Energy differences between Kohn-Sham and Hartree-Fock wave functions yielding the same electron density

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Kohn-Sham wave functions yielding the Hartree-Fock ground-state densities of alkaline-earth and noble-gas atoms are calculated. From the Kohn-Sham wave functions the corresponding noninteracting kinetic energies and the exchange energies are calculated according to the density-functional definition. The difference between the density-functional and the Hartree-Fock exchange energies for a given electron density is found to be surprisingly small. This justifies, at least for the systems studied here, the common practice of using Hartree-Fock exchange energies as reference values to assess the quality of today's approximate density functionals for the exchange energy. The calculated Kohn-Sham wave functions give energies with the atomic Hamiltonian operators which are *de facto* identical to the corresponding values obtained from the optimized potential method. The influence of a coupling parameter turning on the electron-electron interaction on the difference between Kohn-Sham and Hartree-Fock kinetic and exchange energies is investigated. Various hybrid schemes which combine the Kohn-Sham and the Hartee-Fock methods are compared. For the atomic systems investigated here, the different exchange and correlation energies occurring in these schemes are found in most cases to deviate very little from the standard Kohn-Sham exchange and correlation energies. Finally, the formulation and validity of the Hohenberg-Kohn theorem in basis set representations are discussed.

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I. INTRODUCTION

In density-functional theory (DFT) each electron density is associated with a model system of noninteracting electrons described by the N-electron Kohn-Sham (KS) wave function with N being the electron number resulting from the electron density [1]. This model system allows it to define the noninteracting or KS kinetic energy and the DFT or KS exchange energy. On the other hand, a Hartree-Fock ground state also defines a kinetic energy and an exchange energy. Even for a KS model system with the exact same density as that of some given Hartree-Fock (HF) ground state, the KS and the HF kinetic and exchange energies are different. In this work, the magnitude of this difference is calculated for some atomic systems. There are at least two reasons to investigate energetic differences between KS and HF wave functions which yield the same electron density.

(i) For the accurate description of electronic structures within the KS scheme of DFT good approximations to the density functionals for the exchange and the correlation energy which are not known exactly must be available [1]. A good deal of the work in DFT over the last three decades has been devoted to the construction and improvement of such approximations [1]. A common practice in assessing the quality of approximate density functionals for the exchange energy is to evaluate the approximate functional for HF ground-state electron densities and to compare the resulting values with the HF exchange energies [2,3]. However, this procedure is questionable because of the different definitions of the exchange energy within DFT and HF theory. Of course, the magnitude of possible errors introduced by using HF instead of the correct DFT exchange energies as reference values depends on the difference between the two. Recent approximate exchange density functionals [3] yield values which deviate by less than 1% from the corresponding HF exchange energies. It is therefore urgent to clarify this point, in order to have a sound basis for the further development and improvement of approximate exchange density functionals.

(ii) There exist several hybrid methods [4–14] which combine elements from the KS and HF procedures. These hybrid methods give rise to definitions of exchange-correlation energies which differ from those of the standard KS scheme. Subsequently the density functionals corresponding to the various exchange-correlation energies also are different. However, in actual applications of the various methods the same approximations for the exchange and correlation functionals, those derived for the standard KS scheme, are usually employed. To what extend this practice is justified needs to be investigated. The differences between the exchange and correlation functionals for the various methods will be shown to be related to the differences between the KS and HF kinetic and exchange energies.

A systematic investigation of the differences between KS and HF kinetic and exchange energies has not yet been performed. So far, the DFT exchange energy corresponding to a HF density has been calculated only for

lithium and beryllium [15,16]. In Refs. [15–17], the kinetic energies of the KS wave functions yielding the HF densities of lithium and beryllium are presented and in Refs. [9,15–20] the effective KS potentials necessary to obtain KS wave functions corresponding to the HF densities of the atoms Li, Be, and Ne are constructed (see also Ref. [24]). In this work we use a recently introduced basis set method [21] to determine the KS wave functions belonging to the HF ground-state densities of the atoms Ne, Ar, Be, Mg, and Ca. The KS wave functions subsequently allow the calculation of the corresponding noninteracting or KS kinetic energies and of the DFT exchange energies. The differences between these energies and the HF kinetic and exchange energies can then be discussed. We also investigate how these differences depend on a coupling parameter which turns on the electron-electron interaction.

In addition, this work is to our knowledge the first to use a basis set scheme, i.e., the scheme of Ref. [21], to construct KS wave functions from a given electron density. Alternative numerical methods for this purpose have been developed in recent years [9,15–20,22–27] but are usually quite tedious to apply. This probably is the reason KS and HF exchange energies have been compared only in the few cases mentioned above. In the Appendix the method of Ref. [21] is briefly described and problems arising from the fact that a basis set procedure is employed are considered. In particular, the general question of the formulation and validity of the Hohenberg-Kohn theorem within a basis set representation is discussed. Furthermore, it is shown that, for the procedure of Ref. [21], using an iterative scheme which is based on linear response and therefore on perturbation theory does not impose any restrictions on the results.

II. DIFFERENCES BETWEEN KS AND HF ENERGIES

Within the constrained-search formulation [1(d),1(f)] of DFT, the noninteracting kinetic energy $T_s^{KS}[n]$ of an arbitrary N-electron density $n(\mathbf{r})$ is given by

$$T_s^{KS}[n] = \min_{\Psi \to n(\mathbf{r})} \{ \langle \Psi | \hat{T} | \Psi \rangle \} = \langle \Phi^{KS}[n] | \hat{T} | \Phi^{KS}[n] \rangle .$$

(1)

The minimization in Eq. (1), symbolized by $\Psi \to n(\mathbf{r})$, runs over all antisymmetric wave functions yielding the density $n(\mathbf{r})$. The operator of the kinetic energy is denoted by $\hat{T}$. The minimizing wave function $\Phi^{KS}[n]$ is the KS wave function corresponding to the density $n(\mathbf{r})$. The DFT or KS exchange energy $E_x^{KS}[n]$ is then defined by

$$E_x^{KS}[n] = \langle \Phi^{KS}[n] | \hat{V}_{ee} | \Phi^{KS}[n] \rangle - U[n] ,$$

(2)

where $\hat{V}_{ee}$ is the electron-electron interaction operator and $U[n]$ is the classical Coulomb interaction of the charge distribution given by $n(\mathbf{r})$. The expectation value of $\Phi^{KS}[n]$ with an interacting N-electron Hamiltonian operator, $\hat{H}_v = \hat{T} + \hat{V}_{ee} + \hat{v}$, which is characterized by the operator $\hat{v}$ to some local external potential $v(\mathbf{r})$, shall be denoted by $E_v^{KS}[n]$, i.e.,

$$E_v^{KS}[n] = \langle \Phi^{KS}[n] | \hat{T} + \hat{V}_{ee} + \hat{v} | \Phi^{KS}[n] \rangle .$$

(3)

The HF wave function $\Phi^{HF}[n]$ for the same density $n(\mathbf{r})$ is defined here as the minimizing wave function in the expression [1,13]

$$\min_{\substack{\Psi \to n(\mathbf{r}) \\ \Psi \text{ is det}}} \{ \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle \} = \langle \Phi^{HF}[n] | \hat{T} + \hat{V}_{ee} | \Phi^{HF}[n] \rangle$$

(4)

and leads to

$$T^{HF}[n] = \langle \Phi^{HF}[n] | \hat{T} | \Phi^{HF}[n] \rangle$$

(5a)

and

$$E_x^{HF}[n] = \langle \Phi^{HF}[n] | \hat{V}_{ee} | \Phi^{HF}[n] \rangle - U[n] .$$

(5b)

In the minimization (4), the wave functions are not only constrained by the requirement that they have to yield $n(\mathbf{r})$, but additionally by the constraint that they have to be single Slater determinants, denoted by "Ψ is det." $T^{HF}[n]$ and $E_x^{HF}[n]$ are the HF kinetic and exchange energy, respectively. The expectation value of $\Phi^{HF}[n]$ with the Hamiltonian operator $\hat{H}_v$ defines $E_v^{HF}[n]$:

$$E_v^{HF}[n] = \langle \Phi^{HF}[n] | \hat{T} + \hat{V}_{ee} + \hat{v} | \Phi^{HF}[n] \rangle .$$

(6)

If the density $n(\mathbf{r})$ is the HF ground-state density $n_v^{HF}(\mathbf{r})$ of the Hamiltonian operator $\hat{H}_v$, then $E_v^{HF}[n_v^{HF}]$ is just the usual HF energy and $\Phi[n_v^{HF}]$ is the usual HF determinant corresponding to $\hat{H}_v$. This follows from combining the standard definition of the HF determinant as the Slater determinant that minimizes the expectation value of $\hat{H}_v$ with the density-based definition given here in Eq. (4).

The KS wave function $\Phi^{KS}[n]$ can be shown [1] to be the ground-state wave function of a noninteracting Schrödinger equation with an effective local potential $v_s(\mathbf{r})$:

$$[\hat{T} + \hat{v}_s] \Phi^{KS}[n] = E_s \Phi^{KS}[n] .$$

(7)

At this point we make the common assumption that all densities occurring here are noninteracting v representable [1], i.e., that all our densities are ground-state densities of Eq. (7) with an appropriately chosen local potential $v_s(\mathbf{r})$. Note that the energy eigenvalue E_s of $\Phi^{KS}[n]$ is neither the ground-state energy of a real interacting system with density $n(\mathbf{r})$, nor the HF energy of such a system. It follows from the Hohenberg-Kohn theorem [1] that the effective potential $v_s(\mathbf{r})$ is uniquely determined by the density $n(\mathbf{r})$ up to an additive constant. The other way around each ground state of a noninteracting Schrödinger equation with local potential, Eq. (7), fulfills a minimization (1) with the constraining density being the ground-state density of the Schrödinger equation (7) [1]. If, as in the systems considered in this work, no degeneracies occur, then the KS wave function $\Phi^{KS}[n]$, like $\Phi^{HF}[n]$, is a single determinant. The reason for this is that there is no electron-electron interaction present in the minimization (1). Therefore the KS equation (7) decouples naturally into the corresponding one-particle equations. In contrast to this, the HF wave function $\Phi^{HF}[n]$ is a single determinant because of the expli-

cit constraint appearing in the minimization (4).

