

Electronic Structure: Density Functional Theory

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I. INTRODUCTION

Density functional theory (DFT) is a successful theory to calculate the electronic structure of atoms, molecules, and solids. Its goal is the quantitative understanding of materials properties from the fundamental laws of quantum mechanics.

Traditional electronic structure methods attempt to find approximate solutions to the Schrödinger equation of N interacting electrons moving in an external, electrostatic potential (typically the Coulomb potential generated by the atomic nuclei). However, there are serious limitations of this approach: (i) the problem is highly nontrivial, even for very small numbers N and the resulting wave-functions are complicated objects, (ii) the computational effort grows very rapidly with increasing N , so the description of larger systems becomes prohibitive.

A different approach is taken in density functional theory where, instead of the many-body wave-function, the one-body density is used as fundamental variable. Since the density $n(\mathbf{r})$ is a function of only three spatial coordinates (rather than the $3N$ coordinates of the wave-function), density functional theory is computationally feasible even for large systems.

The foundations of density functional theory are the Hohenberg-Kohn and Kohn-Sham theorems which will be reviewed in the following section. In section III, we will discuss various levels of approximation to the central quantity of DFT, the so-called exchange-correlation energy functional. Section IV will present some typical results from DFT calculations for various physical properties that are normally calculated with DFT methods. The original Hohenberg-Kohn and Kohn-Sham theorems can easily be extended from its original formulation to cover a wide variety of physical situations. A number of such extensions is presented in section V, with particular emphasis on time-dependent DFT (section V C).

II. HOHENBERG-KOHN AND KOHN-SHAM THEOREMS

In ground-state DFT one is interested in systems of N interacting electrons described by the Hamiltonian

$$\begin{aligned} \hat{H} &= \hat{T} + \hat{V} + \hat{V}_{ee} \\ &= -\sum_{i=1}^N \frac{\nabla_i^2}{2} + \sum_{i=1}^N v(\mathbf{r}_i) + \frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ i \neq j}}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \end{aligned} \quad (1)$$

with the kinetic, potential and interaction energy operators \hat{T} , \hat{V} and \hat{V}_{ee} , respectively.

The central statement of formal density functional theory is the celebrated Hohenberg-Kohn theorem which, for non-degenerate ground states, can be summarized in the following three statements:

1. The ground state electron density $n(\mathbf{r})$ of a system of interacting electrons uniquely determines the external potential $v(\mathbf{r})$ in which the electrons move and thus the Hamiltonian and all physical properties of the system.
2. The ground-state energy E_0 and the ground-state density $n_0(\mathbf{r})$ of a system characterized by the potential $v_0(\mathbf{r})$ can be obtained from a variational principle which involves only the density, i.e., the ground state energy can be written as a functional of the density, $E_{v_0}[n]$, which gives the ground-state energy E_0 if and only if the true ground-state density $n_0(\mathbf{r})$ is inserted. For all other densities $n(\mathbf{r})$, the inequality

$$E_0 = E_{v_0}[n_0] < E_{v_0}[n] \quad (2)$$

holds.

3. There exists a functional $F[n]$ such that the energy functional can be written as

$$E_{v_0}[n] = F[n] + \int d^3r v_0(\mathbf{r}) n(\mathbf{r}) . \quad (3)$$

The functional $F[n]$ is universal in the sense that, for a given particle-particle interaction (the Coulomb interaction in our case), it is independent of the potential $v_0(\mathbf{r})$ of the particular system under consideration, i.e., it has the same functional form for all systems.

The proof of the Hohenberg-Kohn theorem is based on the Rayleigh-Ritz variational principle and will not be repeated here. The interested reader is referred to excellent reviews given in the Bibliography.

