A generalized local approximation to the exchange potential

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A new method to obtain a local parameterization for the exchange term in the many-body electronic problem is presented. The approach amounts to the introduction of a coordinate dependent electron effective mass. Numerical results for metallic clusters in the jellium model are compared with other standard methods.

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I. INTRODUCTION

One of the major challenges in the density functional theory [1–4] is to improve the treatment of the exchange and correlation energy terms in inhomogeneous systems. Among the most vigorously pursued schemes is the inclusion of generalized gradient corrections to the local density approximation (LDA) [4,5]. One of the persistent problems related to the current formulations of LDA is the fact that the single-particle energies obtained in these methods have no direct relationship with the actual single-particle spectrum of the systems under consideration (with the exception of the ionization energies though). In particular, the gaps in semiconductors are severely underestimated [6]. It has been argued [7] that the origin of this discrepancy is the very nature of the local approximation to the density functional theory. This is one reason why, following an earlier argument [8], the electronic properties of several compounds were recently computed in an exact treatment of the exchange energy [9]. An improvement to the gap problem in semiconductors seems to be provided by the so called self-interaction method [10].

Here we have chosen to explore another line of inquiry, inspired by the so called optimized effective potential (OEP) treatment of the exchange energy. This method was first introduced in atomic physics [11,12] and has been increasingly revisited lately [13]. This recent activity generated some significant developments, for instance, a time dependent extension of the OEP approach [14]. So far, most of the applications of the OEP have been devoted to the exchange only functionals.

As in the OEP method, we shall consider the total energy of a many electron system $E_{\text{tot}}$ in the Hartree–Fock approximation only

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\[ E_{\text{tot}} = \frac{\hbar^2}{2m_0} \sum_{h} \sum_{\sigma} \int dr \nabla \Psi_h^*(r, \sigma) \cdot \nabla \Psi_h(r, \sigma) + e^2 \sum_{i<k} \frac{Z_i Z_k}{|R_i - R_k|} \] 
\[ - e^2 \sum_{i=1}^{N} \int dr \frac{Z_i \rho(r, r)}{|R_i - r|} + e^2 \int dr \int dr' \frac{\rho(r, r) \rho(r', r')}{|r - r'|} \] 
\[ - \frac{e^2}{2} \sum_{\sigma} \int dr \int dr' \frac{\rho_{\sigma}(r, r') \rho_{\sigma}(r', r)}{|r - r'|} , \]  

where \( m_0 \) is the electron mass, \( e \) is its charge, \( R_i \) gives the position of nuclei with charge \( Z_i e \), \( \Psi_h(r, \sigma) \) the single–particle electron wave functions and \( \sigma \) the spin variables. We shall use throughout this work the index \( h \) for labelling the hole (occupied) states and \( p \) for the particle (unoccupied) states. The indices \( h \) and \( p \) will stand for the corresponding quantum numbers of the single–particle states. The single–particle density is given by 
\[ \rho_\sigma(r, r') = \sum_h \Psi_h(r, \sigma) \Psi_h^*(r', \sigma) , \quad \rho(r, r') = \sum_\sigma \rho_\sigma(r, r') . \]  

For the sake of simplicity we shall suppress the spin variables in the following formulas.

The standard approach to self–consistently minimize \( E_{\text{tot}} \) is to solve the Hartree–Fock equations. As customary, those are obtained by varying \( E_{\text{tot}} \) with respect to \( \Psi_h^*(r) \) keeping the single–particle wave functions normalized, leading to 
\[ H_{\text{HF}} \Psi_h(r) \equiv \left( -\frac{\hbar^2}{2m_0} \nabla^2 + V_{\text{dir}}(r) \right) \Psi_h(r) - e^2 \sum_{h'} \int dr' \frac{\Psi_{h'}^*(r') \Psi_{h'}(r)}{|r - r'|} \Psi_h(r') = \varepsilon_h \Psi_h(r) . \]  

The local (direct) part of the potential is given by 
\[ V_{\text{dir}}(r) = V_{\text{ions}}(r) + e^2 \int dr' \frac{\rho(r')}{|r - r'|} . \]  

In the OEP approximation the single–particle wave functions are the solutions of a local Schrödinger equation 
\[ -\frac{\hbar^2}{2m_0} \nabla^2 \Psi_h(r) + V_{\text{OEP}}(r) \Psi_h(r) = \varepsilon_h \Psi_h(r) \]  

and the potential \( V_{\text{OEP}}(r) \) is determined so as to minimize the total energy of the system 
\[ \min \left\{ E_{\text{tot}}(\{ V_{\text{OEP}}(r) \}) \right\} \Rightarrow \frac{\delta E_{\text{tot}}}{\delta V_{\text{OEP}}(r)} = 0 . \]  

At this point a comment about the well known Slater approximation for the exchange energy is in order. We shall call Slater the approximation in which the single–particle wave functions obtained in the LDA with exchange only (LDAX) are used to compute \( E_{\text{tot}} \) according to Eq.(1). Thus, it should be fairly obvious that total energy estimates in these three methods satisfy the following relation
In the same spirit, notice that one cannot vouch for the value of $E_{\text{tot}}$ computed in LDAX (i.e. consistently using the Slater prescription for the exchange energy to calculate $E_{\text{tot}}$) to be either an upper or lower bound estimate for the total energy.

