Electron pair properties for the helium atom from explicitly correlated wave functions

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Abstract

Starting from a compact and accurate explicitly correlated wave function a systematic study of two-body properties in both position and momentum space has been performed for the He atom. A systematic comparison with the values obtained from both a multi-configuration Hartree–Fock and a Hylleraas (when available) wave function is performed. The wave function and the different expectation values are obtained by using the variational Monte Carlo method. The quality of both the wave function and the methodology used are analyzed and discussed.

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1. Introduction

Electron pair intracule and extracule densities in position space have been introduced to study electron–electron correlations in atoms [1]. They are defined as

\[ I(\mathbf{r}_{12}) = \int \sum_{i,j=1}^{N} \delta \left( \mathbf{r}_{12} - (\mathbf{r}_i - \mathbf{r}_j) \right) \left| \psi \left( \mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N \right) \right|^2 \frac{1}{\langle \psi | \psi \rangle} d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_N, \]

\[ E(\mathbf{R}) = \int \sum_{i>j=1}^{N} \delta \left( \mathbf{R} - (\mathbf{r}_i + \mathbf{r}_j) / 2 \right) \left| \psi \left( \mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N \right) \right|^2 \frac{1}{\langle \psi | \psi \rangle} d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_N. \]

The corresponding spherically averaged densities are labeled as \( h(r_{12}) \) and \( d(R) \), respectively, and represent the probability density functions for the interelecronic distance, \( r_{12} \), and the center of mass distance, \( R \). Both the intracule and the extracule densities are normalized to the number of electron pairs, \( N(N - 1)/2 \). The value of the intracule and extracule densities at the origin give us the probability of two electrons to be at the same position and at opposite positions with respect to the nucleus, respectively.

In momentum space the intracule and extracule densities are defined as their counterparts in...
position space but starting from the wave function in momentum space. They give the probability density function for a pair of electrons having a relative momentum \( \vec{p}_{12} \) or a center of mass momentum \( \vec{P} \), respectively. Their spherical averages are denoted by \( \mathcal{H}(p_{12}) \) and \( \mathcal{D}(P) \), respectively.

In position space the intracule density has received much attention. Starting from the seminal work of Coulson and Neilson [2] it has been calculated by using configuration interaction (CI) and Hylleraas-type wave functions [3–7]. This function is of interest to study the electron correlations by means of the so-called Coulomb hole and also it is related to X-ray scattering and high-energy electron scattering cross sections, and it is useful in the interpretation of the Hund’s rules. The extracule density in position space has been less studied than the intracule density. For the helium atom it has been calculated starting from different type of correlated wave functions [8–10]. Banyard and co-workers studied two [11] and three [12] electron atoms within a CI scheme. More recently multi-configuration Hartree–Fock (MCHF) wave functions have been also used to study two-body position and momentum properties for the atoms helium to beryllium [13–15].

The variational Monte Carlo (VMC) method constitutes an efficient method to deal with Quantum Chemistry problems and in particular with the calculation of accurate trial wave functions and the computation of atomic properties starting from those wave functions [16]. It has been applied to study the atoms He through Ne by using explicitly correlated wave functions [10,17–19]. In most of the previous studies the wave function is fixed by minimizing the variance instead of the energy. However, and within the VMC framework it has been recently established that energy optimized wave functions provide not only more accurate values for the ground state energy [20] but also a better description of one- and two-body properties of atomic systems in position space [21,22].

The aim of this work is to obtain two-electron properties in position and momentum spaces starting from an accurate explicitly correlated trial wave function for the He atom. In particular we compute the spherically averaged intracule and extracule densities in position and momentum spaces and some related properties such as their radial moments. The He atom is the simplest system for which analytic solutions cannot be obtained. It has been widely considered in the literature by using different methods and wave functions to obtain the energy and to describe some of its properties. Here we carry out a systematic and complete study of two-electron properties focusing on the properties in momentum space because some properties in position space have been previously reported [22]. The results are compared with others obtained from wave functions based on extensive Slater determinant expansions. To assess the accuracy of the results a comparison with those obtained from a Hylleraas-type wave function that are considered as exact is performed where available, showing a better performance of the functions obtained in this work with respect to the MCHF ones. Finally, some criteria previously used in the literature to evaluate the quality of the results are revised and discussed. Atomic units are used throughout.

