

A 3 The Optimized Effective Potential Method

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Contents

| | | |
|----------|--|-----------|
| 1 | Introduction | 2 |
| 2 | The Optimized Effective Potential Method | 3 |
| 2.1 | Derivation of the OEP integral equation | 4 |
| 2.2 | Approximations to the OEP equation | 5 |
| 2.3 | OEP made simple | 6 |
| 3 | Orbital Functionals for the Exchange-Correlation Energy | 7 |
| 4 | Selection of numerical results | 10 |

1 Introduction

Density functional theory [1, 2] is an ingenious way of reformulating the many-body problem. Instead of trying to solve the Schrödinger equation of interacting electrons directly, the problem is cast in a way such as to make it tractable in an approximate, but in many cases surprisingly accurate way.

Here we briefly summarize the central equations of the Kohn-Sham method [2] in the generalization to spin-densities [3] as it is commonly used today. We seek the ground state energy and spin densities $n_\uparrow(\mathbf{r})$ and $n_\downarrow(\mathbf{r})$ of a system of N interacting electrons. In spin-DFT, the total energy of the interacting system is written as a functional of the spin densities (atomic units are used throughout)

$$E_v[n_\uparrow, n_\downarrow] = T_s[n_\uparrow, n_\downarrow] + \int d^3r v(\mathbf{r})n(\mathbf{r}) + U[n] + E_{xc}[n_\uparrow, n_\downarrow] \quad (1)$$

where

$$T_s[n_\uparrow, n_\downarrow] = \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N_\sigma} \int d^3r \varphi_{i\sigma}^*(\mathbf{r}) \left(-\frac{\nabla^2}{2} \right) \varphi_{i\sigma}(\mathbf{r}) \quad (2)$$

is the kinetic energy functional of *non-interacting* electrons with spin densities n_\uparrow, n_\downarrow and N_σ is the total number of electrons with spin σ where $\sigma = \uparrow, \downarrow$ is the z -component of spin.

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

is the classical electrostatic or Hartree energy of the total charge density $n(\mathbf{r}) = n_\uparrow(\mathbf{r}) + n_\downarrow(\mathbf{r})$ and $E_{xc}[n_\uparrow, n_\downarrow]$ is the so-called exchange-correlation energy functional.

The ground state spin densities of the interacting system may be calculated by self-consistent solution of the auxiliary single-particle equation

$$\left(-\frac{\nabla^2}{2} + v_{s\sigma}(\mathbf{r}) \right) \varphi_{i\sigma}(\mathbf{r}) = \varepsilon_{i\sigma} \varphi_{i\sigma}(\mathbf{r}) \quad (4)$$

where the effective potential is given by

$$v_{s\sigma}(\mathbf{r}) = v(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc\sigma}(\mathbf{r}) . \quad (5)$$

Here we have defined the Hartree potential as

$$v_H(\mathbf{r}) = \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (6)$$

and the exchange-correlation potential

$$v_{xc\sigma}(\mathbf{r}) = \frac{\delta E_{xc}[n_\uparrow, n_\downarrow]}{\delta n_\sigma(\mathbf{r})} . \quad (7)$$

The exchange-correlation functional is the central quantity of density functional theory: although its formal definition has already been given in the original work of Hohenberg and Kohn [1] and further been clarified in the constrained-search formulation of Levy [4, 5], these are formal definitions which cannot be used in practice and one needs to resort to approximations.

Fortunately, it is possible to construct simple approximations which perform, sometimes surprisingly, well. Probably the most widely known approximation is the so called Local Spin Density Approximation (LDA or LSD), which is based on the model of the uniform electron gas. Formally, it is defined as

$$E_{xc}^{LSD}[n_{\uparrow}, n_{\downarrow}] = \int d^3r n(\mathbf{r}) \epsilon_{xc}^{unif}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})) \quad (8)$$

where $\epsilon_{xc}^{unif}(n_{\uparrow}, n_{\downarrow})$ is the exchange-correlation energy per electron of the uniform electron gas with (constant) spin densities n_{\uparrow} and n_{\downarrow} . This function is known from Quantum Monte Carlo calculations [6] and several simple parametrizations have been suggested [7–9]. Despite its simplicity, LSD has proven to be surprisingly accurate and hard to improve upon.

A major breakthrough in the development of more accurate exchange-correlation functionals came with the advent of so-called “generalized gradient approximations” (GGA’s) which have the general form

$$E_{xc}^{GGA}[n_{\uparrow}, n_{\downarrow}] = \int d^3r f(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow}) . \quad (9)$$

While the input $\epsilon_{xc}^{unif}(n_{\uparrow}, n_{\downarrow})$ in LSD is unique, the function f in Eq. (9) is not and many forms have been suggested [10–18]. While the simple LSD approximation proved to be surprisingly accurate especially in solid state physics, only the advent of the so-called generalized gradient approximations (GGA’s) with their increased accuracy led to an explosion of applications of DFT in quantum chemistry.

2 The Optimized Effective Potential Method

Both for LSD and GGA the functional dependence of E_{xc} on the spin densities is known explicitly. More recently it has been realized that functionals which depend explicitly on the Kohn-Sham orbitals may also be viewed as density functionals since the orbitals are, through Eq. (4), functionals of the effective potential $v_s(\mathbf{r})$ which itself is a density functional. Of course, the explicit functional dependence of the orbitals on the density remains unknown and orbital functionals are often called *implicit* density functionals.

Although somewhat surprising at first sight, the idea of orbital functionals is already present in the original Kohn-Sham formalism because the exact form of the kinetic energy $T_s[n_{\uparrow}, n_{\downarrow}]$ of the non-interacting system (see Eq. (2)) is also given in terms of the Kohn-Sham orbitals.