This paper is organized as follows: In the next section we present a generalized local approximation (GLA) and explain the naturalness of introducing a coordinate dependent effective mass. In Section III we describe two strategies for implementing the GLA and discuss in detail the case of spherically symmetric systems. In Section IV we present results for metallic clusters in the jellium approximation. There we compare different approximation schemes. We comment on some further possible extensions of GLA in Section V and present our conclusions in Section VI.

II. THE GENERALIZED LOCAL APPROXIMATION

In this section we shall present an extension of the OEP method, which we shall refer to as the generalized local approximation (GLA). This method is partially inspired by early attempts to treat the exchange term in a systematic way, put forward mostly in nuclear physics [15–18]. The basic idea of the GLA is to replace the OEP Schrödinger equation (5) by a generalized local Schrödinger equation with a coordinate dependent effective mass $m_{\text{eff}}(r) = m_0 \mu(r)$

$$\frac{-\hbar^2}{2m_0} \nabla \psi_h(r) + V(r)\psi_h(r) = \varepsilon_h \psi_h(r).$$

The GLA local potential $V(r)$ and the effective mass $\mu(r)$ are now determined by following set of equations

$$\min \{ E_{\text{tot}}(\{V(r), \mu(r)\}) \} \implies \frac{\delta E_{\text{tot}}}{\delta V(r)} = 0 \quad \text{and} \quad \frac{\delta E_{\text{tot}}}{\delta \mu(r)} = 0.$$

To motivate that a coordinate dependent effective mass is a natural ansatz, we shall invoke two different arguments. The first one, formal and general in nature, is essentially a summary of a more comprehensive reasoning presented in Ref. [18]. The second argument is more physical, but will be presented by putting in perspective the different approximation schemes for the particular case of a jellium model for metallic clusters.

Let us start by writing the Hartree–Fock equations (3) in the form

$$\frac{-\hbar^2}{2m_0} \nabla^2 \psi_h(r) + \int dr' U(r, r') \psi_h(r') = \varepsilon_h \psi_h(r),$$

where the kernel $U(r, r')$ contains the exchange potential which we are interested in, plus a direct term $V_{\text{dir}}(r') \delta(r - r')$ as given by Eq. (4). For convenience, we define the new space coordinates

$$x = \frac{1}{2}(r + r') \quad \text{and} \quad s = r' - r.$$
and change accordingly the kernel to
\[ \tilde{U}(x, s) = U(r, r') . \] (12)

An approximate way to obtain a local equivalent of (10) is to expand the wave functions and the diagonal part of the kernel \( \tilde{U} \) in a Taylor series in \( s \), retaining terms up to the second order in \( s \)
\[ \Psi_h(r') \approx \Psi_h(r) + \nabla_r \Psi_h(r) \cdot s + \frac{1}{2} \sum_{i,j} \partial^2 \Psi_h(r) \frac{\partial^2 \tilde{U}(r, s)}{\partial r_i \partial r_j} s_i s_j \] (13)
and the kernel itself
\[ \tilde{U}(r + \frac{1}{2}s, s) \approx \tilde{U}(r, s) + \frac{1}{2} \nabla_r \tilde{U}(r, s) \cdot s + \frac{1}{8} \sum_{i,j} \partial^2 \tilde{U}(r, s) \frac{\partial^2 \tilde{U}(r, s)}{\partial r_i \partial r_j} s_i s_j , \] (14)
where \( i \) and \( j \) label the axis and \( r_i \) is the component of the vector \( r \) along the axis \( i \). Direct insertion of the approximate \( \Psi_h(r') \) and \( \tilde{U}(r + \frac{1}{2}s, s) \) into Eq. (10) gives an equation of the very same structure as Eq. (8). Furthermore, we can explicitly write for the optimized potential
\[ V(r) = \int ds \tilde{U}(r, s) + \frac{1}{8} \sum_{i,j} \int ds \frac{\partial^2 \tilde{U}(r, s)}{\partial r_i \partial r_j} s_i s_j \] (15)
and for the effective mass
\[ \frac{1}{\mu(r)} = 1 - \frac{m_0}{\hbar^2} \sum_{i,j} \int ds \tilde{U}(r, s) s_i s_j . \] (16)

This set of equations is a good local approximation to the exchange term provided that the range of non–locality \( s_0 \) in \( \tilde{U}(r, s) \) is smaller than the local wave length, or in general, smaller than the typical bulk characteristic length of the direct part, i.e. \( s_0 \ll \frac{2\pi}{k_F} \), where \( k_F \) is the Fermi wave number. This approximation scheme was put forward by Frahn and Lemmer [15]. A comprehensive overview on this and similar approaches is presented in Ref. [18].

One might be tempted to use Eq. (15) and (16) to construct \( V(r) \) and \( \mu(r) \). The problem is that often we cannot assume \( k_F s_0 \) to be small, particularly at surfaces. Unfortunately, a well defined systematic approximate scheme to construct \( V(r) \) and \( \mu(r) \) is only known for non–local potentials in one–dimension [18]. Even for the simple spherically symmetric three dimensional case a satisfactory solution can be found only in some particular cases. In spite of this, the discussion presented above and the insight provided by Refs. [15,16,18] motivated us to consider the variational ansatz in Eq. (8) as a very natural one.

