Accurate effective potential for density amplitude and the corresponding Kohn–Sham exchange–correlation potential calculated from approximate wavefunctions

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Abstract

Over the past few years it has been pointed out that direct inversion of accurate but approximate ground state densities leads to Kohn–Sham exchange–correlation (xc) potentials that can differ significantly from the exact xc potential of a given system. On the other hand, the corresponding wavefunction based construction of exchange-correlation potential as done by Baerends \textit{et al} and Staroverov \textit{et al} obviates such problems and leads to potentials that are very close to the true xc potential. In this paper, we provide an understanding of why the wavefunction based approach gives the exchange–correlation potential accurately. Our understanding is based on the work of Levy, Perdew and Sahni (LPS) who gave an equation for the square root of density (density amplitude) and the expression for the associated effective potential in the terms of the corresponding wavefunction. We show that even with the use of approximate wavefunctions the LPS expression gives accurate effective and exchange–correlation potentials. Based on this we also identify the source of difference between the potentials obtained from a wavefunction and those given by the inversion of the associated density. Finally, we suggest exploring the possibility of obtaining accurate ground-state density from an approximate wavefunction for a system by making use of the LPS effective potential.

Keywords: Levy–Perdew–Sahni equation, exchange–correlation potential, Ryabinkin–Kohut–Staroverov method

(Some figures may appear in colour only in the online journal)

1. Introduction

Density functional theory (DFT) \cite{1, 2} is the most widely used theory \cite{3} of electronic structure and is applied to study systems of all sizes, from atoms to bulk solids. Application of the theory, however, requires approximating the exchange–correlation energy functional and it is usually assumed that better and better approximations for this energy functional will also lead to more accuracy for other quantities. On the other hand, it has been noted \cite{4} that densities do not necessarily improve with improvement in the energy. In light of such observations and the fact that the theory can be applied only approximately—albeit yielding accurate answers with better functionals—it is imperative that exact results be obtained wherever possible. This helps in gaining \cite{5–19} insights into how the theory works in different situations.

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such many studies [20–41] have been carried out to obtain the Kohn–Sham potential for a given near-exact density for a variety of many-electron systems. These densities are obtained by solving the many-body Schrödinger equation as accurately as possible by many different methods, such as integration of the Schrödinger equation directly or application of the variational method. The latter uses the variational principle with appropriately chosen parameterized wavefunction [42–62]. The method of choice in applying the variational scheme, however, is expanding the wavefunction in terms of a basis set and optimizing the expansion parameters. From this wavefunction the density of the system is obtained. Before we proceed further from this point to present our work, we go over some definitions that are going to be used in the paper.

The exact wavefunction of a system of N interacting electrons in an external potential \( v_{\text{ext}} \) is obtained by solving the time-independent Schrödinger equation

\[
H_N \Psi = E \Psi
\]

for the wavefunction \( \Psi(x_1, \ldots, x_N) \) where \( x = (r, \sigma) \) denotes the space \( (r) \), spin \( \sigma \) variables of electrons respectively and \( x_{\sigma,j} = x_j \), \( x_{\sigma,j+1} \cdots x_N \). Here (atomic-units are used throughout the paper)

\[
H_N = \sum_{i=1}^{N} \left( -\frac{1}{2} \nabla_i^2 + v_{\text{ext}}(\mathbf{r}_i) \right) + \frac{1}{2} \sum_{i,j=1}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}
\]

is the Hamiltonian and the eigenvalue \( E \) gives the energy of the system. The density \( \rho(r) \) corresponding to the wavefunction \( \Psi(x_1, \ldots, x_N) \) is given by

\[
\rho(r) = \int |\Psi(x, x_{2-N})|^2 d\sigma \ dx_{2-N}.
\]

Now according to the Hohenberg–Kohn theorem [1] there is a one-to-one correspondence between the external potential \( v_{\text{ext}}(r) \) and the ground state density \( \rho_0(r) \) of a system obtained from ground state wavefunction \( \Psi_0(x_1, \ldots, x_N) \) by using equation (3). Thus either \( v_{\text{ext}}(r) \) or \( \rho_0(r) \) can be used to specify a system. The ground state density for a system can also be obtained by solving self-consistently the Kohn–Sham equation [2]

\[
\left[ -\frac{1}{2} \nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})
\]

where

\[
v_{\text{H}}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \ dx'
\]

is the Hartree potential for a density \( \rho(\mathbf{r}) \) and

\[
v_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}(\rho)}{\delta \rho(\mathbf{r})}
\]

is exchange–correlation potential, calculated as the functional derivative of the exchange–correlation energy functional \( E_{\text{xc}}[\rho] \). The self consistent solution of the Kohn–Sham equation gives orbitals \( \{ \phi_i(\mathbf{r}) \} \) that lead to the density through the formula \( \rho(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2 \). However, since functional \( E_{\text{xc}}[\rho] \) is not known, the corresponding exchange–correlation potential for a given ground state density cannot be calculated exactly using equation (6). Thus other techniques have to be developed to get this potential for a given system. In the following we will denote exact exchange–correlation potential for a given external potential alternatively as \( v_{\text{xc}}[\rho_0(\mathbf{r})] \) or \( v_{\text{xc}}[\rho_0(\mathbf{r})] \), where it is understood that \( \rho_0(\mathbf{r}) \) is the ground-state density corresponding to \( v_{\text{ext}}(\mathbf{r}) \).

To calculate the exact Kohn–Sham exchange–correlation potential \( v_{\text{xc}}(\mathbf{r}) \) from a given density \( \rho(\mathbf{r}) \), the most straightforward method would be to invert the density numerically. In the following we will denote the exchange–correlation potential obtained by inversion of density as \( v_{\text{xc}}^\text{inv}(\mathbf{r}) \). There are several methods [20–26, 33–35, 38, 40, 41, 63–65] proposed for this inversion and most of them have been shown [66] to emanate from a single algorithm based on the Levy–Perdew–Sahni (LPS) equation [67] for the square root of the density. However, these methods are highly sensitive to the correctness of the density and its derivatives for a given \( v_{\text{ext}}(\mathbf{r}) \) and can lead to \( v_{\text{xc}}^\text{inv}(\mathbf{r}) \) having spurious features in them [31, 64, 68–71]. It is easy to understand why this happens: inversion algorithms give the exact potential corresponding to a density and hence even an extremely small deviation of density \( \rho(\mathbf{r}) \) from the exact one \( \rho_0(\mathbf{r}) \) could lead to very different potentials [68]. For example, when densities obtained from wavefunctions expressed in Gaussian basis sets are used, one observes [31, 64, 71] large oscillations in the exchange–correlation potentials of atoms near the nucleus and the potential increases indefinitely in the asymptotic region. This is despite the corresponding density \( \rho(\mathbf{r}) \) being close to the exact density \( \rho_0(\mathbf{r}) \). In this connection, we note it has also been pointed out [72] that use of finite basis in construction of the optimised effective potential (OEP) leads to oscillations in the resulting potential, although for entirely different reasons. Consequently, even with extended basis like plane-waves, very large basis sets containing several thousands of plane waves have to be used for carrying out the calculation of OEP. On the other hand, an alternate approach that has been proposed [37, 39, 73, 74] is to use the wavefunctions directly to get the Kohn–Sham potential. So far all applications of this approach [17, 37, 39, 71, 75–77] have shown that for a given nearly exact wavefunction \( \Psi \), it leads to the exchange–correlation potential–we denote it as \( v_{\text{xc}}^\text{LPS}(\mathbf{r}) \)–that is very close to the exact potential \( v_{\text{xc}}[\rho_0(\mathbf{r})] \) and is free of undesirable features that appear when the corresponding density \( \rho(\mathbf{r}) \) is inverted. This has been attributed to the potential in wavefunction approach being the ‘sum of commensurate, well-behaved terms’ [37] by Staroverov et al. However a perspicuous understanding of why these terms are well behaved is missing.