Orbital-dependent expressions also provide a natural framework for approximations to E_{xc} . In fact, if one performs a power series expansion of the exact functional E_{xc} in terms of the interaction strength e^2 (where e is the elementary charge) one obtains as leading term in this series the exact exchange energy. The functional dependence of the latter on the orbitals is known and reads as

$$E_x^{EXX}[n_{\uparrow}, n_{\downarrow}] = E_x^{EXX}[\{\varphi_{i\sigma}\}] = -\frac{1}{2} \sum_{\sigma=\uparrow, \downarrow} \sum_{j,k=1}^{N_{\sigma}} \int d^3r \int d^3r' \frac{\varphi_{j\sigma}^*(\mathbf{r}) \varphi_{k\sigma}^*(\mathbf{r}') \varphi_{j\sigma}(\mathbf{r}') \varphi_{k\sigma}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \quad (10)$$

which is nothing but the Fock exchange energy but evaluated with Kohn-Sham orbitals.

Once we accept to use an expression for E_{xc} which depends on the Kohn-Sham orbitals, the main question is how to compute the corresponding exchange-correlation potentials of Eq. (7). This is achieved with the so-called Optimized Effective Potential (OEP) method which will be described in the following Sections.

2.1 Derivation of the OEP integral equation

The way to accomplish this task is to use the implicit dependence of the Kohn-Sham orbitals on the spin densities. As a first step we rewrite Eq. (7) by using the chain rule for functional derivatives as

$$v_{xc\sigma}(\mathbf{r}) = \sum_{j=1}^{N_\sigma} \int d^3r' \left(\frac{\delta E_{xc}}{\delta \varphi_{j\sigma}(\mathbf{r}')} \frac{\delta \varphi_{j\sigma}(\mathbf{r}')}{\delta n_\sigma(\mathbf{r})} + c.c. \right). \quad (11)$$

For simplicity, we assumed here that the exchange-correlation functional is given as an explicit functional of the occupied Kohn-Sham orbitals only. Then the functional derivative of E_{xc} with respect to the orbitals can easily be calculated. In order to compute the functional derivative of the orbitals with respect to the spin density, we now view the orbitals as functional of the effective potential $v_{s\sigma}(\mathbf{r})$ and use the chain rule of the functional differentiation once again, i.e.,

$$v_{xc\sigma}(\mathbf{r}) = \sum_{j=1}^{N_\sigma} \int d^3r' \int d^3r'' \left(\frac{\delta E_{xc}}{\delta \varphi_{j\sigma}(\mathbf{r}')} \frac{\delta \varphi_{j\sigma}(\mathbf{r}')}{\delta v_{s\sigma}(\mathbf{r}'')} + c.c. \right) \frac{\delta v_{s\sigma}(\mathbf{r}'')}{\delta n_\sigma(\mathbf{r})} \quad (12)$$

The last functional derivative on the right hand side of this equation may now be identified with the inverse of the static spin-density response function of the Kohn-Sham system which is defined as

$$\chi_{s\sigma}(\mathbf{r}, \mathbf{r}') = \frac{\delta n_\sigma(\mathbf{r})}{\delta v_{s\sigma}(\mathbf{r}')} . \quad (13)$$

Operating with $\chi_{s\sigma}$ on Eq. (12) from the right one obtains

$$\int d^3r' v_{xc\sigma}(\mathbf{r}') \chi_{s\sigma}(\mathbf{r}', \mathbf{r}) = \sum_{j=1}^{N_\sigma} \int d^3r' \left(\frac{\delta E_{xc}}{\delta \varphi_{j\sigma}(\mathbf{r}')} \frac{\delta \varphi_{j\sigma}(\mathbf{r}')}{\delta v_{s\sigma}(\mathbf{r})} + c.c. \right). \quad (14)$$

Now all the terms in this equation can be expressed through the Kohn-Sham orbitals and eigenvalues. The functional derivative of the orbitals with respect to the potential can be calculated exactly from first order perturbation theory and reads

$$\frac{\delta \varphi_{j\sigma}(\mathbf{r}')}{\delta v_{s\sigma}(\mathbf{r})} = G_{s,j\sigma}(\mathbf{r}', \mathbf{r}) \varphi_{j\sigma}(\mathbf{r}) \quad (15)$$

where we have defined

$$G_{s,j\sigma}(\mathbf{r}, \mathbf{r}') = \sum_{k \neq j} \frac{\varphi_{k\sigma}(\mathbf{r}) \varphi_{k\sigma}^*(\mathbf{r}')}{\varepsilon_{j\sigma} - \varepsilon_{k\sigma}} . \quad (16)$$

For simplicity, we have assumed here that the single particle levels are non-degenerate. The static linear density response function of the Kohn-Sham system may be written as

$$\chi_{s\sigma}(\mathbf{r}, \mathbf{r}') = \sum_{j=1}^{N_\sigma} (\varphi_{j\sigma}^*(\mathbf{r}) G_{s,j\sigma}(\mathbf{r}, \mathbf{r}') \varphi_{j\sigma}(\mathbf{r}') + c.c.) \quad (17)$$

Substituting (15) and (17) into (14) yields

$$\sum_{j=1}^{N_\sigma} \int d^3r' (\varphi_{j\sigma}^*(\mathbf{r}') (v_{xc\sigma}(\mathbf{r}') - u_{xc,j\sigma}(\mathbf{r}')) G_{s,j\sigma}(\mathbf{r}', \mathbf{r}) \varphi_{j\sigma}(\mathbf{r}) + c.c.) = 0 \quad (18)$$

where we have defined

$$u_{xc,j\sigma}(\mathbf{r}') = \frac{1}{\varphi_{j\sigma}^*(\mathbf{r}') \delta\varphi_{j\sigma}(\mathbf{r}')} \frac{\delta E_{xc}}{\delta\varphi_{j\sigma}(\mathbf{r}')} . \quad (19)$$

Introducing the so-called orbital shifts [19–21]

$$\psi_{j\sigma}^*(\mathbf{r}) = \int d^3r' \varphi_{j\sigma}^*(\mathbf{r}') (v_{xc\sigma}(\mathbf{r}') - u_{xc,j\sigma}(\mathbf{r}')) G_{s,j\sigma}(\mathbf{r}', \mathbf{r}) \quad (20)$$

allows to rewrite Eq. (18) in a very compact way

$$\sum_{j=1}^{N_\sigma} (\psi_{j\sigma}^*(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}) + c.c.) = 0 \quad (21)$$

which is the standard form of the integral equation of the OEP method.