From the Hohenberg-Kohn variational principle, i.e., the second statement given above, the ground-state density $n(\mathbf{r})$ corresponding to the external potential $v(\mathbf{r})$ can be obtained as solution of the Euler equation

$$\frac{\delta E_v[n]}{\delta n(\mathbf{r})} = \frac{\delta F[n]}{\delta n(\mathbf{r})} + v(\mathbf{r}) = 0 , \quad (4)$$

The formal definition of the Hohenberg-Kohn functional $F[n]$ is well known,

$$F[n] = T[n] + V_{\text{ee}}[n] = \langle \Psi[n] | \hat{T} | \Psi[n] \rangle + \langle \Psi[n] | \hat{V}_{\text{ee}} | \Psi[n] \rangle, \quad (5)$$

where $\Psi[n]$ is that N -electron wave-function which yields the density n and minimizes the expectation value of $\hat{T} + \hat{V}_{\text{ee}}$. However, the explicit density dependence of $F[n]$ remains unknown. Approximations have been suggested, the oldest one being the well-known Thomas-Fermi approximation (which precedes the Hohenberg-Kohn theorem historically). Unfortunately, the accuracy of known approximations to $F[n]$ is rather limited in practical calculations. Therefore Eq. (4) is rarely used in electronic structure calculations today.

Instead, the Hohenberg-Kohn theorem provides the basic theoretical foundation for the construction of an effective single-particle scheme which allows the calculation of the ground-state density and energy of systems of interacting electrons. The resulting equations, the so-called Kohn-Sham equations, are at the heart of modern density functional theory. They have the form of the single-particle Schrödinger equation

$$\left[-\frac{\nabla^2}{2} + v_{\text{s}}(\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}). \quad (6)$$

The density can then be computed from the N single-particle orbitals occupied in the ground state Slater determinant

$$n(\mathbf{r}) = \sum_i^{\text{occ}} |\varphi_i(\mathbf{r})|^2. \quad (7)$$

The central idea of the Kohn-Sham scheme is to construct the single-particle potential $v_{\text{s}}(\mathbf{r})$ in such a way that the density of the auxiliary non-interacting system equals the density of the interacting system of interest. To this end one partitions the Hohenberg-Kohn functional in the following way

$$F[n] = T_{\text{s}}[n] + U[n] + E_{\text{xc}}[n], \quad (8)$$

where

$$U[n] = \frac{1}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (9)$$

is the classical electrostatic energy of the charge distribution $n(\mathbf{r})$, and $E_{\text{xc}}[n]$ is the so-called exchange-correlation energy which is formally defined by

$$E_{\text{xc}}[n] = T[n] + V_{\text{ee}}[n] - U[n] - T_{\text{s}}[n]. \quad (10)$$

From the above definitions one can derive the form of the effective potential entering Eq. (6)

$$v_{\text{s}}[n](\mathbf{r}) = v(\mathbf{r}) + \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{xc}}[n](\mathbf{r}), \quad (11)$$

where the exchange-correlation potential v_{xc} is defined by

$$v_{xc}[n](\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}. \quad (12)$$

Since $v_s[n](\mathbf{r})$ depends on the density, Eqs. (6), (7) and (11) have to be solved self-consistently. This is known as the Kohn-Sham scheme of density functional theory.

III. APPROXIMATIONS FOR THE EXCHANGE-CORRELATION ENERGY

Clearly, the formal definition (10) of the exchange-correlation energy is not helpful for practical calculations and one needs to use an approximation for this quantity. Some of these approximations will be discussed in the following.

While DFT itself does not give any hint on how to construct approximate exchange-correlation functionals, it holds both the promise and the challenge that the true E_{xc} is a *universal* functional of the density, i.e., it has the same functional form for all systems. On one hand this is a promise because an approximate functional, once constructed, may be applied to any system of interest. On the other hand this is a challenge because a good approximation should perform equally well for very different physical situations.

Both the promise and the challenge are reflected by the fact that the simplest of all functionals, the so-called local density approximation (LDA) has remained the approximation of choice for quite many years after the formulation of the Kohn-Sham theorem. In LDA, the exchange-correlation energy is given by

$$E_{xc}^{LDA}[n] = \int d^3r n(\mathbf{r}) e_{xc}^{\text{unif}}(n(\mathbf{r})) \quad (13)$$

where $e_{xc}^{\text{unif}}(n)$ is the exchange-correlation energy per particle of an electron gas with spatially uniform density n . It can be obtained from quantum Monte Carlo calculations and simple parameterizations are available. By its very construction, the LDA is expected to be a good approximation for spatially slowly varying densities. Although this condition is hardly ever met for real electronic systems, LDA has proved to be remarkably accurate for a wide variety of systems.

