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From electron densities to Kohn-Sham kinetic energies, orbital energies, exchange-correlation potentials, and exchange-correlation energies

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By developing our previous method [Phys. Rev. A **46**, 2337 (1992); J. Chem. Phys. **98**, 543 (1993)], we show how to calculate Kohn-Sham kinetic energies, orbitals, orbital energies, and exchange-correlation potentials, starting from accurate ground-state electron densities. In addition, given correct total energies, we also show how to obtain exchange-correlation energies. The scheme used is based on the Levy constrained-search method for determining the Kohn-Sham kinetic energy. In our preferred implementation, the total electron-electron repulsion is written as a Fermi-Amaldi term plus the rest, thereby assuring the correct long-range behavior of the exchange-correlation potential. Results are given for He, Be, Ne, and Ar. It is demonstrated that the exact exchange-correlation functional cannot be local.

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I. INTRODUCTION

In density-functional theory, the density determines the external potential, and therefore determines the system. The energy of the system is a functional of the density and in principle can be determined by the variational principle. Unfortunately, the exact energy density functional is not known at the present time, because the so-called exchange-correlation energy functional which enters is unknown (though there has been much recent progress on approximating it).

On the other hand, the electron density can be determined by experimental methods. There arises a question as to whether there is a density-functional way to determine the system (and its properties) from the experimental density (or from an accurately calculated density). In this paper, we develop, and apply to higher accuracy than before, a method earlier described [1,2] for determining Kohn-Sham orbitals from a given ground-state electron density. Our method is iterative, and it involves substantial self-consistent calculation, but it requires calculating no potential-energy integrals other than classical potentials due to charge distributions. We present detailed calculations on He, Be, Ne, and Ar. Given the total energy as well as the electron density, we then solve the problem of determining the accurate exchange-correlation energy E_{xc} for a system, and we show by calculation that the exact exchange-correlation functional $E_{\mathrm{xc}}[\rho]$ cannot be local. Throughout, we assume that we are dealing with a closed-shell system having a nondegenerate ground state.

II. METHOD FOR DETERMINING KOHN-SHAM ORBITALS AND OTHER QUANTITIES FROM A GIVEN GROUND-STATE ELECTRON DENSITY

Levy [3] and Levy and Perdew [4] have shown that the Kohn-Sham orbitals ϕ_i are delivered by the procedure

$$T_s[\rho]=\min_{D\to\rho_0}\langle D|\hat{T}|D\rangle \ . \tag{1}$$

Here, D is the Slater determinant composed from the Kohn-Sham orbitals ϕ_i and T_s is the corresponding Kohn-Sham kinetic energy. Of course,

$$\sum_{i\ (\mathrm{occ.})}|\phi_i|^2=\rho_0 \ . \tag{2}$$

Levy [3] proposed imposing Eq. (2) using a local Lagrange multiplier $v_{\mathrm{eff}}(r)$. The orbitals then are solutions of the equations

$$[-\tfrac{1}{2}\nabla^2+v_{\mathrm{eff}}(\mathbf{r})]\phi_i=\varepsilon_i\phi_i \ . \tag{3}$$

The orbitals are the Kohn-Sham orbitals, and so Eq. (3) are the Kohn-Sham equations, and the ε_i are the Kohn-Sham orbital energies possibly displaced by some constant. Given ρ_0, determination of v_{eff} so that Eq. (3) are satisfied can be accomplished by self-consistent calculation [5]. The potential $v_{\mathrm{eff}}(\mathbf{r})$ must be the sum of the external (nuclear) potential $v_0(\mathbf{r})$, the classical potential due to ρ_0,

$$v_{J_0}=\int\frac{\rho_0(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' \ , \tag{4}$$

and the exchange-correlation potential

$$v_{\mathrm{xc}}(\mathbf{r})=\frac{\delta E_{\mathrm{xc}}[\rho]}{\delta\rho(\mathbf{r})} \ . \tag{5}$$

One begins with no knowledge of $v_{\mathrm{xc}}(\mathbf{r})$ beyond the fact

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that it decays as $-1/r$ for large r [6]. One never has to deal with E_{xc} itself.

