Universal nature of different methods of obtaining the exact Kohn–Sham exchange-correlation potential for a given density

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Abstract
Finding the external potential or the Kohn–Sham (KS) potential for a given ground state density is a fundamental inverse problem in density functional theory. Furthermore, it is important in generating the exact exchange-correlation potential for a density which can then serve as a benchmark for testing the accuracy of an exchange-correlation energy functional. Over the years different methods have been proposed to do the density-to-potential inversion and all of these appear to be disjoint. In this paper we show that these methods are connected to and can be derived from one general algorithm that utilizes two forms of the equation for the density; these are the KS equation in terms of orbitals and the Euler equation in terms of the density. We obtain the condition for the convergence of the general method and show that all the methods considered by us satisfy this condition. We demonstrate the method and its flexibility by obtaining the KS potential for some spherical systems in a variety of ways.

Keywords: density functional theory, Kohn–Sham potential, exchange-correlation potential

1. Introduction

Density functional theory (DFT) [1–4] is the most widely used method to study the electronic properties of materials [5–7] because of its ever increasing accuracy [8] and computational ease of implementation. As is well known, in DFT the ground state energy is written as a functional $E[\rho]$ of the ground state density $\rho(r)$. In the Kohn–Sham [9] approach to density functional theory (KSDFT) the interacting electron system is mapped to a fictitious non-interacting system and the energy $E[\rho]$ is expressed as the sum of the non-interacting kinetic energy $T_\rho[\rho]$ of the same density, the external energy $\int v_{ext}(r)\rho(r)dr$ where $v_{ext}(r)$ is the external potential, the Hartree energy $E_H[\rho] = \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r-r'|}drdr'$ and the exchange-correlation energy $E_{xc}[\rho]$ which includes all the many-body effects.

The ground state density of the electrons can be obtained by either solving the Euler equation

$$\frac{\delta T_\rho[\rho]}{\delta \rho} + v_{ext}(r) + v_H(r) + v_{xc}(r) = \mu,$$

or equivalently the Kohn–Sham (KS) equation,

$$\left(-\nabla^2 + v_{ext}(r) + v_H(r) + v_{xc}(r)\right)\phi_i(r) = \epsilon_i \phi_i(r).$$

Here

$$v_H(r) = \int \frac{\rho(r')}{|r-r'|}dr'$$

is the Hartree potential and

$$v_{xc}(r) = \frac{\delta E_{xc}[\rho]}{\delta \rho(r)},$$

is the exchange-correlation potential.
In equation (1) \( \mu \) is the Lagrange multiplier to ensure that 
\[
\int \rho(r) \, dr = N = \text{total number of electrons, and has the interpretation of being the chemical potential. The density } \rho(r) \text{ and the kinetic energy } T_\text{K}[\rho] \text{ in terms of the KS orbitals } \{ \phi_i(r) \} \text{ are given as}
\]
\[
\rho(r) = \sum_i f_i |\phi_i(r)|^2,
\]
and
\[
T_\text{K}[\rho] = \sum_i f_i \langle \phi_i(r) | -\frac{1}{2} \nabla^2 |\phi_i(r)\rangle,
\]
where \( f_i \) is the occupancy of each orbital.

Exact expressions for \( T_\text{K}[\rho] \) and \( E_\text{ex}[\rho] \) in terms of the density are not known. As a result, it is the KS equation which is employed in DFT because it treats \( T_\text{K}[\rho] \) exactly in terms of the orbitals. However, in applying KS-DFT, the exchange-correlation energy functional \( E_\text{xc}[\rho] \) is still approximated, and consequently, the KS equation can be solved only approximately. Development of more and more accurate functionals for \( E_\text{xc}[\rho] \) is of central interest for the application of DFT since the accuracy of the energy and density obtained depends on the quality of \( E_\text{xc}[\rho] \) and the corresponding \( v_\text{xc}(\rho); r \).

