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Kohn-Sham equations for multicomponent systems: The exchange and correlation energy functional

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Kohn-Sham equations for multicomponent systems are derived in a rigorous way that permits the precise definition and discussion of the exchange and correlation energy, of the system as a functional of the densities of the components. In the case of a two-component electron-ion system, with n_e, n_I the electron and ion densities, the exchange and correlation energy of the system $E_{\mathrm{xc}}[n_e, n_I]$ is composed of $E_{\mathrm{xc}}[n_e]$ the electron-electron exchange and correlation energy, $E_{\mathrm{xc}}^{II}[n_I]$ the ion-ion exchange and correlation energy, and $E_c^{eI}[n_e, n_I]$ the electron-ion correlation energy. $E_{\mathrm{xc}}[n_e]$ is exactly the functional encountered in the Kohn-Sham theory of electronic systems. The behavior of $E_{\mathrm{xc}}^{II}[n_I]$ is investigated in the limit of a large ion mass and its relation with $E_{\mathrm{xc}}[n_e]$, for $n_e = n_I$, is discussed. The structure of $E_c^{eI}[n_e, n_I]$ is analyzed in the adiabatic approximation. In the special case of perfectly localized ion densities, $E_{\mathrm{xc}}^{II}[n_I]$ results in a self-interaction correction while $E_c^{eI}[n_e, n_I]$ vanishes. [S0163-1829(98)07203-8]

I. INTRODUCTION

The theory of Kohn and Sham (KS) establishes a correspondence between an interacting electronic system and a noninteracting one with the same ground-state energy and single-particle density.[1] The difficulty of course is that the noninteracting system lies in a different density-dependent external potential that has to be approximated. Traditionally, the KS scheme is founded on the Hohenberg-Kohn (HK) theorem,[2] i.e., the 1-1 mapping between the ground-state density of the interacting electronic system and the external potential wherein it lies, a mapping also established for the time-dependent case.[3] The HK theorem has been extended to multicomponent systems establishing the 1-1 mapping between the *vector* of the component densities and the *vector* of the external potentials wherein the components lie.[4–6] Upon reflection, this implies, first, that the existence of an external potential is necessary, and second and less important, that the different components of the system should, strictly speaking, lie in different potentials. A constrained search[7,8] formulation of density-functional theory for multicomponent systems, which followed,[9–11] improved things, as it did not require any more a vector of external potentials. The existence of an external potential however, which would bind the center of mass of the system, is still useful as we shall see in the next section. KS equations for multicomponent systems have been proposed,[5] even in the time-dependent case,[12] based again on the HK theorem. In this work, the derivation is based instead on the constrained search formulation of density-functional theory for multicomponent systems, following an analogous rigorous derivation of the KS scheme for electronic systems.[13] In the resulting scheme, the difference between the exact energy and the energy of the noninteracting system give the exchange and correlation energy of the multicomponent system as a functional of the component densities. This functional is made up of exchange and correlation terms between identical particles (of the same component) and correlation terms between particles of different components. To make the presentation simple, we focus on a two-component fermion system, naming the components electrons and ions. The generalization of the formulation to systems with more components is trivial.

In the following section, the necessary definitions of the various functionals are given, the basic KS theorem is proved, and finally the KS equations are derived. In the next and final section, the exchange and correlation energy of the electron-ion system, is split naturally in the electron-electron exchange and correlation energy, the ion-ion exchange and correlation energy, and the electron-ion correlation energy. The electron-electron exchange and correlation energy is immediately seen to coincide with the exchange and correlation functional encountered in the KS theory for electronic systems. Restricting then the attention to systems where the mass of the ions is indeed much larger than the mass of the electrons, we analyze the structure and discuss the properties of the remaining two functionals.

Finally, it is noted that the method can provide an alternative to the adiabatic or Born-Oppenheimer (BO) approximation, which applies for a full quantum-mechanical treatment of a system, when we can distinguish its components as ‘‘heavy’’ and ‘‘light’’ or ‘‘slow’’ and ‘‘fast.’’ In the adiabatic approximation the wave function of the system is partitioned as a product of an electronic wave function depending parametrically on the ionic positions, multiplied by an ionic wave function. The electronic wave function is chosen to be the ground state of the electronic part of the total Hamiltonian, and it must be calculated for any possible ionic configuration, which becomes computationally forbidding when the number of ions increases. The theory that we develop, in principle, could be applied to calculations requiring accuracy beyond the adiabatic approximation, provided that accurate enough functionals were available. Presently, the analysis of the electron-ion correlation functional is entirely within the adiabatic approximation. Still, the method can be particularly useful for systems where the number of heavy particles (ions) is not very small and the application of the BO approximation is computationally difficult.

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II. THE KOHN-SHAM SCHEME

Let us consider, for simplicity, a two-component, N fermion system, containing S and $N-S$ particles of each component. Having in mind a system of electrons and ions, we shall call the first kind of particles electrons and the other ions. Electrons will be denoted with lower-case letters, and ions with upper-case letters. We further suppress the spin variables. It is understood that the formulas are integrated over the spin variables throughout.

