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Alternative approach to the optimized effective potential method

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We propose an alternative method of calculating so-called optimized effective potentials (OEP's) by directly exploiting the property of the total energy E of an interacting N-electron system to attain a minimum for the true potential of the associated Kohn-Sham equations if E is expressed as a functional of the occupied Kohn-Sham orbitals that solve these equations. The method is based on forming the difference between the sought-for true potential and some local spin-density reference potential corrected to yield the known large r behavior of the OEP. This difference is expanded in terms of attenuated sinusoidal functions that decay exponentially beyond the range of orbital localization. By using this expansion E becomes a function of the expansion coefficients whose values are determined by searching for the minimum of E. This is achieved by employing a variant of a steepest descent method. Due to the flexibility of the method, the exchange-only virial relation can easily be incorporated by performing the minimization in a suitably modified way. The total energy results for a set of atoms (Be-Xe) differ only by about 10^{-3} Ry from those obtained by other authors using different techniques. We have also successfully extended our method to the relativistic case. For the treatment of extended systems we propose a combination of our scheme with an existing approximate OEP method. [S1050-2947(98)02905-9]

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I. INTRODUCTION

Any practical calculation within the framework of density-functional theory (DFT) [1,2] is based on some approximate form of the energy functional and the associated exchange-correlation potential. The optimized effective potential (OEP) method that has originally been put forward by Sharp and Horton [3] and Talman and Shadwick [4] appears to offer the possibility of considerably improving on the standard of approximation set by the expressions for exchange and correlation that are used in present-day DFT calculations. Talman [5] and Shadwick, Talman, and Norman [6] employed an integral-equation approach in calculating the optimized potential within the exchange-only approximation. In further pursuing this line of thought Wang *et al.* [7] applied a refined numerical mesh and ways of improving the systematic accuracy. Also Engel and Vosko [8] worked with a refined numerical mesh and a more accurate asymptotic form of the potential to examine the properties of some currently applied approximate exchange functionals. A relatively successful way of employing the OEP model in an approximate fashion is described by the so-called Krieger-Li-Iafrate (KLI) [9] formalism that avoids the solution of an integral equation. Most recent work by Grabo and Gross [10] rests on the KLI approach but goes beyond the exchange-only approximation by including the correlation energy in the approximate form suggested by Colle and Salvetti [11]. The results prove to be comparable in accuracy with the respective configuration interaction (CI) calculations. The authors have extended this method to diatomic molecules [12]. It appears that a version of the OEP method that includes correlation within a Colle-Salvetti-type approximation constitutes the most promising method of practically improving the capabilities of DFT and at the same time removing the vexing problem of spurious self-interaction that is typical of most non-OEP-based expressions for the exchange-correlation energy. An application of the original KLI method to extended crystalline systems is due to Li *et al.* [13]. The idea has more recently been taken up again by Bylander and Kleinman [14]. The computer coding of the Hartree-Fock exchange expression is relatively clumsy and more time consuming compared to that of a local density approximation. Hence, to alleviate the accessibility of this expression some approximate exchange forms have been suggested very recently [15–17]. An alternative derivation of the KLI formalism has been given by Nagy [18]. Görling and Levy [19] use a perturbation theoretical approach and have also outlined the possibilities of treating extended periodic systems [20].

The present paper deals with an alternative method that aims at the most straightforward calculation of OEP's. The method has already been proposed and applied in a simplified version by Rose and Shore [21] more than 20 years ago. It exploits the fact that the Kohn-Sham (KS) expression for the total energy of an N-electron system attains a minimum if the KS orbitals are solutions to the KS equations for the exact potential. We express this potential by a portion that is based on some local density approximation (LDA) and use a Fourier expansion for the remainder so that the total energy becomes a function of the Fourier coefficients. They can be determined by any sufficiently advanced minimization or optimization code that determines the minimum of the total energy. The present calculations were carried out with the aid of some subroutines of the widely used configuration interaction code CIV3 [22], which is exceedingly efficient and determines the absolute minimum automatically. These subroutines are modifications of some earlier minimization

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codes [23,24]. Our results for a chosen set of atoms (Be-Xe) differ only by about 10^{-3} Ry from those obtained by using the conventional integral-equation technique [7,8], and they are definitely more accurate than the KLI results as far as total energies and the accuracy in satisfying the virial theorem are concerned. The new method of determining optimized potentials proves to be relatively flexible. The energy functional may virtually have any form provided it can be expressed in terms of occupied KS orbitals. We have successfully extended our method to the relativistic case. Moreover, correlation energy functionals that have currently been used in density-functional calculations can also readily be included. As regards numerical accuracy, various criteria have been suggested [7–9,25] that concern errors in satisfying certain equations: the virial relation, the so-called exchange-only virial relation introduced by Ghosh and Parr [26] and by Levy and Perdew [27], and a relation for the eigenvalue of the highest occupied orbital as discussed by Krieger *et al.* [25]. All these relations can readily be incorporated by suitably modifying the expression to be minimized. As a demonstration, we shall be presenting results on satisfying the exchange-only virial relation as a subsidiary condition.

