Using random numbers to obtain Kohn-Sham potential for a given density

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Most of the density-to-potential inversion methods developed over the years follow a general algorithm $v_{xc}^{i+1}(r) = v_{xc}^{i}(r) + \Delta v_{xc}(r)$, where $\Delta v_{xc}(r) = \frac{\delta S[p]}{\delta \rho(r)} |_{\rho(r)} - \frac{\delta S[p]}{\delta \rho(r)} |_{\rho_0(r)}$ and $S[p]$ is an appropriately chosen density functional. In this work we show that this algorithm can be used with random numbers to obtain the exchange-correlation potential for a given density. This obviates the need to evaluate the functional $S[p]$ in each iterative step. The method is demonstrated by calculating exchange-correlation potential of atoms, clusters and the hookium.

Density functional theory (DFT) [1–5] is the most widely used theory of electronic structure [6]. Although exact in principle, its implementation requires making approximations, which have become better and better with the time [7–14]. Developing accurate exchange-correlation functionals has therefore been and continues to be an active area of research in DFT [15]. On the other hand, knowing the exact results, wherever possible, for an operationally approximate theory is also of paramount importance. These results can be used to put the approximations made in proper perspective. Consequently it this can lead to improving the approximations employed.

Most of the DFT calculations are performed using its Kohn-Sham (KS) formulation [2]. In this method the density $\rho(r)$ of an N-electron system is expressed in terms of independent particle orbitals $\{\phi_i\}$ as

$$\rho(r) = \sum_i f_i |\phi_i(r)|^2,$$

where $\{f_i\}$ are the occupation numbers of these orbitals in the ground-state configuration. The orbitals are obtained by solving the KS equation (atomic units are used throughout)

$$\left[ \frac{1}{2} \nabla^2 + v_{ext}(r) + v_{HF}(r) + v_{xc}(r) \right] \phi_i(r) = \varepsilon_i \phi_i(r) \tag{2}$$

self-consistently. Here $v_{ext}(r)$ is the external potential in which electrons are moving,

$$v_{HF}(r) = \int \frac{\rho(r')}{|r-r'|} d\mathbf{r}' \tag{3}$$

is the Hartree potential and $v_{xc}(r)$ is the exchange-correlation potential. In developing KS theory, both Hartree and the exchange-correlation potential are obtained as functional derivatives of the corresponding energy functionals viz. the Hartree energy functional

$$E_H[p] = \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r-r'|} d\mathbf{r}' d\mathbf{r} \tag{4}$$

and the exchange-correlation energy functional $E_{xc}[p]$. As is well understood, the exchange-correlation energy functional $E_{xc}[p]$ is not known exactly and has to be approximated. Thus in implementing KS-DFT, both the exchange-correlation energy functional and the exchange-correlation potential are treated approximately.

In developing exchange-correlation functionals, exactly known results about these quantities help in making them better. For example, development of initial GGA exchange functional by Perdew [7] made use of the exact sum rule satisfied by the exchange hole while that by Becke [8] employed the asymptotic behaviour of the exact exchange energy density. In the context of present work, two exact properties we mention are the exact asymptotic behaviour of the exchange-correlation potential and the ionization-potential theorem. For finite systems $v_{xc}(r)$ goes as $-\frac{1}{r}$ as a function of distance $r$ from the system and for metallic surfaces it behaves as the image potential [16]. The second example is that of ionization potential theorem which states that the value of the highest occupied orbital energy $\varepsilon_{\text{max}}$ of a system is equal to the negative of its exact ionization potential [17, 18].

As is clear from the discussion above, the only component of KS potential that is not known exactly is the exchange-correlation potential. This has led to various investigations into providing the exact exchange-correlation potential and understanding its nature [19–33]. Thus method for getting the exact exchange-correlation potential from the many-body wavefunction [34–37] or by inverting the exact density [38–53] wherever these are available have also been developed over the years. This has led to insights into the behaviour of the exact exchange-correlation potential. Thus development of methods for getting the exact $v_{xc}(r)$ from a given density is an important research activity. In our recent work [54], we have demonstrated that the unified nature of various methods [38–53] proposed and have given a general algorithm that accomplishes this. Based on the insights provided in that work, in this paper we develop a purely numerical method for getting the exchange-correlation potential from a given density by using random numbers. In doing so, we make use of Lieb’s definition [55] for the universal functional of DFT and maximize the related functional using random numbers. In the following we begin by briefly reviewing the method of using Lieb’s definition to invert a given density for getting the corresponding exchange-correlation potential. We then discuss its general nature [54]. This generalization makes it possible to use random numbers to generate the exchange-correlation potential for a given density, thereby providing a novel approach.
to get the exchange-correlation potential. The corresponding results are then presented for a few systems.