For any N-particle state Ψ_{eI} that represents such a system, we shall say that $\Psi_{eI}\rightarrow(n_e,n_I)$, when

$$n_e(\mathbf{r})=S\int\int d\mathbf{R}^{N-S}d\mathbf{r}_2\cdots d\mathbf{r}_S \times|\Psi_{eI}(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_S;\mathbf{R}_1,\ldots,\mathbf{R}_{N-S})|^2, \tag{1}$$

$$n_I(\mathbf{R})=(N-S)\int\int d\mathbf{r}^S d\mathbf{R}_2\cdots d\mathbf{R}_{N-S} \times|\Psi_{eI}(\mathbf{r}_1,\ldots,\mathbf{r}_S;\mathbf{R},\mathbf{R}_2,\ldots,\mathbf{R}_{N-S})|^2, \tag{2}$$

or in second quantization,

$$n_e(\mathbf{r})=\langle\Psi_{eI}|\psi^\dagger(\mathbf{r})\psi(\mathbf{r})|\Psi_{eI}\rangle,$$

$$n_I(\mathbf{r})=\langle\Psi_{eI}|\Psi^\dagger(\mathbf{r})\Psi(\mathbf{r})|\Psi_{eI}\rangle,$$

where $\psi^\dagger(\mathbf{r})$, $\psi(\mathbf{r})$, $\Psi^\dagger(\mathbf{r})$, and $\Psi(\mathbf{r})$ are electron and ion creation and annihilation field operators.

The Hamiltonian that describes the system in second quantization is

$$H=T_e+T_I+V_{ee}+V_{II}+V_{eI}+U,$$

where

$$T_e=-\frac{1}{2}\int d\mathbf{r}\psi^\dagger(\mathbf{r})\nabla^2\psi(\mathbf{r}),$$

$$T_I=-\frac{1}{2M}\int d\mathbf{r}\Psi^\dagger(\mathbf{r})\nabla^2\Psi(\mathbf{r}),$$

$$V_{ee}=\frac{1}{2}\int\int d\mathbf{r}d\mathbf{r}'\,\frac{\psi^\dagger(\mathbf{r})\psi^\dagger(\mathbf{r}')\psi(\mathbf{r}')\psi(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|},$$

$$V_{II}=\frac{Z^2}{2}\int\int d\mathbf{r}d\mathbf{r}'\,\frac{\Psi^\dagger(\mathbf{r})\Psi^\dagger(\mathbf{r}')\Psi(\mathbf{r}')\Psi(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|},$$

$$V_{eI}=-Z\int\int d\mathbf{r}d\mathbf{r}'\,\frac{\psi^\dagger(\mathbf{r})\psi(\mathbf{r})\Psi^\dagger(\mathbf{r}')\Psi(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|},$$

$$U=\int d\mathbf{r}\psi^\dagger(\mathbf{r})\psi(\mathbf{r})U(\mathbf{r})+\int d\mathbf{r}\Psi^\dagger(\mathbf{r})\Psi(\mathbf{r})U(\mathbf{r}).$$

We have used atomic units, setting $\hbar=m=e=1$, where $-e,m$ are the charge and mass of the electron. The charge and mass of an ion, in atomic units are Z,M. $U(\mathbf{r})$ is the external potential of the system. In the formulation it is chosen to be common for the two components. It may in principle differ, but it may not be set to zero without consideration, because then, the center of mass (cm) of the physical system will not be bound, leading to conceptual difficulties regarding whether our functionals (in particular, the KS functional) are bound and well defined or not. One can argue that in nature multicomponent systems, usually, do not need the presence of an external potential to bind them and it would be preferable to formulate the theory in the absence of an external field. This problem is present in any kind of calculation of such systems, and what one usually does is to factor away the cm of the system and deal with the particles that correspond to the remaining relative coordinates. As a result, the wave function becomes complicated with respect to its symmetry properties under exchange of the particles. In an electron-ion system, where the mass of the ions is much larger than the mass of the electrons, the cm of the system coincides with the cm of the ions and, in many cases, the problem of symmetry can be ignored, as exchange effects in ions are often not important. In these cases, one can still use, unchanged, the present formalism. I should remark, with respect to my criticism in the Introduction, that factoring away the cm coordinate can also resolve the situation in the equivalent formulation of the theory that is based on the HK theorem. To conclude, in order not to complicate the formulation with the question of the symmetry of the wave function and, in order to obtain a general method, I prefer to keep, in the derivation of the KS equations, a common external potential.

We next define the following functionals:

$$G[n_e,n_I]=\min_{|\Psi\rangle\rightarrow(n_e,n_I)}\langle\Psi|T_e+T_I+V_{ee}+V_{II}+V_{eI}|\Psi\rangle, \tag{3}$$

$$G_0[n_e,n_I]=\min_{|\Omega\rangle\rightarrow n_I}\langle\Omega|T_I|\Omega\rangle+\min_{|\omega\rangle\rightarrow n_e}\langle\omega|T_e|\omega\rangle, \tag{4}$$

where the minimization in G is over all states Ψ which yield (n_e,n_I), while the minimizations in G_0 are over S and $(N-S)$-particle Slater determinants (noninteracting states) that yield n_e and n_I. The first functional $G[n_e,n_i]$ is the basic functional introduced by Capitani, Nalewajski, and Parr[9] in the constrained search formulation of density-functional theory of molecular systems. The minima in Eqs. (3) and (4) should be rigorously defined as infima; we assume, however, that minimizing states exist and that they are in fact minima. Let us denote the minimizing states by $\Psi_{n_e,n_I},\Omega_{n_I},\omega_{n_e}$. Then

$$G[n_e,n_I]=\langle\Psi_{n_e,n_I}|T_e+T_I+V_{ee}+V_{II}+V_{eI}|\Psi_{n_e,n_I}\rangle, \tag{5}$$

$$G_0[n_e,n_I]=\langle\Omega_{n_I}|T_I|\Omega_{n_I}\rangle+\langle\omega_{n_e}|T_e|\omega_{n_e}\rangle. \tag{6}$$