In Sec. II we briefly summarize the key equations and quantities that define the nonrelativistic Kohn-Sham version of density-functional theory. We furthermore outline the relativistic modification of our approach. In Sec. III we present results obtained for a selected set of atoms (Be-Xe) and discuss particular aspects.

II. THEORETICAL METHOD

A. Basic idea of the new approach

If $s=\pm 1$ denotes the spin orientation with respect to some global axis, the Kohn-Sham expression for the ground-state energy E_0 of the N-electron system under study can be written

$$E_0=\sum_s \sum_{i=1}^{N_s} \int \psi_{is}^*(\vec{r})\left(-\frac{1}{2}\vec{\nabla}^2\right)\psi_{is}(\vec{r}) + \sum_s \int \rho_s(\vec{r})V_{\rm ext}(\vec{r})d^3r+V_c+\overline{E}_{\rm xc}, \qquad (1)$$

where $V_{\rm ext}(\vec{r})$ is the external potential and V_c is defined

$$V_c=\frac{1}{2}\int \rho(\vec{r})V_H(\vec{r})d^3r,$$

with $V_H(\vec{r})$ denoting the Hartree potential. The spin-resolved density is given by

$$\rho_s(\vec{r})=\sum_{i=1}^{N_s} |\psi_{is}(\vec{r})|^2, \qquad (2)$$

where the sum runs (as for the kinetic energy) over the N_s lowest lying one-particle states that solve the Kohn-Sham equations

$$\left[-\frac{1}{2}\vec{\nabla}^2+V_{\rm eff}(\vec{r},s)\right]\psi_{is}(\vec{r})=\epsilon_{is}\psi_{is}(\vec{r}). \qquad (3)$$

The effective potential is usually given the form

$$V_{\rm eff}(\vec{r},s)=V_{\rm ext}(\vec{r})+V_H(\vec{r})+V_{\rm xc}(\vec{r},s),$$

where $V_{\rm xc}(\vec{r},s)$ denotes the exchange-correlation potential. We furthermore have

$$\rho(\vec{r})=\sum_s \rho_s(\vec{r}) \qquad (4)$$

and

$$N=\sum_s N_s\,.$$

The exchange-correlation energy $\overline{E}_{\rm xc}$ may be cast into the form

$$\overline{E}_{\rm xc}=E_x+\overline{E}_c\,, \qquad (5)$$

with E_x being the exchange energy

$$E_x=\frac{1}{2}\sum_s\int\int\frac{\hat{\rho}_{2xo}^{(s,s)}(\vec{r}\,',\vec{r})}{|\vec{r}\,'-\vec{r}|}d^3r'd^3r,$$

where the exchange pair density in the numerator derives from a Slater determinant that is formed from the N lowest lying orbitals solving Eq. (3). The quantity $\overline{E}_c$ in Eq. (5) denotes the λ average of the correlation energy

$$E_c(\lambda)=\frac{1}{2}\sum_{s',s}\int\int\frac{\hat{\rho}_2^{(s',s)}(\lambda,\vec{r}\,',\vec{r})}{|\vec{r}\,'-\vec{r}|}d^3r'd^3r.$$

The real-valued factor λ (ranging from zero to one) describes the strength of the electron-electron interaction, and $\hat{\rho}_2^{(s',s)}(\lambda,\vec{r}\,',\vec{r})$ is defined by

$$\hat{\rho}_2^{(s',s)}(\lambda,\vec{r}\,',\vec{r})=\rho_2^{(s',s)}(\lambda,\vec{r}\,',\vec{r})-\hat{\rho}_{2xo}^{(s,s)}(\vec{r}\,',\vec{r})-\rho_{s'}(\vec{r}\,')\rho_s(\vec{r}),$$

where the first term on the right-hand side is the pair density for coupling strength λ in a modified potential

$$V_{\rm eff}(\lambda,\vec{r},s)=V_{\rm ext}(\vec{r})+\hat{V}_{\rm ext}(\lambda,\vec{r},s)$$

that ensures the conservation of the one-particle density $\rho_s(\vec{r})$ at full coupling strength. [In the following we shall denote the additional potential for $\lambda=0$ by $\hat{V}_{\rm ext}(\vec{r},s)$, which is identical with $V_H(\vec{r})+V_{\rm xc}(\vec{r},s)$.] Colle and Salvetti [11] have derived an approximate expression for $\overline{E}_c$ that has the principal form

$$\overline{E}_c=\overline{E}_c[\rho_s,(\vec{\nabla}\rho_s)^2,\vec{\nabla}^2\rho_s]$$

and has proven to be very successful [10]. Our calculations are also based on an expression of this type but we use a simplified form suggested by Lee, Yang, and Parr [28] where we go beyond the exchange-only approximation.

