

Variational method for inverting the Kohn-Sham procedure

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A procedure based on a variational principle is developed for determining the local Kohn-Sham (KS) potential corresponding to a given ground-state electron density. This procedure is applied to calculate the exchange-correlation part of the effective Kohn-Sham (KS) potential for the neon atom and the methane molecule.

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I. INTRODUCTION

Density functional theory (DFT) [1,2] replaces the N_e -electron wave function $\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_{N_e})$ by the electronic density

$$\rho(\mathbf{r}) = N_e \int |\Psi(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_{N_e})|^2 d\mathbf{s} d\mathbf{x}_2 d\mathbf{x}_3, \dots, \mathbf{x}_{N_e} \quad (1)$$

as the basic quantity describing an interacting N_e -electron system. This is an enormous simplification, and in the past two decades DFT has become the basis for most electronic structure calculations.

DFT is based on two theorems due to Hohenberg and Kohn [1]. The first proves that the external potential is a unique functional of the electronic density, apart from a trivial additive constant. The second establishes a variational principle with respect to the electronic density. However, the direct application of the Hohenberg-Kohn variational principle is hindered because the kinetic energy and the electron-electron interaction energy involve the first- and second-order reduced density matrices. Kohn and Sham (KS) [2] circumvented this difficulty by introducing an auxiliary system of noninteracting electrons with the same density as that of the original interacting system, and arrived at the set of single-particle Schrödinger equations

$$-\frac{1}{2}\nabla^2\phi_i(\mathbf{r}) + V_{KS}(\mathbf{r})\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r}), \quad i = 1, \dots, N_e, \quad (2)$$

where

$$V_{KS}(\mathbf{r}) = V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) \quad (3)$$

is a local effective external potential, the KS potential. The potential consists of the external field $V_{ext}(\mathbf{r})$, the classical Hartree potential

$$V_H(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (4)$$

and the exchange-correlation potential

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} \quad (5)$$

given in terms of the functional $E_{xc}[\rho]$. The exchange-correlation energy functional $E_{xc}[\rho]$ is defined as

$$E_{xc}[\rho] = T[\rho] - T_s[\rho] + V_{ee}[\rho] - \frac{1}{2} \int V_H(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}, \quad (6)$$

where $T[\rho] - T_s[\rho]$ is the difference in kinetic energy of the interacting and noninteracting system of electrons, and $V_{ee}[\rho]$ is the electron-electron interaction energy. The electron density is given by

$$\rho(\mathbf{r}) = \sum_{iocc.} |\phi_i(\mathbf{r})|^2, \quad (7)$$

where the sum is over the occupied KS orbitals.

Since only approximate forms of the exchange-correlation (xc)-energy functional are known, the nature of the effective KS potential is a subject of ongoing research. One approach is to obtain the “exact” KS potential for a sample system from highly correlated electronic densities computed with traditional methods of quantum chemistry such as configuration interaction (CI), and use this information to test and improve approximate xc-energy functionals.

In the past decade, several solutions to this “inverse” KS problem have been suggested. Almladh and Pedroza [3] used a trial and error method based on a parametrized potential to deduce $V_{KS}(\mathbf{r})$. For one-dimensional systems, such as the spherically symmetric atoms neon and beryllium, Ar-yasetiawan and Stott [4] obtained and solved a set of coupled nonlinear differential equations for the KS orbitals in terms of the given electronic density.

A number of iterative methods have been proposed for tackling the inverse problem in which the KS potential at iteration $k+1$ is obtained from that at k using

$$V_{KS}^{k+1}(\mathbf{r}) = f^k(\mathbf{r})V_{KS}^k(\mathbf{r}), \quad (8)$$

where $f(\mathbf{r})$ depends on the method. Van Leeuwen and Baerends [5] used a local updating scheme (8) with

$$f^k(\mathbf{r}) = \frac{\rho^k(\mathbf{r})}{\rho_0(\mathbf{r})}, \quad (9)$$

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where $\rho_0(\mathbf{r})$ is the ‘‘target’’ density, to obtain the xc potential for spherically symmetric atoms of neon and beryllium. Molecular applications (LiH, BH, FH) of this method with slight modifications have been reported [6,7]. Wang and Parr [8] have proposed to use