Another formal reason to introduce an effective electron mass in addition to an optimized local potential was pointed out by Austern [17]. The local and non–local wave functions differ in one rather subtle aspect. A node of a local wave function coincides always with an inflection point of that wave function, as one can easily see from the radial Schrödinger equation, if \( \phi(r) = 0 \) then \( \phi''(r) = 0 \) as well. This is no longer true for non–local wave
functions and the only simple way to remedy this functional difference between local and non–local wave functions is the introduction of a position dependent effective mass [16]. The exact Hartree–Fock single particle wave functions, being solutions of a non–local equation, do not have the property that nodes correspond to inflection points. This is one reason why the trivial exact local effective potentials corresponding to wave functions with nodes have usually pole singularities. The remnants of these poles can be seen, for example, in the local effective potentials determined by Talman and Shadwick [12].

Based on these considerations one should expect that
\[ E_{\text{tot}}^{\text{HF}} < E_{\text{tot}}^{\text{GLA}} < E_{\text{tot}}^{\text{OEP}} < E_{\text{tot}}^{\text{Slater}}, \] (17)
since the GLA variational ansatz is more flexible and more suited for the exchange term than OEP.

In the next sections we shall exemplify how the GLA method can be implemented on alkali atomic clusters [19]. Presently we shall treat the ionic background in the well known jellium approximation and consider only spherical closed shell clusters, when only the valence electrons are explicitly taken into account. One reason for choosing this system is that the electronic density of an alkali cluster is almost constant in the interior of the cluster. Inhomogeneities of the electronic distribution arise only because of the presence of a surface. The surface induces the natural falloff of the electronic density outside of the cluster, as well as Friedel–like oscillations [19]. The simplicity of the jellium approximation and the spherical symmetry of the closed shell clusters allows us to more easily single out the effects originating from inhomogeneities and the role of an effective mass.

One of the appealing features of the OEP method for finite Coulomb systems is the correct asymptotic behaviour of the local potential, namely that for \( r \to \infty \), \( V(r) \to -e^2/r \). This feature is also characteristic of the GLA approach. Besides providing a better estimate for the total energy, which in itself might not be really a significant gain, the GLA method has an additional desirable feature: It generates a better approximation to the single–particle spectrum than the LDA and the OEP methods.

Let us consider, for example, the Na\(_{92}\) cluster in various approximations. For more details see Ref. [20] and Section IV. In the LDAX the width of the occupied band is \( \Delta \varepsilon_{\text{LDAX}} = 2.55 \) eV, while in the Hartree–Fock approximation \( \Delta \varepsilon_{\text{HF}} = 5.27 \) eV. The Fermi gas estimate gives \( \Delta \varepsilon_{\text{Fg}} = p_F^2/2m_0 \), where \( p_F \) is the Fermi momentum. For a Wigner Seitz radius \( r_s = 4 \) a.u., which is approximately the value for bulk sodium, \( \Delta \varepsilon_{\text{Fg}} = 3.13 \) eV. The introduction of the self–interaction correction (SIC) in the exchange energy increases LDA band width from 2.55 eV to 2.94 eV, which is closer to the Fermi gas estimate. This is an indication that the observed smaller occupied band width in clusters than in the bulk is due to electronic spill–out effects. The rather big discrepancy between the Hartree–Fock value and the Fermi gas estimate can be naturally attributed to an electron effective mass arising from the non–local Fock potential [15]. A naive estimate gives \( m_{\text{eff}}/m_0 = \Delta \varepsilon_{\text{Fg}}/\Delta \varepsilon_{\text{HF}} \approx 0.6 \). This value is actually very close to what we determine for this cluster. The reason for this is that in the cluster interior the electronic density is to a fair approximation equal to the jellium model bulk constant density. The occurrence of an electronic effective mass, different from the bare one, can be also interpreted as an energy dependence of the electron self–energy [21].

The trivial exact local potentials, for nodeless wave functions, determined from the exact solution of the Hartree–Fock equations for Na\(_{92}\) system show that \( V_{1s}^{\text{HF}} \approx -9.12 \) eV and
$V_{HF}^{1h} \approx -6.40$ eV \[20\]. These values can be interpreted either as an energy or as an angular momentum dependence of the trivial exact local effective potential. An angular momentum dependence of the effective local potential is in principle present and shall be discussed below. We claim, however, that the potential depth difference between $V_{HF}^{1s}$ and $V_{HF}^{1h}$ can be mainly accounted for by the energy dependence of the local effective potential. In other words, the effect can be interpreted by an electron effective mass smaller than the bare electron mass. In this model, for Na$_{92}$ the last occupied level $1h$ ($\varepsilon_{1h} = -3.38$ eV) is very close in energy to the $3s$ level ($\varepsilon_{3s} = -3.50$ eV), while the lowest occupied level $1s$ has the energy $\varepsilon_{1s} = -8.65$ eV. Had one attributed the energy difference $\varepsilon_{1h} - \varepsilon_{1s} = 5.27$ eV to an angular momentum dependence of the local effective potential, one would have great difficulty in explaining why the energy difference $\varepsilon_{3s} - \varepsilon_{1s} = 5.15$ eV is almost as big and not much closer to the Fermi gas estimate $\varepsilon_{Fg} = 3.13$ eV.