As follows from Eq. (1), E_0 constitutes a known functional of the set $\{\psi_{is}(\vec r)\}$ of occupied orbitals, i.e.,

$$E_0=E_0[\{\psi_{is}(\vec r)\}]$$

provided that the exact expression for $\overline{E_c}=\overline{E_c}[\rho_\uparrow(\vec r),\rho_\downarrow(\vec r)]$ is known. This will be assumed in the following.

If the orbitals are generated in a slightly incorrect potential $V_{\rm ext}(\vec r)+\hat V'_{\rm ext}(\vec r,s)$ by using an approximate form for $\hat V_{\rm ext}(\vec r,s)$, this amounts to replacing $V_{\rm ext}(\vec r)$ in Eq. (1) by a perturbed potential

$$V'_{\rm ext}(\vec r,s)=V_{\rm ext}(\vec r)-\Delta\hat V_{\rm ext}(\vec r,s),$$

with $\Delta\hat V_{\rm ext}(\vec r,s)$ being the difference between the true additional potential $\hat V_{\rm ext}(\vec r,s)$ and its approximation $\hat V'_{\rm ext}(\vec r,s)$. We denote the N-electron wave function pertaining to $V'_{\rm ext}(\vec r,s)$ by Ψ'_0 and the associated energy by E'_0. The latter may be decomposed

$$E'_0=E''_0-\sum_s\int\rho'_s(\vec r)\Delta\hat V_{\rm ext}(\vec r,s)d^3r,$$

where E''_0 is just the expression (1) formed with the perturbed occupied orbitals $\psi'_{is}(\vec r)$ whose square moduli sum up to give $\rho'_s(\vec r)$. Hence

$$\langle\Psi'_0|\hat H|\Psi'_0\rangle=E''_0,$$

where $\hat H$ denotes the N-electron Hamiltonian associated with $V_{\rm ext}(\vec r)$. Because of

$$\langle\Psi'_0|\hat H|\Psi'_0\rangle\geqslant\langle\Psi_0|\hat H|\Psi_0\rangle$$

we have

$$E''_0\geqslant E_0, \tag{6}$$

with the equality sign referring to the case where the KS equations contain $\hat V_{\rm ext}(\vec r,s)=\hat V'_{\rm ext}(\vec r,s)+\Delta\hat V_{\rm ext}(\vec r,s)$ instead of the approximate potential $\hat V'_{\rm ext}(\vec r,s)$. Equation (6) states that E''_0 attains a minimum and becomes equal to the exact total energy if the orbitals are generated in the exact KS potential.

In practically determining $\Delta\hat V_{\rm ext}(\vec r,s)$ we use a modified form of a local spin-density (LSD) potential as an approximation to $\hat V_{\rm ext}(\vec r,s)$. The modification consists in replacing the exponential tail typical of all LSD potentials beyond the classical turning point of the uppermost occupied orbital, by $-1/r-O(1/r)$ where $O(1/r)$ denotes terms of higher order in $1/r$. The first term, $-1/r$, guarantees the correct asymptotic behavior of the exact KS potential. The expression $O(1/r)$ is taken from Hartree-Fock theory [9], which provides an analytical form for it. It may be expected that the r dependence of the exact OEP within that range will closely agree with this asymptotic form. Confining ourselves to spherical atoms we may expand the difference

$$\Delta\hat V_{\rm ext}(\vec r,s)=\hat V_{\rm ext}(r,s)-\hat V'_{\rm ext}(r,s)=\sum_{\nu}^{\nu_{\max}}B_{\nu s}\varphi_\nu(r) \tag{7}$$

in terms of an appropriate set of basis functions $\varphi_\nu(r)$. It turns out that the set of functions

$$\varphi_\nu(r)=\sin(k_\nu r)e^{-r/r_0(k_\nu)} \tag{8}$$

combines practical simplicity with relatively fast convergence. (For a Xe atom one needs only 80 functions to obtain practical convergence, for light atoms one needs considerably fewer, i.e., 20). The quantities k_ν are defined

$$k_\nu=\nu\frac{2\pi}{L},\quad \nu=1,2,\ \ldots$$

where L has been chosen to be approximately the length of the interval that extends from the site of the nucleus to the classical turning point of the uppermost occupied orbital. All the numerical integrations were performed by using the commonly chosen set of grid points whose density drops appropriately as one moves away from the nucleus. The decay length $r_0(k_\nu)$ is chosen to be identical with that distance from the nucleus beyond which the wavelength $2\pi/k_\nu$ of the pertinent basis function is smaller than the distance of consecutive grid points. Thereby unphysical oscillations of our Fourier-type expansion are suppressed in a region where the chosen approximate form of $V_{\rm eff}(\vec r,s)$ is already close to the exact OEP so that the basis functions may there be allowed to have exponentially decaying amplitude.