$$f^k(\mathbf{r}) = \alpha^k [\rho^k(\mathbf{r}) - \rho_0(\mathbf{r})], \quad (10)$$

and, recently, Peirs *et al.* [9] have proposed for the atomic systems

$$f^k(r) = \alpha r^\beta [\rho^k(r) - \rho_0(r)], \quad (11)$$

where α and β are parameters chosen on the basis of trial and error. As far as we know, molecular applications of methods outlined in Refs. [8,9] have not been reported.

The work of Zhao and Parr [10] and Zhao, Morrison, and Parr (ZMP) [11] is also noteworthy. The ZMP method is based on the constrained minimization of the noninteracting kinetic energy of electrons but no direct ‘‘minimization’’ is performed. Instead, one-particle Schrödinger equations are obtained and solved for a series of specific Lagrange multipliers λ , and the results are extrapolated to $\lambda \rightarrow \infty$. To our knowledge, the method has only been applied to spherical atoms. We wish to show that there is an inversion procedure based on minimizing the kinetic energy which is somewhat more straightforward than the ZMP approach.

In this paper, we propose direct application of a variational principle for determining the effective KS potential for a given electronic density. The variational principle, due to Haydock and Foulkes (HF) [12] is based on the constrained search formulation of DFT [13] and involves unconstrained minimization of a functional with respect to the effective potential. The procedure can be applied to both atomic and molecular systems, and as examples, we calculate xc potentials for the neon atom and the methane molecule.

The next section describes the HF variational principle. The applications to neon and methane are given next, followed by a summary of conclusions. Atomic units are used throughout this paper.

II. HAYDOCK-FOULKES VARIATIONAL PRINCIPLE

Suppose, we have a system of N_e noninteracting electrons and we wish to find the single-particle potential $V_0(\mathbf{r})$ which yields a given $\rho_0(\mathbf{r})$ as its ground-state electronic density

$$\begin{aligned} [-\frac{1}{2}\nabla^2 + V_0(\mathbf{r})]\phi_i(\mathbf{r}) &= \varepsilon_i[V_0]\phi_i(\mathbf{r}), \\ \rho_0(\mathbf{r}) &= \sum_{iocc.} |\phi_i(\mathbf{r})|^2, \end{aligned} \quad (12)$$

where $\varepsilon_i[V]$ implies that eigenvalue ε_i is an implicit functional of the potential $V(\mathbf{r})$. The ground-state energy of this system is given by the sum of occupied eigenvalues obtained by solving Eq. (12) with the potential $V_0(\mathbf{r})$

$$E_0 = \sum_{iocc.} \varepsilon_i[V_0]. \quad (13)$$

The ground-state energy of the system of noninteracting electrons in Levy’s constrained search formulation [13] is given by

$$\begin{aligned} E_0[\rho_0] &= \min_{\Psi \in \rho_0} \langle \Psi | \hat{T} + \hat{V}_0 | \Psi \rangle \\ &= \min_{\Psi \in \rho_0} \langle \Psi | \hat{T} | \Psi \rangle + \int V_0(\mathbf{r})\rho_0(\mathbf{r})d\mathbf{r}, \end{aligned} \quad (14)$$

where the search is over all Slater determinants that yield $\rho_0(\mathbf{r})$. Combining Eqs. (13) and (14), we obtain an expression for the kinetic energy of noninteracting electrons

$$T[\rho_0] = \min_{\Psi \in \rho_0} \langle \Psi | \hat{T} | \Psi \rangle = \sum_{iocc.} \varepsilon_i[V_0] - \int V_0(\mathbf{r})\rho_0(\mathbf{r})d\mathbf{r}. \quad (15)$$