The purpose of the present paper is to provide an insight into why the wavefunction based method works better even with wavefunctions which are close to but not exact and how the potential \( v_{\text{xc}}^\text{LPS}(\mathbf{r}) \) obtained through it is connected to the true exchange–correlation potential of a system. For this we make use of the compact expression given by Levy–Perdew & Sahni (LPS) [67] and other researchers [5, 78–82] for the effective potential for the square-root of density and reach our conclusions based on this formula. We focus on the
LPS expression because the wavefunction based formulae [5] for the exchange–correlation potential given in different forms are ultimately related to this expression. Therefore in the following we start our presentation with a discussion of the LPS equation and then derive our main result based on it.

2. The LPS equation and its application

2.1. The LPS equation and the corresponding potential \( v_{\text{eff}}(r) \)

The LPS equation [67] satisfied by the square root of the ground-state density \( \rho_{0}(r) \) for \( N \) electrons corresponding to the Hamiltonian of equation (2) is

\[
\left[ -\frac{1}{2} \nabla^2 + v_{\text{ext}}(r) + v_{\text{eff}}(r) \right] \mu_{0}^{1/2}(r) = \mu_{0}^{1/2}(r) \tag{7}
\]

where \( \mu \) is the chemical potential and effective potential \( v_{\text{eff}}(r) \) is calculated from the wavefunction \( \Psi_{0} \) as

\[
v_{\text{eff}}[\Psi_{0}](r) = \int \rho_{N-1}(r', r) \frac{d r'}{|r - r'|} + \frac{1}{2} \int |\nabla \Phi_{N-1}^{0}(r')|^2 d \sigma d x_{2-N}. \tag{8}
\]

where \( H_{N-1} \) is the Hamiltonian of \( N - 1 \) interacting electrons moving in external potential \( v_{\text{ext}}(r) \) and \( E_{N-1}^{0} \) is the corresponding ground-state energy. \( \rho_{N-1}(r', r) \) is the density of \( N - 1 \) electrons at \( r' \) associated with the function \( \Phi_{N-1}^{0}(x, x_{2-N}) \). Thus

\[
\rho_{N-1}(r, r') = (N - 1) \int \Phi_{N-1}^{0}(x, x', x_{3-N})^2 d \sigma d x_{3-N} \tag{9},
\]

here the function

\[
\Phi_{N-1}^{0}(x, x_{2-N}) = \left( \frac{N}{\rho_{0}(r)} \right)^{1/2} \Psi_{0}(x, x_{2-N}) \tag{10}
\]

is known as the conditional probability amplitude [83]. Evidently the function \( \Phi_{N-1}^{0}(x, x_{2-N}) \) is normalized for every value of \( x \). For a given electron at \( x \), \( |\Phi_{N-1}^{0}(x, x_{2-N})|^2 \) gives the probability of finding other electrons at \( x_{2-N} \).

For the corresponding Kohn–Sham system given by equation (4), the effective potential is known as the Pauli potential [84, 85] and is easily derived to be [82, 85] (see appendix also)

\[
v_{\text{Pauli}}^{N}[\{\phi_{0}^{0}\}](r) = \sum_{i} (\epsilon_{\text{max}} - \epsilon_{i}) |\phi_{i}^{0}(r)|^2 + \sum \left[ |\nabla \phi_{i}^{0}(r)|^2 / 2 \rho_{0}(r) \right]^2 - \frac{1}{8} \left[ |\nabla \rho_{0}(r)|^2 / \rho_{0}(r) \right] \tag{11}
\]

where the sum is over occupied orbitals, \( \epsilon_{i} \) are the eigenenergies of occupied orbitals, \( \epsilon_{\text{max}} \) is the highest occupied orbital eigenenergy and \( \rho_{0}(r) = \sum_{i} |\phi_{i}^{0}(r)|^2 \) is the density. Note that this potential for single orbital systems is zero. In passing we note that this expression along with \( v_{\text{eff}}(r) \) for Hartree–Fock wavefunction (see appendix) has been used [86] in the past to derive the KLI approximation [87] to the exchange-only optimized potential [88]. The exchange–correlation potential \( v_{xc}[\rho_{0}](r) \) appearing in the Kohn–Sham equation is given in terms of these effective potentials as

\[
v_{xc}[\rho_{0}](r) = v_{xc}^{\Psi_{0}}(r) = v_{\text{eff}}[\Psi_{0}](r) - v_{\text{eff}}^{\text{Pauli}}[\{\phi_{0}^{0}\}](r) - v_{\text{H}}(r). \tag{12}
\]

Note that for a given ground-state wavefunction \( \Psi_{0} \), the Kohn–Sham system is not known a priori so the corresponding exchange–correlation potential is obtained by solving the Kohn–Sham equation iteratively starting from an approximate \( v_{xc}^{\Psi_{0}}(r) \) or equivalently \( v_{xc}^{\text{Pauli}}(r) \). The Pauli potential and therefore the exchange–correlation potential improve with each iterative step.

The presentation above has been in terms of the ground-state wavefunction \( \Psi_{0}(x_{1-N}) \) and the associated ground-state density \( \rho_{0}(r) \). The question is what result will one get if an approximate wavefunction \( \Psi_{0}(x_{1-N}) \) is employed in place of \( \Psi_{0}(x_{1-N}) \) in the scheme presented above to calculate the exchange–correlation potential \( v_{xc}^{\Psi_{0}}(r) \) for the same external potential. This is the approach taken by Staroverov et al (see section 4) who have calculated the exchange–correlation potential taking \( \Psi \) to be the Hartree–Fock wavefunction (expressed in terms of Gaussian orbitals) or correlated wavefunctions calculated again using Gaussian basis-set. As noted earlier, they find that the exchange–correlation potential \( v_{xc}^{\Psi_{0}}(r) \) calculated is very close to the true exchange–correlation potential \( v_{xc}^{\Psi_{0}}(r_{\text{eff}}) = v_{xc}[\rho_{0}] = v_{xc}[\rho_{\text{ext}}] \) in contrast to the exchange–correlation potential \( v_{xc}^{\Psi_{0}}(r) \) calculated by inverting the corresponding density. As commented above, \( v_{xc}^{\Psi_{0}}(r) \) contains large oscillations near the nucleus and grows exponentially in the asymptotic regions. In the following we show that results obtained by Staroverov et al are of general nature.