Next, we define the difference $\Delta T[n]$ between the KS and the HF kinetic energies, the difference $\Delta E_x[n]$ between the KS and HF exchange energies, and the sum $\Delta E_c[n]$ of $\Delta T[n]$ and $\Delta E_x[n]$ which is equal to the difference between $E_v^{HF}[n]$ and $E_v^{KS}[n]$ for any potential $v(\mathbf{r})$:

$$\Delta T[n] = T^{HF}[n] - T_s^{KS}[n] \geq 0 , \tag{8a}$$

$$\Delta E_x[n] = E_x^{HF}[n] - E_x^{KS}[n] \leq 0 , \tag{8b}$$

$$\Delta E_c[n] = \Delta T[n] + \Delta E_x[n] = E_v^{HF}[n] - E_v^{KS}[n] \leq 0 . \tag{8c}$$

The inequalities (8a)–(8c) follow from the minimizations (1) and (4) by noting that both $\Phi^{KS}[n]$ and $\Phi^{HF}[n]$ are single determinants [1(f)]. The energy $\Delta E_c[n]$ is a part of the DFT correlation energy $E_c^{KS}[n]$ and is *not* the correlation energy of standard *ab initio* theory, which is defined as the difference between the true ground-state energy and the HF energy of a system. In order to define the DFT correlation energy $E_c^{KS}[n]$, we introduce the Hohenberg-Kohn functional $F[n]$ [1],

$$F[n] = \min_{\Psi \to n(\mathbf{r})} \{ \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle \} . \tag{9}$$

The minimizing wave function in Eq. (9), in contrast to Φ^{KS} and Φ^{HF}, is not a single Slater determinant but rather a linear combination of, in general, infinitely many Slater determinants. If $n(\mathbf{r})$ is the ground-state density of some electronic system, then the minimizing wave function in Eq. (9) is the ground state of the system and $F[n]$ is the sum of the kinetic and electron-electron repulsion energy of this ground state. The DFT [1] correlation energy $E_c^{KS}[n]$ is then given by

$$E_c^{KS}[n] = F[n] - T_s^{KS}[n] - U[n] - E_x^{KS}[n] . \tag{10}$$

A correlation energy $E_c^{HF}[n]$, related to the HF determinant $\Phi^{HF}[n]$, is defined by

$$E_c^{HF}[n] = F[n] - T^{HF}[n] - U[n] - E_x^{HF}[n] . \tag{11}$$

The correlation energy $E_c^{HF}[n]$, like $E_c^{KS}[n]$, is *not* the *ab initio* correlation energy. A fundamental difference between $E_c^{HF}[n]$ as well as $E_c^{KS}[n]$ and the *ab initio* correlation energy is that the former are defined through density functionals which all belong to one density, whereas the latter results from energies connected with different densities, namely, the exact ground-state density and the HF density (see also Sec. V). Therefore the *ab initio* correlation energy cannot be expressed as easily as $E_c^{HF}[n]$ or $E_c^{KS}[n]$ as a pure density functional without referring to an external potential. Equations (8), (10), and (11) show that $\Delta E_c[n]$ is the difference between the correlation energies $E_c^{KS}[n]$ and $E_c^{HF}[n]$:

$$\Delta E_c[n] = E_c^{KS}[n] - E_c^{HF}[n] . \tag{12}$$

From a DFT point of view, the energy $\Delta E_c[n]$ is a part of the correlation energy which is contained in the energy of a HF determinant.

With these formal definitions in hand, we can now report some details of our method and the results obtained.

Within the method of Ref. [21] which is used in this work to determine $\Phi^{KS}[n]$ for a given density $n(\mathbf{r})$, the effective potential $v_s(\mathbf{r})$ of Eq. (7) is expanded in a basis set. The method of Ref. [21] is essentially a procedure to determine the coefficients in the basis set expansion of $v_s(\mathbf{r})$ in a way that, if $v_s(\mathbf{r})$ is substituted into Eq. (7), the resulting ground-state wave function yields the given density $n(\mathbf{r})$ (for details see the Appendix and Refs. [21,28]). The ground-state HF densities which serve as reference densities are obtained by HF calculations using Gaussian basis sets [29]. The corresponding HF energies are identical up to μhartrees to those of numerical calculations given in Ref. [30] (except for Ca, which is not considered in Ref. [30]). For the KS orbitals, the same basis sets as in the HF calculations are used. The basis sets in which the electron densities and the exchange-correlation part of the effective potentials are expanded are derived from the orbital basis sets [28]. The deviations between the original HF densities and the densities recalculated from the corresponding KS wave functions were checked in the range from the origin (located at the nuclei) to ten Slater radii (radii attributed to atoms by an analysis of typical bond distances [31]) on logarithmic grids with about 1000 to 1500 points. The deviations were less than 10 ppm in the region up to one Slater radius (for Be and Mg the deviations are slightly higher). Beyond one Slater radius the relative error increases slowly but always stays under a tenth of a percent for densities higher than 10^{-4} a.u. The Coulomb energies of the original HF and the recalculated KS densities which should be identical differ by less than 10 μhartrees except in the cases of Mg (20 μhartrees) and Ca (120 μhartrees). The same is true for corresponding differences of the electron-nucleus attraction energies. The magnitude of these deviations serves as a criterion for the accuracy of the calculations.

The results for the considered atoms Be, Ne, Mg, Ar, and Ca are displayed in Table I. The Hamiltonian operator $\hat{H}_v$ of Eqs. (3) and (6) which determines the HF ground-state density n_v^{HF} is, of course, the corresponding atomic Hamiltonian operator here. Table I shows that the inequalities (8) are fulfilled. In Ref. [15] values for $E_x^{KS}[n_v^{HF}]$ and $\Delta T[n_v^{HF}]$ for beryllium of 2.667 and 0.0004 hartrees, respectively, are obtained. This is in fair agreement with our results if one takes into account that the deviations of the recalculated KS density from the original HF density are higher in Ref. [15] than in this work. The more accurate calculation of $T_s^{KS}[n_v^{HF}]$ for beryllium in Ref. [17] leads to a value of 14.5720 hartrees ($\Delta T[n_v^{HF}] = 0.0010$ hartrees) which is somewhat different from our result. This discrepancy remains to be solved. In Ref. [16] another very accurate calculation using a completely different approach yields values for $T_s^{KS}[n_v^{HF}]$ and $E_x^{KS}[n_v^{HF}]$ of beryllium which are identical to those found here. Therefore we believe that our result for $T_s^{KS}[n_v^{HF}]$ of beryllium is very close to the exact value. We also report that the value of $T_s^{KS}[n]$ obtained by the method of this work, when $n(\mathbf{r})$ is the *de facto* exact ground-state density of beryllium, differs by only 17 μhartrees from the value found in Ref. [26] by employing the same method as Ref. [16].

Table I shows that the differences $\Delta T[n_v^{HF}]$ and

TABLE I. Results for the atoms: Be, Ne, Mg, Ar, Ca.

	Be	Ne	Mg	Ar	Ca
$T^{HF}[n_v^{HF}]$	14.573 02	128.547 10	199.614 64	526.817 51	676.7582
$T_s^{KS}[n_v^{HF}]$	14.572 46	128.545 45	199.611 72	526.812 48	676.7522
$\Delta T[n_v^{HF}]$	0.000 56	0.001 65	0.002 92	0.005 03	0.0060
$E_x^{HF}[n_v^{HF}]$	−2.666 91	−12.108 35	−15.994 29	−30.184 94	−35.2112
$E_x^{KS}[n_v^{HF}]$	−2.665 76	−12.105 03	−15.988 33	−30.174 75	−35.1989
$\Delta E_x[n_v^{HF}]$	−0.001 15	−0.003 32	−0.005 96	−0.010 19	−0.0123
$E_v^{HF}[n_v^{HF}]$	−14.573 02	−128.547 10	−199.614 64	−526.817 51	−676.7582
E_v^{OPM} [a]	−14.572 43	−128.545 41	−199.611 58	−526.812 21	−676.7519
$E_v^{KS}[n_v^{HF}]$	−14.572 43	−128.545 42	−199.611 60	−526.812 36	−676.7520
$\Delta E_c[n_v^{HF}]$	−0.000 59	−0.001 67	−0.003 04	−0.005 16	−0.0062

[a]From Ref. [32(a)]; Ref. [32(b)] gives essentially the same values.

$\Delta E_x[n_v^{HF}]$ and subsequently $\Delta E_c[n_v^{HF}]$ are extremely small for all considered atoms. The magnitude of the difference $\Delta E_x[n_v^{HF}]$ is only about 0.03% to 0.04% of the total exchange energy. These findings justify, at least for closed shell atomic systems, the common practice of comparing exchange energies from approximate density functionals with HF reference values, as long as they differ by more than one-tenth or two-tenths of a percent. The latter is the case for today's approximations to exchange functionals which typically deviate by about half of one percent from the HF exchange energy [1,3]. If, however, the approximate exchange functionals could be improved further, one should use the correct DFT reference values, like the ones given in the fifth row of Table I, to check them (for example, in Ref. [3(a)], a parameter in an approximate exchange functional is adjusted such that the functional yields exchange energies which deviate only by about a tenth of a percent from the corresponding HF values).

From a formal point of view, these results are somewhat amazing, because they show that it makes almost no difference whether, for a given density, the determinant minimizing the expectation value of just $\hat{T}$ or of $\hat{T} + \hat{V}_{ee}$ is searched. This indicates that the operator $\hat{V}_{ee}$ has almost no influence on the minimization (4). A convincing theoretical explanation for this finding has yet to be found. The results, however, are in agreement with the well-known empirical finding in applications of KS and HF procedures on molecules, that HF and KS orbitals and therefore also the corresponding KS and KF determinants are quite similar. While the present work concentrates on the energies of KS and HF determinants, the similarities found here strongly suggest that other expectation values of KS and HF determinants also exhibit little difference. The similarities of other expectation values, however, may be less pronounced. (See Ref. [7] for the related comparison of determinants obtained by the HF scheme and by the optimized potential method [8] discussed in the next section.)