In DFT the energy $E[\rho]$ of system of ground state density $\rho(r)$ is given by

$$E[\rho] = F[\rho] + \int v_{\text{ext}}(r)\rho(r)\,dr$$

(5)

where $F[\rho]$ is a universal functional of the density and is given by using Levy’s constrained search [56]

$$F[\rho] = \min_{\Psi \to \rho} \left[ E[\rho] - \int v(r)\rho(r)\,dr \right]$$

(6)

where $T$ is the kinetic energy operator and $v_{\text{ext}}$ is the electron-electron interaction energy operator. The search is made over those $\{|\Psi\rangle\}$ that are N-electron antisymmetric functions giving the density $\rho(r)$. The universal functional can also be obtained by finding a potential $v(r)$ such that

$$F[\rho] = \max_{\Psi} \left[ E[\rho] - \int v(r)\rho(r)\,dr \right]$$

(7)

where $E[\rho]$ is the energy of N-electrons moving in potential $v(r)$. It is clear that for a given density $\rho(r)$, the constrained search definition of Eq. (6) leads to many-body wavefunction and from it the corresponding potential. Similarly, use of Eq. (7) gives the potential corresponding to a given density directly. Thus both of these definitions give a method to invert the density to find the corresponding potential. For example in the work of Teale et al. [21] they have used Eq. (7) to obtain the external potential for a given density for varying strength of electron-electron interaction. The same procedures can be applied to get the Kohn-Sham potential if $F[\rho]$ is treated as the expectation value of the kinetic energy operator and therefore $E[\rho]$ as the energy of the non-interacting electrons in the potential $v(r)$. Wu and Yang [47] made the first explicit use of Eq. (7) to obtain the exchange-correlation potential for a given density. They expanded the exchange-correlation potential in terms of appropriately chosen Gaussian functions and optimized the coefficients to maximize right side of Eq. (7). A general prescription [54] for implementing the approach employing Eq. (7) works as follows.

To find the exchange-correlation potential one starts with an approximate exchange-correlation potential $v_{\text{xc}}^{(0)}(r)$, solve Kohn-Sham equation with it, and get a density $\rho_i(r)$. From the density $\rho_i(r)$ the exchange-correlation potential for next iteration, $v_{\text{xc}}^{(i+1)}(r)$, is constructed using the formula

$$v_{\text{xc}}^{(i+1)}(r) = v_{\text{xc}}^{(i)}(r) + \frac{\delta S[\rho]}{\delta \rho(r)} \bigg|_{\rho_i(r)} - \frac{\delta S[\rho]}{\delta \rho(r)} \bigg|_{\rho_0(r)}$$

(8)

and solving the corresponding Kohn-Sham equation. This is done iteratively until a convergence criterion is satisfied. Here $S[\rho]$ is a functional of the dimension of energy and satisfies the condition

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

(9)

As the iterations progress, the exchange-correlation potential becomes close to the true potential and the value of integral in Eq. (9) becomes smaller and smaller. It is this procedure that we make use of in employing random numbers to get the exchange-correlation. This is described next.

In Eq. (8) the correction to the exchange-correlation potential

$$\Delta v_{\text{xc}}^{(i+1)}(r) = \frac{\delta S[\rho]}{\delta \rho(r)} \bigg|_{\rho_i(r)} - \frac{\delta S[\rho]}{\delta \rho(r)} \bigg|_{\rho_0(r)}$$

(10)

during the iterations is obtained through the functional derivative of $S[\rho]$. Question that we ask now is if a search can be made for the change $\Delta v_{\text{xc}}^{(i+1)}(r)$ in the potential directly without being tied down to a functional $S[\rho]$. The motivation for this being that a fixed functional $S[\rho]$ tends to treat all regions in a system on equal footing, irrespective of the value of the density there. It is, however, found that different functionals forms work better in different regions. Thus a more flexible approach is desirable in this regard. One such method has been to use a hybrid $S[\rho]$ [54]. In the present work we completely abandon the use of a functional $S[\rho]$ of density and propose an updating scheme that is based on random numbers and therefore fully flexible. It avoids the need to evaluate functional $S[\rho]$ again and again for each iteration. Furthermore, it provides an advantage over the functional form in those regions where very small densities make the evaluation of the functional derivative $\frac{\delta S[\rho]}{\delta \rho(r)}$ rather difficult. The method works as follows.

Given as potential $v_{\text{xc}}^{(i)}(r)$ for the $i^{th}$ iteration, the correction $\Delta v_{\text{xc}}^{(i)}$ added to it to obtain $v_{\text{xc}}^{(i+1)}(r)$ is constructed using random numbers. For this, at each point of the numerical grid of $\{r\}$ we generate random numbers in the range $\{0, 1\}$, multiply them by a strength parameter (discussed in the next paragraph) and choose its sign such that

$$\Delta v_{\text{xc}}^{(i)}(r)(\rho_i(r) - \rho_0(r)) \geq 0$$

(11)

is satisfied. Note that the satisfaction of Eq. (11) automatically leads to Eq. (9) being satisfied. The last step is taken to ensure the convergence of potential towards the correct one by the use of Lieb’s definition [55] of $F[\rho]$. The condition above makes the potential more positive if $(\rho_i(r) - \rho_0(r)) > 0$ and less positive if $(\rho_i(r) - \rho_0(r)) < 0$. The algorithm to generate the exchange-correlation thus is as follows. We start with an approximate exchange-correlation potential $v_{\text{xc}}^{(0)}(r)$ and solve the KS equation with $v_{\text{xc}}^{(0)}(r)$, get exchange-correlation potential calculated from the given density $\rho_0(r)$, and the approximate exchange-correlation potential. In going from $i^{th}$ iteration to $(i+1)^{th}$ iteration we keep $v_{\text{xc}}^{(i)}(r)$ fixed on it has been calculated exactly, and update only the exchange-correlation potential. We generate a random profile for $\Delta v_{\text{xc}}^{(i)}$ as follows

$$\Delta v_{\text{xc}}^{(i)}(r) = \lambda f_{\text{r}}(r) \delta \rho(r) \big|_{\rho_i(r)} \delta \rho(r) \big|_{\rho_0(r)}$$

