

Construction of accurate Kohn-Sham potentials for the lowest states of the helium atom: Accurate test of the ionization-potential theorem

I. Lindgren*, S. Salomonson†, and F. Möller‡

Department of Physics, Chalmers University of Technology and the Göteborg University, Göteborg, Sweden

Accurate local Kohn-Sham potentials have been constructed for the ground $1s^2\ ^1S$ state and, in particular, for the lowest triplet $1s2s\ ^3S$ state of the helium atom, using electron densities from many-body calculations and the procedure of van Leeuwen and Baerends (Phys. Rev. A **49**, 2138 (1994)). The resulting Kohn-Sham orbitals reproduce the many-body densities very accurately, and furthermore we have demonstrated that the negative of the energy eigenvalue of the outermost electron orbital agrees with the corresponding ionization energy with extreme accuracy. The procedure is also applied to the Hartree-Fock density of the $1s2s\ ^3S$ state, and the Kohn-Sham eigenvalue of the $2s$ orbital is found to agree very well with the corresponding Hartree-Fock eigenvalue, which is the negative of the ionization energy in this model due to Koopmans' theorem. The results clearly 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)).

PACS numbers: 31.15Ew, 31.15Pf, 02.30Sa

I. THE KOHN-SHAM MODEL

According to the Hohenberg-Kohn (HK) theorem [1–3], the energy of any electronic system can be expressed as a functional of the electron density, $\rho(\mathbf{r})$,

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

where $v(\mathbf{r})$ is the external potential and $F_{\text{HK}}[\rho]$ is the universal HK functional, which in the constrained-search formulation is [4, 5]

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

Here, \hat{T} is the kinetic-energy and \hat{W} the electron-electron-interaction operators of the system (in atomic units),

$$\hat{T} = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2; \quad \hat{W} = \sum_{i<j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (3)$$

The wave function, Ψ , is normalized and belongs to the *Sobolev space* $H^1(\mathcal{R}^{3N})$ [5, 6], and the corresponding functional is defined for all N -representable densities [3]. The ground-state energy of the system is obtained by minimizing the energy functional over these densities [3],

$$E_0 = \min_{\rho \rightarrow N} E[\rho] = E[\rho_0]. \quad (4)$$

*ingvar.lindgren@fy.chalmers.se

†f3asos@fy.chalmers.se

‡gu99firmo@dd.chalmers.se

This leads to the Euler-Lagrange equation

$$\frac{\delta F_{\text{HK}}[\rho]}{\delta \rho(\mathbf{r})} + v(\mathbf{r}) = \mu, \quad (5)$$

where μ is the Lagrange parameter for the normalization constraint, $\int d\mathbf{r} \rho(\mathbf{r}) = N$.

In the Kohn-Sham (KS) model the interacting system is replaced by a system of *noninteracting* electrons, moving in the local KS potential, $v_{\text{KS}}(\mathbf{r})$ [7],

$$\left[-\frac{1}{2} \nabla^2 + v_{\text{KS}}(\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}). \quad (6)$$

The energy functional for this system is

$$E_{\text{KS}}[\rho] = T_{\text{KS}}[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) v_{\text{KS}}(\mathbf{r}), \quad (7)$$

where

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2 \quad (8)$$

is the electron density. The kinetic-energy functional is

$$T_{\text{KS}}[\rho] = \min_{\Phi \rightarrow \rho} \langle \Phi | \hat{T} | \Phi \rangle, \quad (9)$$

where $\Phi = \det\{\phi_i\}$ is a single Slater-determinantal wave function. Minimizing this functional leads to the Euler-Lagrange equation

$$\frac{\delta T_{\text{KS}}[\rho]}{\delta \rho(\mathbf{r})} + v_{\text{KS}}(\mathbf{r}) = \mu. \quad (10)$$

Comparing with Eq. (5), leads – apart from an additive constant – to the relation

$$v_{\text{KS}}(\mathbf{r}) = \frac{\delta F_{\text{HK}}[\rho]}{\delta \rho(\mathbf{r})} - \frac{\delta T_{\text{KS}}[\rho]}{\delta \rho(\mathbf{r})} + v(\mathbf{r}). \quad (11)$$

The Hohenberg-Kohn-Sham model was originally proven for the ground state but it was demonstrated by Gunnarsson and Lundqvist [8] that it is valid also for the lowest state of a given symmetry, and it has later been shown to hold also for more general excited states [9, 10].

