Relativistic optimized-potential method: Exact transverse exchange and Møller-Plesset-based correlation potential

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We present a fully relativistic extension of the optimized-potential method (ROPM), including the transverse electron-electron interaction and vacuum corrections. Using perturbation theory on the basis of the Kohn-Sham Hamiltonian an exact representation of the relativistic exchange-correlation energy E_{xc} in terms of Kohn-Sham orbitals and eigenvalues is derived. The most simple, viable approximation to this E_{xc} is obtained by a second-order expansion in powers of e^2, which leads to a Møller-Plesset-type correlation functional $E_c^{(2)}$. Due to this origin $E_c^{(2)}$ allows a first-principles, seamless description of long-range dispersive forces. The ROPM integral equation that determines the full exchange-correlation four potential v_{xc}^μ is presented, and specified in detail for $E_c^{(2)}$. We also analyze the Krieger-Li-Iafrate (KLI) approximation to the exact ROPM integral equation, pointing out an inherent ambiguity of the KLI approximation which arises for eigenvalue-dependent E_{xc}. The gauge properties of E_{xc} and the ROPM integral equation are discussed by examining the transversality of the Kohn-Sham current-current response function. It is demonstrated that due to the multiplicative nature of the total effective potential the density functional definition of the no-pair transverse exchange energy guarantees gauge invariance, in contrast to the relativistic Hartree-Fock scheme. On the other hand, the correlation energy is gauge dependent as soon as the no-pair approximation is applied. In addition, we show that the no-pair approximation automatically implies a definite intrinsic gauge for the spatial components of v_{xc}^μ. The significance of the self-consistent treatment of the transverse interaction for heavy atoms is investigated numerically within the exchange-only limit. By comparing self-consistent with first-order perturbative inclusion of the transverse exchange it is shown that second-order transverse corrections cannot be neglected in calculations of ground state or inner-shell transition energies of heavy atoms, if one aims at spectroscopic accuracy. It is furthermore found that the Breit approximation for the full transverse interaction is not as accurate for the exchange potential as it is for the exchange energy. Finally, the KLI approximation is examined numerically, thereby resolving the ambiguity for the case of the transverse exchange.
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I. INTRODUCTION AND SUMMARY OF RESULTS

Presently, the transition from explicitly density-dependent representations of the exchange-correlation (xc) energy functional E_{xc} to forms depending on the Kohn-Sham orbitals, i.e., to implicit density functionals analogous to the Kohn-Sham kinetic energy T_s, is developing into a major trend in density functional theory (DFT) [1–11]. For these functionals the corresponding multiplicative xc potential v_{xc} is provided by the optimized-potential method (OPM) [12] (for an extension to time-dependent systems see [13]). While the OPM in its exact form is computationally rather demanding and consequently only few full scale applications have been reported [1,2,6,10], orbital-dependent E_{xc} have attracted more and more interest after an efficient approximate variant of the OPM has been presented by Krieger, Li, and Iafrate (KLI) [14].

The concept of orbital-dependent E_{xc} has first been suggested for the exchange-only energy E_x [15]. For E_x the Fock expression, written in terms of Kohn-Sham (KS) orbitals, represents a natural definition within DFT as it guarantees an exact cancellation of the self-interaction between

Hartree and exchange energy and leads to a simple virial relation [16]. Until today, in most applications [6,7] this exact E_x has been combined with conventional density functionals for the correlation energy E_c, i.e., the local density approximation (LDA) or the generalized gradient approximation (GGA). It is well known, however, that the success of LDA or GGA-type functionals relies to some extent on a cancellation of errors between exchange and correlation, which no longer applies if the LDA or GGA for E_c is added to the exact E_x. The simplest orbital-dependent form for E_{xc} that treats exchange and correlation on an equal footing is the self-interaction corrected LDA [17], whose application has also been proposed in the context of the OPM [18]. As an alternative, the semiempirical Colle-Salvetti correlation functional [19] has been suggested for use with the exact E_x [8]. Recently, a systematic scheme for the construction of orbital-dependent E_c has been presented [4]. While this scheme yields a formally exact representation of E_c, its practical implementation requires an expansion in powers of e^2. To lowest order this leads to a functional $E_c^{(2)}$, which also depends on the KS eigenvalues and the inverse KS response function, so that an extension of the original OPM is necessary for the calculation of the corresponding v_c. While applications of $E_c^{(2)}$ are still lacking, its systematic origin nevertheless fosters the hope that now all ingredients for successful quantum chemical applications of the nonrelativistic

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OPM are available. In this contribution we present the fully relativistic extension of the OPM (ROPM), establishing a relativistic analog of the E_{xc} put forward in [4], which includes both the transverse electron-electron interaction and vacuum corrections.

During recent years much effort has been devoted to the formulation of relativistic many-body methods, both in the area of quantum chemistry, aiming at an appropriate description of molecules with heavy constituents, and in atomic physics, mainly focusing on tests of quantum electrodynamics (QED). Starting from the well-established relativistic Hartree-Fock (RHF) approximation [20–23], a variety of correlated many-body concepts has now been generalized to the relativistic domain on the basis of the no-pair Dirac-Coulomb (DC) or Dirac-Coulomb-Breit (DCB) Hamiltonian, namely, many-body perturbation theory (MBPT) [24–26], the multiconfiguration Hartree-Fock approach [27–29], as well as coupled-cluster [30–32] and configuration interaction methods [33–38]. While these schemes are able to adequately deal with electron correlation, use of the no-pair DC(B) Hamiltonian automatically implies the neglect of (higher order) photon retardation effects and of all contributions resulting from negative energy states. Thus, to allow for a comparison with the extremely accurate experimental results (see, e.g., [39]), in particular for highly charged ions for which these QED effects are more important than (higher order) electron correlation, one has to go over to QED-based perturbation theory [40–43] or mixed forms in which the QED effects are added perturbatively (see, e.g., [44]).

While, from a fundamental point of view, QED-based perturbation theory represents the most consistent approach, it is limited to low order (second, at present) and usually starts from a Furry representation in terms of noninteracting orbitals that are strictly hydrogenic. Consequently, important xc effects are not included, so that applications are restricted to high-Z ions with only a few electrons. On the other hand, also for neutral atoms with high Z the Breit interaction gives a substantial contribution to ground-state energies: For example, for neutral mercury the 22.6 hartree difference between the DCB-RHF and DC-RHF ground-state energies [26] is four times larger than E_c (for heliumlike mercury even the second-order Breit contribution of 39 mhartree [41,42] is as large as the total Coulomb correlation energy), indicating that at least this QED effect should be taken into account in quantum chemical calculations. However, evaluating the transverse contribution to the xc energy with the optimized DC(B) orbitals (which form the basis for most of the approaches mentioned), rather than hydrogenic basis functions, raises a fundamental problem: Due to the fact that the DC(B) orbitals experience a nonlocal single-particle potential the resulting transverse exchange energy is gauge dependent [28,45]. Note that gauge-invariant results can also be obtained with RHF orbitals, if a suitable resummation of the perturbation series is used [87]. As a consequence, in the DCB procedure the exchange potential depends on the gauge used for the transverse electron-electron interaction. While this effect is small for two electron systems (differences of 1–10 mhartree between Coulomb and Feynman gauge exchange energies in the high-Z regime on the basis of DC orbitals [45]), it is nevertheless of the same size as many higher-order QED corrections. Moreover, it is not clear to

what extent the gauge dependence of the DCB exchange potential further increases these discrepancies.

Orbital-dependent DFT methods, on the other hand, do not suffer from this problem, as the KS spinors are associated with a multiplicative single-particle potential, which guarantees gauge invariant results for the no-pair exchange [28,46] and, if negative energy states are included, also for the lowest-order correlation energy [47,48]. Consequently, the ROPM put forward in this work represents a self-consistent scheme that allows the inclusion of the transverse interaction in a gauge invariant form. In addition, it may serve as a tool to generate an optimal single-particle basis for QED-based perturbation theory.

In [9] we have extended the OPM to the relativistic domain (ROPM), restricting the discussion to (1) the no-(virtual-) pair approximation, (2) purely orbital-dependent functionals (i.e., the longitudinal exchange energy), and (3) the ''density-only'' (or ''nonmagnetic'') variant of RDFT (in which the absence of external magnetic fields is used to formulate RDFT on the basis of only the density, rather than the complete four current). The corresponding four current version has recently been given in [11]. In this contribution we present a completely general form of the ROPM. Working in the framework of QED, our discussion includes both the transverse electron-electron interaction and vacuum corrections. In addition, we provide the modifications of the ROPM necessary to deal with eigenvalue-dependent functionals and unoccupied excited KS levels, which naturally appear in orbital-dependent forms of E_c.

Using the auxiliary KS Hamiltonian as a basis for a perturbation expansion [4,49,50], we first derive a nonlinear representation of the relativistic E_{xc} in terms of the KS spinors and eigenvalues (in Sec. II). This representation is exact in principle, in the sense that it allows the construction of E_{xc} to all orders of the coupling constant e^2 in a recursive manner: The contribution $E_{xc}^{(n)}$ of order e^{2n} explicitly depends on the KS spinors and eigenvalues and on the $v_{xc}^{(k)}$ resulting from all $E_{xc}^{(k)}$ with $k<n$. These potentials, however, are themselves functionals of the KS spinors and eigenvalues, which can be evaluated by solution of the ROPM integral equations. In practice, at this point only the lowest two orders are investigated, i.e., the relativistic E_x and the correlation functional $E_c^{(2)}$ correct to second order in e^2 (details are given in Secs. II B,IV A). In particular, it is shown that $E_c^{(2)}$ contains the leading contribution to the van der Waals interaction between two atoms in a seamless form.

The crucial ingredient of this E_{xc} is the KS current-current response function $\chi_0^{\mu\nu}$, which, as a kernel of the ROPM integral equation, also determines the gauge dependence of the ROPM procedure. In Sec. III we thus analyze the gauge properties of $\chi_0^{\mu\nu}$ in some detail, which then allows us to review the corresponding properties of E_{xc} in a particularly coherent form. It is demonstrated that there are two possible sources for gauge dependence: (i) the nonlocality of the single-particle potential, which defines the orbitals used to evaluate E_{xc} (thus recovering the observation of [28,45] within an alternative approach), and (ii) the no-pair approximation (compare [48]). In the context of RDFT only the latter is relevant. However, one can explicitly verify that, due to its particular form, the standard no-pair E_x is gauge invariant in spite of the omission of the negative energy continuum states (Sec. III C). Of course, this is no longer the case for

the no-pair E_c, whose gauge dependence is examined quantitatively in a subsequent paper [51].

The extension of the ROPM necessary to deal with transverse exchange, second-order correlation and vacuum corrections is presented in Sec. IV. From the resulting ROPM integral equation, which determines the xc four potential v_{xc}^μ we derive a rigorous identity for an eigenvalue-dependent E_{xc}. While this identity is automatically satisfied by the first-principles functionals E_x and $E_c^{(2)}$, it represents a necessary condition for any semiempirical form of E_{xc}. Furthermore, using the results of Sec. III, the gauge properties of the ROPM are discussed. One finds that the gauge used for the transverse interaction can affect v_{xc}^μ only via the E_{xc}-dependent ingredients of the ROPM integral equation, i.e., if E_{xc} is gauge invariant the same holds for v_{xc}^0. On the other hand, in the no-pair approximation the ROPM integral equation is no longer satisfied by a complete class of v_{xc}^μ, which only differ by static gauge transformations, but rather fixes the intrinsic gauge of the spatial components of v_{xc}^μ.

In Sec. V the KLI approximation for the extended form of the ROPM is discussed. Comparing the two paths for the derivation of the KLI approximation suggested in the literature [1,11,14] we point out an ambiguity that arises for eigenvalue-dependent E_{xc}. It seems difficult to resolve this ambiguity on a purely formal basis, so that detailed numerical studies of a variety of systems and given forms of E_{xc} seem to be necessary.

As a first application of the ROPM for eigenvalue-dependent functionals we present self-consistent exchange-only results for atoms obtained with the full transverse exchange in Sec. VI within the no-pair approximation. The transverse exchange leads to significant corrections compared with the purely longitudinal results presented in [9], both for the ground-state energies and for inner-shell KS eigenvalues, and thus the inner-shell density. In particular, by comparing the self-consistent with the first-order perturbative treatment of the transverse exchange it is demonstrated that second-order transverse corrections to ground-state or inner-shell transition energies of heavy atoms or ions are on the 1-eV level, so that they are not negligible from a spectroscopical point of view. Moreover, this first self-consistent application of the full transverse exchange also shows that the error of the Breit approximation in the case of the exchange potential is an order of magnitude larger than the well-known, rather small deviation found for ground state or exchange energies [23]. Nevertheless, the Breit approximation captures the main physics of the full transverse interaction also for v_x^μ.

The ROPM results are then used to examine the KLI approximation, exploring its non-uniqueness by comparing obvious variants. The findings suggest that complete neglect of the ambiguous contribution to the KLI potential is the optimal choice in the case of the transverse exchange, as the resulting error is no larger than that observed for the nonrelativistic or longitudinal exchange. In fact, the deviations for ground-state energies originating from this KLI potential are roughly a factor of 5 smaller than those introduced by an even simpler approximation to the ROPM, i.e., the combination of a relativistic GGA (RGGA) potential [52] with the exact energy functional. It remains to be investigated, however, whether complete neglect of the ambiguous contribution to the KLI potential also is an option for $E_c^{(2)}$ for which the eigenvalue dependence is much more crucial than for the transverse exchange.

In Appendix A we provide all technical details required for an application of the extended ROPM to spherical systems. On the one hand, this material should allow the incorporation of the ROPM in standard relativistic atomic structure codes. On the other hand, it is required for the discussion of the asymptotic behavior of v_x in finite systems, which is substantially complicated by the spinor structure of the KS orbitals and the presence of the transverse interaction. Relying on Appendix A, we analyze the ROPM integral equation in the asymptotic regime in Appendix B, deriving the relativistic analog of the KLI identity for the highest occupied orbital [14] and verifying explicitly that v_x^0 asymptotically approaches $-e^2/r$. Throughout this paper we use $\hbar = 1$ [$x^0 = ct$, $\partial_0 = \partial/\partial(ct)$—no distinction is made between functions of t and x^0, i.e., $f(t) \hat{=} f(x^0)$].

II. SYSTEMATIC APPROACH TO THE RELATIVISTIC EXCHANGE-CORRELATION ENERGY FUNCTIONAL

The appropriate basis for a first-principles, relativistic description of many electron systems (atoms, molecules, clusters, solids) is QED. In view of the large difference between the electron mass and the nuclear masses, however, it is standard to treat the nuclei as fixed external sources of electromagnetic fields, assuming a common rest frame for all nuclei. Here we thus consider a system of electrons bound by some static external potential $v_{ext}^\mu(\boldsymbol{x})$, which interact via the exchange of photons. In the Heisenberg-representation the corresponding Hamiltonian can be directly derived from the standard QED Lagrangian as the 00 component of the energy-momentum tensor (see, e.g., [53]),

$$\hat{H} = \hat{H}_e(x^0) + \hat{H}_\gamma(x^0) + \hat{H}_{int}(x^0), \qquad (2.1)$$

$$\hat{H}_e(x^0) = \frac{1}{2} \int d^3x [\hat{\bar{\psi}}(x), [-ic\,\boldsymbol{\gamma}\cdot\boldsymbol{\nabla} + mc^2 + \gamma_\mu v_{ext}^\mu(\boldsymbol{x})]\hat{\psi}(x)], \qquad (2.2)$$

$$\hat{H}_\gamma(x^0) = -\frac{1}{8\pi} \int d^3x \{\partial^0 \hat{A}_\nu(x) \partial^0 \hat{A}^\nu(x)$$
$$+ \boldsymbol{\nabla}\hat{A}_\nu(x)\cdot\boldsymbol{\nabla}\hat{A}^\nu(x)\}, \qquad (2.3)$$

$$\hat{H}_{int}(x^0) = e \int d^3x \hat{j}^\mu(x)\hat{A}_\mu(x). \qquad (2.4)$$

Here $\hat{\psi}(x)$ denotes the fermion field operator of the interacting, inhomogeneous system characterized by $\hat{H}$, $\hat{j}^\mu(x)$ is the corresponding fermion four current operator,

$$\hat{j}^\mu(x) = \tfrac{1}{2}[\hat{\bar{\psi}}(x), \gamma^\mu \hat{\psi}(x)], \qquad (2.5)$$

and $\hat{A}_\mu(x)$ represents the field operator of the photons, for which the covariant quantization scheme and Feynman gauge have been used. Note, however, that this particular

choice is irrelevant for the discussion in this section as the specific form of $\hat{H}_\gamma$ will not be used. While the individual components of $\hat{H}$ are time dependent in the Heisenberg representation, the total Hamiltonian (2.1) is stationary as can be shown by examining the four divergence of the corresponding energy-momentum tensor [53]. The transition to the Schrödinger representation, which is more suitable for the subsequent discussion, is thus straightforward: Choosing the Schrödinger representation to coincide with the Heisenberg representation at $x^0=0$, the corresponding Hamiltonian $\hat{H}_S$ can be decomposed into a static noninteracting part $\hat{H}_{0,S}$ and a static interaction Hamiltonian $\hat{H}_{\mathrm{int},S}$,

$$\hat{H}_S = \hat{H} = \hat{H}_{e,S} + \hat{H}_{\gamma,S} + \hat{H}_{\mathrm{int},S}, \qquad (2.6)$$

$$\hat{H}_{e,S} = \hat{H}_e(x^0=0), \ \ldots. \qquad (2.7)$$

The components $\hat{H}_{e,S}$, $\hat{H}_{\gamma,S}$, and $\hat{H}_{\mathrm{int},S}$ are easily written in terms of Schrödinger-picture field operators using the identity with their Heisenberg-picture counterparts at $x^0=0$, e.g., $\hat{\psi}_S(\boldsymbol{x}) = \hat{\psi}(\boldsymbol{x},x^0=0)$.

In the following we analyze the total binding energy of the electrons, E_{tot}, which is given by the energy difference between the ground state $|\Phi\rangle$ of the N-electron sector of the complete Fock space,

$$\hat{H}|\Phi\rangle = E|\Phi\rangle, \qquad (2.8)$$

and the ground state of the zero-charge sector, i.e., the interacting vacuum $|0\rangle$,

$$E_{\mathrm{tot}} = \langle \Phi|\hat{H}|\Phi\rangle - \langle 0|\hat{H}|0\rangle + \mathcal{C}. \qquad (2.9)$$

Here $\mathcal{C}$ indicates the counterterm contributions required to keep E_{tot} UV finite in a perturbative treatment of the expectation values involved (subsequently all counterterms will be suppressed for brevity—their explicit form is not relevant here).

Within the standard many-body framework the individual expectation values in Eq. (2.9) can either be evaluated via the Gell-Mann–Low level shift formula [54] (usually the symmetric form of Sucher [55] is applied—see, e.g., [40,56]) or via a coupling constant integration scheme. Two versions of the latter approach have been introduced in the context of DFT. While the so-called adiabatic connection [57,58] has been particularly useful for the analysis of E_{xc} [16,59,60], the second scheme [49,50] allows a more direct extraction of orbital-dependent forms for E_{xc}. In the following subsections this second variant will be extended to the relativistic domain.

A. Relativistic Kohn-Sham theory

According to the relativistic Hohenberg-Kohn theorem [53,61–63] the (nondegenerate) ground state $|\Phi\rangle$ of any N-electron sector of the complete Fock space is uniquely determined (up to gauge transformations) by the corresponding ground-state four current,

$$j^\mu(x) = \langle \Phi|\hat{j}^\mu(x)|\Phi\rangle, \qquad (2.10)$$

i.e., can be understood as a unique functional of j^μ, $|\Phi[j^\mu]\rangle$. As an immediate consequence all ground-state expectation values are unique functionals of j^μ, as, for instance, the ground-state energy $E=E[j^\mu]$. Moreover, the minimum principle for the (renormalized) ground-state energy allows the determination of both j^μ and E by minimizing $E[j^\mu]$ with respect to j^μ (for a detailed discussion see [53]). Representing j^μ in terms of auxiliary single-particle spinors ϕ_k (assuming noninteracting v representability, as usual),

$$j^\mu(x) = \frac{1}{2}\left[\sum_{\epsilon_k \leq \epsilon_F} \overline{\phi}_k(x)\gamma^\mu \phi_k(x) - \sum_{\epsilon_F < \epsilon_k} \overline{\phi}_k(x)\gamma^\mu \phi_k(x)\right], \qquad (2.11)$$

one can decompose E as

$$E = T_s + \int d^3x\, j_\mu(x) v_{\mathrm{ext}}^\mu(x) + E_H + E_{\mathrm{xc}}. \qquad (2.12)$$

Here T_s denotes the kinetic energy of the "auxiliary particles,"

$$T_s = \frac{1}{2}\int d^3x \left\{\sum_{\epsilon_k \leq \epsilon_F} \overline{\phi}_k[-ic\,\boldsymbol{\gamma}\cdot\boldsymbol{\nabla} + mc^2]\phi_k \right. $$
$$\left. - \sum_{\epsilon_F < \epsilon_k} \overline{\phi}_k[-ic\,\boldsymbol{\gamma}\cdot\boldsymbol{\nabla} + mc^2]\phi_k\right\}, \qquad (2.13)$$

E_H is their "covariant" Hartree energy,

$$E_H = \frac{1}{2}\int d^3x \int d^4y\, D_{\mu\nu}^0(\boldsymbol{x}-\boldsymbol{y},y^0) j^\mu(\boldsymbol{x}) j^\nu(\boldsymbol{y}), \qquad (2.14)$$

with $D_{\mu\nu}^0$ being the noninteracting photon propagator [precisely given in Eq. (2.22)], and the xc energy E_{xc} is defined by Eq. (2.12). Minimization of E with respect to the ϕ_k rather than j^μ then leads to the relativistic KS equations, first introduced by Rajagopal [62] and independently by Mac-Donald and Vosko [63],

$$\{-ic\,\boldsymbol{\alpha}\cdot\boldsymbol{\nabla} + \beta mc^2 + \alpha_\mu v_{\mathrm{KS}}^\mu(x)\}\phi_k(x) = \epsilon_k \phi_k(x), \qquad (2.15)$$

with the multiplicative KS potential v_{KS}^μ consisting of the sum of v_{ext}^μ, the Hartree potential v_H^μ and the xc potential v_{xc}^μ,

$$v_{\mathrm{KS}}^\mu(\boldsymbol{x}) = v_{\mathrm{ext}}^\mu(\boldsymbol{x}) + v_H^\mu(\boldsymbol{x}) + v_{\mathrm{xc}}^\mu(\boldsymbol{x}), \qquad (2.16)$$

$$v_H^\mu(\boldsymbol{x}) = \int d^4y\, D^{0,\mu\nu}(\boldsymbol{x}-\boldsymbol{y},y^0) j_\nu(\boldsymbol{y}), \qquad (2.17)$$

$$v_{\mathrm{xc}}^\mu(\boldsymbol{x}) = \frac{\delta E_{\mathrm{xc}}[j]}{\delta j_\mu(\boldsymbol{x})}. \qquad (2.18)$$

Of course, in order to construct the full current (2.11), the negative energy solutions of the KS equations are required.