While accurate exchange-correlation energy functionals are being developed [13–21] and applied [22], it is equally important to know the exact KS solution for a many-electron density wherever the latter is available. This gives [23–38] the exact KS orbitals, the corresponding non-interacting kinetic energy, and the related quantities. Furthermore, through the construction of the KS systems, we also learn [39–48] about their other interesting aspects. Thus, the exact KS systems set a benchmark to test the accuracy of approximate energy functionals. Note that for the exact density of electrons in a given external potential, constructing the KS system boils down to finding the exact exchange-correlation potential.

The problem of finding the KS system for a given ground state density falls in the general category of inverse problems in physics [49, 50]. In the present context, the direct problem is to find the ground state density of a system of electrons in an external potential by solving the Schrödinger equation for the wave function. The inverse problem [38], whose solution is warranted by the Hohenberg–Kohn theorem [4], is to find the external potential or the wave function for a ground state electronic density. In the context of KS theory, the inverse problem reduces to finding the exchange-correlation potential for the ground state density of electrons in a given external potential. An interesting application [51] of the inverse problem has been to find the Hartree–Fock (HF) wave function for electrons in Be crystal from its x-ray diffraction data. Thus the significance of finding the KS system for a given ground state density can not be overemphasized.

Given its importance, many different methods have been developed over the years to obtain the exact KS system for a given density. Some of these [30, 31] are based on the direct optimization of a functional (see equation (5)) while others are iterative [23–29, 32, 33, 36] (these are displayed in table 1). The latter methods converge towards the exact KS potential by using a density-based quantity to update the potential in each step of the iterative process. For example in reference [33], the iterative method utilizes the difference between a given density and densities obtained during iterative steps to modify the potential. Interestingly, in the same paper, the iterative scheme has also been linked to an optimization method based on Lieb’s definition [52] of \( T_\text{K}[\rho] \). Accordingly, starting from a given \( v_\text{xc}(r) \), the potential is improved iteratively so that \( T_\text{K}[\rho] \) is maximized [33]. Each of the methods referenced above provides a different scheme for this optimization.

The motivation of the present work originates from the speculation that different methods used to update the potential ought to be connected with each other through the fundamental principles of DFT. Therefore we should be able to derive and string them together on the basis of a general prescription. In this paper, we show how this is done for all the inversion schemes (except that of [23]) given above from a single method that utilizes equation (1) and equation (2) in tandem. This method has its origin in the Levy–Perdew–Sahni (LPS) equation [57] for density. Hence in the following we first derive [55] the method for the LPS equation and then generalize it to show how different methods emerge from it. Furthermore, we support this generalization by relating it to the variational principle. Thus, the inversion from density to the KS system through any of these methods is equivalent to the maximization [31, 33] of the functional

\[
J[v, \rho_0] = E[v] - \int v(r) \rho_0(r) \, dr,
\]

with respect to \( v(r) \) to obtain the Levy–Lieb functional [52, 58] for a given density \( \rho_0(r) \). Here \( E[v] \) denotes the energy of a given number of electrons moving in the potential \( v(r) \). Using this approach, we also derive a criterion for the convergence of the generalized inversion process. Although the differential equation for the density coupled with the KS equation has been used [35] in the past to obtain the KS potential, derivation of different inversion methods using these equations has not been done previously to the best of our knowledge.

2. General method to obtain the KS potential

2.1. KS potential from the LPS equation

Consider the LPS equation for the density

\[
\left[ -\frac{1}{2} \nabla^2 + v_{\text{eff}}(r) \right] \rho^{1/2}(r) = \mu \rho^{1/2}(r), \tag{6}
\]

where the expression for \( v_{\text{eff}}(r) \) in the terms of many-body wave function was derived in [57]. However, by writing the non-interacting kinetic energy as

