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Exact Kohn-Sham scheme based on perturbation theory

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An exact formal Kohn-Sham scheme is derived with the help of perturbation theory. Through the introduction of a basis set this Kohn-Sham scheme can be used to perform, in principle, exact Kohn-Sham calculations. As a demonstration, only zeroth- and first-order terms in the underlying perturbation theory are considered. As a result an exact basis set "exchange-only" method is obtained. The presented perturbation theory expansions of the exchange-correlation energy and potential may serve as a starting point for the development of new approximate exchange-correlation functionals based on Kohn-Sham orbitals and eigenvalues and may be used to check conventional exchange-correlation functionals. The formal structures of the *ab initio* and the introduced density-functional treatment of electronic systems are compared.

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I. INTRODUCTION

Recently [1], for an electronic system in its ground state, a perturbation theory expansion for the density-functional energy [2–7] was derived. Each term of the expansion is a functional of the Kohn-Sham orbitals φ_i and eigenvalues ε_i and of the functional derivatives of the lower-order terms with respect to the electron density. This expansion of the correlation energy allows one to express the sum, E, of the kinetic and electron-electron repulsion energies of an electronic system as follows:

$$\begin{aligned} E &= \sum_{j=0}^{\infty} E_j \\ &= \sum_{j=0}^{\infty} E_j[\{\varphi_i\},\{\varepsilon_i\},\{v_1(\mathbf{r}),v_2(\mathbf{r}),\ldots,v_{j-1}(\mathbf{r})\}] \ . \end{aligned} \tag{1}$$

In Eq. (1), the potentials $v_j(\mathbf{r})$ are given by

$$v_j(\mathbf{r}) = \frac{\delta E_j[n]}{\delta n(\mathbf{r})} \ . \tag{2}$$

Although the terms in expansion (1) are explicit functionals of the φ_i, ε_i, and $v_j(\mathbf{r})$ they are implicitly functionals of the ground-state electron density $n(\mathbf{r})$. The reason for this is that the φ_i, ε_i, and $v_j(\mathbf{r})$ are functionals of the density. For the φ_i and ε_i this follows directly from the Hohenberg-Kohn theorem [2]. For the $v_j(\mathbf{r})$, the fact that the *j*th term in expansion (1) contains only potentials $v_j(\mathbf{r})$ of order $j-1$ and lower is also used (see [1] and later on). The terms on Eq. (1) therefore may be written as

$$\begin{aligned} E_j &= E_j[\{\varphi_i[n]\},\{\varepsilon_i[n]\},\{v_1([n];\mathbf{r}),v_2([n];\mathbf{r}),\ldots,v_{j-1}([n];\mathbf{r})\}] \\ &= E_j[n] \ . \end{aligned} \tag{3}$$

The foregoing equation demonstrates that the range of density-functional theory is not left with expansion (1) and that the definitions (2) make sense.

The first terms of expansion (1) are [1]

$$\begin{aligned} E_0 &= T_s = \langle \Phi_s | \hat{T} | \Phi_s \rangle \\ &= \sum_{i}^{\text{occ.}} \int d\mathbf{r}\, \varphi_i^*(\mathbf{r})(-\tfrac{1}{2}\nabla^2)\varphi_i(\mathbf{r}) \ , \\ E_1 &= \langle \Phi_s | \hat{V}_{ee} | \Phi_s \rangle = U + E_x \ , \end{aligned} \tag{4a}$$

with

$$\begin{aligned} U &= 2\sum_{i}^{\text{occ.}}\sum_{j}^{\text{occ.}} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\varphi_i^*(\mathbf{r}_1)\varphi_j^*(\mathbf{r}_2)\varphi_i(\mathbf{r}_1)\varphi_j(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|} \ , \\ E_x &= (-1)\sum_{i}^{\text{occ.}}\sum_{j}^{\text{occ.}} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\varphi_i^*(\mathbf{r}_1)\varphi_j^*(\mathbf{r}_2)\varphi_j(\mathbf{r}_2)\varphi_i(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|} \ , \end{aligned} \tag{4b}$$

$$E_2 = \sum_{i=1}^{\infty} \frac{|\langle \Phi_{s,0} | \hat{V}_{ee} - \hat{v}_1 | \Phi_{s,i} \rangle|^2}{E_{s,0} - E_{s,i}} , \tag{4c}$$

with

$$\hat{v}_1 = \hat{u} + \hat{v}_{\mathrm{x}} = \sum_{k=1}^{N} u(\mathbf{r}_k) + v_{\mathrm{x}}(\mathbf{r}_k)$$

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and

$$u(\mathbf{r})=\frac{\delta U[n]}{\delta n(\mathbf{r})},\quad v_{\mathrm{x}}(\mathbf{r})=\frac{\delta E_{\mathrm{x}}[n]}{\delta n(\mathbf{r})}\ .$$

In Eqs. (4a)–(4c), $\hat{T}$ stands for the operator of the kinetic energy, $\hat{V}_{ee}$ for the operator of the electron-electron repulsion, and Φ_s for the N-electron Kohn-Sham ground-state wave function. (For simplicity, in this work only finite nondegenerate diamagnetic systems with no symmetries in ordinary space are considered. For those systems the Kohn-Sham ground-state wave functions Φ_s are Slater determinants consisting of Kohn-Sham orbitals φ_i. Each Kohn-Sham orbital φ_i is occupied by two electrons with opposite sign. However, the results presented here are also valid for other systems. For example, the findings of this work can easily be transferred to the symmetrized density-functional theory introduced recently [8]). U and E_{x} are the classical electron-electron repulsion energy and the exchange energy, respectively. The corresponding Coulomb potential is denoted by $u(\mathbf{r})$, the exchange potential by $v_{\mathrm{x}}(\mathbf{r})$. In Eq. (4c) the Kohn-Sham wave function Φ_s is written as $\Phi_{s,0}$ to demonstrate that it is the ground-state solution of the Kohn-Sham equation. The ith excited state to the Kohn-Sham equation is denoted by $\Phi_{s,i}$. The energies of $\Phi_{s,0}$ and $\Phi_{s,i}$ are $E_{s,0}$ and $E_{s,i}$, respectively. The higher-order terms of expansion (1) can be obtained by means of perturbation theory [1]. The correlation energy $E_{\mathrm{c}}[n]$ is given by the second- and higher-order terms of expansion (1) leading to the following expression for the exchange-correlation energy $E_{\mathrm{xc}}[n]$:

$$\begin{aligned}E_{\mathrm{xc}}&=E_{\mathrm{x}}+\sum_{j=2}E_j\\&=E_{\mathrm{x}}[\{\varphi_i\}]\\&\quad+\sum_{j=2}^{\infty}E_j[\{\varphi_i\},\{\varepsilon_i\},\{v_1(\mathbf{r}),v_2(\mathbf{r}),\ldots,v_{j-1}(\mathbf{r})\}]\ .\end{aligned}\tag{5}$$

