

Accurate Kohn-Sham potential for the $1s2s^3S$ state of the helium atom: Tests of the locality and the ionization-potential theorems

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Abstract: The local Kohn-Sham potential has been constructed for the $1s2s^3S$ state of the helium atom, using the procedure proposed by van Leeuwen and Baerends (Phys. Rev. A **49**, 2138 (1994)) and the many-body electron density, obtained from the pair-correlation program of Salomonson and Öster (Phys. Rev. A **40**, 5559 (1989)). The Kohn-Sham orbitals reproduce the many-body density very accurately, demonstrating the validity of the Kohn-Sham model and the locality theorem in this case. The ionization-potential theorem, stating that the Kohn-Sham energy eigenvalue of the outermost electron orbital agrees with the negative of the corresponding many-body ionization energy (including electronic relaxation), is verified to nine digits. A Kohn-Sham potential is also constructed to reproduce the Hartree-Fock density of the same state, and the Kohn-Sham $2s$ eigenvalue is then found to agree with the same accuracy with the corresponding Hartree-Fock eigenvalue. This is consistent with the fact that in this model the energy eigenvalue equals the negative of the ionization energy without relaxation due to Koopmans' theorem. Related calculations have been performed previously, particularly for atomic and molecular ground states, but no one of matching accuracy. In particular, our results demonstrate that there is no conflict between the locality of the Kohn-Sham potential and the exclusion principle, as claimed by Nesbet (Phys. Rev. A **58**, R12 (1998)).

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Density-functional theory (DFT) is based upon the Hohenberg-Kohn (HK) energy functional [1, 2, 3] for an interacting system of electrons, moving in an external (nuclear) potential $v(\mathbf{r})$,

$$E[\rho] = F_{\text{HK}}[\rho] + \int d\mathbf{r} \rho(\mathbf{r})v(\mathbf{r}). \quad (1)$$

$F_{\text{HK}}[\rho]$ is the universal HK functional, which is in the constrained-search formulation [4, 5]

$$F_{\text{HK}}[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle, \quad (2)$$

where \hat{T} is the kinetic-energy and \hat{W} the electron-electron-interaction operators of the system. The wave function Ψ is assumed to be normalized and belonging to the *Sobolev space* $H^1(\mathcal{R}^{3N})$ [5, 6]. Were this functional known, minimizing it over normalized densities would yield the ground-state energy of the system,

$$E_0 = \min_{\rho \rightarrow N} E[\rho] = E[\rho_0]. \quad (3)$$

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It is easy to show that the variation principle works also for the lowest eigenstate of certain symmetry [7], and the principle has recently been extended also to more general excited states [8, 9].

According to the Kohn-Sham (KS) model [10], the electron density of the interacting system can be generated by a system of *noninteracting* electrons, moving in the *local* Kohn-Sham potential, $v_{\text{KS}}(\mathbf{r})$,

$$\left[-\frac{1}{2} \nabla^2 + v_{\text{KS}}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}). \quad (4)$$

The energy functional for this system is

$$E_{\text{KS}}[\rho] = T_{\text{KS}}[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) v_{\text{KS}}(\mathbf{r}), \quad (5)$$

where

$$T_{\text{KS}}[\rho] = \min_{\Phi \rightarrow \rho} \langle \Phi | \hat{T} | \Phi \rangle, \quad (6)$$

and Φ is a single Slater-determinantal wave function. The KS potential can be expressed by means of functional derivatives as

$$v_{\text{KS}}(\mathbf{r}) = \frac{\delta F_{\text{HK}}[\rho]}{\delta \rho(\mathbf{r})} - \frac{\delta T_{\text{KS}}[\rho]}{\delta \rho(\mathbf{r})} + v(\mathbf{r}). \quad (7)$$

It has been proven by Englisch and Englisch [11, 12], based on works of Lieb [5], and recently reconfirmed by van Leeuwen [6], that the KS potential is under general conditions strictly *local*, although there are objections to that statement in the literature [13, 14, 15]. In some of our previous works we have also analyzed the differentiability of density functionals and demonstrated the locality under general conditions [16, 17, 18]. In the present work we shall, in addition, give strong numerical support of the locality theorem. More details of this work will be published elsewhere [19].