Let $V(\mathbf{r})$ denote some trial local potential. Then,

$$\begin{aligned} T[\rho_0] &= \sum_{iocc.} \varepsilon_i[V_0] - \int V_0(\mathbf{r})\rho_0(\mathbf{r})d\mathbf{r} \\ &= \min_{\Psi \in \rho_0} \langle \Psi | \hat{T} + \hat{V} | \Psi \rangle - \int V(\mathbf{r})\rho_0(\mathbf{r})d\mathbf{r}. \end{aligned} \quad (16)$$

Since $\rho_0(\mathbf{r})$ is not the ground-state density for the trial potential $V(\mathbf{r})$,

$$\min_{\Psi \in \rho_0} \langle \Psi | \hat{T} + \hat{V} | \Psi \rangle \geq \sum_{iocc.} \varepsilon_i[V], \quad (17)$$

and

$$T[\rho_0] \geq \sum_{iocc.} \varepsilon_i[V] - \int V(\mathbf{r})\rho_0(\mathbf{r})d\mathbf{r}. \quad (18)$$

Consequently, for a system of noninteracting electrons in the local effective potential $V_0(\mathbf{r})$ with $\rho_0(\mathbf{r})$ as its ground-state density, there exists a functional of the potential

$$Y[V] = - \sum_{iocc.} \varepsilon_i[V] + \int V(\mathbf{r})\rho_0(\mathbf{r})d\mathbf{r} \quad (19)$$

which is bounded from below by the negative ground-state kinetic energy of the noninteracting electrons, $-T_s$. This is the variational principle [12] we shall apply.

We will refer to $Y[V]$, given by Eq. (19) as the HF functional. The local potential $V_0(\mathbf{r})$ corresponding to the ground-state density $\rho_0(\mathbf{r})$ can be obtained by minimizing $Y[V]$ with respect to $V(\mathbf{r})$. In practice, minimization of a functional is greatly facilitated if the functional derivative giving the direction of steepest descent, as well as the functional itself, can be evaluated. In such cases, minimization techniques such as the method of conjugate gradients [14] can be used. Applying first-order perturbation theory to the energy eigenvalues in Eq. (19) yields for the functional derivative of $Y[V]$,

$$\frac{\delta Y[V]}{\delta V(\mathbf{r})} = \rho_0(\mathbf{r}) - \rho(\mathbf{r}) \quad (20)$$

which is simply the discrepancy in the electron density. Solving the Schrödinger equation (12) with the trial potential $V(\mathbf{r})$ for the energy eigenvalues gives the value of $Y[V]$, while the corresponding eigenfunctions give $\delta Y[V]/\delta V(\mathbf{r})$.

Consider the electrons moving in the external potential,

$$V_{ext}(\mathbf{r}) = - \sum_{\alpha=1}^{N_n} \frac{Z_{\alpha}}{|\mathbf{r} - \mathbf{R}_{\alpha}|}, \quad (21)$$

due to nuclei at positions $\{\mathbf{R}_{\alpha}, \alpha=1, \dots, N_n\}$. Given the ground-state electron density $\rho_0(\mathbf{r})$, the Hartree potential $V_H(\mathbf{r})$ (4) can be evaluated, and $Y[V_{ext} + V_H + V_{xc}]$ minimized to give the unknown exchange-correlation part of the KS potential.

The numerical procedure begins with an initial guess for the xc potential, for example, the local density approximation (LDA) for the exchange [2]

$$V_{xc}^0(\mathbf{r}) = - \left[\frac{3}{\pi} \rho_0(\mathbf{r}) \right]^{1/3}. \quad (22)$$