Similarly, the exchange-correlation potential $v_{\mathrm{xc}}([n]\!:\!\mathbf{r})$ is given by [see Eq. (2)]

$$v_{\mathrm{xc}}(\mathbf{r})=v_{\mathrm{x}}(\mathbf{r})+\sum_{j=2}^{\infty}v_j(\mathbf{r})\ .\tag{6}$$

Equation (1) was derived [1] from the Taylor series of the total energy of an electronic system with fixed density with respect to the coupling parameter α with the latter turning on and off the electron-electron repulsion. It shall be assumed throughout this work that the Taylor series converges up to a coupling constant $\alpha=1$, i.e., to full electron-electron repulsion, and therefore α was set equal to one in Eq. (1), which for other values of α reads as

$$\begin{aligned}E(\alpha)&=\sum_{j=0}^{\infty}\alpha^jE_j\\&=\sum_{j=0}^{\infty}\alpha^jE_j[\{\varphi_i\},\{\epsilon_i\},\{v_1(\mathbf{r}),v_2(\mathbf{r}),\ldots,v_{j-1}(\mathbf{r})\}]\ .\end{aligned}\tag{7}$$

Density-functional theory today is applied almost exclusively via the Kohn-Sham [3–7] scheme. In a standard Kohn-Sham procedure the exchange-correlation potential in the nth cycle of the self-consistency process, or an approximation to it, respectively, is obtained as a functional of the electron density of the previous cycle. In order to calculate the total energy of the system, the functional for the exchange-correlation energy, or an approximation to it, respectively, is evaluated for the self-consistent electron density obtained when self-consistency is reached. However, if the exchange-correlation potential and energy were known as functionals of the Kohn-Sham orbitals and eigenvalues, and not directly as functionals of the density, the scheme would work as well. Instead of just the electron density, the Kohn-Sham orbitals and eigenvalues would be used to calculate the exchange-correlation potentials and the exchange-correlation energy.

With knowledge of the potentials $v_j(\mathbf{r})$, Eq. (5) gives the exchange-correlation energy as functional of the Kohn-Sham orbitals φ_i and eigenvalues ε_i. Therefore all that remains to have an exact Kohn-Sham scheme at hand is to express the potentials $v_j(\mathbf{r})$ as functionals of the Kohn-Sham orbitals φ_i and eigenvalues ε_i, because then both the exchange-correlation energy through Eq. (5) and the exchange-correlation potential through Eq. (6) would be known as functionals of φ_i and ε_i. All that is necessary to get such expressions for the $v_j(\mathbf{r})$ is a procedure to generate, as a functional of the Kohn-Sham orbitals and eigenvalues, the functional derivative with respect to the density of any quantity which is a functional of Kohn-Sham orbitals and eigenvalues. By having such a procedure, one would start with the lowest-order term in Eq. (5), the exchange energy which depends only on the φ_i [Eq. (4b)], and derive the exchange potential as a functional of the Kohn-Sham orbitals and eigenvalues. Subsequently, the exchange potential, expressed as a functional of Kohn-Sham orbitals and eigenvalues, could be substituted into the second term of Eq. (5), i.e., in Eq. (4c), and then by using the procedure again $v_2(\mathbf{r})$ could be obtained. In this manner all higher terms of the exchange-correlation energy and potential would also be accessible.

In this work, by the strategy outlined in the foregoing an exact formal Kohn-Sham scheme is derived. Furthermore it is demonstrated how this formal scheme can be implemented within the framework of a basis set method. As an example for such an implementation, only the first-order term is considered and as a result an exact basis set method to carry out "exchange-only" Kohn-Sham calculations is obtained.

II. EXACT FORMAL KOHN-SHAM SCHEME

The Hohenberg-Kohn theorem [2] proves that for a fixed number of electrons N, the ground-state electron density $n(\mathbf{r})$ determines, to within an additive constant, the local potential $v(\mathbf{r})$ or $v_s(\mathbf{r})$ of the corresponding interacting or noninteracting Schrödinger equation, respectively. The other way around, of course, the potential $v(\mathbf{r})$, respectively, $v_s(\mathbf{r})$, determines the electron density

$n(\mathbf{r})$ via the corresponding Schrödinger equation. That means that there is a one to one mapping, G, between infinitesimal changes $\delta v(\mathbf{r})$ of the potential $v(\mathbf{r})$ and infinitesimal changes $\delta n(\mathbf{r})$ of the electron density $n(\mathbf{r})$ if constant functions are excluded from the space of functions $\delta v(\mathbf{r})$ and if by the condition

$$\int d\mathbf{r}\, \delta n(\mathbf{r})=0 \tag{8}$$

the space of the functions $\delta n(\mathbf{r})$ is restricted also. Equation (8) follows from the requirement that the number of electrons is fixed. The invertible operator $\hat{G}$ mediates the mapping G,

$$\delta n=\hat{G}\delta v \ . \tag{9}$$

In the following, a noninteracting Schrödinger equation is considered:

$$[\hat{T}+\hat{v}_s]\Phi_s=E_s\Phi_s \ , \tag{10a}$$

where

$$\hat{v}_s=\sum_{i=1}^{N} v_s(\mathbf{r}_i) \ . \tag{10b}$$

In Eqs. (10), $\hat{v}_s$ is the operator belonging to the effective or Kohn-Sham local potential $v_s(\mathbf{r})$, and E_s is the Kohn-Sham energy of the N-electron Kohn-Sham wave function Φ_s. The Kohn-Sham orbitals φ_i and eigenvalues ε_i are obtained by the one particle Kohn-Sham equations corresponding to Eqs. (10). The ground-state electron density $n(\mathbf{r})$ is given by

$$n(\mathbf{r})=2\sum_{i}^{\text{occ.}} \varphi_i^*(\mathbf{r})\varphi_i(\mathbf{r}) \ . \tag{11}$$

First-order perturbation theory gives

$$\frac{\delta\varphi_i(\mathbf{r}_1)}{\delta v_s(\mathbf{r}_2)}=\sum_j{}' \varphi_j(\mathbf{r}_1)\frac{\varphi_j^*(\mathbf{r}_2)\varphi_i(\mathbf{r}_2)}{\varepsilon_i-\varepsilon_j} \ , \tag{12a}$$

$$\frac{\delta\varepsilon_i}{\delta v_s(\mathbf{r}_2)}=\varphi_i^*(\mathbf{r}_2)\varphi_i(\mathbf{r}_2) \ . \tag{12b}$$