III. ENERGIES FROM THE OPTIMIZED POTENTIAL METHOD

The energies E_v^{OPM} in Table I are the expectation values of the atomic Hamiltonian operators $\hat{H}_v$ with

Slater determinants resulting from the optimized potential method (OPM) [8]. The OPM determinant is the one that yields the lowest energy expectation value of a given Hamiltonian operator, here an atomic $\hat{H}_v$, from among all determinants which are ground-state wave functions of a noninteracting Schrödinger equation with some local potential. The latter constraint leads to $E_v^{OPM} \geq E_v^{HF}[n_v^{HF}]$. On the other hand, the inequality $E_v^{KS}[n_v^{HF}] \geq E_v^{OPM}$ holds because, while both the KS determinant $\Phi^{KS}[n_v^{HF}]$ and the OPM determinant belong to a noninteracting Schrödinger equation with a local potential, the KS determinant $\Phi^{KS}[n_v^{HF}]$ is further constrained by the requirement that it has to yield the HF density, while the density from the OPM determinant is completely free. The combination of the two inequalities, consistently with inequality (8c), gives

$$E_v^{KS}[n_v^{HF}] \geq E_v^{OPM} \geq E_v^{HF}[n_v^{HF}] \ . \tag{13}$$

Table I shows that the KS and the OPM energies, $E_v^{KS}[n_v^{HF}]$ and E_v^{OPM}, respectively, are almost identical, i.e., the equal sign practically holds for the left relation (13). (The fact that except for Be the values found for $E_v^{KS}[n_v^{HF}]$ are very slightly lower than the values for E_v^{OPM} has to be attributed to computational inaccuracies.) The OPM determinant, like $\Phi^{KS}[n_v^{HF}]$, is a KS determinant because, by construction, it is the ground state of a noninteracting Schrödinger equation with a local potential. Therefore it fulfills the minimization (1). The constraining density of the minimization (1) for the OPM determinant, however, is not the HF density $n_v^{HF}(\mathbf{r})$ but the OPM density, i.e., the density resulting from the OPM as described above. However, in Refs. [7,32(b)], it is found that the two densities are very close. The fact that the energies $E_v^{KS}[n_v^{HF}]$ and E_v^{OPM} are almost identical shows that this little difference in the density has almost no effect on the energies of the corresponding KS determinants, i.e., the OPM determinant and the KS determinant $\Phi^{KS}[n_v^{HF}]$. The energies of the Slater determinants are affected more strongly by the type of minimization by which they are determined. For $\Phi^{HF}[n_v^{HF}]$ this is minimization (4), whereas for $\Phi^{KS}[n_v^{HF}]$ and the OPM determinant it is minimization (1). For the OPM determinant the minimization has to be performed

with respect to the OPM density, in the other two cases with respect to n_v^{HF}.

IV. SCALING OF THE ELECTRON-ELECTRON INTERACTION BY A COUPLING CONSTANT

Next, the influence of a coupling parameter α, with $0 \le \alpha \le 1$, which turns on the electron-electron interaction, is investigated. We define the α-dependent kinetic and exchange energies, $^{\alpha}T^{HF}[n]$ and $^{\alpha}E_x^{HF}[n]$, respectively, as

$$\langle \,^{\alpha}\Phi^{HF}[n]|\hat{T}+\alpha\hat{V}_{ee}|\,^{\alpha}\Phi^{HF}[n]\rangle$$
$$= \min_{\substack{\Psi \to n(\mathbf{r}) \\ \Psi \text{ is det}}} \{\langle \Psi|\hat{T}+\alpha\hat{V}_{ee}|\Psi\rangle\} \ , \quad (14)$$

$$^{\alpha}T^{HF}[n] = \langle \,^{\alpha}\Phi^{HF}[n]|\hat{T}|\,^{\alpha}\Phi^{HF}[n]\rangle \ , \quad (15a)$$

$$^{\alpha}E_x^{HF}[n] = \langle \,^{\alpha}\Phi^{HF}[n]|\hat{V}_{ee}|\,^{\alpha}\Phi^{HF}[n]\rangle - U[n] \ . \quad (15b)$$

In the above equations, $^{\alpha}\Phi^{HF}[n]$ is the minimizing Slater determinant of Eq. (14). Now the minimization

$$\langle \,^{\alpha}\Phi_v^{HF}[n]|\hat{T}+\alpha\hat{V}_{ee}+\hat{v}|\,^{\alpha}\Phi_v^{HF}[n]\rangle$$
$$= \min_{\Psi \text{ is det}} \{\langle \Psi|\hat{T}+\alpha\hat{V}_{ee}+\hat{v}|\Psi\rangle\} \quad (16)$$

is considered. Its minimizing determinant $^{\alpha}\Phi_v^{HF}$ defines the density $^{\alpha}n_v^{HF}(\mathbf{r})$. The potential $v(\mathbf{r})$ leading to the operator $\hat{T}+\alpha\hat{V}_{ee}+\hat{v}$, of course, is the potential of an atomic nucleus here. Note that this is not the usual coupling constant variation of DFT [1], because the external potential is being held fixed here and not adjusted to keep the density constant. The densities $^{\alpha}n_v^{HF}(\mathbf{r})$ change with α. In Fig. 1 the differences $^{\alpha}T^{HF}[^{\alpha}n_v^{HF}]-T_s^{KS}[^{\alpha}n_v^{HF}]$ and $^{\alpha}E_x^{HF}[^{\alpha}n_v^{HF}]-E_x^{KS}[^{\alpha}n_v^{HF}]$ for various values of α are
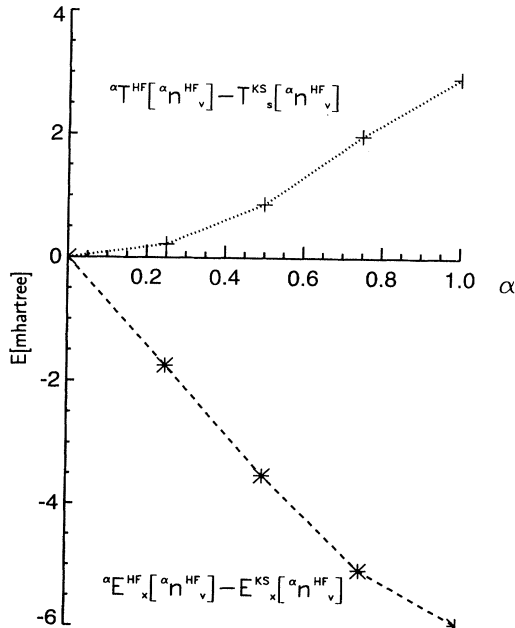

FIG. 1. Differences between KS and HF kinetic and exchange energies with varying coupling constant α.

displayed for magnesium. For $\alpha=0$, the differences are zero because in this case the minimizations (1) and (14) are identical. The results shown in Table I correspond to a coupling constant $\alpha=1$. As expected from theory, the magnitude of the differences displayed in Fig. 1 increases steadily with increasing α.

V. HYBRID METHODS BETWEEN THE KS AND HF SCHEME

In this section, hybrid methods [4-14] lying between the KS and HF schemes are briefly reviewed, focusing on the various exchange and correlation density functionals used and on their differences. In most cases, these differences turn out to be related to the difference $\Delta E_c[n]$ between the correlation energies $E_c^{KS}[n]$ and $E_c^{HF}[n]$ defined in Eqs. (10) and (11), with the pertinent density $n(\mathbf{r})$ being the exact ground-state density or the HF density of the given system. The ground-state energy of an electronic system, which is determined by the external potential $v(\mathbf{r})$, usually the potential of the nuclei, and by the electron number N is given by

$$E_v = F[n_v^0] + \int d\mathbf{r}\, v(\mathbf{r})n_v^0(\mathbf{r}) \ , \quad (17)$$

where the density $n_v^0(\mathbf{r})$ is the exact ground-state density of the system. The various hybrid methods are obtained by decomposing the functional $F[n_v^0]$ or in other cases the energy E_v in different ways. Subsequently one derives different one-particle Schrödinger equations for orbitals. These orbitals build Slater determinants which characterize model systems or approximations to the exact ground state and allow the direct calculation of certain parts of the ground-state energy E_v without using density functionals. The remaining contributions to E_v are determined through density functionals. The various methods we consider here follow.

(i) The standard KS scheme, the reference method, is obtained by the following decomposition of the functional $F[n]$ [1]:

$$F[n_v^0] = T_s^{KS}[n_v^0] + U[n_v^0] + E_x^{KS}[n_v^0] + E_c^{KS}[n_v^0] \ . \quad (18)$$

The corresponding Slater determinant, the KS determinant $\Phi^{KS}[n_v^0]$, is given by the Schrödinger equation

$$(\hat{T}+\hat{v}+\hat{u}[n_v^0]+\hat{v}_x^{KS}[n_v^0]+\hat{v}_c^{KS}[n_v^0])\Phi^{KS}[n_v^0]$$
$$= E_s[n_v^0]\Phi^{KS}[n_v^0] \ . \quad (19)$$

Equation (19) decouples into corresponding single-particle equations for the orbitals building $\Phi^{KS}[n_v^0]$. The potentials $u([n_v^0];\mathbf{r})$, $v_x^{KS}([n_v^0];\mathbf{r})$, and $v_c^{KS}([n_v^0];\mathbf{r})$ leading to the operators $\hat{u}[n_v^0]$, $\hat{v}_x^{KS}[n_v^0]$, and $\hat{v}_c^{KS}[n_v^0]$, respectively, are the functional derivatives with respect to the density of $U[n_v^0]$, $E_x^{KS}[n_v^0]$, and $E_c^{KS}[n_v^0]$, respectively. Of course, Eq. (19) is a nonlinear equation and has to be solved iteratively in order to calculate the KS determinant $\Phi^{KS}[n_v^0]$ and therewith the exact ground-state density $n_v^0(\mathbf{r})$. Whereas the classical Coulomb potential $u([n_v^0];\mathbf{r})$ is known exactly, approximations have to be employed for the potentials $v_x^{KS}([n_v^0];\mathbf{r})$ and $v_c^{KS}([n_v^0];\mathbf{r})$. The contributions to the ground-state energy E_v given by

$T_s^{KS}[n_v^0]$, $U[n_v^0]$, $E_x^{KS}[n_v^0]$, and $\int d\mathbf{r}\, v(\mathbf{r}) n_v^0(\mathbf{r})$, which sum up to $E_v^{KS}[n_v^0]$, can be calculated directly from the KS determinant $\Phi^{KS}[n_v^0]$ and the density $n_v^0(\mathbf{r})$ using Eq. (3), without making further approximations. The contribution of the correlation energy $E_c^{KS}[n_v^0]$ to E_v has to be determined by evaluating an approximation to the density functional $E_c^{KS}[n_v^0]$. In actual implementations of the KS scheme, the exchange energy $E_x^{KS}[n_v^0]$ is usually also calculated via an approximate density functional for technical reasons.