Although the form of the KS potential is generally not known, it can be constructed with arbitrary accuracy in cases where the electron density is known from other sources, e.g., from experiments or from *ab initio* calculations. Essentially two schemes have been developed for this purpose, by Zhao and Parr [11–13] and by van Leeuwen and Baerends [?], respectively.

The KS orbitals were originally assumed to have no other physical significance than generating the exact electron density, but it was later found by Perdew et al. [14–16] and independently by Almbladh and Pendroza [17] that the eigenvalue of the outermost electron (with opposite sign) equals the ionization energy of the system. Perdew et al. have shown that considering densities that integrate to non-integrals,

$$M = \int d\mathbf{r} \rho(\mathbf{r}), \quad (12)$$

the theorem holds in the range $N - 1 < M < N$ and hence when this number approaches N from below. This condition is known as the *ionization-potential theorem* [16].

The validity of the ionization-potential theorem has been challenged by Kleinman [18] with counterarguments supplied by Perdew and Levy [16]. A number of numerical verifications of the theorem have been performed in the past [19? –26], generally with low or moderate accuracy due to problems in representing the density accurately using an analytical basis set [13, 22]. In the

present work we use a numerical basis set, which has made it possible to demonstrate the validity of the theorem with much higher accuracy than in any previous calculation known to us [44].

The construction of the KS potential from the electron density has so far mainly been performed for atomic and molecular ground states. Recently, however, Harbola [26] has constructed the potential for the first excited singlet state, $1s2s\ ^1S$, of the helium atom.

It has been rigorously shown that the KS potential is under general conditions strictly *local* [5, 6, 27, 28], and this has also been demonstrated in some of our previous works [29–31]. Nevertheless, this fact has been disputed in several papers by Nesbet [32–34], who claims that the locality condition is in conflict with the exclusion principle. In the present work we have been able to construct the KS potential for an excited *triplet* state of helium, where the electrons can have the same spin orientation. This has, as far as we know, not been done before, and this makes it possible to test numerically the locality condition. The result confirms the locality condition with extreme accuracy, thereby demonstrating that there is no conflict between locality and the exclusion principle, rebutting the objection of Nesbet.

II. CONSTRUCTION OF THE KOHN-SHAM POTENTIAL FROM ELECTRON DENSITY

In the present work we apply the scheme of van Leeuwen and Baerends to construct accurate KS potentials for the lowest states of the helium atom. Following van Leeuwen and Baerends, we obtain after multiplying the KS equations (6) from the left by $\phi_i^*(\mathbf{r})$ and summing over the N electrons

$$v_{\text{KS}}(\mathbf{r})\rho(\mathbf{r}) = \sum_{i=1}^N \left[\frac{1}{2} \phi_i^*(\mathbf{r}) \nabla^2 \phi_i(\mathbf{r}) + \varepsilon_i |\phi_i(\mathbf{r})|^2 \right], \quad (13)$$

where $\rho(\mathbf{r})$ is the electron density

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2. \quad (14)$$

This leads to a self-consistency problem, which can be solved by iteration. Defining the electronic part of the potential, $v_{\text{el}}(\mathbf{r})$, by

$$v_{\text{KS}}(\mathbf{r}) = -\frac{Z}{r} + v_{\text{el}}(\mathbf{r}) + \text{const.}, \quad (15)$$

the solution is obtained by means of the formula

$$v_{\text{el}}^{k+1}(\mathbf{r}) = \frac{\rho_k(\mathbf{r})}{\rho_0(\mathbf{r})} v_{\text{el}}^k(\mathbf{r}), \quad (16)$$

where $\rho_0(\mathbf{r})$ is the exact many-body density and $\rho_k(\mathbf{r})$ is the density generated with the potential $v_{\text{el}}^k(\mathbf{r})$. This procedure is continued until certain convergence criteria are met.