The summation $\sum_j'$ in Eq. (12a) and in the following Eq. (13) runs over all Kohn-Sham orbitals except the one with the index $j=i$. From Eqs. (11) and (12a), the functional derivative $\delta n(\mathbf{r}_1)/\delta v(\mathbf{r}_2)$ is obtained as

$$\begin{aligned}\frac{\delta n(\mathbf{r}_1)}{\delta v_s(\mathbf{r}_2)}&=2\sum_i^{\text{occ.}}\sum_j{}' \frac{\varphi_i^*(\mathbf{r}_1)\varphi_j(\mathbf{r}_1)\varphi_j^*(\mathbf{r}_2)\varphi_i(\mathbf{r}_2)}{\varepsilon_i-\varepsilon_j}+\text{c.c.}\\ &=G(\mathbf{r}_1,\mathbf{r}_2) \ .\end{aligned} \tag{13}$$

Therefore in coordinate space the operator $\hat{G}$ is given by

$$\int d\mathbf{r}_2 G(\mathbf{r}_1,\mathbf{r}_2) \ . \tag{14}$$

Note that $\hat{G}$ denotes the operator itself whereas $\int d\mathbf{r}_2 G(\mathbf{r}_1,\mathbf{r}_2)$ is the representation of $\hat{G}$ in coordinate space. The operator $\hat{G}$ is the linear response operator giving the reaction of the electron density to infinitesimal changes in the potential. The inverse operator $\hat{G}^{-1}$ with its representation $\int d\mathbf{r}_2 G^{-1}(\mathbf{r}_1,\mathbf{r}_2)$ belongs to the functional derivative $\delta v_s(\mathbf{r}_1)/\delta n(\mathbf{r}_2)$ with

$$\frac{\delta v_s(\mathbf{r}_1)}{\delta n(\mathbf{r}_2)}=G^{-1}(\mathbf{r}_1,\mathbf{r}_2) \ . \tag{15}$$

The function $G^{-1}(\mathbf{r}_1,\mathbf{r}_2)$ and therewith the coordinate space representation of $\hat{G}^{-1}$ is not known analytically. However, as shown later on and in Refs. [10,11] (compare also [12]) a basis set representation of $\hat{G}^{-1}$ is accessible and can be used in actual calculations. Because $\hat{G}^{-1}$ is the inverse operator to $\hat{G}$ the relation

$$\int d\mathbf{r}_3 G(\mathbf{r}_1,\mathbf{r}_3)G^{-1}(\mathbf{r}_3,\mathbf{r}_2)=\delta(\mathbf{r}_1-\mathbf{r}_2) \tag{16}$$

holds.

Next, an arbitrary functional, $F[\{\varphi_i\},\{\varepsilon_i\}]$, of the Kohn-Sham orbitals and eigenvalues is considered. Using Eqs. (12a) and (12b), the functional derivative $\delta F/\delta n(\mathbf{r}_1)$ can be calculated.

$$\begin{aligned}\frac{\delta F}{\delta n(\mathbf{r}_1)}&=\int d\mathbf{r}_2 \frac{\delta F}{\delta v_s(\mathbf{r}_2)}\frac{\delta v_s(\mathbf{r}_2)}{\delta n(\mathbf{r}_1)}\\ &=\int d\mathbf{r}_2 \frac{\delta F}{\delta v_s(\mathbf{r}_2)}G^{-1}(\mathbf{r}_2,\mathbf{r}_1)\\ &=\int d\mathbf{r}_2 d\mathbf{r}_3 \left\{\left[\sum_i \frac{\delta F}{\delta\varphi_i^*(\mathbf{r}_3)}\frac{\delta\varphi_i^*(\mathbf{r}_3)}{\delta v_s(\mathbf{r}_2)}\right]+\left[\sum_i \frac{\delta F}{\delta\varphi_i(\mathbf{r}_3)}\frac{\delta\varphi_i(\mathbf{r}_3)}{\delta v_s(\mathbf{r}_2)}\right]\right\}G^{-1}(\mathbf{r}_2,\mathbf{r}_1)\\ &=\int d\mathbf{r}_2\left[\sum_i \frac{\partial F}{\partial\varepsilon_i}\frac{\delta\varepsilon_i}{\delta v_s(\mathbf{r}_2)}\right]G^{-1}(\mathbf{r}_2,\mathbf{r}_1) \ .\end{aligned} \tag{17}$$

Equation (17) does not give the functional derivative $\delta F/\delta n(\mathbf{r}_1)$ as a functional of the φ_i and ε_i, directly, because of the presence of $G^{-1}(\mathbf{r}_1,\mathbf{r}_2)$ which is not known as a functional of the φ_i and ε_i. Nevertheless Eq. (17) is sufficient to derive an exact Kohn-Sham scheme by the strategy sketched in the Introduction.

First, Eq. (17) is applied to the exchange energy E_x leading to the exchange potential $v_x(\mathbf{r}_1)$,

$$v_{\mathrm{x}}(\mathbf{r}_1)=-\int d\mathbf{r}_2\left\{2\sum_{i}^{\text{occ.}}\sum_{j}^{\text{occ.}}\sum_{k}{}'\int d\mathbf{r}_4 d\mathbf{r}_3\frac{\varphi_i^*(\mathbf{r}_4)\varphi_j^*(\mathbf{r}_3)\varphi_j(\mathbf{r}_4)\varphi_k(\mathbf{r}_3)}{|\mathbf{r}_3-\mathbf{r}_4|}\frac{\varphi_k^*(\mathbf{r}_2)\varphi_i(\mathbf{r}_2)}{\varepsilon_i-\varepsilon_k}+\text{c.c.}\right\}G^{-1}(\mathbf{r}_2,\mathbf{r}_1)\ . \tag{18}$$

Again the summation $\sum_k'$ runs over all Kohn-Sham orbitals except the one with index $k=i$. Equation (18) is an exact expression for the exchange potential (see in this context also Refs. [9,13,14]). In coordinate space the representation of $G^{-1}(\mathbf{r}_1,\mathbf{r}_2)$ is not known explicitly and Eq. (18) therefore is of formal nature. However, a basis set representation of the operator $\hat{G}^{-1}$ is accessible and Eq. (18) can actually be used in basis set calculations (see later on and Refs. [10,11]). Next, $v_{\mathrm{x}}(\mathbf{r}_1)$ is substituted into the first term, E_2, of the correlation energy [Eqs. (5) and (4c)], which in this way is obtained as a functional of the φ_i and ε_i and of $G^{-1}(\mathbf{r}_1,\mathbf{r}_2)$. Although for the potential $v_2(\mathbf{r}_1)$, the equation