Before concluding this section, it is worthwhile to mention that in nuclear physics another approximation beyond the Slater prescription for the exchange energy has been suggested. The method, called density matrix expansion (DME), proved to be very successful for short range nuclear forces between fermions \[22\]. In spirit, the DME method is a generalization of the traditional Slater approximation to inhomogeneous systems. The resulting local self-consistent equations for the single-particle wave functions are similar in structure to Eq.(8). The difference between DME and GLA is that in DME $\mu(r)$ and $V(r)$ are self-consistently obtained from the eigenstates. Unfortunately, when applied to Coulomb systems the ensuing DME equations have inherent instabilities \[23\].

III. NUMERICAL IMPLEMENTATION

The basic novel idea of the present work is entirely contained in Eq.(8), as discussed in the previous section. Nonetheless, in order to have a useful generalized local approximation one needs an efficient minimization algorithm for the total energy $E_{tot}$. This section is devoted to the discussion of two different strategies conceived to determine the best local potential and effective mass in the GLA approximation.

A. Explicit parameterization

In this first approach we shall represent the potential $V(r)$ and effective mass $\mu(r)$ as functions determined by a set of parameters $\{a_k\}$. Hence, the problem of finding the best local potential is equivalent to finding the minimum of the functional $E_{tot}(\{a_k\})$. It is obvious that the quality of the GLA depends on the choice of the variational ansatz. In this section we shall first present the method without specifying any parameterization. We then proceed showing how this method is implemented for a spherically symmetric system. The numerical results shall be discussed in section IV.

Recalling Eq.(11) the partial derivatives of the total energy with respect to $\{a_k\}$ can be written as

$$\frac{\partial E_{tot}}{\partial a_k} = \sum_h \int dr \frac{\partial \Psi_h^*(r)}{\partial a_k} H_{HF} \Psi_h(r) + \text{c.c.} , \quad (18)$$
where \( \partial \Psi_h(r)/\partial a_k \) is the solution of the equation

\[
(\hat{H}_{\text{GLA}} - \varepsilon_h) \frac{\partial \Psi_h(r)}{\partial a_k} + \left( \frac{\partial \hat{H}_{\text{GLA}}}{\partial a_k} - \frac{\partial \varepsilon_h}{\partial a_k} \right) \Psi_h(r) = 0 \tag{19}
\]

where \( \hat{H}_{\text{GLA}} \) is the GLA Schrödinger operator. We stress that the conditions

\[
V(r) \to 0 \quad \text{and} \quad \mu(r) \to 1 \quad \text{for} \quad r \to \infty \tag{20}
\]

are satisfied throughout.

Since the systems we consider in this paper are spherically symmetric one can write \( V(r) \) and \( \mu(r) \) as functions of the radial coordinate \( r \) only. Thus, a suitable variational ansatz reads

\[
V(r) = \sum_{k=-N}^{N} \tilde{V}_k \exp \left[ \frac{(r - r_k)^2}{2a^2} \right] \quad \text{and} \quad \mu(r) = \sum_{k=-N}^{N} \tilde{\mu}_k \exp \left[ \frac{(r - r_k)^2}{2a^2} \right], \tag{21}
\]

where \( r_k = ak \). The sum over \( k \) encompasses negative values in order to guarantee the correct behaviour near the origin, namely \( V'(0) = 0 \) and \( \mu'(0) = 0 \) \[24\], with \( \tilde{V}_k = V_{-k} \) and \( \tilde{\mu}_k = \mu_{-k} \). Working with this ansatz implies that \( \{a_k\} \equiv \{\tilde{V}_k\}, \{\tilde{\mu}_k\} \).

The method is implemented as follows: For a given starting \( V(r) \) and \( \mu(r) \) in the form \( \{\tilde{V}_k\}, \{\tilde{\mu}_k\} \) we solve Eq.(8). New amplitudes \( \{\tilde{V}_k\} \) and \( \{\tilde{\mu}_k\} \) are obtained by using the gradients given by Eq. (18) in a suitable minimization algorithm. In particular, we used the molecular dynamics method described in Ref. [25] and a simplified simulated annealing procedure in order to reach the condition \( \partial E_{\text{tot}}/\partial a_k \approx 0 \) and thus minimize \( E_{\text{tot}} \) as given by Eq.(1).

### B. Unconstrained minimization

In this second approach we have applied the steepest descent method to find directly in coordinate representation the optimized local potential and the effective mass. At a first glance this approach is more attractive than the previous one, since it does not rely on a good variational ansatz. On the other hand, for practical use, an explicit parameterization allows one to reduce the space of minimization variables and obtain very efficiently reasonable solutions. However, if the system in question does exhibit a specific symmetry this method is particularly easy to implement. In the remaining of this section we discuss the particular case of spherical symmetric systems. We believe that this approach can also be implemented for other situations.