We further define the exchange and correlation energy functional,

$$E_{\mathrm{xc}}[n_e,n_I]=G[n_e,n_I]-G_0[n_e,n_I]-\frac{1}{2}\int\int d\mathbf{r}d\mathbf{r}'\,\frac{n_e(\mathbf{r})n_e(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}-\frac{Z^2}{2}\int\int d\mathbf{r}d\mathbf{r}'\,\frac{n_I(\mathbf{r})n_I(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+Z\int\int d\mathbf{r}d\mathbf{r}'\,\frac{n_e(\mathbf{r})n_I(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|};\tag{7}$$

and finally the KS functional,

$$E[\omega,\Omega]=\langle\Omega|\langle\omega|T_e+T_I+U|\omega\rangle|\Omega\rangle+\frac{1}{2}\int\int d\mathbf{r}d\mathbf{r}'\,\frac{n_\omega(\mathbf{r})n_\omega(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+\frac{Z^2}{2}\int\int d\mathbf{r}d\mathbf{r}'\,\frac{n_\Omega(\mathbf{r})n_\Omega(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}-Z\int\int d\mathbf{r}d\mathbf{r}'\,\frac{n_\omega(\mathbf{r})n_\Omega(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+E_{\mathrm{xc}}[n_\omega,n_\Omega].$$

n_ω and n_Ω in an obvious notation mean that $\omega\rightarrow n_\omega$, $\Omega\rightarrow n_\Omega$. The last functional E is not a functional of the densities but a functional of the noninteracting S and $(N-S)$-particle states ω and Ω. The last functional will establish the mapping of the ground state of the interacting two-component system to a noninteracting two-component system, represented by the product $|\omega_0\rangle|\Omega_0\rangle$, where $|\omega_0\rangle$ and $|\Omega_0\rangle$ minimize $E[\omega,\Omega]$. We are now in a position to show the basic theorem.

Theorem. (1) $E[\omega,\Omega]\geqslant E_0$, and further if $(n_\omega,n_\Omega)\neq(n_{e0},n_{I0})$, then $E[\omega,\Omega]>E_0$, where E_0 is the ground-state energy of the system, and n_{e0},n_{I0} are the ground-state electron and ion densities. (2) Noninteracting S and $(N-S)$-particle states ω_0 and Ω_0 exist for which the KS functional E attains its minimum: $E[\omega_0,\Omega_0]=E_0$. For these ω_0 and Ω_0, we have, $(n_{\omega_0},n_{\Omega_0})=(n_{e0},n_{I0})$.

Proof. Using Eqs. (5), (6), and (7) the KS functional can be written

$$E[\omega,\Omega]=\langle\Psi_{n_\omega,n_\Omega}|H|\Psi_{n_\omega,n_\Omega}\rangle+\langle\omega|T_e|\omega\rangle+\langle\Omega|T_I|\Omega\rangle-\langle\omega_{n_\omega}|T_e|\omega_{n_\omega}\rangle-\langle\Omega_{n_\Omega}|T_I|\Omega_{n_\Omega}\rangle.\tag{8}$$

Therefore, $E[\omega,\Omega]\geqslant\langle\Psi_{n_\omega,n_\Omega}|H|\Psi_{n_\omega,n_\Omega}\rangle\geqslant E_0$. When $(n_\omega,n_\Omega)\neq(n_{e0},n_{I0})$ then, $\Psi_{n_\omega,n_\Omega}\neq\Psi_0=\Psi_{n_{e0},n_{I0}}$ and $E[\omega,\Omega]\rangle E_0$. This completes the proof of the first part of the theorem. Consider now the ground-state density (n_{e0},n_{I0}) of the system. Minimizing noninteracting states $\omega_{n_{e0}},\Omega_{n_{I0}}$ exist for $G_0[n_{e0},n_{I0}]$ and the KS functional takes the value $E[\omega_{n_{e0}},\Omega_{n_{I0}}]=\langle\Psi_{n_{e0},n_{I0}}|H|\Psi_{n_{e0},n_{I0}}\rangle=E_0$, which completes the second part of the theorem.