The name of this equation suggests that the resulting potentials are optimal. In which sense are they optimal? In SDFT the value of the ground-state total energy corresponds to the minimum value of the total energy functional. This minimum is obtained only if the exact ground-state spin densities are inserted. Now the idea of the Kohn-Sham method is that these densities can be obtained from single-particle orbitals solving single-particle Schrödinger equations. Hence, in order to produce those single-particle orbitals we need to use a proper *local* spin dependent potential which is nothing but the optimized effective potential. Formally, this potential follows from minimizing the total energy functional [22–25].

2.2 Approximations to the OEP equation

The OEP equations (18) are integral equations to be solved for the exchange-correlation potentials $v_{xc\sigma}(\mathbf{r})$. Historically, this solution first has been achieved for systems with very high symmetry [23]. In order to reduce the computational effort, however, simplifying yet accurate approximations to the full OEP equations have been suggested and will be discussed in this Section.

We see that an important ingredient of the OEP equations is the Green function of Eq. (16) which involves a summation over occupied and unoccupied Kohn-Sham orbitals. Sharp and Horton [22] and later Krieger, Li, and Iafrate (KLI) [26,27] proposed to approximate the Green function by replacing the energy denominators by a constant value, independent of the particle indices j and k , i.e.,

$$\begin{aligned} G_{s,j\sigma}^{KLI}(\mathbf{r}, \mathbf{r}') &= \frac{1}{\Delta} \left(\sum_{k=1}^{\infty} \varphi_{k\sigma}^*(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}') - \varphi_{j\sigma}^*(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}') \right) \\ &= \frac{1}{\Delta} \left(\delta(\mathbf{r} - \mathbf{r}') - \varphi_{j\sigma}^*(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}') \right) \end{aligned} \quad (22)$$

Substitution of this expression into Eq. (20) and solving for $v_{xc\sigma}^{KLI}(\mathbf{r})$ yields

$$v_{xc\sigma}^{KLI}(\mathbf{r}) = \frac{1}{2n_\sigma(\mathbf{r})} \sum_{j=1}^{N_\sigma} n_{j\sigma}(\mathbf{r}) (u_{xc,j\sigma}(\mathbf{r}) + \bar{v}_{xc,j\sigma}^{KLI} - \bar{u}_{xc,j\sigma} + c.c.) \quad (23)$$

where we have defined

$$n_{j\sigma}(\mathbf{r}) = \varphi_{j\sigma}^*(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}) \quad (24)$$

and the constants

$$\bar{v}_{xc,j\sigma}^{KLI} = \int d^3r \varphi_{j\sigma}^*(\mathbf{r}) v_{xc\sigma}^{KLI}(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}) \quad (25)$$

The constants $\bar{u}_{xc,j\sigma}$ are defined in an analogous way as orbital averages of $u_{xc,j\sigma}(\mathbf{r})$ with respect to the orbital $\varphi_{j\sigma}$.

The KLI equation (23) now is an algebraic equation for the potential which only involves the occupied orbitals and therefore is easier to solve in practical applications than the full OEP equation (21). It turns out that results obtained within the KLI approximation are often, but not always, close to those of the full OEP equation.

As we have seen, in the KLI approximation the Kohn-Sham orbital energy differences $\varepsilon_{j\sigma} - \varepsilon_{k\sigma}$ are approximated by one and the same constant, irrespective of the sign of different terms. In a similar spirit, a different approximation known as Common Energy Denominator Approximation (CEDA) [28] or Localized Hartree-Fock (LHF) [29] approximation has been proposed which only replaces the energy differences for occupied-unoccupied orbital pairs by a constant while it retains the energy differences for the occupied-occupied pairs.

Both the KLI as well as the CEDA approximation can easily be implemented within a self-consistent scheme with essentially the same effort. From the theoretical point of view, CEDA has the advantage of being invariant under unitary transformations of the occupied orbitals while KLI is not. From a practical point of view, CEDA and KLI results are often very similar.

2.3 OEP made simple

The orbital shifts $\psi_{j\sigma}(\mathbf{r})$ also play a central role in a iterative scheme to the solution of the full OEP equation recently suggested by Kümmel and Perdew [20, 21]. We start by noting that the non-interacting Green function satisfies the following differential equation

$$\left(\hat{h}_{s\sigma}(\mathbf{r}) - \varepsilon_{j\sigma} \right) G_{s,j\sigma}(\mathbf{r}', \mathbf{r}) = - \left(\delta(\mathbf{r} - \mathbf{r}') - \varphi_{j\sigma}^*(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}') \right) \quad (26)$$

where $\hat{h}_{s\sigma}(\mathbf{r})$ is the Kohn-Sham Hamiltonian. Acting with the operator $(\hat{h}_{s\sigma}(\mathbf{r}) - \varepsilon_{j\sigma})$ on Eq. (20) yields a differential equation which uniquely determines [19] the orbital shifts

$$\left(\hat{h}_{s\sigma}(\mathbf{r}) - \varepsilon_{j\sigma} \right) \psi_{j\sigma}^*(\mathbf{r}) = - \left(v_{xc\sigma}(\mathbf{r}) - u_{xc,j\sigma}(\mathbf{r}) - (\bar{v}_{xc,j\sigma} - \bar{u}_{xc,j\sigma}) \right) \varphi_{j\sigma}^*(\mathbf{r}) . \quad (27)$$