In our previous work [1,2] we wrote $v_{\mathrm{eff}}(\mathbf{r})$ as $v_0(\mathbf{r})$ for the system of interest plus a term that forces ρ to be equal to ρ_0 in a certain limit. If it can been forced, the constraint

$$C[\rho,\rho_0]=\tfrac{1}{2}\int\int\frac{[\rho(\mathbf{r})-\rho_0(\mathbf{r})][\rho(\mathbf{r}')-\rho_0(\mathbf{r}')]}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}'=0 \tag{6}$$

does the job. Attaching a global Lagrange multiplier λ to this, one finds the corresponding effective potential

$$v_c^{\lambda}(\mathbf{r})=\lambda\int\frac{\rho(\mathbf{r}')-\rho_0(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' \tag{7}$$

and the differential equations

$$[-\tfrac{1}{2}\nabla^2+v_0(\mathbf{r})+v_c^{\lambda}(\mathbf{r})]\phi_i^{\lambda}(\mathbf{r})=\varepsilon_i^{\lambda}\phi_i^{\lambda}(\mathbf{r})\ . \tag{8}$$

In the limit $\lambda\rightarrow\infty$, these become Eq. (3), with the orbitals the Kohn-Sham orbitals and the orbital energies the Kohn-Sham orbital energies (up to a constant). One solves Eq. (8) self-consistently for a series of specific λ and extrapolates to $\lambda=\infty$. It works.

To speed convergence and hence to improve numerical accuracy, and also to achieve another property described below, we here propose to add a term to the operator on the left side of Eq. (8), namely, $(1-1/N)v_J$. This can be thought of as the Fermi-Amaldi approximation for the whole electron-electron repulsion effect, v_J being the classical potential due to ρ,

$$v_J(\mathbf{r})=\int\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'\ . \tag{9}$$

Thus we find, using ρ^{λ} to give v_J^{λ},

$$\left[-\tfrac{1}{2}\nabla^2+v_0(\mathbf{r})+\left[1-\frac{1}{N}\right]v_J^{\lambda}+v_c^{\lambda}(\mathbf{r})\right]\phi_i^{\lambda}(\mathbf{r})=\varepsilon_i^{\lambda}\phi_i^{\lambda}(\mathbf{r})\ . \tag{10}$$

For finite λ the orbitals and orbital energies in Eq. (10) will differ from those in Eq. (8), but in the limit $\lambda\rightarrow\infty$ they will be the same (except for a possible shift in the orbital energies), since both achieve solution of Eq. (1) and the Kohn-Sham equations for the problem are unique.

The advantages of Eq. (10) over Eq. (8) are not only numerical. With the choices we have made, the exchange-correlation potential is

$$v_{\mathrm{xc}}=\lim_{\lambda\rightarrow\infty}\left[v_c^{\lambda}-\frac{1}{N}v_J^{\lambda}\right] \tag{11}$$

and the correct long-range behavior of v_{xc} is provided by the last term alone. To leave the Fermi-Amaldi term out of v_{eff}, as is done in Eq. (8), puts a burden on v_c^{λ} that is hard for it to bear for finite λ. This does not mean that the calculations using Eq. (8) are wrong, but that it is much more efficient to employ Eq. (10). That Eq. (10) hold is confirmed by comparison of our results on Be with those of Almbladh and Pedroza [5]. The eigenvalues from Eq. (10) are Kohn-Sham orbital energies *with no energy shift*. Note that Almbladh and Pedroza input the experimental first ionization potential, which we do not.

TABLE I. Kohn-Sham kinetic energies in atomic units.

He	2.8671	(2.8671)[a]
Be	14.5926	(14.5932)[a]
Ne	128.625	
Ar	526.682	

[a]Previously calculated values from Ref. [1].