The noninteracting states ω,Ω in the definition of $E[\omega,\Omega]$, are S and $(N-S)$-particle Slater determinants built on the orbitals $\{\phi_i\}$ and $\{\Phi_j\}$: $\omega=\det[\phi_1,\dots,\phi_S]$ and $\Omega=\det[\Phi_1,\dots,\Phi_{N-S}]$. $E[\omega,\Omega]$ is, therefore, a functional of the orbitals $\{\phi_i\}$ and $\{\Phi_j\}$. Assuming that they are the minimizing orbitals, and by varying the orbitals $\{\phi_i\}$ and $\{\Phi_j\}$ independently, we obtain the KS equations for the multicomponent system:

$$\left\{-\frac{\nabla^2}{2}+U(\mathbf{r})+v_{\mathrm{xc}}[n_\omega,n_\Omega](\mathbf{r})+\int d\mathbf{r}'\,\frac{n_\omega(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}-Z\int d\mathbf{r}'\,\frac{n_\Omega(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\right\}\phi_i(\mathbf{r})=\epsilon_i\phi_i(\mathbf{r}),\tag{9}$$

$$\left\{-\frac{\nabla^2}{2M}+U(\mathbf{r})+V_{\mathrm{xc}}[n_\omega,n_\Omega](\mathbf{r})+Z^2\int d\mathbf{r}'\,\frac{n_\Omega(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}-Z\int d\mathbf{r}'\,\frac{n_\omega(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\right\}\Phi_j(\mathbf{r})=E_j\Phi_j(\mathbf{r}),\tag{10}$$

where

$$v_{\mathrm{xc}}[n_e,n_I]=\frac{\delta E_{\mathrm{xc}}[n_e,n_I]}{\delta n_e}\quad\text{and}\quad V_{\mathrm{xc}}[n_e,n_I]=\frac{\delta E_{\mathrm{xc}}[n_e,n_I]}{\delta n_I},$$

$$n_\omega(\mathbf{r})=\Sigma_{i=1}^{S}|\phi_i(\mathbf{r})|^2,$$

and

$$n_\Omega(\mathbf{r})=\Sigma_{j=1}^{N-S}|\Phi_j(\mathbf{r})|^2,$$

Observe that taking $M=1$, $Z=-1$ we can regard the above equations as the unrestricted KS equations for an N-electron system with $S,N-S$ spin-up and spin-down electrons in the absence of a magnetic field.

III. THE EXCHANGE-CORRELATION ENERGY FUNCTIONAL

We proceed to analyze the structure of the exchange and correlation energy functional. We can split G_0 naturally: $G_0=G_0^e+G_0^I$, with $G_0^e[n_e]=\min_{|\omega\rangle\rightarrow n_e}\langle\omega|T_e|\omega\rangle$ and $G_0^I[n_I]=\min_{|\Omega\rangle\rightarrow n_I}\langle\Omega|T_I|\Omega\rangle$. Then $G_0^e[n_e]=\langle\omega_{n_e}|T_e|\omega_{n_e}\rangle$ and $G_0^I[n_I]=\langle\Omega_{n_I}|T_I|\Omega_{n_I}\rangle$.

We further introduce the functionals: $G^e[n_e]=\min_{|\psi\rangle\rightarrow n_e}\langle\psi|T_e+V_{ee}|\psi\rangle$, $G^I[n_I]=\min_{|\Psi\rangle\rightarrow n_I}\langle\Psi|T_I+V_{II}|\Psi\rangle$. The minimizations are over all (interacting) S and $(N-S)$-particle states, that yield n_e and n_I. $G^e[n_e]$ is the extension of the HK functional introduced by Levy[7] in the constrained search formulation of density-functional theory for electronic systems, and $G^I[n_I]$ is its equivalent for ionic systems. Finally, I define the electron-electron, ion-ion exchange and correlation, and the electron-ion correlation energy functionals as

$$E_{\mathrm{xc}}[n_e]=G^e[n_e]-G_0^e[n_e]-\frac{1}{2}\int\int d\mathbf{r}d\mathbf{r}'\,\frac{n_e(\mathbf{r})n_e(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|},\tag{11}$$

$$E_{\mathrm{xc}}^{II}[n_I]=G^I[n_I]-G_0^I[n_I]-\frac{Z^2}{2}\int\int d\mathbf{r}d\mathbf{r}'\,\frac{n_I(\mathbf{r})n_I(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|},\tag{12}$$

$$E_c^{eI}[n_e,n_I]=G[n_e,n_I]-G^e[n_e]-G^I[n_I]+Z\int\int d\mathbf{r}d\mathbf{r}'\,\frac{n_e(\mathbf{r})n_I(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \tag{13}$$

The exchange-correlation energy functional of the multicomponent system is their sum: $E_{\mathrm{xc}}^{eI}[n_e,n_I]=E_{\mathrm{xc}}[n_e]+E_{\mathrm{xc}}^{II}[n_I]+E_c^{eI}[n_e,n_I]$. $E_{\mathrm{xc}}[n]$ is the exchange and correlation energy of the electronic subsystem, which appears in the usual formulation of the KS equations for electron systems. It is a functional of the electron density only. $E_{\mathrm{xc}}^{II}[n]$ is the exchange and correlation energy of the ionic subsystem. It is a functional of the ion density only. $E_c^{eI}[n_e,n_I]$ is the electron-ion correlation energy and it is a functional of both the electron and ion densities. Approximations in the literature are abundant for the electron-electron exchange-correlation functional. In the rest of the paper, restricting ourselves to the case where the mass of the ions is indeed much larger than the mass of the electrons, we shall try to analyze the structure and discuss the properties of the last two functionals.