The idea of the scheme is to solve Eq. (27) for the orbital shifts directly in the following way: for a given approximate solution $v_{xc\sigma}(\mathbf{r})$ to the OEP equation, compute the right hand side of Eq. (27) and then solve this equation for the orbital shift $\psi_{j\sigma}(\mathbf{r})$ subject to the orthogonality constraint

$$\int d^3r \psi_{j\sigma}^*(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}) = 0 \quad (28)$$

which follows from the definition (20) by the orthonormality of the Kohn-Sham orbitals. With the resulting orbital shifts compute the quantity

$$S_\sigma(\mathbf{r}) = \sum_{j=1}^{N_\sigma} \left(\psi_{j\sigma}^*(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}) + c.c. \right) \quad (29)$$

and then compute a new potential by

$$v_{xc\sigma}^{\text{new}}(\mathbf{r}) = v_{xc\sigma}^{\text{old}}(\mathbf{r}) + c S_\sigma(\mathbf{r}) \quad (30)$$

with some positive constant c . With this new $v_{xc\sigma}$, recompute the right hand side of Eq. (27) and then solve again for a new orbital shift. This is iterated a few times for fixed $\varphi_{j\sigma}$, \hat{h}_s and $\varepsilon_{j\sigma}$ before eventually these quantities are also recomputed during the regular Kohn-Sham self-consistency cycle. This scheme has been applied successfully [20, 21] to compute the OEP potential (in exact exchange approximation) not only for highly symmetric systems such as atoms but also to small sodium clusters where a direct solution of the OEP integral equation (21) is a much more difficult task.

3 Orbital Functionals for the Exchange-Correlation Energy

As we have seen, the OEP method allows treatment of orbital-dependent functionals in the DFT framework. In this Section we will discuss some of the orbital functionals which have been used in the literature.

The exact exchange (EXX) energy functional (10) has been studied extensively in the OEP context. Decomposing E_{xc} into exchange and correlation, $E_{xc} = E_x + E_c$, EXX allows one to treat another component of the total energy (1) exactly and only the correlation energy needs to be approximated.

If one neglects correlation altogether, the resulting energy functional has exactly the form of the Hartree-Fock total energy. In the Hartree-Fock scheme, this total energy functional is minimized with respect to the orbitals leading to the non-local Hartree-Fock potential. In contrast, although in the OEP method one minimizes the same functional, this minimization is done under the restriction that the resulting orbitals come from a *local* potential. As a consequence, evaluating the Hartree-Fock functional with the Hartree-Fock orbitals, one obtains a lower energy than for evaluation of the same functional with EXX orbitals. However, the energy difference is very small in general.

Both Hartree-Fock and EXX theories are free of self-interaction for the occupied orbitals. This means that the orbital $\varphi_{i\sigma}$ does not “feel” the electrostatic potential formally created by itself as part of the Hartree potential because this term is exactly cancelled by a corresponding term in the exchange potential. But it should be noted, that while the Hartree-Fock potential is *not* self-interaction free for unoccupied states, the EXX potential is. As a consequence, Hartree-Fock only leads to few unoccupied bound states. On the other hand, the EXX potential decays asymptotically as $-1/r$ for finite systems for *all* orbitals and therefore supports a whole Rydberg series of unoccupied bound states as well as negative ions.

The statement on the asymptotic behaviour needs some clarification. It is generally said that the EXX potential for finite systems behaves as [23, 26, 30]

$$\lim_{r \rightarrow \infty} v_{x\sigma}^{EXX}(\mathbf{r}) \rightarrow -\frac{1}{r} . \quad (31)$$

Although this statement is true for \mathbf{r} far away from the system in most directions, it has been found [21, 31] that if one approaches the asymptotic region on nodal surfaces of the highest occupied orbital, the Kohn-Sham exchange potential may actually approach a non-vanishing constant value.

Unlike the exact exchange functional, explicit density functionals like LDA or GGA typically are not free of self-interaction, i.e., the exchange-correlation energy does not cancel exactly the self-interaction contained in the Hartree energy (3). One of the consequences is the incorrect exponential asymptotic decay of the corresponding exchange-correlation potentials for finite

systems. Some time ago, Perdew and Zunger [8] suggested to make any approximate E_{xc}^{approx} self-interaction free by removing the self-interaction explicitly for each orbital, i.e.,

$$E_{xc}^{SIC}[n_{\uparrow}, n_{\downarrow}] = E_{xc}^{approx}[n_{\uparrow}, n_{\downarrow}] - \sum_{\sigma=\uparrow, \downarrow} \sum_{j=1}^{N_{\sigma}} \left(U[n_{j\sigma}] + E_{xc}^{approx}[n_{j\sigma}, 0] \right) \quad (32)$$

where the $n_{j\sigma}(\mathbf{r})$ are the orbital densities defined by Eq. (24). In the original work [8], the corresponding total energy functional was minimized with respect to the orbitals, leading to orbital-dependent effective single-particle potentials. However, the resulting functional certainly has an orbital-dependent expression and may therefore be treated with the OEP formalism [32].

An additional advantage of orbital dependent functionals over standard explicit density functionals like LDA or GGA is that they also may reproduce the derivative discontinuity Δ_{xc} of the exchange correlation functional as a function of particle number which occurs at integer particle number N [33–35]. For infinite systems this discontinuity enters into the expression for the so-called fundamental energy gap.

Two other classes of orbital functionals are also discussed in the literature. One of them are the so-called hybrid functionals which are constructed by approximating the exchange energy by a *fraction* of exact exchange plus some GGA part for the remainder, i.e.,

$$E_x^{hyb}[n_{\uparrow}, n_{\downarrow}] = aE_x^{EXX}[n_{\uparrow}, n_{\downarrow}] + (1 - a)E_x^{GGA}[n_{\uparrow}, n_{\downarrow}] \quad (33)$$

where a is a constant parameter. Hybrids have been introduced in quantum chemistry [36–39] and have been found to yield accurate results for many energetic properties. Hybrid functionals are implemented in a wide range of quantum chemistry program packages. Interpretation of the results of these packages, however, requires some care. The reason is that the self-consistency cycle in many cases does not use the OEP method or any approximation to it to evaluate the corresponding effective single-particle potentials. Instead, the results are obtained by minimizing the energy expression with respect to the single-particle orbitals. Due to the appearance of the Fock term E_x^{EXX} in the energy expression, this leads to *non-local* effective single-particle potentials and thus the results are outside the realm of density functional theory.