2. Wave function

The wave function used is the product of the Clementi–Roetti [23] Hartree–Fock solution, \( \Phi \), times a symmetric correlation factor, \( F \), including the dynamical correlation among the electrons

\[
\Psi_{17} = F\Phi,
\]

where

\[
F = e^{\sum_{i<j} U_{ij}}
\]

and

\[
U_{ij} = \sum_{k=1}^{N_e} c_k (\hat{r}_{ik}^m \hat{r}_{jk}^m + \hat{r}_{ik}^p \hat{r}_{jk}^p) \hat{r}_{ij}^p;
\]

\[
\hat{r}_i = \frac{br_i}{1 + br_i}, \quad \hat{r}_{ij} = \frac{dr_{ij}}{1 + dr_{ij}}.
\]

The coefficients \( b \) and \( d \) represent the inverse of the effective range of the correlations which have been fixed at the value of one atomic unit in the present
calculation and \( c_k \) are the variational parameters. This form of the correlation factor is due to Boys and Handy [24]. In this work we use the parameterization proposed by Schmidt and Moskowitz [25] which includes some averaged backflow effects based on the requirement of local current conservation. We have used \( N_c = 17 \), the first coefficient is fixed to satisfy the electron–electron cusp exactly while the others are taken as variational parameters.

In Table 1, we show the values of the integers \( m_k, n_k \) and \( o_k \) that determine the functional form of the wave function and the values of the variational parameters \( c_k \) of this work. They have been obtained by minimizing the total energy instead of the variance of the local energy and then they differ from those of [25]. The value of the energy obtained from this wave function is \( E = -2.903660(5) \) [22].

3. Results

The local effects of electronic correlations are usually studied by means of the difference function \( \Delta M(t) = 4\pi r^2 [M_c(t) - M_{HF}(t)] \) where \( M \) is any of the spherically averaged electron pair densities in position or in momentum spaces, \( t \) is the corresponding variable and the indexes c and HF stand for correlated and Hartree–Fock, respectively. When \( M(t) \) is the intracule density the difference function is the well known Coulomb hole [2].

In Fig. 1, we plot the difference function for the intracule and extracule densities in position space as compared with those obtained from a MCHF wave function [13]. For the extracule we plot the results obtained from a Hylleraas-type wave function that can be considered as exact.

![Fig. 1. Difference function for the intracule (upper plot) and extracule (lower plot) radial densities in position space calculated from the explicitly correlated wave function of this work (\( \Psi_{17} \)) as compared with the MCHF results of [13]. For the intracule we plot the results obtained from a Hylleraas-type wave function that can be considered as exact.](image)

For the intracule difference function some discrepancies in the region of the maximum have been found. We have also plotted the intracule difference function obtained from a very accurate Hylleraas-type wave function that can be considered as exact [26]. As it is clear from the figure, the explicitly correlated results of this work provide a more precise description of the interelectronic electron density than the MCHF results. This is consistent with the fact that the improvement in

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Parameters of the helium wave function</th>
</tr>
</thead>
<tbody>
<tr>
<td>( m_k ), ( n_k ), ( o_k )</td>
<td>( c_k )</td>
</tr>
<tr>
<td>0,0,1</td>
<td>0.25</td>
</tr>
<tr>
<td>0,0,4</td>
<td>1.107188156</td>
</tr>
<tr>
<td>4,0,0</td>
<td>0.758576583</td>
</tr>
<tr>
<td>4,0,2</td>
<td>-2.922689779</td>
</tr>
<tr>
<td>6,0,2</td>
<td>1.137562015</td>
</tr>
<tr>
<td>2,0,6</td>
<td>-1.00133889</td>
</tr>
</tbody>
</table>
the convergence of explicitly correlated wave functions with respect to CI-like expansions at the $m$-hartree level is due to a better description of medium-range correlations [27]. In the CI framework it is mandatory to use a large number of states in order to achieve convergence for the energy and other properties, while more compact wave functions with a better convergence trend are obtained when the interelectronic distance is included. However, a major drawback of the explicitly correlated wave functions is the enormous technical difficulties involved in the calculation of the expectation values. This has lead to the development of approximate schemes as for example, the transcorrelated method [24] or the VMC used here. In general much greater numerical errors are obtained than in the more traditional methods of Quantum Chemistry as CI expansions. In Fig. 2, the difference intracule and extracule densities in momentum space as compared with those obtained from a MCHF wave function [13] are shown. As can be seen there are not appreciable differences between those two different calculations.