(ii) A modified HF procedure [4] which yields the correct ground-state energy and density results if the functional $F[n_v^0]$ is written as

$$F[n_v^0] = T^{HF}[n_v^0] + U[n_v^0] + E_x^{HF}[n_v^0] + E_c^{HF}[n_v^0] \qquad (20a)$$

$$= T^{HF}[n_v^0] + U[n_v^0] + E_x^{HF}[n_v^0]$$
$$+ E_c^{KS}[n_v^0] - \Delta E_c[n_v^0] \,, \qquad (20b)$$

where Eq. (20b) follows from Eq. (20a) by using Eq. (12). The corresponding equations

$$(\hat{T} + \hat{v} + \hat{u}[n_v^0] + \hat{v}_x^{nl}[n_v^0] + \hat{v}_c^{HF}[n_v^0])\Phi^{HF}[n_v^0]$$
$$= E^{nl}[n_v^0]\Phi^{HF}[n_v^0] \qquad (21a)$$

and

$$(\hat{T} + \hat{v} + \hat{u}[n_v^0] + \hat{v}_x^{nl}[n_v^0] + \hat{v}_c^{KS}[n_v^0] - \hat{v}_{\Delta c}[n_v^0])\Phi^{HF}[n_v^0]$$
$$= E^{nl}[n_v^0]\Phi^{HF}[n_v^0] \qquad (21b)$$

for the HF determinant $\Phi^{KS}[n_v^0]$ are identical to the standard HF equations except for the appearance of the operator $\hat{v}_c^{HF}[n_v^0]$ generated by the potential $v_c^{HF}(\mathbf{r})$ which is the functional derivative of $E_c^{HF}[n]$ with respect to the density. In Eq. (21b) the operator $\hat{v}_c^{HF}[n_v^0]$ is written as $\hat{v}_c^{HF}[n_v^0] - \hat{v}_{\Delta c}[n_v^0]$ with $\hat{v}_{\Delta c}[n_v^0]$ being generated by the potential $v_{\Delta c}([n_v^0];\mathbf{r})$ which is the functional derivative of $\Delta E_c[n_v^0]$ with respect to the density. The operator $\hat{v}_x^{nl}[n_v^0]$ is the usual nonlocal HF exchange operator built from the orbitals which generate $\Phi^{HF}[n_v^0]$. Note that the energy eigenvalue $E^{nl}[n_v^0]$ is neither the exact ground-state energy E_v nor the energy $E_v^{HF}[n_v^0]$ which is obtained if $\Phi^{HF}[n_v^0]$ is inserted into Eq. (6). Because of the extra potential $v_c^{HF}([n_v^0];\mathbf{r})$, the HF determinant resulting from Eq. (21) yields the exact ground-state density and not the HF density. For the unknown potential $v_c^{HF}([n_v^0];\mathbf{r})$, or alternatively $v_c^{KS}([n_v^0];\mathbf{r}) - v_{\Delta c}([n_v^0];\mathbf{r})$, a suitable approximation must be employed. All parts of the ground-state energy E_v, except $E_c^{HF}[n_v^0]$, can then be determined directly without further assumptions, from $\Phi^{HF}[n_v^0]$ using Eq. (6). The correlation energy $E_c^{HF}[n_v^0]$, or alternatively $E_c^{KS}[n_v^0] - \Delta E_c[n_v^0]$, must be evaluated through an approximate density functional.

(iii) To obtain an exchange-only KS procedure [6,7], the approximation

$$F[n_v^0] \approx T_s^{KS}[n_v^{XO}] + U[n_v^{XO}] + E_x^{KS}[n_v^{XO}] \qquad (22)$$

for the functional $F[n_v^0]$ is made. The Schrödinger equation for the corresponding exchange-only determinant $\Phi_v^{KS}[n_v^{XO}]$ which, like $\Phi_v^{KS}[n_v^0]$, but unlike $\Phi_v^{HF}[n_v^0]$, is a

KS determinant, is given by

$$(\hat{T} + \hat{v} + \hat{u}[n_v^{XO}] + \hat{v}_x^{KS}[n_v^{XO}])\Phi^{KS}[n_v^{XO}]$$
$$= E_s[n_v^{XO}]\Phi^{KS}[n_v^{XO}] \,. \qquad (23)$$

The exchange-only procedure, due to the neglect of correlation, leads to a single Slater determinant $\Phi_v^{KS}[n_v^{XO}]$ which yields the exchange-only density $n_v^{XO}(\mathbf{r})$ instead of the exact ground-state density $n_v^0(\mathbf{r})$. As in the standard KS scheme, the potential $v_x^{KS}([n_v^{XO}];\mathbf{r})$ must be approximated. The ground-state energy from the exchange-only scheme, of course, is also not exact. It can be calculated directly, without further approximations, as $E_v^{KS}[n_v^{XO}]$ from $\Phi_v^{KS}[n_v^{XO}]$ using Eq. (3). The exchange contribution $E_x^{KS}[n_v^{XO}]$, however, is usually determined via an approximate density functional. The exchange-only method can be considered as a regular KS scheme in which the approximate correlation functional is $\tilde{E}_c^{KS} = 0$, leading to a correlation potential $\tilde{v}_c^{KS}(\mathbf{r}) = 0$. The optimized potential method [8] constitutes a procedure which implements the exchange-only scheme exactly without using an approximate exchange potential. The OPM exploits the fact that the exchange-only determinant $\Phi_v^{KS}[n_v^{XO}]$ is, out of the set of determinants which are ground states to a noninteracting Schrödinger equation (7) with a local multiplicative potential, the one which minimizes the expectation value of the exact interacting Hamiltonian operator of the system [6–9]. The OPM performs this minimization directly and not via Eq. (23). In this way the necessity to use an approximation for the potential $v_x^{KS}([n_v^{XO}];\mathbf{r})$ is circumvented. Instead, the exact potential $v_x^{KS}([n_v^{XO}];\mathbf{r})$ is obtained as a result of the OPM. However, the OPM in most cases leads to integral equations which must be solved numerically and therefore has been applied only to atoms [8,32] and model systems [33] so far.

(vi) A KS scheme leading to the HF energy $E_v^{HF}[n_v^{HF}]$ and density $n_v^{HF}(\mathbf{r})$ is obtained if the HF energy instead of the exact ground-state energy E_v is expressed by density functionals [5–7,9,10],

$$E_v^{HF}[n_v^{HF}] = T^{HF}[n_v^{HF}] + U[n_v^{HF}] + E_x^{HF}[n_v^{HF}]$$
$$+ \int d\mathbf{r}\, v(\mathbf{r}) n_v^{HF}(\mathbf{r}) \qquad (24a)$$

$$= T_s^{KS}[n_v^{HF}] + U[n_v^{HF}] + E_x^{KS}[n_v^{HF}]$$
$$+ \Delta E_c[n_v^{HF}] + \int d\mathbf{r}\, v(\mathbf{r}) n_v^{HF}(\mathbf{r}) \,. \qquad (24b)$$

The corresponding KS determinant $\Phi^{KS}[n_v^{HF}]$ which yields the HF density $n_v^{HF}(\mathbf{r})$ is the ground state to the Schrödinger equation

$$(\hat{T} + \hat{v} + \hat{u}[n_v^{HF}] + \hat{v}_x^{KS}[n_v^{HF}] + \hat{v}_{\Delta c}[n_v^{HF}])\Phi^{KS}[n_v^{HF}]$$
$$= E_s[n_v^{HF}]\Phi^{KS}[n_v^{HF}] \,. \qquad (25)$$

The unknown potentials $v_x^{KS}([n_v^{HF}];\mathbf{r})$ and $v_{\Delta c}([n_v^{HF}];\mathbf{r})$ must be approximated. All contributions to $E_v^{HF}[n_v^{HF}]$, except $\Delta E_c[n_v^{HF}]$, can be obtained directly from the determinant $\Phi^{KS}[n_v^{HF}]$ with Eq. (3). This scheme in Refs. [6,9] has been given the name Hartree-Fock density-functional theory (HFDFT). It is merely of formal in-

terest, because it requires the same effort and similar approximations as the standard KS method, but does not aim on the exact ground-state energy E_v, but only on an approximation to it, namely, the HF energy. The fact that the HFDFT procedure results from a decomposition of $E_v^{HF}[n_v^{HF}]$, and not of E_v or equivalently $F[n_v^0]$, distinguishes this method from the others discussed in this section.

The calculation of the KS determinant $\Phi^{KS}[n_v^{HF}]$ and of the corresponding energies from a given HF density $n_v^{HF}(\mathbf{r})$, which was the central point of this work, leads to the same results as those one would obtain if the HFDFT procedure could be performed exactly. In contrast to the approach of this work, the HFDFT procedure does not require that the HF density is known. Of course, if the HFDFT is actually carried out, by solving Eq. (25), in practice the employment of approximations for $v_x^{KS}([n_v^{HF}];\mathbf{r})$ and $v_{Ac}([n_v^{HF}];\mathbf{r})$ introduces errors. Therefore results from a HFDFT calculation, performed according to Eq. (25), will not be exact, in contrast to the results obtained in this work.