In order to solve Eq.(8) numerically, it is convenient to represent the single-particle wave functions as

\[
\Psi_i(r) \equiv \psi_i(r) Y_{l,m_l}(\hat{r}) = \frac{\mu(r)}{r} \phi_i(r) Y_{l,m_l}(\hat{r}) \tag{22}
\]

where the index \( i \) labels states throughout the spectrum of the \( H_{\text{GLA}} \). After some straightforward manipulations, Eq.(8) can be written as
\[-\phi''_i(r) + \left( U(r) + \frac{l_i(l_i + 1)}{r^2} - \mu(r) \epsilon_i \right) \phi_i(r) = 0 \] (23)

where the energy was rescaled as \( \epsilon_i = 2m_0/\hbar^2 \epsilon_i \) and the potential \( U(r) \) is given by

\[ U(r) = \frac{2m_0}{\hbar^2} \mu(r) V(r) + \left\{ \frac{3}{4} \left[ \frac{\mu'(r)}{\mu(r)} \right]^2 - \frac{1}{2} \frac{\mu''(r)}{\mu(r)} - \mu'(r) \right\} . \] (24)

The normalization and completeness relations for the single–particle wave functions \( \phi_i(r) \) read

\[ \int dr \phi^*_k(r) \mu(r) \phi_l(r) = \langle \phi_k | \mu | \phi_l \rangle = \delta_{kl} , \]
\[ \sum_k \phi^*_k(r') \mu(r) \phi_k(r) = \delta(r - r') . \] (25)

where \( \sum_k \) includes an integration over the continuous (unbound) spectrum of \( H_{\text{GLA}} \). The functional variation of the total energy (\( \Pi \)) can be brought to the following form

\[ \delta E_{\text{tot}} = \int dr \left\{ \delta U(r) \sum_h (2l_h + 1) \phi_h(r) \chi_h(r) - \delta \mu(r) \sum_h (2l_h + 1) \epsilon_h \phi_h(r) \chi_h(r) \right\} + \text{c.c.} . \] (26)

The auxiliary functions \( \chi_h(r) \) are solutions of the following set of equations

\[-\chi''_h(r) + \left[ U(r) + \frac{l_h(l_h + 1)}{r^2} - \mu(r) \epsilon_h \right] \chi_h(r) = r \sqrt{\mu(r)} [1 - \rho]_{l_h} h_{\text{HF}} \psi_h(r) , \] (27)

where \( \rho \) is the single–particle density matrix as in Eq. (3), and \( h_{\text{HF}} \) refers to the radial part of the Hartree–Fock hamiltonian, \( H_{\text{HF}} \). On the right hand side of Eq. (27), \( [1 - \rho] \) is the projection operator outside of the occupied single–particle space and \( [1 - \rho]_{l_h} \) its radial component corresponding to the angular momentum \( l_h \). In Eq. (26) the summation is over the occupied (hole) states \( h \) only. The auxiliary single–particle functions \( \chi_h(r) \) are orthogonal to the occupied single–particle states

\[ \langle \phi_k | \mu | \chi_l \rangle = \int dr \phi^*_k(r) \mu(r) \chi_l(r) = \delta_{kl} , \] (28)

for all occupied states \( k \) and \( l \). It is well known that an equivalent formulation of the Hartree–Fock equations is

\[ [1 - \rho] H_{\text{HF}} \rho = 0 , \]  
\[ \text{or} \quad [H_{\text{HF}}]_{ph} = [H_{\text{HF}}]_{hp} = 0 \]  
\[ \text{or} \quad (1 - \rho) H_{\text{HF}} \Psi_h(r) = 0 , \] (29)

i.e. that all the particle–hole matrix elements of the Hartree–Fock single–particle Hamiltonian vanish. Consequently, if the single–particle wave functions \( \phi_h(r) \) are the solutions of the Hartree–Fock equations (\( \Pi \)), then \( \chi_h(r) \equiv 0 \). One should not construe this as a statement that the Hartree–Fock minimum can be reached exactly in this way though, barring a pure coincidence. According to Eqs. (3) and (8) the single–particle wave functions have to be solutions of both GLA and HF equations at the same time, which in general is very unlikely.
The best one can hope for is that \((29)\) will be rather well satisfied for some \(U(r)\) and \(\mu(r)\). Since the total energy is bounded from below the existence of an optimized local potential and an effective mass is certain. However, the uniqueness of a minimum, \(i.e.,\) the existence of only one global minimum, is not guaranteed. In principle one has the same problem in the exact HF case also. The vanishing of \(\delta E_{tot}\) upon variation of the local potential \(U(r)\) and effective mass \(\mu(r)\) leads to the following equations

\[
\sum_h (2l_h + 1) \phi_h(r) \chi_h(r) = 0 ,
\]

\[
\sum_h (2l_h + 1) \epsilon_h \phi_h(r) \chi_h(r) = 0 .
\]