A. The ion-ion exchange-correlation energy functional

The ion-ion exchange-correlation energy functional $E_{\mathrm{xc}}^{II}[n]$ has a similar form to $E_{\mathrm{xc}}[n]$, the electron-electron exchange-correlation energy functional, the main difference being the parameter $\lambda=1/M$ that appears in front of the kinetic-energy operator. We write, therefore, $E_{\mathrm{xc}}^{II}[n]=E_{\mathrm{xc}}^{II}[\lambda,n]$, where

$$E_{\mathrm{xc}}^{II}[\lambda,n]=\min_{|\Psi\rangle\to n}\langle\Psi|\lambda T+V_{II}|\Psi\rangle-\lambda\min_{|\Omega\rangle\to n}\langle\Omega|T|\Omega\rangle-\frac{Z^2}{2}\int\int d\mathbf{r}d\mathbf{r}'\,\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}, \tag{14}$$

where T is the kinetic-energy operator for fermions of unit mass $T_I=\lambda T$.

We shall investigate the behavior of $E_{\mathrm{xc}}^{II}[\lambda,n]$ as we vary λ. The techniques we are going to use can be equally applied to derive the coupling constant integration formula,[14,15] which is the analogue of Eq. (20). They also resemble the methods employed in the work of Bauer[16] and Bass.[17]

Let the minimizing state of the functional

$$G^I[\lambda,n]=\min_{|\Psi\rangle\to n}\langle\Psi|\lambda T+V_{II}|\Psi\rangle \tag{15}$$

be denoted by Ψ_n^λ. Under some mild assumptions it satisfies the Schrödinger equation,[13,18,19]

$$\left\{\lambda T+V_{II}+\int d\mathbf{r}\Psi^\dagger(\mathbf{r})\Psi(\mathbf{r})U_n^\lambda(\mathbf{r})\right\}|\Psi_n^\lambda\rangle=E_n^\lambda|\Psi_n^\lambda\rangle, \tag{16}$$

where the local external potential U_n^λ appears as an infinite number of Lagrange multipliers to satisfy the density constraint.[13] It is also a function of the parameter λ, because if we consider that λ is varied in some way, keeping the density fixed, U_n^λ will correspondingly change, in such a way that the density of Ψ_n^λ will remain unchanged.

One can show that the functional $G^I[\lambda,n]$ is continuous with respect to λ for fixed density n. It is reasonable then to assume that the minimizing state Ψ_n^λ and the external potential U_n^λ are continuous with respect to λ as well. We further assume that Ψ_n^λ is differentiable with respect to λ, i.e., if $\lambda+\epsilon$ is a neighboring value of the parameter, with $\epsilon\ll\lambda$, we can expand

$$\Psi_n^{\lambda+\epsilon}=\Psi_n^\lambda+\epsilon\Psi'^{\lambda}_n$$

with

$$\langle\Psi'^{\lambda}_n|\Psi_n^\lambda\rangle=0,\ \ \langle\Psi'^{\lambda}_n|T|\Psi'^{\lambda}_n\rangle<\infty,\ \ \langle\Psi'^{\lambda}_n|V_{II}|\Psi'^{\lambda}_n\rangle<\infty. \tag{17}$$

Requiring that $\Psi_n^{\lambda+\epsilon}$ and Ψ_n^λ both have the same density, we have

$$\langle\Psi'^{\lambda}_n|\Psi^\dagger(\mathbf{r})\Psi(\mathbf{r})|\Psi_n^\lambda\rangle+\text{c.c.}=0. \tag{18}$$

If we multiply Eq. (16) on the left by $\langle\Psi'^{\lambda}_n|$ and use Eqs. (17) and (18), we get

$$\langle\Psi'^{\lambda}_n|\lambda T+V_{II}|\Psi_n^\lambda\rangle+\text{ c.c.}=0. \tag{19}$$

Using Eq. (19), the derivative of $G^I[\lambda,n]$ with respect to λ is easily calculated:

$$\frac{\delta G^I[\lambda,n]}{\delta\lambda}\equiv\lim_{\epsilon\to0}\frac{G^I[\lambda+\epsilon,n]-G^I[\lambda,n]}{\epsilon}=\langle\Psi_n^\lambda|T|\Psi_n^\lambda\rangle.$$

This is a version of the Hellman-Feynman theorem, which was not readily applicable because the minimization in the functional $G^I[\lambda,n]$ is under the constraint of fixed density. The ion-ion exchange-correlation functional can be written

$$E_{\mathrm{xc}}^{II}[\lambda,n]=\min_{|\Psi\rangle\to n}\langle\Psi|V_{II}|\Psi\rangle-\frac{Z^2}{2}\int\int d\mathbf{r}d\mathbf{r}'\,\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+\int_0^\lambda d\kappa\langle\Psi_n^\kappa|T|\Psi_n^\kappa\rangle-\lambda\min_{|\Omega\rangle\to n}\langle\Omega|T|\Omega\rangle. \tag{20}$$