\[
T_\text{K}[\rho] = T_\text{K}[\rho] + T_F[\rho], \tag{7}
\]
| Method                                      | $S[\rho]$                                           | Potential improvement scheme                                                                 |
|--------------------------------------------|-----------------------------------------------------|-----------------------------------------------------------------------------------------------|
| 1. van-Leuwen Baerends [29]               | $\frac{1}{2} \int \chi_i^2(r) \rho(r) dr$          | $v_{\text{ex}}^{0}(r) = v_{\text{ex}}^0(r) + \epsilon \sqrt{\frac{\Delta \rho(r)}{\rho_0(r)}} v_{\text{ac}}(r)$ |
| 2. Werden and Davidson [53], Görling [24], Gaudin and Burke [36, 54] | $-\frac{1}{2} \int \chi_i^{-1}(r, r') \rho(r) \rho(r') dr'dr$ | $v_{\text{ex}}^{0}(r) = v_{\text{ex}}^0(r) + \epsilon \sqrt{\frac{\Delta \rho(r)}{\rho_0(r)}} v_{\text{ac}}(r)$ |
| 3. Peirs, Van Neck and Warqueur [32]      | $\int \rho^n(r) dr \quad (n = 2, \beta > 0)$       | $v_{\text{ex}}^{0}(r) = v_{\text{ex}}^0(r) + \epsilon \sqrt{\frac{\Delta \rho(r)}{\rho_0(r)}} v_{\text{ac}}(r)$ |
| 4. Kadantsev and Stott [33]              | $\int \rho^2(r) dr \quad (n = 2)$                  | $v_{\text{ex}}^{0}(r) = v_{\text{ex}}^0(r) + \epsilon \sqrt{\frac{\Delta \rho(r)}{\rho_0(r)}} v_{\text{ac}}(r)$ |
| 5. Hollins, Clark, Refson and Gidopoulos (HCRG) [48] | $-\frac{1}{2} \int \rho^{1/2}(r) \nabla^2 \rho^{1/2}(r) dr$ | $v_{\text{ex}}^{0}(r) = v_{\text{ex}}^0(r) + \epsilon \sqrt{\frac{\Delta \rho(r)}{\rho_0(r)}} v_{\text{ac}}(r)$ |
| 6. Present work [55, 56]                 | $\int \rho^{n+1}(r) dr \quad (0 < n \leq 1)$       | $v_{\text{ex}}^{0}(r) = v_{\text{ex}}^0(r) + \epsilon \sqrt{\frac{\Delta \rho(r)}{\rho_0(r)}} v_{\text{ac}}(r)$ |
| 7. Present work                           | $\int \rho \log \rho dr$                           | $v_{\text{ex}}^{0}(r) = v_{\text{ex}}^0(r) + \epsilon \sqrt{\frac{\Delta \rho(r)}{\rho_0(r)}} v_{\text{ac}}(r)$ |
| 8. Present work                           |                                                     | $v_{\text{ex}}^{0}(r) = v_{\text{ex}}^0(r) + \epsilon \sqrt{\frac{\Delta \rho(r)}{\rho_0(r)}} v_{\text{ac}}(r)$ |
| 9. Present work (hybrid functional)      | $\int [\epsilon(r) \rho^{0.3}(r) + (1 - \epsilon(r)) \rho^{0.5}(r)] dr (\alpha > 0)$ | $v_{\text{ex}}^{0}(r) = v_{\text{ex}}^0(r) + \epsilon \sqrt{\frac{\Delta \rho(r)}{\rho_0(r)}} v_{\text{ac}}(r)$ |

where

$$T_W[\rho] = -\frac{1}{2} \int \rho^{1/2}(r) \nabla^2 \rho^{1/2}(r) dr$$

is the Weizsäcker kinetic energy and $T_P[\rho]$ is the Pauli kinetic energy, it is easy to see that

$$v_{\text{eff}}(r) = v_{\text{ex}}(r) + v_P(r) + v_H(r) + v_{\text{ac}}(r),$$

where $v_P = \frac{\delta E}{\delta \rho}$ is the Pauli potential [59, 60]. With

$$\frac{\delta E}{\delta \rho} = -\frac{1}{2} \frac{\nabla^2 \rho^{1/2}(r)}{\rho^{1/2}(r)},$$

equation (1) for the density is

$$\frac{1}{2} \frac{\nabla^2 \rho^{1/2}(r)}{\rho^{1/2}(r)} + v_{\text{ex}}(r) + v_P(r) + v_H(r) + v_{\text{ac}}(r) = \mu.$$  

