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Orbital structure of the Kohn-Sham exchange potential and exchange kernel and the field-counteracting potential for molecules in an electric field

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Exchange-only Kohn-Sham (KS) theory is developed based on a physically motivated common energy denominator approximation for the orbital Green's function $G_{i\sigma}$. An explicit expression for the exchange potential $v_{x\sigma}$ in terms of the occupied KS orbitals is obtained via the analytical inverse of the resulting density response function $\chi_{s\sigma}$, with $v_{x\sigma}$ being subdivided into the Slater potential $v_{S\sigma}$ and the "response" potential $v_{\mathrm{resp}\sigma}$. The latter exhibits a characteristic orbital structure with "diagonal" contributions from the densities $|\psi_{i\sigma}|^2$ of the occupied KS orbitals as well as "off-diagonal" ones from the occupied-occupied orbital products $\psi_{i\sigma}\psi_{j\sigma}^*$. An expression for the response part $f_{\mathrm{resp}\sigma}$ of the exchange kernel is derived. It is established for the case of a symmetric molecular chain in an applied electric field that the kernel derived from the Krieger-Li-Iafrate potential with the Sharp-Horton approximation for $G_{i\sigma}$ fails to produce the field-counteracting potential $\delta v_{\mathrm{resp}\sigma}$, which is lacking in local-density and generalized-gradient approximations but which is required to obtain realistic (hyper)polarizabilities. On the contrary, as is shown in the case of He_2, the present kernel $f_{\mathrm{resp}\sigma}$ generates a field-counteracting potential $\delta v_{\mathrm{resp}\sigma}^{(\mathrm{fc})}$. The field-counteracting exchange effect is seen to arise from the spatial dependence of the cross product $\psi_g\psi_u\rho^{-1}$ of the symmetric and antisymmetric orbitals which is coupled with an integral over itself times $\delta\rho$. Similar "self-coupling" terms are indicated in the general case of a symmetric molecular chain.

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I. INTRODUCTION

The basic quantity of the Kohn-Sham (KS) density-functional theory (DFT) [1] in the exchange-only approximation is the exchange potential $v_{x\sigma}$ which, as a component of the total KS potential $v_{s\sigma}$

$$v_{s\sigma}(\mathbf{r}_1)=v_{\mathrm{ext}}(\mathbf{r}_1)+v_H(\mathbf{r}_1)+v_{x\sigma}(\mathbf{r}_1), \tag{1.1}$$

determines the KS spin orbitals $\psi_{i\sigma}$

$$\{-\tfrac{1}{2}\nabla^2+v_{s\sigma}(\mathbf{r}_1)\}\psi_{i\sigma}(\mathbf{r}_1)=\epsilon_{i\sigma}\psi_{i\sigma}(\mathbf{r}_1) \tag{1.2}$$

and the electron spin density ρ_σ of a many-electron system. In Eq. (1.1) other components of $v_{s\sigma}$ are the external potential v_{ext} and the Hartree potential v_H of the electrostatic electron repulsion. The exchange potential $v_{x\sigma}$ is defined as the functional derivative of the exchange energy

$$E_x[\{\psi_{i\sigma}\}]=-\frac{1}{2}\sum_\sigma\sum_{ij}^{N_\sigma}\int n_{i\sigma}n_{j\sigma}\times\frac{\psi_{i\sigma}(\mathbf{r}_1)\psi_{j\sigma}^*(\mathbf{r}_1)\psi_{i\sigma}^*(\mathbf{r}_2)\psi_{j\sigma}(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}d\mathbf{r}_1d\mathbf{r}_2 \tag{1.3}$$

with respect to the electron spin density ρ_σ,

$$\begin{aligned}v_{x\sigma}(\mathbf{r}_3)&=\frac{\delta E_x[\{\psi_{i\sigma}\}]}{\delta\rho_\sigma(\mathbf{r}_3)}\\&=-\frac{1}{2}\sum_{ij}^{N_\sigma}n_{i\sigma}n_{j\sigma}\\&\quad\times\int\frac{\delta\psi_{i\sigma}(\mathbf{r}_1)}{\delta\rho_\sigma(\mathbf{r}_3)}\frac{\psi_{j\sigma}^*(\mathbf{r}_1)\psi_{i\sigma}^*(\mathbf{r}_2)\psi_{j\sigma}(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}\\&\quad\times d\mathbf{r}_1d\mathbf{r}_2-\frac{1}{2}\sum_{ij}^{N_\sigma}n_{i\sigma}n_{j\sigma}\\&\quad\times\int\frac{\delta\psi_{j\sigma}(\mathbf{r}_2)}{\delta\rho_\sigma(\mathbf{r}_3)}\frac{\psi_{i\sigma}(\mathbf{r}_1)\psi_{j\sigma}^*(\mathbf{r}_1)\psi_{i\sigma}^*(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}\\&\quad\times d\mathbf{r}_1d\mathbf{r}_2+\mathrm{c.c.}\end{aligned} \tag{1.4}$$

In Eqs. (1.3) and (1.4) the summations run over N_σ occupied KS spin orbitals $\psi_{i\sigma}$.

An accurate $v_{x\sigma}$ can be obtained with the self-consistent solution of the integro-differential equations of the so-called optimized potential method (OPM) [2]. For atomic systems this can be done with the method of Talman and Shadwick [2] by inverting the static KS linear response function $\chi_{s\sigma}$ on a numerical grid. Recently, the OPM has been extended to molecular systems with the exact exchange (EXX) implementation of Ivanov, Hirata, and Bartlett [3], in which basis set expansion [4] is employed to obtain the inverse $\chi_{s\sigma}^{-1}$ and the subsequent $v_{x\sigma}$. The function $\chi_{s\sigma}$ can be inverted on a subspace of its eigenfunctions, such that the eigenfunctions with zero (or near zero for practical purposes) eigenvalues are excluded. To obtain $v_{x\sigma}$ of a high quality with EXX, a large basis is required, in particular, the KS basis should include all occupied and a large number of unoccupied orbitals $\psi_{i\sigma}$. The numerical stability of this inversion becomes a problem, especially for molecular applications. Another EXX method of Görling [5], which also uses basis set expansion, requires no inverse of $\chi_{s\sigma}$. Instead, $v_{x\sigma}(\mathbf{r}_1)$ is obtained with the exchange charge density $\rho_{x\sigma}(\mathbf{r}_2)$ from the solution of the corresponding Poisson's equation with a basis set expansion of $\rho_{x\sigma}(\mathbf{r}_2)$. Numerical problems have been reported also for this variant of EXX.

It has been demonstrated [6], however, that in a certain approximation $\chi_{s\sigma}$ can be inverted analytically, so that the resultant $\chi_{s\sigma}^{-1}$ satisfies the relation

$$\int \chi_{s\sigma}(\mathbf{r}_1,\mathbf{r}_2)\chi_{s\sigma}^{-1}(\mathbf{r}_2,\mathbf{r}_3)d\mathbf{r}_2=\delta(\mathbf{r}_1-\mathbf{r}_3). \tag{1.5}$$

In order to do this, the KS static orbital Green's function $G_{i\sigma}$ that enters the expression for $\chi_{s\sigma}$ is broken up in a local (δ function) part and a remainder that is approximated. An example is the admittedly crude Sharp and Horton (SH) [7,8] approximation for $G_{i\sigma}$, which does not preserve the proper orbital structure of the response function $\chi_{s\sigma}$ (see the next section for discussion). Surprisingly, this approximation yields the good-quality approximate $v_{x\sigma}$ of the Krieger, Li, and Iafrate (KLI) method [8], which is expressed in terms of only the occupied KS orbitals. Such a compact expression for $v_{x\sigma}$ can serve as a basis for further, simpler approximations, which are required for efficient DFT and time-dependent DFT calculations. Simple orbital-dependent approximations to the KLI potential were developed in [9–12].

Having an explicit expression for $v_{x\sigma}$, one can obtain an expression for the exchange kernel $f_{x\sigma}$, the derivative of $v_{x\sigma}$ with respect to ρ_σ

$$f_{x\sigma}(\mathbf{r}_1,\mathbf{r}_2)=\frac{\delta E_{x\sigma}[\rho]}{\delta\rho_\sigma(\mathbf{r}_1)\,\delta\rho_\sigma(\mathbf{r}_2)}=\frac{\delta v_{x\sigma}(\mathbf{r}_1)}{\delta\rho_\sigma(\mathbf{r}_2)}. \tag{1.6}$$

Within time-dependent density-functional perturbation theory (TDDFPT) [13–16], $f_{x\sigma}$ determines the change $\delta v_{x\sigma}$ in response to a changing external field δv_{ext}, which in the static limit is obtained from the static density response $\delta\rho_\sigma(\mathbf{r})$

$$\delta v_{x\sigma}(\mathbf{r}_1)=\int d\mathbf{r}_2 f_{x\sigma}(\mathbf{r}_1,\mathbf{r}_2)\,\delta\rho_\sigma(\mathbf{r}_2). \tag{1.7}$$

As was established within the finite-field approach for extended [17–22] and molecular [23–25] systems, application of a uniform electric field, induces in the exchange-correlation potential v_{xc} and its exchange part $v_{x\sigma}$ characteristic ultranonlocal terms δv_{xc} and $\delta v_{x\sigma}$, which span the entire system and which counteract the external electric field. It was recognized that the absence or presence of a field-counteracting term is a matter of practical importance for DFT calculations. The standard local-density (LDA) and generalized-gradient (GGA) approximations, which all fail to produce the counteracting field, gave quite poor results for the linear and nonlinear polarizabilities of finite polyacetylene chains of varying length and also of the hydrogen chains H_n [23,26]. The corresponding LDA/GGA errors are much larger (by orders of magnitude) than those for "standard molecules" and also much larger than estimates [27] for errors in dielectric constants and nonlinear susceptibilities of solids. Evidently, when in contrast to the LDA and GGA approximations the orbital structure of the exchange functionals (1.3) and (1.4) is properly incorporated in $f_{x\sigma}$, the response formula (1.7) should produce the same field-counteracting term $\delta v_{x\sigma}$ as the finite-field approach with the density $\delta\rho_\sigma(\mathbf{r})$.

It remains to be seen to what extent the failure of LDA/GGA is an exchange effect, or also a correlation effect. In this paper the exchange-only Kohn-Sham theory is developed based on a physically motivated approximation for the orbital Green's function $G_{i\sigma}$, which is presented in Sec. II. An expression for the exchange potential $v_{x\sigma}$ in terms of the occupied KS orbitals is derived in Sec. III, with $v_{x\sigma}$ being subdivided into the Slater potential $v_{S\sigma}$ and the "response" potential $v_{\mathrm{resp}\sigma}$. The latter will be shown to exhibit a characteristic orbital structure with KLI-type "diagonal" contributions from the densities $|\psi_{i\sigma}|^2$ of the occupied KS orbitals as well as with "off-diagonal" ones from orbital products $\psi_{i\sigma}\psi_{j\sigma}^*$. In Sec. IV expressions for the response part $f_{\mathrm{resp}\sigma}$ of the exchange kernel are derived. It is established for the case of a symmetric molecular chain in an electric field, that the kernel derived from the KLI potential with the SH approximation for $G_{i\sigma}$ fails to produce the field-counteracting term $\delta v_{\mathrm{resp}\sigma}$ via Eq. (1.7). Contrary to this, $f_{\mathrm{resp}\sigma}$ obtained with the present approach has a proper spatially nonlocal orbital structure with the occupied-occupied orbital products $\psi_{i\sigma}\psi_{j\sigma}^*$ and this yields a potential $\delta v_{\mathrm{resp}\sigma}$ with field-counteracting terms. In Sec. V implications of these results for DFT and TDDFPT are discussed and the conclusions are drawn.

