Simple iterative construction of the optimized effective potential for orbital functionals, including exact exchange

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For exchange-correlation functionals that depend explicitly on the Kohn-Sham orbitals, the potential $V_{\text{xc}}(r)$ must be obtained as the solution of the optimized effective potential (OEP) integral equation. This is very demanding and has limited the use of orbital functionals. We demonstrate that instead the OEP can be obtained iteratively by solving the partial differential equations for the orbital shifts that exactify the Krieger-Li-Iafrate (KLI) approximation. Unoccupied orbitals do not need to be calculated. Accuracy and efficiency of the method are shown for atoms and clusters using the exact exchange energy. Counter-intuitive asymptotic limits of the exact OEP are presented.

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Density functional theory (DFT) has become one of the most successful methods for electronic structure calculations. This success is largely due to the availability of a "Jacob's ladder" of approximations to the exchange-correlation (xc) energy functional. High hopes for further improvements in functional accuracy rested on third-generation functionals, i.e., functionals that include full or partial exact exchange. One more exact contribution to the total energy can be taken into account, and long-standing DFT problems like the self-interaction error and the inexact high-density limit can be solved. Two problems so far stand in the way of a widespread use of the exact exchange energy in DFT calculations. Finding a correlation functional that is compatible with exact exchange is the first; compatibility can be a severe problem for the atomization energies of molecules. Hyper generalized gradient approximations and hybrid functionals are promising approaches to solve this problem on either a non-empirical or empirical level. But in order to use orbital-dependent functionals in self-consistent Kohn-Sham calculations, a second problem – constructing the corresponding (spin-dependent) exchange-correlation potential $V_{\text{xc}}(r)$ – must be solved as well. In fact, solving the second problem might even help with the first, since known constraints on the potential might be used to constrain the form of $E_c$. But constructing $V_{\text{xc}}(r)$ for a functional that depends explicitly on the Kohn-Sham orbitals (and thus only implicitly on the density) is not straightforward: The potential cannot be calculated directly as the functional derivative of the exchange-correlation energy with respect to the density. $V_{\text{xc}}(r)$ is constructed by directly evaluating the response function. This makes molecular calculations possible, but requires not only occupied but also unoccupied orbitals and may lead to instabilities in the asymptotic regions of the OEP, as discussed in Refs. 14, 15; so alternatives continue to be developed [16]. On the other hand, the KLI [6] and localized Hartree-Fock [13, 18] approximations are easier to implement than the full OEP, yet accurate in many cases [6, 17, 18, 19].

We demonstrate how $V_{\text{xc}}(r) = \delta E_{\text{xc}}/\delta n_\sigma(r)$ can be calculated for any orbital-dependent $E_{\text{xc}}$ without explicitly solving an integral equation. The exact OEP is obtained iteratively by self-consistently solving a system of partial differential equations that is coupled to the Kohn-Sham equations. The iteration converges quickly. We use an essentially asymptotically-correct approximation as the starting point, and the correct asymptotic behavior is preserved during the iteration. The unoccupied Kohn-Sham orbitals need not be calculated. The orbital shifts we evaluate were defined in Refs. [6], [8], but have not been calculated before. However, orbital shifts have been used successfully in linear response theory [21, 22], and the advantages of avoiding explicit evaluation of the response function are discussed in Ref. [22].