Given v_0 and its eigendensity ρ_0, our method for determining Kohn-Sham orbitals and orbital energies is to solve Eq. (10) self-consistently for a series of larger and larger λ values and to extrapolate to $\lambda=\infty$. In practice (and we have made many calculations), we find that we can make accurate extrapolations by expanding any quantity of interest as a power series in $1/\lambda$. If one starts with fairly high λ values (say, 100 or more), linear extrapolation works fairly well, but quadratic terms are needed to achieve the accuracy we want; cubic terms have very little effect. Our preferred procedure is to expand (in $1/\lambda$) and extrapolate just v_{xc}. After determining the extrapolated v_{xc}, we solve the Kohn-Sham equations self-consistently with this v_{xc}, thereby determining all quantities of interest. Note that in the Kohn-Sham effective potential, only v_{xc} depends on λ.

A single calculation for $\lambda=100$ gives reasonable estimates for most quantities. As λ gets larger, the calculations become more tedious. Some type of "critical phenomenon" appears to be involved.

III. KOHN-SHAM KINETIC ENERGIES, ORBITAL ENERGIES, AND EXCHANGE-CORRELATION POTENTIALS

Inputting accurate total electron densities, we solve Eq. (10) self-consistently for $\lambda=100$, 140, and 200. The radi-

TABLE II. Kohn-Sham orbital energies in atomic units.

Atom	ε_{1s}	ε_{2s}	ε_{2p}	ε_{3s}	ε_{3p}	$-I$[a]
He	−0.9039					−0.9037
Be	−4.2142	−0.3384				−0.3424
Ne	−30.812	−1.644	−0.789			−0.7923
Ar	−114.41	−11.11	−8.73	−1.07	−0.56	−0.5792

[a]From Ref. [10]. These values are inferred from experimental ionization potentials with all effects separated out that are not included in the nonrelativistic stationary-point-nucleus Schrödinger equation.

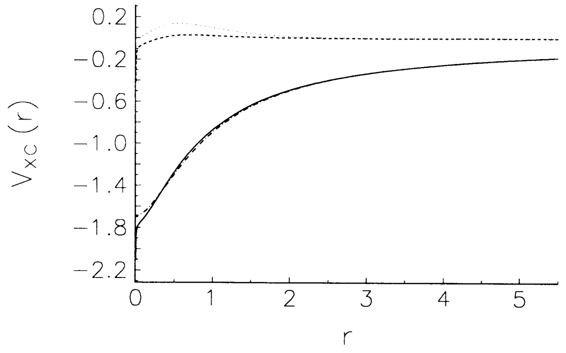

FIG. 1. Exchange-correlation potential for He. The solid curve is v_{xc}, the dot-dashed curve is $-(1/N)v_J$, the dashed curve is v_c, and the dotted curve is the radial density distribution function.

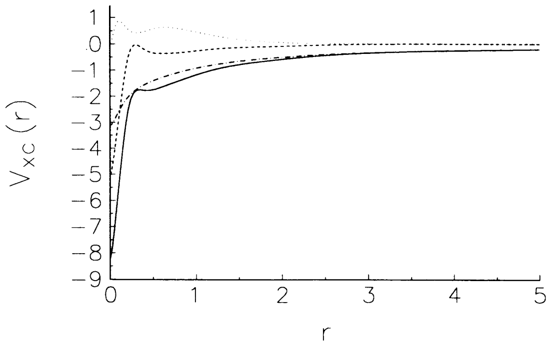

FIG. 3. Exchange-correlation potential for Ne. See Fig. 1 caption.

al parts of the orbitals are constructed by linear combination of orthogonal functions, as described in Ref. [2]. We extrapolate v_{xc} and then solve the Kohn-Sham equations. The accurate densities used for He and Be are from Refs. [7] and [8], and for Ne and Ar, from configuration-interaction (CI) wave functions determined by us.