Thus if an approximate wavefunction \( \Psi \) corresponding to the Hamiltonian of equation (2)—for example that obtained by applying the variational—is employed in equation (8), the effective potential \( v_{\text{eff}}^{\Psi}(r) \) so obtained is close to the true effective potential \( v_{\text{eff}}^{\Psi_{0}}(r) \). Consequently the density \( \rho(r) \) calculated by equation (7) should also be close to the true density and prescription above should lead to the exchange–correlation potential which approximates the potential \( v_{xc}[\rho_{0}] = v_{xc}[\rho_{\text{ext}}] \) well. We first demonstrate this in the following with the example of two-electron atoms and ions.

2.2. Results of applying LPS expression to obtain \( v_{xc}(r) \) using approximate wavefunctions

In this section we describe the results of applying the LPS equation to obtain the exchange–correlation potential from variationally optimized approximate wavefunctions for two-electron interacting systems. These results indicate that even with these wavefunctions, the LPS expression leads to accurate exchange–correlation potentials. On the other hand, inversion of the corresponding densities gives potentials that are
where the potentials obtained in equations (13) and (16) also give rise to wild oscillations in the exchange–correlation potential. In the following we show through the examples of two-electron atoms and ions that the LPS expression leads to well behaved exchange–correlation potential.

The LPS effective potential corresponding to the product wavefunction given in equation (13) is (up to a constant, constant is so chosen that potential goes to zero as \( r \to \infty \))

\[
\psi_{\text{eff}}[\Psi](r) = \frac{1}{2} \int \frac{\rho(r')}{r'^2} \, dr',
\]

where \( \rho(r) = 2|\phi_0(r)|^2 = \frac{2a}{\pi} e^{-2ar} \) is the electronic density of the system. Thus the exchange–correlation potential is given as

\[
v_{\text{xc}}^\Psi(r) = -\frac{1}{2} \int \frac{\rho(r')}{r'^2} \, dr' = -\frac{1}{r} + e^{-2ar} / r(1 + ar).
\]

Note the expression above in terms of the density is the same as in Hartree–Fock theory for two electron systems. On the other hand, direct inversion of the density using Kohn–Sham equation gives (up to a constant)

\[
v_{\text{xc}}^\rho(r) = \frac{1}{2} \frac{\nabla^2 \phi_a}{\phi_a} + Z \frac{r}{r^2} \int \frac{\rho(r')}{|r' - r|} \, dr' = \frac{(Z - a - 2)}{r} + \frac{2e^{-2ar}}{r}(1 + ar).
\]

As is clearly seen from the expressions above, there is a significant difference between the two potentials. This is displayed in figure 1 where the potentials obtained in equations (16) and (17) are plotted for the \( \text{H}^- \) ion and He atom. Also plotted in figure 1 is the exact exchange–correlation potential (27) for the \( \text{H}^- \) ion and He atom. It is evident that exchange–correlation potential obtained using density inversion \( v_{\text{xc}}^\rho(r) \) deviates significantly from the exact potential \( v_{\text{xc}}^{\text{exact}}(r) \) and diverges near the nucleus. However, the potential \( v_{\text{xc}}^\Psi(r) \) obtained using wavefunction is close to \( v_{\text{xc}}^{\text{exact}}(r) \) (27). Equally important, \( v_{\text{xc}}^\Psi(r) \) has the same shape as the exact potential. Figure 1 also shows the exchange–correlation potential \( v_{\text{xc}}^{\text{inversion}}(r) \) obtained numerically using density-to-potential inversion algorithm. For this we have used the hybrid method given in our recent work (66). The potential \( v_{\text{xc}}^{\text{inversion}}(r) \) is close to \( v_{\text{xc}}^\Psi(r) \) and shows divergent behavior near the nucleus. We point out that in principle \( v_{\text{xc}}^\Psi(r) \) and \( v_{\text{xc}}^{\text{inversion}}(r) \) should be exactly the same but are slightly different from each other due to numerical implementation of the inversion algorithm.

Having shown that the two results for the exchange–correlation potential are significantly different for the product wavefunction, next we consider a correlated wavefunction that has the form (89) (with optimization parameters \( a \) and \( b \))

\[
\Psi(r, r') = C_N \left( e^{-ar}e^{-br} + e^{-2ar}e^{-2br} \right),
\]

here

\[
C_N = \frac{1}{\pi} \left[ \frac{1}{\left( \frac{2}{a^2b^2} + \frac{128}{(a+b)^4} \right)} \right]^{1/2}
\]
is the normalization constant. The parameters \( a \) and \( b \) are
optimized by minimizing the expression for the total energy
\[
E(a, b) = (E_K + E_{\text{nucl}} + E_{\text{int}}),
\]
where
\[
E_K = \pi^2 C_N \left( \frac{a^2 + b^2}{a^3 b^3} + \frac{128ab}{(a + b)^3} \right),
\]
\[
E_{\text{nucl}} = -\pi^2 C_N Z \left( \frac{2(a + b)}{a^3 b^3} + \frac{128}{(a + b)^3} \right),
\]
\[
E_{\text{int}} = \pi^2 C_N \left( \frac{2(a^2 + b^2 + 3ab)}{a^2 b^2 (a + b)^3} + \frac{40}{(a + b)^3} \right)
\]
are the kinetic, nuclear and the electron–electron interaction energies, respectively. For \( \text{H}^- \) ion and He atom, the optimized values of parameters \((a, b)\) are \((1.0392, 0.2832)\) and \((2.1832, 1.1885)\), respectively. The corresponding energies are \((-0.5133, -2.8756)\) Hartree, respectively.

This is again a wavefunction where expressions for various quantities and those for \( v_{\text{xc}}^W(r) \) and \( v_{\text{xc}}^I(r) \) can be derived analytically. Those for different components of the total energy have been given above. For the other relevant quantities—the density \( \rho(r) \), Hartree potential \( v_H(r) \), \( v_{\text{eff}} [\Psi](r) \), \( v_{\text{xc}}^W(r) \), \( v_{\text{xc}}^I(r) \)—the expressions are:
\[
\rho(r) = 2\pi C_N^2 \left[ \frac{e^{-2ar}}{b^3} + \frac{e^{-2br}}{a^3} + \frac{16e^{-(a+b)r}}{(a + b)^3} \right]
\]
\[
v_H(r) = \frac{2\pi C_N^2}{r} \left[ \frac{2 - (1 + ar)e^{-2ar} - (1 + br)e^{-2br}}{a^3 b^3} + 128 \left( \frac{1 - (1 + (a+b)r)e^{-(a+b)r}}{(a + b)^3} \right) \right]
\]
\[
v_{\text{eff}}[\Psi](r) = \frac{\pi C_N}{\rho(r)} \left[ \frac{-2e^{-2ar+br}}{r} \left( \frac{1 + ar}{a^3} + \frac{1 + br}{b^3} \right) + \frac{16(1 + (a+b)r)}{(a + b)^3} \right]
\]
The potentials \( v_{\text{xc}}^W(r) \) and \( v_{\text{xc}}^I(r) \) for \( \text{H}^- \) ion and He atom are plotted in figure 2 along with the exact potential \( v_{\text{xc}}^{\text{exact}}(r) \) calculated in reference [27] and potential \( v_{\text{inversion}}(r) \) obtained numerically using inversion algorithm. Again it is evident that \( v_{\text{xc}}^W(r) \) is close to and has the same shape as the exact potential \( v_{\text{xc}}^{\text{exact}}(r) \). On the other hand \( v_{\text{xc}}^I(r) \) and \( v_{\text{inversion}}(r) \) both deviate substantially from \( v_{\text{xc}}^{\text{exact}}(r) \). As these wavefunctions are improved further, the exchange–correlation potential \( v_{\text{xc}}^I(r) \) becomes closer to \( v_{\text{xc}}^{\text{exact}}(r) \). The potential \( v_{\text{xc}}^I(r) \) also improves but may still remain different from the exact potential. For example for the Le Sech wavefunction [53, 55, 90], although energy is quite accurate but \( v_{\text{inversion}}(r) \) still remains different.
from \(v_{xc}(r)\) or \(v_{xc}^{\text{exact}}(r)\) (see figure 3). In passing we note that the expressions given by equations (25)–(27) with the optimized \(a\) and \(b\) can be considered to be reasonably good analytical expressions for the Hartree potential, LPS effective potential and the exchange–correlation potential for the He atom and isoelectronic positive ions.