The second class of functionals we would like to mention here are the so-called meta-GGA's [40–42] which are of the general form

$$E_{xc}^{MGA}[n_{\uparrow}, n_{\downarrow}] = \int d^3r g(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow}, \tau_{\uparrow}, \tau_{\downarrow}) \quad (34)$$

where

$$\tau_{\sigma}(\mathbf{r}) = \frac{1}{2} \sum_{i=1}^{N_{\sigma}} |\nabla \varphi_{i\sigma}(\mathbf{r})|^2 \quad (35)$$

is the kinetic energy density of the Kohn-Sham orbitals. It is through their dependence on τ_{σ} , that meta-GGA's also become orbital functionals, and their exchange-correlation potentials should be calculated with the OEP method. As in the case of the hybrids, this is not always done. However, meta-GGA's have been implemented self-consistently in the LHF approximation to OEP to calculate magnetic response properties [43].

Orbital functionals constitute a natural framework for the systematic construction of approximations for the exchange-correlation functional in the spirit of perturbation theory. Görling and

Levy [44] have suggested a perturbative expansion of the exchange-correlation energy functional in powers of e^2

$$E_{xc} = \sum_{j=1}^{\infty} e^{2j} E_{xc}^{(j)} = e^2 E_x^{EXX} + e^4 E_c^{(2)} + \dots \quad (36)$$

where the exact exchange energy constitutes the first-order term. The series (36) has to be understood as a series expansion of the *functional* E_{xc} which can be evaluated with any set of single-particle orbitals. In particular, it usually is evaluated on the Kohn-Sham orbitals which themselves (through the Kohn-Sham potential v_s) also depend on e^2 . Since the exchange-correlation potential is computed from E_{xc} as the functional derivative (7), Eq. (36) implies that also v_{xc} can be written as a power series in e^2

$$v_{xc}(\mathbf{r}) = \sum_{j=1}^{\infty} e^{2j} v_{xc}^{(j)}(\mathbf{r}) = e^2 v_x^{EXX}(\mathbf{r}) + e^4 v_c^{(2)}(\mathbf{r}) + \dots \quad (37)$$

where the first order term is again the exact exchange contribution.

One of the interesting properties of orbital-dependent correlation energy functionals is their ability to properly describe long-range van-der-Waals interactions for well-separated subsystems. Engel *et al.* [45] have mapped out the binding energy curve of rare gas dimers as a function of atomic separation using the second order functional $E_c^{(2)}$. They found a qualitatively correct description, however, a full quantitative description apparently requires higher-order correlations to be taken into account.

Yet another representation of E_{xc} is related to the dynamic linear density response function of the interacting system of interest. The derivation of this representation requires ideas from time-dependent density functional theory (TDDFT) [46]. For the fundamental ideas underlying TDDFT, the interested reader is referred to the review of Ref. [47] and also to the article by A. Schindlmayr later in this volume. The representation of E_{xc} we are interested in can be derived by using the fluctuation-dissipation theorem at zero temperature and one obtains

$$E_{xc}[n] = \frac{1}{2} \int_0^1 d\lambda \int d^3r \int d^3r' \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \left(-\frac{1}{\pi} \int_0^\infty d\omega \operatorname{Im} \chi^\lambda(\mathbf{r}, \mathbf{r}', \omega) - n(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}') \right). \quad (38)$$

Here we have used the idea of the adiabatic connection method [48–52], i.e., we consider the interacting response function χ^λ for a scaled electron-electron interaction $\lambda e^2/|\mathbf{r} - \mathbf{r}'|$ while the external potential is modified such that the density is fixed for all values of λ .

The time-dependent Kohn-Sham scheme allows to calculate the interacting density response function as solution of the following integral equation which relates χ^λ to the response function χ_s of the non-interacting Kohn-Sham system [53, 54]:

$$\begin{aligned} \chi^\lambda(\mathbf{r}, \mathbf{r}', \omega) &= \chi_s(\mathbf{r}, \mathbf{r}', \omega) \\ &+ \int d^3x \int d^3y \chi_s(\mathbf{r}, \mathbf{x}, \omega) \left(\frac{\lambda e^2}{|\mathbf{x} - \mathbf{y}|} + f_{xc}^\lambda(\mathbf{x}, \mathbf{y}, \omega) \right) \chi^\lambda(\mathbf{y}, \mathbf{r}', \omega). \end{aligned} \quad (39)$$

Here, f_{xc}^λ is the so-called exchange-correlation kernel [53, 54] and has to be approximated in practice. The Kohn-Sham linear density response function χ_s may be expressed in terms of the

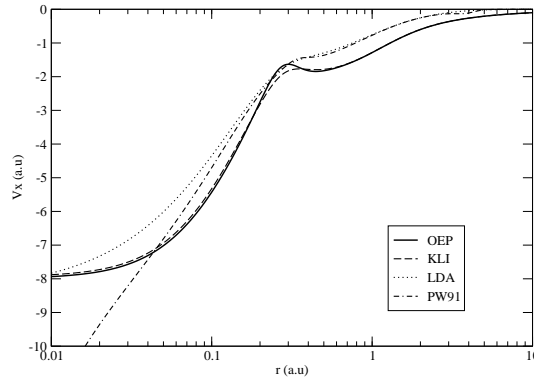


Fig. 1: Exchange potentials for Ne from various self-consistent exchange-only calculations. PW91 denotes the GGA of Ref. [17].

static Kohn-Sham orbitals and orbital energies through

$$\chi_s(\mathbf{r}, \mathbf{r}', \omega) = \sum_{\sigma} \sum_{i,j} (f_{i\sigma} - f_{j\sigma}) \frac{\varphi_{i\sigma}^*(\mathbf{r}) \varphi_{j\sigma}(\mathbf{r}) \varphi_{j\sigma}^*(\mathbf{r}') \varphi_{i\sigma}(\mathbf{r}')}{\omega - (\varepsilon_{j\sigma} - \varepsilon_{i\sigma}) + i\delta} \quad (40)$$

where $f_{i\sigma}$ is the occupation number (0 or 1) of the orbital $\varphi_{i\sigma}(\mathbf{r})$ in the Kohn-Sham ground-state Slater determinant. Insertion of Eqs. (40) and (39) into Eq. (38) represents the exact exchange-correlation energy as an explicitly orbital-dependent and therefore only implicitly density-dependent functional.