$$v_2(\mathbf{r}_1)=\frac{\delta E_2}{\delta n(\mathbf{r}_1)}=\int d\mathbf{r}_2\frac{\delta E_2}{\delta v_s(\mathbf{r}_2)}\frac{\delta v_s(\mathbf{r}_2)}{\delta n(\mathbf{r}_1)}$$
$$=\int d\mathbf{r}_2\frac{\delta E_2}{\delta v_s(\mathbf{r}_2)}G^{-1}(\mathbf{r}_2,\mathbf{r}_1) \tag{19}$$

holds, the potential $v_2(\mathbf{r}_1)$ cannot be obtained directly via Eqs. (17) and (19). The reason is that E_2 is not known as an explicit functional solely of the φ_i and ε_i because of the presence of $G^{-1}(\mathbf{r}_1,\mathbf{r}_2)$ in $v_{\mathrm{x}}(\mathbf{r}_1)$ and therewith in E_2. Nevertheless $\delta E_2/\delta v(\mathbf{r}_1)$ can be calculated by using the following relation which is proven in Appendix A:

$$\frac{\delta G^{-1}(\mathbf{r}_1,\mathbf{r}_2)}{\delta v_s(\mathbf{r}_3)}=-\int d\mathbf{r}_4\int d\mathbf{r}_5 G^{-1}(\mathbf{r}_1,\mathbf{r}_4)\frac{G(\mathbf{r}_4,\mathbf{r}_5)}{\delta v_s(\mathbf{r}_3)}$$
$$\times G^{-1}(\mathbf{r}_5,\mathbf{r}_2)\ . \tag{20}$$

Note that $G(\mathbf{r}_1,\mathbf{r}_2)$ is known as a functional of the φ_i and ε_i. Therefore its functional derivative with respect to $v_s(\mathbf{r}_3)$ can be calculated with Eqs. (12) and (17). This leads to the following expression for $v_2(\mathbf{r}_1)$:

$$\begin{aligned}v_2(\mathbf{r}_1)&=\frac{\delta E_2}{\delta n(\mathbf{r}_1)}\\
&=\int d\mathbf{r}_2\frac{\delta E_2}{\delta v_s(\mathbf{r}_2)}\frac{\delta v_s(\mathbf{r}_2)}{\delta n(\mathbf{r}_1)}\\
&=\int d\mathbf{r}_2\frac{\delta E_2[\{\varphi_i\},\{\varepsilon_i\},\{G^{-1}\}]}{\delta v_s(\mathbf{r}_2)}G^{-1}(\mathbf{r}_2,\mathbf{r}_1)\\
&=\int d\mathbf{r}_2 d\mathbf{r}_3\left\{\left[\sum_i\frac{\delta E_2}{\delta\varphi_i^*(\mathbf{r}_3)}\frac{\delta\varphi_i^*(\mathbf{r}_3)}{\delta v_s(\mathbf{r}_2)}\right]+\left[\sum_i\frac{\delta E_2}{\delta\varphi_i(\mathbf{r}_3)}\frac{\delta\varphi_i(\mathbf{r}_3)}{\delta v_s(\mathbf{r}_2)}\right]\right\}G^{-1}(\mathbf{r}_2,\mathbf{r}_1)\\
&\quad+\int d\mathbf{r}_2\left[\sum_i\frac{\partial E_2}{\partial\varepsilon_i}\frac{\delta\varepsilon_i}{\delta v_s(\mathbf{r}_2)}\right]G^{-1}(\mathbf{r}_2,\mathbf{r}_1)+\int d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4\frac{\delta E_2}{\delta G^{-1}(\mathbf{r}_3,\mathbf{r}_4)}\frac{\delta G^{-1}(\mathbf{r}_3,\mathbf{r}_4)}{\delta v_s(\mathbf{r}_2)}G^{-1}(\mathbf{r}_2,\mathbf{r}_1)\ .\end{aligned} \tag{21}$$

By evaluation of the right-hand side of Eq. (21) [with Eqs. (4c), (12), and (20)] $v_2(\mathbf{r}_1)$ is given as a functional of the φ_i, the ε_i, and of $G^{-1}(\mathbf{r}_1,\mathbf{r}_2)$. In the next step the potential $v_2(\mathbf{r}_1)$ together with $v_{\mathrm{x}}(\mathbf{r}_1)$ can be substituted into E_3 which then is given as functional of the φ_i, ε_i, and of $G^{-1}(\mathbf{r}_1,\mathbf{r}_2)$. Subsequently $v_3(\mathbf{r}_1)$ can be generated in the same way as $v_2(\mathbf{r}_1)$. The higher-order terms of Eqs. (5) and (6) can be treated alike. This results in the exchange-correlation energy and potential as explicit functionals of the φ_i, the ε_i, and of $G^{-1}(\mathbf{r}_1,\mathbf{r}_1)$,

$$E_{\mathrm{xc}}=E_{\mathrm{x}}[\{\varphi_i\}]+\sum_{j=2}^{\infty}E_j[\{\varphi_i\},\{\varepsilon_i\},\{G^{-1}\}]\ , \tag{22a}$$

$$\begin{aligned}v_{\mathrm{xc}}(\mathbf{r}_1)&=\int d\mathbf{r}_2\frac{\delta E_{\mathrm{x}}[\{\varphi_i\}]}{\delta v_s(\mathbf{r}_2)}G^{-1}(\mathbf{r}_2,\mathbf{r}_1)+\sum_{j=2}^{\infty}\left\{\int d\mathbf{r}_2\frac{\delta E_j[\{\varphi_i\},\{\varepsilon_i\},\{G^{-1}\}]}{\delta v_s(\mathbf{r}_2)}G^{-1}(\mathbf{r}_2,\mathbf{r}_1)\right\}\\
&=v_{\mathrm{x}}([\{\varphi_i\},\{\varepsilon_i\},\{G^{-1}\}];\mathbf{r}_1)+\sum_{j=2}^{\infty}v_j([\{\varphi_i\},\{\varepsilon_i\},\{G^{-1}\}];\mathbf{r}_1)\ .\end{aligned} \tag{22b}$$

Equations (22a) and (22b) establish an exact formal Kohn-Sham scheme. By the introduction of a basis set the formal scheme can be used to actually carry out in principle exact Kohn-Sham calculations. Of course, in an actual calculation only a limited number of terms of the series (22a) and (22b) can be taken into account. (See following section and Discussion.)

Note that no additive constants to potentials occur in Eq. (22b) and in previous equations. This is a consequence of the restriction of the space of functions $\delta n(\mathbf{r})$ by Eq. (8). In Appendix B it is shown that the exchange-correlation potential is defined only to within a constant as usual if the space on which the operator $\hat{G}^{-1}$ is defined is extended.

