)$$

The band gap is naturally the difference:

$$E_g = E_c - E_v. \quad (6.3)$$

It is straightforward to show (Sham & Schlüter 1985) from the definition of  $E_v$  and with the help of the variational theorem that the valence band edge is given by the highest occupied density functional eigenenergy:

$$E_v = \epsilon_N. \quad (6.4)$$

Now, the Hohenberg–Kohn theorem is implicitly for a fixed number of electrons,  $M$ . Equation (2.3) and  $v_{xc}$  are implicitly defined as functions of  $M$ . Since  $M = N$  gives the insulating ground state, when an electron is removed, the highest occupied state is changed by a negligible amount [ $O(1/N)$ ] and  $v_{xc}(N-1)$  is the same as  $v_{xc}(N)$  but when an electron is added across the gap, the  $(N+1)$ th state is very different and there is a discontinuity in  $v_{xc}$  as  $N$  is changed to  $N+1$  (Sham & Schlüter 1983; Perdew & Levy 1983):

$$v_{xc}(N+1) = v_{xc}(N) + \Delta_{xc}, \quad (6.5)$$

where  $A_{xc}$  is independent of position. It follows that the difference between the true gap, equation (6.3) and the density functional gap given by

$$\epsilon_g = \epsilon_{N+1} - \epsilon_N, \quad (6.6)$$

is just the potential discontinuity,  $A_{xc}$ .

A persuasive demonstration of the importance of the discontinuity is the calculation of the discontinuity for a number of semiconductors in RPA (Godby *et al.* 1988). RPA for the Green's function using the LDA basis set (Hybertsen & Louie 1987) has been shown to give very good band structures for a number of semiconductors, including the band gaps. The density functional potential for a number of semiconductors, diamond, Si, GaAs, and AlAs, calculated (Godby *et al.* 1988) from the self-energy in RPA by iteration from LDA is then used to construct the Green's function in RPA and to determine the quasi-particle energies. The band gaps are in good agreement with experiment and the  $v_{xc}$  discontinuity accounts for a major part of the correction.

## 7. The Fermi surface problem

The Fermi surface problem is the counterpart of the band gap problem for conductors. The highest occupied energy in the density functional equation (2.3) can easily be shown to be the energy for adding an electron to a metal and is thus the chemical potential. The problem is whether the Fermi surface given by the eigenenergies of equations (2.3) is the same as the true Fermi surface. The true Fermi surface can be constructed from the one-particle Green's function which gives the quasi-particle energies. The LDA-like approximation for the Green's function (Sham & Kohn 1966) yields the same Fermi surface as equation (2.3). Thus, for the case of slowly varying density, the density functional Fermi surface from equation (2.3) is the same as the true Fermi surface. This includes the special case of constant density, where the isotropy of the system ensures both Fermi surfaces to be spherical and where the same total number of electrons enclosed by the Fermi surfaces guarantees the radius to be the same.

Mearns (1988) has demonstrated that the density functional Fermi surface and the true Fermi surface differ to second order in the lattice potential and first order in the Coulomb interaction. This roughly corresponds in the semiconductor case to the demonstration of the discontinuity of  $v_{xc}$  existing in the Hartree-Fock approximation (Sham & Schlüter 1985). Examples abound demonstrating that the LDA Fermi surfaces are very good approximations to the measured ones, even for hybridized f bands (Koelling 1982; Johanson *et al.* 1983). What is needed is first a demonstration of the likely event that the LDA Fermi surface is a good approximation to the density functional Fermi surface and then a theoretical understanding of the difference of the density functional Fermi surface and the true one and of the reason for the small difference.

## 8. Summary

For the ground-state properties, the density functional theory reduces the solution of the many-electron Schrödinger equation to that of an effective one-electron Schrödinger equation, requiring the construction of an exchange-correlation potential. The LDA offers simplicity and universality in the sense that only a knowledge of the exchange-correlation effect of the homogeneous electron gas as a function of density is needed as input. Approximations such as the inclusion of



a gradient correction or a better pair correlation yield improvement in limited instances. For characteristics such as the potential discontinuity in the insulating system, construction of the self-energy for the particular system appears necessary. Simplified approximations for the self-energy (Hanke & Sham 1988) may facilitate computation of  $v_{xc}$  but their accuracy requires extensive testing. A particularly interesting direction would be to utilize the knowledge acquired from the still developing research on models of strong correlation of narrow band electrons to construct functionals for more general solids.