In a sense, the representation (38) of E_{xc} is much more powerful than the Görling-Levy expansion. While the latter provides an order-by-order expansion of E_{xc} , the former provides a prescription for resummation of an infinite power series if for the response function χ^λ one inserts a solution of the integral equation (39). The simplest of these resummed functionals is the so-called random phase approximation (RPA) which results if the exchange-correlation kernel is set to zero, $f_{xc}^{RPA} \equiv 0$. Recently, calculations have been performed in RPA and for other approximate kernels, both for simple model systems such as jellium slabs [55] but also for molecules [56, 57].

4 Selection of numerical results

In this Section we review some results obtained with the OEP method for various systems ranging from atoms and molecules to solids. We concentrate on results obtained with the exact exchange functional.

For atoms, the difference between HF, KLI and OEP total energies is in general very small. As expected, the HF total energies are the lowest, and the KLI values are above the OEP ones. However, at least from the point of view of the total energies, the KLI scheme provides a very good approximation to the full OEP results. This statement is often true also for other quantities such as single-particle eigenvalues and potentials [19, 26].

For the exchange potential this is demonstrated in Fig. 1 where we show self-consistent exchange potentials for the Ne atom in various approximations. The KLI potential follows the OEP potential rather closely in most regions of space. The difference is largest in the atomic

| Atom/Ion | EXX | BLYP | PW91 | exact |
|------------------|--------|--------|--------|--------|
| He | 0.9180 | 0.5849 | 0.5833 | 0.9037 |
| Be ²⁺ | 5.6671 | 4.8760 | 4.8701 | 5.6556 |
| Be | 0.3089 | 0.2009 | 0.2072 | 0.3426 |
| C ²⁺ | 1.6933 | 1.4804 | 1.4856 | 1.7594 |
| Ne | 0.8494 | 0.4914 | 0.4942 | 0.7945 |
| Na ⁺ | 1.7959 | 1.3377 | 1.3416 | 1.7410 |

Table 1: Ionization potentials (in a.u.) from highest occupied Kohn-Sham orbital energies for different functionals. EXX are results for the exact exchange functional in KLI approximation. BLYP are results for the GGA for exchange from Ref. [15] combined with the correlation functional of Ref. [16]. PW91 are results for the GGA of Ref. [17]. Values are taken from [19] and references therein.

inter-shell region where the OEP potentials shows a pronounced hump while in the KLI potential the hump is less prominent. Since both OEP and KLI potentials are free of self-interaction they tend to the correct $-1/r$ asymptotic limit. Since LDA and GGA are not self-interaction free, their potentials incorrectly decay exponentially fast far away from the nucleus.

The self-interaction problem has another consequence as well. Since both LDA and GGA potentials decay exponentially fast, a neutral atom does not exhibit a Rydberg series of excited states in these approximations. Also, negative ions are not stable. On the other hand, OEP and KLI both show a Rydberg series and are also able to support negative ions. Moreover, if one calculates the ionization potential as the negative eigenvalue of the highest occupied Kohn-Sham orbital [58] one finds a much better agreement with experiment in OEP than in GGA. This is illustrated for some atoms and ions in Table 1. It should be noted that the OEP numbers are exchange-only while the GGA numbers include exchange and correlation. While in OEP the self-interaction is absent for both occupied and unoccupied orbitals, in Hartree-Fock only the occupied orbitals are self-interaction free. Therefore the unoccupied orbitals in Hartree-Fock are usually too high in energy leading to HOMO-LUMO gaps which are too large.

In Section 2.2, in addition to the KLI approximation we also mentioned a slightly modified approximate scheme for the solution of the OEP equation, the CEDA approximation. Total energies, single-particle energies and potentials of atoms in CEDA approximation are very close to both KLI and full OEP results [59].

DFT with orbital functionals has been applied to molecular systems as well. The first results were obtained with the KLI approximation [60–62]. Later, both CEDA [59] and full OEP results were reported [21, 63, 64]. For total energies, binding energies and vibrational frequencies the exchange-only KLI, CEDA, and OEP results again are rather close to each other and also close to Hartree-Fock values.

For molecular binding energies, exchange-only KLI, CEDA, and OEP results are of rather poor quality. The errors, which are close to Hartree-Fock errors, are on average more than twice as large as in LDA and almost an order of magnitude worse than GGA results [64]. This is not unexpected since the exchange hole has a long-range component in the dissociation limit which has to be compensated by a corresponding long-range component of the correlation hole. Correlation functionals with this property are notoriously difficult to construct [65]. Combination

| α | H ₄ | H ₆ | H ₈ | H ₁₂ | H ₁₈ |
|----------|----------------|----------------|----------------|-----------------|-----------------|
| HF | 32.0 | 56.4 | 82.3 | 137.6 | 222.3 |
| OEP | 32.2 | 56.6 | 84.2 | 138.1 | |
| CEDA | | 59.3 | | 149.4 | 244.2 |
| KLI | 33.1 | 60.2 | 90.6 | 156.3 | 260.7 |

Table 2: Linear polarizabilities α (in a.u.) for different hydrogen chains in various exchange-only treatments. Values from Ref. [59] and Ref. [66]

of the exact exchange energy with LDA or GGA correlation leads to some improvement, giving errors for the atomization energies of the same order of magnitude as LDA results (but typically with the opposite sign). This shows that the success of explicit functionals relies on an error cancellation between the approximate exchange and correlation parts of the total energy.