By the mean value theorem, μ exists, $0<\mu<\lambda$ such that

$$E_{\mathrm{xc}}^{II}[\lambda,n]=\min_{|\Psi\rangle\to n}\langle\Psi|V_{II}|\Psi\rangle-\frac{Z^2}{2}\int\int d\mathbf{r}d\mathbf{r}'\,\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+\lambda\Big[\langle\Psi_n^\mu|T|\Psi_n^\mu\rangle-\min_{|\Omega\rangle\to n}\langle\Omega|T|\Omega\rangle\Big], \tag{21}$$

where Ψ_n^μ is the minimizing state of $G^I[\mu,n]$. For $\lambda\ll1$ we can regard the term proportional to λ as a small correction only and E_{xc}^{II} can be approximated by the first two terms of the right-hand side Supposing we have the same number of ions and electrons, one may ask the question, for the same electron and ion density n, how are the functionals $E_{\mathrm{xc}}[n]$ and $E_{\mathrm{xc}}^{II}[n]$ related? We can factor out Z^2 from $E_{\mathrm{xc}}^{II}[n]$ introducing V, the repulsion energy operator for fermions of unit charge, $V_{II}=Z^2V$. Then

$$E_{\mathrm{xc}}^{II}[\lambda,n]=Z^2\Bigg\{\min_{|\Psi\rangle\to n}\langle\Psi|V|\Psi\rangle-\frac{1}{2}\int\int d\mathbf{r}d\mathbf{r}'\,\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$+\int_0^{\lambda/Z^2} d\kappa \langle \Psi_n^{\kappa Z^2} | T | \Psi_n^{\kappa Z^2} \rangle$$

$$\left. - \frac{\lambda}{Z^2} \min_{|\Omega\rangle \to n} \langle \Omega | T | \Omega \rangle \right\},$$

where $\Psi_n^{\kappa Z^2}$ is the minimizing state of $\langle \kappa Z^2 T + Z^2 V \rangle = Z^2 \langle \kappa T + V \rangle$. The minimization is independent of Z^2 and we write $\Psi_n^{\kappa Z^2} = \psi_n^\kappa$. We recognize the nonnegative difference $\langle \psi_n^\kappa | \kappa T | \Psi_n^\kappa \rangle - \kappa \min_{|\Omega\rangle \to n} \langle \Omega | T | \Omega \rangle$ as the kinetic component of the exchange and correlation energy functional $T_{\text{xc}}^\kappa[n]$ of a fermion system with particles of unit charge and mass $1/\kappa$. The ion-ion exchange and correlation energy functional finally takes the form

$$\frac{1}{Z^2} E_{\text{xc}}^{II}[n] = \min_{|\Psi\rangle \to n} \langle \Psi | V | \Psi \rangle - \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$+ \int_0^{1/MZ^2} \frac{d\kappa}{\kappa} T_{\text{xc}}^\kappa[n].$$

Putting $M = Z^2 = 1$, we obtain the electron-electron exchange and correlation energy functional. The two functionals are related by

$$E_{\text{xc}}[n] = \frac{1}{Z^2} E_{\text{xc}}^{II}[n] + \int_{\frac{1}{MZ^2}}^{1} \frac{d\kappa}{\kappa} T_{\text{xc}}^\kappa[n] \tag{22}$$

and we see $Z^2 E_{\text{xc}}[n] > E_{\text{xc}}^{II}[n]$. Equation (22) suggests that we use an approximate form for $E_{\text{xc}}[n]$ and subtract the kinetic-energy contribution $T_{\text{xc}}[n]$ (approximating the integral by $T_{\text{xc}}[n]$), to obtain an approximation for $E_{\text{xc}}^{II}[n]$. Properly, one should use $E_{\text{xc}}[n]$ functionals appropriate to describe systems of localized electrons as in the Wigner crystal.[20,21] The kinetic component of an exchange-correlation functional for an electronic system can be easily obtained after Levy and Perdew,[22] introducing the scaled density $n_\gamma(\mathbf{r}) = \gamma^3 n(\gamma \mathbf{r})$,

$$T_{\text{xc}}[n] = -E_{\text{xc}}[n] + \left. \frac{\partial E_{\text{xc}}[n_\gamma]}{\partial \gamma} \right|_{\gamma = 1}.$$

The natural approximation for the ionic densities is the opposite of the uniform density, since the particles are localized. We will, therefore, investigate the form of $E_{\text{xc}}^{II}[n]$, in the limit where the ions are perfectly localized ($\lambda \to 0$). In that case, the zero-order term of the exchange-correlation functional [first two terms on the right-hand side of Eq. (21)] gives a self-interaction correction,

$$-\frac{Z^2}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{\sum_{j=1}^{N-S} |\Phi_j(\mathbf{r})|^2 |\Phi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|},$$

where $n_I(\mathbf{r}) = \Sigma_j |\Phi_j(\mathbf{r})|^2$. Further, the expectation value of V_{II} for states that yield perfectly localized densities is fixed and the minimization in Eq. (15) involves the kinetic-energy operator alone. Hence the two terms in brackets in Eq. (21) cancel and the ion-ion exchange-correlation energy results only in a self-interaction correction in agreement with Gross, Dobson, and Petersilka.[12] Note that the self-interaction correction does not depend on the density directly, but on the arbitrary choice of the orbitals $|\Phi_j(\mathbf{r})|^2$, hence use of this form of E_{xc}^{II} implies that nondiagonal Lagrange multipliers are necessary in Eq. (10) to ensure orthogonality of $\{\Phi_j\}$.

I would like to remark that if the ionic density is approximated as a sum of Gaussian distributions, their width, following the discussion in Refs. 23 and 24, will be of the order of $\lambda^{1/4}$, using the Bohr radius as a unit of length. Therefore, ionic localization is far from perfect[25] and the range of validity of the approximation, in which the ions are assumed perfectly localized, needs to be examined.