(v) A scheme which delivers the exact ground-state energy, but not the exact ground-state density, results from a decomposition of $F[n]$ and the total energy E_v according to [12,13]

$$E_v = T^{HF}[n_v^{HF}] + U[n_v^{HF}] + E_x^{HF}[n_v^{HF}] + \int d\mathbf{r}\, v(\mathbf{r}) n_v^{HF}(\mathbf{r})$$
$$+ \left[T^{HF}[n_v^0] - T^{HF}[n_v^{HF}] + U[n_v^0] - U[n_v^{HF}] + E_x^{HF}[n_v^0] - E_x^{HF}[n_v^{HF}] + E_c^{HF}[n_v^0] + \int d\mathbf{r}\, v(\mathbf{r})[n_v^0(\mathbf{r}) - n_v^{HF}(\mathbf{r})] \right] \tag{26a}$$

$$= E_v^{HF}[n_v^{HF}] + E_{c,v}^{QM}, \tag{26b}$$

where

$$E_{c,v}^{QM} = E_c^{HF}[n_v^0] + \{ T^{HF}[n_v^0] - T^{HF}[n_v^{HF}] + U[n_v^0] - U[n_v^{HF}] + E_x^{HF}[n_v^0] - E_x^{HF}[n_v^{HF}] + \int d\mathbf{r}\, v(\mathbf{r})[n_v^0(\mathbf{r}) - n_v^{HF}(\mathbf{r})] \} \tag{27a}$$

$$= E_c^{KS}[n_v^{HF}] - \Delta E_c[n_v^{HF}] + \left[T_s^{KS}[n_v^0] - T_s^{KS}[n_v^{HF}] + U[n_v^0] - U[n_v^{HF}] + E_x^{KS}[n_v^0] - E_x^{KS}[n_v^{HF}] \right.$$
$$\left. + E_c^{KS}[n_v^0] - E_c^{KS}[n_v^{HF}] + \int d\mathbf{r}\, v(\mathbf{r})[n_v^0(\mathbf{r}) - n_v^{HF}(\mathbf{r})] \right]. \tag{27b}$$

The energy $E_{c,v}^{QM}$ is the correlation energy as defined in *ab initio* theory because $E_v^{HF}[n_v^{HF}]$ [see Eq. (6)] is the standard HF energy. Next, one exploits the fact that the HF density $n_v^{HF}(\mathbf{r})$ formally determines the exact ground-state density $n_v^0(\mathbf{r})$, which therefore can be considered as functional $n_v^0([n_v^{HF}];\mathbf{r})$ of $n_v^{HF}(\mathbf{r})$ [12,13]. This follows from the fact that the Hohenberg-Kohn theorem is also valid within the HF formalism [5], which implies that the HF density determines the external potential $v(\mathbf{r})$. For a given electron number N which is also given by the HF density the potential $v(\mathbf{r})$ subsequently determines the exact ground-state density. This allows us to interpret $E_{c,v}^{QM}$ as a functional of the HF density $n_v^{HF}(\mathbf{r})$, and to write Eq. (27b) as

$$E_{c,v}^{QM}[n_v^{HF}] = E_c^{KS}[n_v^{HF}] - \Delta E_c[n_v^{HF}] + \left[T_s^{KS}[n_v^0[n_v^{HF}]] - T_s^{KS}[n_v^{HF}] + U[n_v^0[n_v^{HF}]] - U[n_v^{HF}] \right.$$
$$+ E_x^{KS}[n_v^0[n_v^{HF}]] - E_x^{KS}[n_v^{HF}] + E_c^{KS}[n_v^0[n_v^{HF}]] - E_c^{KS}[n_v^{HF}]$$
$$\left. + \int d\mathbf{r}\, v(\mathbf{r})\{ n_v^0([n_v^{HF}];\mathbf{r}) - n_v^{HF}(\mathbf{r}) \} \right]. \tag{28}$$

Within this scheme, the exact ground-state energy is calculated by carrying out a standard HF calculation. This leads to the HF density and to all contributions of E_v given in Eq. (26), except $E_{c,v}^{QM}$. The correlation energy $E_{c,v}^{QM}$ must be taken into account by an approximation to the density functional $E_{c,v}^{QM}[n_v^{HF}]$ of Eq. (28). In Ref. [14] this scheme is applied and called HFDFT procedure, just as the preceding scheme (iv) was. Of course, the two methods are different and using the same name for both might lead to confusion. In this work the term HFDFT is used exclusively for the scheme (iv).

Approximate exchange and correlation density functionals currently available [1] are derived to describe the exchange and correlation energies $E_x^{KS}[n]$ and $E_c^{KS}[n]$, as well as the corresponding potentials $v_x^{KS}(\mathbf{r})$ and $v_c^{KS}(\mathbf{r})$ which emerge in the standard KS formalism. Therefore, from a strict and formal point of view, today's approximate exchange-correlation functionals should be employed only in the standard KS procedure (i) and the related exchange-only scheme (iii). However, the results of

this work, i.e., the small value of the difference $\Delta E_c[n]$, suggests that it leads only to very small errors, if the quantities $E_c^{HF}[n]$ and $v_c^{HF}(\mathbf{r})$ appearing in the method (ii) are treated by approximations to the formally different quantities $E_c^{KS}[n]$ and $v_c^{KS}(\mathbf{r})$ of the standard KS formalism. This is not an absolutely strict conclusion, mainly for two reasons. First, we have investigated only closed shell atoms and it remains to be seen whether our findings for these systems can be generalized also to molecules and solids. Secondly, small differences between the functionals $E_c^{KS}[n]$ and $E_c^{HF}[n]$ for certain densities are not a strict proof that differences between the corresponding functional derivatives, $v_c^{KS}(\mathbf{r})$ and $v_c^{HF}(\mathbf{r})$, are small too.

The HFDFT scheme (iv) yields the HF energy $E_v^{HF}[n_v^{HF}]$ and density $n_v^{HF}(\mathbf{r})$. However, if the terms $\Delta E_c[n_v^{HF}]$ and $v_{\Delta c}([n_v^{HF}];\mathbf{r})$ in Eqs. (24b) and (25) are neglected scheme (iv) becomes identical to the exchange-only scheme (iii). The small differences between the results from the exchange-only procedure (or equivalently the OPM) and the HF procedure found for atoms [7,32] must therefore originate in the quantities $\Delta E_c[n_v^{HF}]$ and $v_{\Delta c}([n_v^{HF}];\mathbf{r})$. Scheme (iv), if performed exactly, leads to the HF density $n_v^{HF}(\mathbf{r})$ and not to the exchange-only or OPM density $n_v^{XO}(\mathbf{r})$ of scheme (iii). The difference between $n_v^{HF}(\mathbf{r})$ and $n_v^{XO}(\mathbf{r})$ is caused by the potential $v_{\Delta c}([n_v^{HF}];\mathbf{r})$. The difference between the corresponding HF and OPM energies is caused by $\Delta E_c[n_v^{HF}]$ and also indirectly by $v_{\Delta c}([n_v^{HF}];\mathbf{r})$ through the difference between the densities $n_v^{HF}(\mathbf{r})$ and $n_v^{XO}(\mathbf{r})$ which also affects all other parts of the energy. The latter contribution is negligible for the systems considered here. This can be concluded from the results of Sec. III, which show that the determinants $\Phi^{KS}[n_v^{HF}]$ and $\Phi^{KS}[n_v^{XO}]$, for closed shell atoms, yield practically identical energies, despite their somewhat different densities. For the model system of the cubic electron gas this does not hold. In this case, unlike as for closed shell atoms, the differences between the HFDFT scheme (iv) and the OPM turn out to be quite significant, at least as far as the one-particle eigenvalues are concerned [33].

The question of how far it is justified to employ approximations to $E_c^{KS}[n_v^{HF}]$ for the calculation of $E_{c,v}^{QM}[n_v^{HF}]$ cannot be answered completely by the results of this work. The difference between the correlation energies $E_{c,v}^{QM}[n_v^{HF}]$ and $E_c^{KS}[n_v^{HF}]$ consists of two contributions, the term $(-)\Delta E_c[n_v^{HF}]$, plus the sum of the terms in the large parentheses of the right-hand side of Eq. (28). The results of this work suggest that the first contribution, $(-)\Delta E_c[n_v^{HF}]$, is small. The second contribution has its origin in the different involved densities, namely, the HF density $n_v^{HF}(\mathbf{r})$ and the exact ground-state density $n_v^0(\mathbf{r})$. Its magnitude remains to be investigated. The functional $E_{c,v}^{QM}[n_v^{HF}]$, from a formal point of view, is much more difficult to study than the correlation energy functionals $E_c^{KS}[n]$ or $E_c^{HF}[n]$. The reason is that $E_c^{KS}[n]$ or $E_c^{HF}[n]$ are functionals of a density $n(\mathbf{r})$ and give an energy which is determined by wave functions belonging to that density $n(\mathbf{r})$, whereas $E_{c,v}^{QM}[n_v^{HF}]$ is a functional of one density, the HF density, and gives an energy which depends in part on a wave function, that of the exact ground state, to another density, namely, the exact ground-state density. In other words the functional $E_{c,v}^{QM}[n_v^{HF}]$, in contrast to the other correlation functionals, formally contains the additional step of deducing the exact ground-state density from the HF density. Therefore method (v) introduces additional formal difficulties. On the other hand, from a practical point of view, method (v) is very appealing, because it is conceptually simple and requires only a single evaluation of a density functional after a standard HF procedure has been carried out.