III. MANY-BODY THEORY

The many-body electron density needed for this procedure has been evaluated by means of many-body perturbation technique [35], using the nonrelativistic pair-correlation program developed by Salomonson and Öster [36]. We shall briefly indicate this procedure here.

We want to solve the Schrödinger equation

$$H\Psi = E\Psi \quad (17)$$

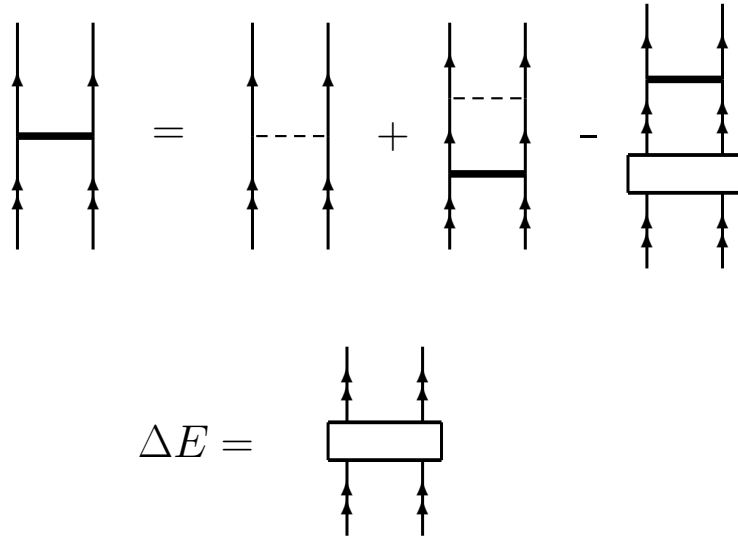


FIG. 1: Upper line: Graphical representation of the pair equation (Eq. (26)). The vertical lines represent the valence orbitals (double arrows) and virtual orbitals (single arrow). The thick horizontal line represents Ω_2 , the dotted line the electrostatic interaction between the electrons and the box the effective two-body interaction W_2 (27). Lower line: Graphical representation of the energy shift due to the perturbation (Eq. (28)).

and partition the Hamiltonian into a zeroth-order hamiltonian and a perturbation

$$H = H_0 + H'. \quad (18)$$

We start from a zeroth-order or *model function* Ψ_0 , which is an eigenfunction of H_0 ,

$$H_0 \Psi_0 = E_0 \Psi_0. \quad (19)$$

The exact solution can be expressed

$$\Psi = \Omega \Psi_0, \quad (20)$$

where Ω is the *wave operator*, satisfying the *generalized Bloch equation* in the *linked-diagram form*

$$[\Omega, H_0]P = (H'\Omega - \Omega W)_{\text{linked}}P. \quad (21)$$

Here, W is the *effective interaction*, in intermediate normalization ($\Psi_0 = P\Psi$) given by $W = PH'\Omega P$. P is the projection operator for the model space, which in this simple case is assumed to contain only a single model state, Ψ_0 . Only so-called linked diagrams will contribute according to the linked-diagram theorem [35].

Using second quantization, the wave operator can be separated into normal-ordered one-, two-,... body parts

$$\Omega = 1 + \Omega_1 + \Omega_2 + \dots \quad (22)$$

or

$$\Omega = 1 + \{a_i^\dagger a_j\} x_j^i + \frac{1}{2!} \{a_i^\dagger a_j^\dagger a_l a_k\} x_{kl}^{ij} + \dots \quad (23)$$

using the sum convention. a^\dagger/a are the electron creation/annihilation operators, and the curly brackets denote the normal-ordering. The n -body part of the wave operator then satisfies the equation

$$[\Omega_n, H_0]P = (H'\Omega - \Omega W)_{\text{linked},n}P. \quad (24)$$

IV. APPLICATION TO THE LOWEST STATES OF THE HELIUM ATOM

For heliumlike systems, starting from hydrogenlike orbitals, the wave operator can be expressed by means of the two-body part only of the wave operator,