We present self-consistent exact-exchange OEP calculations for atoms and three-dimensional sodium clusters to demonstrate the accuracy and efficiency of the method. Excellent reviews of the OEP method have been published [10, 12, 13], so we restrict ourselves to the central equations. Following [10, 12], the OEP integral equation is written in the form

$$\sum_{i=1}^{N_e} \psi_{i\sigma}^*(r) \varphi_{i\sigma}(r) + \text{c.c.} = 0. \quad (1)$$

Here, c.c. denotes the complex conjugate of the previous term, and $\varphi_{i\sigma}(r)$ denotes Kohn-Sham orbitals, i.e., the solutions of

$$\left(\hat{H}_{\text{KS}} - \varepsilon_{i\sigma} \right) \varphi_{i\sigma}(r) = 0, \quad (2)$$

constructed by directly evaluating the response function.
where \( \hat{h}_{\text{KS}, \sigma} = \left(-\frac{\hbar^2}{2m}\nabla^2 + V_\sigma(r) \right) \) is the Kohn-Sham Hamiltonian, \( V_\sigma(r) = V_{\text{ext}}(r) + V_{1f}(r) + V_{\text{xc}}(r) \) is the Kohn-Sham potential with \( V_{\text{ext}}(r) \) the external potential and \( V_{1f}(r) = \int d^3r' e^2 n(r')/|r-r'| \) the Hartree potential. The unnormalized orbital shifts are defined by

\[
\psi^*_\sigma(r) = \sum_{j=1}^{N_s} \int \frac{d^3r'}{\epsilon_{\sigma} - \epsilon_{j\sigma}} [V_{\text{xc}}(r') - u_{\text{scs}}(r')] \varphi_{j\sigma}(r') \varphi^*_{\sigma}(r),
\]

where

\[
u_{\text{scs}}(r) = \frac{1}{\psi^*_\sigma(r)} \frac{\delta E_{\text{xc}}}{\delta \varphi_{\sigma}(r)}.
\]

(Ref. [8] uses \( p_\sigma(r) = -\psi^*_\sigma(r)/\varphi^*_\sigma(r) \).) The \( -\psi^*_\sigma(r) \) are the first-order perturbation theory corrections to the \( \varphi_{\sigma}(r) \) for the perturbing potential \( u_{\text{scs}}(r) - V_{\text{xc}}(r) \). Thus, Eq. (1) asserts that the density shift vanishes to first order, and perturbation theory shows that \( \psi^*_\sigma(r) \) must fulfill the partial differential equation

\[
(\hat{h}_{\text{KS}, \sigma} - \epsilon_{\sigma})\varphi^*_{\sigma}(r) = -[V_{\text{xc}}(r) - u_{\text{scs}}(r) - (V_{\text{ext}} - \bar{u}_{\text{scs}})]\varphi_{\sigma}(r). \tag{5}
\]

In Eq. (6), the orbital averages are \( \bar{V}_{\text{xc}} = \int \varphi^*_{\sigma}(r)V_{\text{xc}}(r)\varphi_{\sigma}(r) d^3r \) and \( \bar{u}_{\text{scs}} = \int \varphi^*_{\sigma}(r)u_{\text{scs}}(r)\varphi_{\sigma}(r) d^3r \). Multiplying Eq. (1) by \( V_{\text{ext}}(r) \) and inserting Eq. (6), solved for \( \bar{V}_{\text{xc}}(r) \), into the resulting expression, an equation is obtained that can be solved for \( \bar{V}_{\text{xc}}(r) \), and a few further manipulations then lead to the form

\[
V_{\text{xc}}(r) = \frac{1}{2n_{\sigma}} \sum_{i=1}^{N_s} \left| \varphi_{\sigma}(r) \right|^2 \left[ u_{\text{scs}}(r) + (V_{\text{ext}} - \bar{u}_{\text{scs}}) \right] - \frac{\hbar^2}{m} \nabla \cdot \left[ \psi^*_{\sigma}(r) \nabla \varphi_{\sigma}(r) \right] + c.c. \tag{6}
\]

The KLI potential is obtained by setting \( \psi^*_\sigma(r) = 0 \forall i \) in the above equation, a choice that can be motivated in the sense of a mean-field approximation.