APPENDIX: LINEAR RESPONSE METHOD TO DETERMINE KOHN-SHAM WAVE FUNCTIONS FROM ELECTRON DENSITIES

In this appendix, the method of Ref. [21] to generate the KS wave functions to a given electron density is briefly reviewed and the implementation of the procedure employed in this work is discussed. The method of Ref. [21] is based on the noninteracting N-electron Schrödinger equation

$$[\hat{T}+\hat{v}_s]\Phi^{KS}=E_s\Phi^{KS} , \tag{A1}$$

characterized by the potential $v_s(\mathbf{r})$ generating the operator $\hat{v}_s$ [Eq. (A1) is identical to Eq. (7) of the main text; it is repeated here for clarity]. At this point, $v_s(\mathbf{r})$ is an arbitrary local multiplicative potential. The ground-state wave function Φ^{KS} of the Schrödinger equation (A1) is that N-electron wave function which gives the minimal expectation value with the Hamiltonian operator $[\hat{T}+\hat{v}_s]$. As a consequence Φ^{KS} is, among all wave functions which yield the ground-state density to the Schrödinger Eq. (A1) and which therefore give the same expectation value with the operator $\hat{v}_s$, that one which minimizes the expectation value with the operator of the kinetic energy $\hat{T}$. This property is precisely the one used in Eq. (1) to define the KS wave function to a given density. Therefore each ground-state wave function Φ^{KS} of a Schrödinger equation (A1) is the KS wave function of the corresponding ground-state density. This justifies the superscript KS attached to Φ^{KS}. Note that for the identification of the ground-state wave function of Eq. (A1) with the KS determinant of the corresponding ground-state density, the Hohenberg-Kohn theorem [1] is not involved if the KS determinant is defined according to Eq. (1). Indeed, if two different potentials $v_s(\mathbf{r})$ were to lead to the same ground-state density, the above argument remains valid, and shows that the two potentials $v_s(\mathbf{r})$ would also have the same ground-state wave func-

tion, namely, the KS determinant corresponding to the common ground-state density. The ground-state wave function of a Schrödinger equation (A1), of course, determines up to an additive constant uniquely the potential $v_s(\mathbf{r})$. To see this simply divide the representation of Eq. (A1) in ordinary space by the ground-state wave function Φ^{KS}. Therefore no two potentials $v_s(\mathbf{r})$ differing by more than a constant yield the same ground-state density or the same ground-state wave function. Thus the identification of Φ^{KS} of Eq. (A1) as the KS determinant also leads to a proof, the constrained-search proof [1], of the Hohenberg-Kohn theorem, which states that there can be, within the addition of a constant, at most one potential $v_s(\mathbf{r})$ generating via Eq. (A1) a ground-state wave function Φ^{KS} which yields a given density $n(\mathbf{r})$. The other way around, a potential $v_s(\mathbf{r})$ determines uniquely a ground-state density $n(\mathbf{r})$, if no degeneracies are present. (For simplicity we assume throughout this work that no degeneracies are present; for a discussion of degeneracies and symmetries see Ref. [34].) Therefore the Hohenberg-Kohn theorem establishes a one to one mapping between ground-state densities and potentials.

The method of Ref. [21] is a procedure to determine that local multiplicative potential $v_s([n];\mathbf{r})$ which leads via Eq. (A1) to a ground-state density which is identical to some given reference density $n(\mathbf{r})$. The corresponding ground-state wave function then is the KS wave function $\Phi^{KS}[n]$ corresponding to $n(\mathbf{r})$. The discussion of the preceding paragraph shows that the two conditions that a wave function yields the reference density $n(\mathbf{r})$ and that it is the ground state to a Schrödinger equation (A1) are sufficient to guarantee that the wave function is the KS wave function $\Phi^{KS}[n]$ to $n(\mathbf{r})$. In other words, once it is demonstrated that the solution Φ^{KS} of Eq. (A1) yields $n(\mathbf{r})$ any possible shortfalls of the method used to obtain the corresponding potential $v_s([n];\mathbf{r})$ are irrelevant. The Hohenberg-Kohn theorem which guarantees that the potential $v_s([n];\mathbf{r})$ is unique, except for an addition of a constant, is not used to identify $\Phi^{KS}[n]$ as the KS wave function of $n(\mathbf{r})$. The Hohenberg-Kohn theorem or the uniqueness of $v_s([n];\mathbf{r})$, however, is exploited by the method of Ref. [21] to determine the $v_s([n];\mathbf{r})$ corresponding to a given reference density $n(\mathbf{r})$.

In the absence of degeneracies the ground-state wave function Φ^{KS} of Eq. (A1) is a single Slater determinant. The N-electron equation (A1) decouples in N one-electron equations for the orbitals $\varphi_i(\mathbf{r})$ forming the determinant Φ^{KS}:

$$[\hat{T}+\hat{v}_s]\varphi_i(\mathbf{r})=\varepsilon_i\varphi_i(\mathbf{r}) \ . \tag{A2}$$

The symbol $\varphi_i(\mathbf{r})$ stands for the ith orbital including its spin degree of freedom, i.e., $\varphi_i(\mathbf{r})$ represents a two-dimensional spinor.

The method of Ref. [21] uses the linear response operator $\hat{G}$ which connects infinitesimal changes δv_s of the potential v_s with changes δn of the ground-state density $n(\mathbf{r})$ of Φ^{KS} of Eq. (A1), i.e.,

$$\delta v_s=\hat{G}\delta n \ . \tag{A3}$$

The representation of Eq. (A3) in ordinary space, which

we denote as $\mathbf{r}$ space, reads as [21]

$$\delta v_s(\mathbf{r})=\int d\mathbf{r}\, G(\mathbf{r},\mathbf{r}')\delta n(\mathbf{r}') \ , \tag{A4}$$

with

$$G(\mathbf{r},\mathbf{r}')=\sum_i^{occ}\sum_s^{unocc}\frac{\varphi_i^*(\mathbf{r})\varphi_s(\mathbf{r})\varphi_s^*(\mathbf{r}')\varphi_i(\mathbf{r}')}{\varepsilon_i^{KS}-\varepsilon_s^{KS}}+c.c. \tag{A5}$$

In Eq. (A5) the summations run over the occupied (occ) and unoccupied (unocc) KS orbitals $\varphi_i(\mathbf{r})$, respectively. The former are the orbitals building the determinant Φ^{KS}, while the latter are the energetically higher solutions of Eq. (A2). The linear response operator $\hat{G}$ cannot be inverted for arbitrary changes δv_s and δn. The reason is that the operator $\hat{G}$ has an eigenfunction, namely, δv_s being a constant function, with an eigenvalue of zero. Additionally only changes δn which integrate to zero are generated by $\hat{G}$ from changes δv_s, because the electron number of Φ^{KS} is not affected by a change of the potential v_s. However, if constant functions are excluded from the space of the changes δv_s and also from the space of the changes δn, then the linear response operator is invertible (see Refs. [21,35] for a discussion). This follows from the one to one mapping between densities and potentials established by the Hohenberg-Kohn theorem. At this point the additional assumption is made that all involved densities are noninteracting v representable [1]. Through the latter assumption it is guaranteed that all involved densities are ground-state densities for which the one to one mapping with potentials v_s exists.

One cycle of the iterative scheme of Ref. [21] to determine $v_s([n];\mathbf{r})$ for a given reference density $n(\mathbf{r})$ consists of the following steps.

(i) Solve Eqs. (A2) with an approximate potential $\tilde{v}_s$ obtained in the previous cycle.

(ii) Determine the corresponding ground-state density $\tilde{n}$ and the difference Δn to the reference density n ($\Delta n = n - \tilde{n}$).

(iii) Determine the linear response operator $\hat{G}$ and its inverse $\hat{G}^{-1}$ on the space in which constant functions are excluded.

(iv) Calculate a potential $\tilde{v}_s$ for the next cycle by adding $\Delta v_s = \hat{G}^{-1}\Delta n$ to the potential $\tilde{v}_s$ of the current cycle.

After convergence of the process, the final potential $\tilde{v}_s(\mathbf{r})$ is equal to the effective potential $v_s([n];\mathbf{r})$ belonging to the reference density $n(\mathbf{r})$ and the corresponding Slater determinant is the KS wave function Φ^{KS} of $n(\mathbf{r})$. This determinant $\Phi^{KS}[n]$, of course, is built from the KS orbitals to Eq. (A2) of the last iteration cycle and $\Phi^{KS}[n]$ also is the ground-state wave function to Eq. (A1) with the effective potential $v_s([n];\mathbf{r})$. At the start of the iteration process a first potential $\tilde{v}_s(\mathbf{r})$ has to be chosen. A suitable choice, made in this work, is to take as starting potential $\tilde{v}_s(\mathbf{r})$ the sum of the external potential, here the potential of the nucleus, plus the classical Coulomb potential to the reference density $n(\mathbf{r})$ plus the local-density approximation to the exchange potential of $n(\mathbf{r})$. Because the first two contributions are exactly known parts

of $v_s([n];\mathbf{r})$ only the last contribution which is interpreted as a first approximation to the exchange-correlation potential has to be optimized. The process then effectively determines the exact exchange-correlation potential to the reference density $n(\mathbf{r})$ starting from the local-density approximation to the exchange potential to $n(\mathbf{r})$.

To obtain a converging scheme the approximate potentials $\tilde{v}_s(\mathbf{r})$ occurring during the process have to be close enough to the exact potential $v_s([n];\mathbf{r})$ so that it is possible to apply a linear response approach in which infinitesimal changes δv_s and δn are substituted by finite changes Δv_s and Δn. Also problems originating in the v-representable assumption may not interfere. However, once the scheme has converged, these points become irrelevant with respect to the question of whether the correct KS wave function to the reference density $n(\mathbf{r})$ has been generated. For this, as discussed above, two conditions are sufficient, namely, that $\Phi^{KS}[n]$ is the ground state to a noninteracting Schrödinger equation with a local multiplicative potential and that $\Phi^{KS}[n]$ yields $n(\mathbf{r})$. Both conditions are fulfilled if convergence has been reached.