By acting with the operator $\int d\mathbf{r}_2 G(\mathbf{r}_1,\mathbf{r}_2)$ on both sides of Eq. (18) and subsequent usage of Eq. (16) the following relation for the exchange potential is obtained:

$$\int d\mathbf{r}_2 v_x(\mathbf{r}_2) G(\mathbf{r}_2,\mathbf{r}_1) = -2 \sum_i^{\text{occ.}} \sum_j^{\text{occ.}} {\sum_k}' \int d\mathbf{r}_4 d\mathbf{r}_3 \frac{\varphi_i^*(\mathbf{r}_4)\varphi_j^*(\mathbf{r}_3)\varphi_j(\mathbf{r}_4)\varphi_k(\mathbf{r}_3)}{|\mathbf{r}_3-\mathbf{r}_4|} \frac{\varphi_k^*(\mathbf{r}_1)\varphi_i(\mathbf{r}_1)}{\varepsilon_i-\varepsilon_k} + \text{c.c.} \tag{23}$$

As always the summation $\sum'_k$ runs over all Kohn-Sham orbitals except the one with index $k=i$. Equation (23), for the exchange potential, also was derived in Ref. [9] and is the basis for the optimized-effective-potential method (compare also [13]). Relations equivalent to Eq. (23) exist for all functionals of the Kohn-Sham orbitals φ_i and eigenvalues ε_i.

III. BASIS SET FORMULATION OF THE EXACT KOHN-SHAM SCHEME

In order to derive a basis set formulation of the exact Kohn-Sham scheme presented in the preceding section, orthonormal basis sets $\{\chi_j\}$, $\{f'_k\}$, and $\{g'_m\}$ to represent the Kohn-Sham orbitals φ_i, the Kohn-Sham potential $v_s(\mathbf{r})$ with changes $\delta v_s(\mathbf{r})$, and the electron densities $n(\mathbf{r})$ with changes $\delta n(\mathbf{r})$, respectively, are introduced. The basis sets $\{f'_k\}$ and $\{g'_m\}$ shall have the same dimension and furthermore consist of real functions because the densities and potentials are real. In contrast, the χ_j in general are complex functions. However, in actual calculations usually real orbitals φ_i are assumed and then the χ_j also are real functions. Of course, an arbitrary, nonorthonormal, linearly independent, basis set always can be transformed to an orthonormal one with the help of the eigenvectors and eigenvalues of the corresponding overlap matrix. To take the constraint (8) for $\delta n(\mathbf{r})$ into account, the basis set $\{f'_k\}$ is transformed into the new basis set $\{f_k\}$. The first basis function f_1 of the new basis set is given by

$$f_1 = A_f^{-1} \sum_k \left[\int d\mathbf{r}\, f'_k(\mathbf{r}) \right] f'_k \;, \tag{24}$$

with

$$A_f = \left[\sum_k \left[\int d\mathbf{r}\, f'_k(\mathbf{r}) \right]^2 \right]^{1/2} .$$

The remaining basis functions f_k are linear combinations of the original basis functions f'_k such that the new basis set $\{f_k\}$ again is an orthonormal basis set. This is always possible, for example, by a Schmidt orthogonalization procedure. The new basis set has the property

$$\int d\mathbf{r}\, f_k(\mathbf{r}) = 0 \quad \text{for } k \neq 1 \;. \tag{25}$$

From Eqs. (24) and (25) it follows that the contribution of f_1 to a density $n(\mathbf{r})$ is given by N/A_f, i.e., the electron number N divided by the normalization constant A_f, whereas f_1 does not contribute to any change $\delta n(\mathbf{r})$. In a similar way, the basis set $\{g'_m\}$ is transformed into a new orthonormal basis set $\{g_m\}$ with the basis function g_1 being the basis function corresponding to a constant. The basis function g_1 can be shown to have the same structure as f_1 (see Appendix B):

$$g_1 = \left[\sum_m \left[\int d\mathbf{r}\, g'_m(\mathbf{r}) \right]^2 \right]^{-1/2} \times \sum_m \left[\int d\mathbf{r}\, g'_m(\mathbf{r}) \right] g'_m \;. \tag{26}$$

Next, for the representation of $\delta n(\mathbf{r})$ and $\delta v(\mathbf{r})$, the basis functions f_1 and g_1 are excluded from the basis sets $\{f_k\}$ and $\{g_m\}$, respectively. For simplicity the shortened basis sets also are denoted by $\{f_k\}$ and $\{g_m\}$. The basis set representation of the linear response operator $\hat{G}$, as defined in Eq. (9) [see also Eqs. (13) and (14)], is then given by the matrix $\mathbf{G}$ with matrix elements G_{km}:

$$\begin{aligned} G_{km} &= \int d\mathbf{r}_1 d\mathbf{r}_2 f_k(\mathbf{r}_1) G(\mathbf{r}_1,\mathbf{r}_2) g_m(\mathbf{r}_2) \\ &= 2 \sum_i^{\text{occ.}} {\sum_j}' \frac{\int d\mathbf{r}_1 f_k(\mathbf{r}_1)\varphi_i^*(\mathbf{r}_1)\varphi_j(\mathbf{r}_1) \int d\mathbf{r}_2 \varphi_j^*(\mathbf{r}_2)\varphi_i(\mathbf{r}_2) g_m(\mathbf{r}_2)}{\varepsilon_i-\varepsilon_j} + \text{c.c.} \end{aligned} \tag{27}$$

As before, the summation $\sum'_j$ runs over all the Kohn-Sham orbitals except the one with index $j=i$. The basis set representation of the inverse of $\hat{G}$, i.e., of $\hat{G}^{-1}$, is given by the inverse $\mathbf{G}^{-1}$ of the matrix $\mathbf{G}$.

Alternatively, a basis set representation of the operators $\hat{G}$ and $\hat{G}^{-1}$ can be obtained by generating a matrix $\mathbf{G}'$ by using the original basis sets $\{f'_k\}$ and $\{g'_m\}$ in the evaluation of Eq. (27) followed by a singular value decomposition [15] of $\mathbf{G}'$ which subsequently allows one to determine the basis functions f_1 and g_1 and finally the matrix $\mathbf{G}$. For the case that the basis sets $\{f'_k\}$ and $\{g'_m\}$ are identical, the singular value decomposition of $\mathbf{G}'$ is equivalent to a determination of the eigenvalues and eigenvectors of $\mathbf{G}'$, i.e., a diagonalization of $\mathbf{G}'$. For further details concerning the basis set representation of the operators G and G^{-1} see Refs. [10,11].