$$\Omega = 1 + \Omega_2, \quad (25)$$

satisfying the 'pair equation'

$$[\Omega_2, H_0]P = (H'\Omega - \Omega W_2)_{\text{linked},2}P. \quad (26)$$

This equation is depicted in the upper part of Fig. 1. Here, the thick line represents Ω_2 and the box the two-body part of the effective interaction

$$W_2 = (PH'\Omega P)_2. \quad (27)$$

The total energy of the system is

$$E = E_0 + \Delta E, \quad (28)$$

where the energy shift, ΔE , is in this case given by

$$\Delta E = \langle \Psi_0 | H'\Omega | \Psi_0 \rangle = \langle \Psi_0 | W_2 | \Psi_0 \rangle \quad (29)$$

and represented graphically by all 'closed' two-body diagrams, as indicated at the bottom part of Fig. 1. Since the final state of the ionization process is in our cases the ground state of the He^+ ion, with the exact nonrelativistic energy of -2 H, the binding energy of the outermost electron becomes (in atomic units)

$$\text{BE} = -2 - E. \quad (30)$$

In the present work the pair equation (26) has been solved, using the numerical procedure developed by Salomonson and Öster [36], and densities for the $1s^2\ ^1S$ ground state and the lowest triplet state, $1s2s\ ^3S$, of the helium atom have been evaluated. These densities are then used to construct the corresponding KS potentials, as discussed above. The wave functions obtained in this way are virtually exact, apart from relativistic, mass-polarization and quantum-electrodynamical effects. In a similar fashion we have also used the Hartree-Fock density to construct the corresponding KS potential.

It can be argued that the procedure used here corresponds to approaching the electron-density integral (12) to the electron number from below, $M \rightarrow N-0$ [16], and hence the ionization-potential theorem can be tested.

In order to achieve good accuracy, particularly for the eigenvalue of the outermost electron orbital, it is important to have the exact density in an accurate form and to have this density well reproduced by the Kohn-Sham orbitals. In the present work we have generated the many-body density using a large numerical grid, and the convergence criteria are set so that the Kohn-Sham density should not deviate from the many-body density by more than one part in 10^9 at any point. The convergence rate was usually quite slow, and several thousands of iterations were often needed to reach this level of accuracy. 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 is also important to keep the electronic part, v_{el} , of the KS-potential positive at all points by adjusting the constant in Eq. (15). After the iteration procedure was completed, the constant is determined so that the potential approaches zero as $r \rightarrow \infty$.

As in our earlier works [36], we apply an exponential radial grid $r_i = e^{x_i}/Z$, where x_i is a discrete linear lattice with equally spaced points with x typically ranging from $x_{\text{min}} = -11$ to about $x_{\text{max}} = 4$. For the triplet state at least four different grids were used, and the results extrapolated in the standard way. Also the end point of the grid, x_{max} , is varied, as it was found that the Kohn-Sham results were quite sensitive to that value (See Fig. 6), most likely due

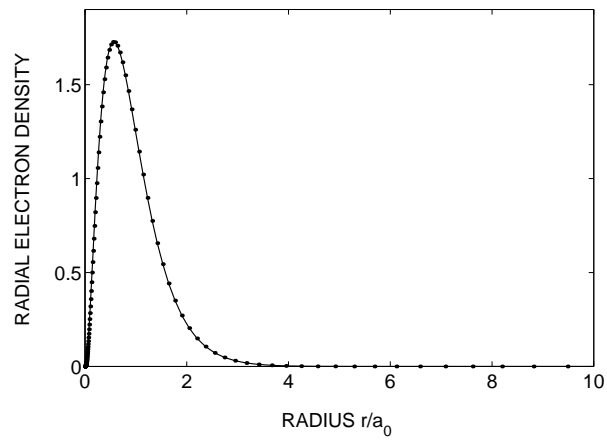


FIG. 2: The Kohn-Sham density (dots) superimposed on the many-body density (solid line) for the helium ground state.