In Table 2, some two-body momentum properties obtained in this work are reported. For the sake of comparison we have also included the Hartree–Fock values and those calculated from a MCHF wave function. The electron–electron coalescence, $\langle h(0) \rangle$ and the electron–electron counterbalance, $d(0)$, densities as well the radial expectation values $\langle r^2 \rangle$, $\langle P^2 \rangle$ and $\langle \vec{p}_1 \cdot \vec{p}_2 \rangle$, and the angular correlation factor in momentum space, $\tau_\vec{p}$

Fig. 2. Difference function for the intracule (upper plot) and extracule (lower plot) radial densities in momentum space calculated from the explicitly correlated wave function of this work ($\Psi_{17}$) as compared with the MCHF results of [13].

<table>
<thead>
<tr>
<th></th>
<th>$\langle \rho^2 \rangle$</th>
<th>$\langle \rho_{12}^2 \rangle$</th>
<th>$\langle P^2 \rangle$</th>
<th>$\langle \vec{p}_1 \cdot \vec{p}_2 \rangle$</th>
<th>$\tau_\vec{p}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF$^a$</td>
<td>5.72336</td>
<td>5.72336</td>
<td>1.43084</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>MCHF$^b$</td>
<td>5.807215</td>
<td>5.48855</td>
<td>1.53147</td>
<td>0.15934</td>
<td>0.05487</td>
</tr>
<tr>
<td>$\Psi_{17}$</td>
<td>5.796(1)</td>
<td>5.483(1)</td>
<td>1.5274(4)</td>
<td>0.1568(4)</td>
<td>0.0541(1)</td>
</tr>
</tbody>
</table>

Table 2
Two-body momentum properties of the helium atom

<table>
<thead>
<tr>
<th></th>
<th>$\langle \rho^{*2} \rangle$</th>
<th>$\langle P^{-2} \rangle$</th>
<th>$\langle P^{-1} \rangle$</th>
<th>$\langle P \rangle$</th>
<th>$\langle P^3 \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF$^a$</td>
<td>0.0522763</td>
<td>0.811757</td>
<td>0.688027</td>
<td>2.05863</td>
<td>21.9</td>
</tr>
<tr>
<td>MCHF$^b$</td>
<td>0.0495798</td>
<td>0.795530</td>
<td>0.686667</td>
<td>2.02905</td>
<td>20.4</td>
</tr>
<tr>
<td>$\Psi_{17}$</td>
<td>0.04953(2)</td>
<td>0.795</td>
<td>0.687</td>
<td>2.027</td>
<td>20.3</td>
</tr>
</tbody>
</table>

In parentheses we give the statistical error in the last digit.

$^a$ Refs. [30,31].

$^b$ Ref. [13].
[28], are quantities directly obtained in the Monte Carlo run and are shown in the upper part of Table 2. Some other quantities such as the expectation values $\langle r^n \rangle$, $n = -2, -1, 1, \text{and } 3$ defined as

$$
\langle r^n \rangle = \int \mathcal{D} \hat{r} \, r^n \Gamma(T),
$$

where $(t, \Gamma)$ stand for $(\mathcal{p}_{12}, \mathcal{h}(\mathcal{p}_{12}))$ and $(P, \mathcal{d}(P))$ cannot be directly calculated in the Monte Carlo run and it is necessary to consider the asymptotic behavior of the corresponding momentum distribution in order to obtain approximate values for them [29]. The moments so-calculated are affected of some systematic errors which are not easily obtainable. But, as can be seen in Table 2 they compare quite well with those obtained from a MCHF wave function which uses a numerically more stable calculation. Despite the approximations used to calculate them, the values obtained for all those quantities allow to distinguish perfectly the effects of electronic correlations.