The Schrödinger equation (2) is solved for the potential $V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}^0(\mathbf{r})$, the values of $Y[V]$ and its functional derivative are computed, and the xc potential is adjusted to minimize the value of the HF functional. After k iterations, the adjustment to the xc potential is

$$V_{xc}^{k+1}(\mathbf{r}) = V_{xc}^k(\mathbf{r}) + \alpha^k f^k(\mathbf{r}), \quad (23)$$

where α^k is the line minimization parameter and $f^k(\mathbf{r})$ is the search direction related to the functional derivative (20). In the case of steepest descent minimization $f^k(\mathbf{r}) = \rho^k(\mathbf{r}) - \rho_0(\mathbf{r})$ is the direction of steepest descent; for conjugate gradient minimization $f^k(\mathbf{r})$ is a linear combination of $\rho^k(\mathbf{r}) - \rho_0(\mathbf{r})$ and the previous search direction $f^{k-1}(\mathbf{r})$. Iterations continue until the integral error in the electronic density

$$I_{error} = \int |\rho^k(\mathbf{r}) - \rho_0(\mathbf{r})| d\mathbf{r} \quad (24)$$

becomes smaller than some preset value.

III. APPLICATION TO NEON

The xc potential for the neon atom has been studied extensively (see, for example, Refs. [4,5,11]) largely because the system is spherical and there exists an accurate ground-state CI electronic density calculated by Bunge and Esquivel [15]. This density is accurate to 0.1% for $r < 3$ bohrs and to 0.5% for $3 < r < 6$ bohrs, and the cusp condition at the nucleus is accurate to 0.5%. Figure 1 shows the radial electron density distribution for neon reported by Bunge and Esquivel [15]. Note that the density has a minimum at about 0.31 bohrs corresponding to the region between the 1s and 2s shells.

The HF functional was minimized for the target density

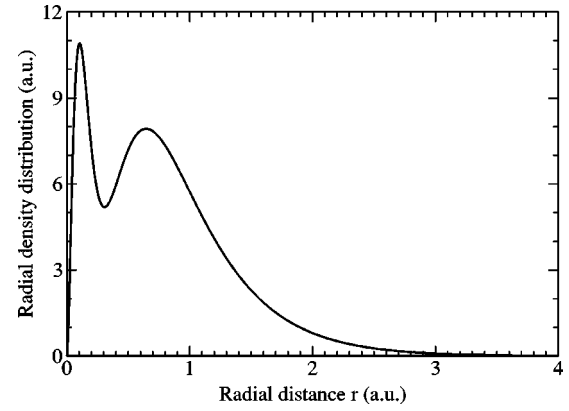


FIG. 1. Radial density distribution $4\pi\rho_0(r)r^2$ for the neon atom as a function of radial distance r computed by Bunge *et al.* [15].

[15] to determine the xc potential for neon, using as an initial guess for the xc potential the LDA for exchange (22). The xc potential was defined and varied on a radial logarithmic grid of 5000 points extending from $r_i = 4.5 \times 10^{-6}$ a.u. to about $r_f = 14$ a.u. The minimization of $Y[V]$ was accomplished in 150 steps each consisting of one steepest descent and two conjugate gradient line minimizations.

The resulting xc potential for neon shown on Fig. 2 has a characteristic peak at 0.31 bohrs coinciding with the minimum in the density and represents exchange repulsion between electrons of the same spin in the 1s- and 2s-shells. The kinetic energy of the system of noninteracting electrons was found to be 128.609 a.u. The integral error in the electron density $\int |\rho(\mathbf{r}) - \rho_0(\mathbf{r})| d\mathbf{r} = 1.0 \times 10^{-3}$, and the maximum error in density does not exceed 0.3% for $r < 3.0$ bohrs. In general, we find good agreement between the results obtained using the HF variational principle and those obtained earlier (see Table I).

Finally, we note that the minimization procedure determines the xc potential to within a constant. At the end of each step, a constant was added to the xc potential so that the highest occupied KS eigenvalue equalled -0.79 a.u., the neon ionization potential [16,17].