With the basis set representation of the operators $\hat{G}$ and $\hat{G}^{-1}$, the evaluation of the integrals, expectation values, and operators occurring in Eqs. (22a) and (22b) are straightforward. Therefore, in principle, it is possible to perform exact basis set Kohn-Sham calculations. As an example, when Eqs. (22a) and (22b) are considered only up to first order, a basis set "exchange-only" calculation results. To generate the basis set representation of the exchange potential $v_{\mathrm{x}}(\mathbf{r})$ first the vector $\mathbf{w}$ representing the functional derivative $\delta E_{\mathrm{x}}[n]/\delta v(\mathbf{r})$ is defined through its components w_m:

$$w_m=-2\sum_i^{\mathrm{occ.}}\sum_j^{\mathrm{occ.}}\sum_k{}' \int d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 \frac{\varphi_i^*(\mathbf{r}_4)\varphi_j^*(\mathbf{r}_3)\varphi_j(\mathbf{r}_4)\varphi_k(\mathbf{r}_3)}{|\mathbf{r}_3-\mathbf{r}_4|}\frac{\varphi_k^*(\mathbf{r}_2)\varphi_i(\mathbf{r}_2)g_m(\mathbf{r}_2)}{\varepsilon_i-\varepsilon_k}+\text{c.c.} \tag{28}$$

Again the summation $\sum_k'$ runs over all Kohn-Sham orbitals except the one with index $k=i$. The basis set representation $\mathbf{v}_{\mathrm{x}}$ of the functional derivative $\delta E_{\mathrm{x}}[n]/\delta n(\mathbf{r})$, i.e., the function $v_{\mathrm{x}}(\mathbf{r})$, is given by

$$\mathbf{v}_{\mathrm{x}}^T=\mathbf{w}^T\mathbf{G}^{-1} . \tag{29}$$

This immediately leads to the basis set representation $\mathbf{V}_{\mathrm{x}}$ with elements $V_{\mathrm{x},ij}$ of the operator $\hat{v}_{\mathrm{x}}$ connected with the function $v_{\mathrm{x}}(\mathbf{r})$:

$$V_{\mathrm{x},ij}=\sum_k v_{\mathrm{x},k}V_{\mathrm{x},ij}^k , \tag{30}$$

with

$$V_{\mathrm{x},ij}^k=\int d\mathbf{r}\,\chi_i^*(\mathbf{r})f_k(\mathbf{r})\chi_j(\mathbf{r}) .$$

In Eq. (30), $v_{\mathrm{x,k}}$ are the elements of the vector $\mathbf{v}_{\mathrm{x}}$ of Eq. (29). Note that the basis set representations of the $\mathbf{r}$ dependent function $v_{\mathrm{x}}(\mathbf{r})$, which is the functional derivative $\delta E_{\mathrm{x}}[n]/\delta n(\mathbf{r})$, and of the operator $\hat{v}_{\mathrm{x}}$ belonging to $v_{\mathrm{x}}(\mathbf{r})$, are different.

The first-order or linear change ΔE_{x} of the exchange energy corresponding to a change $\Delta n(\mathbf{r})$ is given by the scalar product

$$\Delta E_{\mathrm{x}}=\mathbf{v}_{\mathrm{x}}^T\boldsymbol{\Delta}_n , \tag{31}$$

with the elements $\Delta_{n,k}$ of $\boldsymbol{\Delta}_n$ being

$$\Delta_{n,k}=\int d\mathbf{r}\,f_k(\mathbf{r})\Delta n(\mathbf{r}) ,$$

whereas the action of the operator $\hat{v}_{\mathrm{x}}$ on a Kohn-Sham orbital φ_i is given by the product $\mathbf{V}_{\mathrm{x}}\mathbf{c}_i$ of the matrix $\mathbf{V}_{\mathrm{x}}$ with the vector $\mathbf{c}_i$ representing φ_i in the basis set $\{\chi_j\}$. The elements $c_{i,j}$ of $\mathbf{c}_i$ are given by

$$c_{i,j}=\int d\mathbf{r}\,\chi_j^*(\mathbf{r})\varphi_i(\mathbf{r}) . \tag{32}$$

Now, to carry out an "exchange-only" Kohn-Sham calculation, just a standard Kohn-Sham calculations has to be performed with the only difference that instead of some approximation to the exchange potential, the exchange operator $\mathbf{V}_{\mathrm{x}}$ of Eq. (30), is used. That means, in every iteration of the self-consistent process, Eqs. (27) and (28) have to be evaluated and $\mathbf{V}_{\mathrm{x}}$ has to be constructed according to Eqs. (29) and (30).

IV. DISCUSSION AND CONCLUSIONS

The results derived in this paper give new insight into the nature of theories for the description of electronic structures. Equations (22a) and (22b) not only allow the formulation of an exact formal Kohn-Sham procedure, they also unveil parallels between *ab initio* [16] and density-functional [2–7] theories. In *ab initio* theory, the Hartree-Fock wave function is the zero-order wave function which is obtained in a self-consistency procedure. The exact energy of the system then may be determined by perturbation theory (MØller-Plesset perturbation theory [16], for instance). In density-functional theory, the Kohn-Sham wave function is the zero-order wave function and the corresponding perturbation theory is given through expansions (1), (22a), and (22b). Whereas the Hartree-Fock wave function is that "one-determinantal" wave function which gives the lowest-energy expectation value with the full interacting Hamiltonian, the Kohn-Sham wave function gives the correct ground-state electron density. An important difference between the *ab initio* approach and the density-functional approach, as given in this work, is that the self-consistency procedure to determine the Kohn-Sham wave function, in contrast to the one leading to the Hartree-Fock wave function, already depends on perturbation theory which therefore comes into play at an earlier stage.

With the basis set formulation of the exact Kohn-Sham scheme, the formal results of this paper may also be applied in computational procedures as outlined in Sec. III. The performance of exact "exchange-only" calculations according to Eqs. (27)–(30), i.e., Eqs. (22a) and (22b) to first order, should not cast up any significant computational difficulties. Note, in this context, that a basis set representation of the operator $\hat{G}^{-1}$ already has been used successfully in actual calculations [11]. In these calculations the property that the operator $\hat{G}^{-1}$ gives the linear response of the Kohn-Sham potential on changes of the electron density was used to generate the Kohn-Sham potentials for given electron densities. Whether higher-order Kohn-Sham calculations within the suggested scheme can compete with *ab initio* methods (configuration interaction, MØller-Plesset perturbation theory) depends on how rapidly expansions (22a) and (22b) converge. The computational demands of exact basis set Kohn-Sham calculations is of the same order as those of Hartree-Fock calculations as far as the evaluation of the necessary integrals is concerned. On a first glance the evaluation of Eqs. (22a) and (22b) leads to three (and higher) electron integrals, e.g., Eq. (18) for the first-order term. However, due to their origin in perturbation theory and due to the use of a basis set representation of $\hat{G}^{-1}$ these integrals factorize and can be resolved into sums of at most two-electron integrals [see Eqs. (27)–(30) for the first-order term]. The extent of the necessary linear algebra depends on the order up to which the calculation is performed. Hereby one should keep in mind that linear algebra is carried out highly efficiently on modern computers. Nevertheless, before being applicable in higher-order calculations the scheme probably has to be modified because now the required amount of computer time would scale very unfavorably with the size of electronic systems to which the procedure would be applied. It should be mentioned here that the disadvantage that the operator $\hat{G}^{-1}$ is not known analytically, but only in its basis set representation, is not that serious because calculations on the electronic structure of larger systems are usually done within basis set methods anyway.