(10)

Now for a given exact density $\rho_0(r)$, if we denote the corresponding quantities with superscript ‘0’, equation (10) can be rewritten for the exact exchange-correlation potential as

$$v_{\text{ex}}^{0}(r) = \mu + \frac{1}{2} \frac{\nabla^2 \rho_0^{1/2}(r)}{\rho_0^{1/2}(r)} - v_{\text{ex}}(r) - v_P^{0}(r) - v_H^{0}(r),$$

and for the exact Pauli potential as

$$v_{P}^{0}(r) = \mu + \frac{1}{2} \frac{\nabla^2 \rho_0^{1/2}(r)}{\rho_0^{1/2}(r)} - v_{\text{ex}}(r) - v_H^{0}(r) - v_{\text{ac}}^{0}(r).$$

(12)

Note that $'\mu'$ is given by density $\rho_0(r)$ from its asymptotic behavior. Now suppose we have an approximate potential $v_{\text{ex}}^{1}(r)$ at the ith iteration that gives density $\rho_i(r)$ as an approximation to $\rho_0(r).$ We use equation (11) and equation (12) to write the exchange-correlation potential for the $(i + 1)$th iteration as follows:

$$v_{\text{ex}}^{i+1}(r) = \mu + \frac{1}{2} \frac{\nabla^2 \rho_i^{1/2}(r)}{\rho_i^{1/2}(r)} - v_{\text{ex}}(r) - v_P^{i}(r) - v_H^{i}(r),$$

(13)

where

$$v_P^{i}(r) = \mu_{i} + \frac{1}{2} \frac{\nabla^2 \rho_i^{1/2}(r)}{\rho_i^{1/2}(r)} - v_{\text{ex}}(r) - v_H^{i}(r) - v_{\text{ac}}^{i}(r).$$

(14)

Thus the potential for next iteration is improved by replacing $\rho_i(r)$ by $\rho_0(r)$ in the term arising from the Weizsäcker kinetic energy. Substituting equation (14) in equation (13) gives $(\mu - \mu_{i})$ (we have dropped the constant term)

$$v_{\text{ex}}^{i+1}(r) = v_{\text{ex}}^{i}(r) - \frac{1}{2} \frac{\nabla^2 \rho_0^{1/2}(r)}{\rho_0^{1/2}(r)} + \frac{1}{2} \frac{\nabla^2 \rho_i^{1/2}(r)}{\rho_i^{1/2}(r)}.$$  

(15)

The constant $(\mu - \mu_{i})$ can be fixed either by adjusting the potential to get the correct $\mu$ or by setting it equal to its value at a large distance. Equation (15) is the working equation for obtaining the exchange-correlation potential $v_{\text{ex}}^{i}(r)$ up to a constant for the ground state density $\rho_0(r).$

Using equation (15), the algorithm to find the exchange-correlation potential for a ground state density $\rho_0(r)$ is as follows.

- Start with a trial exchange-correlation potential $v_{\text{ex}}^{0}(r)$ and solve the KS equation to obtain the corresponding orbitals, the density and $\mu_{i} = \epsilon_{\text{max}}.$ The external and Hartree potentials in the KS equations are the exact ones with the latter being calculated from the density $\rho_0(r).$
• Find the new potential using equation (15). At this step one can either use \( \mu - \epsilon_{\text{max}} \) explicitly or fix the potential asymptotically by using the boundary condition for it.
• Use the new potential in the KS equation again until the density obtained from it matches to \( \rho_0(r) \).

For completeness we note that if \( \frac{1}{2} \frac{\nabla r^2}{\rho_0} \) and \( \frac{1}{2} \frac{\nabla r^2}{\rho_0} \) in equation (15) are replaced by \( v_p(r) \) derived from the true wave function and the KS orbitals in the \( n \)th iteration, respectively, an expression for \( v_{i+1}^{\alpha}(r) \) is obtained in terms of the quantities that depend explicitly on the wave function and the KS orbitals. This approach has been utilized [35] to get \( v_{xc} \) or \( v_\alpha \) in the HF theory, directly from the wave function and get rid of basis-set effects. For further discussion on the method of [35], we refer the reader to [61, 62]. We note that the approach given above has also been developed independently in [56].