Combining Eqs. (2) and (6) to calculate \( V_{\text{xc}}(r) \) in a self-consistent iteration is the basic idea of our method. Calculating the \( \psi^*_\sigma(r) \) is thus the first crucial step. The first problem to be addressed is which boundary conditions are appropriate. Since the \( \psi^*_\sigma(r) \) are orbital shifts, the boundary condition to be employed in the solution of Eq. (6) must be the same as the one used in solving Eq. (2), i.e., for our finite systems, \( \psi^*_\sigma(r) \to 0 \) for \( r \to \infty \). But at first sight, calculating \( \psi^*_\sigma(r) \) still seems a hopeless task: Evaluating Eq. (3) is highly impractical and Eq. (5) is singular. It does not have a unique solution because to any one solution \( \psi_{\sigma}(r) \), the Kohn-Sham orbital \( \varphi_{\sigma}(r) \) multiplied by an arbitrary constant can be added to find another solution.

That Eq. (5) can nevertheless be solved efficiently is based on two facts. First, it is clear from Eq. (6) that the particular solution of Eq. (5) that is relevant for the OEP must be orthogonal to the KLI orbital \( \varphi_{\sigma}(r) \). Second, the right hand side of Eq. (5) is orthogonal to \( \varphi_{\sigma}(r) \). The orbital shift therefore can be calculated elegantly by the conjugate gradient method in short, if the operator on the left hand side of Eq. (5) is abbreviated by \( \hat{A}_i \) and the right hand side by \( b_i \), then the conjugate gradient method constructs the solution of \( \hat{A}_i \varphi^*_i = b_i \) by calculating a sequence of additive corrections to a starting guess \( \varphi^*_i \). The first correction in the sequence is, up to a constant factor, given by the expression \( b_i - \hat{A}_i \varphi^*_i \). Since \( b_i \) is orthogonal to \( \varphi_i \), and since \( \varphi_i \) spans the nullspace of \( \hat{A}_i \), the whole correction is orthogonal to \( \varphi_i \). Since the following steps in the sequence proceed analogously, the desired orthogonal solution is obtained if \( \varphi^*_i \) is chosen orthogonal. In practice, numerical inaccuracies might lead to small contributions of \( \varphi_i \) to the calculated \( \psi_i \), but they can easily be removed by orthogonalizing the final \( \psi_i \) (or, in the case of degeneracies, to all Kohn-Sham orbitals having the eigenvalue \( \epsilon_i \)). Real space and basis-set implementations should be equally unproblematic since \( V_{\text{ext}}(r) \to \infty \) is essentially correct in the starting approximation.

One way of constructing the OEP would be to insert the orbital shifts into Eq. (5). But this is numerically cumbersome for finite systems: Evaluating the last term on the right hand side of Eq. (5) requires dividing derivatives of exponentially decaying functions by the exponentially decaying density. For large distances where all orbitals have decayed to the extent that their numerical representation comes close to zero, inaccuracies can be introduced into the iteration. We found that, with appropriate cut-offs, the iteration converged quickly for the Be atom. However, for non-spherical systems this procedure becomes cumbersome.

An alternative way of using the orbital shifts to construct the OEP is based on the fact that once the \( \varphi^*_{\sigma}(r) \) have been calculated for a given \( V_{\text{xc}}(r) \), one obtains from them an estimate for how close the given \( V_{\text{xc}}(r) \) is to the true OEP in the region of nonvanishing density by defining the function

\[
S_{\sigma}(r) = \sum_{i=1}^{N_s} \psi^*_{\sigma}(r)\varphi_{\sigma}(r) + c.c. \tag{7}
\]

For the exact OEP, Eq. (7) reduces to Eq. (1), i.e., \( S_{\sigma}(r) = 0 \forall \sigma \). But if \( \varphi_{\sigma}(r) \) and \( \psi^*_{\sigma}(r) \) have been calculated via Eqs. (2) and (5) for an approximate \( V_{\text{xc}}(r) \), then \( S_{\sigma}(r) \) does not vanish. As an example, the left half of Fig. 1 shows the OEP and KLI potentials for the Ne atom, and the full line in the right half of Fig. 1 shows the \( S(r) \) obtained for the KLI potential. (When there is no spin polarization, we drop the index \( \sigma \).) Although \( S(r) \) is not an exact representation of the difference be-
between the two potentials, as can be seen by comparing $S(r)$ to Fig. 2 of Ref. [6], it nevertheless indicates where and qualitatively how the approximation deviates from the OEP: $S(r)$ vanishes in the asymptotic region where KLI is correct, but features the greater intershell bump and lower core value of the OEP.

