Wave functions and two-electron probability distributions of the Hooke's-law atom and helium

Darragh P. O'Neill and Peter M. W. Gill
School of Chemistry, University of Nottingham, Nottingham NG7 2RD, United Kingdom

(Received 3 April 2003; published 21 August 2003)

The Hooke's-law atom (hookium) provides an exactly soluble model for a two-electron atom in which the nuclear-electron Coulombic attraction has been replaced by a harmonic one. Starting from the known exact position-space wave function for the ground state of hookium, we present the momentum-space wave function. We also look at the intracules, two-electron probability distributions, for hookium in position, momentum, and phase space. These are compared with the Hartree-Fock results and the Coulomb holes (the difference between the exact and Hartree-Fock intracules) in position, momentum, and phase space are examined. We then compare these results with analogous results for the ground state of helium using a simple, explicitly correlated wave function.

DOI: 10.1103/PhysRevA.68.022505 PACS number(s): 31.25.Eb

I. INTRODUCTION

Contrary to the claims of most textbooks, systems with two electrons do not inevitably have intractable Schrödinger equations. This is exemplified by a curious ''atom'' wherein two electrons repel Coulombically but are bound to a nucleus by a harmonic potential and is governed by the Hamiltonian

$$\hat{H}=-\frac{1}{2}\nabla_1^2-\frac{1}{2}\nabla_1^2+\frac{1}{2}kr_1^2+\frac{1}{2}kr_2^2+\frac{1}{r_{12}}. \tag{1}$$

It was first considered 40 years ago by Kestner and Sinanoglu [1] but it was not until 1989 that Kais *et al.* discovered [2] that, if the harmonic force constant is $k=1/4$, its *exact* ground-state wave function can be written in closed form and the associated energy is $E=2$. Since then, interest in this unusual system has grown steadily [3–22] and its study has shed light on the behavior of strongly correlated electrons.

A consensus on a name for the atom has not yet been reached. It has been variously termed the Hooke's-law model, Hooke's atom, the Hookean atom, harmonium, and the harmonic quantum dot. However, in this paper, we will use the term ''hookium'' to refer specifically to the ($k=1/4,E=2$) system.

If the harmonic potential is replaced by a Coulombic one, the Hamiltonian becomes

$$\hat{H}=-\frac{1}{2}\nabla_1^2-\frac{1}{2}\nabla_1^2-\frac{2}{r_1}-\frac{2}{r_2}+\frac{1}{r_{12}}, \tag{2}$$

and hookium is transformed into helium. Unfortunately, no exact helium wave functions are known but a number of simple near-exact wave functions were developed by Hylleraas in the early days of quantum mechanics [23]. Although hookium and helium are quantitatively different—hookium being a more diffuse species, and the overlap of the two wave functions being ~ 0.6—meaningful qualitative comparisons can be made between the two.

We have recently commenced a systematic study of position, momentum, and phase-space two-electron probability distributions, intracules, of atoms and molecules. The position intracule $P(u)$, which gives the probability of finding two electrons separated by a distance u, is given by [24]

$$P(u)=\int\int\int|\Psi(\mathbf{r}_1,\mathbf{r}_2)|^2\delta(\mathbf{r_{12}}-\mathbf{u})d\mathbf{r}_1d\mathbf{r}_2d\Omega_{\mathbf{u}}, \tag{3}$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the positions of electrons 1 and 2, $\mathbf{r}_{12}=\mathbf{r}_1-\mathbf{r}_2$, and $\Omega_{\mathbf{u}}$ is the angular component of $\mathbf{u}$.

The momentum intracule $M(v)$, which gives the probability of finding two electrons moving with a relative momentum v, is given by [25]

$$M(v)=\int\int\int|\Phi(\mathbf{p}_1,\mathbf{p}_2)|^2\delta(\mathbf{p_{12}}-\mathbf{v})d\mathbf{p}_1d\mathbf{p}_2d\Omega_{\mathbf{v}}, \tag{4}$$

where $\Phi(\mathbf{p}_1,\mathbf{p}_2)$ is the momentum wave function, $\mathbf{p}_1$ and $\mathbf{p}_2$ are the momenta of electrons 1 and 2, $\mathbf{p}_{12}=\mathbf{p}_1-\mathbf{p}_2$, and $\Omega_{\mathbf{v}}$ is the angular component of $\mathbf{v}$.