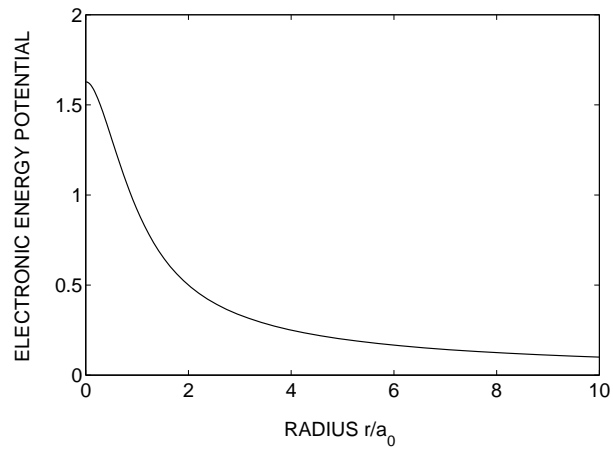


FIG. 3: The electronic part of the Kohn-Sham potential for the helium ground state.

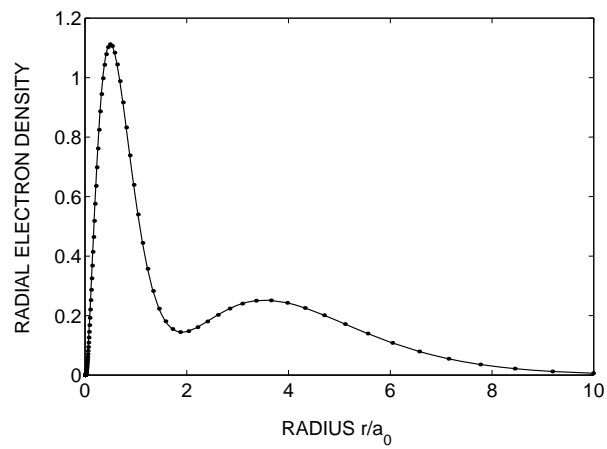


FIG. 4: The Kohn-Sham density (dots) superimposed on the many-body density (solid line) for $1s2s^3S$.

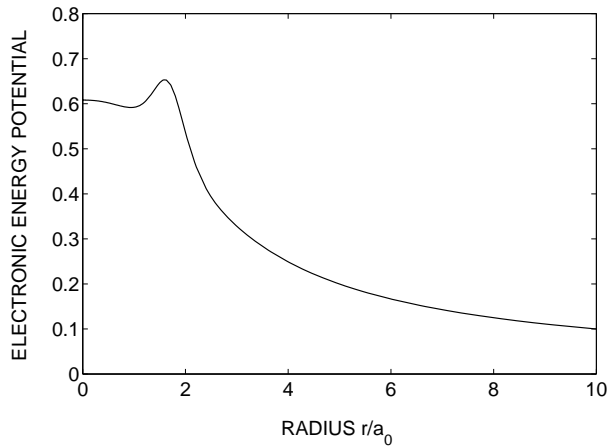


FIG. 5: The electronic part of the Kohn-Sham potential for the $1s2s^3S$ state of helium.

to the fact that our pair functions are forced to be zero at the end point. This has very little effect on standard many-body calculations, but the KS eigenvalue depends strongly upon the tail of the density distribution and therefore more affected by the boundary condition. Hence, an extrapolation of x_{\max} is required in the KS case. It is likely that the results could be improved by more sophisticated boundary conditions.

In the evaluation of the many-body electron density a partial-wave expansion is used [36], normally up to $l_{\max} = 10$, and an extrapolation performed in the standard way. In our procedure, however, the Kohn-Sham potential is evaluated for successive truncations of the partial-wave expansion, and the above-mentioned ionization-potential theorem could be tested for each truncation separately, as well as after the l_{\max} extrapolation.

A. The many-body density of the helium ground state

As a preliminary test of our procedure, we have applied our procedure to the ground state of the helium atom, where the Kohn-Sham potential has previously been constructed [22, 26]. The electron density obtained from the KS orbitals is shown in Fig. 2 (dots) superimposed on the many-body density (dots). In this figure, the two densities are indistinguishable. The resulting KS potential is shown in Fig. 3.