The orbitals of the KS model generate the exact density but were originally believed to have no other physical significance. It has been shown, though, that the negative of the eigenvalue of the outermost electron orbital (HOMO) equals the ionization energy of the system. This was first shown by Perdew et al. [20, 21] and is known as the *ionization-potential theorem*. This has been challenged by Kleinman [22], but there are numerous calculations supporting the theorem [23]. In our present work this theorem is verified with much higher numerical accuracy than in any other calculation known to us.

Generally, the HK and KS energy functionals and the KS potential are not known, but more or less sophisticated approximations exist and are widely used in quantum-mechanical calculations [24, 25]. In certain cases, however, the electron density is accurately known, either from experiments or from *ab initio* calculations, and then the KS potential can be constructed with the corresponding accuracy. Essentially two schemes have been developed for this purpose, based upon works of Zhao and Parr [26, 27, 28] and of van Leeuwen and Baerends [29], respectively.

In the present work we have constructed accurate KS potentials for the lowest states of the helium atom, using the scheme of van Leeuwen and Baerends. In this procedure, the electronic part of the Kohn-Sham potential, $v_{\text{el}}(\mathbf{r})$, defined by (in atomic units)

$$v_{\text{KS}}(\mathbf{r}) = -\frac{Z}{r} + v_{\text{el}}(\mathbf{r}) + \text{const.}, \quad (8)$$

is obtained by iterations, using the formula

$$v_{\text{el}}^{i+1}(\mathbf{r}) = \frac{\rho_i(\mathbf{r})}{\rho_{\text{ex}}(\mathbf{r})} v_{\text{el}}^i(\mathbf{r}), \quad (9)$$

where $\rho_{\text{ex}}(\mathbf{r})$ is the exact many-body density and $\rho_i(\mathbf{r})$ is the density generated with the potential $v_{\text{el}}^i(\mathbf{r})$.

The electron density of the helium atom is in the present work generated by using the pair-correlation program of Salomonson and Öster [30]. The wave function is here expanded in partial waves, and after convergence the wave function is for this two-electron system virtually exact.

The convergence criteria in the iterative process (9) was set so that the iterated density should agree with the exact density within one part in 10^9 at all points. The rate of convergence is usually quite slow in this process — several thousands of iterations were often needed to achieve this kind of convergence. In order to improve the convergence rate and avoid 'oscillations', it was sometimes helpful to take some average of the last two iterations as the input for the next one. It was also found important to keep the electronic part of the potential positive at all points during the iterations by adjusting the constant in the expression (8). After convergence the constant is adjusted so that the potential approaches zero at infinity.

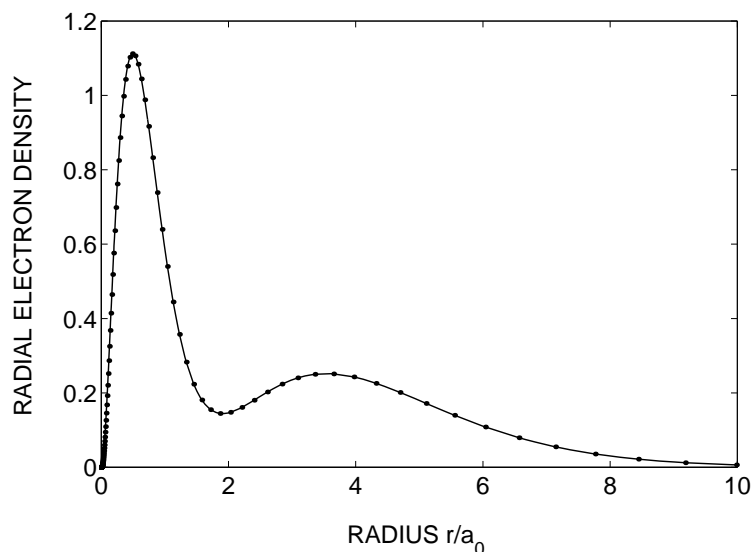


Fig. 1. The Kohn-Sham density (dots) superimposed on the many-body density (solid line) for the $1s2s^3S$ state of the helium atom (atomic units).

The final KS density for the $1s2s^3S$ system is shown in Fig. 1, superimposed on the exact many-body density. With the resolution of this figure, the two densities are indistinguishable. The corresponding KS potential is shown in Fig. 2. The potential has a 'bump' near the node of the outermost electron, which is characteristic of 'optimized local potentials' [31]. This is an effect of the electron self interaction (SIC), which varies strongly near the node of the valence wave function due to the $\rho^{1/3}$ dependence [32, 33].