Although the method suggested by equation (15) is quite straightforward in principle, it is difficult to implement numerically because of the Laplacian of the density in it. Furthermore, it also involves division by the density and that at times leads to difficulty in regions of very small densities. Thus, one would like to generalize equation (15) to use some other function of density for updating the potential. The question is how to do it.

At this stage, we recall that the LPS equation was derived by splitting the functional \( T_3[\rho] \) into the Weizsäcker functional which is known exactly in terms of the density and the Pauli kinetic energy functional. In the inversion scheme above, the unknown Pauli potential in the LPS equation has been eliminated. We now ask if the method above can be generalized by decomposing the kinetic energy functional in terms of some other known functional and its ‘Pauli’ counterpart and then eliminating the latter. This can indeed be done as we show in the following.

2.2. Use of a general functional \( S[\rho] \) to obtain the KS potential

To develop a general algorithm for KS density-potential inversion we split the kinetic energy functional \( T_3[\rho] \) as

\[
T_3[\rho] = S[\rho] + \tilde{T}_F[\rho],
\]

where \( S[\rho] \) is a known functional with the dimensions of energy and \( \tilde{T}_F[\rho] = T_3[\rho] - S[\rho] \) is the generalized Pauli kinetic energy. In terms of \( S[\rho] \), the equation for the density is

\[
\frac{\delta S}{\delta \rho} + v_{xc}(r) + \tilde{v}_F(r) + v_H[\rho(r)] + v_\alpha(r) = \mu,
\]

where \( \tilde{v}_F = \frac{\delta S}{\delta \rho} \) and is not known. Analogous to the manner in which equation (10) leads to equation (15) relating \( v_{i+1}^{\alpha}(r) \) to \( v_i^{\alpha}(r) \), equation (17) gives

\[
v_{i+1}^{\alpha}(r) = v_i^{\alpha}(r) + \frac{\delta S}{\delta \rho} \bigg|_{\rho_{i+1}} - \frac{\delta S}{\delta \rho} \bigg|_{\rho_i},
\]

where \( \frac{\delta S}{\delta \rho} \bigg|_{\rho_{i+1}} \) implies that the functional derivative is evaluated at density \( \rho_{i+1}(r) \). This is the general working equation for obtaining the exchange-correlation potential \( v_{i+1}^{\alpha}(r) \) corresponding to a given density \( \rho_i(r) \). Following the steps as given above, it can be employed iteratively to obtain the exact exchange-correlation potential for a given density \( \rho_0(r) \) with the functional \( S[\rho] \).

An important aspect of the development above is that with equation (18) we have the flexibility of choosing \( S[\rho] \) and that leads to a variety of methods. To give a few examples, \( S[\rho] \) can be chosen to be the Weizsäcker functional leading to equation (15) or the functional \( \int f(r)' \rho''(r)dr \) \((n > 1)\), where \( f(r) \) is an appropriately chosen function, the Hartree energy \( \frac{1}{2} \int \rho''(r)dr \) or \( \int \rho(r)\log \rho(r)dr \). Furthermore, many new functionals can be obtained by mixing the functionals given above. However, the functional \( S[\rho] \) must satisfy a condition derived from the variational principle.

3. Condition on functional \( S[\rho] \) using the Lieb functional

The condition for admissible forms of \( S[\rho] \) is obtained by using the Levy–Lieb functional [52, 58] defined by Lieb [52] as

\[
F[\rho_0] = \sup_{\nu} J[\nu, \rho_0],
\]

where \( J[\nu, \rho_0] \) is given in equation (5) and the search for the supremum is done over different potentials \( \nu(r) \). For the true ground state densities the supremum is a maximum. Thus a properly chosen \( S[\rho] \) should make \( J[\nu, \rho_0] \) larger and larger (i.e. \( \Delta J > 0 \)) in each iterative step converging finally to the correct \( F[\rho_0] \). For this to happen, consider the potentials \( \nu^i \) and \( \nu^{i+1} \) for the \( i \)th and \( (i + 1) \)th steps and calculate the difference:

\[
\Delta J = J[\nu^{i+1}, \rho_0] - J[\nu^i, \rho_0] = E[\nu^{i+1}] - E[\nu^i] - \int (\nu^{i+1} - \nu^i) \rho_0(r)dr.
\]