In the quest for improved functionals, an important breakthrough was achieved with the emergence of the so-called generalized gradient approximations (GGAs). Within GGA, the exchange-correlation energy for spin-unpolarized systems is written as

$$E_{xc}^{\text{GGA}}[n] = \int d^3r f(n(\mathbf{r}), \nabla n(\mathbf{r})). \quad (14)$$

While the input e_{xc}^{unif} in LDA is unique, the function f in GGA is not and many different forms have been suggested. When constructing a GGA one usually tries to incorporate a number of known properties of the exact functional into the restricted functional form of the approximation. The impact of GGAs has been quite dramatic, especially in quantum chemistry where DFT is now competitive in accuracy with more traditional methods while being computationally less expensive.

In recent years, still following the lines of GGA development, a new class of “meta-GGA” functionals has been suggested. In addition to the density and its first gradient, meta-GGA functionals depend on the kinetic energy density of the Kohn-Sham orbitals,

$$\tau(\mathbf{r}) = \frac{1}{2} \sum_i^{\text{occ}} |\nabla\varphi_i(\mathbf{r})|^2, \quad (15)$$

The meta-GGA functional then takes the form

$$E_{xc}^{\text{MGGA}}[n] = \int d^3r g(n(\mathbf{r}), \nabla n(\mathbf{r}), \tau(\mathbf{r})). \quad (16)$$

The additional flexibility in the functional form gained by the introduction of the new variable can be used to incorporate more of the exact properties into the approximation. In this way it has been possible to improve upon the accuracy of GGA for some physical properties without worsening the results for others.

Unlike LDA or GGA, which are *explicit* functionals of the density, meta-GGAs also depend explicitly on the Kohn-Sham orbitals. It is important to note, however, that we are still in the domain of DFT since, through the Kohn-Sham equation (6), the orbitals are functionals of the Kohn-Sham potential and therefore, by virtue of the Hohenberg-Kohn theorem, also functionals of the density.

Orbital functionals, or *implicit* density functionals, constitute a wide field of active research. Probably the most familiar orbital functional is the exact exchange energy functional (EXX)

$$E_x^{\text{EXX}}[n] = -\frac{1}{2} \sum_{\sigma} \int d^3r \int d^3r' \sum_{i,j}^{\text{occ}} \frac{\varphi_{i\sigma}(\mathbf{r})\varphi_{i\sigma}^*(\mathbf{r}')\varphi_{j\sigma}(\mathbf{r}')\varphi_{j\sigma}^*(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}. \quad (17)$$

At this point, some remarks about similarities and differences to Hartree-Fock theory are in order. If one uses the exact exchange functional (17) and neglects correlation, the resulting total energy functional is exactly the Hartree-Fock functional. However, in exact-exchange DFT this functional is evaluated with Kohn-Sham rather than Hartree-Fock orbitals. Furthermore, the Hartree-Fock orbitals are obtained from a minimization without constraints

(except for orthonormality) which leads to the nonlocal Hartree-Fock potential. The exact-exchange Kohn-Sham orbitals, on the other hand, are obtained by minimizing the same functional under the additional constraint that the single-particle orbitals come from a *local* potential. Therefore the total Hartree-Fock energy is always lower than the total energy in exact-exchange DFT but the difference has turned out to be very small. However, single-particle properties such as orbitals and orbital eigenvalues can be quite different in both approaches. For example, Kohn-Sham exact exchange energy spectra are usually much closer to experiment than Hartree-Fock spectra, indicating that exact-exchange DFT might be a better starting point to include correlation than Hartree-Fock.