The reported results [Eqs. (22a) and (22b)] allow the calculation of the exact exchange-correlation energy and potential (up to some finite order) belonging to an arbitrary Kohn-Sham wave function or equivalently to the ground-state wave function of a noninteracting Schrödinger equation with an arbitrary effective potential. The only requirement for the effective potential is that it is a local potential and that the corresponding noninteracting Schrödinger equation therefore can be interpreted as a Kohn-Sham equation. The effective potential need not be the correct Kohn-Sham potential of a real system like an atom or a molecule. Instead it can be arbitrarily chosen or it can be an approximate potential obtained by one of the commonly used standard Kohn-Sham methods. Being able to obtain, up to some finite order, the exact exchange-correlation energy and potential for any Kohn-Sham wave function may be very helpful in the construction of new or improved approximate functionals for the exchange-correlation energy and potential. For any chosen effective potential, respectively, for its corresponding Kohn-Sham wave function and electron density, the exchange-correlation energy, and potential, from approximate functionals can be compared to the exact values.

In combination with the recently introduced basis set procedure to generate the Kohn-Sham wave function and potential for a given electron density [10,11], Eqs. (22a) and (22b) also allow one to determine the exact exchange-correlation energy and potential for this given electron density. Again, this is of interest in the development and improvement of approximate exchange-correlation functionals.

With knowledge of the exact expressions for the exchange-correlation energy and potential, as given in Eqs. (22a) and (22b), it seems reasonable to pursue more thoroughly attempts to construct approximate exchange-correlation functionals directly from the Kohn-Sham orbitals and eigenvalues. Most approximate exchange-correlation functionals are based on the density; the Kohn-Sham orbitals are merely used to obtain the density. As demonstrated in this work, it is not necessary to know how exchange-correlation functionals, based directly on the Kohn-Sham orbitals and eigenvalues, can be formulated as explicit functionals of the density in order to use them in a Kohn-Sham scheme. As discussed in the Introduction, those functionals are always implicitly functionals of the density. By considering functionals based directly on the Kohn-Sham orbitals and eigenvalues as approximate exchange-correlation functionals more freedom in the construction of the latter is gained.

The expansion for the exchange-correlation potential [Eq. (22b)] and the exact Kohn-Sham scheme derived in this work are a consequence of the results of Ref. [1], i.e., the perturbation theory expansion of the exchange-correlation energy. Further investigations starting from the formalism introduced are desirable.

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APPENDIX A: FUNCTIONAL DERIVATIVE OF $G^{-1}(\mathbf{r}_1,\mathbf{r}_2)$ WITH RESPECT TO $v_s(\mathbf{r})$

The functions $G(\mathbf{r}_1,\mathbf{r}_2)$ and $G^{-1}(\mathbf{r}_1,\mathbf{r}_2)$, through the Kohn-Sham orbitals φ_i and eigenvalues ε_i, are functionals of the potential $v_s(\mathbf{r})$. This may be expressed by writing $G([v_s];\mathbf{r}_1,\mathbf{r}_2)$ and $G^{-1}([v_s];\mathbf{r}_1,\mathbf{r}_2)$. The equation

$$\int d\mathbf{r}_3 G([v_s];\mathbf{r}_1,\mathbf{r}_3)G^{-1}([v_s];\mathbf{r}_3,\mathbf{r}_2)=\delta(\mathbf{r}_1-\mathbf{r}_2) \tag{A1}$$

is valid independently of the choice of the potential $v_s(\mathbf{r})$. Next, the Taylor series of the functions $G([v_s+\Delta v_s];\mathbf{r}_1,\mathbf{r}_2)$ and $G^{-1}([v_s+\Delta v_s];\mathbf{r}_1,\mathbf{r}_2)$ with respect to $\Delta v_s(\mathbf{r})$ is given:

$$\begin{aligned}G([v_s+\Delta v_s];\mathbf{r}_1,\mathbf{r}_2)={}&G([v_s];\mathbf{r}_1,\mathbf{r}_2)\\&+\int d\mathbf{r}_3\frac{\delta G([v_s];\mathbf{r}_1,\mathbf{r}_2)}{\delta v_s(\mathbf{r}_3)}\\&\times\Delta v_s(\mathbf{r}_3)+O(2)\ ,\end{aligned} \tag{A2}$$

$$\begin{aligned}G^{-1}([v_s+\Delta v_s];\mathbf{r}_1,\mathbf{r}_2)={}&G^{-1}([v_s];\mathbf{r}_1,\mathbf{r}_2)\\&+\int d\mathbf{r}_3\frac{\delta G^{-1}([v_s];\mathbf{r}_1,\mathbf{r}_2)}{\delta v_s(\mathbf{r}_3)}\\&\times\Delta v_s(\mathbf{r}_3)+O(2)\ .\end{aligned} \tag{A3}$$

In Eqs. (A2) and (A3) $O(2)$ stands for second- and higher-order terms. Substitution of Eqs. (A2) and (A3) in Eq. (A1) leads to

$$\int d\mathbf{r}_3 d\mathbf{r}_5 G([v_s];\mathbf{r}_4,\mathbf{r}_5)\frac{\delta G^{-1}([v_s];\mathbf{r}_5,\mathbf{r}_2)}{\delta v_s(\mathbf{r}_3)}\Delta v_s(\mathbf{r}_3)+\int d\mathbf{r}_3 d\mathbf{r}_5\frac{\delta G([v_s];\mathbf{r}_4,\mathbf{r}_5)}{\delta v_s(\mathbf{r}_3)}\Delta v_s(\mathbf{r}_3)G^{-1}([v_s];\mathbf{r}_5,\mathbf{r}_2)+O(2)=0\ . \tag{A4}$$

Equation (A4) has to be valid for arbitrary $\Delta v_s(\mathbf{r})$ and therefore each contribution to the left side of Eq. (A4) of an order different from zero has to be zero independently of the specific $\Delta v_s(\mathbf{r})$. For the first order this results in

$$\int d\mathbf{r}_5 G([v_s];\mathbf{r}_4,\mathbf{r}_5)\frac{\delta G^{-1}([v_s];\mathbf{r}_5,\mathbf{r}_2)}{\delta v_s(\mathbf{r}_3)} = -\int d\mathbf{r}_5 \frac{\delta G([v_s];\mathbf{r}_4,\mathbf{r}_5)}{\delta v_s(\mathbf{r}_3)} G^{-1}([v_s];\mathbf{r}_5,\mathbf{r}_2) \; . \tag{A5}$$