Not for all properties are KLI, CEDA and OEP results so similar as for total energies and related quantities. Quite large differences emerge [59] for linear and non-linear response properties of molecular chains where the high mobility of the valence electrons along the backbone leads to a large directional electronic response. The response properties of these molecular chains can be characterized by the linear polarizabilities α and the hyperpolarizabilities γ , defined as the first and third derivatives, $\partial\mu_z/\partial E_z$ and $\partial^3\mu_z/\partial^3 E_z$, of the dipole moment μ_z with respect to the electric field E_z along the direction of the chain, respectively.

In LDA and GGA α and γ are usually overestimated by orders of magnitude in comparison to Hartree-Fock results which are in reasonable agreement with results obtained from correlated quantum chemical methods [59, 66]. As can be seen in Tables 2 and 3, for KLI and CEDA the deviations are not orders of magnitude but can still be quite large. The improvement compared to standard functionals is due to the orbital structure of the CEDA and KLI exchange potentials which produces an exchange field counteracting the external field. Moreover, there are pronounced differences between KLI and CEDA results. The latter gives considerable improvement as compared to KLI, but in order to reach Hartree-Fock quality a full solution of the OEP equations is required [66].

A number of successful applications of the exact exchange functional have been reported for solids. The first application is due to Kotani [67], who treated the exact exchange potential within the linear muffin-tin-orbital method in the atomic-sphere approximation. Later Görling

| $\gamma/10^3$ | H ₄ | H ₆ | H ₈ | H ₁₂ | H ₁₈ |
|---------------|----------------|----------------|----------------|-----------------|-----------------|
| HF | | 29.8 | | 147 | 301.3 |
| OEP | 9.3 | 30 | 68 | 144 | |
| CEDA | | 34.7 | | 209.2 | 468.4 |
| KLI | 10.7 | 36 | 90 | 300 | 778.1 |

Table 3: Hyperpolarizabilities γ (in a.u.) for different hydrogen chains in various exchange-only treatments. Values from Ref. [59] and Ref. [66]

| Solid | xcLDA | EXX+cLDA | Δ_x | Exp. |
|------------------|-------|----------|------------|------|
| Si | 0.52 | 1.43 | 5.84 | 1.17 |
| C | 4.16 | 5.06 | 8.70 | 5.47 |
| GaN (Γ) | 1.90 | 3.46 | 7.63 | 3.30 |
| InN (Γ) | -0.18 | 1.40 | 6.14 | 1.95 |

Table 4: *Calculated Kohn-Sham and measured (Exp.) energy gap in in semiconductors (in eV). EXX stands for OEP in pure exact exchange-only. cLDA stands for correlation in LDA approximation. Values in eV, all taken from [69] and reference there in.*

[68] proposed a procedure to solve the OEP equation for a solid exactly in a plane wave basis. This technique was then applied [69, 70] to several semiconductors.

Lattice constants predicted by exact exchange plus LDA correlation generally agree as well with experiment as the full LDA ones [70]. On the other hand, bulk moduli are overestimated and a treatment of correlations beyond LDA is needed [70].

Probably the most interesting result of these calculations are the ones for the band gaps of semiconductors. Standard functionals such as LDA or GGA typically give Kohn-Sham band gaps which are too small, often by a factor of two. This is a manifestation of two main shortcomings of these functionals: on one hand there is the self-interaction error and on the other hand they fail to reproduce a finite derivative discontinuity in the exchange-correlation potential.

The exact exchange functional eliminates the self-interaction problem and the corresponding Kohn-Sham gaps often provide excellent estimates for the experimental gaps, as can be seen in Table 4. On the other hand, EXX also leads to a derivative discontinuity Δ_x which is actually quite large. If this is included in the calculation of the gap, the agreement is ruined and the gaps are too large.

Not always are the EXX Kohn-Sham gaps in such a good agreement with experimental gaps as in semiconductors. In fact, results for noble-gas solids [71] show that the Kohn-Sham gaps differ from the fundamental band gaps by several eV and reproduce about of 80% of the experimental optical gaps.

As a final application of the OEP formalism to extended systems we mention a very recent calculation within the non-collinear spin-DFT framework [72] for a magnetically frustrated monolayer of chromium which shows how intra-atomic non-collinearity may be underestimated by local functionals.

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References

- [1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

- [2] W. Kohn and L.J. Sham, Phys. Rev. **140**, A1133 (1965).
- [3] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).
- [4] M. Levy, Proc. Natl. Acad. Sci. USA **76**, 6062 (1979).
- [5] M. Levy, Phys. Rev. A **26**, 1200 (1982).
- [6] D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
- [7] S.H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).
- [8] J.P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
- [9] J.P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).
- [10] S.-K. Ma and K.A. Brueckner, Phys. Rev. **165**, 18 (1968).
- [11] M. Rasolt and D.J.W. Geldart, Phys. Rev. B **34**, 1325 (1986).
- [12] J.P. Perdew, Phys. Rev. Lett. **55**, 1665 (1985).
- [13] J.P. Perdew and Y. Wang, Phys. Rev. B **33**, 8800 (1986), *ibid.* **40**, 3399 (1989) (E).
- [14] A.D. Becke, J. Chem. Phys. **84**, 4524 (1986).
- [15] A.D. Becke, Phys. Rev. A **38**, 3098 (1988).
- [16] C. Lee, W. Yang, and R.G. Parr, Phys. Rev. B **37**, 785 (1988).
- [17] J.P. Perdew, in *Electronic Structure of Solids '91*, edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991), p. 11.
- [18] J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996), *ibid.* **78**, 1396 (1997)(E).
- [19] T. Grabo, T. Kreibich, S. Kurth, and E.K.U. Gross, in *Strong Coulomb Correlations in Electronic Structure Calculations: Beyond Local Density Approximations*, edited by V. Anisimov (Gordon and Breach, Amsterdam, 2000), p. 203.
- [20] S. Kümmel and J.P. Perdew, Phys. Rev. Lett. **90**, 043004 (2003).
- [21] S. Kümmel and J.P. Perdew, Phys. Rev. B **68**, 035103 (2003).
- [22] R. Sharp and G. Horton, Phys. Rev. **90**, 317 (1953).
- [23] J.D. Talman and W.F. Shadwick, Phys. Rev. A **14**, 36 (1976).
- [24] V. Sahni, J. Gruenebaum, and J.P. Perdew, Phys. Rev. B **26**, 4371 (1982).
- [25] J.P. Perdew and M.R. Norman, Phys. Rev. B **26**, 5445 (1982).
- [26] J.B. Krieger, Y. Li, and G.J. Iafrate, Phys. Rev. A **45**, 101 (1992).
- [27] J. Krieger, Y. Li, and G. Iafrate, Phys. Rev. A **46**, 5453 (1992).