While the KS approach is based on auxiliary single-particle quantities with (almost) no physical meaning, the total KS potential v_{KS}^μ nevertheless allows the definition of a corresponding noninteracting Hamiltonian $\hat{H}_{\mathrm{KS}}$,

$$\hat{H}_{\mathrm{KS}} = \frac{1}{2} \int d^3x [\, \hat{\bar{\psi}}_S(\boldsymbol{x}), (-ic\boldsymbol{\gamma}\cdot\boldsymbol{\nabla} + mc^2)\hat{\psi}_S(\boldsymbol{x})]$$

$$+ \int d^3x \hat{j}_{S,\mu}(\boldsymbol{x}) v_{\mathrm{KS}}^\mu(\boldsymbol{x}) + \hat{H}_\gamma(x^0 = 0), \qquad (2.19)$$

with ground state $|\Phi_{\mathrm{KS}}\rangle$ and eigenvalue E_{KS},

$$\hat{H}_{\mathrm{KS}} |\Phi_{\mathrm{KS}}\rangle = E_{\mathrm{KS}} |\Phi_{\mathrm{KS}}\rangle. \qquad (2.20)$$

As in $\hat{H}_{\mathrm{KS}}$ electrons and photons do not interact directly they can be dealt with separately. Thus the KS ground state $|\Phi_{\mathrm{KS}}\rangle$ factorizes into a product of the photon vacuum $|0_\gamma\rangle$ (no free photons are present in the ground state) and an electronic ground state $|\Phi_{\mathrm{KS},e}\rangle$,

$$|\Phi_{\mathrm{KS}}\rangle = |\Phi_{\mathrm{KS},e}\rangle \times |0_\gamma\rangle; \quad \langle 0_\gamma | \hat{A}_0^\mu(x) | 0_\gamma \rangle = 0, \quad (2.21)$$

where $\hat{A}_0^\mu(x)$ denotes the free photon field operator. As a consequence, in any perturbative approach based on $\hat{H}_{\mathrm{KS}}$ the standard vacuum QED results can be used for the photon sector of the KS problem, as, e.g., the free photon propagator

$$D^{0,\mu\nu}(x-y) = -i\frac{e^2}{c}\langle 0_\gamma | T\hat{A}_0^\mu(x)\hat{A}_0^\nu(y) | 0_\gamma \rangle. \quad (2.22)$$

On the other hand, in the electronic sector the presence of v_{KS}^μ leads to an inhomogeneous reference system (Furry picture). In terms of the KS spinors ϕ_k the corresponding noninteracting field operators are thus given by

$$\hat{\psi}_0(x) = e^{i\hat{H}_{\mathrm{KS}}x^0/c} \hat{\psi}_S(\boldsymbol{x}) e^{-i\hat{H}_{\mathrm{KS}}x^0/c}$$

$$= \sum_{-mc^2 < \epsilon_k} \hat{b}_k \phi_k(\boldsymbol{x}) e^{-i\epsilon_k x^0/c}$$

$$+ \sum_{\epsilon_k \leq -mc^2} \hat{d}_k^\dagger \phi_k(\boldsymbol{x}) e^{-i\epsilon_k x^0/c}, \qquad (2.23)$$

where the $\hat{b}_k$ ($\hat{b}_k^\dagger$) and $\hat{d}_k$ ($\hat{d}_k^\dagger$) are annihilation (creation) operators for positive and negative energy KS states. This then allows the construction of the noninteracting electron propagator,

$$G^0(x,y) \equiv G^0(\boldsymbol{x},\boldsymbol{y},x^0-y^0)$$

$$= -i\langle \Phi_{\mathrm{KS},e} | T\hat{\psi}_0(x)\hat{\bar{\psi}}_0(y) | \Phi_{\mathrm{KS},e}\rangle \qquad (2.24)$$

$$= -i\Theta(x^0 - y^0) \sum_{\epsilon_F < \epsilon_k} \phi_k(\boldsymbol{x})\bar{\phi}_k(\boldsymbol{y}) e^{-i\epsilon_k(x^0-y^0)/c}$$

$$+ i\Theta(y^0 - x^0) \sum_{\epsilon_k \leq \epsilon_F} \phi_k(\boldsymbol{x})\bar{\phi}_k(\boldsymbol{y}) e^{-i\epsilon_k(x^0-y^0)/c},$$

$$(2.25)$$

where in $|\Phi_{\mathrm{KS},e}\rangle$ the electronic single-particle states are assumed to be filled up to the Fermi level ϵ_F,

$$|\Phi_{\mathrm{KS},e}\rangle = \prod_{-mc^2 < \epsilon_k \leq \epsilon_F} \hat{b}_k^\dagger |0_e\rangle. \qquad (2.26)$$

Using Eqs. (2.5), (2.23), and (2.26) the corresponding four current

$$j^\mu(\boldsymbol{x}) = \langle \Phi_{\mathrm{KS}} | \hat{j}^\mu(x) | \Phi_{\mathrm{KS}}\rangle \qquad (2.27)$$

is given by Eq. (2.11), while for E_{KS} one obtains

$$E_{\mathrm{KS}} = T_s + \int d^3x j_\mu(\boldsymbol{x}) v_{\mathrm{KS}}^\mu(\boldsymbol{x}). \qquad (2.28)$$

In fact, the field theoretical formulation of the KS problem via Eqs. (2.19)–(2.28) is the actual origin of the forms (2.11),(2.13) for the KS four current and T_s. Note that in Eqs. (2.11),(2.13) the counterterms inherent in any field theoretical treatment have been suppressed.

B. Perturbation theory on Kohn-Sham basis

In order to obtain a formula for the energy difference between the complete ground-state energy E and the KS energy E_{KS}, and thus for E_{xc}, the coupling constant integration technique is utilized. To this end one decomposes the total $\hat{H}$ into $\hat{H}_{\mathrm{KS}}$ and an interaction Hamiltonian $\hat{H}_1$, for which a dimensionless coupling strength parameter g is introduced,

$$\hat{H}(g) = \hat{H}_{\mathrm{KS}} + \hat{H}_{1,S}, \qquad (2.29)$$

$$\hat{H}_1(x^0) = \int d^3x \hat{j}_\mu(x)[g^{1/2}e\hat{A}^\mu(x) - gv_{H\mathrm{xc}}^\mu(\boldsymbol{x})], \qquad (2.30)$$

$$v_{H\mathrm{xc}}^\mu(\boldsymbol{x}) \equiv v_{\mathrm{KS}}^\mu(\boldsymbol{x}) - v_{\mathrm{ext}}^\mu(\boldsymbol{x}) = v_H^\mu(\boldsymbol{x}) + v_{\mathrm{xc}}^\mu(\boldsymbol{x}). \quad (2.31)$$

Here the scaling of the two perturbations with g has been adjusted to their dependence on the actual coupling constant e^2 (at least to lowest order). The original Hamiltonian (2.1) is then obtained from Eq. (2.29) for $g = 1$. By differentiation of the corresponding g-dependent ground-state energy

$$E(g) = \langle \Phi(g) | \hat{H}(g) | \Phi(g)\rangle \qquad (2.32)$$

with respect to g one finds

$$\frac{\partial}{\partial g} E(g) = \int d^4x \, \delta(x^0)\langle \Phi(g) | \hat{j}_\mu(x)$$

$$\times \left[\frac{e}{2g^{1/2}} \hat{A}^\mu(x) - v_{H\mathrm{xc}}^\mu(\boldsymbol{x}) \right] | \Phi(g)\rangle, \quad (2.33)$$

where the normalization of $|\Phi(g)\rangle$,

$$\langle \Phi(g) | \Phi(g)\rangle = 1, \qquad (2.34)$$

has been used. Consequently, integration over g leads to

$$E(1)-E(0)=E-E_{\text{KS}}\equiv E_1$$

$$=\int_0^1 dg\int d^4x\,\delta(x^0)\langle\Phi(g)|\hat{j}_\mu(x)$$

$$\times\left[\frac{e}{2g^{1/2}}\hat{A}^\mu(x)-v_{\text{Hxc}}^\mu(\boldsymbol{x})\right]\Bigg|\Phi(g)\rangle.$$

$$(2.35)$$

In order to obtain a more explicit form of Eq. (2.35), we use the concept of adiabatic switching for $\hat{H}_1$. This allows us to relate $|\Phi(g)\rangle$ (assumed to be nondegenerate) to $|\Phi_{\text{KS}}\rangle$ (also assumed to be nondegenerate) via the interaction-picture time-evolution operator $\hat{U}_{I,\epsilon}$,

$$|\Phi\rangle=A\;\lim_{\epsilon\to0}\frac{\hat{U}_{I,\epsilon}(0,\mp\infty)|\Phi_{\text{KS}}\rangle}{\langle\Phi_{\text{KS}}|\hat{U}_{I,\epsilon}(0,\mp\infty)|\Phi_{\text{KS}}\rangle},\qquad(2.36)$$

$$A=\lim_{\epsilon_1,\epsilon_2\to0}\left[\frac{\langle\Phi_{\text{KS}}|\hat{U}_{I,\epsilon_1}(+\infty,0)|\Phi_{\text{KS}}\rangle}{\langle\Phi_{\text{KS}}|\hat{U}_{I,\epsilon_1}(+\infty,0)}\right.$$

$$\left.\times\frac{\langle\Phi_{\text{KS}}|\hat{U}_{I,\epsilon_2}(0,-\infty)|\Phi_{\text{KS}}\rangle}{\hat{U}_{I,\epsilon_2}(0,-\infty)|\Phi_{\text{KS}}}\right]^{1/2},\qquad(2.37)$$

$$\hat{U}_{I,\epsilon}(t,t')=\sum_{n=0}^\infty\frac{(-i)^n}{n!}\int_{t'}^t dt_1\cdots\int_{t'}^t dt_n$$

$$\times\exp[-\epsilon(|t_1|+\cdots+|t_n|)]$$

$$\times T[\hat{H}_{1,I}(t_1)\cdots\hat{H}_{1,I}(t_n)],\qquad(2.38)$$

$$\hat{H}_{1,I}(x^0)=e^{i\hat{H}_{\text{KS}}x^0/c}\hat{H}_{1,S}e^{-i\hat{H}_{\text{KS}}x^0/c}$$

$$=\int d^3x\hat{j}_{0,\mu}(x)[g^{1/2}e\hat{A}_0^\mu(x)-gv_{\text{Hxc}}^\mu(\boldsymbol{x})]$$

$$(2.39)$$

(for brevity, the g dependence of the various operators and states involved is no longer noted explicitly, whenever it is not essential). Together with the normalization of $\langle\Phi_{\text{KS}}|\Phi_{\text{KS}}\rangle=1$ the factor (2.37) ensures the validity of Eq. (2.34) for all g. Equation (2.36) holds for any charge sector of the complete Fock space, i.e., not only for the N-electron ground states (charge $-Ne$), but also for the corresponding vacua $|0\rangle$ and $|0_0\rangle=|0_e\rangle\times|0_\gamma\rangle$. Insertion of Eq. (2.36) into Eq. (2.35) and use of the additivity of the time-evolution operator gives

$$E_1=\lim_{\epsilon\to0}\int_0^1 dg\int d^4x\;\delta(x^0)\sum_{n=0}^\infty\frac{(-i)^n}{n!}\int_{-\infty}^\infty dt_1\cdots\int_{-\infty}^\infty dt_n\;e^{-\epsilon(|t_1|+\cdots+|t_n|)}$$

$$\times\frac{\langle\Phi_{\text{KS}}|T\hat{j}_{0,\mu}(x)[(e/2g^{1/2})\hat{A}^\mu(x)-v_{\text{Hxc}}^\mu(\boldsymbol{x})]\hat{H}_{1,I}(t_1)\cdots\hat{H}_{1,I}(t_n)|\Phi_{\text{KS}}\rangle}{\langle\Phi_{\text{KS}}|\hat{U}_{I,\epsilon}(+\infty,-\infty)|\Phi_{\text{KS}}\rangle},\qquad(2.40)$$

where, as usual, it has been assumed that all ϵ limits involved can be combined to a single limiting procedure. With Eq. (2.30) one then obtains a perturbative expansion of E_1 in powers of e,

$$E_1=\lim_{\epsilon\to0}\int_0^1 dg\sum_{n=0}^\infty\frac{(-i)^n}{n!c^n}\sum_{k=0}^n\binom{n}{k}g^{n-k/2}\int d^4x\,\delta(x^0)\int d^4x_1\cdots\int d^4x_n e^{-\epsilon(|x_1^0|+\cdots+|x_n^0|)}$$

$$\times\langle\Phi_{\text{KS},e}|T\hat{j}_0^\mu(x)\hat{j}_0^{\mu_1}(x_1)\cdots\hat{j}_0^{\mu_n}(x_n)|\Phi_{\text{KS},e}\rangle_c(-1)^{n-k}v_{\text{Hxc},\mu_{k+1}}(\boldsymbol{x}_{k+1})\cdots v_{\text{Hxc},\mu_n}(\boldsymbol{x}_n)$$

$$\times e^k\left\{\frac{e}{2g^{1/2}}\langle0_\gamma|T\hat{A}_{0,\mu}(x)\hat{A}_{0,\mu_1}(x_1)\cdots\hat{A}_{0,\mu_k}(x_k)|0_\gamma\rangle-v_{\text{Hxc},\mu}(\boldsymbol{x})\langle0_\gamma|T\hat{A}_{0,\mu_1}(x_1)\cdots\hat{A}_{0,\mu_k}(x_k)|0_\gamma\rangle\right\},\qquad(2.41)$$

where the index c indicates that only those diagrammatic contributions are to be included in which all vertices $x_1\cdots x_n$ are connected to the vertex x [the remaining terms are exactly canceled by the denominator of Eq. (2.40)]. The expansion (2.41) can be reordered as an explicit expansion in powers of e^2 by eliminating all photon operators in favor of the photon propagator (2.22), using the fact that due to Eq. (2.21) the vacuum expectation value of an odd number of $\hat{A}_0$ vanishes, while for an even number all possible contractions, i.e., permutations of the $\hat{A}_0$, are obtained by

$$\langle0_\gamma|T\hat{A}_0^{\mu_1}(x_1)\cdots\hat{A}_0^{\mu_{2n}}(x_{2n})|0_\gamma\rangle=\sum_{k=2}^{2n}\langle0_\gamma|T\hat{A}_0^{\mu_1}(x_1)\hat{A}_0^{\mu_k}(x_k)|0_\gamma\rangle\langle0_\gamma|T\hat{A}_0^{\mu_2}(x_2)\cdots\hat{A}_0^{\slashed{\mu}_k}(x_k)\cdots\hat{A}_0^{\mu_{2n}}(x_{2n})|0_\gamma\rangle\quad(2.42)$$

[here $\hat{A}_0^{\slashed{\mu}_k}(x_k)$ indicates that this operator has to be dropped from the series $k=2,\ldots,2n$]. As a consequence of Eq. (2.21) k must be odd in the first term inside the curly brackets in Eq. (2.41) and even in the second. In order to separate the contributions with even from those with odd k, it is convenient to interchange the summation order of k and n. Subsequently

the photon vacuum expectation values are evaluated using Eq. (2.42). Taking into account the multiplicity originating from the number of possible contractions of the $\hat{A}_0$ (Wick's theorem) this leads to

$$
E_1 = \lim_{\epsilon \to 0} \int_0^1 dg \sum_{l=0}^{\infty} \frac{(ig)^l}{l! c^l} \sum_{k=0}^{l} \binom{l}{k} \left(-\frac{1}{2} \right)^k \int d^4x \ \delta(x^0) \int d^4x_1 \cdots \int d^4x_{l+k} e^{-\epsilon(|x_1^0|+\cdots+|x_{l+k}^0|)}
$$

$$
\times D^0_{\mu_1\mu_2}(x_1-x_2)\cdots D^0_{\mu_{2k-1}\mu_{2k}}(x_{2k-1}-x_{2k}) v_{Hxc,\mu_{2k+1}}(\boldsymbol{x}_{2k+1})\cdots v_{Hxc,\mu_{l+k}}(\boldsymbol{x}_{l+k}) \left\{ \frac{1}{2} \int d^4y \, e^{-\epsilon|y^0|} D^0_{\mu\nu}(x-y) \right.
$$

$$
\left. \times \langle \Phi_{KS,e}|T\hat{\jmath}_0^\mu(x)\hat{\jmath}_0^\nu(y)\hat{\jmath}_0^{\mu_1}(x_1)\cdots\hat{\jmath}_0^{\mu_{l+k}}(x_{l+k})|\Phi_{KS,e}\rangle_c - v_{Hxc,\mu}(\boldsymbol{x})\langle \Phi_{KS,e}|T\hat{\jmath}_0^\mu(x)\hat{\jmath}_0^{\mu_1}(x_1)\cdots\hat{\jmath}_0^{\mu_{l+k}}(x_{l+k})|\Phi_{KS,e}\rangle_c \right\}.
$$

$$(2.43)$$

Finally, the binomial structure of Eq. (2.43) can be utilized to eliminate the summation over k. Extracting the xc contribution to E_1 via Eqs. (2.12), (2.28), and (2.35) and introducing the interaction operator

$$
\hat{W}(x^0) = \frac{1}{2} \int d^3x \int d^4y \, e^{-\epsilon(|x^0|+|y^0|)} \ \hat{\jmath}_0^\mu(x) D^0_{\mu\nu}(x-y)\hat{\jmath}_0^\nu(y) - \int d^3x \, e^{-\epsilon|x^0|} \{v_{H,\mu}(\boldsymbol{x})+v_{xc,\mu}(\boldsymbol{x})\}\hat{\jmath}_0^\mu(x), \qquad (2.44)
$$

the final result for E_{xc} can be written as

$$
E_{xc} = \frac{1}{2} \int d^4x \ \delta(x^0) \int d^4y \, e^{-\epsilon|y^0|} \ D^0_{\mu\nu}(x-y)\{\langle \Phi_{KS}|T\hat{\jmath}_0^\mu(x)\hat{\jmath}_0^\nu(y)|\Phi_{KS}\rangle - j^\mu(\boldsymbol{x})j^\nu(\boldsymbol{y})\}
$$

$$
+ \lim_{\epsilon \to 0} \sum_{n=1}^{\infty} \frac{(-i)^n}{(n+1)!} \int_{-\infty}^{\infty} dt_1 \cdots \int_{-\infty}^{\infty} dt_n \langle \Phi_{KS}|T\hat{W}(0)\hat{W}(t_1)\cdots\hat{W}(t_n)|\Phi_{KS}\rangle_c, \qquad (2.45)
$$

with the understanding that, in analogy to the time evolution operator, the time ordering in Eq. (2.45) also applies inside Eq. (2.44), i.e., before performing the time integrations in the individual $\hat{W}$ the overall time ordering of Eq. (2.45) has to be established.