Besides the examples given above, we now describe results available in the literature. These consider approximate wavefunctions expressed in finite basis set and construct [37, 39, 71, 75, 77] the exchange–correlation potential according to the details given in section 4 below. The potential so obtained is again found to be close to the true potential.

As is clear from the discussion above, use of the LPS expression leads to exchange–correlation potentials which are close to the exact results. This is in contrast to those constructed by inversion of the density. In an extreme example, use of Gaussian basis in calculations give [64, 69–71] wild oscillation in the potentials; these can make the resulting potential deviate from the actual potential so much that there is no resemblance between the two. These oscillations have been attributed [64, 68] to the Gaussian basis orbitals being the solution for a harmonic oscillator potential. The question arises why the LPS expression leads to such accurate results. We answer this question in this paper by analyzing \(v_{\text{eff}}(\Psi)(r)\) for approximate wavefunctions \(\Psi\). The approximate nature of the wavefunction may be due to the form chosen for it or due to the use of finite basis set. The analysis is based on a comparison between \(v_{\text{eff}}(\Psi)(r)\) and \(v_{\text{eff}}(\rho)(r)\), where the latter is obtained from the use of density directly in the LPS equation. The expression of \(v_{\text{eff}}(\rho)(r)\) is given below in equation (29).

### 3. Theory: well behaved nature of \(v_{\text{eff}}(\Psi)(r)\) and \(v_{xc}^{\text{exact}}(r)\) for approximate wavefunctions

The understanding of why the inversion of an approximate density generally leads to the exchange–correlation potential with large deviations from the exact one and why the LPS effective potential gives the exchange–correlation potential close to the exact one can be summarized in one sentence: the external potential \(v_{\text{ext}}(\rho)\) corresponding to an approximate ground state density is different from the true external potential \(v_{\text{ext}}(\rho)\) and this difference between the two potentials appears in the exchange–correlation potential. Such a correlation between density and potential has been suggested earlier in a qualitative manner [64, 68]. This is further supported by the observation [91] that the oscillations in the Kohn–Sham exchange–correlation potential obtained from the inversion of a density or equivalently the Kohn–Sham orbitals depend primarily on the basis set used for the calculation and is independent of the functional used for generating the density. In this section we prove the statement above mathematically. Furthermore, observing that the expression for the effective potential \(v_{\text{eff}}(\Psi)(r)\) has the true external potential in it (see equation (36) below), we show that the difference between \(v_{\text{eff}}(\rho)(r)\) and \(v_{\text{eff}}(\Psi)(r)\) arises from the difference \(\Delta v_{\text{ext}}(r)\) between \(v_{\text{ext}}(r)\) and \(v_{\text{ext}}(\rho)(r)\).

The LPS effective potential is given in terms of the density \(\rho(r)\) as

\[
v_{\text{eff}}(\rho)(r) = \frac{1}{2} \frac{\nabla^2 \rho^{1/2}(r)}{\rho^{1/2}(r)} - v_{\text{ext}}(r) + \mu
\]

\[
= \frac{\nabla^2 \rho(r)}{4\rho(r)} \left[ \frac{1}{8} \frac{\nabla \rho(r)}{\rho(r)} \right] - v_{\text{ext}}(r) + E_N^0 - E_{N-1}^0, \tag{29}
\]

here we have used the fact [92] that \(\mu = -\text{ionization potential} = E_N^0 - E_{N-1}^0\), where \(E_N^0\) and \(E_{N-1}^0\) are the ground state energies of the \(N\) and \(N-1\) electron systems. It is clear from the equation above that the ratio of the gradient of density to the density and the ratio of the Laplacian of density to the density determine the structure of \(v_{\text{eff}}(\rho)(r)\) and that may lead to large deviations from the exact structure if the density is approximate. For example, let us see what will happen if the density fails to satisfy the nuclear cusp condition [93] in an atom exactly i.e. \(\frac{\rho(r)}{r^2} \neq -2Z\rho\). In that case \(\frac{\nabla^2 \rho^{1/2}(r)}{\rho^{1/2}(r)}\) does not have the term \(-\frac{2}{r}\) to cancel \(-v_{\text{ext}}(r)\) and therefore the effective potential diverges as \(\frac{2}{r}\) for \(r \to 0\). This is what is seen in figures 1 and 2 for such wavefunctions. Consider another example where an
To derive this relation, start by calculating the deviation from the exact LPS effective potential arises from the difference \( \Delta v_{\text{ext}}(r) = v_{\text{ext}}(r) - v_{\text{eff}}(r) \) in the external potential \( v_{\text{ext}}(r) \) corresponding to the approximate density—and the wavefunction—and the exact external potential \( v_{\text{ext}}(r) \). We show this explicitly in the following. Notice that the maximum deviation occurs when the density is dominated by one orbital or one basis function.

Consider the conditional probability amplitude \([83]\)

\[
\Phi_{N-1}(x, x_{2-N}) = \left( \frac{N}{\rho(r)} \right)^{1/2} \Psi(x, x_{2-N})
\]  

(30)

constructed from the wavefunction \( \Psi(x, x_{2-N}) \) and the corresponding density \( \rho(r) \). If \( \Psi \) is exact then the external potential is \( v_{\text{ext}}(r) \) and if \( \Psi \) is approximate the external potential is denoted as \( v_{\text{eff}}(r) \). We proceed as follows. First we can easily show that

\[
\frac{1}{2} \frac{\nabla^2 \Psi(r)}{\rho^{1/2}(r)} = \frac{N}{2\rho(r)} \int \Psi^* \frac{\nabla^2 \Psi}{\rho} \, d\sigma \, dx_{2-N} + \frac{1}{2} \int |\nabla \phi_{N-1}|^2 \, d\sigma \, dx_{2-N}.
\]  

(31)

To derive this relation, start by calculating \( \frac{1}{2} \int |\nabla \phi_{N-1}|^2 \, d\sigma \, dx_{2-N} \) and rearrange terms in the resulting expression. We now consider an approximate wavefunction \( \tilde{\Psi} \). Then in the equation above the first term

\[
\frac{N}{2\rho(r)} \int \Psi^* \frac{\nabla^2 \Psi}{\rho} \, d\sigma \, dx_{2-N} = -E_N^0 + \Phi_{N-1}[\mathcal{H}_{N-1}] \Phi_{N-1} + \tau_{\text{ext}}(r) + \int \frac{\rho_{N-1}(r, r')}{|r - r'|} \, dr'.
\]  