II. COMMON DENOMINATOR APPROXIMATIONS FOR THE GREEN'S FUNCTION

In order to obtain from Eq. (1.4) the orbital-dependent expression for $v_{x\sigma}$, one has to evaluate the functional derivative $\delta\psi_{i\sigma}(\mathbf{r}_1)/\delta\rho_\sigma(\mathbf{r}_3)$ of the KS orbital with respect to the density. Following Ref. [6], we evaluate the derivative with the functional chain rule differentiation

$$\frac{\delta\psi_{i\sigma}(\mathbf{r}_1)}{\delta\rho_\sigma(\mathbf{r}_2)}=\int\frac{\delta\psi_{i\sigma}(\mathbf{r}_1)}{\delta v_{s\sigma}(\mathbf{r}_3)}\frac{\delta v_{s\sigma}(\mathbf{r}_3)}{\delta\rho_\sigma(\mathbf{r}_2)}d\mathbf{r}_3 \tag{2.1}$$

through the derivative of $\psi_{i\sigma}$ with respect to the KS potential $v_{s\sigma}$ and the derivative of $v_{s\sigma}$ with respect to the density ρ_σ. The latter derivatives are determined with the KS static orbital Green's function $G_{i\sigma}$

$$G_{i\sigma}(\mathbf{r}_1,\mathbf{r}_2)=\sum_{j\neq i}\frac{\psi_{j\sigma}(\mathbf{r}_1)\psi_{j\sigma}^*(\mathbf{r}_2)}{\epsilon_{j\sigma}-\epsilon_{i\sigma}}, \tag{2.2}$$

which yields the change of $\psi_{i\sigma}$ in response to a variation $\delta v_{s\sigma}$,

$$\delta\psi_{i\sigma}(\mathbf{r}_1)=-\int d\mathbf{r}_2 G_{i\sigma}(\mathbf{r}_1,\mathbf{r}_2)\psi_{i\sigma}(\mathbf{r}_2)\,\delta v_s(\mathbf{r}_2). \tag{2.3}$$

The orbital derivative in the right-hand side (RHS) of Eq. (2.1) follows from Eq. (2.3),

$$\frac{\delta\psi_{i\sigma}(\mathbf{r}_1)}{\delta v_s(\mathbf{r}_3)} = -G_{i\sigma}(\mathbf{r}_1,\mathbf{r}_3)\,\psi_{i\sigma}(\mathbf{r}_3). \tag{2.4}$$

The other derivative is just the inverse

$$\frac{\delta v_{s\sigma}(\mathbf{r}_3)}{\delta\rho_\sigma(\mathbf{r}_2)} = \chi_{s\sigma}^{-1}(\mathbf{r}_3,\mathbf{r}_2) \tag{2.5}$$

of the static KS linear response function $\chi_{s\sigma}$,

$$\chi_{s\sigma}(\mathbf{r}_2,\mathbf{r}_3) = \frac{\delta\rho_\sigma(\mathbf{r}_2)}{\delta v_{s\sigma}(\mathbf{r}_3)}, \tag{2.6}$$

which is also determined with the help of the Green's function $G_{i\sigma}$,

$$\begin{aligned}\chi_{s\sigma}(\mathbf{r}_2,\mathbf{r}_3) &= -\sum_{i=1}^{N_\sigma} n_{i\sigma}\psi_{i\sigma}^*(\mathbf{r}_2)G_{i\sigma}(\mathbf{r}_2,\mathbf{r}_3)\,\psi_{i\sigma}(\mathbf{r}_3) + \text{c.c.}\\ &= -\sum_{i=1}^{N_\sigma} n_{i\sigma}\psi_{i\sigma}^*(\mathbf{r}_2)\,\psi_{i\sigma}(\mathbf{r}_3)\\ &\quad\times\sum_{j\neq i}\frac{\psi_{j\sigma}(\mathbf{r}_2)\,\psi_{j\sigma}^*(\mathbf{r}_3)}{\epsilon_{j\sigma}-\epsilon_{i\sigma}} + \text{c.c.}\\ &= -\sum_{i=1}^{N_\sigma} n_{i\sigma}\psi_{i\sigma}^*(\mathbf{r}_2)\,\psi_{i\sigma}(\mathbf{r}_3)\\ &\quad\times\sum_{c>N_\sigma}\frac{\psi_{c\sigma}(\mathbf{r}_2)\,\psi_{c\sigma}^*(\mathbf{r}_3)}{\epsilon_{c\sigma}-\epsilon_{i\sigma}} + \text{c.c.}\end{aligned} \tag{2.7}$$

Note an important difference between the orbital expansions (2.2) and (2.7) of the functions $G_{i\sigma}$ and $\chi_{s\sigma}$. In Eq. (2.2) all the orbitals, except the orbital $\psi_{i\sigma}$ itself, contribute to $G_{i\sigma}$, so that there are contributions from other occupied orbitals $\psi_{j\sigma}$, $j_\sigma \leqslant N_\sigma$. However, in the double sum of Eq. (2.7) the contributions from the pairs of the occupied orbitals $\psi_{i\sigma}$ and $\psi_{j\sigma}$ cancel each other, since they contain the orbital energy differences $\Delta\epsilon_{ij\sigma} = \epsilon_{j\sigma} - \epsilon_{i\sigma}$ and $\Delta\epsilon_{ji\sigma} = \epsilon_{i\sigma} - \epsilon_{j\sigma} = -\Delta\epsilon_{ij\sigma}$ of the opposite signs. Thus, the occupied-occupied orbital mixing does not contribute to the response function $\chi_{s\sigma}$, which contains only contributions corresponding to excitations from an occupied orbital $\psi_{j\sigma}$ to an unoccupied one $\psi_{c\sigma}$. Strictly speaking, the above-mentioned cancellation is possible, if $n_{i\sigma}$ of all occupied orbitals are equal to each other, for instance, $n_{i\sigma}=1$ as for a pure KS state. This cancellation will be the physical basis for our further derivation, so that throughout the paper we assume that for all occupied orbitals $n_{i\sigma}=n_{j\sigma}$.

Finding an explicit expression for the orbital derivative (2.1) requires an approximation to the Green's function (2.2). In KLI [8] the simple Sharp-Horton approximation [7] has been employed, according to which various differences $\Delta\epsilon_{ij\sigma} = \epsilon_{j\sigma} - \epsilon_{i\sigma}$ in Eq. (2.2) are represented by a single constant $\epsilon_{j\sigma} - \epsilon_{i\sigma} \approx \Delta\tilde{\epsilon}_\sigma$. With this approximation, summation over the complete spectrum produces a δ function and the functions $G_{i\sigma}$ and $\chi_{s\sigma}$ assume the form

$$G_{i\sigma}(\mathbf{r}_1,\mathbf{r}_2) \approx \frac{1}{\Delta\tilde{\epsilon}_\sigma}\{\delta(\mathbf{r}_1-\mathbf{r}_2) - \psi_{i\sigma}(\mathbf{r}_1)\,\psi_{i\sigma}^*(\mathbf{r}_2)\}, \tag{2.8}$$

$$\begin{aligned}\chi_{s\sigma}(\mathbf{r}_1,\mathbf{r}_2) \approx -\frac{2}{\Delta\tilde{\epsilon}_\sigma}\Bigg\{ &\delta(\mathbf{r}_1-\mathbf{r}_2)\rho_\sigma(\mathbf{r}_1)\\ &-\sum_{i=1}^{N_\sigma} n_{i\sigma}\left|\psi_{i\sigma}(\mathbf{r}_1)^2\right|\left|\psi_{i\sigma}(\mathbf{r}_2)^2\right|\Bigg\}.\end{aligned} \tag{2.9}$$

The approximation (2.8) appears to be a crude one. Indeed, it levels large energy differences $\Delta\epsilon_{ic\sigma}$ for the occupied-unoccupied orbital pairs and relatively small differences $\Delta\epsilon_{ij\sigma}$ for the occupied-occupied pairs and in the latter case it neglects the change of the sign when going from $\Delta\epsilon_{ij\sigma}$ to $\Delta\epsilon_{ji\sigma}$. Because of this, in the SH density response function (2.9) only the self-interaction is excluded and it effectively contains contributions from mixing of different occupied orbitals, unlike the exact KS function (2.7).

In this paper we propose to use a more physically motivated common energy denominator approximation for $G_{i\sigma}$. Within the present approximation, only the energy differences $\Delta\epsilon_{ic\sigma}$ for the occupied-unoccupied orbital pairs are approximated with the mean energy $\Delta\tilde{\epsilon}_\sigma$

$$\Delta\epsilon_{ic\sigma} = \epsilon_{c\sigma} - \epsilon_{i\sigma} \approx \Delta\tilde{\epsilon}_\sigma, \quad i \leqslant N_\sigma, \quad c > N_\sigma, \tag{2.10}$$

while the true differences $\Delta\epsilon_{ij\sigma}$ for the occupied-occupied pairs are retained. This gives for $G_{i\sigma}$

$$\begin{aligned}G_{i\sigma}(\mathbf{r}_1,\mathbf{r}_2) \approx &\sum_{j\neq i}^{N_\sigma}\frac{1}{\Delta\epsilon_{ij\sigma}}\,\psi_{j\sigma}(\mathbf{r}_1)\,\psi_{j\sigma}^*(\mathbf{r}_2)\\ &+\frac{1}{\Delta\tilde{\epsilon}_\sigma}\sum_{c>N_\sigma}\psi_{c\sigma}(\mathbf{r}_1)\,\psi_{c\sigma}^*(\mathbf{r}_2).\end{aligned} \tag{2.11}$$

Adding to and subtracting from the RHS of Eq. (2.11) contributions of the occupied orbitals with the common denominator $\Delta\tilde{\epsilon}_\sigma$, we obtain the master expressions for $G_{i\sigma}$,

$$\begin{aligned}G_{i\sigma}(\mathbf{r}_1,\mathbf{r}_2) \approx &\frac{\delta(\mathbf{r}_1-\mathbf{r}_2)}{\Delta\tilde{\epsilon}_\sigma} - \frac{1}{\Delta\tilde{\epsilon}_\sigma}\sum_{j}^{N_\sigma}\psi_{j\sigma}(\mathbf{r}_1)\,\psi_{j\sigma}^*(\mathbf{r}_2)\\ &+\sum_{j\neq i}^{N_\sigma}\frac{1}{\Delta\epsilon_{ij\sigma}}\,\psi_{j\sigma}(\mathbf{r}_1)\,\psi_{j\sigma}^*(\mathbf{r}_2),\end{aligned} \tag{2.12}$$

and for the corresponding density response function

$$
\begin{aligned}
\chi_{s\sigma}(\mathbf{r}_1,\mathbf{r}_2)\approx&-\frac{1}{\Delta\tilde{\epsilon}_\sigma}\,\delta(\mathbf{r}_1-\mathbf{r}_2)\rho_\sigma(\mathbf{r}_1)\\
&+\frac{1}{\Delta\tilde{\epsilon}_\sigma}\sum_i^{N_\sigma} n_{i\sigma}\psi^*_{i\sigma}(\mathbf{r}_1)\psi_{i\sigma}(\mathbf{r}_2)\\
&\times\sum_j^{N_\sigma}\psi_{j\sigma}(\mathbf{r}_1)\psi^*_{j\sigma}(\mathbf{r}_2)\\
&-\sum_i^{N_\sigma} n_{i\sigma}\psi^*_{i\sigma}(\mathbf{r}_1)\psi_{i\sigma}(\mathbf{r}_2)\sum_{j\neq i}^{N_\sigma}\frac{1}{\Delta\epsilon_{ij\sigma}}\psi_{j\sigma}(\mathbf{r}_1)\\
&\times\psi^*_{j\sigma}(\mathbf{r}_2)+\text{c.c.}\\
=&-\frac{1}{\Delta\tilde{\epsilon}_\sigma}\sum_i^{N_\sigma} n_{i\sigma}\psi^*_{i\sigma}(\mathbf{r}_1)\psi_{i\sigma}(\mathbf{r}_2)\\
&\times\sum_{c>N_\sigma}\psi_{c\sigma}(\mathbf{r}_1)\psi^*_{c\sigma}(\mathbf{r}_2)+\text{c.c.}
\end{aligned}
\qquad (2.13)
$$

One can see from Eq. (2.13) that, just as for the exact function (2.7), the terms with the occupied-occupied mixing are properly excluded from the approximate $\chi_{s\sigma}$ of Eq. (2.13). In particular, the second sum in the RHS of Eq. (2.13) disappears due to the mutual cancellation of its terms (under the assumption that $n_{i\sigma}=n_{j\sigma}$) and the first sum cancels the corresponding contribution to the δ function. As a result, only the terms with the occupied-unoccupied mixing are properly retained within the common energy denominator approximation. In this sense, the present approximation preserves the proper orbital structure of the density response function. In the next section it will be applied to evaluate the orbital derivative (2.1) and, as a consequence, to obtain an explicitly orbital-dependent expression for the exchange potential $v_{x\sigma}$.