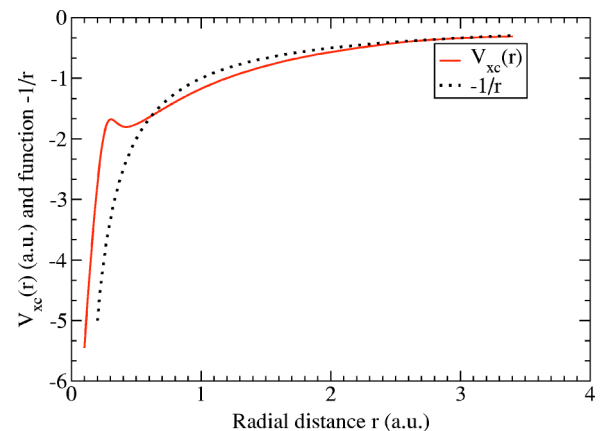


FIG. 2. Exchange-correlation potential for the neon atom obtained from the HF functional after 150 steps, along with correct asymptotic behavior of the xc potential, $-1/r$.

TABLE I. Some characteristics of the xc potential of neon. Kinetic energy of noninteracting system of electrons, T_s in a.u. and differences in KS eigenvalues in a.u. ZMP—results of Zhao *et al.* [11], AS—Aryasetiawan and Stott [4], SGB—Schipper *et al.* [26], HF—the present work. Results of Refs. [4,26] and HF were obtained using the same target density.

Scheme	T_s	$\sigma_{2p} - \sigma_{1s}$	$\sigma_{2p} - \sigma_{2s}$
HF	128.61	30.03	0.86
ZMP	128.63	30.02	0.86
AS		30.03	0.86
SGB	128.61		

IV. APPLICATION TO METHANE

With the objective of investigating exchange and correlation effects in the regions of chemical bonds the HF minimization scheme has also been applied to the methane molecule. The target CI density was computed using the GAUSSIAN98 [18] electronic structure code [19]. The 6-311(*d,p*) 6D basis set was used in all the calculations.

First, the methane geometry was optimized with CISD level of theory to find the CH bond length, and a value of 1.090 Å was obtained. Then, for this geometry the CISD electronic density was computed. The target ground-state electronic density can be written as

$$\rho_0(\mathbf{r}) = \sum_{p=1}^{MO} n_p \sum_{i=1}^{PR} \sum_{j=1}^{PR} c_{pi} c_{pj} g_i(\mathbf{r}) g_j(\mathbf{r}), \quad (25)$$

where MO is the number of molecular orbitals, PR is the number of primitive Gaussians, n_p is the occupancy of the p th natural orbital, c_{pi} and c_{pj} are coefficients, and $g_i(\mathbf{r})$ and $g_j(\mathbf{r})$ are primitive Gaussians. This density served as input to the variational procedure for finding the molecular KS potential, but improved ground-state densities could equally well be implemented in the scheme.

TABLE II. SCF DFT calculations for CH₄ (CH bond length is 1.090 Å) using 6-311(*d,p*) 6D basis set. Difference in KS eigenvalues (a.u.), kinetic energy of noninteracting system of electrons T_s (a.u.), total energy E (a.u.), and the integral error in the electron density with CI density as a reference $\int |\rho(\mathbf{r}) - \rho_0(\mathbf{r})| d\mathbf{r}$. LDAX—LDA exchange [2], LDAXC—LDA exchange with Perdew-Zunger correlation [23], B88—Becke’s 1988 exchange [22], BLYP—Becke’s 1988 exchange with Lee-Yang-Parr correlation [25], and B3LYP—Becke’s hybrid functional [24] with Lee-Yang-Parr correlation. HFB88 and HFLDAX: the results obtained after 160 steepest descent minimizations of HF functional for the Becke’s exchange and the LDA initial guesses, respectively; in T_s column—the upper bound for the noninteracting kinetic energy $-Y[V_{KS}] = \sum_{iocc} \epsilon_i[V_{KS}] - \int V_{KS}(\mathbf{r}) \rho_0(\mathbf{r}) d\mathbf{r}$.

xc energy	$\sigma_3 - \sigma_1$	$\sigma_3 - \sigma_2$	T_s	E	I_{error}
LDAX	9.3893	0.2747	39.6425	-39.5225	0.3136
LDAXC	9.4111	0.2757	39.7727	-40.1115	0.2596
B88	9.5417	0.2762	40.2789	-40.2023	0.1546
BLYP	9.5432	0.2767	40.3188	-40.4968	0.1517
B3LYP	9.7591	0.3015	40.2586	-40.5343	0.1064
HFB88	9.6526	0.2834	40.2046		0.0125
HFLDAX	9.6434	0.2835	40.2046		0.0103