Equation (2.45) can be further evaluated by applying Wick's theorem to the electronic sector, utilizing the KS propagator (2.25). Taking into account the explicit form (2.17) for v_H^μ [64], Eq. (2.45) thus provides an exact representation of E_{xc} in terms of the KS orbitals, the KS eigenvalues, and v_{xc}^μ, $E_{xc}[\phi_k^{(\dagger)}, \epsilon_k, v_{xc}^\mu]$. However, the $\phi_k^{(\dagger)}$, ϵ_k as well as v_{xc}^μ are functionals of the four current, so that E_{xc} is in fact an implicit functional of j^μ. As via Eq. (2.18) v_{xc}^μ is itself defined as the functional derivative of E_{xc} with respect to j^μ, Eq. (2.45) is a highly nonlinear equation for E_{xc}. Nevertheless, this equation allows an iterative solution after an expansion in powers of e^2,

$$
E_{xc} = \sum_{i=1}^{\infty} e^{2i} E_{xc}^{(i)}; \quad v_{xc}^\mu = \sum_{i=1}^{\infty} e^{2i} v_{xc}^{\mu,(i)}. \qquad (2.46)
$$

In fact, after insertion of Eq. (2.46) in Eq. (2.45) one notices that the lowest-order contribution in e^2, the exchange energy $E_x = e^2 E_{xc}^{(1)}$, does not depend on v_{xc}^μ. Thus E_x is a well-defined functional of the $\phi_k^{(\dagger)}$ and ϵ_k only, so that the corresponding exchange potential v_x^μ can be evaluated using the ROPM (see Sec. IV) to order e^2. This then defines the e^4 contribution to E_{xc}, as only $v_x^\mu = e^2 v_{xc}^{\mu,(1)}$ enters in this order [65],

$$
E_c^{(2)} = \frac{i}{2c}\lim_{\epsilon \to 0} \int d^4x \, \delta(x^0) \int d^4y \, e^{-\epsilon|y^0|} \left\{ -v_{x,\mu}(\boldsymbol{x})v_{x,\nu}(\boldsymbol{y}) \text{tr}[\gamma^\mu G^0(x,y)\gamma^\nu G^0(y,x)] + i\int d^4z \, e^{-\epsilon|z^0|}[D^0_{\mu\rho}(x-z)v_{x,\nu}(\boldsymbol{y}) \right.
$$

$$
+ D^0_{\nu\rho}(y-z)v_{x,\mu}(\boldsymbol{x})]\text{tr}[\gamma^\mu G^0(x,y)\gamma^\nu G^0(y,z)\gamma^\rho G^0(z,x)] - \frac{1}{2}\int d^4z \int d^4u \, e^{-\epsilon(|z^0|+|u^0|)} D^0_{\mu\nu}(x-z)D^0_{\rho\lambda}(y-u)
$$

$$
\times \{\text{tr}[\gamma^\mu G^0(x,y)\gamma^\rho G^0(y,x)]\text{tr}[\gamma^\nu G^0(z,u)\gamma^\lambda G^0(u,z)] - 2\,\text{tr}[\gamma^\mu G^0(x,z)\gamma^\nu G^0(z,u)\gamma^\lambda G^0(u,y)\gamma^\rho G^0(y,x)]
$$

$$
\left. - \text{tr}[\gamma^\mu G^0(x,y)\gamma^\rho G^0(y,z)\gamma^\nu G^0(z,u)\gamma^\lambda G^0(u,x)]\} \right\}. \qquad (2.47)
$$

This procedure can be repeated to all orders as $E_{xc}^{(n)}$ only depends on the $v_{xc}^{\mu,(i)}$ with $i<n$, establishing a recursive definition of E_{xc} as a functional of the ϕ_k and ϵ_k.

While the expansion (2.46) immediately shows that Eq. (2.45) represents a practically viable approach to E_{xc}, Eq. (2.46) is not really required for establishing the ROPM, which can be based directly on the general nonlinear form (2.45) for E_{xc}. We just remark that a representation of E_{xc} that is equivalent to Eq. (2.45) can be derived from the Gell-Mann–Low–Sucher level shift formula [54,55].

III. GAUGE PROPERTIES OF THE EXCHANGE-CORRELATION ENERGY

A. Basic definitions

The relativistic DF exchange energy E_x is most suitably defined as the lowest order contribution to Eq. (2.45). Introducing the time-ordered KS current-current response function,

$$\chi_0^{\mu\nu}(x,y) \equiv \chi_0^{\mu\nu}(\boldsymbol{x},\boldsymbol{y},x^0-y^0)$$
$$= -i[\langle \Phi_{KS}|T\hat{j}_0^\mu(x)\hat{j}_0^\nu(y)|\Phi_{KS}\rangle - j^\mu(\boldsymbol{x})j^\nu(\boldsymbol{y})],$$
$$(3.1)$$

E_x can be written as

$$E_x = \frac{i}{2}\int d^3x \int d^4y \, D_{\mu\nu}^0(\boldsymbol{x}-\boldsymbol{y},y^0)\chi_0^{\mu\nu}(\boldsymbol{x},\boldsymbol{y},y^0). \quad (3.2)$$

$\chi_0^{\mu\nu}$ can be easily expressed in terms of KS orbitals via the KS propagator (2.25),

$$\chi_0^{\mu\nu}(\boldsymbol{x},\boldsymbol{y},x^0-y^0)$$
$$= -i \, \mathrm{tr}[\gamma^\mu G^0(\boldsymbol{x},\boldsymbol{y},x^0-y^0)\gamma^\nu G^0(\boldsymbol{y},\boldsymbol{x},y^0-x^0)] \quad (3.3)$$

$$= -i\left\{ \Theta(x^0-y^0)\sum_{\epsilon_l\leq\epsilon_F<\epsilon_k} + \Theta(y^0-x^0)\sum_{\epsilon_k\leq\epsilon_F<\epsilon_l} \right\}$$
$$\times \overline{\phi}_l(\boldsymbol{x})\gamma^\mu\phi_k(\boldsymbol{x})\overline{\phi}_k(\boldsymbol{y})\gamma^\nu\phi_l(\boldsymbol{y})$$
$$\times \exp[-i(\epsilon_k-\epsilon_l)(x^0-y^0)/c]. \quad (3.4)$$

While Eqs. (3.1)–(3.4) define the exchange energy in the context of DFT, these expressions are equally valid for the case of the standard HF exchange, as soon as the ϕ_k are understood as HF spinors. Thus, in order to allow a direct comparison of the gauge properties of DF and HF exchange, we consider a more general form of single-particle orbitals in this section: The ϕ_k defining $\chi_0^{\mu\nu}$ via Eq. (3.4) are assumed to satisfy the single-particle equations

$$0 = \{-ic\boldsymbol{\alpha}\cdot\boldsymbol{\nabla} + \beta mc^2 - \epsilon_k\}\phi_k(\boldsymbol{x}) + \int d^3z \, V_k(\boldsymbol{x},\boldsymbol{z})\phi_k(\boldsymbol{z}),$$
$$(3.5)$$

with either a given or a self-consistently determined, Hermitian potential, which can be both nonlocal and state dependent,

$$V_k^\dagger(\boldsymbol{x},\boldsymbol{z}) = V_k(\boldsymbol{z},\boldsymbol{x}) \quad (3.6)$$

(we here use the term "state dependent" to indicate that each orbital experiences a different potential, in distinction to the term "orbital dependent," which refers to the fact that a potential or energy can be expressed as functional of the orbitals). In particular, in the DF context $V_k(\boldsymbol{x},\boldsymbol{z})$ would be the multiplicative, non-state-dependent Kohn-Sham potential v_{KS},

$$V_k(\boldsymbol{x},\boldsymbol{z}) = \alpha_\mu v_{KS}^\mu(\boldsymbol{x})\delta^{(3)}(\boldsymbol{x}-\boldsymbol{z}). \quad (3.7)$$

Alternatively, $V_k(\boldsymbol{x},\boldsymbol{z})$ could be a self-consistent relativistic HF potential. Restricting the self-consistent calculation to the instantaneous Coulomb interaction and utilizing the no-pair approximation its exchange component is nonlocal, but not state dependent,

$$V_x^{HF,C}(\boldsymbol{x},\boldsymbol{z}) = -e^2 \sum_{-mc^2<\epsilon_l\leq\epsilon_F} \frac{\phi_l(\boldsymbol{x})\phi_l^\dagger(\boldsymbol{z})}{|\boldsymbol{x}-\boldsymbol{z}|}. \quad (3.8)$$

On the other hand, the HF exchange potential becomes state dependent if the complete transverse interaction is taken into account self-consistently. For instance, in the Feynman gauge for the photon propagator one has

$$V_{x,k}^{HF,C+T}(\boldsymbol{x},\boldsymbol{z}) = -e^2 \sum_{-mc^2<\epsilon_l\leq\epsilon_F} \frac{\cos(\omega_{kl}|\boldsymbol{x}-\boldsymbol{z}|)}{|\boldsymbol{x}-\boldsymbol{z}|}$$
$$\times \gamma^0\gamma_\mu\phi_l(\boldsymbol{x})\overline{\phi}_l(\boldsymbol{z})\gamma^\mu, \quad (3.9)$$

with the single-particle transition frequencies

$$\omega_{kl} = |\epsilon_k-\epsilon_l|/c. \quad (3.10)$$

However, for $D_{\mu\nu}^0$ a number of gauges are in use: While the Feynman and Landau gauge forms of $D_{\mu\nu}^0$ correspond to the $\lambda=1$ and $\lambda=\infty$ limits of

$$D_{\mu\nu}^{0,F \text{ or } L}(x-y) = \int \frac{d^4q}{(2\pi)^4} \, e^{-iq(x-y)} D_{\mu\nu}^{0,F \text{ or } L}(q),$$
$$(3.11)$$

$$D_{\mu\nu}^{0,F \text{ or } L}(q) = D(q^2)\left(g_{\mu\nu} - \frac{\lambda-1}{\lambda}\frac{q_\mu q_\nu}{q^2}\right), \quad (3.12)$$

$$D(q^2) = \frac{-4\pi e^2}{q^2+i\eta}, \quad (3.13)$$

in Coulomb gauge (usually applied in quantum chemistry) $D_{\mu\nu}^0$ reads

$$D_{\mu\nu}^{0,C}(q) = \begin{pmatrix} D(-\boldsymbol{q}^2) & 0 \\ 0 & D(q^2)\left(g_{ij}+\dfrac{q_iq_j}{\boldsymbol{q}^2}\right) \end{pmatrix}. \quad (3.14)$$

Furthermore, in most applications only the (weakly relativistic) Breit limit,

$$D_{\mu\nu}^{0,C,B}(q)=D(-\boldsymbol{q}^2)\begin{pmatrix}1 & 0 \\ 0 & g_{ij}+\dfrac{q_iq_j}{\boldsymbol{q}^2}\end{pmatrix},$$

of the Coulomb gauge propagator (3.14) is used.

The exchange energy (3.2) remains independent of the gauge chosen for $D_{\mu\nu}^0$ as long as $\chi_0^{\mu\nu}$ satisfies the transversality relation

$$\partial_\mu\chi_0^{\mu\nu}(\boldsymbol{x},\boldsymbol{y},x^0-y^0)=0. \tag{3.15}$$

Moreover, $D_{\mu\nu}^0\chi_0^{\nu\lambda}$ is not only the basic ingredient of E_x, but also appears in $E_c^{(2)}$, Eq. (2.47), and all higher-order correlation contributions to Eq. (2.45). For instance, a RPA-like resummed expression for E_c could be based on the ''RPA'' response function

$$\chi_{\mathrm{RPA}}^{\mu\nu}(x,y)=\chi_0^{\mu\nu}(x,y)+\frac{1}{c}\int d^4z\,d^4u\,\chi_0^{\mu\rho}(x,z)$$
$$\times D_{\rho\kappa}^0(z-u)\chi_{\mathrm{RPA}}^{\kappa\nu}(u,y). \tag{3.16}$$

In addition, $\chi_0^{\mu\nu}$ represents the kernel of the ROPM integral equation for the xc potential v_{xc}^μ (see Sec. IV). In order to determine the gauge properties of both E_{xc} and v_{xc}^μ it is thus necessary to investigate the transversality of $\chi_0^{\mu\nu}$ in some detail.

B. Transversality of the current-current response function

Starting from Eq. (3.4) and using the single-particle equations (3.5) as well as their Hermitian conjugate one directly obtains

$$\partial_\mu\chi_0^{\mu\nu}(\boldsymbol{x},\boldsymbol{y},x^0-y^0)=\left\{\Theta(x^0-y^0)\sum_{\epsilon_F<\epsilon_k}\sum_{\epsilon_l\leqslant\epsilon_F}+\Theta(y^0-x^0)\sum_{\epsilon_k\leqslant\epsilon_F}\sum_{\epsilon_F<\epsilon_l}\right\}\frac{1}{c}\,\overline{\phi}_k(\boldsymbol{y})\gamma^\nu\phi_l(\boldsymbol{y})$$

$$\times\exp[-i(\epsilon_k-\epsilon_l)(x^0-y^0)/c]\int d^3z[\phi_l^\dagger(\boldsymbol{z})V_l(\boldsymbol{z},\boldsymbol{x})\phi_k(\boldsymbol{x})-\phi_l^\dagger(\boldsymbol{x})V_k(\boldsymbol{x},\boldsymbol{z})\phi_k(\boldsymbol{z})]$$

$$-i\delta(x^0-y^0)\left\{\sum_{\epsilon_F<\epsilon_k}\sum_{\epsilon_l\leqslant\epsilon_F}-\sum_{\epsilon_k\leqslant\epsilon_F}\sum_{\epsilon_F<\epsilon_l}\right\}\phi_l^\dagger(\boldsymbol{x})\phi_k(\boldsymbol{x})\overline{\phi}_k(\boldsymbol{y})\gamma^\nu\phi_l(\boldsymbol{y}). \tag{3.17}$$

Equation (3.17) clearly demonstrates that $\chi_0^{\mu\nu}$ in general violates the transversality relation (3.15) as long as $V_k(\boldsymbol{x},\boldsymbol{z})$ is nonlocal or state dependent. In particular, this is the case for the RHF potentials (3.8) and (3.9), as can be explicitly shown by insertion of Eq. (3.8) or Eq. (3.9) into Eq. (3.17). Thus, if one used the RHF orbitals resulting from the exchange potentials (3.8),(3.9) to calculate either the complete E_x (which would amount to a perturbative evaluation of the contributions beyond the no-pair approximation) or $E_c^{(2)}$ the results would be gauge dependent [28,46,47].

On the other hand, as soon as the single-particle potential is not state dependent one can use the completeness of the single-particle spectrum,

$$\sum_k\phi_k(\boldsymbol{x})\phi_k^\dagger(\boldsymbol{y})=\delta^{(3)}(\boldsymbol{x}-\boldsymbol{y}) \tag{3.18}$$

[after rewriting the sums in Eq. (3.17) via $\Sigma_{\epsilon_F<\epsilon_k}=\Sigma_k-\Sigma_{\epsilon_k\leqslant\epsilon_F}$] to show that the second term on the right-hand side of Eq. (3.17) vanishes. Finally, for local, non-state-dependent single-particle potentials the first term on the right-hand side of Eq. (3.17) automatically vanishes, so that the resulting $\chi_0^{\mu\nu}$ in fact satisfies the transversality requirement (3.15). Note that this result not only holds for given (external) local potentials, but also for local, non-state-dependent potentials, which are generated by some self-consistent procedure.

This last statement, however, is only correct if in $\chi_0^{\mu\nu}$ the complete single-particle spectrum is used, i.e., if the negative energy continuum states are included. As soon as the no-pair approximation is applied, which amounts to projecting out these states completely,

$$\chi_{0,\mathrm{np}}^{\mu\nu}(\boldsymbol{x},\boldsymbol{y},x^0-y^0)=-i\left\{\Theta(x^0-y^0)\sum_{-mc^2<\epsilon_l\leqslant\epsilon_F<\epsilon_k}+\Theta(y^0-x^0)\sum_{-mc^2<\epsilon_k\leqslant\epsilon_F<\epsilon_l}\right\}\overline{\phi}_l(\boldsymbol{x})\gamma^\mu\phi_k(\boldsymbol{x})\overline{\phi}_k(\boldsymbol{y})\gamma^\nu\phi_l(\boldsymbol{y})$$

$$\times\exp[-i(\epsilon_k-\epsilon_l)(x^0-y^0)/c], \tag{3.19}$$

the completeness relation (3.18) no longer allows the elimination of the second term on the right-hand side of Eq. (3.17). In the case of a local, non-state-dependent single-particle potential one then obtains

$$\partial_\mu\chi_{0,\mathrm{np}}^{\mu\nu}(\boldsymbol{x},\boldsymbol{y},x^0-y^0)=-i\delta(x^0-y^0)\left\{\sum_{\epsilon_l\leqslant-mc^2<\epsilon_k\leqslant\epsilon_F}-\sum_{\epsilon_k\leqslant-mc^2<\epsilon_l\leqslant\epsilon_F}\right\}\phi_l^\dagger(\boldsymbol{x})\phi_k(\boldsymbol{x})\overline{\phi}_k(\boldsymbol{y})\gamma^\nu\phi_l(\boldsymbol{y}), \tag{3.20}$$

so that $\chi_{0,np}^{\mu\nu}$ violates the transversality condition even for the relativistic KS potential (3.7) [66]. One thus concludes that a gauge dependence of the crucial product $D_{\mu\nu}^0\chi_0^{\nu\rho}$ can originate from two sources: (i) the state dependence and nonlocality of the single-particle potential, on which $\chi_0^{\mu\nu}$ is based, and (ii) from the no-pair approximation.

For the subsequent discussion it is useful to examine the components of $\chi_0^{\mu\nu}$ individually. Decomposing the single-particle propagator as

$$G^0(x,y)=G_V^0(x,y)+G_D^0(x,y), \qquad (3.21)$$

$$G_V^0(x,y)=-i\left\{\Theta(x^0-y^0)\sum_{-mc^2<\epsilon_k}-\Theta(y^0-x^0)\sum_{\epsilon_k\leqslant-mc^2}\right\}$$
$$\times\phi_k(\boldsymbol{x})\overline{\phi}_k(\boldsymbol{y})e^{-i\epsilon_k(x^0-y^0)/c}, \qquad (3.22)$$

$$G_D^0(x,y)=i\sum_{-mc^2<\epsilon_k\leqslant\epsilon_F}\phi_k(\boldsymbol{x})\overline{\phi}_k(\boldsymbol{y})e^{-i\epsilon_k(x^0-y^0)/c}, \qquad (3.23)$$

one can write $\chi_0^{\mu\nu}$ as

$$\chi_0^{\mu\nu}=\chi_{VV}^{\mu\nu}+\chi_{DV}^{\mu\nu}+\chi_{VD}^{\mu\nu}+\chi_{DD}^{\mu\nu}, \qquad (3.24)$$

with

$$\chi_{DD}^{\mu\nu}(x,y)=-i\ \mathrm{tr}[\gamma^\mu G_D^0(x,y)\gamma^\nu G_D^0(y,x)] \qquad (3.25)$$

and analogous definitions for $\chi_{VV}^{\mu\nu}$ and $\chi_{DV}^{\mu\nu}$ [$\chi_{DV}^{\mu\nu}(x,y)=\chi_{VD}^{\nu\mu}(y,x)$]. $\chi_{VV}^{\mu\nu}$ agrees with the full $\chi_0^{\mu\nu}$ in the limit $\epsilon_F=-mc^2$. The preceding statements on the transversality of $\chi_0^{\mu\nu}$ thus also apply to $\chi_{VV}^{\mu\nu}$. On the other hand, for $\chi_{DD}^{\mu\nu}$ one finds

$$c\partial_\mu\chi_{DD}^{\mu\nu}(\boldsymbol{x},\boldsymbol{y},x^0-y^0)$$
$$=-\sum_{-mc^2<\epsilon_k,\epsilon_l\leqslant\epsilon_F}\overline{\phi}_k(\boldsymbol{y})\gamma^\nu\phi_l(\boldsymbol{y})e^{-i(\epsilon_k-\epsilon_l)(x^0-y^0)/c}$$
$$\times\int d^3z[\phi_l^\dagger(\boldsymbol{z})V_l(\boldsymbol{z},\boldsymbol{x})\phi_k(\boldsymbol{x})-\phi_l^\dagger(\boldsymbol{x})V_k(\boldsymbol{x},\boldsymbol{z})\phi_k(\boldsymbol{z})]. \qquad (3.26)$$

Consequently the transversality of $\chi_{DD}^{\mu\nu}$ does not depend on the completeness of the states involved, but only relies on the structure of $V_k(\boldsymbol{x},\boldsymbol{z})$. Any non-state-dependent, local potential thus leads to a gauge invariant $\chi_{DD}^{\mu\nu}$.

C. Gauge dependence of the no-pair exchange energy

While the transversality of the complete $\chi_0^{\mu\nu}$ determines the gauge properties of the full exchange energy (3.2), in practice the no-pair approximation to E_x is of particular interest. In order to define the no-pair approximation, one decomposes the complete E_x according to Eq. (3.24). Introducing the vacuum self-energy,

$$\Sigma_V(x,y)=iD_{\mu\nu}^0(x-y)\gamma^\mu G_V^0(x,y)\gamma^\nu, \qquad (3.27)$$

one can write E_x as

$$E_x=\frac{i}{2}\int d^3x\,d^4y\{D_{\mu\nu}^0(x-y)[\chi_{DD}^{\mu\nu}(x,y)+\chi_{VV}^{\mu\nu}(x,y)]$$
$$-2\,\mathrm{tr}[\Sigma_V(x,y)G_D^0(y,x)]\}. \qquad (3.28)$$

The no-pair approximation for E_x is obtained by neglecting all radiative corrections (which automatically eliminates the need for renormalization),

$$E_{x,np}=\frac{i}{2}\int d^3x\int d^4y\ D_{\mu\nu}^0(x-y)\chi_{DD}^{\mu\nu}(x,y). \qquad (3.29)$$

The gauge dependence of $E_{x,np}$ is thus determined by Eq. (3.26), so that any local, non-state-dependent single-particle potential will lead to a gauge invariant $E_{x,np}$ [28,46,47]. Consequently, in contrast to the case of the HF approximation the no-pair DF exchange based on the KS orbitals does not introduce a gauge dependence of $E_{x,np}$ [67]. The gauge dependence of the no-pair correlation energy is studied within the relativistic LDA [58] in a subsequent paper [51].

IV. RELATIVISTIC OPTIMIZED-POTENTIAL METHOD

The ROPM can either be formulated within the field theoretical framework or on the basis of the no-pair approximation. The starting point for the derivation of the former version is the ground-state energy (2.12), using the DF representations (2.13),(2.14),(2.45) for the individual components. The resulting ROPM equations, however, differ from their no-pair limit only by the inclusion of the negative continuum states in the quantities involved. We will thus simultaneously discuss the full ROPM and its no-pair approximation, giving all explicit formulas for the more practical no-pair form and just noting the modifications necessary for the general variant (for brevity, the index np is dropped from now on).