In actual implementations of this scheme, the problem arises that the r-space representation of the operator $\hat{G}^{-1}$, i.e., $G^{-1}(\mathbf{r},\mathbf{r}')$, is unknown. There is no simple way to exclude constant functions from the complete r space. Therefore the occurring potentials and densities as well as their changes Δv_s and Δn are expanded in an orthonormal basis set $\{g_k\}$ consisting of M_g real basis functions $g_k(\mathbf{r})$. The basis set $\{g_k\}$ is obtained by excluding from an original basis set of dimension M_g+1 that uniquely defined linear combination of basis functions which corresponds to a constant function. (See Refs. [21,35] for details. In Ref. [21] two different basis sets for potentials and densities are introduced. This, however, leads to unnecessary complications and therefore is not done here.)

$$n(\mathbf{r}) \rightarrow \sum_{k=1}^{M_g} a_k g_k(\mathbf{r}), \quad \tilde{n}(\mathbf{r}) \rightarrow \sum_{k=1}^{M_g} \tilde{a}_k g_k(\mathbf{r}),$$

$$\Delta n(\mathbf{r}) = \sum_{k=1}^{M_g} b_k g_k(\mathbf{r}),$$
(A6)

$$v_s([n];\mathbf{r}) = \sum_{k=1}^{M_g} c_k g_k(\mathbf{r}), \quad \tilde{v}_s(\mathbf{r}) = \sum_{k=1}^{M_g} \tilde{c}_k g_k(\mathbf{r}),$$
(A7)

$$\Delta v_s(\mathbf{r}) = \sum_{k=1}^{M_g} d_k g_k(\mathbf{r}).$$

The densities $n(\mathbf{r})$ and $\tilde{n}(\mathbf{r})$ cannot be identified with the corresponding sums in Eqs. (A6) because they contain a contribution of the linear combination of basis functions of the original (M_g+1)-dimensional basis set which belongs to a constant function. The magnitude of such a contribution is determined by the requirement on the density to integrate to a fixed electron number N. This requirement is met by any density built from N orthonormal orbitals. Therefore the coefficients a_k and $\tilde{a}_k$ are sufficient to characterize an N-electron density. The

change Δn does not contain a contribution of a constant function and therefore can be completely represented by the basis set $\{g_k\}$. The potentials $v_s[n]$ and $\tilde{v}_s$ as well as the changes Δv_s can be chosen not to contain a contribution belonging to a constant function. The coefficients of Eqs. (A6) and (A7) are collected in the vectors $\mathbf{a}$, $\tilde{\mathbf{a}}$, $\mathbf{b}$, $\mathbf{c}$, $\tilde{\mathbf{c}}$, and $\mathbf{d}$, respectively. The operator $\hat{G}$ is represented by a symmetric matrix $\mathbf{G}$ with matrix elements $G_{kl} = \langle g_k | \hat{G} | g_l \rangle$ in the basis set $\{g_k\}$. The inverse $\mathbf{G}^{-1}$ of $\mathbf{G}$ is the representation of $\hat{G}^{-1}$ and the equation $\Delta v_s = \hat{G}^{-1}\Delta n$ of step (iv) of the iteration process turns into the matrix equation $\mathbf{d} = \mathbf{G}^{-1}\mathbf{b}$. The determination of the orbitals in step (i) of the iteration process can be carried out essentially exactly by solving the corresponding Eqs. (A2) numerically. The iteration scheme is converged if the coefficient vectors $\mathbf{a}$ and $\tilde{\mathbf{a}}$ are identical.

In this work, for technical reasons, the KS orbitals φ_i are also expanded into an orthonormal basis set $\{\chi_j\}$ of dimension M_χ. To simplify the presentation, the basis $\{\chi_j\}$ is assumed to be real. The basis functions actually used in this work contain complex spherical harmonics. The basis set representation of the orbitals leads to additional complications, because in this case the Hohenberg-Kohn theorem constituting the foundation of the method [21] is not strictly valid, as will be demonstrated next. (A general and comprehensive investigation of basis set representations of densities, density matrices, and potentials, as well as a thorough discussion of the mappings between these quantities can be found in Refs. [36,37].) In order to discuss problems arising from the employment of finite orbital basis sets, we first have to formulate the Hohenberg-Kohn theorem within the basis set representation. If the orbitals are expanded in a basis set, then Eq. (A2) turns into the matrix equation

$$[\mathbf{T}+\mathbf{V}_s]\mathbf{w}_i = \varepsilon_i \mathbf{w}_i .$$
(A8)

The vector $\mathbf{w}_i$ is the representation of the orbital φ_i with respect to the basis set $\{\chi_j\}$. The matrices $\mathbf{T}$ and $\mathbf{V}_s$ with matrix elements $T_{ij} = \langle \chi_i | \hat{T} | \chi_j \rangle$ and $V_{s,ij} = \langle \chi_i | \hat{v}_s | \chi_j \rangle$, respectively, represent the operators $\hat{T}$ and $\hat{v}_s$ in the basis set $\{\chi_j\}$.

If one adds a matrix $\mathbf{V}_{ad}$, given by the sum

$$\mathbf{V}_{ad} = \sum_{i=1}^{M_\chi} \mu_i \mathbf{w}_i \mathbf{w}_i^T ,$$
(A9)

to the matrix $\mathbf{V}_s$, the M_χ eigenvectors of Eq. (A8) remain unchanged. The eigenvalues are changed from ε_i to $\varepsilon_i + \mu_i$, with the μ_i being constants. As long as the μ_i are chosen in such a way that the eigenvalues $\varepsilon_i + \mu_i$ resulting for the N lowest eigenvalues ε_i are again the N lowest eigenvalues in the new spectrum of eigenvalues $\varepsilon_i + \mu_i$, the occupied orbitals and therewith the density are not affected by the modification of the matrix $\mathbf{V}_s$. This demonstrates that $\mathbf{V}_s$ can be substituted by an infinite number of symmetric matrices without changing the corresponding ground-state density. This is not a contradiction of the Hohenberg-Kohn theorem, because an arbitrary symmetric matrix is not, in general, the representation of an operator to a local potential. For nonlocal po-

tentials, however, the Hohenberg-Kohn theorem does not hold. Indeed the addition of the nonlocal operator $\sum_i \mu_i |\varphi_i\rangle\langle\varphi_i|$ to the operator $\hat{v}_s$ of the local potential $v_s(\mathbf{r})$ in Eqs. (A1) and (A2) with appropriately chosen constants μ_i also does not affect the corresponding ground-state density [38]. For Schrödinger equations with nonlocal potentials there exist one to one mappings between the density matrices and the wave functions to ground states [39]. These mappings exhibit some formal similarities to the mappings established by the Hohenberg-Kohn theorem. However, in contrast to Ref. [39], the term Hohenberg-Kohn theorem shall be used here exclusively for the original mapping between densities and potentials. Equations (A8) do not give the most general form of a matrix $\mathbf{V}_{ad}$ which can be added to $\mathbf{V}_s$ without affecting the corresponding ground-state density. Any matrix which mixes the occupied and unoccupied orbitals only among themselves and keeps the eigenvalues emerging from the set of occupied orbitals lower than those emerging from the set of unoccupied orbitals qualifies as $\mathbf{V}_{ad}$.

Within the basis set representations used here the criterion of whether a symmetric matrix is a matrix $\mathbf{V}_s$ belonging to a local potential shall be whether the matrix can be expanded according to

$$\mathbf{V}_s = \sum_{k=1}^{M_g} c_k \mathbf{V}_k \; ,$$

with matrix elements $V_{k,ij} = \langle \chi_i | g_k | \chi_j \rangle \; ,$ (A10)

and with the matrices $\mathbf{V}_k$ being the basis set representation of operators $\hat{v}_k$ generated by the basis functions $g_k(\mathbf{r})$. The vector $\mathbf{c}$ collecting the coefficients c_k represents through Eq. (A7) a local potential $v_s(\mathbf{r})$ connected with $\mathbf{V}_s$. The Hohenberg-Kohn theorem within the representation defined by the basis sets $\{\chi_i\}$ and $\{g_k\}$ is given by the statement that two different vectors $\mathbf{c}$ cannot lead via Eqs. (A10) and (A8) to two sets of occupied orbitals $\mathbf{w}_i$ which give rise to the same vector $\mathbf{a}$ characterizing the corresponding ground-state density. To demonstrate that the Hohenberg-Kohn theorem in this form is not, in general, obeyed we show that different vectors $\mathbf{c}$ lead to identical orbitals $\mathbf{w}_i$ and therefore to an identical vector $\mathbf{a}$. (How the vector $\mathbf{a}$ corresponding to a set of occupied orbitals $\mathbf{w}_i$ is determined is demonstrated later.) The matrix $\mathbf{V}_s$ is symmetric and therefore consists of $(M_\chi + 1)M_\chi/2$ independent elements. That means for a given $\mathbf{V}_s$ Eq. (A10) is equivalent to $(M_\chi + 1)M_\chi/2$ linear equations for the M_g variables c_k. If the dimension M_g of the basis set $\{g_k\}$ is greater than $(M_\chi + 1)M_\chi/2$, then the system of equations is underdetermined and different sets of coefficients c_k, i.e., different vectors $\mathbf{c}$, result in the same matrix $\mathbf{V}_s$ and therefore lead to the same orbitals, the same determinant Φ^{KS}, and the same vector $\mathbf{a}$ characterizing the corresponding ground-state density. This clearly violates the basis set formulation of the Hohenberg-Kohn theorem given above. The representations $v_s(\mathbf{r})$ of the potential in ordinary space resulting from the two different vectors $\mathbf{c}$ by Eq. (A6) are not the same for the different sets of coefficients.

If the inequality $M_g \leq (M_\chi + 1)M_\chi/2$ holds, then different vectors $\mathbf{c}$ nevertheless may lead to the same matrix $\mathbf{V}_s$ if the M_g vectors of dimension $(M_\chi + 1)M_\chi/2$ which are built by the elements of the unique matrix elements of the M_g matrices $\mathbf{V}_k$ are linearly dependent. Whether this happens depends on how balanced the basis sets $\{g_k\}$ and $\{\chi_j\}$ are chosen. Even if $M_g \leq (M_\chi + 1)M_\chi/2$ and if the vectors built from the matrix elements of the $\mathbf{V}_k$ are linearly independent, this does not guarantee that the Hohenberg-Kohn theorem is obeyed. In the latter case different vectors $\mathbf{c}$ result in different matrices $\mathbf{V}_s$. However, there may exist vectors $\mathbf{c}_{ad}$ which lead through Eq. (A10) to matrices $\mathbf{V}_{ad}$ [see Eq. (A9) and text thereafter]. The addition of such a vector $\mathbf{c}_{ad}$ to a given vector $\mathbf{c}$ changes $\mathbf{V}_s$ but not the eigenvectors of Eq. (A8) and therefore leads to the same density matrix and the same vector $\mathbf{a}$ characterizing the corresponding ground-state density.