In the case when \(\mu(r) \equiv 1\), Eq. \((30)\) can be readily rewritten in the form of the equation for OEP derived by Talman and Shadwick \([12]\). To implement the steepest descent method one has to change the local optimized potential and the effective mass according to the simple rules

\[
U(r) \rightarrow U(r) + \delta U(r) \quad \text{and} \quad \mu(r) \rightarrow \mu(r) + \delta \mu(r)
\]

where

\[
\delta U(r) = -2\lambda \sum_h (2l_h + 1) \phi_h(r) \chi_h(r)
\]

\[
\delta \mu(r) = 2\lambda \sum_h (2l_h + 1) \epsilon_h \phi_h(r) \chi_h(r) .
\]

The step size \(\lambda\) has to be gauged with a certain care, so that Eq. \((33)\) leads to new single-particle wave functions corresponding to a lower total energy \(E_{tot}\). It is worth mentioning that the corrections to \(U(r)\) and \(\mu(r)\) introduced above satisfy the following constraints

\[
\int dr \mu(r) \delta U(r) = 0 \quad \text{and} \quad \int dr \mu(r) \delta \mu(r) = 0 ,
\]

which in particular imply that one cannot change the real effective local potential \(V(r)\) by a constant only, \(i.e.,\) \(V(r) \rightarrow V(r) + \text{const}\) is not a possible change within this scheme.

**IV. RESULTS**

In our numerical study we used the jellium model to illustrate and compare the previously discussed approximation schemes. The model is defined by replacing \(V_{ions}(r)\) as appears in Eq.(1), by the potential given by an uniform positive background charge density. We analyzed the following alkali clusters: \(\text{Na}_{40}, \text{Na}_{92}, \text{Na}_{138}\) and \(\text{Na}_{196}\). For those, corresponding to electronic magic numbers, the spherical jellium approximation provides remarkably good results for the ground state properties and optical response \([19]\). The spherical geometry and the bulk Wigner–Seitz radius for sodium, \(r_s = 4\) a.u., determine the model entirely. In this section we examine the results of different schemes to solve the problem posed by Eq.(1) in the jellium approximation, namely Hartree–Fock, OEP, GLA and Slater.
Since the discussed schemes are approximations to the exchange potential, we first need to solve the jellium Hartree-Fock problem to have a standard to compare with. For this purpose we wrote a code that uses the same kind of algorithm as Ref. [20]. Apparently the method used by Hansen and Nishioka [26] is more accurate, but since we had no problems with obtaining converged results for cluster sizes up to $N_{a_{196}}$, we did not improve further our code. As for the Slater functional, we used a method very similar to the one described in Ref. [27], but with a series of refinements to ensure a higher numerical accuracy and increase the speed of computation. To obtain the solution of Eq. (8) and (9) we typically used the explicit parameterization method with $N = 20, \cdots, 30$, depending on cluster size and $a = 1 \text{Å}$. By starting with a reasonable guess for $\mu(r)$ and $V(r)$ we were always able to find a value for $E_{\text{tot}}$ very close to the Hartree–Fock value (see Tables I-III). Using the unconstrained minimization we could only marginally improve the minima obtained by explicit parameterization. In order to get a feeling of how well the GLA method works for different electronic densities we have varied the jellium density by a factor of two in both directions, i.e. smaller and higher densities ($3 \text{a.u.} < r_s < 5 \text{a.u.}$). Again the results were always in very good agreement with the Hartree–Fock ones.

We should mention, however, that for alkali clusters in the jellium model the GLA has likely several very close lying energy minima and often the corresponding $U(r)$ and $\mu(r)$ differ quite considerably from each other. Furthermore, even for the states we have identified, we can only claim that our numerical solutions are very close to the actual minimum. The direct minimization procedures we have used, meet with considerable numerical accuracy problems close to a minimum and one can hardly improve on the quality of an approximate solution. The total energy of alkali clusters, as of any many–electron system as well, comes as a result of a strong cancellations of different contributions. Thus, a numerically accurate solution (relative accuracy better than $\approx 10^{-5}$) is very difficult to obtain.

In Tables I–III we show the kinetic, Hartree, exchange, electron–ion and total energies for various sodium clusters in Slater, OEP, GLA and Hartree–Fock approximations. As one can see from these tables the GLA results are very close to the Hartree-Fock minimum and are of better quality than the OEP and Slater results. In Fig. 1 we compare the electron density profiles obtained in OEP, GLA and Hartree–Fock methods. Again, even though our solution might not exactly correspond to a local minimum, it is much closer to Hartree–Fock than the OEP solution. The local effective potential $V(r)$ for the GLA and OEP cases are displayed in Fig. 2 and in Fig. 3 we show the renormalized effective potential $U(r)$, see Eq. (23), and the effective mass $\mu(r)$. We have not imposed the “correct” asymptotic behavior $-e^2/r$ on the local potential as was done, for example, by Talman and Shadwick [12]. Since at radii a few Å larger than the jellium radius the electronic density is very small, any change of the potential or of the effective mass in this region has little effect on the hole single–particle wave functions. This is the origin of possible unexpected features in the local effective potential, such as non–monotonic behavior beyond the jellium radius. If unphysical characteristics appear in the local potential for large $r$ at the early minimization stages, they are very difficult to correct. Such unwanted features can only significantly alter the particle (unoccupied) states. Whenever we encountered such problems, after obtaining an approximate local minimum in the GLA, we proceeded as follows: Using the parameterized minimization method we constrained the amplitudes $\{\tilde{\mu}_k\}$ and $\{\tilde{V}_k\}$ for gaussians inside the jellium radius to be fixed, varying only the others. Although these corrections have a
negligible effect on $E_{\text{tot}}$, the effective potential tends slowly to acquire the correct form for large $r$.