(32)

by using the Schrödinger equation \( \mathcal{H}_N \Psi = E_N \Psi \). Here

\[
\mathcal{H}_N = \sum_{i=1}^{N} \left( -\frac{1}{2} \nabla_i^2 + \tau_{\text{ext}}(r_i) \right) + \sum_{i>j}^{N} \frac{1}{|r_i - r_j|},
\]  

(33)

\[
\mathcal{H}_{N-1}(x_2-N) = \sum_{i=2}^{N} \left( -\frac{1}{2} \nabla_i^2 + \tau_{\text{ext}}(r_i) \right) + \sum_{i>j}^{N} \frac{1}{|r_i - r_j|},
\]  

(34)

and \( \rho_{N-1}(r; r') \) is the density of \( N - 1 \) particle at \( r' \) calculated from \( \Phi_{N-1}(x, x_{2-N}) \). Furthermore, in calculating the expectation value of \( \mathcal{H}_{N-1} \), integration over \( \sigma \) is implied. Thus the LPS effective potential using equation (29) is given as

\[
v_{\text{eff}}(\rho)(r) = \int \frac{\rho_{N-1}(r, r')}{|r - r'|} \, dr' + \Phi_{N-1}[\mathcal{H}_{N-1}] - E_N^0 \Phi_{N-1} + \frac{1}{2} \int |\nabla \phi_{N-1}|^2 \, d\sigma \, dx_{2-N} + \Delta v_{\text{ext}}(r) + (E_N^0 - E_N^0),
\]  

(35)

where we recall that \( \Delta v_{\text{ext}}(r) = \tau_{\text{ext}}(r) - v_{\text{ext}}(r) \). Notice that the expression for \( v_{\text{eff}}(\rho)(r) \) contains \( \tau_{\text{ext}}(r) \). On the other hand, \( v_{\text{eff}}(\Psi)(r) \) corresponds to \( \Psi \) is evaluated as

\[
v_{\text{eff}}(\Psi)(r) = \int \frac{\rho_{N-1}(r, r')}{|r - r'|} \, dr' + \Phi_{N-1}[H_{N-1} - E_N^0 \Phi_{N-1}] + \frac{1}{2} \int |\nabla \phi_{N-1}|^2 \, d\sigma \, dx_{2-N},
\]  

(36)

where \( H_{N-1} \) is given by equation (34) by replacing \( v_{\text{ext}}(r) \) by \( v_{\text{eff}}(r) \). Thus the difference

\[
v_{\text{eff}}(\rho)(r) - v_{\text{eff}}(\Psi)(r) = (E_N^0 - E_N^0) + \Delta v_{\text{ext}}(r) + \int \Delta v_{\text{ext}}(r) \rho_{N-1}(r, r') \, dr'.
\]  

(37)

As is clear from the expression above, the difference between the effective potentials calculated by inverting the density and that obtained from the wavefunction using the LPS expression arises from the difference between the external potential \( \tau_{\text{ext}}(r) \) corresponding to the approximate wavefunction \( \Psi \) and the true external potential \( v_{\text{ext}}(r) \). It is this difference that appears between the exchange–correlation potential \( v_{xc}^0(r) \) calculated from the density-to-potential inversion and \( v_{xc}^0(r) \) obtained using the effective potential \( v_{\text{eff}}(\Psi)(r) \).

Having obtained the difference between the effective LPS potential \( v_{\text{eff}}(\rho)(r) \) calculated by inverting the density and \( v_{\text{eff}}(\Psi)(r) \) by the use of wavefunction dependent expression, we now pay attention to the behavior of \( v_{\text{eff}}(\Psi)(r) \). We focus on understanding whether it deviates from the exact potential by a large amount. For this expand the conditional probability amplitude as

\[
\Phi_{N-1}(x, x_{2-N}) = \sum_j f_j(x) \Psi_{N-1}^{(0)}(x_{2-N})
\]  

(38)

where because of \( \phi_{N-1} \) being normalized, \( \sum_j |f_j(x)|^2 = 1 \) so that \( |f_j(x)|^2 \leq 1 \) for every value of \( x \); here \( \Psi_{N-1}^{(0)} \) are the eigenfunction for \( N - 1 \) electron in the Hamiltonian with external potential \( v_{\text{ext}}(r) \). We do this expansion so that \( v_{\text{eff}}(r) \) is shown to be well behaved independent of the expressions given in equations (30) and (31).

For well behaved \( \Psi \) [94–96] and because \( \rho(r) \) for the ground-state is nonzero except when \( r \to \infty \), \( f_j \) and its gradient will be finite and smooth. Thus, all the terms in \( v_{\text{eff}}(\Psi)(r) \) viz

\[
\int \frac{\rho_{N-1}(r, r')}{|r - r'|} \, dr' = (N - 1) \sum_{i, j} \int f_j^*(x) f_j(x) d\sigma \times \int \frac{\Psi_{N-1}^{(0)} \Psi_{N-1}^{(0)}}{|r - r'|} \, dx_{2-N},
\]  

(39)

\[
\Phi_{N-1}[H_{N-1} - E_N^0 \Phi_{N-1}] = \sum_{i \neq 0} (E_{N-1}^0 - E_{N-1}^0) \int |f_i(x)|^2 \, d\sigma.
\]  

(40)
As is apparent $\delta_{\text{LPS}}(r)$ has terms that do not grow large erroneously. Furthermore, for small $\{\delta f_i\}$, the difference is linear in $\{\delta f_i\}$. Thus it can be safely concluded that $v_{\text{eff}}[\Psi](r)$ is close to $v_{\text{eff}}[\Psi_0](r)$. The next question that arises is about the behavior of the corresponding density and the exchange–correlation potential. We now address that.

The density corresponding to $v_{\text{eff}}[\Psi](r)$ is obtained by solving the LPS equation [67]

\[
\left[ -\frac{1}{2} \nabla^2 + v_{\text{ext}}(r) + v_{\text{eff}}[\Psi](r) \right] \rho^{1/2}(r) = \mu \rho^{1/2}(r).\]

Let us call this density $\rho_1(r)$. Since $v_{\text{eff}}[\Psi](r) \approx v_{\text{eff}}[\Psi_0](r)$, density $\rho_1(r)$ will be closer to the exact density $\rho_0(r)$ (given by $\Psi_0$) than the density $\rho^0(r)$ corresponding to the approximate wavefunction $\Psi$ used. This is shown in figures 4 and 5 for H$^{-}$ ion and He atom using the product and correlated wavefunctions given in equation (13) and equation (18), respectively. In these figures we have plotted $\rho_0(r)$ and $\rho^0(r)$ associated with these wavefunctions. Also plotted is the exact density $\rho_0(r)$ [48]. We see that in all the cases, $\rho_1(r)$ is much closer to $\rho_0(r)$ in comparison to $\rho^0(r)$ (The maximum deviation is when product wavefunction is used for H$^{-}$ ion.) This then also suggests a possible method of obtaining accurate ground state densities using an approximate wavefunction. This will be explored in the future. Note that for two electron systems Pauli potential $v_{\text{Pauli}}(r)$ is zero and therefore the LPS effective potential for two electron systems contains only the Hartree and the exchange–correlation potential.