The single-particle Schrödinger equation for the trial potential was solved using the same basis set as in the CI calculation. The “core” Hamiltonian matrix elements

$$H_{ij}^{core} = \left\langle i \left| \left(-\frac{\nabla^2}{2} + \hat{V}_{ext} + \hat{V}_H \right) \right| j \right\rangle \quad (26)$$

were computed analytically and need not be recalculated during the minimization. The xc potential was defined and varied on the Becke multicenter numerical grid [21] with 40 radial and 302 angular points per atom. At iteration k the following steps were followed. The matrix elements

$$H_{ij}^{xck} = \langle i | \hat{V}_{xc}^k | j \rangle \quad (27)$$

were computed numerically on the Becke grid, the total Hamiltonian

$$H_{ij}^k = H_{ij}^{core} + H_{ij}^{xck} \quad (28)$$

was formed, the eigenvalue-eigenfunction problem was solved for Hamiltonian (28), the search direction $f^k(\mathbf{r})$ was found; line minimization was performed, and the new xc potential $V_{xc}^{k+1}(\mathbf{r}) = V_{xc}^k(\mathbf{r}) + \alpha^k f^k(\mathbf{r})$ was calculated.

We performed 300 steepest descent minimizations of the HF functional with the target electronic density (25) for two different initial $V_{xc}(\mathbf{r})$: using LDA exchange (22), and using Becke’s 1988 exchange [22]. Both initial potentials were computed from the target CISD density. The results of KS calculations on methane with commonly used xc functionals and the results obtained using the HF variational principle are summarized in Table II.

Table II shows that for both initial potentials, our variational procedure results in the same value of the HF functional and the same difference between the two highest occupied KS eigenvalues. The differences between the highest and the lowest occupied KS eigenvalue differ slightly. The eigenvalue differences obtained by our variational procedure lie between the results obtained from self-consistent-field re-

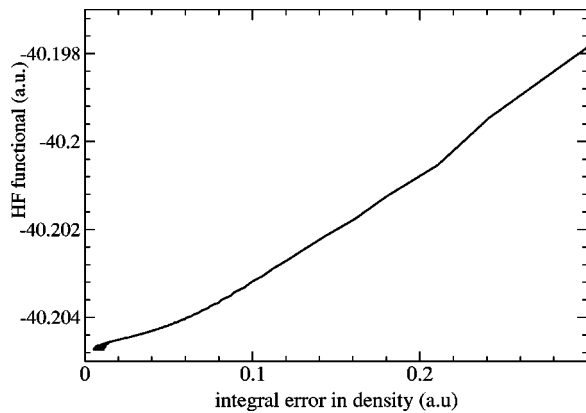


FIG. 3. Value of the HF functional for methane as a function of the integral error in density $\int |\rho(\mathbf{r}) - \rho_0(\mathbf{r})| d\mathbf{r}$ computed using 6-311G(d,p) 6D basis set for three hundred steepest descent minimizations of the HF functional.

sults (SCF) DFT calculations using the B3LYP functional (Becke's 3-parameter hybrid functional [24] with Lee, Yang, and Parr correlation [25]) and other model functionals.

Figure 3 shows the value of the HF functional as a function of the integral error in the density when the LDA exchange potential (22) was used as the initial guess. As the iterations continued, the integral error and the value of the HF functional decreased. The integral error in the density diminished to $\int |\rho(\mathbf{r}) - \rho_0(\mathbf{r})| d\mathbf{r} \approx 0.01$ in the first 100–160 iterations. Further iterations did not result in a significant change in the integral error or the other quantities of interest.