III. ORBITAL STRUCTURE OF $v_{x\sigma}$

The form of the approximate density response function (2.13) allows us to obtain its inverse with a generalization of the analytical inverse procedure of Ref. [6] after fixing the long-range asymptotics of the inverse $\chi^{-1}_{s\sigma}$ and the gauge of the resultant potential $v_{x\sigma}$. The problem with the inverse is that Eq. (1.5) has no unique solution for $\chi^{-1}_{s\sigma}$ as adding a constant to $\chi^{-1}_{s\sigma}$ gives another solution for Eq. (1.5). As is shown in the Appendix, $\chi^{-1}_{s\sigma}$ (and, eventually, $v_{x\sigma}$) can be forced to go to zero asymptotically by exclusion of the diagonal term $2n_{N\sigma}\psi^*_{N\sigma}(\mathbf{r}_1)\psi_{N\sigma}(\mathbf{r}_2)\psi_{N\sigma}(\mathbf{r}_1)\psi^*_{N\sigma}(\mathbf{r}_2)/\Delta\tilde{\epsilon}_\sigma$ with the densities $|\psi_{N\sigma}(\mathbf{r}_1)|^2$ and $|\psi_{N\sigma}(\mathbf{r}_2)|^2$ of the highest occupied molecular orbital (HOMO) $\psi_{N\sigma}$ from the first sum in Eq. (2.13):

$$
\begin{aligned}
\chi_{s\sigma}(\mathbf{r}_1,\mathbf{r}_2)\approx&-\frac{2}{\Delta\tilde{\epsilon}_\sigma}\,\delta(\mathbf{r}_1-\mathbf{r}_2)\rho_\sigma(\mathbf{r}_1)\\
&+\frac{2}{\Delta\tilde{\epsilon}_\sigma}{\sum_{ij}}'\, n_{i\sigma}\psi^*_{i\sigma}(\mathbf{r}_1)\psi_{i\sigma}(\mathbf{r}_2)\psi_{j\sigma}(\mathbf{r}_1)\psi^*_{j\sigma}(\mathbf{r}_2).
\end{aligned}
\qquad (3.1)
$$

The double summation in Eq. (3.1) goes over all occupied orbitals and the primed sum indicates the above-mentioned exclusion. Due to the symmetry with respect to the orbital indices and electron coordinates the second term of Eq. (3.1) is real under our assumption $n_{i\sigma}=n_{j\sigma}$.

The exact inverse of this function is derived in the Appendix and has the following form:

$$
\begin{aligned}
\chi^{-1}_{s\sigma}(\mathbf{r}_1,\mathbf{r}_2)=&-\frac{\Delta\tilde{\epsilon}_\sigma}{2\rho_\sigma(\mathbf{r}_1)}\,\delta(\mathbf{r}_1-\mathbf{r}_2)\\
&-\frac{\Delta\tilde{\epsilon}_\sigma}{2\rho_\sigma(\mathbf{r}_1)\rho_\sigma(\mathbf{r}_2)}\sum_{ijkl}^{N_\sigma} n_{i\sigma}\xi^\sigma_{ijkl}\psi_{i\sigma}(\mathbf{r}_1)\\
&\times\psi^*_{j\sigma}(\mathbf{r}_1)\psi_{k\sigma}(\mathbf{r}_2)\psi^*_{l\sigma}(\mathbf{r}_2),\\
&\xi^\sigma_{ijN\sigma N\sigma}=\xi^\sigma_{N\sigma N\sigma kl}=0.
\end{aligned}
\qquad (3.2)
$$

Just like $\chi_{s\sigma}$, its inverse $\chi^{-1}_{s\sigma}$ consists of a local δ function part and a nonlocal orbital-dependent part, the latter being represented by orbital cross products $\psi_{i\sigma}(\mathbf{r}_1)\psi^*_{j\sigma}(\mathbf{r}_1)$ of electron coordinate $\mathbf{r}_1$ coupled with the products $\psi_{k\sigma}(\mathbf{r}_2)\psi^*_{l\sigma}(\mathbf{r}_2)$ of $\mathbf{r}_2$. The coupling coefficients ξ^σ_{ijkl} are the elements of the matrix inverse

$$
\xi^\sigma_{ijkl}=(\overline{\mathbf{I}}-\overline{\mathbf{N}}^\sigma)^{-1}_{ijkl},
\qquad (3.3)
$$

$\overline{\mathbf{N}}^\sigma$ is the overlap matrix of the orbital products $\psi_{i\sigma}\psi^*_{j\sigma}$ and $\psi_{k\sigma}\psi^*_{l\sigma}$

$$
N^\sigma_{ijkl}=n_k\int\frac{\psi_{i\sigma}(\mathbf{r}_1)\psi^*_{j\sigma}(\mathbf{r}_1)\psi_{k\sigma}(\mathbf{r}_1)\psi^*_{l\sigma}(\mathbf{r}_1)}{\rho_\sigma(\mathbf{r}_1)}\,d\mathbf{r}_1,
\qquad (3.4)
$$

and $\overline{\mathbf{I}}$ is the unit matrix

$$
I_{ijkl}=\delta_{ik}\delta_{jl}.
\qquad (3.5)
$$

The terms with at least one HOMO density $|\psi_{N\sigma}|^2$ are excluded from the sums in Eq. (3.2), which provides the zero asymptotics of $\chi^{-1}_{s\sigma}$,

$$
\lim_{|\mathbf{r}_1|\to\infty}\{\chi^{-1}_{s\sigma}(\mathbf{r}_1,\mathbf{r}_2)\}=\lim_{|\mathbf{r}_2|\to\infty}\{\chi^{-1}_{s\sigma}(\mathbf{r}_1,\mathbf{r}_2)\}=0.
\qquad (3.6)
$$

This is taken into account by zeroing the corresponding coefficients $\xi^\sigma_{ijN\sigma N\sigma}$ and $\xi^\sigma_{N\sigma N\sigma kl}$. Inserting Eq. (3.2) in Eq. (2.5), Eq. (2.12) in Eq. (2.4), and then Eqs. (2.4) and (2.5) in Eq. (2.1), we determine the orbital derivative

$$
\begin{aligned}
\frac{\delta\psi_{i\sigma}(\mathbf{r}_1)}{\delta\rho_\sigma(\mathbf{r}_3)}=&-\int G_{i\sigma}(\mathbf{r}_1,\mathbf{r}_2)\psi_{i\sigma}(\mathbf{r}_2)\chi^{-1}_{s\sigma}(\mathbf{r}_2,\mathbf{r}_3)d\mathbf{r}_2\\
=&-\int\Bigg[\frac{\delta(\mathbf{r}_1-\mathbf{r}_2)}{\Delta\tilde{\epsilon}_\sigma}-\sum_j^{N_\sigma}\left(\frac{1}{\Delta\tilde{\epsilon}_\sigma}-\frac{1}{\Delta\epsilon_{ij\sigma}}\right)\\
&\times\psi_{j\sigma}(\mathbf{r}_1)\psi^*_{j\sigma}(\mathbf{r}_2)\Bigg]\psi_{i\sigma}(\mathbf{r}_2)\chi^{-1}_{s\sigma}(\mathbf{r}_2,\mathbf{r}_3)d\mathbf{r}_2
\end{aligned}
$$

$$
\begin{aligned}
&= -\frac{1}{\Delta\tilde{\epsilon}_{\sigma}}\psi_{i\sigma}(\mathbf{r}_1)\chi_{s\sigma}^{-1}(\mathbf{r}_1,\mathbf{r}_3)\\
&+\sum_{j}^{N_\sigma}\left(\frac{1}{\Delta\tilde{\epsilon}_{\sigma}}-\frac{1}{\Delta\epsilon_{ij\sigma}}\right)\psi_{j\sigma}(\mathbf{r}_1)\\
&\times\int\psi_{i\sigma}(\mathbf{r}_2)\psi_{j\sigma}^{*}(\mathbf{r}_2)\chi_{s\sigma}^{-1}(\mathbf{r}_2,\mathbf{r}_3)d\mathbf{r}_2 .
\end{aligned}
\tag{3.7}
$$

To make Eq. (3.7) more compact, we have combined two sums in Eq. (2.12), extending the last sum of Eq. (2.12) to all occupied orbitals and formally assuming $\Delta\epsilon_{ii\sigma}=\infty$, in order to properly exclude the term with $\Delta\epsilon_{ii\sigma}$ from the sums in Eq. (3.7). The last integral in Eq. (3.7) can be worked out as, using $\xi_{mnkl}^{\sigma}=\xi_{klmn}^{\sigma}$,

$$
\begin{aligned}
&\int\psi_{i\sigma}(\mathbf{r}_2)\psi_{j\sigma}^{*}(\mathbf{r}_2)\chi_{s\sigma}^{-1}(\mathbf{r}_2,\mathbf{r}_3)d\mathbf{r}_2\\
&\quad=-\frac{\Delta\tilde{\epsilon}_{\sigma}}{2\rho_{\sigma}(\mathbf{r}_3)}\psi_{i\sigma}(\mathbf{r}_3)\psi_{j\sigma}^{*}(\mathbf{r}_3)-\frac{\Delta\tilde{\epsilon}_{\sigma}}{2}\sum_{klmn}^{N_\sigma}n_{k\sigma}\xi_{klmn}^{\sigma}\\
&\quad\times\int\frac{\psi_{m\sigma}(\mathbf{r}_2)\psi_{n\sigma}^{*}(\mathbf{r}_2)\psi_{i\sigma}(\mathbf{r}_2)\psi_{j\sigma}^{*}(\mathbf{r}_2)}{\rho_{\sigma}(\mathbf{r}_2)}d\mathbf{r}_2\\
&\quad\times\frac{\psi_{k\sigma}(\mathbf{r}_3)\psi_{l\sigma}^{*}(\mathbf{r}_3)}{\rho_{\sigma}(\mathbf{r}_3)}\\
&\quad=-\frac{\Delta\tilde{\epsilon}_{\sigma}}{2\rho_{\sigma}(\mathbf{r}_3)}\psi_{i\sigma}(\mathbf{r}_3)\psi_{j\sigma}^{*}(\mathbf{r}_3)-\frac{\Delta\tilde{\epsilon}_{\sigma}}{2}\sum_{klmn}^{N_\sigma}\frac{n_{k\sigma}}{n_{i\sigma}}\\
&\quad\times(\bar{\mathbf{I}}-\bar{\mathbf{N}}^{\sigma})_{klmn}^{-1}N_{mnij}^{\sigma}\frac{\psi_{k\sigma}(\mathbf{r}_3)\psi_{l\sigma}^{*}(\mathbf{r}_3)}{\rho_{\sigma}(\mathbf{r}_3)}
\end{aligned}
\tag{3.8}
$$

using the matrix relation

$$
(\bar{\mathbf{I}}-\bar{\mathbf{N}}^{\sigma})^{-1}\bar{\mathbf{N}}^{\sigma}=\bar{\mathbf{N}}^{\sigma}(\bar{\mathbf{I}}-\bar{\mathbf{N}}^{\sigma})^{-1}=(\bar{\mathbf{I}}-\bar{\mathbf{N}}^{\sigma})^{-1}-\bar{\mathbf{I}}
\tag{3.9}
$$

and assuming that $n_{k\sigma}=n_{i\sigma}$. Inserting Eq. (3.9) in Eq. (3.8), one obtains

$$
\begin{aligned}
&\int\psi_{i\sigma}(\mathbf{r}_2)\psi_{j\sigma}^{*}(\mathbf{r}_2)\chi_{s\sigma}^{-1}(\mathbf{r}_2,\mathbf{r}_3)d\mathbf{r}_2\\
&\quad=-\frac{\Delta\tilde{\epsilon}_{\sigma}}{2\rho_{\sigma}(\mathbf{r}_3)}\left\{\psi_{i\sigma}(\mathbf{r}_3)\psi_{j\sigma}^{*}(\mathbf{r}_3)\right.\\
&\quad\left.+\sum_{kl}^{N_\sigma}(\xi_{ijkl}^{\sigma}-\delta_{ik}\delta_{jl})\psi_{k\sigma}(\mathbf{r}_3)\psi_{l\sigma}^{*}(\mathbf{r}_3)\right\}\\
&\quad=-\frac{\Delta\tilde{\epsilon}_{\sigma}}{2}\sum_{kl}^{N_\sigma}\xi_{ijkl}^{\sigma}\frac{\psi_{k\sigma}(\mathbf{r}_3)\psi_{l\sigma}^{*}(\mathbf{r}_3)}{\rho_{\sigma}(\mathbf{r}_3)} .
\end{aligned}
\tag{3.10}
$$