Next, we observe the following. Since $v_{\text{eff}}[\Psi](r)$ is free from spuriously large deviations from $v_{\text{eff}}[\Psi_0](r)$, it is anticipated that $v_{\text{Pauli}}(r)$ will also not deviate much from $v_{\text{Pauli}}(r)$. We now show this to be the case irrespective of whether the Kohn–Sham calculation is done exactly (fully numerically on a grid) or by employing a finite basis set, as long as a wavefunctional (orbital) based expression is used for the calculation of Pauli potential.

The exchange–correlation potential $v_{\text{xc}}(r)$ is obtained from $v_{\text{eff}}[\Psi](r)$ by subtracting from it $v_{\text{Pauli}}(\{\phi_i\})(r)$. The convergence towards true $v_{\text{xc}}(r)$ is done by an iterative process. The resulting potential $v_{\text{xc}}(r)$ will be smooth and will not have erroneously large deviation from the exact potential if the Pauli potential...
\( v_{\text{Pauli}}^n[\{\phi_i\}](\mathbf{r}) \) is well behaved at each iteration for approximate \( \{\phi_i\} \). That this is the case can be shown exactly in the same manner as done above for \( v_{n\text{eff}}[\Psi](\mathbf{r}) \). For this, at the \( n \)th iteration, we write

\[
\Phi_{N-1}^{KS}(\mathbf{x}, x_{2-N}) = \sum_i f_i^{KS(n)}(\mathbf{x}) \Psi_{N-1}^{KS}(\mathbf{x}_{2-N}), \quad (45)
\]

where \( \Psi_{N-1}^{KS}(\mathbf{x}_{2-N}) \) represent the determinant for \( N-1 \) exited state of the KS Hamiltonian corresponding to the \( n \)th iteration and \( \{f_i^{KS(n)}\} \) have the same properties as in the fully interacting case (see equation (38) above). Then during each iteration

\[
v_{\text{Pauli}}^n[\{\phi\}][\mathbf{r}] = \sum_{i \neq 0} (E_i^{KS(n)} - E_{N-1}^{KS}) \int |f_i^{KS(n)}(\mathbf{x})|^2 d\sigma \\
+ \frac{1}{2} \sum_i \int |\nabla f_i^{KS(n)}(\mathbf{x})|^2 d\sigma. \quad (46)
\]

Thus if we start iterations with a reasonable approximation (say LDA) to \( v_{xc} \), this potential is always going to be free of erroneous large terms and close to the exact Pauli potential for the \( n \)th iteration, thereby leading to a smooth exchange–correlation potential as iterations proceed. Furthermore, as shown in equation (43), this exchange–correlation potential will be close to the true exchange–correlation potential after convergence.

4. Analysis of Ryabinin, Kohut, and Staroverov (RKS) [37, 39] and modified RKS (mRKS) [76] methods

Having shown that the LPS potential calculated from wavefunction is well behaved and close to the true potential, we now use this to develop an understanding of why the method of Ryabinin, Kohut, Staroverov (RKS) [37, 39] and modified RKS (mRKS) [76] method give accurate exchange–correlation potential and mRKS improves the RKS further.

The main equation used by Staroverov et al is

\[
v_{xc}(\mathbf{r}) = v_{\psi}^\Psi(\mathbf{r}) + \frac{\tau^\Psi(\mathbf{r})}{\rho^\Psi(\mathbf{r})} - \frac{\nabla^2 \rho(\mathbf{r})}{4\rho(\mathbf{r})} - \epsilon^\Psi(\mathbf{r}) = \frac{\tau^{KS}(\mathbf{r})}{\rho^{KS}(\mathbf{r})} + \frac{\nabla^2 \rho^{KS}(\mathbf{r})}{4\rho^{KS}(\mathbf{r})} + \epsilon^{KS}(\mathbf{r}). \quad (47)
\]

The quantities on the right side of above equation are given in terms of many-body wavefunction \( \Psi \) and the corresponding density \( \rho(\mathbf{r}) \). Here

\[
v_{\psi}^\Psi(\mathbf{r}) = \int \frac{\rho_{xc}(\mathbf{r}, \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (48)
\]

\[
\tau^\Psi(\mathbf{r}) = \frac{1}{2} \int \left| \nabla \psi^2 \right| d\sigma d\mathbf{x}_{2-N}, \quad (49)
\]

and

\[
\epsilon^\Psi(\mathbf{r}) = \frac{N}{\rho^\Psi(\mathbf{r})} \int \psi^*(E_N - H_{N-1}) \psi d\sigma d\mathbf{x}_{2-N} \quad (50)
\]

are potential of Fermi–Coulomb hole \( \rho_{xc}(\mathbf{r}, \mathbf{r}') \), kinetic energy density and average energy respectively. Similarly, quantities are obtained from Kohn–Sham orbitals \( \{\phi_i^{KS}\} \) with the corresponding eigenenergies \( \{\epsilon_i^{KS}\} \) are the kinetic energy density \( \tau^{KS}(\mathbf{r}) = \frac{1}{2} \sum_i |\nabla \phi_i^{KS}(\mathbf{r})|^2 \) and the average ionization energy

\[
\epsilon^{KS}(\mathbf{r}) = \frac{1}{\rho^{KS}(\mathbf{r})} \sum_i |\phi_i^{KS}(\mathbf{r})|^2. 
\]

In their first algorithm for the construction of exchange–correlation potential, Ryabinin, Kohut, and Staroverov (RKS) [37, 39] took the term

\[
\nabla^2 \rho^{KS}(\mathbf{r})/4\rho^{KS}(\mathbf{r}) - \nabla^2 \rho(\mathbf{r})/4\rho(\mathbf{r})
\]

in equation (47) to be zero. Then the equation for updating of the exchange–correlation potential becomes