In practice, one starts out by giving the coefficients $B_{\nu s}$ some values of plausible magnitude. The potential $V_{\rm ext}(\vec r)+\hat V'_{\rm ext}(\vec r,s)+\Delta\hat V_{\rm ext}(\vec r,s)$ in the one-particle equations (3) is fixed then and one can solve these equations to obtain the N lowest lying orbitals $\psi_{is}(\vec r)$ that are used to calculate the density according to Eqs. (2) and (4), the kinetic energy and $\overline{E_x},\overline{E_c}$. One hence obtains

$$E_0=E_0(\{B_{\nu s}\}).$$

The minimum of E_0 in the space of the expansion coefficients $B_{\nu s}$ can be determined by using any reasonably efficient steepest descent method which automatically changes the assumed starting values of $B_{\nu s}$ in an appropriate way. The present calculations were carried out with the aid of some subroutines of the widely used code CIV3 [22]. These subroutines are modifications of some earlier minimization codes [23,24].

B. Extending the OEP method to the relativistic case

We replace the scalar orbitals by four-component spinors according to

$$\psi_{is}(\vec r)\to\vec\psi_\kappa(\vec r)=\sum_{\alpha=1}^{2}\sum_s f^{(s)}_{\kappa\alpha}(\vec r)\vec\chi^{(s)}_\alpha,$$

where

$$\sum_{\alpha,s}\int|f^{(s)}_{\kappa\alpha}(\vec r)|^2d^3r=1$$

TABLE I. Ground-state energy ($-E_{\text{tot}}$) of some closed-shell atoms or spherical spin-polarized atoms, in Ry.

Atoms	Hartree-Fock[a]	Engel-Vosko[b]	Krieger *et al.*[c]	Present
Be	29.1460	29.1449	29.1447	29.1449
Ne	257.0942	257.0910	257.0897	257.0910
Mg	399.2292	399.2232	399.2214	399.2234
Ar	1053.6350	1053.6246	1053.6210	1053.6248
Ca	1353.5164	1353.5040	1353.4994	1353.5038
Zn	3555.6962	3555.6690	3555.6614	3555.6679
Kr	5504.1100	5504.0862	5504.0796	5504.0855
Sr	6263.0914	6263.0672	6263.0598	6263.0660
Cd	10930.2662	10930.2292	10930.2168	10930.2272
Xe	14464.2768	14464.2426	14464.2297	14464.2403
Li	14.8656	14.8650	14.8644	14.8650
N	108.8090	108.8068	108.8061	108.8067
Na	323.7180	323.7134	323.7099	323.7131
P	681.4386	681.4300	681.4274	681.4297
K	1198.3298	1198.3184	1198.3142	1198.3173

[a] Spin-unrestricted Hartree-Fock for non-closed-shell atoms.
[b] Engel and Vosko [8].
[c] Krieger *et al.* [9].

and $\vec{\chi}_\alpha^{(s)}$ denote four-component unit spinors. The large and small components of $\vec{\psi}_\kappa$ are labeled by a suffix $\alpha=1$ and $\alpha=2$, respectively.

The kinetic energy expression in Eq. (1) has to be replaced by

$$\langle T\rangle_0=\sum_{\substack{\kappa\\ (\text{occup})}}\int \vec{\psi}_\kappa^{+}(\vec{r})[-ic\vec{\alpha}\cdot\vec{\nabla}+\epsilon_0(\beta-1)]\vec{\psi}_\kappa(\vec{r})d^3r,$$

where $\vec{\alpha}$ and β are the four fundamental Dirac matrices and ϵ_0 denotes the electron rest energy. The spin-resolved densities are given by

$$\rho_s(\vec{r})=\sum_{\substack{\kappa\\ (\text{occup})}}\sum_{\alpha}|f_{\kappa\alpha}^{(s)}(\vec{r})|^2.$$

The one-particle equations that are obtained by employing the familiar procedure of adiabatically switching off the electron-electron interaction, are analogous to the KS equations, and read

$$\{[-c\vec{\alpha}\cdot\vec{\nabla}+\epsilon_0(\beta-1)]+V_{\text{ext}}(\vec{r})+\hat{\mathbf{V}}_{\text{ext}}(\vec{r},s)\}\vec{\psi}_\kappa(\vec{r})$$
$$=\epsilon_\kappa\vec{\psi}_\kappa(\vec{r}),$$

where $\hat{\mathbf{V}}_{\text{ext}}(\vec{r},s)$ is a diagonal 4×4 matrix containing the additional external potential $\hat{V}_{\text{ext}}(\vec{r},s)$ that guarantees the conservation of the interacting densities $\rho_s(\vec{r})$ as one performs the switching. (For details see Fritsche *et al.* [29].)