In order to go beyond exact-exchange DFT one might be tempted to use the exact exchange functional in combination with a traditional approximation such as LDA or GGA for correlation. Since both LDA and GGA benefit from a cancellation of errors between their exchange and correlation pieces, an approach using LDA or GGA for only one of these energy components is bound to fail. The obvious alternative are approximate, orbital-dependent correlation energy functionals. One systematic way to construct such functionals is known as Görling-Levy perturbation theory. Structurally, this is similar to what is known as Møller-Plesset perturbation theory in quantum chemistry. However, it is only practical for low orders. A more promising route uses the fluctuation-dissipation theorem which establishes a connection to linear response theory in time-dependent DFT.

A final class of approximations to the exchange-correlation energy are the so-called hybrid functionals which mix a fraction of exact exchange with GGA exchange,

$$E_x^{\text{HYB}}[n] = aE_x^{\text{EXX}}[n] + (1 - a)E_x^{\text{GGA}}[n], \quad (18)$$

where a is the (empirical) mixing parameter. This exchange functional is then combined with some GGA for correlation. Hybrid functionals are tremendously popular and successful in quantum chemistry but much less so in solid-state physics.

This last fact highlights a problem pertinent to the construction of improved functionals: available approximations are already very accurate and hard to improve upon. In addition, and this makes it a *very* difficult problem, one would like to have improved performance not only for just one particular property or one particular class of systems but for as many properties and systems as possible. After all, the true exchange-correlation energy is a *universal* functional of the density.

IV. RESULTS FOR SOME SELECTED SYSTEMS

Over the years, a vast number of DFT calculations has been reported and only the scantiest of selections can be given here. Results are given for different functionals in order to illustrate the performance of the different levels of approximation. It should be kept in mind, however, that while there is only one LDA functional there are several GGA, meta-GGA, or hybrid functionals which have been suggested and whose results for a given system will vary.

In solid-state physics, typical quantities calculated with ground-state DFT are structural properties. In table I, we present equilibrium lattice constants and bulk moduli for a few solids. LDA lattice constants are usually accurate to within a few percent. On average, GGA and meta-GGA give some improvement. For bulk moduli, the relative errors are much larger and improvement of GGA and meta-GGA as compared to LDA is statistical and not uniform. There are however some properties that are systematically improved by GGA. For example, GGA cohesive energies for transition metals are on average better by almost half an order of magnitude than the LDA values.

Possibly the best known success of GGA is the correct prediction of the ferromagnetic bcc ground state of iron for which LDA incorrectly gives a non-magnetic fcc ground state. The calculated magnetic moments shown in table II illustrates the improved performance of GGA also for this quantity.

One of the standard uses of DFT in solid state physics is the calculation of band structures. Usually one interprets and compares the Kohn-Sham band structure directly with experimental energy bands. Strictly speaking this interpretation has no sound theoretical justification since the Kohn-Sham eigenvalues are only auxiliary quantities. Experience has shown, however, that LDA or GGA band structures are often rather close to experimental ones, especially for simple metals. On the other hand, a well-known problem in semiconductors and insulators is that both LDA and GGA seriously underestimate the band gap. This deficiency is corrected when using the exact exchange functional (see Table III).

Since DFT also has gained a tremendous popularity in the world of quantum chemistry we finally present some results for the atomization energies of small molecules in Table IV. Similar to the cohesive energy of solids one sees a clear improvement as one goes from LDA to GGA. Further improvement is achieved on the meta-GGA level but, for this particular

quantity, the accuracy of the hybrid functional is truly remarkable. Unfortunately, however, the accuracy of hybrid functionals for molecular properties does not translate into an equally good performance for solids.

V. EXTENSIONS OF DFT

The original theory of Hohenberg, Kohn and Sham can only be applied to quantum systems in their (non-degenerate) ground-state. Over the years a number extensions have been put forth (with varying degree of success). In fact, density functional theories have been formulated for relativistic systems, superconductors, ensembles, etc. Here we only review a small selection of extensions of DFT. We will pay special attention to time-dependent DFT, as this theory is becoming particularly popular in the calculation of excited-state properties.