The single–particle spectrum we have obtained for the occupied states is in very good agreement with the HF one. The corresponding single–particle spectra for the occupied states in either LDAX, Slater or OEP methods is much more compressed, as is shown in Fig. 4. These differences arise because the effective mass in GLA is smaller than $m_0$ inside the cluster ($m_{\text{eff}} \approx 0.6m_0$), as we have alluded to in Section II.

The unoccupied single–particle states show very interesting features. In the Hartree–Fock approximation the level density of the unoccupied states is too small and the gap at the Fermi level is too large. The reason is well known: the particle states in this approximation are computed in the field of a complete screened positive charge. On the other hand, in the OEP method the level density of the unoccupied states is large and the gap at the Fermi level is small. The main reason for it is that the $V_{\text{OEP}}(r)$ exhibits the correct asymptotic behaviour as $r \to \infty$. This causes the major difference between the OEP and the LDAX single–particle spectra. In LDAX one observes an overall upward shift of the spectrum, mainly due to the too sharp fall–off of the potential. One can reconcile almost perfectly the HF and the GLA particle spectra by rescaling the Hartree–Fock potential by a factor $(N_e - 1)/N_e$, where $N_e$ is the total number of electrons. In this way we force by hand the HF potential to have the “correct” $-e^2/r$ asymptotic behaviour for particle states. Notice that the hole states automatically have the correct asymptotic behaviour built in. The pleasant feature of the GLA approach is that one obtains not only a correct band width for the occupied states, but also a correct asymptotic behaviour for the effective potential of the particle states. As a result the gap at the Fermi level is larger in the GLA method than in the OEP method and smaller than in the HF approximation.

V. FURTHER GENERALIZATIONS

The GLA we have presented here is not yet the most general one. As we have mentioned in the introduction, one can extend it by considering an arbitrary angular momentum dependence of either the effective local potential or of the effective mass. (In general, an arbitrary angular dependence of the effective local potential leads strictly speaking to a non–local potential.) For example, one can consider a GLA Schrödinger equation of the following type

\begin{align}
-\frac{\hbar^2}{2m_0} \nabla \hat{M}(r) \nabla \Psi_h(r) + V(r)\Psi_h(r) = \varepsilon_h \Psi_h(r).
\end{align}

(35)

where $\hat{M}(r)$ is a symmetric tensor of rank two. One can chose this tensor in an appropriate manner such that the Schrödinger equation still preserves the spherical symmetry. For example, in the case of spherical systems one can choose

\begin{align}
\left[ \hat{M}(r) \right]_{ij} &= \frac{1}{\mu(r)} \delta_{ij} + \frac{b(r)}{\mu(r)} (\delta_{ij} - \hat{r}_i \hat{r}_j),
\end{align}

(36)

where $i$ and $j$ are axis labels; and rewrite Eq. (23) as
$- \phi''_i(r) + \left[ U(r) + \frac{l_i(l_i + 1)}{r^2} (1 + b(r)) - \mu(r)\epsilon_i \right] \phi_i(r) = 0. \quad (37)$

In this case one can interpret the appearance of a tensor inverse effective mass as an angular momentum dependence of the effective local potential $U(r)$. This ambiguity occurs only in the case of spherical symmetry. A simple analysis of the HF single–particle spectra of the clusters discussed in the previous section suggests that such a correction exists. The fact that the splitting between consecutive $s$–levels is smaller than between $p$–levels, which in its turn is smaller than the splitting between $d$–levels and so forth, gives room for such speculation. On the other hand, the total energy and the electronic density distribution of the alkali clusters we have considered here is very little affected by this type of correction. We have investigated to some extent this possibility as well, but not very thoroughly.

One can consider some further generalizations, e.g. to introduce a pseudovector component (or equivalently an antisymmetric component of $\mathbf{M}(r)$) of the inverse effective mass and/or also the introduction of a vector effective potential as well and still have a local Schrödinger equation which is a partial differential equation of at most second order. For example, a natural candidate for a pseudovector is the spin density. One can expect that in spin unsaturated systems a term with this symmetry might arise not only in the local effective potential but also in the inverse effective mass as well. One has to keep in mind that this type of correction violates time–reversal symmetry (which is violated in these systems anyway) and consider it with care. Whether there will be a reason to introduce a vector effective potential as well is still unclear at the present moment. The presence of an effective vector potential might signal also the existence of nonvanishing currents in the ground state, since in such a case the GLA Hamiltonian would not automatically be invariant under the transformation $\mathbf{p} \rightarrow -\mathbf{p}$, which will occur for example if the system is in an external magnetic field.