III. RESULTS AND DISCUSSION

The accuracy of the energy of free atoms constitutes the most obvious criterion for the competitiveness of our alternative method. In Table I we have listed the pertinent results obtained from exchange-only calculations ($\overline{E_c}=0$) on some closed-shell and spherical spin-polarized free atoms along with Hartree-Fock results and respective OEP data of Engel and Vosko [8]. The latter authors used the conventional integral-equation method. We have also included total energies obtained from exchange-only KLI calculations [9]. Obviously, our results are in better agreement with those of the very accurate integral-equation method than the corresponding KLI data. The difference between our results and those of Engel and Vosko is virtually zero on the scale of interest for the lighter atoms up to Ar and is about 1 mRy or less up to Xe, where the largest error occurs, i.e., 2.3 mRy. By contrast, the KLI method yields sizably less accurate results that differ by more than 10 mRy for the Xe atom. All our data lie above the corresponding values of Engel and Vosko except for the case of Mg and Ar, where our results are about 0.2 mRy lower. As we have carefully checked our results in this case it seems that the integral-equation method in the implementation used by Engel and Vosko cannot in all cases guarantee an accuracy up to the fourth decimal place. Calculations within the relativistic extension of our method compare in accuracy to our nonrelativistic results. The pertinent results are presented in Table II for a few atoms along with Dirac-Fock results obtained by using the well-known code of Grant *et al.* [30]. The calculations are based on the nuclear point-charge model. The differences between our results and the corresponding Dirac-Fock values are nearly the same as for the nonrelativistic results if compared to the Hartree-Fock data in Table I. This lends credence to the conceptual and numerical consistency of our approach also in the relativistic case.

The exchange energy itself represents another quantity that is sizably sensitive to the accuracy of the effective potential. The pertinent values are given in Table III together with those obtained from a pure Hartree-Fock calculation and from the OEP calculations by Wang *et al.* [7] and by

TABLE II. Relativistic ground-state total energy ($-E_{\text{tot}}$), in Ry.

Atoms	Dirac-Fock	Present	Present (including correlation)
Ne	257.3839	257.3802	258.1478
Ar	1057.3689	1057.3603	1058.8627
Kr	5577.7690	5577.7450	5581.2463
Xe	14894.3245	14894.2930	14899.7929

Engel and Vosko [8]. Obviously, our data agree very well with those exceedingly accurate OEP results. The accuracy of the OEP in the exchange-only approximation can very sensitively be checked by using the exchange-only virial theorem derived by Levy and Perdew [27] which states

$$E_{xs}=-\int \rho_s(\vec{r})\vec{r}\cdot\vec{\nabla}V_{xs}(\vec{r})d^3r, \tag{9}$$

where E_{xs} and ρ_s are determined by using the OEP, and $V_{xs}(\vec{r})$ is just the exchange portion of the latter. Another criterion that is particularly suited for checking the accuracy of the potential in the asymptotic region is due to Krieger *et al.* [25] and consists in the equality

$$\epsilon_s=\epsilon_s^{\text{HF}} \tag{10}$$

for the highest occupied level for either spin direction. Here ϵ_s and ϵ_s^{HF} denote, respectively, the orbital eigenvalue pertaining to the exchange-only OEP and the Hartree-Fock one-particle expectation value formed with the corresponding OEP orbital. Our method lends itself to incorporating Eq. (9) in a particularly simple way by minimizing

$$E_{\text{tot}}+\sum_s |E_{xs}-E_{xs}^{vr}|,$$

where E_{xs}^{vr} represents the right-hand side of Eq. (9). The results obtained for the total energy by employing this kind of modified minimization are compiled in Table I where we have listed a selected set of atoms. The remaining errors in satisfying the virial theorem and Eqs. (9), (10) are listed in Table IV. Considering the accuracy of our total energies (Table I) within the mRy range, the small magnitude of the error in satisfying Eq. (9) indicates that our procedure achieves, in fact, what it is designed for. At the same time the error in satisfying Eq. (10) becomes obviously very small. This is different from the KLI method where one finds Eq. (10) satisfied exactly which is not surprising as this result can be shown to follow analytically from the particular construction of $V_{\text{xc}}(\vec{r},s)$. By contrast, in satisfying the virial theorem as well as the exchange-only virial theorem, Eq. (9), the KLI method yields sizable errors which can be as large as 3.6 Ry for the Xe atom. The eigenvalues obtained for the highest occupied orbitals and the Hartree-Fock one-particle expectation values are listed in Table V and compared to the corresponding Hartree-Fock eigenvalues and the OEP results of Engel and Vosko [8]. There is a good overall agreement within a few mRy between their data and ours.