A. Spin Density Functional Theory

Most practical applications of DFT make use of an extension of the original theory which uses the partial densities of electrons with different spin σ as independent variables,

$$n_{\sigma}(\mathbf{r}) = \sum_i^{\text{occ}} |\varphi_{i\sigma}(\mathbf{r})|^2, \quad (19)$$

rather than using the total density of Eq. (7). Again, the single-particle orbitals are solutions of a non-interacting Schrödinger equation (6), but the effective potential Eq. (11) now becomes spin-dependent by using the exchange-correlation potential

$$v_{\text{xc}\sigma}[n_{\uparrow}, n_{\downarrow}](\mathbf{r}) = \frac{\delta E_{\text{xc}}[n_{\uparrow}, n_{\downarrow}]}{\delta n_{\sigma}(\mathbf{r})} \quad (20)$$

instead of the one given in Eq. (12). Spin-density functional theory (SDFT) relates to the original formulation of DFT as spin-unrestricted Hartree-Fock relates to spin-restricted Hartree-Fock theory. It allows for a straightforward description of systems with a spin-polarized ground state such as, e.g., ferromagnets.

B. Density functional theory for superconductors

In 1988, triggered by the remarkable discovery of the high- T_c materials, Oliveira, Gross and Kohn proposed a density functional theory for the superconducting state. Their theory

uses two independent variables, the "normal" density, $n(\mathbf{r})$, and a non-local "anomalous" density $\chi(\mathbf{r}, \mathbf{r}')$. This latter quantity reduces, under the appropriate limits, to the order-parameter in Ginzburg-Landau theory. With these two densities it is straightforward to derive a Hohenberg-Kohn-like theorem and a Kohn-Sham scheme. The resulting equations are very similar to the traditional Bogoliubov-de Gennes equations for inhomogeneous superconductors, but include exchange and correlation effects through a "normal",

$$v_{\text{xc}}[n, \chi](\mathbf{r}) = \frac{\delta E_{\text{xc}}[n, \chi]}{\delta n(\mathbf{r})}, \quad (21)$$

and an "anomalous" exchange-correlation potential,

$$\Delta_{\text{xc}}[n, \chi](\mathbf{r}, \mathbf{r}') = -\frac{\delta E_{\text{xc}}[n, \chi]}{\delta \chi^*(\mathbf{r}, \mathbf{r}')}. \quad (22)$$

Unfortunately, only few approximations to the exchange-correlation functionals have been proposed so far. From these we would like to mention an LDA-like functional aimed at describing electron-electron correlations, and the development of an OEP-like scheme that incorporates both strong electron-phonon interactions and electron screening. In this framework it is now possible to calculate transition temperatures and energy gaps of superconductors from first principles.

C. Time-dependent density functional theory

Several problems in physics require the solution of the time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}\Psi(\underline{\mathbf{r}}, t) = \hat{H}(t)\Psi(\underline{\mathbf{r}}, t), \quad (23)$$

where Ψ is the many-body wave-function of N electrons with coordinates $\underline{\mathbf{r}} = (\mathbf{r}_1, \mathbf{r}_2 \cdots \mathbf{r}_N)$, and $\hat{H}(t)$ is the operator (1) generalized to the case of time-dependent external potentials. This equation describes the time evolution of a system subject to the initial condition $\Psi(\underline{\mathbf{r}}, t = t_0) = \Psi_0(\underline{\mathbf{r}})$. The initial density is n_0 .