For quasi-particle energies, the density functional eigenvalues, especially the LDA values, form a convenient approximation though unjustified. To include the exchange-correlation effect properly, there is no avoiding the construction of the self-energy. RPA has been shown to be adequate for the band structures but not total energies in the covalent semiconductors. For metals, as in jellium, corrections to RPA are important (Hybertsen & Louie 1987). The LDA orbitals form a good starting basis for the construction of the self-energy but it appears that to improve on LDA a simple universal approximation may no longer be adequate.

I acknowledge the benefit of helpful discussions from many persons, especially my collaborators, R. Godby, W. Kohn and M. Schlüter, over the years. This work is supported in part by NSF Grant no. DMR 88-15068.

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*Discussion*

Z. REUT (*City University, London, U.K.*). It may be more appropriate to define the pseudo- or effective potential by an integral, rather than by the usual gradient that might not exist, or be of a dubious meaning in the case of many-electron systems. The effective potential in such cases can be velocity dependent and subject to relativistic effects.

L. J. SHAM. For a physical system, small changes of the electron density generally produce small changes in  $E_{xc}[n]$  (except across the band gap of a semiconductor). Therefore,  $\delta E_{xc}[n]/\delta n$  is well defined. For a semiconductor, it is well defined for either side of the hyperface of the constant total electron number.

J. W. WILKINS (*Ohio State University, U.S.A.*). In strained superlattices – such as GaAs/GaInAs grown in the [III] direction – there are large, strain-induced, electric fields of order  $10^5$  V cm<sup>-1</sup> or 1 meV Å<sup>-1</sup>. Can density functional theory adequately explain excitations between the valence and conduction bands in such a situation?

L. J. SHAM. The band structure computation itself at the present stage is unable to reproduce accurately the band edge features in the meV range. It is, therefore, necessary to use the effective mass theory with the relevant band edge position and curvature taken from experiment.

V. HEINE (*Cambridge, U.K.*). Professor Sham emphasized the corrections beyond the LDA to band gaps, where there are experimental data to compare with. That is natural, but I wonder whether in the long run some chemical effects may not be more important. For example in a transition metal, the exchange and correlation hole seen by a d electron will be quite different from the hole seen by an sp electron, unlike the situation in LDA. Thus the relative position of the sp and d band will be incorrect, which in turn affects the amount of hybridization. Similarly in high  $T_c$  superconductors, much hangs on the balance between the Cu 3d level and the oxygen 2p level, which one cannot expect to give well by the LDA.

L. J. SHAM. For the states close to the Fermi level, the density functional theory (DFT) gives quite good Fermi surface even though not exact. So improvement from

the construction of the DFT self-energy should be small. But for deeper levels, such as the sp and d band separation, the construction of the one-particle Green's function is necessary.

L. M. FALICOV (*University of California, Berkeley, U.S.A.*). For moderately correlated systems (ferromagnets, antiferromagnets) the DFT gives qualitatively the correct Fermi surface only if the correct symmetry breaking is considered from the start. For highly correlated heavy fermions, where symmetry breaking normally takes place and is much more subtle, why does Professor Sham 'hope' to obtain the correct Fermi surface?

L. J. SHAM. LDA has given Fermi surfaces even in heavy Fermion metals quite close to the measured ones. One needs to understand the reason.

D. M. EDWARDS (*Imperial College, London, U.K.*). Professor Sham discussed the formulations of the exact exchange correlation potential using perturbation theory. Since even the exact functional does not give the exact Fermi surface isn't there a problem with the anomalous diagrams of Kohn and Luttinger?

L. J. SHAM. No, in the perturbation expansion starting from the density functional Green's function  $G_0$ , one can avoid the anomalous diagrams by keeping the unperturbed and perturbed Fermi levels the same, which they naturally are in DFT.