In Fig. 1(a) we have plotted the exchange potential for the Xe atom as it results from our exchange-only calculation. It displays the shell-derived structures (‘‘bumps’’) that Wang *et al.* discuss in their OEP paper [7] which is based on a refined integral-equation approach. The close one-to-one cor-

TABLE III. Exchange energy ($-E_x$), in Ry.

Atoms	Hartree-Fock[a]	Wang *et al.*[b]	Engel-Vosko[c]	Present
Be	5.3338	5.3317	5.3316	5.3318
Ne	24.2167	24.2098	24.2100	24.2136
Mg	31.9886	31.9758	31.9768	31.9821
Ar	60.3699	60.3486	60.3496	60.3531
Ca	70.4224	70.3968	70.3982	70.4036
Zn	139.2824	139.2352	139.2378	139.2274
Kr	187.7120	187.6615	187.6662	187.6782
Sr	203.9100	203.8459	203.8528	203.8445
Cd	297.8284	297.7525	297.7596	297.7751
Xe	358.1942	358.1182	358.1276	358.1526
Li	3.5624		3.5616	3.5617
N	13.2134		13.2088	13.2082
Na	28.0352		28.0262	28.0295
P	45.2846		45.2684	45.2662
K	65.3562		65.3338	65.3407

[a] Spin-unrestricted Hartree-Fock for non-closed-shell atoms.

[b] Wang *et al.* [7].

[c] Engel and Vosko [8].

TABLE IV. Errors in satisfying the virial theorem and Eqs. (9), (10), in mRy. The suffix h stands for "highest occupied level."

Atoms	$E_{\text{tot}}+E_{\text{kin}}$	$E_x-E_x^{vr}$	$-\varepsilon_h+\varepsilon_h^{\text{HF}}$
Be	-0.33	0.0006	-0.90
Ne	-1.88	-0.0006	4.72
Mg	-1.81	-0.0013	-1.52
Ar	-3.73	-0.0031	0.64
Ca	-2.87	0.0033	-1.22
Zn	-6.04	0.0037	6.25
Kr	-0.89	0.0027	4.01
Sr	-0.81	0.0050	-0.75
Cd	-1.09	-0.0008	6.14
Xe	0.26	0.0004	-0.01
Li(↑)	-0.20	-0.0005	0.13
Li(↓)		0.0001	-16.35
N(↑)	-0.68	0.0001	-1.02
N(↓)		-0.0002	-0.56
Na(↑)	-1.18	-0.0000	-0.69
Na(↓)		-0.0000	0.13
P(↑)	-1.70	0.0005	-3.48
P(↓)		0.0001	-2.18
K(↑)	-2.37	0.0005	-0.38
K(↓)		0.0002	-1.20

respondences of these features (also in their absolute values) demonstrates even more convincingly the adequacy of the two methods. This applies as well to the exchange potentials for spin up and spin down shown in Fig. 1(b) for the example of the P atom which presents a spherical spin-polarized system.

TABLE V. Eigenvalues $-\varepsilon_{nl}$ of the highest occupied orbitals and the Hartree-Fock single-particle expectation values $-\varepsilon_{nl}^{\text{HF}}$, in Ry.

Atoms	Hartree-Fock[a] $(-\varepsilon_{nl})$	Engel-Vosko[b] $(-\varepsilon_{nl})$	Present $(-\varepsilon_{nl})$	Present $(-\varepsilon_{nl}^{\text{HF}})$
Be(2s)	0.6185	0.6184	0.6177	0.6186
Ne(2p)	1.7008	1.7014	1.7042	1.6995
Mg(3s)	0.5061	0.5060	0.5046	0.5061
Ar(3p)	1.1820	1.1816	1.1817	1.1810
Ca(4s)	0.3911	0.3912	0.3899	0.3911
Zn(4s)	0.5850	0.5856	0.5913	0.5851
Kr(4p)	1.0484	1.0468	1.0498	1.0458
Sr(5s)	0.3569	0.3572	0.3569	0.3577
Cd(5s)	0.5297	0.5310	0.5360	0.5299
Xe(5p)	0.9146	0.9128	0.9124	0.9124
Li(2s↑)	0.3928	0.3926	0.3925	0.3926
Li(1s↓)	4.9374	4.9376	4.9537	4.9373
N(2p↑)	1.1418	1.1424	1.1416	1.1426
N(2s↓)	1.4516	1.4514	1.4509	1.4514
Na(3s↑)	0.3644	0.3642	0.3635	0.3641
Na(2p↓)	3.0340	3.0354	3.0334	3.0333
P(3p↑)	0.7842	0.7832	0.7799	0.7834
P(3s↓)	1.1124	1.1122	1.1106	1.1128
K(4s↑)	0.2954	0.2954	0.2951	0.2954
K(3p↓)	1.9070	1.9068	1.9053	1.9065