A. No-pair limit of RDFT

The no-pair limit of RDFT is obtained by consistently eliminating all vacuum effects, i.e., by suppressing the creation of virtual electron-positron pairs. In the case of the KS four current (2.11) and the KS kinetic energy (2.13) this leads to

$$j^\mu(\boldsymbol{r})=\sum_{-mc^2<\epsilon_k\leqslant\epsilon_F}\phi_k^\dagger(\boldsymbol{r})\alpha^\mu\phi_k(\boldsymbol{r}), \qquad (4.1)$$

$$T_s=\int d^3r\sum_{-mc^2<\epsilon_k\leqslant\epsilon_F}\overline{\phi}_k[-ic\boldsymbol{\gamma}\cdot\boldsymbol{\nabla}+mc^2]\phi_k. \qquad (4.2)$$

Performing the time integration in both the no-pair Hartree energy, obtained by insertion of Eq. (4.1) into Eq. (2.14), and in the no-pair exchange energy (3.29), using Eqs. (3.23), (3.25), one finds

$$E_H=\frac{e^2}{2}\int d^3r\int d^3r'\frac{j_\mu(\boldsymbol{r})j^\mu(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}, \qquad (4.3)$$

$$E_x = -\frac{e^2}{2} \int d^3r \int d^3r'$$

$$\times \sum_{-mc^2 < \epsilon_k, \epsilon_l \leq \epsilon_F} \frac{\cos(\omega_{kl}|\boldsymbol{r}-\boldsymbol{r}'|)}{|\boldsymbol{r}-\boldsymbol{r}'|}$$

$$\times \phi_k^\dagger(\boldsymbol{r}) \alpha_\mu \phi_l(\boldsymbol{r}) \phi_l^\dagger(\boldsymbol{r}') \alpha^\mu \phi_k(\boldsymbol{r}'), \qquad (4.4)$$

where $\omega_{kl} = |\epsilon_k - \epsilon_l|/c$ is now defined in terms of the KS eigenvalues. In Eq. (4.4) we have chosen to work in Feynman gauge, which is technically simplest to handle. This choice does not introduce any gauge dependence, as demonstrated in Sec. III. In order to facilitate comparison with standard many-body methods and for later reference, we also note the decompositions of the total Hartree and exchange energies, (4.3),(4.4), into their longitudinal (Coulomb, C) and transverse (retarded Breit, T) components,

$$E_H^C = \frac{e^2}{2} \int d^3r \int d^3r' \frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}, \qquad (4.5)$$

$$E_H^T = -\frac{e^2}{2} \int d^3r \int d^3r' \frac{\boldsymbol{j}(\boldsymbol{r}) \cdot \boldsymbol{j}(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}, \qquad (4.6)$$

$$E_x^C = -\frac{e^2}{2} \int d^3r \int d^3r' \sum_{-mc^2 < \epsilon_k, \epsilon_l \leq \epsilon_F}$$

$$\times \frac{\phi_k^\dagger(\boldsymbol{r}) \phi_l(\boldsymbol{r}) \phi_l^\dagger(\boldsymbol{r}') \phi_k(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}, \qquad (4.7)$$

$$E_x^T = E_x - E_x^C, \qquad (4.8)$$

where the density j^0 has been denoted by the more familiar n [note that due to Eq. (4.1) $\boldsymbol{j}$ differs from the standard current by a factor of $1/c$]. The Breit limit E_x^B of E_x^T is obtained from Eq. (4.8) by keeping only the leading contribution in $1/c$. As a correlation functional to be used with Eqs. (4.1)–(4.4) the no-pair limit of Eq. (2.47) suggests itself: While the no-pair approximation can be introduced for the complete E_{xc}, Eq. (2.45), without further approximations, for practical purposes either a low-order expansion or a partial resummation of E_{xc} is imperative. In addition, one would expect the transverse interaction to play only a minor role in E_c, so that we restrict ourselves to giving the longitudinal limit of $E_c^{(2)}$ at this point,

$$E_c^{(2),C} = \frac{e^4}{2} \sum_{-mc^2 < \epsilon_i, \epsilon_j \leq \epsilon_F < \epsilon_k, \epsilon_l} \frac{1}{\epsilon_i + \epsilon_j - \epsilon_k - \epsilon_l} \int d^3r_1 \int d^3r_2 \frac{\phi_i^\dagger(\boldsymbol{r}_1)\phi_k(\boldsymbol{r}_1)\phi_j^\dagger(\boldsymbol{r}_2)\phi_l(\boldsymbol{r}_2)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|} \int d^3r_3 \int d^3r_4$$

$$\times \left\{ \frac{\phi_k^\dagger(\boldsymbol{r}_3)\phi_i(\boldsymbol{r}_3)\phi_l^\dagger(\boldsymbol{r}_4)\phi_j(\boldsymbol{r}_4)}{|\boldsymbol{r}_3-\boldsymbol{r}_4|} - \frac{\phi_k^\dagger(\boldsymbol{r}_3)\phi_j(\boldsymbol{r}_3)\phi_l^\dagger(\boldsymbol{r}_4)\phi_i(\boldsymbol{r}_4)}{|\boldsymbol{r}_3-\boldsymbol{r}_4|} \right\} + \sum_{-mc^2 < \epsilon_k \leq \epsilon_F < \epsilon_l} \frac{1}{\epsilon_k - \epsilon_l}$$

$$\times \left| \int d^3r_1 \phi_k^\dagger(\boldsymbol{r}_1) \alpha^\mu \phi_l(\boldsymbol{r}_1) v_{x,\mu}^C(\boldsymbol{r}_1) + e^2 \sum_{-mc^2 < \epsilon_j \leq \epsilon_F} \int d^3r_1 \int d^3r_2 \frac{\phi_k^\dagger(\boldsymbol{r}_1)\phi_j(\boldsymbol{r}_1)\phi_j^\dagger(\boldsymbol{r}_2)\phi_l(\boldsymbol{r}_2)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|} \right|^2. \qquad (4.9)$$

The approximation (4.9) consists of two contributions: The first term is formally identical to the second-order Møller-Plesset energy, derived as a perturbative correction to the total HF energy. The second term reflects the conceptual difference between the exchange-only ROPM and the RHF approach. However, the differences between exchange-only ROPM and RHF ground-state energies are comparatively small, at least for atoms (see [9] and Table I). In fact, for heliumlike systems both energies coincide. One would thus expect the second term in Eq. (4.9) to contribute much less than the Møller-Plesset-type correction. Although no corresponding estimate of the quantitative impact of the second term on the self-consistent $v_c^{(2)}$ is available (cf. Sec. IV C), this suggests that neglect of the second term is a reasonable approximation to (4.9). This would eliminate the v_x dependence of $E_c^{(2),C}$.

In view of the origin of the approximation (4.9) one would expect that $E_c^{(2),C}$ includes long-range dispersive forces. In order to verify this important property of $E_c^{(2),C}$ we consider two neutral atoms A and B, whose centers are sepa-

rated by a distance R large enough so that the corresponding electronic densities have no substantial overlap (i.e., the overlap vanishes exponentially with R). The KS single-particle orbitals are then localized around the two atomic centers (if required, degenerate molecular orbitals can be combined to generate localized atomic orbitals). Each sum in Eq. (4.9) can thus be split into two sums over orbitals belonging to the centers A and B,

$$\sum_{\epsilon_i} \rightarrow \sum_{\epsilon_{i_A}} + \sum_{\epsilon_{i_B}}.$$

As a consequence, in the Møller-Plesset-type term the sums over i and k and those over j and l are restricted to the same atom by the $\boldsymbol{r}_1, \boldsymbol{r}_2$ integrations, due to the vanishing overlap of orbitals that correspond to different centers. Moreover, in the exchange contribution to the Møller-Plesset-type term the $\boldsymbol{r}_3, \boldsymbol{r}_4$ integrations in addition require that i and l as well as j and k belong to the same atom, so that all four sums correspond to the same atom. Similarly, in the second term of Eq.

TABLE I. Self-consistent exchange-only ground-state energies from ROPM and RHF calculations for neutral atoms with closed subshells: Coulomb (C) and Coulomb-Breit (C+B) limit in comparison with complete transverse exchange (C+T). For the RHF approximation the energy difference with respect to the ROPM is given, $\Delta E = E_{\text{tot}}(\text{RHF}) - E_{\text{tot}}(\text{ROPM})$, providing results both from fully numerical calculations (a) [74] and from a basis set expansion (b) [26]. Note that in contrast to all other calculations reported in this paper here a speed of light of 137.037 a.u. has been used and the nuclear radii have been set according to $R_{\text{nuc}} = 2.2677 \times 10^{-5} A^{1/3}$ bohr in order to allow a comparison with [26] (all energies in mhartree).

Atom	$-E_{\text{tot}}^{\text{C}}$ ROPM	ΔE^{C} RHF[a]	ΔE^{C} RHF[b]	$-E_{\text{tot}}^{\text{C+B}}$ ROPM	$\Delta E^{\text{C+B}}$ RHF[b]	$-E_{\text{tot}}^{\text{C+T}}$ ROPM
He	2862	0	0	2862	0	2862
Be	14575	-1		14575		14575
Ne	128690	-2	-2	128674	-2	128674
Mg	199932	-3		199900		199900
Ar	528678	-5	-5	528546	-5	528546
Ca	679704	-6		679513		679513
Zn	1794599	-14	-12	1793838	-12	1793841
Kr	2788849	-13	-12	2787423	-12	2787431
Sr	3178069	-13		3176350		3176360
Pd	5044388	-16		5041074		5041101
Cd	5593303	-20	-17	5589466	-15	5589500
Xe	7446882	-19	-6	7441115	-3	7441179
Ba	8135632	-19		8129091		8129168
Yb	14067635	-48		14053517		14053764
Hg	19648836	-39	-13	19626225	9	19626715
Rn	23601947	-35	-19	23572625	11	23573332
Ra	25027992	-34		24996118		24996912
No	36740241	-57		36685157		36686790

(4.9) j, k, and l are restricted to the same center. Thus the Møller-Plesset-type exchange term and the complete second term can be decomposed into additive contributions of the two atoms. However, only terms that involve both atoms, i.e., that depend on R, contribute to the interaction energy between the atoms. Taking into account the symmetry of Eq. (4.9), one obtains as a correlation contribution to the interaction energy for large R,

$$
\begin{aligned}
E_{\text{c,int}}^{(2),\text{C}} = & \sum_{-mc^2 < \epsilon_{i_A} \leq \epsilon_F < \epsilon_{k_A}} \\
& \times \sum_{-mc^2 < \epsilon_{j_B} \leq \epsilon_F < \epsilon_{l_B}} \frac{e^4}{\epsilon_{i_A} + \epsilon_{j_B} - \epsilon_{k_A} - \epsilon_{l_B}} \\
& \times \int d^3r_1 \int d^3r_2 \frac{\phi_{i_A}^\dagger(\mathbf{r}_1)\phi_{k_A}(\mathbf{r}_1)\phi_{j_B}^\dagger(\mathbf{r}_2)\phi_{l_B}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \\
& \times \int d^3r_3 \int d^3r_4 \frac{\phi_{k_A}^\dagger(\mathbf{r}_3)\phi_{i_A}(\mathbf{r}_3)\phi_{l_B}^\dagger(\mathbf{r}_4)\phi_{j_B}(\mathbf{r}_4)}{|\mathbf{r}_3 - \mathbf{r}_4|}.
\end{aligned}
\tag{4.10}
$$

Now one can use the time-ordered KS response function (3.4) of the individual atoms to rewrite Eq. (4.10) as

$$
\begin{aligned}
E_{\text{c,int}}^{(2),\text{C}} = & -\frac{e^4}{2} \int d^3r_1 \cdots d^3r_4 \\
& \times \int \frac{d\omega}{2\pi i} \frac{\chi_{0,A}^{00}(\mathbf{r}_1,\mathbf{r}_3,\omega)\chi_{0,B}^{00}(\mathbf{r}_4,\mathbf{r}_2,\omega)}{|\mathbf{r}_1 - \mathbf{r}_2||\mathbf{r}_3 - \mathbf{r}_4|}.
\end{aligned}
\tag{4.11}
$$

For time-reversal invariant systems this expression can be given a more familiar form [68],

$$
\begin{aligned}
E_{\text{c,int}}^{(2),\text{C}} = & -e^4 \int_0^\infty \frac{du}{2\pi} \int d^3r_1 \cdots d^3r_4 \\
& \times \frac{\chi_{0,A}^{R,00}(\mathbf{r}_1,\mathbf{r}_3,iu)\chi_{0,B}^{R,00}(\mathbf{r}_2,\mathbf{r}_4,iu)}{|\mathbf{r}_1 - \mathbf{r}_2||\mathbf{r}_3 - \mathbf{r}_4|},
\end{aligned}
\tag{4.12}
$$

where $\chi_{0,A}^{R,\mu\nu}$ denotes the retarded KS current-current response function. Choosing the center of atom A as origin for the $\mathbf{r}_1$ and $\mathbf{r}_3$ integrations and the center of atom B as origin for the $\mathbf{r}_2$ and $\mathbf{r}_4$ integrations, one can easily expand the Coulomb interaction,

$$\frac{1}{|\boldsymbol{r}_1-\boldsymbol{r}_2|} \rightarrow \frac{1}{|\boldsymbol{R}+\boldsymbol{r}_1-\boldsymbol{r}_2|} = \frac{1}{R}\left\{1 - \frac{(\boldsymbol{r}_1-\boldsymbol{r}_2)\cdot\boldsymbol{R}}{R^2} + \frac{3[(\boldsymbol{r}_1-\boldsymbol{r}_2)\cdot\boldsymbol{R}]^2}{2R^4}\right.$$
$$\left. - \frac{(\boldsymbol{r}_1-\boldsymbol{r}_2)^2}{2R^2} + \cdots \right\}.$$

The two leading terms of this expansion, however, do not contribute to Eq. (4.12) due to charge conservation, so that

$$E_{c,int}^{(2),C} = -\frac{e^4}{R^6}\int_0^\infty \frac{du}{2\pi}\left(g^{ij}+3\frac{R^iR^j}{R^2}\right)$$
$$\times\left(g^{kl}+3\frac{R^kR^l}{R^2}\right)\alpha_{A,ik}(iu)\alpha_{B,jl}(iu), \quad (4.13)$$

where $\alpha_{A,ik}$ is the atomic KS polarizability tensor,

$$\alpha_A^{ik}(\omega) = \int d^3r_1 \int d^3r_2\, r_1^i r_2^k \chi_{0,A}^{R,00}(\boldsymbol{r}_1,\boldsymbol{r}_2,\omega). \quad (4.14)$$

Equation (4.13) explicitly shows that $E_c^{(2),C}$ contains the leading contribution to the van der Waals interaction between the two atoms, the deviation from the full van der Waals interaction resulting from the difference between the KS and the complete response function. One would thus expect $E_c^{(2),C}$ to be particularly useful for a seamless DFT description of van der Waals binding. Of course, if the transverse interaction is included, $E_{c,int}^{(2)}$ approaches the Casimir-Polder form proportional to $1/R^7$ for very large separations.

B. Complete nonlinear ROPM equation

In contrast to approximations like the LDA or GGA, Eqs. (2.45), (4.4), (4.9) provide E_{xc} as a functional of the KS orbitals and eigenvalues, rather than as a functional of j^μ. However, as long as the ϕ_k and ϵ_k satisfy single-particle equations with a multiplicative potential they are unique

functionals of j^μ by virtue of the Hohenberg-Kohn theorem for noninteracting particles, the functional dependences $\phi_k([j];\boldsymbol{r})$ and $\epsilon_k[j]$ being established implicitly via solution of the single-particle equations. This fact allows the derivation of the standard KS equations (2.15) as in the case of an explicitly current dependent E_{xc}.

Given an orbital- and eigenvalue-dependent xc-energy functional in the nonlinear form $E_{xc}[\phi_k^{(\dagger)},\epsilon_k,v_{xc}^\mu]$ the next task is to explicitly construct the xc potential (2.18). This is achieved by the optimized-potential method (OPM), which has first been introduced in the context of nonrelativistic DFT [12,15,50,69] and recently been extended to the relativistic domain [9,70]. Although this procedure originally had been suggested for the exchange-only limit of DFT it can be applied to any functional of the KS orbitals and eigenvalues. Two equivalent derivations of the OPM formalism are available [4,12], both relying on the unique correspondence between the ground-state density (here, four current) and the associated KS potential. We follow here the more direct approach, in which the functional derivative of E_{xc} with respect to j^μ is replaced by derivatives with respect to those quantities on which E_{xc} explicitly depends, using the chain rule for functional differentiation.

Again two variants are possible: One can either base the discussion on the recursive solution of Eq. (2.45) via Eq. (2.46), i.e., expand in powers of e^2 before introducing the OPM. The OPM equation for the lowest order, in which E_{xc} only depends on the $\phi_k^{(\dagger)}$ and ϵ_k, then allows the elimination of the lowest-order potential, i.e., the exchange potential v_x^μ, from all higher orders in E_{xc} in favor of the $\phi_k^{(\dagger)}$ and ϵ_k. As a consequence, the second-order contribution to E_{xc} is a functional of the $\phi_k^{(\dagger)}$ and ϵ_k only, allowing one to repeat the procedure. Alternatively, the expansion in powers of e^2 can be introduced after the derivation of the ROPM equation. In this case E_{xc} is a functional of the $\phi_k^{(\dagger)}$ and ϵ_k as well as of v_{xc}^μ, so that

$$\frac{\delta E_{xc}[\phi_k^{(\dagger)},\epsilon_k,v_{xc}^\mu]}{\delta j^\nu(\boldsymbol{r})} = \int d^3r' \frac{\delta v_{KS}^\rho(\boldsymbol{r}')}{\delta j^\nu(\boldsymbol{r})}\sum_k\left\{\int d^3r''\left[\frac{\delta\phi_k^\dagger(\boldsymbol{r}'')}{\delta v_{KS}^\rho(\boldsymbol{r}')}\frac{\delta E_{xc}}{\delta\phi_k^\dagger(\boldsymbol{r}'')}\bigg|_{expl.} + c.c.\right] + \frac{\delta\epsilon_k}{\delta v_{KS}^\rho(\boldsymbol{r}')}\frac{\partial E_{xc}}{\partial\epsilon_k}\bigg|_{expl.}\right\}$$
$$+ \int d^3r' \frac{\delta v_{xc}^\rho(\boldsymbol{r}')}{\delta j^\nu(\boldsymbol{r})}\frac{\delta E_{xc}}{\delta v_{xc}^\rho(\boldsymbol{r}')}\bigg|_{expl.}, \quad (4.15)$$

where the unique correspondence between j^μ and v_{KS}^μ has been used to insert the functional differentiation with respect to v_{KS}^μ (in the following the derivatives of E_{xc} are always understood with respect to the explicit dependence on $\phi_k^{(\dagger)}$, ϵ_k, and v_{xc}^μ, so that we drop the index expl. from now on). The k summation on the right-hand side of Eq. (4.15) runs over all KS levels, including the negative continuum. As soon as the no-pair approximation is used for E_{xc}, however, it effectively reduces to the states with $\epsilon_k > -mc^2$. The various ingredients of Eq. (4.15) require the evaluation of the

linear response of the $\phi_k^{(\dagger)}$ and ϵ_k to a variation of v_{KS}^ρ, which can be directly obtained from first-order perturbation theory,

$$\frac{\delta\phi_k^\dagger(\boldsymbol{r})}{\delta v_{KS}^\rho(\boldsymbol{r}')} = -\phi_k^\dagger(\boldsymbol{r}')\alpha_\rho G_k(\boldsymbol{r}',\boldsymbol{r}), \quad (4.16)$$

$$G_k(\boldsymbol{r},\boldsymbol{r}') = \sum_{l\neq k}\frac{\phi_l(\boldsymbol{r})\phi_l^\dagger(\boldsymbol{r}')}{\epsilon_l-\epsilon_k}, \quad (4.17)$$

$$\frac{\delta\epsilon_k}{\delta v_{\mathrm{KS}}^{\rho}(\boldsymbol{r})} = \phi_k^{\dagger}(\boldsymbol{r})\alpha_{\rho}\phi_k(\boldsymbol{r}). \qquad (4.18)$$

Equation (4.15) can be recast, using the static KS response function, as

$$\chi_0^{\mu\nu}(\boldsymbol{r},\boldsymbol{r}') = \frac{\delta j^{\mu}(\boldsymbol{r})}{\delta v_{\mathrm{KS},\nu}(\boldsymbol{r}')} = \int_{-\infty}^{\infty} d\tau \ \chi_0^{\mu\nu}(\boldsymbol{r},\boldsymbol{r}',\tau)$$

$$= - \sum_{-mc^2 < \epsilon_k \leqslant \epsilon_F} \phi_k^{\dagger}(\boldsymbol{r})\alpha^{\mu}G_k(\boldsymbol{r},\boldsymbol{r}')\alpha^{\nu}\phi_k(\boldsymbol{r}') + \mathrm{c.c.},$$

$$(4.19)$$

where the no-pair form (4.1) has been used for j^{μ}. Multiplying Eq. (4.15) by $\chi_0^{\mu\nu}$ and integrating over $\boldsymbol{r}$ leads to the ROPM integral equations for the xc potential,

$$\int d^3r' \chi_0^{\mu\nu}(\boldsymbol{r},\boldsymbol{r}')v_{\mathrm{xc},\nu}(\boldsymbol{r}') = \Lambda_{\mathrm{xc}}^{\mu}(\boldsymbol{r}), \qquad (4.20)$$

with the inhomogeneity

$$\Lambda_{\mathrm{xc}}^{\mu}(\boldsymbol{r}) = -\sum_k \int d^3r' \left[\phi_k^{\dagger}(\boldsymbol{r})\alpha^{\mu}G_k(\boldsymbol{r},\boldsymbol{r}')\frac{\delta E_{\mathrm{xc}}}{\delta\phi_k^{\dagger}(\boldsymbol{r}')} + \mathrm{c.c.} \right]$$

$$+ \sum_k \phi_k^{\dagger}(\boldsymbol{r})\alpha^{\mu}\phi_k(\boldsymbol{r})\frac{\partial E_{\mathrm{xc}}}{\partial\epsilon_k}$$

$$+ \int d^3r' \int d^3r'' \chi_0^{\mu\nu}(\boldsymbol{r},\boldsymbol{r}')\frac{\delta v_{\mathrm{xc}}^{\rho}(\boldsymbol{r}'')}{\delta j^{\nu}(\boldsymbol{r}')}\frac{\delta E_{\mathrm{xc}}}{\delta v_{\mathrm{xc}}^{\rho}(\boldsymbol{r}'')}.$$

$$(4.21)$$

Note that the ROPM concept can be directly extended to the field theoretical level by using the full current (2.11), rather than its no-pair limit: In this case Eq. (4.19) has to be replaced by the corresponding full static KS response function [obtained by Fourier transformation of (3.4)].