Next we consider the consequences of such a violation of the Hohenberg-Kohn theorem on the basis set version of the scheme of Ref. [21] to generate KS determinants to a given density. If the Hohenberg-Kohn theorem is violated then the matrix representation $\mathbf{G}$ of the linear response operator has zero eigenvalues and cannot be inverted directly. The symmetric matrix $\mathbf{G}$ always can be written as

$$\mathbf{G} = \mathbf{U}\lambda\mathbf{U}^T \; ,$$ (A11)

with λ being the diagonal matrix of the eigenvalues of $\mathbf{G}$ and with $\mathbf{U}$ being an orthonormal matrix consisting of the eigenvectors of $\mathbf{G}$. For step (iii) of the iteration scheme an effective inverse of $\mathbf{G}$ is generated by inverting all nonzero diagonal elements of λ and keeping any zero eigenvalues unchanged. In actual calculations those diagonal elements with a magnitude smaller than a certain threshold are set equal to zero. If that effective inverse of $\mathbf{G}$ is used to calculate in step (iv) of the iteration scheme the change Δv_s from the difference Δn, only that part of the density $\bar{n}$ of a certain cycle which can be represented by eigenvectors of $\mathbf{G}$ with nonzero eigenvalues is moved towards the corresponding part of the reference density $n(\mathbf{r})$. The remaining part of $\bar{n}$ which belongs to eigenvectors of $\mathbf{G}$ with zero eigenvalue is not optimized through the iteration procedure. The linear response operator and therefore its matrix representation $\mathbf{G}$ depend on the orbitals $\mathbf{w}_i$ and consequently change from cycle to cycle. Therefore, in each cycle, a different singular value decomposition (A11) of the matrix $\mathbf{G}$ is obtained. The iterative scheme is converged if the contributions to $n(\mathbf{r})$ and $\bar{n}(\mathbf{r})$ of that linear combination of basis functions $\{g_k\}$ belonging to eigenvectors of $\mathbf{G}$ with nonzero eigenvalues are identical (or in practice sufficiently close).

After convergence of the iteration scheme, it has to be checked whether the contributions to $n(\mathbf{r})$ and $\bar{n}(\mathbf{r})$ connected with the zero eigenvalues of $\mathbf{G}$ also are identical (or in practice sufficiently close). Only if this is true is the complete final density $\bar{n}(\mathbf{r})$ identical (or sufficiently close) to the reference density $n(\mathbf{r})$. This is the case for all systems considered in this work. To check this, a transformation of the basis set $\{g_k\}$ defined by the matrix $\mathbf{U}$ of

Eq. (A11) from the last iteration cycle has been carried out. The coefficients of the basis set representations of $n(\mathbf{r})$ and $\tilde{n}(\mathbf{r})$ for those new basis functions belonging to zero eigenvalues of $\mathbf{G}$ differ by less than 10 ppm, if the magnitude of the coefficients is similar to that of a typical coefficient to a new basis function belonging to a nonzero eigenvalue of $\mathbf{G}$. For each order of magnitude the absolute value of the "zero eigenvalue" coefficients to $n(\mathbf{r})$ and $\tilde{n}(\mathbf{r})$ decreases, the absolute value of their difference increases by at most one order of magnitude. Therefore the absolute error remains small and is within the accuracy of the method.

If the vectors $\mathbf{a}$ and $\tilde{\mathbf{a}}$, characterizing the densities $n(\mathbf{r})$ and $\tilde{n}(\mathbf{r})$, are identical (in practice sufficiently close) then the KS determinant to $\mathbf{a}=\tilde{\mathbf{a}}$ is the determinant built by the orbitals represented by the $\mathbf{w}_i$ of the final Eq. (A8) from the iteration scheme. The crucial point now is that, for the identification of the Slater determinant built by the orbitals represented by the $\mathbf{w}_i$ with the KS determinant of a density $n(\mathbf{r})$ characterized by the vector $\mathbf{a}$ [Eq. (A6)], the following two conditions alone are sufficient: The $\mathbf{w}_i$ are eigenfunctions to an equation of the type of Eq. (A8) with a matrix $\mathbf{V}_s$ given by Eq. (10), and the $\mathbf{w}_i$ lead to a density characterized by $\mathbf{a}$. The way in which the vector $\mathbf{c}$ determining $\mathbf{V}_s$ has been obtained is irrelevant. Therefore the fact that the Hohenberg-Kohn theorem is violated does not matter, as long as at the end of the iteration scheme the condition $\mathbf{a}=\tilde{\mathbf{a}}$ is obeyed. The reasons this condition turns out to be fulfilled here despite the difficulties with the invertibility of the matrix $\mathbf{G}$ originating in the violation of the Hohenberg-Kohn theorem lies in the relations of the basis sets $\{g_k\}$ and $\{\chi_j\}$ [40].

Next the above statement for the identification of the KS determinant is proven. The one-electron equations (A2) for the orbitals with the N lowest eigenvalues are equivalent to the N-electron equation (A1) for the determinant built from them. In the basis set representation considered here, Eq. (A2) turns into Eq. (A7) and Eq. (A1) [or, to be precise, the minimization equivalent to Eq. (A1)] is given by

$$E_s = \min \left\{ \sum_{i=1}^{N} \mathbf{p}_i^T [\mathbf{T}+\mathbf{V}_s] \mathbf{p}_i \right\} = \min \{ \mathrm{Tr}(\mathbf{P}[\mathbf{T}+\mathbf{V}_s]) \} .$$

(A12)

The minimization (A12) runs over all sets of N orthonormal vectors $\mathbf{p}_i$. The matrices $\mathbf{P}$ have the form

$$\mathbf{P} = \sum_{i=1}^{N} \mathbf{p}_i \mathbf{p}_i^T .$$

(A13)

The minimizing matrix $\mathbf{P}$ is the matrix built from the N energetically lowest orbitals $\mathbf{w}_i$ to the corresponding

one-electron equation (A8) leading to the energy E_s:

$$E_s = \sum_{i=1}^{N} \mathbf{w}_i^T [\mathbf{T}+\mathbf{V}_s] \mathbf{w}_i = \sum_{i=1}^{N} \varepsilon_i .$$

(A14)

The density $n'(\mathbf{r})$ to a trial matrix $\mathbf{P}$ is characterized by the vector $\mathbf{a}'$ of Eq. (A6) for $n'(\mathbf{r})$. The components a_k' of $\mathbf{a}'$ are given by

$$a_k' = \mathrm{Tr}[\mathbf{PV}_k] .$$

(A15)

Inserting Eq. (A10) and subsequently Eq. (A15) into Eq. (A12) leads to

$$E_s = \min \{ \mathrm{Tr}[\mathbf{PT}] + \mathbf{a}' \cdot \mathbf{c} \} .$$

(A16)

Next, the subset of matrices $\mathbf{P}$ yielding a density which has expansion coefficients $\mathbf{a}'$ equal to the coefficients $\mathbf{a}$ of the ground-state density of Eq. (A12) is considered. The coefficients a_k of the "ground-state vector" $\mathbf{a}$ are obtained if the matrix $\mathbf{P}$ in Eq. (A15) is replaced by $\sum_{i=1}^{N} \mathbf{w}_i \mathbf{w}_i^T$. From minimization (A16), which searches over all matrices $\mathbf{P}$, it follows that among the subset of matrices $\mathbf{P}$ leading via Eq. (15) to the ground-state vector $\mathbf{a}$, the one that minimizes the kinetic energy is the one fulfilling minimization (A12) or equivalently (A16)

$$T_s^{\mathrm{KS}}[\mathbf{a}] = \min_{\mathbf{P} \to \mathbf{a}} \{ \mathrm{Tr}[\mathbf{PT}] \} .$$

(A17)

In Eq. (17) by "$\mathbf{P} \to \mathbf{a}$" it is indicated that the minimization runs over all matrices $\mathbf{P}$ which yield via Eq. (A15) the vector $\mathbf{a}$. Equation (A17) is the equivalent of the definition (1) of a KS determinant with respect to the basis sets $\{\chi_j\}$ and $\{g_k\}$. The foregoing argumentation is valid for arbitrary vectors $\mathbf{c}$ occurring in Eq. (A16) and characterizing via Eq. (A10) the effective potential $\mathbf{V}_s$ in Eqs. (A12) and (A14). That means if a vector $\mathbf{c}$ is found which leads via Eqs. (A10) and (A8) to a set of vectors $\mathbf{w}_i$ yielding via Eq. (A15) with $\mathbf{P} = \sum_{i=1}^{N} \mathbf{w}_i \mathbf{w}_i^T$ to the coefficients a_k of a vector $\mathbf{a}$ which in addition also characterizes the reference density $n(\mathbf{r})$ then the vectors $\mathbf{w}_i$ represent the KS orbitals φ_i which generate the KS determinant to $n(\mathbf{r})$.

Finally, we mention that the method of Ref. [21] to calculate KS determinants to a given density as it is implemented in this work can be derived directly as a basis set constrained-search procedure according to Eq. (A17) [28]; this means as a procedure which directly searches the set of orthogonal orbitals which minimize the kinetic energy among all sets of orthogonal orbitals yielding a given reference density. The vector $\mathbf{c}$ in this derivation emerges not as the representation of a local external potential but is obtained as Lagrange multipliers originating from the constraint that the orbitals yield a certain density. In $\mathbf{r}$ space the equivalent interpretation of $v_s(\mathbf{r})$ as Lagrange multiplier is well known [1].

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