The results we have obtained are $-0.903\,7246$ H for the KS $1s$ eigenvalue and $0.903\,7248$ H for the many-body ionization energy, which verifies the above-mentioned ionization-potential theorem to at least six digits. The result agrees well with the very accurate value obtained by Frankowski and Pekeris [37] and by Freund et al. [38] of $0.903\,724\,377$ H (uncorrected for relativity, mass-polarization and QED effects).

In the corresponding calculation by Harbola [26], an electron density taken from the literature [39] was used. Two different configurations, $1s^2\,^1S$ and $1s2s\,^1S$, respectively, were used, and the energy eigenvalue of the highest occupied orbital was in both cases found to be 0.899 H.

B. The many-body density of the lowest triplet state of helium

As mentioned, our primary goal of the present work has been to construct the Kohn-Sham potential from the many-body density for the lowest triplet state, $1s2s\,^3S$ of the helium atom, in order to test the possible conflict between locality and the exclusion principle, claimed by Nesbet [32–

TABLE I: Comparison between the Kohn-Sham $2s$ eigenvalue and the many-body ionization energy for the $1s2s^3S$ state of helium with $l_{\max} = 10$ and different end points of the numerical grid.

x_{\max}	KS eigenvalue	Many-body IP
3.8	-0.175 228 7967	0.175 229 3578
4.0	-0.175 229 1111	0.175 229 3634
4.2	-0.175 229 2488	0.175 229 3649
4.4	-0.175 229 3135	0.175 229 3634
extrapol	-0.175 229 3630	0.175 229 3639

TABLE II: Comparison between the Kohn-Sham $2s$ eigenvalue and the many-body ionization energy for the $1s2s^3S$ state of helium with different truncations of the partial-wave expansion.

l_{\max}	KS eigenvalue	Many-body IP
4	-0.175 228 6206	0.175 228 6214
6	-0.175 229 2341	0.175 229 2354
8	-0.175 229 3366	0.175 229 3379
10	-0.175 229 3630	0.175 229 3639
extrapol	-0.175 229 3794	0.175 229 3797

34]. Therefore, we have in this case performed more extensive extrapolations on order to improve the accuracy.

The final KS-density for the $1s2s^3S$ system is shown in Fig. 4 (dots), together with the many-body density (solid line). The corresponding KS-potential is shown in Fig. 5. It is interesting to note that the potential has a 'bump' close to the node of the outermost (valence) electron. This is typical of this kind of potential and is an effect of the electron *self interaction* (SIC) [40–42]. This depends approximately on $\rho_{\text{val}}^{1/3}$, where ρ_{val} is the density of the valence electron, and hence varies strongly near the node of the valence orbital.

In Table I we show the KS $2s$ eigenvalue and the corresponding many-body ionization energy after grid extrapolation with the partial-wave expansion truncated at $l_{\max} = 10$ and different values of the grid end point, x_{\max} . This extrapolation is illustrated graphically for two values of l_{\max} in Fig. 6. It is found that the KS eigenvalue is – in contrast to the many-body ionization energy – quite sensitive to the end point. After the x_{\max} extrapolation, the values are found to agree to nine

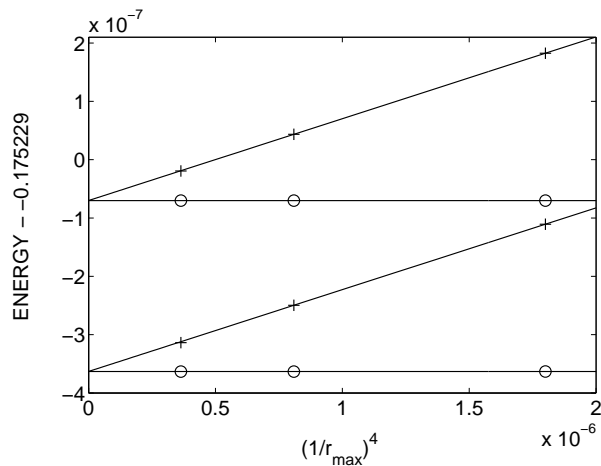


FIG. 6: x_{\max} extrapolation of the $2s$ eigenvalue (crosses) and the negative ionization energy (rings) for the $1s2s^3S$ state of helium with $l_{\max} = 5$ (upper part) and $l_{\max} = 10$ (lower part).