Finally, inserting Eqs. (3.10) and (3.2) in Eq. (3.7), one finds the expression for the orbital derivative (2.1)

$$
\begin{aligned}
\frac{\delta\psi_{i\sigma}(\mathbf{r}_1)}{\delta\rho_{\sigma}(\mathbf{r}_3)}&=\frac{\psi_{i\sigma}(\mathbf{r}_1)}{2\rho_{\sigma}(\mathbf{r}_3)}\delta(\mathbf{r}_1-\mathbf{r}_3)\\
&+\sum_{mn}^{N_\sigma}\left\{\frac{\psi_{i\sigma}(\mathbf{r}_1)}{2\rho_{\sigma}(\mathbf{r}_1)}\sum_{kl}^{N_\sigma}n_{k\sigma}\xi_{klmn}^{\sigma}\psi_{k\sigma}(\mathbf{r}_1)\psi_{l\sigma}^{*}(\mathbf{r}_1)\right.\\
&\left.-\sum_{k}^{N_\sigma}\left(1-\frac{\Delta\tilde{\epsilon}_{\sigma}}{\Delta\epsilon_{ik\sigma}}\right)\frac{\psi_{k\sigma}(\mathbf{r}_1)}{2}\xi_{ikmn}^{\sigma}\right\}\\
&\times\frac{\psi_{m\sigma}(\mathbf{r}_3)\psi_{n\sigma}^{*}(\mathbf{r}_3)}{\rho_{\sigma}(\mathbf{r}_3)} .
\end{aligned}
\tag{3.11}
$$

Straightforward substitution of this expression for the orbital derivative in Eq. (1.4) produces the exchange potential $v_{x\sigma}$ in our common denominator approximation. The derivatives of $\psi_{i\sigma}(\mathbf{r}_1)$ and $\psi_{j\sigma}(\mathbf{r}_2)$ yield identical terms, which results in the following expression:

$$
\begin{aligned}
v_{x\sigma}(\mathbf{r}_3)=&-\frac{1}{2}\sum_{ij}^{N_\sigma}\frac{n_{i\sigma}n_{j\sigma}}{\rho_{\sigma}(\mathbf{r}_3)}\\
&\times\int\frac{\psi_{i\sigma}(\mathbf{r}_1)\psi_{j\sigma}^{*}(\mathbf{r}_1)\psi_{i\sigma}^{*}(\mathbf{r}_2)\psi_{j\sigma}(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}\\
&\times\delta(\mathbf{r}_1-\mathbf{r}_3)d\mathbf{r}_1d\mathbf{r}_2-\frac{1}{2}\sum_{mn}^{N_\sigma}\frac{\psi_{m\sigma}(\mathbf{r}_3)\psi_{n\sigma}^{*}(\mathbf{r}_3)}{\rho_{\sigma}(\mathbf{r}_3)}\\
&\times\sum_{ij}^{N_\sigma}n_{i\sigma}n_{j\sigma}\times\left\{\sum_{kl}^{N_\sigma}n_{k\sigma}\xi_{klmn}^{\sigma}\int\frac{\psi_{k\sigma}(\mathbf{r}_1)\psi_{l\sigma}^{*}(\mathbf{r}_1)}{\rho_{\sigma}(\mathbf{r}_1)}\right.\\
&\times\frac{\psi_{i\sigma}(\mathbf{r}_1)\psi_{j\sigma}^{*}(\mathbf{r}_1)\psi_{i\sigma}^{*}(\mathbf{r}_2)\psi_{j\sigma}(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}d\mathbf{r}_1d\mathbf{r}_2\\
&-\sum_{k}^{N_\sigma}\left(1-\frac{\Delta\tilde{\epsilon}_{\sigma}}{\Delta\epsilon_{ik\sigma}}\right)\xi_{ikmn}^{\sigma}\\
&\left.\times\int\frac{\psi_{k\sigma}(\mathbf{r}_1)\psi_{j\sigma}^{*}(\mathbf{r}_1)\psi_{i\sigma}^{*}(\mathbf{r}_2)\psi_{j\sigma}(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}d\mathbf{r}_1d\mathbf{r}_2\right\}\\
&+\text{c.c.}
\end{aligned}
\tag{3.12}
$$

As a result, $v_{x\sigma}$ is subdivided naturally into two physically meaningful components: the first term in the RHS of Eq. (3.12), taken together with its complex conjugate, turns after the δ function integration into an attractive long-range Slater potential $v_{S\sigma}$ [28], while the rest represents a repulsive short-range response potential $v_{\text{resp}\sigma}$ [29]

$$
v_{x\sigma}(\mathbf{r}_3)=v_{S\sigma}(\mathbf{r}_3)+v_{\text{resp}\sigma}(\mathbf{r}_3).
\tag{3.13}
$$

$v_{S\sigma}$ is the potential of the Fermi (exchange) hole density distribution $\rho_{x\sigma}(\mathbf{r}_2|\mathbf{r}_3)$,

$$
v_{S\sigma}(\mathbf{r}_3)=\int\frac{\rho_{x\sigma}(\mathbf{r}_2|\mathbf{r}_3)}{|\mathbf{r}_2-\mathbf{r}_3|}d\mathbf{r}_2 ,
\tag{3.14}
$$

$$\rho_{x\sigma}(\mathbf{r}_2|\mathbf{r}_3)=-\sum_{ij}^{N_\sigma} n_{i\sigma}n_{j\sigma}\frac{\psi_{i\sigma}(\mathbf{r}_3)\psi^*_{j\sigma}(\mathbf{r}_3)\psi^*_{i\sigma}(\mathbf{r}_2)\psi_{j\sigma}(\mathbf{r}_2)}{\rho_\sigma(\mathbf{r}_3)}, \tag{3.15}$$

so that the orbital structure of $v_{S\sigma}$ reflects that of the Fermi hole function $\rho_{x\sigma}(\mathbf{r}_2|\mathbf{r}_3)$. The potential has Coulombic long-range asymptotics $v_{S\sigma}(\mathbf{r}_3)\rightarrow -1/|\mathbf{r}_3|$ at $|\mathbf{r}_3|\rightarrow\infty$.

In turn, the potential $v_{\text{resp}\sigma}$ can be expressed in the following form by rearrangement of the corresponding terms in Eq. (3.12):

$$v_{\text{resp}\sigma}(\mathbf{r}_3)=\frac{1}{2}\sum_{mn}^{N_\sigma}\frac{\psi_{m\sigma}(\mathbf{r}_3)\psi^*_{n\sigma}(\mathbf{r}_3)}{\rho_\sigma(\mathbf{r}_3)}\times\sum_{ik}^{N_\sigma} n_{i\sigma}\xi^\sigma_{ikmn}\left\{\overline{v}^{S}_{ik\sigma}-\left(1-\frac{\Delta\tilde{\epsilon}_\sigma}{\Delta\epsilon_{ik\sigma}}\right)\overline{v}^{xi}_{ik\sigma}\right\}+\text{c.c.}, \tag{3.16}$$

where $\overline{v}^{S}_{ik\sigma}$ and $\overline{v}^{xi}_{ik\sigma}$ are the expectation values for the product $\psi^*_{i\sigma}\psi_{k\sigma}$ of the Slater potential (3.14) and the Hartree-Fock orbital potential $v^i_{x\sigma}$ calculated with the KS orbitals

$$v^i_{x\sigma}(\mathbf{r}_3)=-\frac{1}{\psi^*_{i\sigma}(\mathbf{r}_3)}\sum_{j=1}^{N_\sigma} n_{j\sigma}\psi^*_{j\sigma}(\mathbf{r}_3)\int\frac{\psi^*_{i\sigma}(\mathbf{r}_2)\psi_{j\sigma}(\mathbf{r}_2)}{|\mathbf{r}_2-\mathbf{r}_3|}d\mathbf{r}_2, \tag{3.17}$$

i.e.,

$$\overline{v}^{S}_{ik\sigma}=\int\psi^*_{i\sigma}(\mathbf{r}_1)\psi_{k\sigma}(\mathbf{r}_1)v_{S\sigma}(\mathbf{r}_1)d\mathbf{r}_1 \tag{3.18}$$

and

$$\overline{v}^{xi}_{ik\sigma}=\int\psi^*_{i\sigma}(\mathbf{r}_1)\psi_{k\sigma}(\mathbf{r}_1)v^i_{x\sigma}(\mathbf{r}_1)d\mathbf{r}_1. \tag{3.19}$$

Due to the symmetry of the quantities and summations in Eq. (3.16), the term containing the orbital energy difference $\Delta\epsilon_{ik\sigma}$ cancels with the corresponding term in the complex conjugate part with $\Delta\epsilon_{ki\sigma}=-\Delta\epsilon_{ik\sigma}$ under our assumption $n_{k\sigma}=n_{i\sigma}$. With this in mind, one can rewrite Eq. (3.16) in a form that reveals the characteristic orbital step structure of $v_{\text{resp}\sigma}$,

$$v_{\text{resp}\sigma}(\mathbf{r}_3)=\sum_{mn}^{N_\sigma} w^\sigma_{mn}\frac{\psi_{m\sigma}(\mathbf{r}_3)\psi^*_{n\sigma}(\mathbf{r}_3)}{\rho_\sigma(\mathbf{r}_3)} \tag{3.20}$$

with the step heights w^σ_{mn}

$$w^\sigma_{mn}=\sum_{ik}^{N_\sigma} n_{i\sigma}\xi^\sigma_{ikmn}\{\overline{v}^{S}_{ik\sigma}-\overline{v}^{xi}_{ik\sigma}\},\quad w^\sigma_{N\sigma N\sigma}=0, \tag{3.21}$$

corresponding to the individual products $\psi_{m\sigma}\psi^*_{n\sigma}$ of the occupied orbitals. It follows from Eq. (3.20) that in the region, where a particular orbital density $|\psi_{i\sigma}|^2$ brings a dominant contribution to the total density ρ_σ, the potential $v_{\text{resp}\sigma}$ is close to the corresponding weight w^σ_{ii}, thus producing the step structure of $v_{\text{resp}\sigma}$. As a consequence of the fixing of the asymptotics (3.6) of $\chi^{-1}_{s\sigma}$, the last diagonal weight $w^\sigma_{N\sigma N\sigma}$ is zero, which effectively removes the HOMO density $|\psi_{N\sigma}|^2$ from the numerator of Eq. (3.20). Since $|\psi_{N\sigma}|^2$ is present in the total density ρ_σ in the denominator and it dominates the density at $|\mathbf{r}_3|\rightarrow\infty$, $v_{\text{resp}\sigma}$ is a short-range potential, which decays asymptotically faster than the Coulombic asymptotics.