The computed Kohn-Sham kinetic energies are given in Table I, the computed occupied orbital energies in Table II. It is known that the highest Kohm-Sham occupied orbital energy is the negative of the first ionization potential [9]. In Table II we list the accurate ionization potentials [10]. There are small differences between these values and our calculated highest Kohn-Sham occupied orbital energies, probably because the densities we employed are not the exact experimental ones. Our experience shows that the highest orbital energies are the most difficult of all quantities to compute accurately. They are small numbers, and they are very sensitive to details of the density for large r.

In Figs. 1 to 4, we give the exchange-correlation potentials (solid curve) for all four atoms. Also shown is the Fermi-Amaldi term in Eq. (11), $(-1/N)v_J$ (dot-dashed curve) (which reproduces the correct long-range behavior), and the constraint term v_c (dashed curve) (which is responsible for the shell-structure-like behavior of v_{xc}). The Fermi-Amaldi term mainly functions to sub-

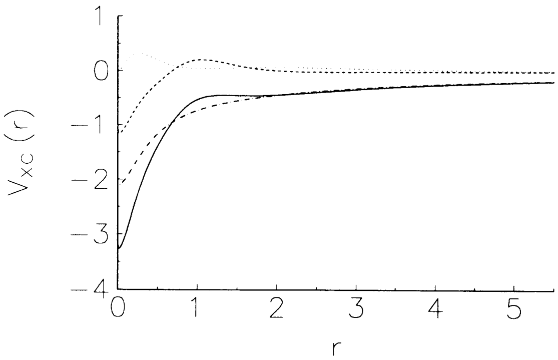

FIG. 2. Exchange-correlation potential for Be. See Fig. 1 caption.

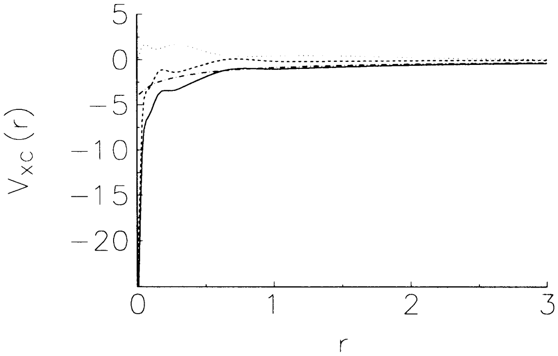

FIG. 4. Exchange-correlation potential for Ar. See Fig. 1 caption.

TABLE III. Kinetic-energy components in atomic units.

	T_s	T_c	T
He	2.867	0.037	2.904
Be	14.593	0.074	14.667
Ne	128.63	0.29	128.92
Ar	526.68	0.71	527.37

TABLE IV. Exchange-correlation energies in atomic units.

	E_{xc}	Corresponding conventional value[a]
He	−1.068	−1.069
Be	−2.776	−2.761
Ne	−12.52	−12.50
Ar	−31.25	−30.97

[a] These values are not expected to be the same as the density-functional values in the second column. The values are from Ref. [12].

TABLE V. Effective homogeneity numbers for $E_{xc}[\rho]$. See the text for definitions. k is the effective homogeneity of the functional $E_{xc}[\rho]$.

	E_{xc}	$\int \rho v_{xc} d\mathbf{r}$	L_{xc}	k_{eff}
He	-1.068	-2.021	0.953	1.89
Be	-2.776	-4.429	1.653	1.60
Ne	-12.52	-19.28	6.76	1.54
Ar	-31.25	-43.98	12.73	1.41

tract out the self-repulsion in v_J that does not belong there, while the constraint term is representing correlation plus the interorbital exchange. Radial density distribution functions (dotted curve) are superposed for comparison purposes.