Equations (4.19)–(4.21) differ from previous forms of the ROPM given in [9,11] by the appearance of the functional derivatives of E_{xc} with respect to both the ϵ_k as well as v_{xc}^{μ}. Of course, for the orbital-dependent E_{xc} considered previously, i.e., the longitudinal exchange (4.7) and the Colle-Salvetti correlation functional [19], Eqs. (4.19)–(4.21) reduce to the published forms. On the other hand, the full exchange (4.4) depends on the ϵ_k due to photon retardation. Moreover, as soon as some first-principles, orbital-dependent E_{c} based on the approach of Sec. II is to be applied, also the static xc kernel

$$\frac{\delta v_{\mathrm{xc}}^{\mu}(\boldsymbol{r})}{\delta j_{\nu}(\boldsymbol{r}')} = f_{\mathrm{xc}}^{\mu\nu}(\boldsymbol{r},\boldsymbol{r}')$$

has to be evaluated in accordance with the actual approximation used for E_{xc}. Two strategies are conceivable: One could either hope that this ingredient of $\Lambda_{\mathrm{xc}}^{\mu}$ is only of minor importance for the solution of the ROPM integral equation, thus allowing the use of some approximation for $f_{\mathrm{xc}}^{\mu\nu}$, as, e.g., the LDA. This would immediately open the possibility

to deal with larger classes of diagrammatic contributions to Eq. (2.45), as, e.g., the ring diagrams, thus establishing an RPA-type approximation. On the other hand, a rigorous treatment of $f_{\mathrm{xc}}^{\mu\nu}$ requires some well-defined recursive definition of E_{xc} that allows the iteration of the left-hand and right-hand sides of Eq. (4.20), as discussed in Sec. IV C for the expansion in powers of e^2.

The ROPM integral equation (4.20) has to be solved self-consistently together with the KS equations (2.15). In this procedure one also has to fix the gauge of v_{xc}^{μ}. First of all, analogous to the situation without magnetic fields, v_{xc}^0 is only defined up to a global constant, as

$$\int d^3r' \chi_0^{\mu 0}(\boldsymbol{r},\boldsymbol{r}') = \int d^3r \ \chi_0^{0\mu}(\boldsymbol{r},\boldsymbol{r}') = 0 \qquad (4.22)$$

(charge conservation). This constant, however, is not a real problem. For instance, for finite systems it is usually defined by requiring that

$$v_{\mathrm{xc}}^0(\boldsymbol{r}) \xrightarrow[|\boldsymbol{r}|\to\infty]{} 0. \qquad (4.23)$$

As far as the spatial components of v_{xc}^{μ} are concerned, the situation is somewhat more complicated. In particular, in the no-pair approximation not only the "external" k summation in Eq. (4.19) is restricted to $\epsilon_k > -mc^2$, but also the l summation inside G_k does not include the negative continuum states. Consequently Eq. (3.26) applies, i.e., in the static limit one has

$$\partial_i \chi_0^{i\nu}(\boldsymbol{r},\boldsymbol{r}') \neq 0. \qquad (4.24)$$

Thus three-vector potentials $\boldsymbol{v}_{\mathrm{xc}}$, which differ by static gauge transformations, lead to different results for the left-hand side of Eq. (4.20). As a consequence, in the no-pair approximation there is only one unique solution of Eq. (4.20) for the spatial components of v_{xc}^{μ}, i.e., the no-pair ROPM procedure automatically fixes the gauge of $\boldsymbol{v}_{\mathrm{xc}}$. On the other hand, the field theoretical version of the ROPM is based on the full response function (3.4), which satisfies Eq. (3.15). In this case Eq. (4.20) determines $\boldsymbol{v}_{\mathrm{xc}}$ only up to an arbitrary static gauge transformation, so that the gauge of $\boldsymbol{v}_{\mathrm{xc}}$ has to be fixed by some additional requirement.

It should be emphasized, however, that in both situations the gauge used for the photon propagator (not to be confused with the gauge of v_{xc}^{μ}) only enters Eq. (4.20) via the E_{xc} dependence of $\Lambda_{\mathrm{xc}}^{\mu}$. Thus v_{xc}^{μ} is independent of the gauge of $D_{\mu\nu}^0$ as long as E_{xc} is gauge invariant.

A rigorous condition for $E_{\mathrm{xc}}[\phi_k^{(\dagger)},\epsilon_k,v_{\mathrm{xc}}^{\mu}]$ is obtained by integrating the zeroth component of Eq. (4.20) over $\boldsymbol{r}$. Using the projection property of the Greens function,

$$\int d^3r \phi_k^{\dagger}(\boldsymbol{r})G_k(\boldsymbol{r},\boldsymbol{r}') = 0, \qquad (4.25)$$

one finds

$$\sum_k \frac{\partial E_{\mathrm{xc}}}{\partial\epsilon_k} = 0. \qquad (4.26)$$

Equation (4.26) can be directly verified for the exchange-only energy (4.4) and for the second-order expression (4.9).

For approximate correlation functionals, on the other hand, it provides an important consistency criterion.

Equations (4.19)–(4.21) can also be used to extract the behavior of the xc potential in the asymptotic regime of finite systems. Unfortunately, the spinor structure of the quantities involved substantially complicates the discussion even in the exchange-only limit. Nevertheless, restricting the analysis to spherically averaged systems, a somewhat tedious analysis (of which the essential points are given in Appendix B) leads to a relativistic variant of the KLI identity for the highest occupied orbital ϕ_h [14],

$$\int d^3 r \phi_h^\dagger(\boldsymbol{r}) \left\{ \phi_h(\boldsymbol{r}) v_{\rm x}^0(\boldsymbol{r}) - \frac{\delta E_{\rm x}}{\delta \phi_h^\dagger(\boldsymbol{r})} \right\} + {\rm c.c.} = 0, \tag{4.27}$$

and the expected behavior of $v_{\rm x}^0$,

$$v_{\rm x}^0(r) \underset{r \to \infty}{\sim} -\frac{e^2}{r}. \tag{4.28}$$

C. Second-order ROPM equations

In order to provide a practical computational scheme, the general ROPM equation (4.20) is now specialized to the second-order xc energy functional

$$E_{\rm xc} \to E_{\rm x} + E_{\rm c}^{(2)}. \tag{4.29}$$

Expanding the corresponding xc potential in powers of e^2 allows the separation of the orders e^2 and e^4 also in the ROPM equation,

$$\int d^3 r_2 \chi_0^{\mu\nu}(\boldsymbol{r}_1, \boldsymbol{r}_2) v_{{\rm x},\nu}(\boldsymbol{r}_2) = \Lambda_{\rm x}^\mu(\boldsymbol{r}_1), \tag{4.30}$$

$$\int d^3 r_2 \chi_0^{\mu\nu}(\boldsymbol{r}_1, \boldsymbol{r}_2) v_{{\rm c},\nu}^{(2)}(\boldsymbol{r}_2) = \Lambda_{\rm c}^{(2),\mu}(\boldsymbol{r}_1), \tag{4.31}$$

where the inhomogeneities are given by

$$\Lambda_{\rm x}^\mu(\boldsymbol{r}_1) = -\sum_k \int d^3 r_2 \left[\phi_k^\dagger(\boldsymbol{r}_1) \alpha^\mu G_k(\boldsymbol{r}_1, \boldsymbol{r}_2) \frac{\delta E_{\rm x}}{\delta \phi_k^\dagger(\boldsymbol{r}_2)} + {\rm c.c.} \right]$$

$$+ \sum_k \phi_k^\dagger(\boldsymbol{r}_1) \alpha^\mu \phi_k(\boldsymbol{r}_1) \frac{\partial E_x}{\partial \epsilon_k}, \tag{4.32}$$

$$\Lambda_{\rm c}^{(2),\mu}(\boldsymbol{r}_1) = -\sum_k \int d^3 r_2$$

$$\times \left[\phi_k^\dagger(\boldsymbol{r}_1) \alpha^\mu G_k(\boldsymbol{r}_1, \boldsymbol{r}_2) \frac{\delta E_{\rm c}^{(2)}}{\delta \phi_k^\dagger(\boldsymbol{r}_2)} + {\rm c.c.} \right]$$

$$+ \sum_k \phi_k^\dagger(\boldsymbol{r}_1) \alpha^\mu \phi_k(\boldsymbol{r}_1) \frac{\partial E_{\rm c}^{(2)}}{\partial \epsilon_k}$$

$$+ \int d^3 r_2 \frac{\delta v_{\rm x}^\nu(\boldsymbol{r}_2)}{\delta v_{{\rm KS},\mu}(\boldsymbol{r}_1)} \frac{\delta E_{\rm c}^{(2)}}{\delta v_{\rm x}^\nu(\boldsymbol{r}_2)} \tag{4.33}$$

[the unique correspondence between j^μ and $v_{\rm KS}^\mu$ has been used to simplify the last term in Eq. (4.33)]. The evaluation

of the functional derivatives of $E_{\rm x}$ and $E_{\rm c}^{(2)}$ is lengthy but straightforward, so that we limit ourselves to giving an explicit formula for the only nontrivial term in Eq. (4.33), i.e., $\delta v_{\rm x}^\nu / \delta v_{{\rm KS},\mu}$. Taking the functional derivative of Eq. (4.30) with respect to $v_{\rm KS}^\mu$ one finds (after subsequent multiplication with the inverse KS response function $\chi_0^{-1,\nu\lambda}$ and integration over $\boldsymbol{r}_1$)

$$\frac{\delta v_{\rm x}^\nu(\boldsymbol{r}_2)}{\delta v_{\rm KS}^\mu(\boldsymbol{r}_1)} = \int d^3 r_3 \chi_0^{-1,\nu\lambda}(\boldsymbol{r}_2, \boldsymbol{r}_3) \left\{ \frac{\delta \Lambda_{{\rm x},\lambda}(\boldsymbol{r}_3)}{\delta v_{\rm KS}^\mu(\boldsymbol{r}_1)} \right.$$

$$\left. - \int d^3 r_4 \frac{\delta \chi_{0,\lambda\rho}(\boldsymbol{r}_3, \boldsymbol{r}_4)}{\delta v_{\rm KS}^\mu(\boldsymbol{r}_1)} v_{\rm x}^\rho(\boldsymbol{r}_4) \right\}. \tag{4.34}$$

The first term on the right-hand side of Eq. (4.34) can be evaluated using the standard OPM replacement of functional derivatives [utilizing Eqs. (4.16)–(4.18)],

$$\frac{\delta \Lambda_{\rm x}^\lambda(\boldsymbol{r}_2)}{\delta v_{\rm KS}^\mu(\boldsymbol{r}_1)} = -\sum_k \int d^3 r_3$$

$$\times \left[\phi_k^\dagger(\boldsymbol{r}_1) \alpha_\mu G_k(\boldsymbol{r}_1, \boldsymbol{r}_3) \frac{\delta \Lambda_{\rm x}^\lambda(\boldsymbol{r}_2)}{\delta \phi_k^\dagger(\boldsymbol{r}_3)} + {\rm c.c.} \right]$$

$$+ \sum_k \phi_k^\dagger(\boldsymbol{r}_1) \alpha_\mu \phi_k(\boldsymbol{r}_1) \frac{\partial \Lambda_{\rm x}^\lambda(\boldsymbol{r}_2)}{\partial \epsilon_k}. \tag{4.35}$$

The second term on the right-hand side of Eq. (4.34) contains the quadratic response function,

$$\frac{\delta \chi_{0,\mu_1\mu_2}(\boldsymbol{r}_1, \boldsymbol{r}_2)}{\delta v_{\rm KS}^{\mu_3}(\boldsymbol{r}_3)}$$

$$= \frac{\delta^2 j_{\mu_1}(\boldsymbol{r}_1)}{\delta v_{\rm KS}^{\mu_3}(\boldsymbol{r}_3) \delta v_{\rm KS}^{\mu_2}(\boldsymbol{r}_2)}$$

$$= \sum_{-mc^2 < \epsilon_k \leq \epsilon_F} H_{k,\mu_1\mu_2\mu_3}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3)$$

$$+ \text{ all permutations of } \boldsymbol{r}_1\mu_1 \leftrightarrow \boldsymbol{r}_2\mu_2 \leftrightarrow \boldsymbol{r}_3\mu_3, \tag{4.36}$$

with

$$H_{k,\mu_1\mu_2\mu_3}(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3)$$

$$= \phi_k^\dagger(\boldsymbol{r}_1) \alpha_{\mu_1} G_k(\boldsymbol{r}_1, \boldsymbol{r}_2) \alpha_{\mu_2} G_k(\boldsymbol{r}_2, \boldsymbol{r}_3) \alpha_{\mu_3} \phi_k(\boldsymbol{r}_3)$$

$$- \phi_k^\dagger(\boldsymbol{r}_1) \alpha_{\mu_1} \phi_k(\boldsymbol{r}_1) \phi_k^\dagger(\boldsymbol{r}_2) \alpha_{\mu_2}$$

$$\times \int d^3 r_4 G_k(\boldsymbol{r}_2, \boldsymbol{r}_4) G_k(\boldsymbol{r}_4, \boldsymbol{r}_3) \alpha_{\mu_3} \phi_k(\boldsymbol{r}_3). \tag{4.37}$$

Equations (4.30)–(4.37) together with (4.4), (4.9), (4.17), and (4.19) provide all the necessary ingredients for the determination of $v_{\rm x}$ and $v_{\rm c}^{(2)}$.

V. KRIEGER-LI-IAFRATE APPROXIMATION

The numerical solution of the integral equation (4.20) is computationally rather demanding. Thus an approximate analytical solution is of great interest. In the nonrelativistic context such an analytical scheme has been suggested by Krieger, Li, and Iafrate [14]. Very recently the KLI approximation has also been extended to the relativistic domain (RKLI) [11]. For the derivation of the KLI approximation for the OPM integral equation two different routes have been followed in the literature: One can either rely on a closure approximation for the Greens function (4.17) [14] or rewrite the OPM integral equation in a form that suggests neglecting certain complicated ''higher-order'' contributions [1,11].

Both approaches, however, have so far only been formulated for purely orbital-dependent E_{xc}. In the general situation discussed in Secs. II and IV E_{xc} also depends on the ϵ_k and may even be specified in the nonlinear form $E_{xc}[\phi_k^{(\dagger)}, \epsilon_k, v_{xc}^\mu]$. As a consequence of the v_{xc}^μ dependence of E_{xc} any approximation for v_{xc}^μ also affects the associated E_{xc}, and thus has to be consistently applied to $\delta v_{xc}^\mu / \delta j_\nu$. This problem is most easily resolved by the recursive procedure of Sec. IV C, i.e., by successively addressing exchange and correlation of the second-order functional $E_x + E_c^{(2)}$. Starting from Eqs. (4.30) and (4.32), a KLI approximation for v_x^μ can be devised, which itself is an implicit functional of the $\phi_k^{(\dagger)}$ and ϵ_k, $v_x^\mu[\phi_k^{(\dagger)}, \epsilon_k]$. This $v_x^\mu[\phi_k^{(\dagger)}, \epsilon_k]$ can then be used to construct a KLI approximation for $v_c^{(2),\mu}$ via Eqs. (4.31) and (4.33). Alternatively, after insertion of $v_x^\mu[\phi_k^{(\dagger)}, \epsilon_k]$ into $E_c^{(2)}$ the KLI approximation for $v_c^{(2),\mu}$ can be derived from the ROPM integral equation for functionals of the linear type $E_{xc}[\phi_k^{(\dagger)}, \epsilon_k]$, so that for brevity we restrict ourselves to formulating the RKLI scheme for functionals of this form.

For purely orbital-dependent E_{xc} the KLI approximation is most easily obtained via the closure approach: Replacing the denominator in Eq. (4.17) by some average eigenvalue difference $\Delta\bar{\epsilon}$ one has

$$G_k(\mathbf{r},\mathbf{r}') \approx \sum_{l \neq k} \frac{\phi_l(\mathbf{r})\phi_l^\dagger(\mathbf{r}')}{\Delta\bar{\epsilon}} = \frac{\delta^{(3)}(\mathbf{r}-\mathbf{r}') - \phi_k(\mathbf{r})\phi_k^\dagger(\mathbf{r}')}{\Delta\bar{\epsilon}}. \tag{5.1}$$

Insertion into Eq. (4.20) (reduced to functionals of the type $E_{xc}[\phi_k^{(\dagger)}, \epsilon_k]$ and within the no-pair approximation) leads to

$$\sum_{-mc^2 < \epsilon_k \leq \epsilon_F} \phi_k^\dagger(\mathbf{r})\{\alpha^\mu, \alpha^\nu\}\phi_k(\mathbf{r})v_{xc,\nu}(\mathbf{r})$$

$$= \sum_k \left\{ \phi_k^\dagger(\mathbf{r})\alpha^\mu \frac{\delta E_{xc}}{\delta \phi_k^\dagger(\mathbf{r})} - j_k^\mu(\mathbf{r})\bar{e}_k + \text{c.c.} \right\}$$

$$+ 2\sum_{-mc^2 < \epsilon_k \leq \epsilon_F} j_k^\mu(\mathbf{r})\bar{v}_k - \Delta\bar{\epsilon}\sum_k j_k^\mu(\mathbf{r})\frac{\partial E_{xc}}{\partial \epsilon_k}, \tag{5.2}$$

with

$$\bar{e}_k = \int d^3r \; \phi_k^\dagger(\mathbf{r})\frac{\delta E_{xc}}{\delta \phi_k^\dagger(\mathbf{r})}, \tag{5.3}$$

$$\bar{v}_k = \int d^3r \; j_{k,\lambda}(\mathbf{r})v_{xc}^\lambda(\mathbf{r}), \tag{5.4}$$

$$j_k^\mu(\mathbf{r}) = \phi_k^\dagger(\mathbf{r})\alpha^\mu \phi_k(\mathbf{r}). \tag{5.5}$$

Inversion of the tensor on the left-hand side of Eq. (5.2) then gives

$$v_{xc}^\mu(\mathbf{r}) = \frac{1}{2j_0(\mathbf{r})}\left\{ -g_\nu^\mu + g^{\mu 0}g_{\nu 0} + \frac{j^\mu(\mathbf{r})j_\nu(\mathbf{r})}{j^\rho(\mathbf{r})j_\rho(\mathbf{r})} \right\}$$

$$\times \left\{ \sum_k \left[\phi_k^\dagger(\mathbf{r})\alpha^\nu \frac{\delta E_{xc}}{\delta \phi_k^\dagger(\mathbf{r})} - j_k^\nu(\mathbf{r})\bar{e}_k + \text{c.c.} \right] \right.$$

$$\left. + 2\sum_{-mc^2 < \epsilon_k \leq \epsilon_F} j_k^\nu(\mathbf{r})\bar{v}_k - \Delta\bar{\epsilon}\sum_k j_k^\nu(\mathbf{r})\frac{\partial E_{xc}}{\partial \epsilon_k} \right\}. \tag{5.6}$$

While for purely orbital-dependent xc functionals (as the Coulomb exchange) the term proportional to $\Delta\bar{\epsilon}$ vanishes, this is no longer the case for eigenvalue-dependent functionals [as the transverse exchange (4.4) or the correlation (4.9)]. In order to reinstall the universality of the approximation (5.6), one has to specify $\Delta\bar{\epsilon}$ as a functional of the ϵ_k and ϕ_k (leaving $\Delta\bar{\epsilon}$ as a parameter to be adjusted by hand would explicitly introduce a characteristic energy scale of the system into the functional).

Such a universal representation for $\Delta\bar{\epsilon}$ automatically emerges from the second approach to the KLI approximation: Following exactly the steps given in [11] and neglecting the same terms one ends up with

$$v_{xc}^\mu(\mathbf{r}) = \frac{1}{2j_0(\mathbf{r})}\left\{ -g_\nu^\mu + g^{\mu 0}g_{\nu 0} + \frac{j^\mu(\mathbf{r})j_\nu(\mathbf{r})}{j^\rho(\mathbf{r})j_\rho(\mathbf{r})} \right\}$$

$$\times \left\{ \sum_k \left[\phi_k^\dagger(\mathbf{r})\alpha^\nu \frac{\delta E_{xc}}{\delta \phi_k^\dagger(\mathbf{r})} - j_k^\nu(\mathbf{r})\bar{e}_k + \text{c.c.} \right] \right.$$

$$\left. + 2\sum_{-mc^2 < \epsilon_k \leq \epsilon_F} j_k^\nu(\mathbf{r})\bar{v}_k - v_{KS}^0(\mathbf{r})\sum_k j_k^\nu(\mathbf{r})\frac{\partial E_{xc}}{\partial \epsilon_k} \right\}, \tag{5.7}$$

which suggests the use of v_{KS}^0 as the characteristic energy scale which multiplies $\partial E_{xc}/\partial \epsilon_k$. Indeed, v_{KS}^0 is a rough measure of the ϵ_k for the individual shells, as long as these shells are localized. However, while the ''derivation'' of Eq. (5.7) is straightforward, it is by no means clear whether Eq. (5.7) represents a physically reasonable extension of the RKLI approximation to eigenvalue-dependent functionals.