The derivation presented in this section highlights the structure of the KS theory at the exchange-only level. Separation of the δ function within the Green's function (2.12) leads to the separation within $v_{x\sigma}$ of the Slater potential (3.14), the latter originates eventually from the δ function part of the orbital derivative (3.11). Then, the orbital sum in Eq. (2.12), which produces the proper exclusion of the occupied-occupied mixing from the density response function (2.13), yields the response potential (3.20), a weighted sum of the occupied-occupied orbital products. As was argued in [30], the repulsive potential $v_{\text{resp}\sigma}$ represents the effect of the Pauli repulsion of the occupied orbitals on the KS potential.

It is interesting to note that, although both functions $G_{i\sigma}$ and $\chi_{s\sigma}$ contain the mean energy $\Delta\tilde{\epsilon}_\sigma$ of excitation to unoccupied orbitals, the final expressions (3.13)–(3.15), (3.20), and (3.21) for $v_{x\sigma}$ contain only occupied orbitals and the related quantities. A formal explanation for this is that the expression (3.7) for the orbital derivative contains the product $G_{i\sigma}\chi^{-1}_{s\sigma}$ and then $G_{i\sigma}$ is inversely proportional to $\Delta\tilde{\epsilon}_\sigma$, while $\chi^{-1}_{s\sigma}$ is proportional to it, so that $\Delta\tilde{\epsilon}_\sigma$ cancels out for the product. Note, on a broader view, that the ground-state exchange energy functional (1.3) itself represents interaction only between the occupied orbitals. Thus, one can expect that its derivative, the ground-state exchange potential $v_{x\sigma}$, can be described in a good approximation just with this interaction. And our common denominator approximation for $G_{i\sigma}$ appears to be such an approximation. With its mean excitation energy $\Delta\tilde{\epsilon}_\sigma$, it treats the spectrum of unoccupied orbitals as a structureless entity and these orbitals serve effectively as intermediate quantities in the description of interaction between the occupied orbitals. Indeed, summation in Eq. (2.11) over unoccupied orbitals contributes to the δ function of Eq. (2.12), which eventually yields the Slater potential of the exchange interaction between occupied orbitals.

At the end of this section, we compare the structure of the present exchange potential (3.13), (3.14), and (3.20) with that of the KLI approximation [8]. $v^{\text{KLI}}_{x\sigma}$ can be obtained with the SH approximation (2.8) for the Green's function in the same way as the potential (3.20) is obtained with the Green's function (2.12) (for the details of the $v^{\text{KLI}}_{x\sigma}$ derivation, see Refs. [6], [8]). Starting from Eq. (2.8) and inverting the corresponding response function (2.9), one can get the KLI SH expression for the orbital derivative $\delta\psi_{i\sigma}(\mathbf{r}_1)/\delta\rho_\sigma(\mathbf{r}_3)$:

$$\frac{\delta\psi_{i\sigma}(\mathbf{r}_1)}{\delta\rho_\sigma(\mathbf{r}_3)}=\frac{\psi_{i\sigma}(\mathbf{r}_1)}{2\rho_\sigma(\mathbf{r}_3)}\delta(\mathbf{r}_1-\mathbf{r}_3)+\sum_m^{N_\sigma}\left\{\frac{\psi_{i\sigma}(\mathbf{r}_1)}{2\rho_\sigma(\mathbf{r}_1)}\sum_k^{N_\sigma} n_{k\sigma}\xi^\sigma_{km}|\psi_{k\sigma}(\mathbf{r}_1)|^2-\frac{\xi^\sigma_{im}\psi_{i\sigma}(\mathbf{r}_1)}{2}\right\}\frac{|\psi_{m\sigma}(\mathbf{r}_3)|^2}{\rho_\sigma(\mathbf{r}_3)}, \tag{3.22}$$

where the coefficients ξ^σ_{km} are the elements of the inverse matrix

$$\xi^\sigma_{im}=(\overline{\mathbf{I}}-\overline{\mathbf{N}}^\sigma)^{-1}_{im} \tag{3.23}$$

with

$$N^\sigma_{im}=n_m\int\frac{|\psi_{i\sigma}(\mathbf{r}_1)|^2|\psi_{m\sigma}(\mathbf{r}_1)|^2}{\rho_\sigma(\mathbf{r}_1)}d\mathbf{r}_1,\quad I_{im}=\delta_{im}. \tag{3.24}$$

Inserting Eq. (3.22) into Eq. (1.4), one arrives at the KLI expression for $v_{x\sigma}$. Due to separation of the δ function in Eq. (2.8), $v^{\mathrm{KLI}}_{x\sigma}$ also contains the Slater and response parts:

$$v^{\mathrm{KLI}}_{x\sigma}(\mathbf{r}_3)=v_{S\sigma}(\mathbf{r}_3)+v^{\mathrm{KLI}}_{\mathrm{resp}\sigma}(\mathbf{r}_3). \tag{3.25}$$

However, because of the incomplete exclusion of the occupied-occcupied orbital mixing from Eq. (2.9), the KLI response potential contains only "diagonal steps,"

$$v^{\mathrm{KLI}}_{\mathrm{resp}\sigma}(\mathbf{r}_3)=\sum_m^{N_\sigma}w^\sigma_m\frac{|\psi_{m\sigma}(\mathbf{r}_3)|^2}{\rho_\sigma(\mathbf{r}_3)}, \tag{3.26}$$

$$w^\sigma_m=\sum_i^{N_\sigma}n_{i\sigma}\xi^\sigma_{im}\{\overline{v}^S_{ii\sigma}-\overline{v}^{xi}_{ii\sigma}\},\quad w^\sigma_{N\sigma}=0. \tag{3.27}$$

Having both diagonal (with w^σ_{mm}) and off-diagonal (with w^σ_{mn}, $m\neq n$) steps the present potential (3.20) provides a more detailed orbital structure compared to the KLI potential (3.25).

The KLI potential already approximates quite well the exact local KS exchange potential. Still, a qualitative improvement will result from the use of our response potential, Eq. (3.20). Essential differences are introduced by the occurrence of the occupied-occupied mixing terms when the functional derivative of the potential is required, as is the case for the kernel $f_{x\sigma}$, in particular its response part $f_{\mathrm{resp}\sigma}$, in response calculations, notably in time-dependent DFT. We shall analyze this case in the next section.

IV. ORBITAL STRUCTURE OF $f_{\mathrm{resp}\sigma}$ AND THE FIELD-COUNTERACTING EFFECT

In this section the orbital structure of the response part $f_{\mathrm{resp}\sigma}$ of the exchange kernel is analyzed in connection with the field-counteracting exchange effect in an external electric field. We concentrate on the response part, since (as was established in Refs. [23], [25] in the finite-field approach) the field-counteracting term is a part of the field-induced change $\delta v_{\mathrm{resp}\sigma}$ of the response potential. Straightforward differentiation (1.6) of the potential (3.20) derived in the previous section gives for the corresponding $f_{\mathrm{resp}\sigma}$ the following expression:

$$\begin{aligned}f_{\mathrm{resp}\sigma}(\mathbf{r}_1,\mathbf{r}_2)&=\delta\left[\sum_{ij}^{N_\sigma}w^\sigma_{ij}\psi_{i\sigma}(\mathbf{r}_1)\psi^*_{j\sigma}(\mathbf{r}_1)/\rho_\sigma(\mathbf{r}_1)\right]\\&\quad/\delta\rho_\sigma(\mathbf{r}_2)|_{\rho_\sigma=\rho_{0\sigma}}\\&=\sum_{ij}^{N_\sigma}\frac{\psi_{i\sigma}(\mathbf{r}_1)\psi^*_{j\sigma}(\mathbf{r}_1)}{\rho_\sigma(\mathbf{r}_1)}\frac{\delta w^\sigma_{ij}}{\delta\rho_\sigma(\mathbf{r}_2)}\\&\quad-\sum_{ij}^{N_\sigma}w^\sigma_{ij}\frac{\psi_{i\sigma}(\mathbf{r}_1)\psi^*_{j\sigma}(\mathbf{r}_1)}{\rho^2_\sigma(\mathbf{r}_1)}\delta(\mathbf{r}_1-\mathbf{r}_2)\\&\quad+\left\{\sum_{ij}^{N_\sigma}w^\sigma_{ij}\frac{\psi^*_{j\sigma}(\mathbf{r}_1)}{\rho_\sigma(\mathbf{r}_1)}\frac{\delta\psi_{i\sigma}(\mathbf{r}_1)}{\delta\rho_\sigma(\mathbf{r}_2)}+\text{c.c.}\right\}.\end{aligned} \tag{4.1}$$

As indicated in the first equality of Eq. (4.1), the derivative is taken at the ground-state density, for which we use just the notation ρ_σ throughout the paper. Inserting in Eq. (4.1) the expression (3.11) for the orbital derivative $\delta\psi_{i\sigma}(\mathbf{r}_1)/\delta\rho_\sigma(\mathbf{r}_3)$ in Eq. (4.1), one obtains for $f_{\mathrm{resp}\sigma}$

$$\begin{aligned}f_{\mathrm{resp}\sigma}(\mathbf{r}_1,\mathbf{r}_2)&=\sum_{ij}^{N_\sigma}\frac{\psi_{i\sigma}(\mathbf{r}_1)\psi^*_{j\sigma}(\mathbf{r}_1)}{\rho_\sigma(\mathbf{r}_1)}\frac{\delta w^\sigma_{ij}}{\delta\rho_\sigma(\mathbf{r}_2)}\\&\quad-\sum_{ij}^{N_\sigma}w^\sigma_{ij}\frac{\psi_{i\sigma}(\mathbf{r}_1)\psi^*_{j\sigma}(\mathbf{r}_1)}{\rho^2_\sigma(\mathbf{r}_1)}\delta(\mathbf{r}_1-\mathbf{r}_2)\\&\quad+\sum_{ij}^{N_\sigma}w^\sigma_{ij}\frac{\psi_{i\sigma}(\mathbf{r}_1)\psi^*_{j\sigma}(\mathbf{r}_1)}{\rho_\sigma(\mathbf{r}_1)\rho_\sigma(\mathbf{r}_2)}\delta(\mathbf{r}_1-\mathbf{r}_2)\\&\quad+\frac{1}{2}\left\{\sum_{ij}^{N_\sigma}w^\sigma_{ij}\frac{\psi^*_{j\sigma}(\mathbf{r}_1)}{\rho_\sigma(\mathbf{r}_1)}\right.\\&\quad\times\sum_{mn}^{N_\sigma}\left[\psi_{i\sigma}(\mathbf{r}_1)\sum_{kl}^{N_\sigma}n_{k\sigma}\xi^\sigma_{klmn}\frac{\psi_{k\sigma}(\mathbf{r}_1)\psi^*_{l\sigma}(\mathbf{r}_1)}{\rho_\sigma(\mathbf{r}_1)}\right.\\&\quad\left.+\sum_k^{N_\sigma}\frac{\Delta\tilde{\epsilon}_\sigma-\Delta\epsilon_{ik\sigma}}{\Delta\epsilon_{ik\sigma}}\xi^\sigma_{ikmn}\psi_{k\sigma}(\mathbf{r}_1)\right]\\&\quad\left.\times\frac{\psi_{m\sigma}(\mathbf{r}_2)\psi^*_{n\sigma}(\mathbf{r}_2)}{\rho_\sigma(\mathbf{r}_2)}+\text{c.c.}\right\}.\end{aligned} \tag{4.2}$$