Recently it has been suggested [13] that the results obtained with the Monte Carlo algorithm from wave functions as that of the present work are inconsistent and insufficiently accurate. Therefore some comments on the quality of both the wave function and the results obtained by using the VMC are in order. The criticisms are mainly based upon two reasons: the virial theorem and the fulfillment of some sum rules. With respect to the former it is based on the assumption that the better a trial wavefunction satisfies the virial theorem the better the trial function is. Nevertheless this rule of thumb must be applied with care, because if it is used inconsistently it will lead to misleading conclusions as it is the case. In particular, the use of the accuracy on the virial theorem to compare different trial function is only valid when both, the wave functions are obtained within the same framework and the same numerical technique is used to compute the expectation values. Thus, if one approaches from the HF solution to the exact one through a MCHF set of solutions, each of them satisfies the virial theorem and therefore deviations from it only indicate numerical inaccuracy in the integrals. On the other hand, if one uses a basis set of Hylleraas-type wave functions it is known that the energy and the virial theorem improve as the dimension of the basis increases. In spite of that the accuracy in the virial theorem of extensive Hylleraas-tye expansions is below that provided by the HF solution [26]. As far as we know it has not been proved that the wave functions used here must satisfy the virial theorem. However, it is well known [32] that for atomic systems a simple scaling of the coordinates allows to verify exactly this theorem. We have checked this for our wave functions and no significant change, within the statistical errors, has been found in the energy. Finally, one has to take into account that the Monte Carlo method will provide the results with a statistical error that, with the statistics usually employed, is much greater than the numerical errors in a standard calculation of CI or MCHF-type when the same wave function is used. Clearly the lack of accuracy in the fulfillment of the virial theorem is not because of the wave function but it is completely due to the limitations inherent to any statistical method such as the Monte Carlo one. Consequently a criterion of quality based on the virial theorem when comparing calculations done by using wave functions of different type and/or performed in a completely different framework cannot be used.

The second argument used to evaluate the quality and consistency of the VMC results is based on the following sum rules [33]:

$$
\delta_{\text{pos}} = 4\langle R^2 \rangle + \langle r_{12}^2 \rangle - 2(N-1)\langle r^2 \rangle = 0, \quad (7)
$$

$$
\delta_{\text{mom}} = 4\langle P^2 \rangle + \langle p_{12}^2 \rangle - 2(N-1)\langle p^2 \rangle = 0, \quad (8)
$$

that must be fulfilled by any wave function in the domain of the Hamiltonian.

First, and because any wave function must satisfy these sum rules independently of the upper bound to the energy that provides, they are useless to assess the accuracy of any variational wave function. Nevertheless the sum rules could be of some interest when testing the precision of a given integration method but their utility depends strongly on the technique. For example, if one is using a scheme where some systematic errors are present, as for instance the Fermi hyper netted chain theory, the fulfillment of these and other sum rules such as the normalization condition will provide valuable information on the error in these
expectation values. However, in the case of the VMC method employed by us, the use of these sum rules to test the reliability of the results, unfortunately makes no sense. The reason lies in the nature of the Monte Carlo quadrature. In the VMC method a very large set of configurations distributed according to a given probability distribution function is generated. Then any given expectation value is evaluated by averaging on these configurations the corresponding local operator. On the other hand, the sum rules (7) and (8) are simply identities and hence they hold exactly, within the computer accuracy, for any of the configurations. Therefore they are verified exactly in any Monte Carlo calculation no matter if it is performed with ten or with ten millions of configurations. Notwithstanding this is not readily apparent in the final results due, exclusively, to the round off errors which appear when the results obtained in a given run must be rounded at some decimal place to be consistent with the statistical error in the Monte Carlo calculation. Then, the results of a MC calculation for the sum rules contribute nothing to elucidate either the quality of any wave function or the accuracy of a particular calculation. Finally, it is worth to stress that when comparing results obtained either in two different calculations or in the same one, it is crucial to take into account the statistical errors.

4. Conclusions

A systematic study of two-electron properties in both position and momentum spaces has been carried out for the atomic helium starting from accurate and compact explicitly correlated wave functions. The interelectronic and the center of mass distribution functions and some related properties such as their radial expectation values have been obtained. A comparison with the values calculated starting from an extensive CI wave function is performed. The Coulomb hole, related to the interelectronic density, has been compared with the results that can be considered as exact obtained form a very accurate Hylleraas-type wave function. The conclusion drawn is that the simple and compact wave function obtained in this work used along with the Monte Carlo methods provides very accurate two-body properties with a precision, in the numerical sense, enough to elucidate the effects of electronic correlations. The quality of the results is superior to that of the MCHF values of [13] that needs to include more configurations to describe accurately interelectronic properties, specially at intermediate electron–electron distances. Finally, a discussion of some criteria previously used in the literature to study the quality of a given wave function is carried out.

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