In fact, consistency with the approximation (5.1) might require that one also drops the term with $\partial E_{xc}/\partial \epsilon_k$ in the ROPM integral equation. In addition, there is an indication that the v_{KS}^0 scale may not be appropriate, as it can be shown that for neutral, closed-subshell atoms an incorrect asymptotic form of v_x^0 emerges. In this case one has

$$v_{xc}^0 = \frac{1}{2j_0}\left\{\sum_k \left[\phi_k^\dagger \frac{\delta E_{xc}}{\delta \phi_k^\dagger} - j_k^0 \bar{e}_k + \text{c.c.}\right]\right.$$

$$\left. + 2\sum_{-mc^2 < \epsilon_k \leqslant \epsilon_F} j_k^0 \bar{v}_k - v_{KS}^0 \sum_k j_k^0 \frac{\partial E_{xc}}{\partial \epsilon_k}\right\}, \quad (5.8)$$

as the spatial components of the current vanish and j_0, v_{KS}^0, and v_{xc}^0 are spherical. In the asymptotic regime the correct $v_{KS}^0(r)$ then approaches $-e^2/r$, thus adding an additional

$$-\frac{v_{KS}^0}{2j_0}\sum_k j_k^0 \frac{\partial E_{xc}}{\partial \epsilon_k} \underset{r \to \infty}{\sim} \frac{e^2}{2r}\frac{\partial E_{xc}}{\partial \epsilon_h}$$

(h here denotes the highest occupied level) to the $-e^2/r$ resulting from

$$\frac{1}{2j_0}\sum_k \left[\phi_k^\dagger \frac{\delta E_{xc}}{\delta \phi_k^\dagger} + \text{c.c.}\right]\underset{r \to \infty}{\sim} -\frac{e^2}{r}$$

on the right-hand side of Eq. (5.8). Thus v_{xc}^0 and, via Eq. (2.16), also v_{KS}^0 no longer have the correct asymptotic r dependence.

The quality of the approximation (5.7) depends on the explicit functional form of E_{xc} as well as on the specific system under consideration. As a consequence, the question of whether to use Eq. (5.7) with or without the $\partial E_{xc}/\partial \epsilon_k$ contribution can only be answered on the basis of explicit results, which are given in Sec. VI for the case of the transverse exchange.

Notwithstanding the question of the $\partial E_{xc}/\partial \epsilon_k$ contribution, Eq. (5.7) still represents an integral equation, which, however, is much more easily solved than Eq. (4.20): The v_{xc}^ν dependence on the right-hand side can either be eliminated by solving a set of linear equations for the $\bar{v}_k$ [obtained by multiplication of Eq. (5.7) with $j_{l,\mu}(r)$ and subsequent summation over l and integration over r]. Alternatively, Eq. (5.7) can be solved iteratively, using the left-hand side of iteration number n to evaluate $\bar{v}_k$ (and v_{KS}^0, if required) on the right-hand side of iteration number $n+1$ (and some suitable starting guesses for $\bar{v}_k$ and v_{KS}^0). Note that this procedure is most easily implemented in any iteration towards self-consistency.

VI. EXCHANGE-ONLY RESULTS FOR CLOSED SUBSHELL ATOMS

A. ROPM including transverse interaction

Standard relativistic *ab initio* calculations for many-electron systems are usually based on either the no-pair DC or the no-pair DCB Hamiltonian. Consequently, as soon as the transverse xc energy is not completely neglected, the resulting ground-state energies are gauge dependent, even in the exchange-only limit [28,45]. The ROPM, on the other hand, can be applied self-consistently for all three relevant forms of the electron-electron interaction, i.e., the instantaneous Coulomb (C), the Coulomb-Breit (CB), and the full (CT) interaction, without introducing a gauge dependence in E_x^T. The ROPM thus offers the possibility to unambiguously

analyze the impact of the transverse interaction on a variety of quantities. In particular, while the size of transverse corrections to ground-state energies has already been known from first-order perturbation theory on DC basis for quite some time [23], the ROPM allows an explicit examination of microscopic (local) quantities such as single-particle energies or the xc potential, and therefore of higher-order transverse corrections to ground-state energies.

Within the framework of DFT the role of the transverse exchange potential has first been investigated by Das, Rajagopal, and co-workers [71–73] on the basis of the relativistic LDA (RLDA) [62,63]. However, while the RLDA provides a gauge invariant approach to the transverse exchange, it misrepresents atomic E_x^T substantially [63,71,73]. Thus, to obtain conclusive results, the ROPM, which gives very accurate exchange and ground-state energies in the C limit [9], has to be used.

We have performed self-consistent exchange-only ROPM calculations for closed subshell atoms, including the transverse interaction either completely or in its Breit approximation (throughout this section we restrict ourselves to exchange-only DFT and the no-pair approximation, so that $E = E_{tot}$—all subsequent statements are to be understood within these limits). The technical details are given in Appendix A. All ROPM results in this paper have been obtained by coupled solution of the relativistic KS equations (A31) and the integral equation specified in Eqs. (A38)–(A40) and (A54) with standard finite differences methods on a grid of 800–1600 mesh points (without any further approximation).

We start our analysis by a comparison of ROPM and RHF results, both on the C and the CB level, in order to show that the local ROPM potential is physically equivalent to the nonlocal RHF potential. In Table I we list self-consistent exchange-only ground-state energies for closed subshell atoms (in Table I we have used a different nuclear radius and speed of light as in all other tables of this paper and in [9], in order to allow a comparison with [26]). In the case of the C interaction two different sets of RHF energies are given, resulting from (a) a completely numerical solution of the DC-RHF equations [74], and from (b) a basis set expansion [26]. Focusing on the fully numerical RHF data first, one observes that throughout the periodic system the RHF energies are slightly below the corresponding ROPM results, reflecting the somewhat larger variational freedom of the RHF scheme. Nevertheless, the differences between ROPM and RHF values are only on the 1-eV level, which clearly supports the DFT concept of multiplicative potentials. One also notices that for heavy atoms the differences between the fully numerical RHF results and those obtained by finite basis expansion [26] are of the same order of magnitude as the differences between the fully numerical ROPM and RHF data. For instance, for Hg, which we use as a prototype for all heavy atoms considered, the former difference amounts to 26 mhartree, while the latter is 39 mhartree. Note that in spite of the similarity of the ground-state energies the single-particle energies of the ROPM are quite different from their RHF counterparts (see Table II), just as in the nonrelativistic case [2] (and within the RLDA [71]).

Table I also gives a corresponding comparison for the CB interaction, for which, however, only RHF results obtained with a basis set expansion [26] are available. In this case the

TABLE II. Exchange-only single-particle energies $(-\epsilon_{nlj})$ for neutral Hg from self-consistent ROPM, RHF, and RKLI calculations, using (i) the complete relativistic exchange-only potential (C+T), (ii) its Coulomb-Breit approximation (C+B), and (iii) its longitudinal (C) limit. For the RKLI approximation two variants are shown: (a) Eq. (5.7) without the $\partial E_x / \partial \epsilon_k$ contribution, (b) Eq. (5.7) including the $\partial E_x / \partial \epsilon_k$ contribution. Also given are RGGA results that have been obtained with the relativistic extension of the Becke parametrization [52], either in exchange-only mode (RB) or including the Lee-Young-Parr correlation GGA (RBLYP) [76] (all energies in hartree [86]).

Level	ROPM			RHF	RKLIa	RKLIb	RB	RBLYP
	C+T	C+B	C	C	C+T	C+T	C+T	C+T
$1s1/2$	3036.871	3032.278	3047.431	3074.229	3037.244	3029.982	3036.453	3036.485
$2s1/2$	538.444	537.853	540.057	550.251	538.343	536.425	538.051	538.085
$2p1/2$	516.198	515.546	518.062	526.855	516.083	513.925	516.097	516.132
$2p3/2$	445.422	445.013	446.683	455.157	445.302	443.541	445.276	445.311
$3s1/2$	127.956	127.858	128.273	133.113	127.906	127.163	127.703	127.738
$3p1/2$	117.994	117.885	118.351	122.639	117.966	117.178	117.857	117.893
$3p3/2$	102.302	102.236	102.537	106.545	102.274	101.583	102.152	102.187
$3d3/2$	86.069	86.036	86.202	89.437	86.062	85.387	85.959	85.994
$3d5/2$	82.692	82.665	82.808	86.020	82.687	82.036	82.582	82.617
$4s1/2$	28.361	28.351	28.428	30.648	28.303	27.986	28.037	28.072
$4p1/2$	24.090	24.075	24.162	26.124	24.050	23.724	23.819	23.854
$4p3/2$	20.321	20.315	20.364	22.189	20.269	19.967	20.024	20.059
$4d3/2$	13.397	13.397	13.412	14.797	13.372	13.083	13.151	13.186
$4d5/2$	12.689	12.690	12.701	14.053	12.663	12.380	12.441	12.476
$4f5/2$	3.766	3.770	3.757	4.473	3.764	3.509	3.571	3.607
$4f7/2$	3.613	3.616	3.603	4.312	3.611	3.358	3.417	3.453
$5s1/2$	4.394	4.394	4.404	5.103	4.399	4.251	4.278	4.313
$5p1/2$	3.004	3.002	3.013	3.538	3.004	2.870	2.886	2.920
$5p3/2$	2.360	2.360	2.364	2.842	2.348	2.236	2.219	2.253
$5d3/2$	0.507	0.507	0.506	0.650	0.496	0.417	0.367	0.399
$5d5/2$	0.440	0.441	0.440	0.575	0.430	0.354	0.300	0.332
$6s1/2$	0.330	0.330	0.330	0.328	0.332	0.283	0.222	0.249

CB ROPM ground-state energies become even more attractive than their CB-RHF counterparts for very heavy atoms: While for Hg the basis set expansion loses 26 mhartree with respect to the finite differences calculation for the C interaction, this difference increases to 48 mhartree in the CB case. Whether this fact is an indication of the gauge dependence of the DCB-RHF data or is just due to a particular sensitivity of the Breit term to the basis chosen is not clear at this point. Nevertheless, the order of magnitude of this discrepancy is consistent with the gauge dependencies observed by Gorceix, Indelicato, and Desclaux [28,45] in the case of two electron systems: For example, for the $1s2p\,^3P_0$ state they found differences of 1.2 mhartree for $Z=54$ and 3.3 mhartree for $Z=92$ between the expectation values of the weakly relativistic limits of the transverse interaction in Coulomb and Feynman gauge, when using C-RHF orbitals.

In addition to E_{tot}^{C} and E_{tot}^{C+B} also the complete E_{tot}^{C+T} are shown in Table I, so that one can extract the absolute size of the Breit and beyond Breit corrections to ground-state energies. For example for Hg E_{tot}^{C+T} is more attractive by 490 mhartree than E_{tot}^{C+B}, which is 22.6 hartree above E_{tot}^{C}. Thus, as far as ground-state energies are concerned, the self-consistent ROPM results show the same trend as the well-known perturbative RHF results [23].

We now turn to an analysis of the exchange-only potential, addressing in particular the importance of its transverse component v_x^T for ground-state and excitation energies. In

Table III we again list total exchange-only ground-state energies for closed subshell atoms, this time comparing three ROPM variants (and using the nuclear shape and the value of the speed of light of [9]—for completeness and in order to correct some slightly incorrect numbers [75] in Table VI of [9] the corresponding E_x^T are recorded in Table IV). First of all, the fully self-consistent ROPM energies E_{tot}^{C+T} are given, obtained by solution of Eqs. (2.15) and (4.20) for the complete exchange energy (4.4). In addition, we show the E_{tot}^{C+T} obtained by restricting v_x to either the C or the CB limit, i.e., by only including Eq. (4.7) or the Breit limit of Eq. (4.4) in Eq. (4.21) and evaluating the remainder of Eq. (4.4) by first-order perturbation theory. As the ROPM procedure yields the multiplicative exchange potential that minimizes the energy expression of interest, the E_{tot}^{C+T} resulting from the C or CB exchange potentials are somewhat above the fully self-consistent values. Nevertheless, the CB-exchange potential leads to energies that are only a few mhartree away from the self-consistent E_{tot}^{C+T}, demonstrating that the CB potential is a rather accurate approximation of the full v_x for atomic systems. In other words, the second-order contribution of the transverse corrections not included in the B interaction are of the order of 5–10 mhartree. On the other hand, treating only the C interaction self-consistently produces E_{tot}^{C+T}, which, for heavy atoms, differ from the fully self-consistent results on the 1-eV level. In fact, the second-order transverse exchange

TABLE III. Exchange-only ground-state energies from ROPM, RHF, RKLI, and RGGA calculations for neutral atoms with closed subshells: In the case of the ROPM the self-consistent (s) treatment of the complete transverse exchange (T) is compared with a self-consistent inclusion of only its Breit (B) limit [together with a perturbative (p) calculation of the beyond Breit contributions — T−B] as well as a fully perturbative evaluation of E_x^T. The latter procedure has also been used for the RHF calculations [74]. For the RKLI approximation two variants are shown: (a) Eq. (5.7) without the $\partial E_x/\partial \epsilon_k$ contribution, (b) Eq. (5.7) including the $\partial E_x/\partial \epsilon_k$ contribution. The RGGA results have been obtained with the relativistic extension of the Becke parametrization (RB) [52] for v_x, while using Eq. (4.4) for the calculation of E_x (all energies in mhartree [86]).

Atom	$-E_{tot}^{C+T}$	$E_{tot}^{C+T}-E_{tot}^{C+T}$[ROPM: s(C+T)]					
	ROPM s: C+T p:	ROPM C+B T−B	ROPM C T	RHF C T	RKLIa C+T	RKLIb C+T	RB C+T
He	2862	0	0	0	0	0	2
Be	14575	0	0	−1	0	0	2
Ne	128674	0	0	−2	1	1	13
Mg	199900	0	0	−3	1	1	9
Ar	528546	0	0	−5	2	2	10
Ca	679513	0	0	−6	2	2	8
Zn	1793840	0	1	−14	4	4	40
Kr	2787429	0	2	−12	3	3	21
Sr	3176359	0	2	−11	3	5	18
Pd	5041098	0	5	−13	4	6	35
Cd	5589496	1	6	−16	6	9	30
Xe	7441173	1	10	−11	6	16	22
Ba	8129161	1	11	−9	6	39	21
Yb	14053750	3	29	−21	11	82	74
Hg	19626705	6	50	8	10	118	51
Rn	23573354	8	68	29	9	224	45
Ra	24996946	9	75	38	9		44
No	36687173	16	140	82	13		87

contributions are of the same order of magnitude as the energy gain from the additional variational freedom of the non-local RHF potential, so that the fully self-consistent ROPM energies are below the perturbative RHF energies for heavy atoms (also given in Table III).

While this is a negligible energy contribution in the quantum chemical context, it has to be corrected by second-order perturbation theory to achieve spectroscopic accuracy [39]: This is most easily seen from Tables V and VI in which some ionization potentials (IPs) and inner-shell excitation energies are given. For none of the atoms considered do the IPs from the first order perturbative and the self-consistent treatment of E_x^T differ by more than 1 mhartree, reflecting the fact that the transverse corrections essentially cancel out of all chemically relevant energy differences. On the other hand, for the $(1s_{1/2})^2 \rightarrow 1s_{1/2}2p_{3/2}$ transition in heliumlike uranium one finds a difference of 0.68 eV between the two schemes. However, this effect is reduced substantially as soon as no K electron participates in the excitation process: For the $(1s_{1/2})^2 2s_{1/2} \rightarrow (1s_{1/2})^2 2p_{3/2}$ transition energy in lithiumlike uranium the deviation only amounts to 0.18 eV.

These observations are corroborated by the corresponding single-particle energies and the exchange potentials themselves. In Figs. 1 and 2 we analyze the relative importance of the transverse exchange, i.e., the relativistic treatment of the electron-electron interaction, and the relativistic corrections to the Coulomb exchange, i.e., the relativistic treatment of

TABLE IV. Transverse exchange-only energies (E_x^T) for closed subshell atoms: Self-consistent ROPM results (s) in comparison with values obtained perturbatively (p) with orbitals from longitudinal ROPM and RHF (Coulomb gauge for E_x^T) calculations [75] (all energies in hartree [86]).

Atom	ROPM: s	ROPM: p	RHF: p
He	0.000064	0.000064	0.000064
Be	0.00070	0.00070	0.00070
Ne	0.0167	0.0167	0.0166
Mg	0.0318	0.0319	0.0318
Ar	0.132	0.132	0.132
Ca	0.191	0.191	0.191
Zn	0.758	0.759	0.759
Kr	1.417	1.420	1.419
Sr	1.706	1.711	1.710
Pd	3.282	3.291	3.290
Cd	3.797	3.809	3.808
Xe	5.693	5.712	5.711
Ba	6.453	6.475	6.473
Yb	13.842	13.900	13.898
Hg	22.071	22.171	22.168
Rn	28.547	28.683	28.680
Ra	31.006	31.156	31.153
No	53.313	53.593	53.591

TABLE V. Ionization potentials of neutral atoms calculated from ground-state energy differences: For the ROPM the self-consistent inclusion of the transverse exchange (C+T) is compared with complete neglect of E_x^T (C). The RGGA data have been obtained by combining the relativistic extension of the Becke parametrization (RB) [52] for v_x with Eq. (4.4) for E_x (all energies in mhartree [86]).

Atom	ROPM		RKLIa	RB
	C+T	C	C+T	C+T
Li	196	196	196	195
Be	296	296	295	296
Na	181	181	181	181
Mg	243	243	243	243
K	147	147	147	147
Ca	189	189	189	189
Cu	234	234	232	229
Zn	284	284	283	279
Rb	139	139	139	139
Sr	175	175	175	174
Ag	229	229	228	227
Cd	269	269	268	267
Cs	127	127	127	127
Ba	157	157	157	157
Au	279	280	278	279
Hg	312	313	312	312
Fr	132	132	131	131
Ra	161	161	161	160

the electrons, for v_x, again using Hg. While Fig. 1 gives an idea of the absolute size of these corrections, their relative impact is most clearly seen in Fig. 2, where the percentage relativistic correction

$$\Delta v_x(r) = \frac{v_x^{ROPM}(r) - v_x^{NROPM}(r)}{v_x^{NROPM}(r)} \qquad (6.1)$$

is plotted. For all three variants of v_x one observes an oscillatory behavior of $\Delta v_x(r)$, reflecting the shell structure of the atom. The specific structure results from the contraction

TABLE VI. Transition energies of He- and Li-like ions from exchange-only ROPM calculations: Self-consistent (ST) versus first-order perturbative (PT) treatment of E_x^T (all energies in hartree [86]).

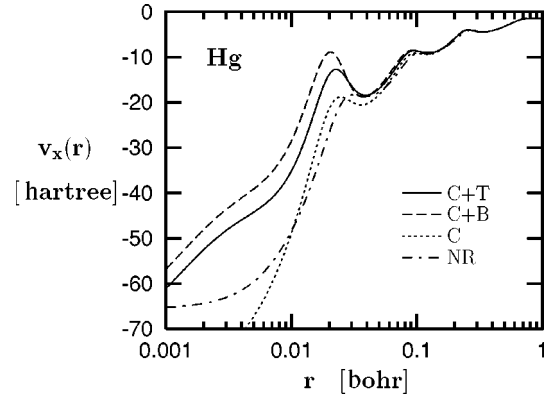| Ion	ST	PT
	$(1s_{1/2})^2 \rightarrow 1s_{1/2}2p_{3/2}$	
Hg^{78+}	2666.819	2666.805
U^{90+}	3704.916	3704.891
No^{100+}	4793.688	4793.652
	$(1s_{1/2})^2 2s_{1/2} \rightarrow (1s_{1/2})^2 2p_{1/2}$	
Hg^{77+}	9.061	9.065
U^{89+}	11.895	11.901
No^{99+}	14.077	14.087

FIG. 1. ROPM exchange-only potentials for neutral Hg: Self-consistent Coulomb (C), Coulomb-Breit (C+B), and fully transverse (C+T) results in comparison with nonrelativistic limit (NR).

of most orbitals (in particular the $s_{1/2}$ and $p_{1/2}$ orbitals) when going from a nonrelativistic to a relativistic description: As there is a unique correspondence between the density $n(r)$ and the exchange potential, $\Delta v_x(r)$ is a direct measure of the inward shifts of the maxima of the radial density $r^2 n(r)$ caused by the orbital contraction. This effect originates from the relativistic treatment of the electron kinetic energy, so that the oscillatory structure in $\Delta v_x(r)$ is independent of the transverse interaction. The latter starts to show up in $v_x(r)$ for the M shell, although becoming sizable only for the L and K shells: While the $3p_{3/2}$ level is destabilized by 235 mhartree when going from the C to the CT level, the $2p_{3/2}$ eigenvalue already experiences a 1.26-hartree shift (see Table II). On the other hand, the corresponding percentage correction of the eigenvalues, i.e., the ratio between the transverse exchange and the total KS potential, is similar for all levels: It amounts to 0.35% for the $1s_{1/2}$, 0.23% for the $3p_{3/2}$, 0.28% for the $4f_{7/2}$, and 0.15% for the $6s_{1/2}$ orbital. Even for the $4f$ levels the 10-mhartree shift due to v_x^T is of the same order of magnitude as the effect of v_c: The inclusion of v_c via the LYP-GGA [76] leads to a 36 mhartree correction of the $4f_{7/2}$ eigenvalue. Correlation completely dominates over transverse exchange only for the valence electrons.