[a] Quoted from Wang *et al.* [7] for closed-shell atoms and from Engel and Vosko [8] for open-shell atoms.
[b] Engel and Vosko [8].

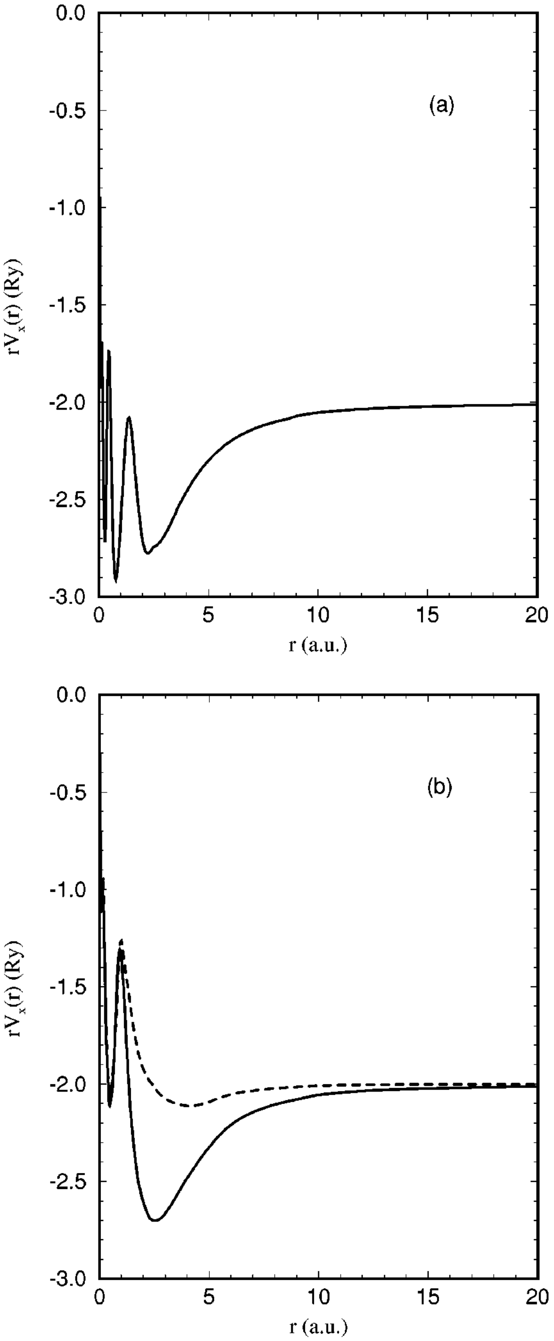

FIG. 1. The exchange potentials of Xe and P atoms as examples demonstrating the capability of our method to reproduce the detailed structure of the exchange potential that results from a different OEP technique (see Wang *et al.* [7]). (a) Exchange potential of Xe, (b) exchange potential for, respectively, majority spin (solid line) and minority spin (dashed line) of a P atom.

The flexibility of the present method allows the incorporation of a wide class of energy functionals. Its application to the relativistic N-electron problem, the results of which are given in Table II, presents one of the examples that demonstrates this flexibility. Another example constitutes the inclusion of approximate correlation energy functionals [28]. The incorporation of this or similar functionals into the integral-equation approach to the OEP method poses a serious difficulty. Grabo and Gross therefore resort to the KLI approach in order to achieve this incorporation of correlation [10]. Notwithstanding the error introduced by using a modified expression for the correlation energy compared to the Colle-Salvetti expression employed by Grabo and Gross there is a relatively satisfactory agreement between their results on E_c and ours, the maximum difference being less than 5%.

In conclusion it may be stated that the accuracy of our alternative DFT method in calculating OEP's appears to compare well with that of the integral-equation method. The new method is flexible and lends itself to incorporating various kinds of energy functionals.