(12)

where $f_{\text{r}}(r)$ takes random values between 0 and 1 at each $r$. 

In Eq. (12) \( \lambda \) is the strength parameter and is calculated for each iteration based on the difference between \( \rho_i(\mathbf{r}) \) and \( \rho_0(\mathbf{r}) \). For example it could be chosen to be the maximum of \( |\rho_i(\mathbf{r}) - \rho_0(\mathbf{r})| \). Thus the form of potential upgradation in Eq. (12) ensures the condition of Eq. (11) being satisfied. Using \( \Delta v_{xc}^{i+1}(\mathbf{r}) \), the exchange-correlation potential for the next iteration is given as

\[
v_{xc}^{i+1}(\mathbf{r}) = (1 - \varepsilon)^{-1} v_{xc}(\mathbf{r}) + \varepsilon(v_{xc}(\mathbf{r}) + \Delta v_{xc}(\mathbf{r})).
\]  

(13)

where \( \varepsilon \) (0 < \( \varepsilon \) < 1) is the mixing parameter. The process is iterated until desired accuracy in density is achieved.

We have applied the method above to generate the exchange-correlation potential for Hartree-Fock density of atoms [57] Be, Ne and Ar. Here the external potential is proportional to \(-r^2\) and for the jellium spheres it is proportional to \( r^2 \) inside the sphere and proportional to \(-\frac{1}{r}\) for \( r \) outside the sphere. The potentials calculated by us are compared with the exact results. In our calculations we have chosen parameter \( \varepsilon \) in Eq. (13) to be of order of \( 10^{-3} \) for \( n = 0.01 \) for the Hookium atom and jellium spheres. The initial potential \( v_{xc}^{0}(\mathbf{r}) \) is taken to be the Fermi-Amaldi potential \(-\frac{\omega(\mathbf{r})}{N}\) where \( N \) is the total number of electrons and \( v_{HF}(\mathbf{r}) \) is the Hartree potential corresponding to the input density \( \rho_0(\mathbf{r}) \). We have also fixed the exchange-correlation potential to its exact value \(-\frac{1}{r}\) [16] in the asymptotic region. Calculations has been performed using a modified Herman-Skillman code [61]. In all the calculations reported we have run the code until the integral \( \int \rho(\mathbf{r}) - \rho_0(\mathbf{r}) \, d\mathbf{r} \) becomes smaller than \( 1.0 \times 10^{-5} \) for atoms and smaller than \( 1.0 \times 10^{-6} \) for jellium spheres and Hookium atom.

In Fig (1), we display the exchange potential for atoms mentioned above and compare it with the exact exchange potential of these atoms obtained through the optimized potential method [62–64]. It is evident from the figure that output exchange potential is very close to the corresponding exact
results although there are some fluctuations due to the use of random numbers. When these fluctuations are made smooth, the resulting potential becomes essentially exact as shown in Fig (2). We note, however, that smoothing softens the bump in the intershell region slightly. Next in Fig. (3), we have plotted the exchange potential for jellium spheres [59, 60] having $N = 18, 34$ and 58 atoms. Here the density of jellium sphere is obtained by solving the Kohn-Sham equation with the exchange potential taken to be the Harbola-Sahni (HS) potential $\varepsilon_{\text{max}} = \mu$ obtained in our method is the satisfaction of the ionization potential theorem to high degree of accuracy.

To conclude, in the present work we have proposed an inversion method to get the exchange-correlation potential for a given density by updating the exchange-correlation potential by employing random numbers. This method circumvents the need to calculate a functional during the update and thus avoids any difficulties faced in low density region in the calculation of the functional. The method has been applied to different spherical systems and the calculated exchange-correlation potentials are found to be close to exact results.

We are grateful to Prof. Dr. Eberhard Engel for providing optimized effective potential data of atoms.

A hallmark of the accuracy of of an exchange-correlation potential is the satisfaction of the ionization potential theorem [17, 18]. We have tested the results of $\varepsilon_{\text{max}}$ obtained in our calculations against the corresponding exact results. These are shown in Table I. This is clear that the two are quite close. It is important since we fix behaviour of the potential $\varepsilon_{\text{corr}}$ quite far from the origin; it is the point where the density becomes order of $10^{-6} - 10^{-5}$ for atoms and Hookium and less than $10^{-15}$ for clusters. Thus the potentials of all system calculated by us using the random numbers satisfy the ionization theorem to high degree of accuracy.

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