Acting with the operator $\int d\mathbf{r}_4 G^{-1}(\mathbf{r}_1,\mathbf{r}_4)$ on both sides of Eq. (A5) and using Eq. (16) leads to the desired result

$$\frac{\delta G^{-1}([v_s];\mathbf{r}_1,\mathbf{r}_2)}{\delta v_s(\mathbf{r}_3)} = -\int d\mathbf{r}_4 d\mathbf{r}_5 G^{-1}([v_s];\mathbf{r}_1,\mathbf{r}_4) \times \frac{\delta G([v_s];\mathbf{r}_4,\mathbf{r}_5)}{\delta v_s(\mathbf{r}_3)} \times G^{-1}([v_s];\mathbf{r}_5,\mathbf{r}_2) \; . \tag{A6}$$

APPENDIX B: INTRODUCTION OF AN ADDITIVE CONSTANT TO THE EXCHANGE-CORRELATION POTENTIAL

At the outset it has to be mentioned that the emphasis of this appendix lies not on mathematical rigor but rather on giving some physical and mathematical insight. Therefore aspects of mostly mathematical nature are not discussed in detail.

The operator $\hat{G}^{-1}$ mediates a mapping between the space of changes $\delta n(\mathbf{r})$ of the electron density, hereafter denoted as space δn, and the space of changes $\delta v_s(\mathbf{r})$ of the effective potential, hereafter denoted as space δv_s. The space δv_s does not include constant functions whereas the space δn is characterized by

$$\int d\mathbf{r}\, \delta n(\mathbf{r})=0 \; . \tag{B1}$$

The space δn is a vector subspace of the vector space of all functions because a linear combination of functions out of δn is again a function out of δn. Therefore there exists an orthonormal basis for the space δn and the mapping G^{-1} is defined by the images of the basis functions of δn in the space δv_s. Next, it will be shown that the space δn, like the space δv, is obtained from the full space of functions by excluding constant functions, i.e., the spaces δn and δv are identical. For this a function $f(\mathbf{r})$ is assumed which is orthogonal to the space δn and which is not a constant function. Then there exist at least two points $\mathbf{r}_1$ and $\mathbf{r}_2$ with $f(\mathbf{r}_1)\neq f(\mathbf{r}_2)$. However, the function $g(\mathbf{r})=\delta(\mathbf{r}-\mathbf{r}_1)-\delta(\mathbf{r}-\mathbf{r}_2)$ out of the space δn, in contrast to the assumption, is not orthogonal to $f(\mathbf{r})$.

$$\int d\mathbf{r} f(\mathbf{r})g(\mathbf{r})=\int d\mathbf{r} f(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}_1)-\int d\mathbf{r} f(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}_2) = f(\mathbf{r}_1)-f(\mathbf{r}_2)\neq 0 \; . \tag{B2}$$

This is a contradiction and therefore, as in the case of the space δv_s the only functions needed to supplement the space δn to the space of all functions are constant functions. The foregoing is the reason that Eqs. (24) and (26) of the main text have the same structure.

Now, a mapping $G^{-1'}$ with the operator $\hat{G}^{-1'}$ and with the corresponding function $G^{-1'}(\mathbf{r}_1,\mathbf{r}_2)$ is defined as follows. The image of the basis functions of δn is given by the original mapping G^{-1}, the image of the constant functions is determined by the image of one constant function, e.g., of $f(\mathbf{r})=1$. This image is chosen arbitrarily within the space δv_s. Note that the space δv_s remains unchanged, i.e., $G^{-1'}$ is a mapping of the full space of functions on the space δv_s. This leads to potentials $v_j'(\mathbf{r}_1)$ [see Eqs. (2) and (17)] defined by

$$v_j'(\mathbf{r}_1)=\int d\mathbf{r}_2 \frac{\delta E_j}{\delta v_s(\mathbf{r}_2)} G^{-1'}(\mathbf{r}_2,\mathbf{r}_1) \tag{B3}$$

instead of potentials $v_j(\mathbf{r}_1)$ defined according to Eqs. (2) and (17) by

$$v_j(\mathbf{r}_1)=\int d\mathbf{r}_2 \frac{\delta E_j}{\delta v_s(\mathbf{r}_2)} G^{-1}(\mathbf{r}_2,\mathbf{r}_1) \; . \tag{B4}$$

The difference between the potentials $v_j(\mathbf{r}_1)$ and $v_j'(\mathbf{r}_1)$ is a constant which depends on the arbitrary choice made for the image of the constant functions in the definition of the mapping $G^{-1'}$. The exchange potential $v_{\mathrm{xc}}'(\mathbf{r}_1)$ obtained by substituting the potentials $v_{\mathrm{x}}(\mathbf{r}_1)$ and $v_j(\mathbf{r}_1)$ by the corresponding potentials $v_{\mathrm{x}}'(\mathbf{r}_1)$ and $v_j'(\mathbf{r}_1)$ then, like the potentials $v_{\mathrm{x}}'(\mathbf{r}_1)$ and $v_j'(\mathbf{r}_1)$ itself, is defined only to within an arbitrary constant. That means, the generalization of the mapping G^{-1} to the mapping $G^{-1'}$ introduces an arbitrary constant in the exchange-correlation potential.

For a given change $\delta n(\mathbf{r})$ out of the space δn the change δE_j does not depend on whether the functional derivative $\delta E_j/\delta n(\mathbf{r})$ is set equal to $v_j(\mathbf{r})$ or $v_j'(\mathbf{r})$ because $\delta n(\mathbf{r})$ contains no contributions of constant functions and therefore the integrals

$$\int d\mathbf{r}\, v_j'(\mathbf{r})\delta n(\mathbf{r})=\int d\mathbf{r}\, v_j(\mathbf{r})\delta n(\mathbf{r}) \tag{B5}$$

give the same value. This means each functional derivative $\delta E_j/\delta n(\mathbf{r})$ can be identified with $v_j'(\mathbf{r})$ as well as $v_j(\mathbf{r})$ and therefore as usual is defined only to within a constant for changes $\delta n(\mathbf{r})$ out of the space δn.

Note that in this appendix as throughout in this work the number of electrons is fixed. This is a necessary condition for Eq. (B5) to be valid. If the number of electrons is allowed to vary the functional derivative of the total energy, of the exchange-correlation energy, and of their parts with respect to the density are no longer undefined with respect to the addition of a constant. See in this context the discussion of the treatment of the chemical potential and the ionization potential in density-functional theory (e.g., Refs. [17–19]).

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