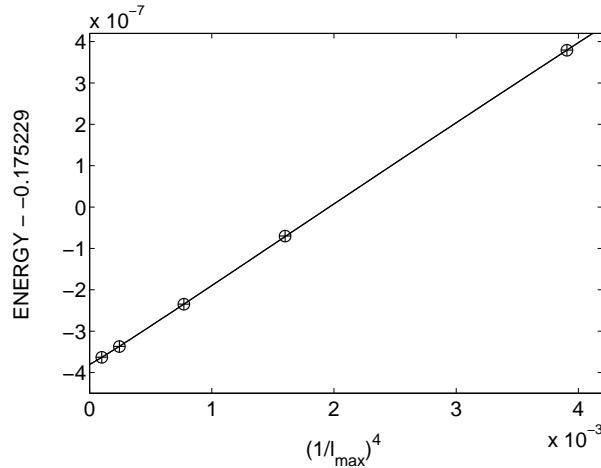


FIG. 7: Partial-wave extrapolation of the $2s$ eigenvalue (crosses) and the negative ionization energy (rings) for $1s2s^3S$ of helium.

digits for each partial wave truncation. The dependence on the end point is in our calculations due to the way we truncate the wave functions at the high end. In ordinary many-body calculations this is insignificant, but in the present case the performance at this end is of more importance.

In order to find the "true" values of these quantities, it is necessary also to extrapolate the partial-wave expansion, with the result shown in Table II. This is illustrated in Fig. 7. These final values represents the nonrelativistic ionization energy, as before, uncorrected for mass polarization as well as for relativistic and QED effects. Then our two values differ by only a few units in the tenth decimal place, and they differ by only one unit in the ninth place from the corresponding value 0,175 229 3782 H, obtained by Pekeris [43].

C. The Hartree-Fock density of the lowest triplet state of helium

As an additional test of the procedure described here, we have applied this also to the Hartree-Fock density of lowest triplet state of the helium atom. This density is generated by solving the standard HF equations and then inserted into the generating formula (16) in place of the many-body density. The resulting densities are quite similar to those given above, as is the resulting KS potential, since HF is quite a good approximation for this system.

In the HF approximation the orbital eigenvalues correspond exactly to the corresponding ionization energies (with opposite sign), and therefore a comparison of the Hartree-Fock-Kohn-Sham (HFKS) $2s$ eigenvalue with the corresponding HF value would constitute a further test of the above-mentioned ionization-potential theorem. Here, the x_{\max} extrapolation is less important. For a particular value of x_{\max} we obtained after grid extrapolation the HFKS $2s$ eigenvalue -0.174 256 072 542 H and the corresponding HF value -0.174 256 072 544 H – an agreement to 11 digits! After complete extrapolations the result is -0.174 256 0724 H, which is expected to be accurate to 8-9 digits.

V. SUMMARY AND COMMENTS

We have demonstrated that it is possible to construct with extreme accuracy a local Kohn-Sham potential for the lowest states of the helium atom, including the lowest triplet state. The agreement between the absolute values of the ionization potential and highest-lying KS orbital

energy eigenvalue is verified to at least nine digits, which – as far as we know – represents by far the most accurate numerical test of the ionization-potential theorem performed to date. This result for the triplet state also clearly demonstrates that there is no conflict between the locality theorem and the exclusion principle, as claimed by Nesbet [32–34].