In principle, the derivative $\delta w^\sigma_{ij}/\delta\rho_\sigma(\mathbf{r}_2)$ in the first term of the RHS can be elaborated further through a straightforward differentiation of Eq. (3.21); however, for our purposes just Eq. (4.2) suffices. The orbital structure of the nonlocal terms of $f_{\mathrm{resp}\sigma}$ is characterized by the two-electron "coupling" of cross products $\psi_{m\sigma}(\mathbf{r}_2)\psi^*_{n\sigma}(\mathbf{r}_2)$ with $\psi_{k\sigma}(\mathbf{r}_1)\psi^*_{l\sigma}(\mathbf{r}_1)$ of the occupied orbitals, with the coupling coefficients ξ^σ_{klmn}. Note that, unlike in the expression (3.16) for $v_{\mathrm{resp}\sigma}$, the terms with the orbital energy differences $\Delta\epsilon_{ik\sigma}$ do not cancel each other in Eq. (4.2). Indeed, the ratio $\Delta\tilde{\epsilon}_\sigma/\Delta\epsilon_{ik\sigma}$ with a certain $\Delta\epsilon_{ik\sigma}$ is attached in Eq. (4.2) to the orbital $\psi_{k\sigma}$, while its counterpart $\Delta\tilde{\epsilon}_\sigma/\Delta\epsilon_{ki\sigma}$ with $\Delta\epsilon_{ki\sigma}=-\Delta\epsilon_{ik\sigma}$ is attached to a different orbital $\psi_{i\sigma}$, so that the corresponding terms do not cancel each other. Inserting Eq. (4.2) in Eq. (1.7), one can get a change of the potential $\delta v_{\text{resp}\sigma}$ for the density change $\delta\rho_\sigma$. After integration over $\mathbf{r}_2$ in Eq. (1.7), the terms with δ functions cancel each other, which gives for $\delta v_{\text{resp}\sigma}$ the following expression:

$$\begin{aligned}\delta v_{\text{resp}\sigma}(\mathbf{r}_1)=&\sum_{ij}^{N_\sigma}\frac{\psi_{i\sigma}(\mathbf{r}_1)\psi_{j\sigma}^*(\mathbf{r}_1)}{\rho_\sigma(\mathbf{r}_1)}\int\frac{\delta w_{ij}^\sigma}{\delta\rho_\sigma(\mathbf{r}_2)}\delta\rho_\sigma(\mathbf{r}_2)d\mathbf{r}_2\\&+\frac{1}{2}\left\{\sum_{ij}^{N_\sigma}w_{ij}^\sigma\frac{\psi_{j\sigma}^*(\mathbf{r}_1)}{\rho_\sigma(\mathbf{r}_1)}\right.\\&\times\sum_{mn}^{N_\sigma}\left[\psi_{i\sigma}(\mathbf{r}_1)\sum_{kl}^{N_\sigma}n_{k\sigma}\xi_{klmn}^\sigma\frac{\psi_{k\sigma}(\mathbf{r}_1)\psi_{l\sigma}^*(\mathbf{r}_1)}{\rho_\sigma(\mathbf{r}_1)}\right.\\&\left.+\sum_{k}^{N_\sigma}\frac{\Delta\tilde{\epsilon}_\sigma-\Delta\epsilon_{ik\sigma}}{\Delta\epsilon_{ik\sigma}}\xi_{ikmn}^\sigma\psi_{k\sigma}(\mathbf{r}_1)\right]\\&\left.\times\int\frac{\psi_{m\sigma}(\mathbf{r}_2)\psi_{n\sigma}^*(\mathbf{r}_2)}{\rho_\sigma(\mathbf{r}_2)}\delta\rho_\sigma(\mathbf{r}_2)d\mathbf{r}_2+\text{c.c.}\right\}.\end{aligned}\tag{4.3}$$

It is instructive to compare Eq. (4.2) with the KLI SH kernel $f_{\text{resp}\sigma}^{\text{KLI SH}}$, which can be obtained via the differentiation of the KLI response potential (3.26) with the KLI SH approximation (3.22) for the orbital derivative. In complete analogy with Eqs. (4.1) and (4.2), one obtains for $f_{\text{resp}\sigma}^{\text{KLI SH}}$

$$\begin{aligned}f_{\text{resp}\sigma}^{\text{KLI SH}}(\mathbf{r}_1,\mathbf{r}_2)=&\sum_{i}^{N_\sigma}\frac{|\psi_{i\sigma}(\mathbf{r}_1)|^2}{\rho_\sigma(\mathbf{r}_1)}\frac{\delta w_i^\sigma}{\delta\rho_\sigma(\mathbf{r}_2)}\\&-\sum_{i}^{N_\sigma}w_i^\sigma\frac{|\psi_{i\sigma}(\mathbf{r}_1)|^2}{\rho_\sigma^2(\mathbf{r}_1)}\delta(\mathbf{r}_1-\mathbf{r}_2)\\&+\sum_{i}^{N_\sigma}w_i^\sigma\frac{|\psi_{i\sigma}(\mathbf{r}_1)|^2}{\rho_\sigma(\mathbf{r}_1)\rho_\sigma(\mathbf{r}_2)}\delta(\mathbf{r}_1-\mathbf{r}_2)\\&+\sum_{i}^{N_\sigma}w_i^\sigma\frac{|\psi_{i\sigma}(\mathbf{r}_1)|^2}{\rho_\sigma(\mathbf{r}_1)}\sum_{m}^{N_\sigma}\left[\sum_{k}^{N_\sigma}n_{k\sigma}\xi_{km}^\sigma\right.\\&\left.\times\frac{|\psi_{k\sigma}(\mathbf{r}_1)|^2}{\rho_\sigma(\mathbf{r}_1)}-\xi_{im}^\sigma\right]\frac{|\psi_{m\sigma}(\mathbf{r}_2)|^2}{\rho_\sigma(\mathbf{r}_2)}.\end{aligned}\tag{4.4}$$

The difference between the kernels $f_{\text{resp}\sigma}$ of Eq. (4.2) and $f_{\text{resp}\sigma}^{\text{KLI SH}}$ resembles that between the corresponding potentials $v_{\text{resp}\sigma}$ of Eq. (3.20) and $v_{\text{resp}\sigma}^{\text{KLI}}$ of Eq. (3.26). While $f_{\text{resp}\sigma}^{\text{KLI SH}}$ depends on the orbital densities $|\psi_{i\sigma}|^2$, $f_{\text{resp}\sigma}$ includes also cross products $\psi_{i\sigma}\psi_{j\sigma}^*$ of different orbitals. $f_{\text{resp}\sigma}^{\text{KLI SH}}$ produces the change $\delta v_{\text{resp}\sigma}^{\text{KLI SH}}$

$$\begin{aligned}\delta v_{\text{resp}\sigma}^{\text{KLI SH}}(\mathbf{r}_1)=&\sum_{i}^{N_\sigma}\frac{|\psi_{i\sigma}(\mathbf{r}_1)|^2}{\rho_\sigma(\mathbf{r}_1)}\int\frac{\delta w_i^\sigma}{\delta\rho_\sigma(\mathbf{r}_2)}\delta\rho_\sigma(\mathbf{r}_2)d\mathbf{r}_2\\&+\sum_{i}^{N_\sigma}w_i^\sigma\frac{|\psi_{i\sigma}(\mathbf{r}_1)|^2}{\rho_\sigma(\mathbf{r}_1)}\\&\times\sum_{m}^{N_\sigma}\left[\sum_{k}^{N_\sigma}n_{k\sigma}\xi_{km}^\sigma\frac{|\psi_{k\sigma}(\mathbf{r}_1)|^2}{\rho_\sigma(\mathbf{r}_1)}-\xi_{im}^\sigma\right]\\&\times\int\frac{|\psi_{m\sigma}(\mathbf{r}_2)|^2}{\rho_\sigma(\mathbf{r}_2)}\delta\rho_\sigma(\mathbf{r}_2)d\mathbf{r}_2.\end{aligned}\tag{4.5}$$

The difference between Eqs. (4.2),(4.3) and Eqs. (4.4),(4.5) appears to be of crucial importance for the generation of the field-counteracting term in the KS potential when an external electric field is applied over a chainlike molecule. In order to show this, we consider the response of a symmetric molecular chain X_n with arbitrary fragments X, which has a mid-molecule center of inversion or a mirror plane (or both) as the symmetry element, to an antisymmetric external field $\delta v_{\text{ex}}(\mathbf{r})=-Ez$ (z is the main symmetry axis of the chain, with $z=0$ being the molecular midpoint). Obviously, the density response $\delta\rho_\sigma$ of the chain will also be an antisymmetric function of z with a positive buildup $\delta\rho_\sigma>0$ $(z>0)$ of the density in the down-field region and with a negative depletion $\delta\rho_\sigma<0$ $(z<0)$ in the up-field region. Then, the field-counteracting exchange effect should manifest itself in the appearance of the term $\delta v_{\text{resp}\sigma}^{(\text{fc})}$ in Eq. (4.3) or Eq. (4.5), which counters $\delta v_{\text{ext}}(\mathbf{r})$, i.e., it should be an antisymmetric function of z and $\delta v_{\text{resp}\sigma}^{(\text{fc})}$ should be positive in the down-field region $z>0$ and negative in the up-field region $z<0$.

However, the KLI SH kernel (4.4) fails to generate any field-counteracting term, as can be shown by analyzing the corresponding potential change (4.5). In particular, the second sum in the RHS of Eq. (4.5) vanishes due to the integration over $\mathbf{r}_2$. Indeed, all the orbital-density terms $|\psi_{m\sigma}(\mathbf{r}_2)|^2/\rho_\sigma(\mathbf{r}_2)$ in the integrands are symmetric functions of z, while $\delta\rho_\sigma(\mathbf{r}_2)$ is antisymmetric, so that the integral of the resultant antisymmetric integrand vanishes. Although nonzero, the first term of Eq. (4.5) is, clearly, a symmetric function, since its spatial dependence is represented with the symmetric orbital-density functions $|\psi_{i\sigma}(\mathbf{r}_1)|^2/\rho_\sigma(\mathbf{r}_1)$, while the counterfield term should be an antisymmetric function. This proves the absence of the field-counteracting term in the KLI SH approach.

In contrast to this, the present kernel (4.2) displays an orbital structure that is able to generate a field-counteracting term $\delta v_{\text{resp}\sigma}^{(\text{fc})}$. In order to establish this, we start with the simplest chain with Pauli repulsion between the fragments, the four-electron system of two distant He atoms. The occupied orbitals of He$_2$ are the symmetric orbital ψ_g of σ_g type and the antisymmetric orbital ψ_u of σ_u type (here real orbitals are considered and the spin index is suppressed due to the closed-shell character of the system). Then, the potential (3.20) consists just of a single step:

$$\begin{aligned}v_{\text{resp}}(\mathbf{r}_3)=&\,w_{gg}\frac{2|\psi_g(\mathbf{r}_3)|^2}{\rho(\mathbf{r}_3)}+w_{uu}\frac{2|\psi_u(\mathbf{r}_3)|^2}{\rho(\mathbf{r}_3)}\\&+2w_{gu}\frac{2\psi_g(\mathbf{r}_3)\psi_u(\mathbf{r}_3)}{\rho(\mathbf{r}_3)}\\=&\,w_{gg}\frac{2|\psi_g(\mathbf{r}_3)|^2}{\rho(\mathbf{r}_3)},\end{aligned}\tag{4.6}$$

since the weights w_{uu} and w_{gu} in Eq. (4.6) vanish, the first due to the condition $w_{N\sigma N\sigma}=w_{uu}=0$ [cf. Eq. (3.21)], and the second due to the symmetry of the orbitals entering the Slater and exchange integrals in w_{gu}, [cf. Eq. (3.21)]. Thus, for He_2 the potential (3.20) reduces to the KLI potential and the difference between the present approach and the KLI SH one becomes manifest only when the symmetry is broken, due to an applied unsymmetric finite field, or equivalently, in a response calculation through the different expressions (3.11) and (3.22) for the orbital derivatives, which produce different kernels (4.2) and (4.4). Unlike Eq. (4.4) the kernel (4.2) contains the cross product $\psi_g\psi_u$, which transforms as z under the symmetry operations. Collecting the corresponding terms in Eq. (4.3) applied to He_2, one can obtain the following expression:

$$\begin{aligned}\delta v_{\mathrm{resp}}^{(\mathrm{fc})}(\mathbf{r}_1)=&\Bigg\{2w_{gg}(\xi_{gugu}+\xi_{guug})\frac{\psi_g(\mathbf{r}_1)\psi_u(\mathbf{r}_1)}{\rho(\mathbf{r}_1)}\\&\times\left[\frac{2|\psi_g(\mathbf{r}_1)|^2}{\rho(\mathbf{r}_1)}+\frac{\Delta\tilde{\epsilon}-\Delta\epsilon_{gu}}{\Delta\epsilon_{gu}}\right]\\&\times\int\frac{\psi_g(\mathbf{r}_2)\psi_u(\mathbf{r}_2)}{\rho(\mathbf{r}_2)}\delta\rho(\mathbf{r}_2)d\mathbf{r}_2\Bigg\}\\&+\frac{4\psi_g(\mathbf{r}_1)\psi_u(\mathbf{r}_1)}{\rho(\mathbf{r}_1)}\int\frac{\delta w_{gu}}{\delta\rho(\mathbf{r}_2)}\delta\rho(\mathbf{r}_2)d\mathbf{r}_2,\end{aligned}\tag{4.7}$$

which represents a potential $\delta v_{\mathrm{resp}\sigma}^{(\mathrm{fc})}$ counteracting the external field $\delta v_{\mathrm{ext}}(\mathbf{r})=-Ez$. Indeed, the integrals over $\mathbf{r}_2$ in Eq. (4.7) are nonzero due to the antisymmetry of both $\psi_g(\mathbf{r}_2)\psi_u(\mathbf{r}_2)$ and $\delta\rho(\mathbf{r}_2)$, then $\delta v_{\mathrm{resp}\sigma}^{(\mathrm{fc})}(\mathbf{r}_1)$ itself is an antisymmetric function because of the product $\psi_g(\mathbf{r}_1)\psi_u(\mathbf{r}_1)$.

In order to establish the sign of the term in the curly brackets of Eq. (4.7) in the down- and up-field regions, note that apart from the obviously positive first term in the square brackets of Eq. (4.7), the second term is also positive, since the energy difference $\Delta\epsilon_{gu}$ between the occupied orbitals is smaller for two distant He atoms, than the average one $\Delta\tilde{\epsilon}$ between the occupied and unoccupied orbitals. In the round brackets of Eq. (4.7) the leading term is the element ξ_{gugu} of the inverse matrix, which corresponds to the "diagonal" positive element $(1-N_{gugu})$ of the four-index matrix $(\mathbf{I}-\mathbf{N})$ in Eq. (3.3). Thus, one can expect that ξ_{gugu} and the sum $(\xi_{gugu}+\xi_{guug})$ will also be positive, and our numerical experience with the inverse matrix (3.3) confirms this expectation. Furthermore, the diagonal weight w_{gg} is also positive. Since the product $\psi_g\psi_u$ appears twice, for $\mathbf{r}_1$ and $\mathbf{r}_2$, the location of the positive and negative parts of Eq. (4.7) does not depend on the choice of phase of ψ_u and it is determined by that of $\delta\rho(\mathbf{r}_2)$. So let us choose the sign of ψ_u positive at the $+z$ axis, in the down-field region, where also $\delta\rho$ is positive, then the integral over $\mathbf{r}_2$ is positive, and the factor $\psi_g(\mathbf{r}_1)\psi_u(\mathbf{r}_1)$ makes $\delta v_{\mathrm{resp}}^{(\mathrm{fc})}(\mathbf{r}_1)$ of Eq. (4.7) positive in the down-field region and negative in the up-field region, as it should be for the field-counteracting potential. We have derived an analytical expression also for the derivative $\delta w_{gu}/\delta\rho(\mathbf{r}_2)$ in the second term of Eq. (4.7); but it appears to be too complicated to establish the sign of this antisymmetric term. However, our preliminary calculations show that the term with $\delta w_{gu}/\delta\rho(\mathbf{r}_2)$ adds to the field-counteracting potential, while the dominant contribution comes from the term in the curly brackets in Eq. (4.7).

Considering the orbital structure of the field-counteracting response potential $\delta v_{\mathrm{resp}}^{(\mathrm{fc})}(\mathbf{r}_1)$ of Eq. (4.7), we note that a distinguishing feature is a "self-coupling" in the term in the curly brackets, in which the orbital product $\psi_g\psi_u\rho^{-1}$ at $\mathbf{r}_1$ is coupled with an integral of itself over $\mathbf{r}_2$, with the coupling coefficients $(\xi_{gugu}+\xi_{guug})$. Returning to the general case of a symmetric molecular chain, we collect analogous "self-coupling" terms within the potential $\delta v_{\mathrm{resp}\sigma}^{(\mathrm{fc\text{-}sc})}$

$$\begin{aligned}\delta v_{\mathrm{resp}\sigma}^{(\mathrm{fc\text{-}sc})}(\mathbf{r}_1)=&\frac{1}{2}\Bigg\{\sum_{ij}^{N_\sigma}(ss)w_{ij}^{\sigma}\frac{\psi_{i\sigma}(\mathbf{r}_1)\psi_{j\sigma}^{*}(\mathbf{r}_1)}{\rho_\sigma(\mathbf{r}_1)}\\&\times\sum_{kl}^{N_\sigma}(gu)n_{k\sigma}\xi_{klkl}^{\sigma}\frac{\psi_{k\sigma}(\mathbf{r}_1)\psi_{l\sigma}^{*}(\mathbf{r}_1)}{\rho_\sigma(\mathbf{r}_1)}\\&\times\int\frac{\psi_{k\sigma}^{*}(\mathbf{r}_2)\psi_{l\sigma}(\mathbf{r}_2)}{\rho_\sigma(\mathbf{r}_2)}\delta\rho_\sigma(\mathbf{r}_2)d\mathbf{r}_2\\&+\sum_{ik}^{N_\sigma}(gu)w_{ii}^{\sigma}\frac{\Delta\tilde{\epsilon}_\sigma-\Delta\epsilon_{ik\sigma}}{\Delta\epsilon_{ik\sigma}}\\&\times\xi_{ikik}^{\sigma}\frac{\psi_{i\sigma}^{*}(\mathbf{r}_1)\psi_{k\sigma}(\mathbf{r}_1)}{\rho_\sigma(\mathbf{r}_1)}\\&\times\int\frac{\psi_{i\sigma}(\mathbf{r}_2)\psi_{k\sigma}^{*}(\mathbf{r}_2)}{\rho_\sigma(\mathbf{r}_2)}\delta\rho_\sigma(\mathbf{r}_2)d\mathbf{r}_2+\mathrm{c.c.}\Bigg\}.\end{aligned}\tag{4.8}$$

In Eq. (4.8) the brackets (ss) in the sum over i and j mean that only the orbitals ψ_i and ψ_j of the same symmetry are involved in the summation. The brackets (gu) in the sums over k,l and i,k mean that in the orbital products involved in the summations one orbital is a symmetric function of z, while another is an antisymmetric one. Then, because of the reasons presented above for He_2, one can expect that in the general case $\delta v_{\mathrm{resp}\sigma}^{(\mathrm{fc\text{-}sc})}$ of Eq. (4.8) also represents a field-counteracting potential.

V. CONCLUSIONS

In this paper the exchange-only Kohn-Sham theory is developed based on a physically motivated common energy denominator approximation for the KS static orbital Green's function $G_{i\sigma}$. Within the proposed approximation, contributions from the occupied-occupied orbital mixing are correctly excluded from the density response function $\chi_{s\sigma}$ associated with $G_{i\sigma}$. The approximations for $G_{i\sigma}$ and $\chi_{s\sigma}$ make it possible to analytically invert the latter after fixing of the asymptotics of $\chi_{s\sigma}^{-1}$.

An explicit expression for the exchange potential $v_{x\sigma}$ in terms of the occupied KS orbitals is derived via the analytical inverse of $\chi_{s\sigma}$. The resultant $v_{x\sigma}$ is naturally subdivided into the attractive long-range Slater potential $v_{S\sigma}$ and a repulsive short-range "response" potential $v_{\text{resp}\sigma}$. The present potential $v_{\text{resp}\sigma}$ is compared with the corresponding potential $v_{\text{resp}\sigma}^{\text{KLI}}$ of the KLI approximation. In addition to the "diagonal" structure of $v_{\text{resp}\sigma}^{\text{KLI}}$ with contributions from the densities $|\psi_{i\sigma}|^2$ of the occupied KS orbitals, $v_{\text{resp}\sigma}$ possesses also an "off-diagonal" structure with contributions from the occupied-occupied orbital products $\psi_{i\sigma}\psi_{j\sigma}^*$. The difference between $v_{\text{resp}\sigma}$ and $v_{\text{resp}\sigma}^{\text{KLI}}$ might be small, in particular, for atomic systems, for which the diagonal steps represent the atomic shell structure, while the off-diagonal steps produce the intershell corrections. However, $v_{\text{resp}\sigma}$ might provide a definite improvement over $v_{\text{resp}\sigma}^{\text{KLI}}$ in applications to various molecular properties. In particular, application within the finite-field approach of $v_{\text{resp}\sigma}$ can improve polarizabilities and hyperpolarizabilities of molecular chains calculated with DFT, because, as was shown in Refs. [23], [25], the proper treatment of the occupied-occupied orbital mixing in the orbital-dependent KS potential is of importance for these properties. Preliminary results of finite-field calculations for the hydrogen chains H_n confirm these expectations.

An expression for the response part $f_{\text{resp}\sigma}$ of the exchange kernel is derived through a direct differentiation of the present $v_{\text{resp}\sigma}$. The orbital structure of $f_{\text{resp}\sigma}$ has as a distinguishing feature an "off-diagonal" orbital structure with the two-electron coupling of cross products $\psi_{m\sigma}(\mathbf{r}_2)\psi_{n\sigma}^*(\mathbf{r}_2)$ and $\psi_{k\sigma}(\mathbf{r}_1)\psi_{l\sigma}^*(\mathbf{r}_1)$ of the occupied orbitals. Unlike this, the kernel $f_{\text{resp}\sigma}^{\text{KLI SH}}$ derived from the KLI potential with the SH approximation for $G_{i\sigma}$ depends on the orbital densities $|\psi_{i\sigma}|^2$ only.

The difference between $f_{\text{resp}\sigma}$ and $f_{\text{resp}\sigma}^{\text{KLI SH}}$ is shown to be crucial for the corresponding potentials $\delta v_{\text{resp}\sigma}$ and $\delta v_{\text{resp}\sigma}^{\text{KLI SH}}$ generated by the kernels in an external electric field. It is established for the case of a symmetric molecular chain that $f_{\text{resp}\sigma}^{\text{KLI SH}}$ fails to produce any field-counteracting term. Contrary to this, as is shown in the simple case of He_2, the present $f_{\text{resp}\sigma}$ generates a field-counteracting term $\delta v_{\text{resp}\sigma}^{(\text{fc})}$. The mechanism behind $\delta v_{\text{resp}\sigma}^{(\text{fc})}$ is the "self-coupling" of the cross product $\psi_g\psi_u$ of the symmetric and antisymmetric orbitals. Similar self-coupling terms are indicated for the general case of a symmetric molecular chain.

The established spatial nonlocal orbital structure of $f_{\text{resp}\sigma}$ is expected to be of importance for a proper description of the response properties (polarizabilities, hyperpolarizabilities, excitation energies) of molecular chains with TDDFPT. Evidently, the standard TDDFPT approximation, the adiabatic LDA completely lacks this structure, which is the reason for the poor results mentioned in the Introduction. Thus, the present expression for $f_{\text{resp}\sigma}$ might serve as a basis for improved models and approximations. Another important direction of further development is an extension of the present exchange functionals $v_{x\sigma}$ and $f_{\text{resp}\sigma}$ to full exchange-correlation ones with a proper incorporation of the effects of Coulomb correlation. Work along these directions is in progress.