Figures 4 and 5 show the differences of KS eigenvalues for methane as functions of the integral error in the density. The exchange potential (22) was used as the initial guess. Both Figs. 4 and 5 show an oscillatory behavior with the amplitude of oscillations decreasing as the iterations continued. The eigenvalue differences in Figs. 4 and 5 have plateaux, which also appear after the first 100–160 iterations. We estimated that at this point we achieved the best approximation to the true xc potential. Further iterations will build

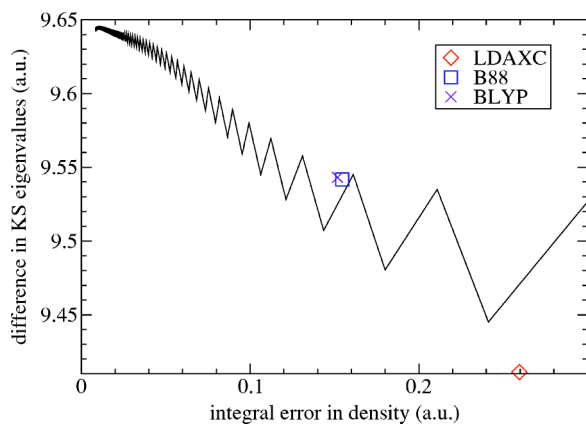


FIG. 4. Difference between KS eigenvalues corresponding to the highest and lowest occupied KS orbital in methane as a function of the integral error in density $\int |\rho(\mathbf{r}) - \rho_0(\mathbf{r})| d\mathbf{r}$ computed using 6-311G(d,p) 6D basis set for three hundred steepest descent minimizations of the HF functional.

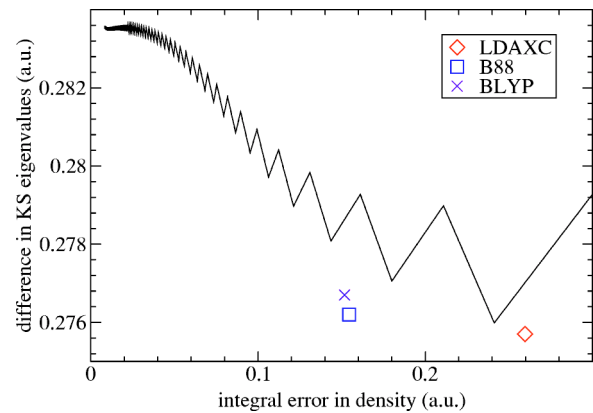


FIG. 5. Difference between KS eigenvalues corresponding to the highest and the next highest occupied KS orbitals in methane as a function of the integral error in density $\int |\rho(\mathbf{r}) - \rho_0(\mathbf{r})| d\mathbf{r}$ computed using 6-311G(d,p) 6D basis set for three hundred steepest descent minimizations of the HF functional.

up oscillations in the xc potential, particularly in the bond region. These oscillations are due to the finite basis set expansion of molecular orbitals and should not be present in the exact potential [26].

If the minimization of the HF functional is started with potential [22], the plateaux of Fig. 4 is prolonged; the curve for the functional value and the curve in Fig. 5 look very similar.

Figure 6 shows LDA and Becke's 1988 exchange potentials along the direction of the CH bond in the methane molecule computed from the CISD reference density, and two xc potentials obtained after 160 steepest descent minimizations of the HF functional for these two initial guesses. The carbon atom is located at zero and the hydrogen atom is at approximately 2.1 bohrs from the carbon atom.

The two xc potentials in Fig. 6 obtained from the variational scheme are very similar except for the small regions