REFERENCES

- [1] P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).
- [2] R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford Univ. Press, New York, 1989).
- [3] R. M. Dreizler and E. K. U. Gross, *Density Functional Theory* (Springer-Verlag, Berlin, 1990).
- [4] M. Levy, *Proc. Natl. Acad. Sci. USA* **76**, 6062 (1979).
- [5] E. H. Lieb, *Int. J. Quantum Chem.* **24**, 243 (1983).
- [6] R. van Leeuwen, *Adv. Quantum Chem.* **43**, 25 (2003).
- [7] W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- [8] O. Gunnarsson and B. I. Lundqvist, *Phys. Rev. B* **10**, 4274 (1976).
- [9] A. Görling, *Phys. Rev. A* **59**, 3359 (1999).
- [10] M. Levy and A. Nagy, *Phys. Rev. Lett.* **83**, 4361 (1999).
- [11] Q. Zhao and R. G. Parr, *J. Chem. Phys.* **98**, 543 (1993).
- [12] Y. Wang and R. G. Parr, *Phys. Rev. A* **47**, R1591 (1993).
- [13] Q. Zhao, R. C. Morrison, and R. G. Parr, *Phys. Rev. A* **50**, 2138 (1994).
- [14] J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balducci, *Phys. Rev. Lett.* **49**, 1691 (1982).
- [15] M. Levy, J. P. Perdew, and V. Sahni, *Phys. Rev. A* **30**, 2745 (1984).
- [16] J. P. Perdew and M. Levy, *Phys. Rev. B* **56**, 16021 (1997).
- [17] C.-O. Almbladh and A. C. Pedroza, *Phys. Rev. A* **29**, 2322 (1984).
- [18] L. Kleinman, *Phys. Rev. B* **56**, 12042 (1997).
- [19] Q. Zhao and R. G. Parr, *J. Chem. Phys.* **98**, 543 (1993).
- [20] O. V. Gritsenko, R. van Leeuwen, and E. J. Baerends, *Phys. Rev. A* **52**, 1870 (1995).
- [21] M. Levy and A. Görling, *Phys. Rev. B* **53**, 969 (1996).
- [22] M. E. Mura, P. J. Knowles, and C. A. Reynolds, *J. Chem. Phys.* **106**, 9659 (1997).
- [23] Á. Nagy and M. Levy, *Chem. Phys. Letters* **296**, 313 (1998).
- [24] D. P. Chong, O. V. Gritsenko, and E. J. Baerends, *J. Phys. Chem.* **116**, 1760 (2002).
- [25] C.-G. Zhan, J. A. Nichols, and D. Dixon, *J. Phys. Chem. A* **107**, 4184 (2003).
- [26] M. K. Harbola, *Phys. Rev. A* **69**, 042512 (2004).
- [27] H. Englisch and R. Englisch, *Phys. Stat. Sol.* **123**, 711 (1984).
- [28] H. Englisch and R. Englisch, *Phys. Stat. Sol.* **124**, 373 (1984).
- [29] I. Lindgren and S. Salomonson, *Phys. Rev. A* **67**, 056501 (2003).
- [30] I. Lindgren and S. Salomonson, *Adv. Quantum Chem.* **43**, 95 (2003).
- [31] I. Lindgren and S. Salomonson, *Phys. Rev. A* p. (accepted) (2004).
- [32] R. K. Nesbet, *Phys. Rev. A* **58**, R12 (1998).
- [33] R. K. Nesbet, *Phys. Rev. A* **65**, 010502(R) (2001).
- [34] R. K. Nesbet, *Adv. Quantum Chem.* **43**, 1 (2003).
- [35] I. Lindgren and J. Morrison, *Atomic Many-Body Theory* (Second edition, Springer-Verlag, Berlin, 1986).
- [36] S. Salomonson and P. Öster, *Phys. Rev. A* **40**, 5559 (1989).
- [37] K. Frankowski and C. L. Pekeris, *Phys. Rev.* **146**, 46 (1966).
- [38] D. E. Freund, B. D. Huxtable, and J. D. Morgan, *Phys. Rev. A* **29**, 980 (1984).
- [39] T. Koga, Y. Kasai, and A. J. Thakkar, *Int. J. Quantum Chem.* **46**, 689 (1993).
- [40] I. Lindgren, *Int. J. Quantum Chem.* **5**, 411 (1971).
- [41] J. D. Talman and W. S. Shadwick, *Phys. Rev. A* **14**, 36 (1976).
- [42] J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
- [43] C. L. Pekeris, *Phys. Rev.* **115**, 1216 (1959).
- [44] A short version of this work has been submitted for publication in *Phys. Rev. Letters*