This observation motivates the following simple iterative construction of the OEP: Using an approximation to the exact OEP, calculate $\varphi_{i\sigma}(r)$ and $\psi^*_{i\sigma}(r)$ via Eqs. (2) and (5) and $S_\sigma(r)$ via Eq. (7). An improved approximation to the OEP is then constructed as

$$V_{xc}^{\text{new}}(r) = V_{xc}^{\text{old}}(r) + cS_\sigma(r),$$

where $c$ is a positive constant having the dimension of energy over density. The idea of this iteration is to remove the error – for which $S_\sigma(r)$ is a measure – from the current approximation to obtain a better one. The numerical value of $c$ is a system-dependent parameter of the iteration. Larger values lead to faster convergence, but too large a value will ultimately lead to divergence. $c$ is thus similar to the parameter introduced in the over-relaxation method [2] or the mixing parameter in self-consistent calculations. In the calculations discussed below we used values of about 1 for the atoms and of about 30 for the clusters on a trial-and-error basis. A rationale for these values will be presented in future work. In a simple but important second step, it must be ensured that the improved approximation satisfies the relation $V_{xc,N_\sigma} = \hat{u}_{xc,N_\sigma}$ which is obeyed by the exact OEP [6, 8]. This can easily be achieved by adding the constant $\hat{u}_{xc,N_\sigma} - \int \varphi_{i\sigma}^*(r)V_{xc}^{\text{new}}(r)\varphi_{i\sigma}(r)\,d^3r$ to the $V_{xc}^{\text{new}}(r)$ computed from Eq. (8). With this new approximation for $V_{xc}^{\text{new}}(r)$, Eqs. (2) and (5) can be solved anew to start another cycle until convergence is achieved.

In our calculations the most efficient way of doing one iteration of Eq. (2) is to do several cycles of iterating $\{\psi^*_{i\sigma}(r)\}$ and $V_{xc\sigma}(r)$ while keeping $\{\varphi_{i\sigma}(r)\}$, $\{u_{xc\sigma}(r)\}$, $\hbar\varepsilon_\sigma$ and $\varepsilon_i$ in Eq. (5) fixed. Only then are the Kohn-Sham equations solved anew. The reason for this is that in our real-space finite difference calculations, solving Eq. (5) requires only roughly as much computational effort as calculating the Hartree potential, whereas solving the Kohn-Sham eigenvalue equations is more demanding.

We first employed this scheme to calculate OEP total energies and eigenvalues of spherical atoms in the exchange-only approximation. The corresponding equations were solved on a logarithmic grid. The right half of Fig. 1 shows that each iteration reduces $S$, as it should. The first line of Table I shows the KLI energies, the starting point of our iteration. The second line gives the same values for the OEP, and the first column indicates how many iterations were necessary to converge to 0.0001 hartree accuracy. Our simple iteration converges within a few steps to very high accuracy. We have carefully checked that these numbers correspond to the ones obtained by the much more involved direct solution of the OEP integral equation, by re-running the program used in Refs. [6, 8] on fine grids.