The central statement of time-dependent density functional theory (TDDFT), the Runge-Gross theorem, states that, if Ψ_0 is the ground state of $\hat{H}(t = t_0)$, there exists a one-to-one correspondence between the time-dependent density $n(\mathbf{r}, t)$ and the external potential, $v(\mathbf{r}, t)$. All observables of the system can then be written as functionals of the density only. The Runge-Gross theorem provides the theoretical foundation of TDDFT. The practical

framework of the theory is given by the Kohn-Sham scheme. We define a system of non-interacting electrons, obeying the one-particle Schrödinger equation

$$i\frac{\partial}{\partial t}\varphi_i(\mathbf{r}, t) = \left[-\frac{\nabla^2}{2} + v_s(\mathbf{r}, t) \right] \varphi_i(\mathbf{r}, t). \quad (24)$$

Similar to static Kohn-Sham theory, the Kohn-Sham potential is usually written as

$$v_s[n](\mathbf{r}, t) = v(\mathbf{r}, t) + \int d^3r' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}[n](\mathbf{r}, t), \quad (25)$$

where $v(\mathbf{r}, t)$ includes both the static Coulomb potential of the nuclei and the explicitly time-dependent contribution of an external electromagnetic field. The exchange-correlation potential, v_{xc} , is chosen such that the density of the Kohn-Sham electrons,

$$n(\mathbf{r}, t) = \sum_i^{\text{occ}} |\varphi_i(\mathbf{r}, t)|^2, \quad (26)$$

is equal to the density of the *interacting* system. Clearly, v_{xc} is a very complex quantity – it encompasses all non-trivial many-body effects – that has to be approximated. The most common approximation to $v_{xc}(\mathbf{r}, t)$ is the adiabatic local density approximation (ALDA). In the ALDA we assume that the exchange-correlation potential at time t is equal to the ground-state LDA potential evaluated with the density $n(\mathbf{r}, t)$, i.e

$$v_{xc}^{\text{ALDA}}[n](\mathbf{r}, t) = v_{xc}^{\text{unif}}(n(\mathbf{r}, t)). \quad (27)$$

Following the same reasoning it is simple to derive an adiabatic GGA or meta-GGA.

Two regimes can usually be distinguished in TDDFT (or more generally in time-dependent quantum mechanics), depending on the strength of the external time-dependent potential. If this potential is “weak”, the solution of the time-dependent Kohn-Sham equations can be circumvented by the use of linear (or low-order) response theory. In linear response, we look at the linear change of the density produced by a small (infinitesimal) change in the external potential – information which is contained in the so-called linear density response function χ . Within TDDFT, χ can be calculated from the Dyson-like equation

$$\begin{aligned} \chi(\mathbf{r}t, \mathbf{r}'t') &= \chi_s(\mathbf{r}t, \mathbf{r}'t') + \int d^3x \int d^3x' \int d\tau \int d\tau' \\ &\chi_s(\mathbf{r}t, \mathbf{x}\tau) \left[\frac{\delta(\tau - \tau')}{|\mathbf{x} - \mathbf{x}'|} + f_{xc}(\mathbf{x}\tau, \mathbf{x}'\tau') \right] \chi(\mathbf{x}'\tau', \mathbf{r}'t'), \end{aligned} \quad (28)$$

where χ_s is the (non-interacting) Kohn-Sham response function. The exchange-correlation kernel f_{xc} is defined as

$$f_{xc}(\mathbf{r}t, \mathbf{r}'t') = \left. \frac{\delta v_{xc}(\mathbf{r}, t)}{\delta n(\mathbf{r}', t')} \right|_{n_0} \quad (29)$$

where the functional derivative is evaluated at the initial ground state density n_0 . If we put $f_{xc} = 0$ in (28) we recover the well-known random phase approximation (RPA) to the excitation energies. Knowledge of χ allows for the calculation of linear absorption spectra. Here we have to distinguish between finite and extended systems. The optical absorption spectrum of a finite system is essentially given by the poles of χ . For an extended system, the spectrum is obtained from the imaginary part of the dielectric function, which can be written (in frequency space) as

$$\varepsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega) = \delta(\mathbf{r} - \mathbf{r}') + \int d^3x \frac{\chi(\mathbf{x}, \mathbf{r}', \omega)}{|\mathbf{r} - \mathbf{x}|}. \quad (30)$$