B. The electron-ion correlation energy functional

The electron-ion correlation energy functional remains which, to my knowledge has not been considered or defined previously in the literature. It can be equivalently defined as

$$E_c^{eI}[n_e, n_I]$$

$$= \min_{\Psi_{eI} \to (n_e, n_I)} \langle \Psi_{eI} | T_e + T_I + V_{ee} + V_{II} + V_{eI} | \Psi_{eI} \rangle$$

$$- \min_{\substack{\psi \to n_e \\ \Psi \to n_I}} \langle \Psi | \langle \psi | T_e + T_I + V_{ee} + V_{II} + V_{eI} | \psi \rangle | \Psi \rangle.$$

In the second term of the right-hand side the minimization is over states that can be written as a product of an electronic state that yields n_e and an ionic state, which yields n_I, and hence electron-ion correlation in the expectation value is ignored. The minimizing state Ψ_{n_e, n_I} of $G[n_e, n_I]$ satisfies the Schrödinger equation,

$$\left\{ T_e + T_I + V_{ee} + V_{II} + V_{eI} + \int d\mathbf{r} \psi^\dagger(\mathbf{r}) \psi(\mathbf{r}) v_{n_e}(\mathbf{r}) \right.$$

$$\left. + \int d\mathbf{r} \Psi^\dagger(\mathbf{r}) \Psi(\mathbf{r}) U_{n_I}(\mathbf{r}) \right\} | \Psi_{n_e, n_I} \rangle = E_{n_e, n_I} | \Psi_{n_e, n_I} \rangle. \tag{23}$$

The external potentials v_{n_e} and U_{n_I} appear again as Lagrange multipliers to satisfy the density constraint. In the adiabatic or BO approximation the minimizing wave function is factored:

$$\Psi_{n_e, n_I}(\mathbf{r}_1, \ldots, \mathbf{r}_S, \mathbf{R}_1, \ldots, \mathbf{R}_{N-S})$$

$$= \psi_{\text{BO}}[\mathbf{R}_1, \ldots, \mathbf{R}_{N-S}](\mathbf{r}_1, \ldots, \mathbf{r}_S)$$

$$\times \Psi_{\text{BO}}(\mathbf{R}_1, \ldots, \mathbf{R}_{N-S}), \tag{24}$$

where the electronic state $\psi_{\text{BO}}[\{\mathbf{R}_i\}]$, $1 \leqslant i \leqslant N - S$, in a mixed second quantization notation, is the ground state for fixed $\{\mathbf{R}_i\}$ of the electronic Hamiltonian $H_e[\{\mathbf{R}_i\}] = T_e + V_{ee} + \int d\mathbf{r} \psi^\dagger(\mathbf{r}) \psi(\mathbf{r}) \{ v_{n_e}(\mathbf{r}) - Z \Sigma_j 1/|\mathbf{r} - \mathbf{R}_j| \}$ with eigenvalue $E[\{\mathbf{R}_i\}] + \int d\mathbf{r} n_e(\mathbf{r}) v_{n_e}(\mathbf{r})$. The wave function $\Psi_{\text{BO}}(\{\mathbf{R}_i\})$ is the ground state of the effective Hamiltonian

$$H_{\text{eff}} = E[\{\mathbf{R}_i\}] + \sum_{j=1}^{N-S} \left\{ -\frac{1}{2M} (\boldsymbol{\nabla}_{\mathbf{R}_j} - i \mathbf{A}_j)^2 + \frac{Z^2}{2} \sum_{i, i \neq j}{}' \frac{1}{|\mathbf{R}_{ij}|} \right.$$

$$+\frac{1}{2M}\left(\langle\nabla_{\mathbf{R}_j}\psi_{\mathrm{BO}}|\nabla_{\mathbf{R}_j}\psi_{\mathrm{BO}}\rangle-A_j^2\right)+U_{n_I}(\mathbf{R}_j)\Bigg\},\tag{25}$$

where the vector potential is given by

$$\begin{aligned}\mathbf{A}_j[\{\mathbf{R}_i\}]&=i\langle\psi_{\mathrm{BO}}[\{\mathbf{R}_i\}]|\nabla_{\mathbf{R}_j}\psi_{\mathrm{BO}}[\{\mathbf{R}_i\}]\rangle\\&=-i\langle\nabla_{\mathbf{R}_j}\psi_{\mathrm{BO}}[\{\mathbf{R}_i\}]|\psi_{\mathrm{BO}}[\{\mathbf{R}_i\}]\rangle\end{aligned}$$