The impact of v_x^T on the density can be extracted from Fig. 3, where the percentage deviations of self-consistent CT
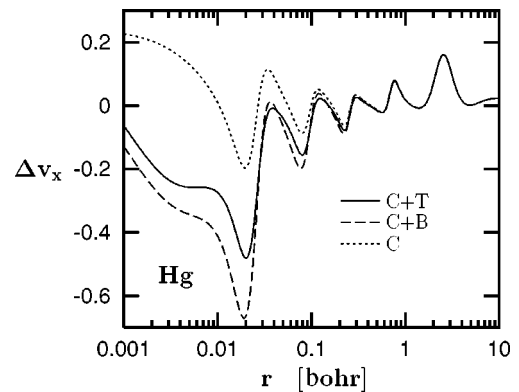

FIG. 2. Relativistic contribution to the ROPM exchange-only potential for neutral Hg: Percentage correction (6.1) from self-consistent calculations, using (i) the complete relativistic x-only potential (C+T), (ii) its Coulomb-Breit approximation (C+B), and (iii) its longitudinal (C) limit.
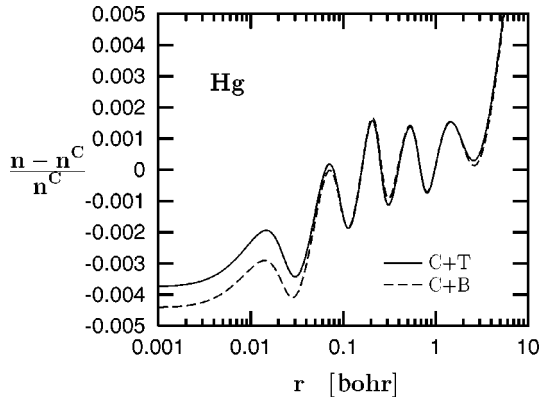
FIG. 3. Percentage deviations of fully transverse (C+T) and Coulomb-Breit (C+B) densities from purely longitudinal (C) result for neutral Hg.

and CB densities from the pure C result are plotted for Hg. One observes direct shifts of roughly 0.4% for the innermost shell and indirect effects of the order of 0.1% for all other shells. The increasing deviation for very large r reflects the 0.5 mhartree change of the $6s$ eigenvalue, resulting from the inclusion of v_x^T.

Finally, Figs. 1–3 and Table II show that the Breit approximation is reasonably accurate also on the local level. As in the case of the exchange energies, the Breit corrections to v_x and the eigenvalues overshoot the exact transverse results. However, while for E_x^T the error of the Breit approximation is 2% for Hg, it, e.g., amounts to 36% for the $2s_{1/2}$ eigenvalue. Obviously, v_x^T is much more sensitive to the retardation corrections to the Breit interaction than E_x^T.

B. RKLI approximation

By definition of the exchange-only limit of RDFT, the ROPM results represent the exact exchange-only energies within RDFT, given some form of the relativistic electron-electron interaction. On the basis of the ROPM results one can thus examine approximations, both on the global (ground-state energies) and on the local (eigenvalues, potentials) level. In the following we investigate the ambiguity in the treatment of the eigenvalue dependence of E_x^T within the RKLI scheme. We compare two RKLI variants, namely, Eq. (5.7) without the $\partial E_x/\partial \epsilon_k$ contribution (RKLIa) and Eq. (5.7) including the $\partial E_x/\partial \epsilon_k$ contribution (RKLIb).

Table III shows that the RKLIa potential is an accurate representation of the exact ROPM potential: The differences between the E_{tot}^{C+T} found with RKLIa and ROPM are smaller than those between ROPM and RHF energies, the RKLIa energies always being slightly above the ROPM values (consistent with the variational character of the ROPM potential). As a further measure for the quality of the RKLI exchange potential one can use the E_{tot}^{C+T} obtained by combining the exact representation of E_x, Eq. (4.4), with one of the available explicit density functionals for v_x. In Table III we thus give the E_{tot}^{C+T}, resulting from a RGGA for v_x, using the relativistic extension of the Becke GGA (RB) [52,77]. The error in these numbers is roughly a factor of 5 larger than that of the RKLIa energies, while still being of the same order of magnitude as the differences between ROPM and
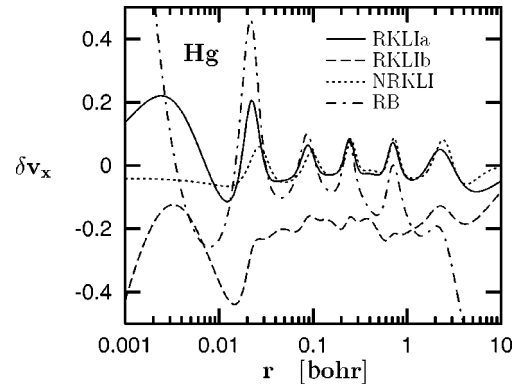

FIG. 4. Self-consistent RKLI and RGGA exchange-only potentials for neutral Hg: Percentage deviation (6.2) from ROPM result. For the RKLI approximation two variants are shown: (a) Eq. (5.7) without the $\partial E_x/\partial \epsilon_k$ contribution, (b) Eq. (5.7) including the $\partial E_x/\partial \epsilon_k$ contribution. Also plotted is the deviation of the nonrelativistic KLI potential from the nonrelativistic OPM potential (NRKLI). The RGGA results have been obtained with the RB parametrization [52].

RHF results. A similar picture emerges from the IPs of Table V. The error resulting from the RKLIa potential is in the range of 0.2–1.5 mhartree, thus being roughly a factor of 3 smaller than that found with the RGGA potential. We remark that, in contrast to the RKLIa potential, the exchange-only RGGA potential does not give stable negative ions due its incorrect asymptotic behavior [78] (compare Fig. 4).

The RKLIb version, on the other hand, yields energies that for heavy elements differ significantly from the ROPM standard. In fact, we have not found converged solutions with this scheme for the heaviest atoms (Ra, No), which suggests that the inclusion of the $\partial E_x/\partial \epsilon_k$ contribution in the form (5.7) is not appropriate.

This conclusion is confirmed in Table II and Fig. 4 from a more microscopic point of view. While the single-particle energies from the RKLIa are in good agreement with their ROPM counterparts, the RKLIb eigenvalues deviate substantially, with even the valence levels being destabilized. An analogous observation can be made on the basis of Fig. 4, where the percentage deviation of the RKLI approximations from the exact exchange-only potential,

$$\delta v_x(r) = \frac{v_x^{Test}(r) - v_x^{ROPM}(r)}{v_x^{ROPM}(r)}, \qquad (6.2)$$

is shown. The RKLIb potential is shifted upward by the $\partial E_x/\partial \epsilon_k$ contribution even for shells that should not be affected by the transverse exchange.

At first glance one might think that this is a consequence of the incorrect asymptotic behavior of the RKLIb potential, as discussed in Sec. V. In order to resolve this question, we have examined a RKLI variant in which v_{KS}^0 in Eq. (5.7) had been replaced by $v_{KS}^0 - v_x^0$, thus correcting the asymptotic behavior. This *ad hoc* procedure seems legitimate as no really systematic derivation of the energy scale in front of $\partial E_x/\partial \epsilon_k$ seems to be possible, thus allowing "educated guesses." However, the results obtained with this modified RKLIb approximation are only marginally different from the

original RKLIb data, so that the failure of the RKLIb scheme cannot be attributed to the asymptotic behavior.

The RKLIa potential, on the other hand, is as accurate as its Coulomb [11] or nonrelativistic limit (see Fig. 4). It is superior to the RGGA potential, in particular, in the asymptotic regime. This fact is also reflected by the corresponding eigenvalues: While for the innermost levels the RGGA is essentially as accurate as RKLIa, the valence levels are much better reproduced by RKLIa, as a consequence of the correct asymptotic behavior of $v_x(r)$ (see Table II). Although there are exceptional cases in which the RKLI approximation predicts an incorrect eigenvalue ordering in the valence regime (as, e.g., for neutral Yb), one thus concludes that, at least for the transverse exchange, the neglect of the $\partial E_x / \partial \epsilon_k$ contribution in Eq. (5.7) is superior to any inclusion of this term. It remains to be investigated whether the same holds true for correlation functionals as $E_c^{(2)}$, in which the eigenvalue dependence is expected to play a more prominent role than in E_x.

VII. OUTLOOK

In this paper we have established a first-principles, parameter-free density functional scheme in which all exchange-correlation effects are consistently represented in terms of the Kohn-Sham orbitals and eigenvalues, rather than the density (four current) used in the conventional Kohn-Sham approach. Due to its perturbative origin the practical version of the scheme provided here should be particularly suited for atomic physics and quantum chemical applications. One would, for instance, expect that the correlation potential resulting from this systematic approach has the correct sign in the asymptotic regime of atoms [79], in contrast, e.g., to the Colle-Salvetti potential. On the other hand, the ability of the nonempirical, orbital-dependent functional to deal with van der Waals bonds in a seamless form opens a whole new range of applications.

A possible path to an approximate treatment of resummed forms of the orbital-dependent exchange-correlation energy functional, which should be more appropriate for the description of solids, has been sketched. The proposed approximate handling of the exchange-correlation kernel f_{xc} may also be useful for applications to complex molecules, as the rigorous evaluation of the correlation potential requires knowledge of the quadratic response function. Alternatively, the improved description of atoms could be utilized to construct more accurate pseudopotentials [80].

The procedure has been formulated in a fully relativistic form, indicating that a consistent inclusion of quantum electrodynamical effects is possible. While we have given explicit self-consistent results for the transverse electron-

electron interaction, the statement also applies to vacuum corrections. This should, e.g., allow a study of ''overcritical'' atomic systems [81,82] in a self-consistent fashion.

APPENDIX A: ROPM FOR SPHERICAL SYSTEMS

The ROPM equations for spherical systems can either by obtained by directly reducing Eqs. (4.19)–(4.21) to spherical systems or by evaluating the spherical limit of the ground-state energy and subsequently rederiving the ROPM integral equation. In fact, the second procedure is somewhat simpler as the spherical form of the xc energy is required for Eq. (4.21) in any case. We thus briefly summarize the spherical average for both the Hartree and the exchange energy (in A 1) and then discuss the resulting ROPM equations (in A 2), in order to provide the technical details necessary for the inclusion of the exchange-only ROPM in standard codes and for the examination of the behavior of the exchange potential in the asymptotic regime of finite systems (in Appendix B).

1. Relativistic exchange-only energy for spherical systems

For spherical systems the KS four spinors can be written as

$$\phi_{nljm}(\mathbf{r}) = \frac{1}{r} \begin{pmatrix} a_{nlj}(r) & \Omega_{jlm}(\theta, \varphi) \\ ib_{nlj}(r) & \Omega_{j\bar{l}m}(\theta, \varphi) \end{pmatrix}, \qquad \text{(A1)}$$

where the quantum numbers are defined as usual [$\bar{l} = 2j - l$, $\kappa = -2(j-l)(j+1/2)$] and the angular momentum eigenfunctions Ω_{jlm} agree with the convention of Rose [83]. In the following, we will frequently use a shorthand notation for the quantum numbers nlj,

$$nlj = q, \quad n'l'j' = q'.$$

Due to the different angular momentum coupling schemes the complete relativistic exchange-only energy (4.4) (in Feynman gauge) is most conveniently decomposed into a ''retarded Coulomb'' (RC) and a ''retarded Gaunt'' (RG) contribution,

$$E_x^{C+T} = E_{x,RC} + E_{x,RG}, \qquad \text{(A2)}$$

$$E_{x,RC}^{qm,q'm'} = -\frac{e^2}{2} \int d^3r \int d^3r' \frac{\cos(\omega_{qq'}|\mathbf{r}-\mathbf{r'}|)}{|\mathbf{r}-\mathbf{r'}|} \phi_{qm}^\dagger(\mathbf{r}) \phi_{q'm'}(\mathbf{r}) \phi_{q'm'}^\dagger(\mathbf{r'}) \phi_{qm}(\mathbf{r'}), \qquad \text{(A3)}$$

$$E_{x,RG}^{qm,q'm'} = \frac{e^2}{2} \int d^3r \int d^3r' \frac{\cos(\omega_{qq'}|\mathbf{r}-\mathbf{r'}|)}{|\mathbf{r}-\mathbf{r'}|} \phi_{qm}^\dagger(\mathbf{r}) \boldsymbol{\alpha} \phi_{q'm'}(\mathbf{r}) \cdot \phi_{q'm'}^\dagger(\mathbf{r'}) \boldsymbol{\alpha} \phi_{qm}(\mathbf{r'}) \qquad \text{(A4)}$$

$(\omega_{q,q'} = |\epsilon_q - \epsilon_{q'}|/c)$. The corresponding matrix elements of the Hartree energy read

$$E_{H,C}^{qm,q'm'} = E_{H,RC}^{qm,q'm'} = \frac{e^2}{2} \int d^3r \int d^3r' \frac{1}{|\boldsymbol{r} - \boldsymbol{r'}|} \phi_{qm}^\dagger(\boldsymbol{r}) \phi_{qm}(\boldsymbol{r}) \phi_{q'm'}^\dagger(\boldsymbol{r'}) \phi_{q'm'}(\boldsymbol{r'}), \tag{A5}$$

$$E_{H,T}^{qm,q'm'} = E_{H,RG}^{qm,q'm'} = -\frac{e^2}{2} \int d^3r \int d^3r' \frac{1}{|\boldsymbol{r} - \boldsymbol{r'}|} \phi_{qm}^\dagger(\boldsymbol{r}) \boldsymbol{\alpha} \phi_{qm}(\boldsymbol{r}) \cdot \phi_{q'm'}^\dagger(\boldsymbol{r'}) \boldsymbol{\alpha} \phi_{q'm'}(\boldsymbol{r'}). \tag{A6}$$

The matrix elements (A3)–(A6) can be evaluated [20–22] by using the multipole expansion of the retarded interaction,

$$\frac{\cos(\omega_{qq'}|\boldsymbol{r} - \boldsymbol{r'}|)}{|\boldsymbol{r} - \boldsymbol{r'}|} = \sum_{L=0}^{\infty} \frac{4\pi}{2L+1} U_{qq',L}(r,r') \sum_{M=-L}^{L} Y_{LM}^*(\theta,\varphi) Y_{LM}(\theta',\varphi'), \tag{A7}$$

$$U_{qq',L}(r,r') = \frac{r_<^L}{r_>^{L+1}} \tilde{j}_L(\omega_{qq'} r_<) \tilde{y}_L(\omega_{qq'} r_>), \tag{A8}$$

where $\tilde{j}_L(x)$ and $\tilde{y}_L(x)$ represent spherical Bessel functions of first and second kind [84], normalized to 1 at $x=0$,

$$\tilde{j}_L(x) = \frac{(2L+1)!!}{x^L} j_L(x),$$

$$\tilde{y}_L(x) = -\frac{x^{L+1}}{(2L-1)!!} y_L(x).$$

However, before providing xplicit formulas for the individual matrix elements (A3)–(A6) we restrict the discussion to the spherical average. In the case of open shells only the average over all possibilities to distribute the $\Theta_q \leq 2j+1$ electrons over the $2j+1$ available m states lead to a spherical KS potential. For this m average one has to distinguish between diagonal and off-diagonal matrix elements for both the exchange-only and the Hartree energy [85]. In the more simple off-diagonal case, i.e., for $q \neq q'$, one is led to consider two independent averages for the two relevant shells, so that one ends up with

$$\bar{E}^{qq'} = \frac{\Theta_q}{2j+1} \frac{\Theta_{q'}}{2j'+1} \sum_{m=-j}^{j} \sum_{m'=-j'}^{j'} E^{qm,q'm'}. \tag{A9}$$

On the other hand, for the m average of the diagonal matrix elements one has to take into account the reduced probability to find two electrons in the two distinct states m and m' [85],

$$\bar{E}^{qq} = \frac{\Theta_q}{2j+1} \left(1 - \frac{\Theta_q - 1}{2j}\right) \sum_{m=-j}^{j} E^{qm,qm} + \frac{\Theta_q(\Theta_q - 1)}{(2j+1)2j} \sum_{m=-j}^{j} \sum_{m'=-j}^{j} E^{qm,qm'}. \tag{A10}$$

Equations (A9) and (A10) apply to the individual components (A3)–(A6) of both the exchange and the Hartree energy. The DFT Hartree energy (4.3), however, is defined in terms of the four current (4.1), and thus the m average of its matrix elements is given by Eq. (A9) also for $q=q'$,

$$\bar{E}_H^{qq} = \left(\frac{\Theta_q}{2j+1}\right)^2 \sum_{m=-j}^{j} \sum_{m'=-j}^{j} E_H^{qm,qm'}. \tag{A11}$$

As a consequence, the difference between the true m-averaged Hartree energy of the form (A10) and its DFT counterpart (A11) has to be interpreted as part of the m-averaged exchange energy. Using $E_H^{qm,qm} = -E_x^{qm,qm}$ one obtains as diagonal exchange matrix elements

$$\bar{E}_x^{qq} = \frac{\Theta_q(\Theta_q - 1)}{(2j+1)2j} \sum_{m=-j}^{j} \sum_{m'=-j}^{j} E_x^{qm,qm'} + \frac{\Theta_q(\Theta_q - 2j-1)}{2j(2j+1)^2} \sum_{m=-j}^{j} \sum_{m'=-j}^{j} E_H^{qm,qm'}. \tag{A12}$$

Decomposing Eqs. (A9), (A11), and (A12) into the retarded Coulomb and retarded Gaunt contributions one finally ends up with

$$\bar{E}_{H,RC}^{qq'} = \frac{e^2}{2} \Theta_q \Theta_{q'} \int_0^\infty dr \int_0^\infty dr' \frac{1}{r_>} \{a_q(r)^2 + b_q(r)^2\} \{a_{q'}(r')^2 + b_{q'}(r')^2\}, \tag{A13}$$

$$\bar{E}_{H,\mathrm{RG}}^{qq'}=0 \tag{A14}$$

for the Hartree energy, while for E_x one has to distinguish between $q\neq q'$,

$$\bar{E}_{\mathrm{x,RC}}^{qq'}=-\frac{e^2}{2}\Theta_q\Theta_{q'}\int_0^\infty dr\int_0^\infty dr'\sum_{L=0}^\infty U_{qq',L}(r,r')\{a_q(r)a_{q'}(r)+b_q(r)b_{q'}(r)\}\{a_q(r')a_{q'}(r')+b_q(r')b_{q'}(r')\}\bar{B}_{jl,j'l',L}, \tag{A15}$$

$$\bar{E}_{\mathrm{x,RG}}^{qq'}=\frac{e^2}{2}\Theta_q\Theta_{q'}\int_0^\infty dr\int_0^\infty dr'\sum_{L=0}^\infty U_{qq',L}(r,r')\{2a_q(r)b_{q'}(r)a_{q'}(r')b_q(r')\bar{F}_{jl,j'l',L}+a_q(r)b_{q'}(r)a_q(r')b_{q'}(r')\bar{E}_{jl,j'\bar{l}',L}$$

$$+a_{q'}(r)b_q(r)a_{q'}(r')b_q(r')\bar{E}_{j'l',j\bar{l},L}\}, \tag{A16}$$

and $q=q'$,

$$\bar{E}_{\mathrm{x,RC}}^{qq}=-\frac{e^2}{2}\int_0^\infty dr\int_0^\infty dr'\sum_{L=0}^\infty U_{qq,L}(r,r')\{a_q(r)^2+b_q(r)^2\}\ \{a_q(r')^2+b_q(r')^2\}$$

$$\times\left\{\frac{\Theta_q(\Theta_q-1)(2j+1)}{2j}\bar{B}_{jl,jl,L}+\frac{\Theta_q(2j+1-\Theta_q)}{2j}\bar{A}_{jl,jl,L}\right\}, \tag{A17}$$

$$\bar{E}_{\mathrm{x,RG}}^{qq}=\frac{e^2}{2}\int_0^\infty dr\int_0^\infty dr'\sum_{L=0}^\infty U_{qq,L}(r,r')2a_q(r)b_q(r)a_q(r')b_q(r')\frac{\Theta_q(\Theta_q-1)(2j+1)}{2j}\{\bar{F}_{jl,jl,L}+\bar{E}_{jl,j\bar{l},L}\}. \tag{A18}$$

The angular momentum coupling coefficients in Eqs. (A15)–(A18) are given by [20–22]

$$\bar{A}_{jl,j'l',L}=\delta_{L0}, \tag{A19}$$

$$\bar{B}_{jl,j'l',L}=\frac{1+(-1)^{l+l'+L}}{2(2L+1)}C\left(jj'L;\frac{1}{2},-\frac{1}{2},0\right)^2, \tag{A20}$$

$$\bar{E}_{jl,j'\bar{l}',L}=\begin{cases}\dfrac{1+(-1)^{l+\bar{l}'+L}}{2(2L+1)(j'+1)}\left[j'C\left(j,j',L;\frac{1}{2},-\frac{1}{2},0\right)^2+(2j'+3)C\left(j,j'+1,L;\frac{1}{2},-\frac{1}{2},0\right)^2\right] & \text{if } j'=\bar{l}'-\dfrac{1}{2},\\[1.5em] \dfrac{1+(-1)^{l+\bar{l}'+L}}{2(2L+1)j'}\left[(j'+1)C\left(j,j',L;\frac{1}{2},-\frac{1}{2},0\right)^2+(2j'-1)C\left(j,j'-1,L;\frac{1}{2},-\frac{1}{2},0\right)^2\right] & \text{if } j'=\bar{l}'+\dfrac{1}{2},\end{cases} \tag{A21}$$

$$\bar{F}_{jl,j'l',L}=\frac{1+(-1)^{l+l'+L+1}}{2(2L+1)}\ C\left(jj'L;\frac{1}{2},-\frac{1}{2},0\right)^2. \tag{A22}$$

We just remark that the Clebsch-Gordan coefficients required for Eqs. (A19)–(A22) can be expressed in closed form [70].