Finally, the Wigner intracule $W(u,v)$ [26], which gives the quasiprobability of finding two electrons at a distance u and moving with relative momentum v, is given for a two-electron singlet by

$$W(u,v)=\frac{v^2}{2\pi^2}\int\int\int\Psi(\mathbf{r},\mathbf{r}+\mathbf{q}+\mathbf{u})\Psi(\mathbf{r}+\mathbf{q},\mathbf{r}+\mathbf{u})\times j_0(qv)d\mathbf{r}d\mathbf{q}d\Omega_{\mathbf{u}}, \tag{5}$$

where $j_0(x)$ is the zeroth-order spherical Bessel function [27].

In this paper, we present and discuss intracules for hookium and helium, using both (near-)exact and Hartree-Fock (HF) wave functions. Atomic units $h=m=c=1$ are used throughout and $1E_h=1$ hartree.

II. CORRELATED WAVE FUNCTIONS AND INTRACULES

A. Hookium

The normalized exact position wave function [4] for hookium is given by

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{2\sqrt{8\pi^{5/2}+5\pi^3}}\left(1+\frac{r_{12}}{2}\right)\exp\left(-\frac{r_1^2+r_2^2}{4}\right). \tag{6}$$

The position intracule derived from this [19] is given by

$$P(u)=\frac{1}{8+5\pi^{1/2}}u^2\left(1+\frac{u}{2}\right)^2\exp\left(-\frac{u^2}{4}\right). \tag{7}$$

To derive the analogous momentum intracule, the normalized momentum wave function for hookium, which is related to the position wave function via a Fourier transform, was determined and is given by

$$\Phi(\mathbf{p}_1,\mathbf{p}_2)=\frac{4\exp(-p_1^2-p_2^2)}{\sqrt{8\pi^{5/2}+5\pi^3}}\left[1+\sqrt{\frac{2}{\pi}}\exp\left(\frac{p_{12}^2}{2}\right)+\left(\frac{1}{p_{12}}-p_{12}\right)\text{erfi}\left(\frac{p_{12}}{\sqrt{2}}\right)\right], \tag{8}$$

where $\text{erfi}(z)=\text{erf}(iz)/i$ and $\text{erf}(z)$ is the error function [27]. The exact momentum intracule for hookium is thus

$$M(v)=\frac{8v^2}{8+5\sqrt{\pi}}\left[\sqrt{\frac{2}{\pi}}+\exp\left(-\frac{v^2}{2}\right)+\left(\frac{1}{v}-v\right)\exp\left(-\frac{v^2}{2}\right)\text{erfi}\left(\frac{v}{\sqrt{2}}\right)\right]^2. \tag{9}$$

We have not been able to obtain the Wigner intracule for hookium in closed form yet and must currently use quadrature [28] to approximate the single integral

$$W(u,v)=\frac{u^2v^2e^{-u^2/4}}{\pi(8+5\sqrt{\pi})}\int_0^\infty q^2e^{-q^2/4}j_0(qv)f(q,u)dq, \tag{10}$$

where

$$f(q,u)=\begin{cases} 2+2u+\dfrac{2q^2}{3u}+\dfrac{u^2-q^2}{4}+\dfrac{(q^2+u^2)^2}{4qu}\arctan\left(\dfrac{q}{u}\right) & (q\leqslant u)\\ 2+2q+\dfrac{2u^2}{3q}+\dfrac{q^2-u^2}{4}+\dfrac{(q^2+u^2)^2}{4qu}\arctan\left(\dfrac{u}{q}\right) & (q>u). \end{cases} \tag{11}$$

B. Helium

The near-exact wave function we have chosen is that of Hylleraas [23] and is given by