| iter | $E$     | $\varepsilon_1$ | $\varepsilon_2$ | $\varepsilon_3$ | $\varepsilon_4$ | $\varepsilon_5$ |
|------|---------|------------------|------------------|------------------|------------------|------------------|
| 0    | -128.5448 | -30.8021         | -1.7073          | -0.8494          |                  |                  |
| 3    | -128.5454 | -30.8200         | -1.7181          | -0.8507          |                  |                  |
| 0    | -526.8105 | -114.4279        | -11.1820         | -8.7338          | -1.0942          | -0.5893          |
| 6    | -526.8122 | -114.4522        | -11.1532         | -8.7338          | -1.0993          | -0.5908          |

FIG. 1: Left: $V_x(r)$ for the Ne atom versus radial coordinate $r$ in bohr ($a_0$). Dashed: KLI. Full: OEP. Right: $S(r)$ at different stages of the iteration. Full: $S(r)$ for KLI potential. Long dashed, short dashed and dotted: $S(r)$ after first, second and third iteration. Note that the magnitude of $S(r)$ is reduced by each iteration and goes to zero.
Our scheme can easily be used to calculate the OEP for three-dimensional systems without particular symmetry. To demonstrate this, we have calculated the OEP for the sodium clusters Na$_4$ and Na$_8$, using the pseudopotential and geometries from Ref. [24]. A three-dimensional Cartesian grid with 129 points in each direction and of spacing 0.5\(a_0\) was employed to obtain an accuracy of 0.0001 hartree. Eq. [2] was solved by damped gradient iteration with multigrid relaxation, and Eq. [5] by our own conjugate gradient routine. In Table II we list total energies and eigenvalues obtained with the exact exchange functional, iterating from KLI to OEP. The first thing to note is that, even for the clusters, KLI is a rather good approximation to the OEP. But it should also be noted that the relative error in the KLI energies is nearly two orders of magnitude higher for the clusters than for the atoms. Nevertheless, just five steps of our iteration refine KLI to OEP energies. The relative error in the Levy-Perdew virial relation [25] falls to \(\sim 10^{-5}\) during the first five iterations, and to \(\sim 10^{-7}\) upon further iteration, demonstrating the accuracy and stability of our method.

Finally, we investigated the asymptotic behavior of the Kohn-Sham potential. Contrary to common belief, the exchange potential does not fall off asymptotically like \(-e^2/r\) everywhere for finite systems, but approaches \(-e^2/(r+C)\), where \(C\) is a nonvanishing constant, on nodal surfaces of the energetically-highest occupied orbital. For Na$_4$ we find \(C = 0.0307\) for OEP and \(C = 0.0298\) hartree for KLI. This unexpected behavior of \(V_x(r)\) can be understood on the basis of Eq. [6]. It is not reproduced by any of the common methods such as the local density approximation, and also not by the OEP construction presented in Ref. [17]. Our work thus demonstrates the existence of non-vanishing asymptotic constants in the exact OEP, and confirms the arguments recently put forward in Ref. [20].

In conclusion, our simple iterative construction of the OEP does not require solving an integral equation or calculating unoccupied Kohn-Sham orbitals. We discussed the surprising asymptotic behavior of \(V_x(r)\). All-electron calculations for atoms and three-dimensional pseudopotential calculations for clusters demonstrate the accuracy and broad range of applicability of our approach. It thus opens a path for employing orbital functionals, in particular the exact exchange energy, in self-consistent Kohn-Sham calculations.

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TABLE II: KLI and OEP total energies and eigenvalues from three-dimensional cluster calculations, listed as in Table I.

| iter | E   | \(\varepsilon_1\) | \(\varepsilon_2\) | \(\varepsilon_3\) | \(\varepsilon_4\) |
|------|-----|-------------------|-------------------|-------------------|-------------------|
| 0    | -0.7528 | -0.1776          | -0.1394          |                   |                   |
| 5    | -0.7531 | -0.1762          | -0.1401          |                   |                   |
| 0    | -1.5282 | -0.1963          | -0.1591          | -0.1458          | -0.1458          |
| 5    | -1.5285 | -0.1954          | -0.1592          | -0.1459          | -0.1459          |

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