IV. EXCHANGE-CORRELATION ENERGIES AND THE KINETIC-ENERGY CORRECTION T_c

Provided that we know not only the ground-state electron density but also the true total energy E, we can proceed to determine the exchange-correlation energy E_{xc}, which we now do. Note that E_{xc} in density-functional theory is not the same as in conventional quantum chemistry. The density-functional definition is

$$E_{xc}[\rho]=(V_{ee}[\rho]-J[\rho])+(T[\rho]-T_s[\rho]) , \qquad (12)$$

where $V_{ee}[\rho]$ is the total electron-electron repulsion. The kinetic-energy difference in this formula is conventionally called T_c,

$$T_c[\rho]=T[\rho]-T_s[\rho] . \qquad (13)$$

Tables III and IV give values of T_c and E_{xc} for He, Be, Ne, and Ar, determined as will be immediately described. The values obtained are reasonable. Systematic further calculation and development of the theory of these quantities would appear to be highly desirable.

To determine T_c and E_{xc}, given E, T_s, and the potential v_{xc} determined as above, we proceed as follows: The virial theorem applies, and so

$$T=-E=T_s+T_c , \quad T_c=-E-T_s . \qquad (14)$$

This gives T_c. E_{xc} and T_c are related through [10]

$$E_{xc}[\rho]+T_c[\rho]=-\int \rho(\mathbf{r})\mathbf{r}\cdot\nabla v_{xc}(\mathbf{r})d\mathbf{r} . \qquad (15)$$

The integral can be calculated, and this gives E_{xc}. A check is provided by the exact density-functional formula [11]

$$E[\rho]=\sum_i \varepsilon_i-J[\rho]+E_{xc}-\int \rho(\mathbf{r})v_{xc}(\mathbf{r})d\mathbf{r} . \qquad (16)$$

This requires calculation of the last integral.

For the "exact" energies employed in calculating the results in Tables III and IV, we have taken the values -2.9037, 14.6669, -128.918, and -527.388 a.u. These are the values of total energy associated with the electron densities we have employed, the "true" values being, respectively, -2.9037, -14.6674, -128.9376, and -527.540 [10].

V. TESTS OF HOMOGENEITY AND LOCALITY

The hypothetical exact functional E_{xc}, values of which we have determined in the foregoing for exact ground-state densities for four atoms, may or may not be approximately homogeneous in ρ, and may or may not be approximately or accurately local in ρ. We can provide tests. See the Appendix for definitions and key properties of homogeneous and local functionals.

From Eq. (16), we see that we may regard as the basic quantity of interest for determining E its Legendre transform,

$$L_{xc}[\rho]\equiv E_{xc}[\rho]-\int \rho(\mathbf{r})v_{xc}(\mathbf{r})d\mathbf{r} . \qquad (17)$$

Our questions are, may $E_{xc}[\rho]$ be homogeneous and still give the correct value of L_{xc} (that we compute)? May E_{xc} be local?

Table V addresses the homogeneity issue. We calculate an effective homogeneity parameter [see the Appendix, Eqs. (A1) and (A2)],

$$k_{eff}=1+\frac{L_{xc}}{E_{xc}} , \qquad (18)$$

and compute it for the four atoms. We would in fact expect, since the term v_J/N is a principal part of v_{xc} [see Eq. (11) above], a leading part of E_{xc} to be homogeneous of degree 2. Also, a high-N $\rho^{4/3}$ dependence is expected. So for the "effective" values to smoothly change from 2 to $\frac{4}{3}$, as they seem to do, is reasonable. There is, however, no simple general homogeneity.

Table VI addresses the locality issue. For this we may test whether Eq. (A4) holds, with $Q=E_{xc}$. It is clear from the results in the Table that it does not. The unknown exact exchange-correlation functional is not local.

VI. CONCLUSIONS

To summarize, we have established a method for finding, starting from a ground-state density, Kohn-Sham

TABLE VI. Test for locality of $E_{xc}[\rho]$. If E_{xc} were local, the numbers in the first column would be the same as those in the second column. See text.

	E_{xc}	$-\frac{1}{3}\int v_{xc} r(d\rho/dr)d\mathbf{r}$
He	-1.068	-1.677
Be	-2.776	-3.527
Ne	-12.52	-15.16
Ar	-31.25	-33.33

orbitals, orbital energies, exchange-correlation potentials, and kinetic energies T_s. If, further, we know the exact total energy, we have shown how to determine the exchange-correlation energy E_{xc}. From calculations on He, Be, Ne, and Ar, we have shown that the accurate $E_{\mathrm{xc}}[\rho]$ cannot be local and that it does not have single homogeneity properties.