VI. CONCLUSIONS

Our analysis suggests a possible way to generalize the popular LDA treatment of Coulomb systems by enlarging the class of considered functionals. There is no a priori or fundamental reason why one should consider a total energy functional of the Kohn–Sham type only and not allow for terms, in which the inverse mass is replaced, e.g., by a density dependent function. One can find typical examples of such functionals in nuclear physics [22]. By considering such type of generalized local energy density functionals one can improve the quality of the description of inhomogeneous systems (total energy, electronic density distribution) and at the same time achieve a significant improvement of the single–particle spectrum as well, which is a long standing unsolved issue in LDA. We would like to remind the reader of one potential problem with using the present approach in infinite homogeneous systems. It is well known that the electron self–energy in the HF approximation for a pure Coulomb interaction between electrons has a logarithmic singularity at the Fermi level [21]. In principle that should prevent us from introducing an effective mass the way we have described here. On the other hand the Coulomb interaction between electrons is strongly renormalized in medium, see e.g. Ref. [28], and this fact in particular leads to Coulomb screening. (In its
simplest classical form that is the Thomas–Fermi screening at large distances.) This should be sufficient to remove such singularities of the electron self–energy and thus lends support to a GLA approach.

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TABLE I. Results for Na\textsubscript{92}. Note that in LDAX and Slater the entries for the total kinetic energy $E_{\text{kin}}$, Hartree energy $E_{\text{Hartree}}$, total electron–ion interaction energy $E_{\text{Coulomb}}$ are identical (since these quantities have identical functional forms) and the only differences are in Fock or exchange energy $E_{\text{Fock}}$ and total energy of the cluster $E_{\text{total}}$ respectively. Energies are in eV.

|        | LDAX     | Slater   | OEP      | GLA      | HF       |
|--------|----------|----------|----------|----------|----------|
| $E_{\text{kin}}$ | 160.80   | 160.80   | 161.59   | 161.94   | 161.73   |
| $E_{\text{Hartree}}$ | 7,560.71 | 7,560.71 | 7,565.32 | 7,565.09 | 7,564.02 |
| $E_{\text{Coulomb}}$ | -15,210.17 | -15,210.17 | -15,214.67 | -15,214.47 | -15,213.37 |
| $E_{\text{Fock}}$ | -269.39  | -277.28  | -278.38  | -279.18  | -279.04  |
| $E_{\text{total}}$ | -188.41  | -196.30  | -196.50  | -196.97  | -197.01  |

TABLE II. Results for Na\textsubscript{138}. See caption for Table I for notation and additional remarks.

|        | LDAX     | Slater   | OEP      | GLA      | HF       |
|--------|----------|----------|----------|----------|----------|
| $E_{\text{kin}}$ | 242.51   | 242.51   | 243.30   | 243.68   | 243.66   |
| $E_{\text{Hartree}}$ | 14,889.18 | 14,889.18 | 14,902.39 | 14,902.44 | 14,901.75 |
| $E_{\text{Coulomb}}$ | -28,926.61 | -28,926.61 | -29,939.80 | -29,939.84 | -29,939.15 |
| $E_{\text{Fock}}$ | -406.51  | -415.98  | -416.91  | -417.85  | -417.94  |
| $E_{\text{total}}$ | -268.37  | -277.84  | -277.96  | -278.51  | -278.61  |

TABLE III. Results for Na\textsubscript{196}. See caption for Table I for notation and additional remarks.

|        | LDAX     | Slater   | OEP      | GLA      | HF       |
|--------|----------|----------|----------|----------|----------|
| $E_{\text{kin}}$ | 346.40   | 346.40   | 348.04   | 348.54   | 347.73   |
| $E_{\text{Hartree}}$ | 26,776.91 | 26,776.91 | 26,791.67 | 26,792.13 | 26,781.13 |
| $E_{\text{Coulomb}}$ | -53,764.64 | -53,764.64 | 53,779.52 | -53,779.76 | -53,768.72 |
| $E_{\text{Fock}}$ | -580.21  | -591.13  | -592.97  | -594.33  | -593.73  |
| $E_{\text{total}}$ | -365.16  | -376.08  | -376.41  | -377.05  | -377.21  |
FIGURES

FIG. 1. Electronic densities (in Å⁻³) as a function of the radial coordinate \( r \) (in Å) for Na\(_{92}\) and Na\(_{132}\) in the Hartree–Fock, GLA (solid line), OEP (dashed line) and LDAX (dot–dashed line) approximations respectively. On this scale the GLA and Hartree–Fock densities are visually indistinguishable.

FIG. 2. The optimized effective potential \( V(r) \) (in eV) for Na\(_{92}\) in the GLA (solid line) and OEP (dashed line) approximations as a function of the radial coordinate \( r \) (in Å).

FIG. 3. For Na\(_{92}\) the effective mass \( \mu(r) \) (in dimensionless units) is displayed in the top panel. The renormalized optimized effective potential \( U(r) \) (in Å⁻²), see Eq. (23), for the GLA (solid line) and OEP (dashed line) approximations as a function of the radial coordinate \( r \) (in Å) is shown in the bottom panel.

FIG. 4. Single–particle level scheme for Na\(_{92}\) (in eV) in different approximation schemes. Solid lines correspond to the occupied spectrum and the dashed lines to several lowest unoccupied levels. For further details see text.