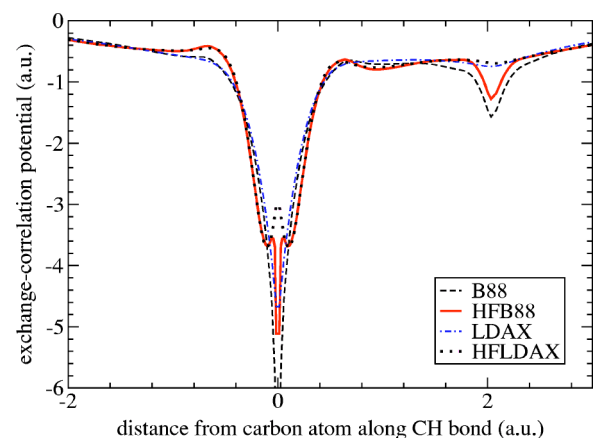


FIG. 6. (Color online) Exchange-correlation potential for methane in the direction of the CH bond. LDAX and B88 are the LDA exchange potential (22) and Becke's 1988 exchange potential computed from CI target density. HFLDAX and HFB88 are potentials obtained using the HF variational principle after 160 steepest descent minimizations with LDAX and B88 initial guess, respectively. Hydrogen atom is located approximately in 2.1 a.u. from carbon.

close to the carbon and hydrogen atoms that we will address shortly. Both xc potentials exhibit characteristic peaks at $r \approx \pm 0.6$ bohrs that correspond to the local minimum in the density distribution. Note that these two peaks are more pronounced than the corresponding ones in the model potentials, and the xc potentials obtained by our procedure are more “asymmetric” near the carbon atom.

The two potentials obtained from the HF functional minimization with different starting points deviate from one another in the region close to the atoms. In the case of the xc potential obtained with the LDA exchange initial guess, there is a counterpeak at the position of the carbon atom which is an artifact of the Gaussian expansion of the target CI density. The CI density computed with a Gaussian basis set does not have the required cusp at a nucleus and therefore is not a ground-state density for the external potential behaving as $-Z/r$ near a nucleus. Consequently, an erroneous counterpeak appears in the “exact” xc potential corresponding to the Gaussian density to compensate for this. As the iterations continued, the magnitude of this counterpeak oscillated together with the eigenvalue differences shown in Figs. 4 and 5. In the case of the xc potential obtained from the Becke’s exchange initial guess, there are two counterpeaks. All the counterpeaks near the carbon nucleus are erroneous. They are due to deficiencies in the Gaussian density and should not be present in the “real” xc potential. One of the possible solutions to the counterpeak problem at the carbon nucleus is to replace the external Coulomb potential due to the point nucleus by that of a smeared out charge distribution.

In addition, Fig. 6 shows that our variational procedure does not converge completely in the region close to the hydrogen atom; the two different initial guesses produce slightly different xc potentials. This is because the direction of steepest descent in the minimization process is proportional to $\rho(\mathbf{r}) - \rho_0(\mathbf{r})$ so that the rate of minimization is dominated by the regions with high electronic density, and we note that the electron density at the C nucleus is approximately 260 times larger than that at the H nucleus. However, as minimization progresses, erroneous features appear near the nuclei due to inadequacies in the Gaussian density and these begin to interfere with the minimization. These difficulties did not arise for neon where the cusp condition is accurately met.

V. CONCLUSIONS

A variational procedure to obtain a KS potential is based on the HF functional of a single-particle potential. If the external field is known, the HF functional can be minimized to obtain the xc part of the effective KS potential corresponding to some target density. Minimization of the HF functional can be carried out using techniques that require knowledge not only of the value of the functional but also of its functional derivative, for example, the conjugate gradient or the steepest descent methods.

The proposed variational principle was successfully applied to calculate the xc potential for the neon atom, and also for the methane molecule but with reservations. The results for neon are in agreement with results of other methods. To our knowledge, it is the first time the xc potential for a molecular system as complicated as methane has been obtained, but unfortunately, the results are limited by the quality of the target density and the basis set incompleteness.

Our molecular KS potential procedure which employs Gaussian basis sets allows computation of the xc potential for any molecule, no input except the positions of the ions and the target density is needed. In particular, no empirical parameters are used in the calculation. But, we note that the degree of success for this or any other KS inversion procedure depends on two factors. The first one is an accurate and highly correlated target density. The deficiencies of Gaussian-based densities are well known, the Gaussian-based density does not satisfy the cusp condition at the nuclei and falls off too rapidly. The second factor is our ability to solve accurately the one-electron Schrödinger equation. The basis set employed in molecular calculations should be as complete as possible.

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