The fact that we can generate the the exact many-body density in the Kohn-Sham model with a single local potential, proves the locality theorem in this case — at least within our numerical accuracy of nine digits.

In order to test the ionization-potential theorem mentioned above, the eigenvalue of the Kohn-Sham $2s$ orbital is compared with the many-body ionization energy. According to this theorem these quantities should be equal, with opposite signs. We have found the KS eigenvalue to be $-0.175\ 229\ 3794$ H to be compared with our many-body ionization energy (including relaxation) of $0.175\ 229\ 3794$ H, i.e., a numerical agreement to nine digits also in this case. These values agree also very well with the value $0.175\ 229\ 3782$ H, obtained by Pekeris [34], using accurate Hylleraas-type wave functions (uncorrected for relativity, mass-polarization and QED effects).

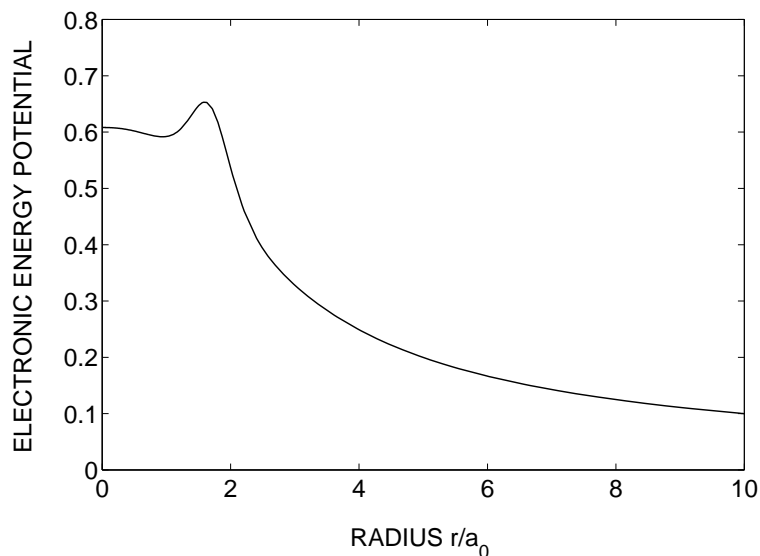


Fig. 2. The electronic part of the Kohn-Sham potential for the helium $1s2s^3S$ state. Note the 'bump' near the node of the $2s$ orbital, characteristic of 'optimized' local potentials [31] (atomic units).

As a further test we have constructed the Kohn-Sham potential that reproduces the Hartree-Fock (HF) density of the same state. This density is easily generated by solving the standard HF equations and inserted into the generating formula (9) in place of the many-body density. The resulting KS potential was found to yield a $2s$ energy eigenvalue of $-0.174\ 256\ 072$ H, which agreed with the HF value to all digits given. This represents further tests of the locality and ionization-potential theorems.

A comparison between the ionization energy and Hartree-Fock eigenvalue shows that the effect of relaxation enters here already in the third decimal place. This demonstrates that this effect is reproduced to six digits by the Kohn-Sham eigenvalue.

Numerical construction of the KS potentials for the ground state of the helium atom as well as other noble-gas atoms were first performed by Zhao, Morrison and Parr [28], and the ionization-potential theorem was verified for helium to about two parts in 10000. Similar work on the ground as well as the first excited singlet states of helium has recently been performed by Harbola [35]. These calculations, which are partly based upon old density data available in the literature, are less accurate, though, and the ionization-potential theorem is verified only on percent level. Related calculations have also been performed on other small atoms and molecules, but none of the calculations we have found in the literature can match the accuracy of the present work.

In summary, we have demonstrated that it is possible to construct a local Kohn-Sham potential that generates the many-body density for the lowest-lying triplet state of the helium atom with extreme accuracy. The validity of the ionization-potential theorem, i.e., the agreement between the absolute values of the ionization potential and highest-lying orbital eigenvalue, is confirmed with to nine digits. In the triplet state the electrons can have the same spin orientation, demonstrating that there is no conflict between locality and the exclusion principle, as claimed by Nesbet [13, 14, 15].

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