For small \((\nu^{i+1} - \nu^i)\)—and this can always be ensured by proper mixing [63] of \( \nu^i \) and the potential calculated from equation (18)—we have by the first-order perturbation theory

\[
E[\nu^{i+1}] - E[\nu^i] = \int (\nu^{i+1} - \nu^i) \rho_i(r)dr,
\]

and therefore

\[
\Delta J = \int (\nu^{i+1} - \nu^i) \rho(r) - \rho_0(r)dr,
\]

\[
= \int \left( \frac{\delta S}{\delta \rho} \bigg|_{\nu_i} - \frac{\delta S}{\delta \rho} \bigg|_{\nu_i} \right) \rho_i(r) - \rho_0(r)dr.
\]

For the iterative process to converge towards the correct potential, the condition \( \Delta J \geq 0 \) and equation (22) imply that the functional \( S[\rho] \) be such that

\[
\int \left( \frac{\delta S}{\delta \rho} \bigg|_{\nu_i} - \frac{\delta S}{\delta \rho} \bigg|_{\nu_i} \right) (\rho(r) - \rho_0(r))dr \geq 0.
\]
Equation (23) therefore is the condition on \( S[\rho] \) for finding the KS potential using iterative methods. The proof above is akin to the demonstration [63, 64] that the iterative KS solution always converges towards minimum energy. However, there is a subtle difference. In the proof [63, 64] of convergence, the term \( (\rho_i(r) - \rho_0(r)) \), i.e. the density difference between consecutive iterations so that the condition reads 

\[
\int (v_{i+1}(r) - v_i(r))(\rho_{i+1}(r) - \rho_i(r))dr \geq 0. 
\]

Finally, we note that for the KS system, \( F[\rho_i] = T_0[\rho_i] \) and the proof reduces to that given in [31, 33]. However, the general proof indicates that the procedure can also be applied to find the external potential for a given density [36].

A strong condition on \( S[\rho] \) will be that the integrand

\[
\left( \frac{\delta S}{\delta \rho} \bigg|_{v_i(r)} - \frac{\delta S}{\delta \rho} \bigg|_{v_0(r)} \right)(\rho_i(r) - \rho_0(r)) \geq 0. 
\]

This condition is easy to understand physically: it means that in each iterative step the potential increases (decreases) if the density \( \rho(r) \) in the previous step is larger (smaller) than the target density \( \rho_0(r) \).

### 4. Results

In table 1, we have listed many different density-based inversion schemes that exist in the literature and show that they all have a corresponding \( S[\rho] \) functional that satisfies either equation (23) or equation (24). Additionally we have also listed some new inversion methods based on the \( S[\rho] \) proposed in this work. We have applied new, different methods presented above to four distinct spherically symmetric systems.

All the calculations reported here are carried out using the Herman–Skillman program [65] by modifying it suitably. The starting exchange-correlation potential for all the calculations is taken to be \( \frac{v_H(r)}{N} \) where \( v_H(r) \) is the Hartree potential calculated from a given density \( \rho_0(r) \) and \( N \) is the number of electrons. We find this choice to be the best as it gives the same \( v_H(r) \) for all methods. For other choices, the resulting potential may differ slightly near the nucleus where the external potential dominates. During the iterative process, the potential for the \( (i + 1) \) iteration is taken to be

\[
v_{i+1}(r) = v_i(r) + \epsilon \left( \frac{\delta S}{\delta \rho} \bigg|_{v_i(r)} - \frac{\delta S}{\delta \rho} \bigg|_{v_0(r)} \right)
\]