\[
v_{xe}^{\text{RKS}}(\mathbf{r}) = v_{\psi}^\Psi(\mathbf{r}) + \frac{\tau^\Psi(\mathbf{r})}{\rho^\Psi(\mathbf{r})} - \epsilon^\Psi(\mathbf{r}) - \frac{\tau^{KS}(\mathbf{r})}{\rho^{KS}(\mathbf{r})} + \epsilon^{KS}(\mathbf{r}). \quad (51)
\]
To apply the above equation one starts with a trial \( \{ \phi_i^{\text{KS}}, \epsilon_i^{\text{KS}} \} \) and the corresponding \( v_{\text{xc}}^{\text{RKS}}(r) \) is used in the Kohn–Sham equation
\[
\left[ -\frac{\nabla^2}{2} + v_{\text{ext}}(r) + v_{\text{H}}[\rho](r) + v_{\text{xc}}^{\text{RKS}}(r) \right] \phi_i^{\text{KS}}(r) = \epsilon_i^{\text{KS}} \phi_i^{\text{KS}}(r)
\]
(52)
to get the next set of Kohn–Sham orbitals and eigenenergies. This process is applied until convergence condition of Kohn–Sham density obtained during two consecutive iterations is achieved. In the basis-set limit the calculation above gives \( \rho^{\text{KS}}(r) = \rho(r) \) and the resulting potential is the true exchange–correlation potential of density \( \rho(r) \). For a finite basis set calculation the \( \rho^{\text{KS}}(r) \neq \rho(r) \) and the resulting potential is an approximation to the true potential conjugate to density \( \rho(r) \). The exchange–correlation potential obtained from other existing popular density-to-potential inversion methods \([20–26, 33–35, 38, 40, 41, 63–66]\) depends upon what type of density it corresponds to and for a basis-set density it could show unphysical behavior. However, exchange–correlation potential obtained by RKS method is found to be free from such pathological features. According to Staroverov \textit{et al.} \[76\] the RKS method gives good results because by taking \( \nabla^2 \rho^{\text{KS}}(r)/\rho^{\text{KS}}(r) = -\nabla^2 \rho(r)/\rho(r) = 0 \) one sets it to its basis set limit value even if \( \rho^{\text{KS}}(r) \neq \rho(r) \) so the resulting exchange–correlation potential gets close to its basis set limit. We point out that apart from imposing basis-set limit value on few quantities, it is the use of wavefunction dependent quantities in RKS method which play important role in giving the proper structure to the exchange–correlation potential obtained from it. This becomes transparent by writing equation (51) in terms of the LPS potential \( v_{\text{eff}}(r) \). Now using relations
\[
\int \frac{\rho_{N-1}(r'; r)}{|r' - r|} \, dr' = v_{\text{eff}}(r) + v_{\text{H}}[\rho](r),
\]
(53)
and
\[
\langle \Phi_{N-1} | H_{N-1} - E_{N-1} | \Phi_{N-1} \rangle = -v_{\text{eff}}(r),
\]
(54)
and
\[
\frac{1}{2} \int [\nabla \Phi_{N-1}]^2 \, ds_{2N} = \frac{1}{\rho(r)} \left( \tau_{\text{eff}} - \frac{1}{8} \frac{\nabla \rho(r)}{\rho(r)} \right)
\]
(55)
equation (51) is written (up to a constant) as
\[
v_{\text{xc}}^{\text{RKS}}(r) = v_{\text{eff}}[\Psi](r) + \frac{1}{8} \frac{\nabla \rho(r)}{\rho(r)}^2 - v_{\text{eff}}[\{ \phi_i^{\text{KS}} \}](r) - \frac{1}{8} \frac{\nabla \rho_{\text{KS}}(r)}{\rho_{\text{KS}}(r)}^2 - v_{\text{H}}[\rho](r).
\]
(56)

From the equation above it is seen that the RKS method utilizes the LPS potential written in terms of wavefunction for the construction of exchange–correlation potential. Since we have shown that the LPS potential \( v_{\text{eff}}(r) \) obtained from many-body wavefunction \( \Psi \) and Kohn–Sham orbitals \( \{ \phi_i^{\text{KS}} \} \) is well behaved, so the resulting exchange–correlation potential obtained from RKS method is also expected to show proper structure. However, equation (56) also contains density dependent term \( \frac{\nabla \rho(r)}{\rho(r)}^2 - \frac{\nabla \rho_{\text{KS}}(r)}{\rho_{\text{KS}}(r)}^2 \) in it whose effect may appear in the resulting potential. For \( \rho^{\text{KS}}(r) \approx \rho(r) \) the contribution of density dependent term is vanishingly small. However, for the finite basis set calculation \( \rho^{\text{KS}}(r) \neq \rho(r) \) and the quantity \( \frac{\nabla \rho(r)}{\rho(r)}^2 - \frac{\nabla \rho_{\text{KS}}(r)}{\rho_{\text{KS}}(r)}^2 \) may give significant contribution and the resulting potential could have pathological features. This is seen for Ar atom \[76\] where exchange–correlation potential shows well behaved nature only for a large basis-set calculation. However, by taking the \( \frac{\nabla \rho(r)}{\rho(r)}^2 - \frac{\nabla \rho_{\text{KS}}(r)}{\rho_{\text{KS}}(r)}^2 = 0 \) the above equation becomes
\[
v_{\text{xc}}^{m}\rho_{\text{RKS}}(r) = v_{\text{eff}}[\Psi](r) - v_{\text{eff}}[\{ \phi_i^{\text{KS}} \}](r) - v_{\text{H}}[\rho](r).
\]
(57)
which is the equation (expressed in natural orbitals) for the exchange–correlation potential used in the modified RKS method \(m\text{RKS}\) \[76\] and it is the same as equation (12). Now, since the \(m\text{RKS}\) method uses only the LPS potential \( v_{\text{eff}}[\Psi](r) \) and \( v_{\text{eff}}[\{ \phi_i \}](r) \) so the resulting exchange–correlation potential is expected to be well behaved. This is indeed observed in application \[76\] of the \(m\text{RKS}\) method to the Ar atom.

5. Conclusion

Previous work in the literature has shown that use of wavefunction based formula derived from LPS formulation leads to highly accurate exchange–correlation potential from wavefunctions calculated by expansion in finite basis set. In this study we have proved analytically and demonstrated numerically a general result: that the use of properly constructed approximate wavefunction—whether given in a functional form or in terms of basis-set expansion—in the LPS expression for potential leads to good approximation to the exact exchange–correlation potential for a given Hamiltonian specified by \( v_{\text{ext}}(r) \). Furthermore, we have shown that the difference between the exchange–correlation potential so obtained and that calculated by the inversion of the corresponding approximate density arises from the difference between \( v_{\text{ext}}(r) \) and the potential \( \tau_{\text{eff}}(r) \) corresponding to a given density. Our work thus extends the previous studies to all kinds of approximate wavefunctions and it gives a method to calculate accurate exchange–correlation potential by employing these. Additionally, we have also shown that the use of the LPS effective potential obtained from approximate wavefunction in the corresponding equation gives a density which is more accurate than that given by the wavefunction itself. This may pave the way to calculating accurate densities by employing approximate wavefunctions.

Appendix A. LPS potential calculated from Slater determinant wavefunction

In this section we calculate LPS effective potential for the \(N\) particle Slater-determinant wavefunction
constructed using one particle orthogonal spin–orbitals \( \{ \phi_i(x) \} \). For the Hartree–Fock spin–orbitals \( \{ \phi_i(x) = \phi_i^\text{HF}(x) \} \) those are the solutions of the Hartree–Fock (HF) equation

\[
-\frac{\nabla^2}{2} + v_{\text{ext}}(r) + \int \frac{d^3r'}{|r-r'|} \phi_i^\text{HF}(x') \phi_j^\text{HF}(x) = \epsilon_i^\text{HF} \phi_i^\text{HF}(x),
\]

with \( \epsilon_i^\text{HF} \) being the eigenenergy corresponding to \( \phi_i^\text{HF} \). \( \Phi_{S,N} \) is an approximation to the ground state wavefunction for interacting system and it is known as HF Slater determinant wavefunction. Here \( \phi_i^\text{HF}(x) \) is HF exchange operator and it operates on spin–orbitital \( \phi_i^\text{HF}(x) \) as

\[
\phi_i^\text{HF}(x) \phi_j^\text{HF}(x) = -\sum_j \int \frac{\phi_i^\text{HF}(x) \phi_j^\text{HF}(x') \phi_j^\text{HF}(x')}{|r-r'|} d'x'.
\]

Similarly if one employs \( \{ \phi_i(x) = \phi_i^\text{KS}(x) \} \) with \( \{ \phi_i^\text{KS}(x) \} \) being solution of the Kohn–Sham equation then \( \Phi_{S,N} \) represents the ground-state wavefunction of the corresponding Kohn–Sham system.