We should like to hope for more, and we are laboring toward that end. Can we find the accurate total energy from the density alone? Of course, $E\sim -T_s$, and this is a more accurate estimate of E than a full Hartree-Fock calculation provides. But what about the accurate E? Understanding better the quantity L_{xc} of Eq. (17) might do the job, or integrating the equation $v_{\mathrm{xc}}=\delta E_{\mathrm{xc}}/\delta\rho$ from a known reference state to the system of interest.

Second, the method that we have developed is not variational. Can it be made variational? If so, one would then have achieved an explicit solution of the original Hohenberg-Kohn problem involving only classical Coulomb integrals and self-consistent calculations simpler than Hartree-Fock calculations. A $\lambda\rightarrow\infty$ limiting process is required, but no one would be concerned about that.

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APPENDIX: LEMMAS FOR HOMOGENEOUS AND LOCAL FUNCTIONALS

For any well-defined and well-behaved functional $Q[\rho(\mathbf{r})]$ of the three-dimensional electron density ρ, for which the functional derivative $v_Q[\rho]=\delta Q[\rho]/\delta\rho(\mathbf{r})$ exists and is well behaved, we focus on the Legendre transform of Q,

$$L[\rho]\equiv Q[\rho]-\int v_Q[\rho]\rho(\mathbf{r})d\mathbf{r}\ . \tag{A1}$$

We then have two lemmas.

Lemma 1. If Q is a *homogeneous* functional of degree k in ρ,

$$L[\rho]=(1-k)Q[\rho]=\left[\frac{1-k}{k}\right]\int v_Q[\rho]\rho(\mathbf{r})d\mathbf{r}\ . \tag{A2}$$

Proof. Q is homogeneous of degree k in ρ if and only if $\int v_Q[\rho]\rho(\mathbf{r})d\mathbf{r}=kQ$. Equation (A2) follows.

Lemma 2. Let $\rho(\mathbf{r})$ be a typical atomic electron density: spherically symmetric and monotonically decreasing in r. Then for any functional $Q[\rho]$ that is a *local* functional of ρ, that is, has the form

$$Q[\rho]=\int f(\rho)d\mathbf{r}\ , \tag{A3}$$

where $f(\rho)$ is a function of ρ vanishing strongly at $r=\infty$, we have

$$\begin{aligned}Q[\rho]&=-\tfrac{1}{3}\int v_Q(r)\left[r\frac{d}{dr}\right]\rho(r)d\mathbf{r}\\&=-\tfrac{1}{3}\int v_Q(r)\rho(r)\frac{d\ln\rho(r)}{d\ln r}d\mathbf{r}\end{aligned} \tag{A4}$$

and

$$L[\rho]=-\int v_Q(r)\rho(r)\left[1+\frac{1}{3}\left[\frac{d\ln\rho(r)}{d\ln r}\right]\right]d\mathbf{r}\ . \tag{A5}$$

If either (A4) or (A5) is not satisfied, $Q[\rho]$ is not local. *Proof.*

$$\frac{\delta Q}{\delta\rho}=\frac{df}{d\rho}=\frac{df}{dr}\left[\frac{dr}{d\rho}\right]=v_Q\ .$$

Hence,

$$\frac{df}{dr}=v_Q\left[\frac{d\rho}{dr}\right]=f'\ , \tag{A6}$$

and we find, on integrating Eq. (A3) by parts,

$$Q=\int f(r)r^2dr\,d\Omega=-\tfrac{1}{3}\int f'dr\,d\Omega=-\tfrac{1}{3}\int v_Q\frac{d\rho}{dr}d\mathbf{r}\ . \tag{A7}$$

Equations (A4) and (A5) follow.

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