where \( \epsilon \) (0 < \( \epsilon \) < 1) is a mixing coefficient. In our calculations we have taken it to be 0.05. Furthermore, the potential is taken to be \( -\frac{1}{r} \) in the asymptotic region. The program is iterated until it meets the convergence criterion chosen by us. We have chosen the criterion based on the difference in the potential produced. For this, we have taken

\[
|\Delta V_{i+1}| \leq 5 \times 10^{-5}, \quad \text{where} \quad \Delta V_{i+1} = |\frac{\delta S}{\delta \rho} \bigg|_{v_i(r)} - \frac{\delta S}{\delta \rho} \bigg|_{v_0(r)}|
\]

i.e. without the mixing coefficient between two iterations. The number of iterations in each system considered varies depending on the method and the mixing coefficient used. For example the Weizsacker functional, when applied with the mixing coefficient \( \epsilon = 0.05 \), takes only 1000 iterations for clusters, while it takes 50 000 iterations for an Ar atom. Similarly, the value of \( \Delta \) varies according to the mixing coefficient used. For our calculations it starts with \( 10^{-4} \) and soon goes down by several orders of magnitude for a Hookium atom. Similar trends are observed for other systems. By the time convergence is achieved, \( \Delta J \) is of the order of \( 10^{-10} - 10^{-13} \) for different systems. Now we present our results.

In figure 1 we show the exchange potential for the HF density of Na and Ar atoms [66] using methods 6, 7, and 8 given in the table. The output exchange potential matches the corresponding optimized effective potential [67] for all the functional forms mentioned above with \( n \) varying over a large number of values. We have also tested the hybrid functional given in the table and found that due to \( \rho^{0.05} \) in it, the potential in the asymptotic region is reproduced with ease. We comment on this further in the paragraph below.
Next in figure 2 we display the correlation potential of a Hookium atom calculated using $S[\rho] = -\frac{1}{2} \int \rho(r)^{1/2} \nabla^2 \rho(r)^{1/2} dr$, $\int \rho^{1.05}(r) dr$ and the hybrid functional given in table 1. The output potential matches perfectly with the exact correlation potential [68]. We wish to point out that although the functional $S[\rho] = \int \rho^{1.05}(r) dr$ gives an exact result here, for inner regions a functional with a larger power of $\rho$ is equally good. It is in the outer regions where the density becomes very small, because of its $e^{-r}$ dependence on $r$, that the functional $\int \rho^{1.05}(r) dr$ becomes particularly advantageous. This then is a good example of how hybrid functionals are useful in such situations.

Finally, in figure 3, we employ the density for a neutral jellium sphere [69, 70] carrying a total background charge $N$ (and the same number of electrons) to get the KS exchange potential. These densities are obtained using the Harbola-Sahni (HS) exchange potential [71]. The method proposed in this paper reproduces the HS exchange potential for different forms of $S[\rho]$ viz. $\int \rho^{1.05}(r) dr$ and $\frac{1}{2} \int \rho(r)^{1/2} \nabla^2 \rho(r)^{1/2} dr$. For other forms stated above, deviation from the exact potential starts for $r > 20$ as the density becomes very low.

The general theory proposed in the preset work can also be applied to understand the Zhao–Morrison–Parr (ZMP) method [28] which has similarity to updating the potential using the electrostatic potential given by $\rho_i(r) - \rho_0(r)$; we present this in the appendix later.

5. Conclusion

To conclude, we have shown that all the density-based methods for density-to-potential inversion emerge from the Euler equation for density and have also provided an understanding of these methods on the basis of Lieb’s definition of the Hohenberg–Kohn universal functional $F[\rho]$. Our work thus unifies these different methods through the fundamental principle of DFT and gives a general theory for the construction of a KS system for a given density. As a result, it also provides flexibility in ways through which a KS system can be constructed for a given density, as has been demonstrated in this paper.

Before ending this paper, in the present work we have demonstrated the unified theory of density-to-potential inversion using simple spherical systems. All these methods will work equally well with an exact density for any system. However, we note that the majority of calculations for densities of different systems are performed using suitable basis sets and this may lead some pathological features [72, 73] in the resulting exchange-correlation potential. In particular Gaussian basis sets give wild oscillations in the exchange-correlation potential. To overcome these oscillations, a wave-function-based method, derived from the LPS equation, has previously been proposed [35, 37]. We are working on how density-based methods discussed in this work can also be used in conjunction with the LPS equation to avoid these oscillations. The work will be reported in a separate communication.