- [28] O.V. Gritsenko and E.J. Baerends, Phys. Rev. A **64**, 42506 (2001).
- [29] F. Della Sala and A. Görling, J. Chem. Phys. **115**, 5718 (2001).
- [30] T. Kreibich, S. Kurth, T. Grabo, and E.K.U. Gross, Adv. Quantum Chem. **33**, 31 (1999).
- [31] F. Della Sala and A. Görling, J. Chem. Phys. **116**, 5374 (2002).
- [32] J. Chen, J.B. Krieger, Y. Li, and G.J. Iafrate, Phys. Rev. A **54**, 3939 (1996).
- [33] J.P. Perdew, R.G. Parr, M. Levy, and J.L. Balduz, Phys. Rev. Lett. **49**, 1691 (1982).
- [34] L. Sham and M. Schlüter, Phys. Rev. Lett. **51**, 1888 (1983).
- [35] L. Sham and M. Schlüter, Phys. Rev. B **32**, 3883 (1985).
- [36] A.D. Becke, J. Chem. Phys. **98**, 1372 (1993).
- [37] A.D. Becke, J. Chem. Phys. **98**, 5648 (1993).
- [38] A.D. Becke, J. Chem. Phys. **104**, 1040 (1996).
- [39] C. Adamo and V. Barone, J. Chem. Phys. **110**, 6158 (1999).
- [40] J.P. Perdew, S. Kurth, A. Zupan, and P. Blaha, Phys. Rev. Lett. **82**, 2544 (1999), *ibid.* **82**, 5179 (1999)(E).
- [41] S. Kurth, J.P. Perdew, and P. Blaha, Int. J. Quantum Chem. **75**, 889 (1999).
- [42] J. Tao, J.P. Perdew, V.N. Staroverov, and G.E. Scuseria, Phys. Rev. Lett. **91**, 146401 (2003).
- [43] A.V. Arbuznikov and M. Kaupp, Chem. Phys. Lett. **381**, 495 (2003).
- [44] A. Görling and M. Levy, Phys. Rev. B **47**, 13105 (1993).
- [45] E. Engel, A. Höck, and R.M. Dreizler, Phys. Rev. A **61**, 032502 (2000).
- [46] E. Runge and E.K.U. Gross, Phys. Rev. Lett. **52**, 997 (1984).
- [47] E.K.U. Gross, J.F. Dobson, and M. Petersilka, in *Density Functional Theory II*, edited by R.F. Nalewajski (Springer, Berlin, 1996), vol. 181 of *Topics in Current Chemistry*, p. 81.
- [48] J. Harris and R.O. Jones, J. Phys. F **4**, 1170 (1974).
- [49] D.C. Langreth and J.P. Perdew, Solid State Commun. **17**, 1425 (1975).
- [50] D.C. Langreth and J.P. Perdew, Phys. Rev. B **15**, 2884 (1977).
- [51] O. Gunnarsson and B.I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).
- [52] A. Görling, M. Levy, and J.P. Perdew, Phys. Rev. B **47**, 1167 (1993).
- [53] E.K.U. Gross and W. Kohn, Adv. Quantum Chem. **21**, 255 (1990).

- [54] M. Petersilka, U. Gossmann, and E.K.U. Gross, Phys. Rev. Lett. **76**, 1212 (1996).
- [55] J.F. Dobson, J. Wang, and T. Gould, Phys. Rev. B **66**, 081108(R) (2002).
- [56] F. Furche, Phys. Rev. B **64**, 195120 (2001).
- [57] F. Furche and T. V. Voorhis, J. Chem. Phys. **122**, 164106 (2005).
- [58] C.O. Almbladh and U. von Barth, Phys. Rev. B **31**, 3231 (1985).
- [59] M. Grüning, O.V. Gritsenko, and E.J. Baerends, J. Chem. Phys. **116**, 6435 (2002).
- [60] T. Grabo and E.K.U. Gross, Int. J. Quantum Chem. **64**, 95 (1997).
- [61] Y.-H. Kim, M. Städele, and R.M. Martin, Phys. Rev. A **60**, 3633 (1999).
- [62] E. Engel, A. Höck, and R.M. Dreizler, Phys. Rev. A **62**, 042502 (2000).
- [63] S. Ivanov, S. Hirata, and R.J. Bartlett, Phys. Rev. Lett. **83**, 5455 (1999).
- [64] A. Görling, Phys. Rev. Lett. **83**, 5459 (1999).
- [65] M. Seidl, J.P. Perdew, and S. Kurth, Phys. Rev. Lett. **84**, 5070 (2000).
- [66] S. Kümmel, L. Kronik, and J.P. Perdew, Phys. Rev. Lett. **93**, 213002 (2004).
- [67] T. Kotani, Phys. Rev. B **50**, 14816 (1994).
- [68] A. Görling, Phys. Rev. B **53**, 7024 (1996).
- [69] M. Städele, J.A. Majewski, P. Vogl, and A. Görling, Phys. Rev. Lett. **79**, 2089 (1997).
- [70] M. Städele, M. Moukara, J.A. Majewski, P. Vogl, and A. Görling, Phys. Rev. B **59**, 10031 (1999).
- [71] R. Magyar, A. Fleszar, and E.K.U. Gross, Phys. Rev. B **69**, 045111 (2004).
- [72] S. Sharma, J.K. Dewhurst, C. Ambrosch-Draxl, N. Helbig, S. Kurth, E.K.U. Gross, S. Shallcross, and L. Nordström, cond-mat/0510800 (2005).