The relative simplicity of the KLI approach and the flexibility of our method in dealing with relativistic modifications and extensions beyond the exchange-only approximation suggests a combination of the two methods. Instead of using a LSD-reference potential and expanding $\Delta\hat{V}_{\text{ext}}(\vec{r},s)$ in terms of basis functions $\varphi_\nu(\vec{r})$ [as given by Eq. (7)] we could just as well use the KLI potential as a reference. Since the latter already displays the wiggles that are characteristic of the potential correction $\Delta\hat{V}_{\text{ext}}(\vec{r},s)$, one might surmise that a redefined correction $\Delta\hat{V}_{\text{ext}}^{\text{KLI}}(\vec{r},s)$ would vary much more smoothly, and hence its Fourier-type expansion should converge much faster. We have checked this property of $\Delta\hat{V}_{\text{ext}}^{\text{KLI}}(\vec{r},s)$ for the case of Xe. As shown in Fig. 2, $\hat{V}_{\text{ext}}^{\text{KLI}}(\vec{r},s)$ and $\hat{V}_{\text{ext}}^{\text{exact}}(\vec{r},s)$ display, in fact, a very similar wiggly dependence, but differ sizably in the amplitude of their oscillations around an identical smooth r dependence. (This difference may be the source of error one observes with the KLI method in satisfying the virial theorem.) Consequently, $\Delta\hat{V}_{\text{ext}}^{\text{KLI}}(\vec{r},s)$ still exhibits sharp structures, which, however, can be represented by an expansion as defined by Eq. (7), but with $\varphi_\nu(\vec{r})$ now denoting spline functions. In that case the number of necessary basis functions drops from 80 to 20.

In the case of nonspherical atoms one could think of expanding

$$\Delta\hat{V}_{\text{ext}}^{\text{KLI}}(\vec{r},s)=\sum_{L}^{l_{\max}}\sum_{\nu}^{\nu_{\max}} B_{L\nu s}\varphi_{l\nu}(r)Y_L(\hat{\vec{r}}), \tag{11}$$

where L is shorthand for l, m and $Y_L(\hat{\vec{r}})$ denotes spherical harmonics. For insulating periodic structures it would be suggestive to split $\Delta\hat{V}_{\text{ext}}^{\text{KLI}}(\vec{r},s)$ into two portions which refer to contributions of the core states and the valence states, respectively. The contribution of the latter could be expanded in terms of plane waves $\exp[i\vec{G}\cdot\vec{r}]$ where $\vec{G}$ denotes vectors of the associated reciprocal lattice. The orbitals $\psi_{is}^{\text{KLI}}(\vec{r})$ generated within the KLI scheme are Bloch states in this case, and it would be convenient to use a full-potential linearized augmented plane wave (FLAPW) representation for the valence states. For an insulating periodic structure the sum (2) for the densities and analogous expressions that occur in the KLI scheme can be reduced to a few contributions from ''magic $\vec{k}$ points'' (see Baldereschi [31], Chadi and Cohen [32]). The core states could still be treated as atomic states. The remaining portion of $\Delta\hat{V}_{\text{ext}}^{\text{KLI}}(\vec{r},s)$ associated with them could then be expanded according to Eq. (7) by using spline functions so that E_0 would become a function of these two sets of expansion coefficients whose values are found by applying the same steepest descent method as in the present paper. The FLAPW method allows one to treat small molecules as well, as has been shown by Freeman and associates [33].

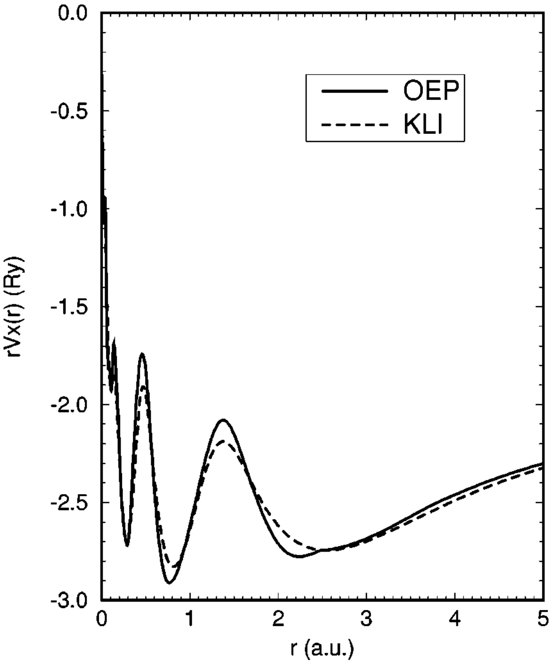

FIG. 2. The OEP exchange portion: ''exact OEP'' (present work) vs the result of the KLI approximation for the Xe atom.

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