(since $\psi_{\mathrm{BO}}[\{\mathbf{R}_i\}]$ is normalized) and has a vanishing curl if $\psi_{\mathrm{BO}}[\{\mathbf{R}_i\}]$ can be chosen to be real, single valued and continuous with respect to $\{\mathbf{R}_i\}$.[26] The ions, therefore, are subject to the influence of the following terms: (i) The scalar potential $E[\{\mathbf{R}_i\}]$, which is the ground-state energy of the interacting electronic system in the presence of localized ions at positions $\{\mathbf{R}_i\}$. The expectation value of this term gives the main contribution to the correlation energy after subtracting $G_e[n_e]-Z\int\int d\mathbf{r}d\mathbf{r}'(n_e(\mathbf{r})n_I(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|)$. (ii) The ion kinetic energy in the presence of the vector potential $\mathbf{A}_j[\{\mathbf{R}_i\}]$ and the ion repulsion energy. The vector potential has nonvanishing circulation around the points in the configuration space of ion coordinates where the electronic ground state $\psi_{\mathrm{BO}}[\{\mathbf{R}_i\}]$ is degenerate. This term gives a Berry phase correction to $G_I[n_I]$.[27] (iii) The small potential energy $(1/2M)(\langle\nabla_{\mathbf{R}_j}\psi_{\mathrm{BO}}|\nabla_{\mathbf{R}_j}\psi_{\mathrm{BO}}\rangle-A_j^2)$, which appears in an analogous way to the centrifugal energy term in the equations of motion of a classical system when one adopts a rotating system of reference.[23]

The complexity of the electron-ion correlation energy functional is evident. Both the scalar potential $E[\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}_{N-S}]$ and the vector potential $\mathbf{A}_j[\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}_{N-S}]$ represent $(N-S)$-body interactions. Further, the appearance of the vector potential suggests that, in the case of the ionic subsystem, it might be more appropriate to use single-particle equations, formally similar to those in current-density–functional theory,[28] in which the vector potential appears explicitly. It should be noted that the vector potential appears only in the context of the adiabatic approximation and depends on the electron and ion densities. It does not correspond to an external magnetic field and, therefore, current-density–functional theory is not applicable. The question remains valid, however, and elsewhere we shall attempt to partially take into account the electron-ion correlation by including additional potential terms (like the vector potential) in the single-particle equations, so that the correlation energy functional, remaining to be approximated, will be smaller.

Further analysis of the electron-ion correlation functional at this point is difficult. In the rest of the present work, we restrict ourselves to investigating whether, in the limit of perfectly localized ion densities, the electron-ion correlation functional vanishes or gives a correction. In this limit, we have seen that the ions are uncorrelated. One could imagine, however, that, in the adiabatic approximation, some electron-ion correlation could remain at least for the Berry phase correction.

Let us consider an artificial parameter λ that couples the electron-ion interaction only and varies in the interval $0\leqslant\lambda\leqslant1$. We can easily obtain a coupling constant integration formula[14,15] for the electron-ion correlation:

$$\begin{aligned}E_c^{eI}[n_e,n_I]=&\int_0^1 d\lambda\langle\Psi^{\lambda}_{n_e,n_I}|V_{eI}|\Psi^{\lambda}_{n_e,n_I}\rangle\\&+Z\int\int d\mathbf{r}d\mathbf{r}'\frac{n_e(\mathbf{r})n_I(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|},\end{aligned}\tag{26}$$

where $\Psi^{\lambda}_{n_e,n_I}$ is that multicomponent state that minimizes $\langle T_e+T_I+V_{ee}+V_{II}+\lambda V_{eI}\rangle$ under the constraint of fixed electronic and ionic densities n_e,n_I. Employing the adiabatic approximation we factor $\Psi^{\lambda}_{n_e,n_I}(\{\mathbf{r}_i\};\{\mathbf{R}_j\})=\psi^{\lambda}_{\mathrm{BO}}[\{\mathbf{R}_j\}](\{\mathbf{r}_i\})\Psi^{\lambda}_{\mathrm{BO}}(\{\mathbf{R}_j\})$, and since $\Psi^{\lambda}_{n_e,n_I}\rightarrow(n_e,n_I)$ we have $\Psi^{\lambda}_{\mathrm{BO}}\rightarrow n_I$ and

$$\begin{aligned}&\int d\mathbf{R}^{N-S}|\Psi^{\lambda}_{\mathrm{BO}}(\{\mathbf{R}_j\})|^2\langle\psi^{\lambda}_{\mathrm{BO}}[\{\mathbf{R}_j\}]|\psi^{\dagger}(\mathbf{r})\psi(\mathbf{r})|\psi^{\lambda}_{\mathrm{BO}}[\{\mathbf{R}_j\}]\rangle\\&\quad=n_e(\mathbf{r}).\end{aligned}\tag{27}$$

Taking the limit in which the ions are perfectly localized, in the positions, say, $\{\mathbf{R}_1^0,\ldots,\mathbf{R}_{N-S}^0\}$, the ion density has the form $n_I(\mathbf{R})=\Sigma_j\delta(\mathbf{R}-\mathbf{R}_j^0)$. We have, therefore,

$$|\Psi_{\mathrm{BO}}(\{\mathbf{R}_j\})|^2=\frac{1}{(N-S)!}\sum_{\text{permutations of }\{\mathbf{R}_j\}}\prod_{i=1}^{N-S}\delta(\mathbf{R}_i-\mathbf{R}_i^0),$$

where the sum is over all $(N-S)!$ permutations of the coordinates $\{\mathbf{R}_1,\ldots,\mathbf{R}_{N-S}\}$. Using Eq. (27) we have $\psi^{\lambda}_{\mathrm{BO}}[\mathbf{R}_1^0,\ldots,\mathbf{R}_{N-S}^0]\rightarrow n_e(\mathbf{r})$. Substituting the above in the first integral in Eq. (26), we see that it cancels with the second integral and hence the correlation energy vanishes exactly.

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