Most calculations performed within this scheme approximate the exchange-correlation kernel by the ALDA. For finite systems, excitation energies are of excellent quality for a variety of atoms, organic and inorganic molecules, clusters, etc. Unfortunately, the situation is different for extended systems, especially for large gap semiconductors. In Fig. 1 we show the ALDA optical absorption spectrum of silicon together with an RPA calculation, a Bethe-Salpeter calculation (a method based on many-body perturbation theory), and experimental results. It is clear that ALDA fails to give a significant correction over RPA. In momentum space, the Coulomb interaction is simply $1/q^2$. It is then clear from (28) that if f_{xc} is to contribute for small q – which is the relevant regime for optical absorption – it will have to behave asymptotically as $1/q^2$. The ALDA kernel approaches a constant for $q \rightarrow 0$ and is therefore incapable to correct the RPA results. Recently several new kernels have been proposed that overcome this problem. In the figure we show one of them, the RORO kernel, which has the simple form

$$f_{xc}^{\text{RORO}}(\mathbf{r}, \mathbf{r}') = -\frac{\alpha}{4\pi} \frac{1}{|\mathbf{r} - \mathbf{r}'|}, \quad (31)$$

where α is a phenomenologically determined parameter. Taking $\alpha = 0.12$ yields the curve shown in Fig. 1, which is already very close to the experimental results.

VI. CONCLUSIONS

There is no doubt that DFT has become a mature theory for electronic structure calculations. The success of DFT is based on the availability of increasingly accurate approximations to the exchange-correlation energy. Research into the development of still more accurate approximations continues. In static DFT, orbital functionals seem to be promising candidates to achieve this goal. In time-dependent DFT as well as in other extensions of DFT, development of approximations is still at a much earlier stage.

Applications of DFT abound. In solid state physics, DFT is the method of choice for the calculation materials properties from first principles. While traditional, static DFT calculations have mainly focussed on structural ground state properties such as, e.g., lattice parameters, TDDFT also allows for the calculation of excited state properties such as, e.g., absorption spectra. In quantum chemistry, the decade-long dream of electronic structure calculations with “chemical accuracy” appears within reach with DFT. Due to the favorable scaling of the computational effort with increasing system size and also to the ever-increasing computational power of modern computers, DFT calculations are now feasible for systems containing several thousand atoms. This opens the way for applications of DFT to biologically relevant systems.

Further Reading

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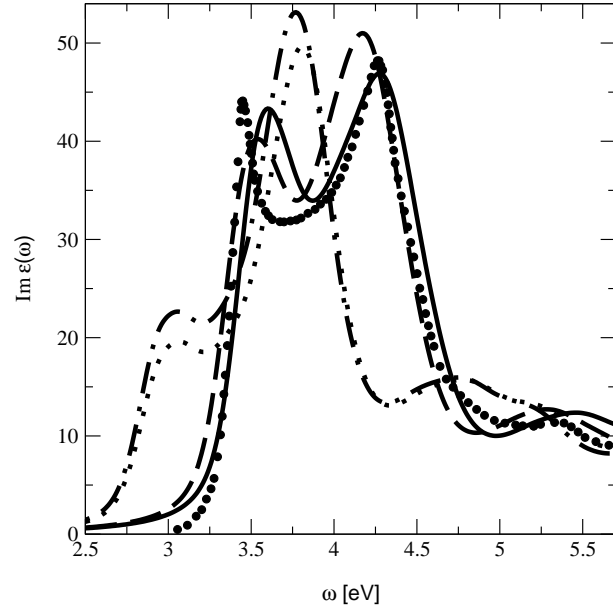


FIG. 1: Optical absorption spectrum of silicon^c. The curves are: thick dots – experiment^c; dotted curve – RPA; dot-dashed curve – TDDFT using the ALDA; solid curve – TDDFT using the RORO kernel^c; dashed curve – Bethe-Salpeter equation.

^aFigure reproduced from G. Onida, L. Reining, and A. Rubio, *Rev. Mod. Phys.* **74**, 601 (2002).

^bP. Lautenschlager, M. Garriga, L. Viña, and M. Cardona, *Phys. Rev. B* **36**, 4821 (1987).