For the calculation purpose we consider LPS potential in reduced density-matrix representation. In reduced density-matrix representation the Pth order reduced density-matrix \( \gamma_p(x', x_{2-p}, x, x_{2-p}) \) is defined using many-body wavefunction \( \Psi \) as

\[
\gamma_p(x', x_{2-p}, x, x_{2-p}) = \frac{1}{N_p} \int \Psi(x', x_{2-p}, x_{p+1-N}) \times \Psi^*(x, x_{2-N}) d(x_{p+1-N}).
\]

In particular for \( \Psi = \Phi_{S,N} \), the Pth order reduced density-matrix \( \gamma_p(x', x_{2-p}, x, x_{2-p}) \) is related to the first order reduced density matrix \( \gamma_1(x'; x) \) by

\[
\gamma_p(x', x_{2-p}, x, x_{2-p}) = \frac{1}{\sqrt{p!}} \left[ \left( \gamma_1(x'; x) \right) \gamma_1(x_{2}; x_{2}) \ldots \gamma_1(x_{2-p}; x_{2-p}) \right]_{p=0}^{N}
\]

where \( \gamma_1(x'; x) = \sum_{i=1}^{N} \phi_i(x') \phi_i^*(x) \). The density \( \rho(r) \) in reduced density representation is calculated by

\[
\rho(r) = \int \gamma_1(x; x) d\sigma.
\]

Using the above relations one finds that different term of LPS potential in equation (8) for Slater determinant wavefunction \( \Phi_{S,N} \) are

\[
\int \frac{\rho_{N-1}(r'; r')}{|r-r'|} d'x' = \frac{2}{\rho(r)} \int \frac{\gamma_2(x', x'; x, x')}{|r-r'|} d'x' d\sigma - \frac{1}{\rho(r)} \int \frac{\gamma_1(x'; x)}{|r-r'|} d'x' d\sigma
\]

\[
= \eta_1(r) + v_2(r).
\]
\[ - \sum_{i=1}^{N} \int \frac{\phi_i^*(\mathbf{x}) \phi_j^*(\mathbf{x})}{\rho(\mathbf{r})} d\sigma \left\{ \int \frac{\phi_j^*(\mathbf{x}')}{-\frac{\nabla^2}{2} + v_{ext}(\mathbf{r}') + \int \frac{\rho(\mathbf{r}'')}{|\mathbf{r}' - \mathbf{r}|} d\sigma' \} \phi_i(\mathbf{x}') d\sigma' \right\} \\
\[ \sum_{k=1}^{N} \int \frac{\phi_i^*(\mathbf{x}^k) \phi_j^*(\mathbf{x}') \phi_k^*(\mathbf{x}^k) \phi_j^*(\mathbf{x}')}{|\mathbf{r} - \mathbf{r}'|} d\sigma' d\sigma'' \right\} \quad \text{(A.8)} \]

and

\[ \frac{1}{2} \int |\nabla \Phi_{N-1}|^2 d\sigma d\mathbf{x}_2 \ldots d\mathbf{x}_N = \frac{1}{2 \rho(\mathbf{r})} \int \nabla \gamma_i(\mathbf{x},\mathbf{x}') |_{\mathbf{x} = \mathbf{x}'} d\sigma - \frac{1}{8} \left| \frac{\nabla v(\mathbf{r})}{\rho(\mathbf{r})} \right|^2 = \frac{1}{2 \rho(\mathbf{r})} \int \sum_{i=1}^{N} |\nabla \phi_i(\mathbf{x})|^2 d\sigma - \frac{1}{8} \left| \frac{\nabla v(\mathbf{r})}{\rho(\mathbf{r})} \right|^2. \quad \text{(A.9)} \]

In equation (A.7) \( v_S(\mathbf{r}) \) is known as the Slater potential [98] and it is given by

\[ v_S(\mathbf{r}) = - \frac{1}{\rho(\mathbf{r})} \int \frac{\gamma_i(\mathbf{x}',\mathbf{x}) \gamma_j(\mathbf{x}',\mathbf{x})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{x}' d\sigma \\
= \frac{1}{\rho(\mathbf{r})} \sum_{i=1}^{N} \int \frac{\phi_i^*(\mathbf{x}) \phi_j(\mathbf{x}) \phi_j(\mathbf{x}) \phi_i(\mathbf{x})}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{x}' d\sigma. \quad \text{(A.10)} \]

Having calculated different quantities of the LPS potential in equation (8), on applying equations (A.7)–(A.9) with equation (A.2) for Hartree–Fock wavefunction \( \phi(\mathbf{x}) = \phi_{\text{HF}}(\mathbf{x}) \) the corresponding LPS potential is found to be

\[ v_{\text{eff}}^{\text{HF}}(\mathbf{r}) = v_0(\mathbf{r}) + v_S(\mathbf{r}) + \frac{1}{\rho^{\text{HF}}(\mathbf{r})} \int \sum_{i=1}^{N} (\mu^{\text{HF}} - \epsilon_i^{\text{HF}}) |\phi_i^{\text{HF}}(\mathbf{x})|^2 d\sigma \\
= \frac{1}{2 \rho^{\text{HF}}(\mathbf{r})} \int \sum_{i=1}^{N} |\nabla \phi_i^{\text{HF}}(\mathbf{x})|^2 d\sigma - \frac{1}{8} \left| \frac{\nabla \rho^{\text{HF}}(\mathbf{r})}{\rho^{\text{HF}}(\mathbf{r})} \right|^2. \quad \text{(A.11)} \]

The quantity \( \mu^{\text{HF}} \) is calculated using

\[ \mu^{\text{HF}} = E_{\text{0-HF}} - E_{\text{0-HF}}, \quad \text{(A.12)} \]

and is the chemical potential of HF system in Koopman’s approximation. In the calculation of LPS potential for the Kohn–Sham system \( \{ \phi(\mathbf{x}) = \phi^{\text{KS}}(\mathbf{x}) \} \), all the terms corresponding to interaction term \( 1/|\mathbf{r} - \mathbf{r}'| \) drop out of equation (A.11). Then using equations (A.8) and (A.9) leads to

\[ v_{\text{Pauli}}^{\text{KS}}(\mathbf{r}) = \frac{1}{\rho^{\text{KS}}(\mathbf{r})} \int \sum_{i=1}^{N} (\mu^{\text{KS}} - \epsilon_i^{\text{KS}}) |\phi_i^{\text{KS}}(\mathbf{x})|^2 d\sigma \\
= \frac{1}{2 \rho^{\text{KS}}(\mathbf{r})} \int \sum_{i=1}^{N} |\nabla \phi_i^{\text{KS}}(\mathbf{x})|^2 d\sigma - \frac{1}{8} \left| \frac{\nabla \rho^{\text{KS}}(\mathbf{r})}{\rho^{\text{KS}}(\mathbf{r})} \right|^2, \quad \text{(A.13)} \]

here \( \mu^{\text{KS}} = \epsilon^{\text{KS}}_{\text{max}} \) is the eigenenergy of the highest occupied Kohn–Sham orbital.