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APPENDIX

In this appendix the analytical expression for the inverse $\chi_{s\sigma}^{-1}$ of the density response function is derived with the technique developed in Ref. [6]. As the term with the orbital energy differences $\Delta\epsilon_{ij\sigma}$ vanishes in Eq. (2.13), one can rewrite $\chi_{s\sigma}$ as follows:

$$\chi_{s\sigma}(\mathbf{r}_1,\mathbf{r}_2)=-\frac{2}{\Delta\tilde{\epsilon}_\sigma}\delta(\mathbf{r}_1-\mathbf{r}_2)\rho_\sigma(\mathbf{r}_1)+\frac{2}{\Delta\tilde{\epsilon}_\sigma}\sum_{ij}^{N_\sigma}n_{i\sigma}\psi_{i\sigma}^*(\mathbf{r}_1)\psi_{i\sigma}(\mathbf{r}_2)\psi_{j\sigma}(\mathbf{r}_1)\psi_{j\sigma}^*(\mathbf{r}_2). \tag{A1}$$

Then, our goal is to construct the inverse $\chi_{s\sigma}^{-1}$, which satisfies the condition (1.5). Note, however, that (1.5) determines $\chi_{s\sigma}^{-1}$ only up to a constant, i.e., adding a constant to $\chi_{s\sigma}^{-1}$ gives another solution of Eq. (1.5). To fix this constant according to the procedure of Ref. [6], we exclude the diagonal term $2n_{N\sigma}\psi_{N\sigma}^*(\mathbf{r}_1)\psi_{N\sigma}(\mathbf{r}_2)\psi_{N\sigma}(\mathbf{r}_1)\psi_{N\sigma}^*(\mathbf{r}_2)/\Delta\tilde{\epsilon}_\sigma$ with the densities $|\psi_{N\sigma}(\mathbf{r}_1)|^2$ and $|\psi_{N\sigma}(\mathbf{r}_2)|^2$ of the HOMO $\psi_{N\sigma}$ from the sum in Eq. (A1)

$$\chi_{s\sigma}(\mathbf{r}_1,\mathbf{r}_2)=-\frac{2}{\Delta\tilde{\epsilon}_\sigma}\delta(\mathbf{r}_1-\mathbf{r}_2)\rho_\sigma(\mathbf{r}_1)+\frac{2}{\Delta\tilde{\epsilon}_\sigma}\sum_{ij}{}'\,n_{i\sigma}\psi_{i\sigma}^*(\mathbf{r}_1)\psi_{i\sigma}(\mathbf{r}_2)\psi_{j\sigma}(\mathbf{r}_1)\psi_{j\sigma}^*(\mathbf{r}_2) \tag{A2}$$

and the primed sum in Eq. (A2) indicates the abovementioned exclusion. As will be shown below, $\chi_{s\sigma}^{-1}$ corresponding to Eq. (A2) goes to zero asymptotically [cf. Eq. (3.6)], which eventually produces the zero long-range asymptotics of the potential $v_{x\sigma}$. To construct $\chi_{s\sigma}^{-1}$ which, taken together with Eq. (A2), would satisfy Eq. (1.5), we split $\chi_{s\sigma}^{-1}$ into a local δ function part and a remainder,

$$\chi_{s\sigma}^{-1}(\mathbf{r}_1,\mathbf{r}_2)=-\frac{\Delta\tilde{\epsilon}_\sigma}{2\rho_\sigma(\mathbf{r}_1)}\delta(\mathbf{r}_1-\mathbf{r}_2)+c_\sigma(\mathbf{r}_1,\mathbf{r}_2). \tag{A3}$$

For the function c_σ an equation follows from Eqs. (1.5), (A2), and (A3):

$$\delta(\mathbf{r}_1-\mathbf{r}_2)=\int\chi_{s\sigma}(\mathbf{r}_1,\mathbf{r}_3)\chi_{s\sigma}^{-1}(\mathbf{r}_3,\mathbf{r}_2)d\mathbf{r}_3$$

$$=\delta(\mathbf{r}_1-\mathbf{r}_2)-\frac{1}{\rho_\sigma(\mathbf{r}_2)}\times\sum_{ij}{}'\,n_{i\sigma}\psi_{i\sigma}^*(\mathbf{r}_1)\psi_{i\sigma}(\mathbf{r}_2)\psi_{j\sigma}(\mathbf{r}_1)\psi_{j\sigma}^*(\mathbf{r}_2)$$

$$-\frac{2}{\Delta\tilde{\epsilon}_\sigma}\rho_\sigma(\mathbf{r}_1)c_\sigma(\mathbf{r}_1,\mathbf{r}_2)$$
$$+\frac{2}{\Delta\tilde{\epsilon}_\sigma}\sum_{ij}{}' n_{i\sigma}\psi^*_{i\sigma}(\mathbf{r}_1)\psi_{j\sigma}(\mathbf{r}_1)$$
$$\times\int \psi_{i\sigma}(\mathbf{r}_3)\psi^*_{j\sigma}(\mathbf{r}_3)c_\sigma(\mathbf{r}_3,\mathbf{r}_2)d\mathbf{r}_3, \tag{A4}$$

so that

$$c_\sigma(\mathbf{r}_1,\mathbf{r}_2)=-\frac{\Delta\tilde{\epsilon}_\sigma}{2\rho_\sigma(\mathbf{r}_1)\rho_\sigma(\mathbf{r}_2)}$$
$$\times\sum_{ij}{}' n_{i\sigma}\psi^*_{i\sigma}(\mathbf{r}_1)\psi_{i\sigma}(\mathbf{r}_2)\psi_{j\sigma}(\mathbf{r}_1)\psi^*_{j\sigma}(\mathbf{r}_2)$$
$$+\frac{1}{\rho_\sigma(\mathbf{r}_1)}\sum_{ij}{}' n_{i\sigma}\psi^*_{i\sigma}(\mathbf{r}_1)\psi_{j\sigma}(\mathbf{r}_1)$$
$$\times\int \psi_{i\sigma}(\mathbf{r}_3)\psi^*_{j\sigma}(\mathbf{r}_3)c_\sigma(\mathbf{r}_3,\mathbf{r}_2)d\mathbf{r}_3. \tag{A5}$$

Then, for the function d_σ defined as

$$d_\sigma(\mathbf{r}_1,\mathbf{r}_2)=\frac{4\rho_\sigma(\mathbf{r}_1)\rho_\sigma(\mathbf{r}_2)}{(\Delta\tilde{\epsilon}_\sigma)^2}c_\sigma(\mathbf{r}_1,\mathbf{r}_2) \tag{A6}$$

one has

$$d_\sigma(\mathbf{r}_1,\mathbf{r}_2)=-\frac{2}{\Delta\tilde{\epsilon}_\sigma}\sum_{ij}{}' n_{i\sigma}\psi^*_{i\sigma}(\mathbf{r}_1)\psi_{i\sigma}(\mathbf{r}_2)\psi_{j\sigma}(\mathbf{r}_1)\psi^*_{j\sigma}(\mathbf{r}_2)$$
$$-\frac{2}{\Delta\tilde{\epsilon}_\sigma}\sum_{ij}{}' n_{i\sigma}\psi^*_{i\sigma}(\mathbf{r}_1)\psi_{j\sigma}(\mathbf{r}_1)\alpha_{ij\sigma}(\mathbf{r}_2), \tag{A7}$$

where

$$\alpha_{ij\sigma}(\mathbf{r}_2)=-\frac{\Delta\tilde{\epsilon}_\sigma}{2}\int\frac{\psi_{i\sigma}(\mathbf{r}_3)\psi^*_{j\sigma}(\mathbf{r}_3)d_\sigma(\mathbf{r}_3,\mathbf{r}_2)}{\rho_\sigma(\mathbf{r}_3)}d\mathbf{r}_3. \tag{A8}$$

Inserting Eq. (A7) in Eq. (A8), one obtains a system of equations for the functions $\alpha_{ij\sigma}$:

$$\alpha_{ij\sigma}(\mathbf{r}_2)=\sum_{kl}{}' N^\sigma_{ijkl}[\psi_{k\sigma}(\mathbf{r}_2)\psi^*_{l\sigma}(\mathbf{r}_2)+\alpha_{kl\sigma}(\mathbf{r}_2)] \tag{A9}$$

with the coefficients N^σ_{ijkl} being defined in Eq. (3.4). The prime over the sum means that both the orbital density $|\psi_{N\sigma}|^2$ and the function $\alpha_{N\sigma N\sigma}$ are excluded from the summation. A general solution to Eqs. (A9) can now be found. As the products $\psi_{k\sigma}\psi^*_{l\sigma}$ are only finite in number, the most general expression for $\alpha_{ij\sigma}$ is a linear combination of these functions,

$$\alpha_{ij\sigma}(\mathbf{r}_2)=\sum_{kl}{}' \beta^\sigma_{ijkl}\psi_{k\sigma}(\mathbf{r}_2)\psi^*_{l\sigma}(\mathbf{r}_2). \tag{A10}$$

This gives an equation for the coefficients β^σ_{ijkl},

$$\beta^\sigma_{ijkl}=N^\sigma_{ijkl}+\sum_{mn}{}' N^\sigma_{ijmn}\beta^\sigma_{mnkl}, \tag{A11}$$

or in matrix form

$$\overline{\beta}^\sigma=\overline{\mathbf{N}}^\sigma(\overline{\mathbf{I}}-\overline{\mathbf{N}}^\sigma)^{-1}=(\overline{\mathbf{I}}-\overline{\mathbf{N}}^\sigma)^{-1}\overline{\mathbf{N}}^\sigma=(\overline{\mathbf{I}}-\overline{\mathbf{N}}^\sigma)^{-1}-\overline{\mathbf{I}}, \tag{A12}$$

where $\overline{\mathbf{I}}$ is the matrix (3.5).

From Eqs. (A10)–(A12) it follows for d_σ that

$$d_\sigma(\mathbf{r}_1,\mathbf{r}_2)=-\frac{2}{\Delta\tilde{\epsilon}_\sigma}\sum_{ijkl}^{N_\sigma} n_{i\sigma}\xi^\sigma_{ijkl}\psi_{i\sigma}(\mathbf{r}_1)\psi^*_{j\sigma}(\mathbf{r}_1)$$
$$\times\psi_{k\sigma}(\mathbf{r}_2)\psi^*_{l\sigma}(\mathbf{r}_2),$$
$$\xi^\sigma_{ijN\sigma N\sigma}=\xi^\sigma_{N\sigma N\sigma kl}=0. \tag{A13}$$

We then have our final expression for the inverse density response function,

$$\chi^{-1}_{s\sigma}(\mathbf{r}_1,\mathbf{r}_2)=-\frac{\Delta\tilde{\epsilon}_\sigma}{2\rho_\sigma(\mathbf{r}_1)}\delta(\mathbf{r}_1-\mathbf{r}_2)-\frac{\Delta\tilde{\epsilon}_\sigma}{2\rho_\sigma(\mathbf{r}_1)\rho_\sigma(\mathbf{r}_2)}$$
$$\times\sum_{ijkl}^{N_\sigma} n_{i\sigma}\xi^\sigma_{ijkl}\psi_{i\sigma}(\mathbf{r}_1)\psi^*_{j\sigma}(\mathbf{r}_1)\psi_{k\sigma}(\mathbf{r}_2)\psi^*_{l\sigma}(\mathbf{r}_2),$$
$$\xi^\sigma_{ijN\sigma N\sigma}=\xi^\sigma_{N\sigma N\sigma kl}=0. \tag{A14}$$

The function $\chi^{-1}_{s\sigma}$ has the zero long-range asymptotic behavior (3.6) due to the exclusion of the HOMO orbital density $|\psi_{N\sigma}|^2$ (which dominates at the asymptotics $|\mathbf{r}_1|\to\infty$ and $|\mathbf{r}_2|\to\infty$) from the numerator of Eq. (A14), while it is present in the densities in the denominator.

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