^cL. Reining, V. Olevano, A. Rubio, and G. Onida, *Phys. Rev. Lett.* **88**, 066404 (2002).

TABLE I: Equilibrium lattice constants a (in Å) and bulk moduli B_0 (in GPa) for some solids calculated with LDA, GGA, and meta-GGA approximations in comparison to experimental results. m.a.e. is the mean absolute error. ^a

Solid	a^{LSD}	a^{GGA}	a^{MGGA}	a^{exp}	B_0^{LSD}	B_0^{GGA}	B_0^{MGGA}	B_0^{exp}
Na	4.05	4.20	4.31	4.23	9.2	7.6	7.0	6.9
NaCl	5.47	5.70	5.60	5.64	32.2	23.4	28.1	24.5
Al	3.98	4.05	4.02	4.05	84.0	77.3	90.5	77.3
Si	5.40	5.47	5.46	5.43	97.0	89.0	93.6	98.8
Ge	5.63	5.78	5.73	5.66	71.2	59.9	64.6	76.8
GaAs	5.61	5.76	5.72	5.65	74.3	60.7	65.1	74.8
Cu	3.52	3.63	3.60	3.60	191	139	154	138
W	3.14	3.18	3.17	3.16	335	298	311	310
m.a.e.	0.078	0.051	0.043	-	12.8	7.0	7.6	-

^aLattice constants from J. P. Perdew, S. Kurth, A. Zupan, and P. Blaha, Phys. Rev. Lett. **82** 2544 (1999), ibid. **82**, 5179 (1999)(E); bulk moduli from S. Kurth, J. P. Perdew, and P. Blaha, Int. J. Quantum Chem. **75**, 889 (1999).

TABLE II: Magnetic moments (in μ_B) for some ferromagnetic solids. ^a

Solid	M^{LSD}	M^{GGA}	M^{exp}
Fe	2.01	2.32	2.22
Co	1.49	1.66	1.72
Ni	0.60	0.64	0.61

^afrom J. H. Cho and M. Scheffler, Phys. Rev. **B** 53, 10685 (1996).

TABLE III: Fundamental band gaps (in eV) of some semiconductors and insulators.

Solid	LSD	EXX	exp
Ge ^a	-0.05	0.99	0.74
Si ^a	0.66	1.51	1.2
C ^a	4.17	4.92	5.50
GaAs ^b	0.49	1.49	1.52
AlN ^a	3.2	5.03	5.11
BeTe ^b	1.60	2.47	2.7
MgSe ^b	2.47	3.72	4.23

^afrom W. G. Aulbur, M. Städele, A. Görling, Phys. Rev. **B** 62, 7121 (2000).

^bfrom A. Fleszar, Phys. Rev. **B** 64, 245204 (2001).

TABLE IV: Atomization energies (in units of 1 kcal mol⁻¹ = 0.0434 eV) of 20 small molecules.

Zero-point vibration has been removed from experimental energies. ^a

Molecule	ΔE^{LSD}	ΔE^{GGA}	ΔE^{MGGA}	ΔE^{HYB}	ΔE^{exp}
H ₂	113.2	104.6	114.5	107.5	109.5
LiH	61.0	53.5	58.4	54.7	57.8
CH ₄	462.3	419.8	421.1	420.3	419.3
NH ₃	337.3	301.7	298.8	297.5	297.4
H ₂ O	266.5	234.2	230.1	229.9	232.2
CO	299.1	268.8	256.0	256.5	259.3
N ₂	267.4	243.2	229.2	226.5	228.5
NO	198.7	171.9	158.5	154.3	152.9
O ₂	175.0	143.7	131.4	125.6	120.5
F ₂	78.2	53.4	43.2	37.1	38.5
m.a.e.	34.3	9.7	3.6	2.1	-

^aLSD, GGA, and meta-GGA results from S. Kurth, J. P. Perdew, and P. Blaha, Int. J. Quantum Chem. **75**, 889 (1999); results for the hybrid functional from A. D. Becke, J. Chem. Phys. **98**, 5648 (1998).