2. ROPM integral equation for spherical systems

For spherically averaged systems the total energy functional thus reads

$$E=T_s+\int_0^\infty dr[4\pi r^2 n(r)]v(r)+E_H+E_{\mathrm{xc}}, \tag{A23}$$

$$T_s=\sum_{nlj}\Theta_{nlj}\int_0^\infty dr\ \varphi_{nlj}^T(r)\vec{T}_{lj}(r)\varphi_{nlj}(r), \tag{A24}$$

$$E_H=\frac{1}{2}\int_0^\infty dr[4\pi r^2 n(r)]v_H(r), \tag{A25}$$

$$v_H=4\pi e^2\left\{\frac{1}{r}\int_0^r dr'r'^2 n(r')+\int_r^\infty dr'r'n(r')\right\}, \tag{A26}$$

$$E_\mathrm{x}=\sum_{nlj,n'l'j'}\{\bar{E}_{\mathrm{x,RC}}^{nlj,n'l'j'}+\bar{E}_{\mathrm{x,RG}}^{nlj,n'l'j'}\}, \tag{A27}$$

$$n=\sum_{nlj}\Theta_{nlj}\varphi_{nlj}^T(r)\varphi_{nlj}(r), \tag{A28}$$

where we have used the abbreviations

$$\varphi_{nlj}(r) = \begin{pmatrix} a_{nlj}(r) \\ b_{nlj}(r) \end{pmatrix}, \qquad \text{(A29)}$$

$$\vec{T}_{lj}(r) = c \begin{pmatrix} 0 & -\vec{\partial}_r + \dfrac{\kappa}{r} \\ \vec{\partial}_r + \dfrac{\kappa}{r} & -2mc \end{pmatrix} \qquad \text{(A30)}$$

and the rest mass has been subtracted from T_s. While the transverse Hartree energy vanishes due to Eq. (A14), E_c can be any explicit or implicit functional of the density $n(r)$. The spherical KS equations may be obtained by minimizing E with respect to the radial spinors φ_{nlj}, taking into account that the latter are implicit functionals of $n(r)$,

$$\{\vec{T}_{lj}(r) + v_{\text{KS}}(r)\}\varphi_{nlj}(r) = \epsilon_{nlj}\varphi_{nlj}(r), \qquad \text{(A31)}$$

$$v_{\text{KS}}(r) = v(r) + v_H(r) + v_{\text{xc}}(r), \qquad \text{(A32)}$$

$$v_{\text{xc}}(r) = \frac{\delta E_{\text{xc}}}{\delta[4\pi r^2 n(r)]}. \qquad \text{(A33)}$$

In the case of orbital- and eigenvalue-dependent functionals, given in the nonlinear form $E_{\text{xc}}[\varphi,\epsilon,v_{\text{xc}}]$, the functional derivative with respect to the radial density $4\pi r^2 n(r)$ is replaced by functional derivatives with respect to the real radial orbitals φ_{nlj}, the eigenvalues ϵ_{nlj}, and the xc potential v_{xc}, using the chain rule for functional differentiation,

$$\frac{\delta E_{\text{xc}}[\varphi,\epsilon,v_{\text{xc}}]}{\delta[4\pi r^2 n(r)]} = \int_0^\infty dr' \frac{\delta v_{\text{KS}}(r')}{\delta[4\pi r^2 n(r)]} \sum_{nlj} \int_0^\infty dr'' \frac{\delta \varphi_{nlj}^T(r'')}{\delta v_{\text{KS}}(r')} \frac{\delta E_{\text{xc}}}{\delta \varphi_{nlj}^T(r'')} + \sum_{nlj} \frac{\delta \epsilon_{nlj}}{\delta v_{\text{KS}}(r')} \frac{\partial E_{\text{xc}}}{\partial \epsilon_{nlj}}$$

$$+ \int_0^\infty dr' \frac{\delta v_{\text{xc}}(r')}{\delta[4\pi r^2 n(r)]} \frac{\delta E_{\text{xc}}}{\delta v_{\text{xc}}(r')}.$$

Multiplication with $\delta[4\pi r^2 n(r)]/\delta v_{\text{KS}}(x)$ and subsequent integration over r then yields an integral equation for the unknown potential v_{xc},

$$\int_0^\infty dr \; \frac{\delta[4\pi r^2 n(r)]}{\delta v_{\text{KS}}(x)} v_{\text{xc}}(r) = \sum_{nlj} \int_0^\infty dr'' \frac{\delta \varphi_{nlj}^T(r'')}{\delta v_{\text{KS}}(x)} \frac{\delta E_{\text{xc}}}{\delta \varphi_{nlj}^T(r'')} + \sum_{nlj} \frac{\delta \epsilon_{nlj}}{\delta v_{\text{KS}}(x)} \frac{\partial E_{\text{xc}}}{\partial \epsilon_{nlj}} + \int_0^\infty dr'' \frac{\delta v_{\text{xc}}(r'')}{\delta v_{\text{KS}}(x)} \frac{\delta E_{\text{xc}}}{\delta v_{\text{xc}}(r'')}. \quad \text{(A34)}$$

Defining the Greens function

$$G_{nlj}(r,r') = \sum_{n'\neq n} \frac{\varphi_{n'lj}(r)\varphi_{n'lj}^T(r')}{\epsilon_{n'lj} - \epsilon_{nlj}}, \qquad \text{(A35)}$$

the linear response of the orbitals and eigenvalues with respect to a variation of v_{KS} can be written as

$$\frac{\delta \varphi_{nlj}(r)}{\delta v_{\text{KS}}(r')} = -G_{nlj}(r,r')\varphi_{nlj}(r'), \qquad \text{(A36)}$$

$$\frac{\delta \epsilon_{nlj}}{\delta v_{\text{KS}}(r)} = \varphi_{nlj}^T(r)\varphi_{nlj}(r), \qquad \text{(A37)}$$

$$\frac{\delta[4\pi r^2 n(r)]}{\delta v_{\text{KS}}(r')} = -2\sum_{nlj} \Theta_{nlj}\varphi_{nlj}^T(r)G_{nlj}(r,r')\varphi_{nlj}(r')$$

$$\equiv -2K(r,r'), \qquad \text{(A38)}$$

where $K(r,r')$ essentially represents the radial KS response function. Insertion of Eqs. (A36)–(A38) into Eq. (A34) then leads to the ROPM integral equation for spherical systems,

$$\int_0^\infty dr' K(r,r')v_{\text{xc}}(r') = Q_{\text{xc}}(r), \qquad \text{(A39)}$$

$$Q_{\text{xc}}(r) = \frac{1}{2}\left\{ \sum_{nlj} \int_0^\infty dr' \varphi_{nlj}^T(r) G_{nlj}(r,r') \frac{\delta E_{\text{xc}}}{\delta \varphi_{nlj}^T(r')} \right.$$

$$- \sum_{nlj} \varphi_{nlj}^T(r)\varphi_{nlj}(r)\frac{\partial E_{\text{xc}}}{\partial \epsilon_{nlj}}$$

$$\left. - \int_0^\infty dr' \frac{\delta v_{\text{xc}}(r')}{\delta v_{\text{KS}}(r)} \frac{\delta E_{\text{xc}}}{\delta v_{\text{xc}}(r')} \right\}. \qquad \text{(A40)}$$

As in the general situation discussed in Sec. IV, further discussion of Eqs. (A39) and (A40) requires an explicit approximation at least for $\delta v_{\text{xc}}(r')/\delta v_{\text{KS}}(r)$. While using the LDA for $\delta v_{\text{xc}}(r')/\delta v_{\text{KS}}(r)$ in the ROPM equation for some orbital-dependent E_{xc} might represent an accurate and efficient approximation to the exact ROPM, we here focus on the more systematic e^2-expansion scheme of Sec. IV. Using the fact that the exchange energy (A27) does not depend on v_{xc}, Eqs. (A39) and (A40) can be examined order by order, so that only the functional derivative of v_x with respect to v_{KS} is required in the order e^4,

$$\frac{\delta v_x(r)}{\delta v_{KS}(r')} = \int_0^\infty dr'' K^{-1}(r,r'')$$

$$\times \left\{ \frac{\delta Q_x(r'')}{\delta v_{KS}(r')} - \int_0^\infty dr''' \frac{\delta K(r'',r''')}{\delta v_{KS}(r')} v_x(r''') \right\},$$

$$(A41)$$

where

$$\frac{\delta Q_x(r)}{\delta v_{KS}(r')} = -\sum_{nlj} \int_0^\infty dr'' \varphi_{nlj}^T(r') G_{nlj}(r',r'') \frac{\delta Q_x(r)}{\delta \varphi_{nlj}^T(r'')}$$

$$+ \sum_{nlj} \varphi_{nlj}^T(r') \varphi_{nlj}(r') \frac{\partial Q_x(r)}{\partial \epsilon_{nlj}},$$

$$(A42)$$

and K^{-1} is the inverse response function. Utilizing second-order perturbation theory one easily obtains an expression for the quadratic response function,

$$\frac{\delta K(r,r')}{\delta v_{KS}(r'')} = -\frac{1}{2} \frac{\delta^2[4\pi r^2 n(r)]}{\delta v_{KS}(r'') \delta v_{KS}(r')}$$

$$= -\sum_{nlj} \Theta_{nlj}\{H_{nlj}(r,r',r'') + H_{nlj}(r',r'',r)$$

$$+ H_{nlj}(r'',r,r')\},$$

$$(A43)$$

with

$$H_{nlj}(r,r',r'') = \varphi_{nlj}^T(r) G_{nlj}(r,r') G_{nlj}(r',r'') \varphi_{nlj}(r'')$$

$$- \varphi_{nlj}^T(r) \varphi_{nlj}(r) \varphi_{nlj}^T(r')$$

$$\times \int_0^\infty dr''' G_{nlj}(r',r''') G_{nlj}(r''',r'') \varphi_{nlj}(r'').$$

$$(A44)$$

The Greens function (A35) can equivalently be defined by the differential equation

$$\{\vec{T}_{lj}(r) + v_{KS}(r) - \epsilon_{nlj}\} G_{nlj}(r,r')$$

$$= \delta(r-r') - \varphi_{nlj}(r) \varphi_{nlj}^T(r'),$$

$$(A45)$$

with the boundary conditions

$$\int_0^\infty dr' G_{nlj}(r,r') \varphi_{nlj}(r') = 0,$$

$$(A46)$$

$$G_{nlj}^T(r,r') = G_{nlj}(r',r),$$

$$(A47)$$

where Eq. (A46) is required to enforce the normalization of φ_{nlj},

$$\int_0^\infty dr\ \varphi_{nlj}^T(r) \delta\varphi_{nlj}(r) = 0.$$

As a practically useful alternative to the formal solution (A35) of Eqs. (A45)–(A47), one can thus express $G_{nlj}(r,r')$ in terms of the complementary, non-normalizable solutions χ_{nlj} of (A31) [70],

$$\{\vec{T}_{lj}(r) + v_{KS}(r)\}\chi_{nlj}(r) = \epsilon_{nlj}\chi_{nlj}(r),$$

$$(A48)$$

$$\partial_r[\varphi_{nlj}^T(r) i\sigma_y \chi_{nlj}(r)] = 0.$$

$$(A49)$$

Normalizing χ_{nlj} so that

$$c\varphi_{nlj}^T(r) i\sigma_y \chi_{nlj}(r) = 1,$$

$$(A50)$$

one has the matrix relation

$$\varphi_{nlj}(r)\chi_{nlj}^T(r) - \chi_{nlj}(r)\varphi_{nlj}^T(r) = \frac{i\sigma_y}{c}.$$

$$(A51)$$

This allows the definition of the auxiliary Greens function $\Gamma_{nlj}(r,r')$,

$$\Gamma_{nlj}(r,r') = \Theta(r-r')\varphi_{nlj}(r)\chi_{nlj}^T(r')$$

$$+ \Theta(r'-r)\chi_{nlj}(r)\varphi_{nlj}^T(r'),$$

$$(A52)$$

which, using Eq. (A51), satisfies

$$\{\vec{T}_{lj}(r) + v_{KS}(r) - \epsilon_{nlj}\}\Gamma_{nlj}(r,r') = \delta(r-r').$$

$$(A53)$$

With Eq. (A52) $G_{nlj}(r,r')$ can finally be written as

$$G_{nlj}(r,r') = \Gamma_{nlj}(r,r') + C_{nlj}\varphi_{nlj}(r)\varphi_{nlj}^T(r')$$

$$- \int_0^\infty dr'' \Gamma_{nlj}(r,r'')\varphi_{nlj}(r'')\varphi_{nlj}^T(r')$$

$$- \int_0^\infty dr'' \varphi_{nlj}(r)\varphi_{nlj}^T(r'')\Gamma_{nlj}(r'',r'),$$

$$(A54)$$

$$C_{nlj} = \int_0^\infty dr \int_0^\infty dr' \varphi_{nlj}^T(r)\Gamma_{nlj}(r,r')\varphi_{nlj}(r').$$

APPENDIX B: ASYMPTOTIC BEHAVIOR OF V_X FOR FINITE SYSTEMS

The discussion of the asymptotic behavior of the exchange-only potential for finite, spherical systems is based on the large-r limit of the ROPM integral equation (A39), which can be analyzed using the asymptotic forms of φ_{nlj} and χ_{nlj},

$$\varphi_{nlj}(r) \underset{r\to\infty}{\sim} \frac{\alpha_{nlj}}{c\gamma_{nlj}}\begin{pmatrix} c\gamma_{nlj} \\ \epsilon_{nlj} \end{pmatrix} r^{\beta_{nlj}} e^{-\gamma_{nlj}r},$$

$$(B1)$$

$$\chi_{nlj}(r) \underset{r\to\infty}{\sim} \frac{-1}{2c\alpha_{nlj}\epsilon_{nlj}}\begin{pmatrix} c\gamma_{nlj} \\ -\epsilon_{nlj} \end{pmatrix} r^{-\beta_{nlj}} e^{\gamma_{nlj}r},$$

$$(B2)$$

where

$$\gamma_{nlj} = \left[-\epsilon_{nlj} \left(2m + \frac{\epsilon_{nlj}}{c^2} \right) \right]^{1/2},$$

and the precise form of β_{nlj} depends on the asymptotic decay of the KS potential. Using Eqs. (B1) and (B2) in Eqs. (A38)–(A40) and (A54) one can explicitly verify that for large r only the highest occupied orbital is relevant in Eq. (A39). Dropping the index nlj one thus finds as asymptotic ROPM equation,

$$
\begin{aligned}
0 = & \left\{ \varphi^T(r)\varphi(r) \left[\int_0^r dr' \chi^T(r') + C \int_0^\infty dr' \varphi^T(r') \right. \right. \\
& - \int_0^r dr'' \chi^T(r'')\varphi(r'') \int_0^\infty dr' \varphi^T(r') \\
& \left. - \int_0^\infty dr' \int_0^{r'} dr'' \varphi^T(r'')\Gamma(r'',r') \right] + \chi^T(r)\varphi(r) \\
& \times \left[\int_r^\infty dr' \varphi^T(r') - \int_r^\infty dr'' \varphi^T(r'')\varphi(r'') \int_0^\infty dr' \varphi^T(r') \right] \right\} \\
& \times \left\{ \Theta \varphi(r')v_x(r') - \frac{1}{2} \frac{\delta E_x}{\delta \varphi^T(r')} \right\} + \varphi^T(r)\varphi(r) \frac{1}{2} \frac{\partial E_x}{\partial \epsilon}.
\end{aligned}
$$
$$(\text{B3})$$

Now the individual terms in Eq. (B3) have to be examined. First of all, due to the selection rules for the retarded Gaunt term, Eqs. (A20)–(A22), only multipoles with $L \neq 0$ contribute to Eq. (A18), so that $\delta E_x / \delta \varphi^T$ is asymptotically dominated by the Coulomb exchange,

$$\frac{\delta E_x}{\delta \varphi^T(r)} \underset{r \to \infty}{\sim} -2\Theta \frac{e^2}{r} \varphi(r), \tag{B4}$$

all corrections decaying faster by at least a factor $1/r$. Using

$$\varphi^T(r)\varphi(r) \underset{r \to \infty}{\sim} \alpha^2 \left[1 + \left(\frac{\epsilon}{c\gamma} \right)^2 \right] r^{2\beta} e^{-2\gamma r},$$

$$\chi^T(r)\varphi(r) \underset{r \to \infty}{\sim} -\frac{\gamma}{2\epsilon} \left[1 - \left(\frac{\epsilon}{c\gamma} \right)^2 \right]$$

and the fact that $v_x(r)$ asymptotically approaches zero, one finds

$$\int_r^\infty dr' \varphi^T(r')\varphi(r') \sim \varphi^T(r)\varphi(r),$$

$$\int_0^r dr' \chi^T(r')\varphi(r') \sim r,$$

$$\int_r^\infty dr' \varphi^T(r') \left[\Theta \varphi(r')v_x(r') - \frac{1}{2} \frac{\delta E_x}{\delta \varphi^T(r')} \right] \sim \varphi^T(r)\varphi(r),$$

and that

$$\int_0^r dr' \chi^T(r') \left\{ \Theta \varphi(r')v_x(r') - \frac{1}{2} \frac{\delta E_x}{\delta \varphi^T(r')} \right\}$$

asymptotically increases more slowly than r. The leading term in Eq. (B3) is thus given by

$$
\begin{aligned}
0 = & -\varphi^T(r)\varphi(r) \int_0^r dr'' \chi^T(r'')\varphi(r'') \int_0^\infty dr' \varphi^T(r') \\
& \times \left\{ \Theta \varphi(r')v_x(r') - \frac{1}{2} \frac{\delta E_x}{\delta \varphi^T(r')} \right\},
\end{aligned}
$$

all other contributions being suppressed by at least some small power of r or a factor of $\ln(r)/r$. This directly leads to the relativistic extension of the KLI identity [14],

$$0 = \int_0^\infty dr \ \varphi^T(r) \left\{ \Theta \varphi(r)v_x(r) - \frac{1}{2} \frac{\delta E_x}{\delta \varphi^T(r)} \right\} \tag{B5}$$

(φ is the highest occupied orbital). Insertion of Eq. (B5) into Eq. (B3) then leaves as a leading term

$$
\begin{aligned}
0 &= \varphi^T(r)\varphi(r) \int_0^r dr' \chi^T(r') \left\{ \Theta \varphi(r')v_x(r') - \frac{1}{2} \frac{\delta E_x}{\delta \varphi^T(r')} \right\} \\
&= \Theta \varphi^T(r)\varphi(r) \int_0^r dr' \chi^T(r')\varphi(r') \left\{ v_x(r') + \frac{e^2}{r'} \right\}.
\end{aligned}
$$

Consequently, one finds the same asymptotic behavior as in the nonrelativistic case,

$$v_x(r) \underset{r \to \infty}{\sim} -\frac{e^2}{r}. \tag{B6}$$

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$$\frac{1}{2}\int d^3x \int d^4y\, e^{-\epsilon(|x^0|+|y^0|)}\, \hat{j}_0^\mu(x)D_{\mu\nu}^0(x-y)\hat{j}_0^\nu(y),$$

the two field operators in $\hat{j}_0^\mu(x)$ can either be contracted with themselves or with any other field operator in a given expectation value $\langle\Phi_{KS}|T\hat{W}(0)\hat{W}(t_1)\cdots\hat{W}(t_n)|\Phi_{KS}\rangle_c$. The former type of contractions, and only this type, leads to the so-called tadpole diagrams in which one or several simple fermion loops are connected to the remainder of the diagram by a single photon line. The same holds for $\hat{j}_0^\nu(y)$, of course. The tadpole contractions can be taken care of by explicitly including them in $\hat{W}$ via addition of

$$\int d^3x \int d^4y\, e^{-\epsilon(|x^0|+|y^0|)}\, \hat{j}_0^\mu(x)D_{\mu\nu}^0(x-y)j^\nu(\mathbf{y})$$

(where symmetry under exchange of x and y has been used) and simultaneously excluding this type of contraction from the expectation value $\langle\Phi_{KS}|T\hat{W}(0)\hat{W}(t_1)\cdots\hat{W}(t_n)|\Phi_{KS}\rangle_c$. However, using Eq. (2.17) the additional term exactly cancels with

$$-\int d^3x\, e^{-\epsilon|x^0|}v_{H,\mu}(\mathbf{x})\hat{j}_0^\mu(x).$$

This allows us to drop v_H^μ in Eq. (2.44) if at the same time all tadpole contributions are omitted in the expectation value appearing in Eq. (2.45).

[65] Note that Eq. (2.47) includes all photon retardation and vacuum effects, so that renormalization is required to obtain finite results.

[66] Only the real part of the timelike component satisfies the transversality relation,

$$\partial_\mu \mathrm{Re}[\chi_{0,np}^{\mu 0}(\boldsymbol{x},\boldsymbol{y},x^0-y^0)]=0.$$

[67] Note that in spite of the nontransversality of $\chi_{DD}^{\mu\nu}$ the corresponding no-pair ground state current is conserved,

$$\boldsymbol{\nabla}\cdot\boldsymbol{j}_{\mathrm{np}}^{\mathrm{HF}}(\boldsymbol{r}) \;=\; \sum_{-mc^2<\epsilon_k\leqslant\epsilon_F} \partial_i[\,\phi_k^\dagger(\boldsymbol{r})\alpha^i\phi_k(\boldsymbol{r})\,] \;=\; 0.$$

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