Appendix. Zhao–Morrison–Parr [28] method

In the ZMP method, the KS potential is obtained as the Hartree potential of difference in a given density $\rho_0(r)$ and solution density $\rho(r)$ multiplied by a large constant $\lambda$. The method has been used to obtain the exchange-correlation potential for atoms [28], molecules [74, 75] and the excited-state of atoms [76]. The equation to be solved in the ZMP method is

$$
\left[-\frac{1}{2} \nabla^2 + v_{ex}(r) + (1 - \frac{1}{N})v_0^{\phi}(r) + v_{ZMP}(r)\right] \phi_i = \epsilon_i \phi_i,
$$

(A1)

with

$$
v_{ZMP}(r) = \lambda \int \frac{\rho(r') - \rho_0(r')}{|r - r'|} dr'.
$$

(A2)

Here $v_0^{\phi}(r)$ is Hartree potential of a given density $\rho_0(r)$ and $\rho(r) = \sum |\phi_i(r)|^2$. We point out that the self-interaction component of the exchange-correlation potential has been included with the Hartree potential and that makes achieving self-consistency easier. In using this method, one usually starts with a small value of $\lambda$ and then increases it to obtain a better and better density $\rho(r)$. Finally the exchange-correlation potential is obtained as

$$
v_{ex}(r) = \lim_{\lambda \to \infty} v_{ZMP}(r) - \frac{v_0^{\phi}(r)}{N}.
$$

(A3)

For a given $\lambda$ equation (A1) is solved self-consistently. Thus, one starts with an initial guess of $v_{ZMP}(r)$, say $v_{ZMP}^{0}(r)$, and at the $(i + 1)$th cycle of the self-consistent procedure the potential is updated as

$$
v_{ZMP}^{i+1}(r) = (1 - \alpha)v_{ZMP}^{i}(r) + \alpha \lambda \int \frac{\rho(r') - \rho_0(r')}{|r - r'|} dr',
$$

(A4)
From equation (23) for the ZMP method, the value of $\alpha$ should be very small. This is because

$$v_{2ZMP}^i(r) = \lambda \left[ \int \rho_i^e(r') - \rho_0^e(r') \, dr' \right].$$

(A5)

In the HCRG method (No. 5 in table 1), the potential $v_{2ZMP}^i(r)$ in equation (A1) is replaced by $v_{HCRG}^i(r)$ and it is updated as

$$v_{HCRG}^{i+1}(r) = v_{HCRG}^i(r) + \epsilon \int \rho_i^e(r') - \rho_0^e(r') \, dr'.$$

(A6)

After achieving the convergence, the exchange-correlation potential $v_{xc}(r)$ is calculated as

$$v_{xc}(r) = v_{HCRG}(r) - \frac{v_0^Z}{N}.$$  

(A7)

Again taking $v_{HCRG}^i(r) = 0$, equation (A6) becomes

$$v_{HCRG}^{i+1}(r) = \epsilon \left[ \sum_{m=1}^i \int \frac{\rho_m(r') - \rho_0(r')}{|r - r'|} \, dr' \right].$$

(A8)

We note that to satisfy the convergence condition of equation (23) for the ZMP method, the value of $\alpha$ should be very small. This is because

$$v_{2ZMP}^i(r) - v_{2ZMP}^{i+1}(r) = \lambda \left[ \int \rho_i^e(r') - \rho_0^e(r') \, dr' \right] - \alpha^2 \left[ \int \rho_0^e(r') \, dr' \right].$$

Therefore the contribution to $\Delta J$ from the term proportional to $\alpha$ (which is always positive) will be larger than that proportional to $\alpha^2$ (which could be positive or negative) if $\alpha \ll 1$, thereby ensuring $\Delta J \geq 0$ for each iterative step. This is seen to be the case while performing the ZMP calculations.

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