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=\frac{4\alpha^4}{\pi\sqrt{16\alpha^2+70\alpha c+96c^2}}(1+cr_{12})e^{-\alpha(r_1+r_2)}, \tag{12}$$

where c and α are such that they minimize the energy. The position intracule is then given by

$$P(u)=\frac{4\alpha^5u^2(1+cu)^2(3+6u\alpha+4u^2\alpha^2)}{3(8\alpha^2+35\alpha c+48c^2)}e^{-2\alpha u}. \tag{13}$$

The momentum wave function proves to be too difficult to derive so to obtain the momentum and Wigner intracules, we expand the position wave function using a set of Gaussians to represent the Slater functions

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=M(1+cr_{12})\sum_{i=1}^{n}a_i\phi_i(\zeta_i,\mathbf{r}_1)\sum_{j=1}^{n}a_j\phi_j(\zeta_j,\mathbf{r}_2), \tag{14}$$

where the $\phi_i(\mathbf{r})$ are Gaussian functions with contraction coefficients a_i and exponents ζ_i, and M is a normalization constant. Using this expansion, the Wigner intracule can be reduced to a one-dimensional integral, analogous to that of hookium, and the momentum intracule is then calculated from this by integrating over u using 50-point Euler-Maclaurin [29] quadrature.

An energy of $-2.891\,121E_h$ is achieved using $c=0.365\,796$ and $\alpha=1.849\,685$. Using an appropriately scaled expansion of six Gaussians (STO-6G) in Eq. (14) yields an energy of $-2.889\,978E_h$.

III. HARTREE-FOCK WAVE FUNCTIONS AND INTRACULES

A. Hookium

Whereas the exact wave function of hookium (6) is known in closed form, the corresponding HF wave function is known only from numerical calculation. The normalized HF orbital $\psi(r)$ satisfies the integrodifferential equation

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}-\frac{1}{r}\frac{d}{dr}+\frac{r^2}{8}+\frac{1}{r}\int_0^r 4\pi x^2\Psi^2(x)dx+\int_r^\infty 4\pi x\Psi^2(x)dx\right]\Psi(r)=\epsilon\Psi(r), \tag{15}$$

and the HF energy is $E_{\text{HF}}=E_1+E_2$, where

$$E_1=2\int\psi(r)\left[-\frac{1}{2}\frac{d^2}{dr^2}-\frac{1}{r}\frac{d}{dr}+\frac{r^2}{8}\right]\psi(r)d\mathbf{r}, \tag{16}$$

$$E_2=\int\int\psi^2(r_1)\frac{1}{r_{12}}\psi^2(r_2)d\mathbf{r}_1d\mathbf{r}_2. \tag{17}$$

It is difficult to solve Eq. (15) directly but, if we expand $\psi(r)$ in an orthonormal basis,

TABLE I. Convergence of the Hartree-Fock energy with Hermite basis set size.

N	$E(N)$	$E(N)-E(N-1)$	c_2	c_3	c_4	c_5
1	2.06418958					
2	2.03878780	−0.02540178	0.10994405			
3	2.03845337	−0.00033443	0.10833978	−0.00951451		
4	2.03843949	−0.00001388	0.10825043	−0.00940132	0.00157574	
5	2.03843889	−0.00000061	0.10824442	−0.00939263	0.00156292	−0.000284251
6	2.03843887	−0.00000001	0.10824412	−0.00939209	0.00156212	−0.000283023
7	2.03843887	−0.00000000	0.10824414	−0.00939212	0.00156212	−0.000283102

$$\psi(r) \approx \psi_N(r) = \sum_{k=1}^{N} c_k \phi_k(r), \tag{18}$$

and choose the appropriate basis functions, then all of the required integrals can be evaluated in closed form. We choose the basis functions to be the harmonic-oscillator eigenfunctions

$$\phi_k(r) = \frac{H_{2k-1}(r/\sqrt{2})}{2^k \sqrt{(2k-1)!}\, r/\sqrt{2}} \frac{\exp(-r^2/4)}{(2\pi)^{3/4}} \tag{19}$$

(where H_k is the kth Hermite polynomial) and the expansion converges very rapidly, as Table I shows. We observe that the expansion coefficients c_k decay roughly exponentially. Our limiting energy ($2.038\,438\,87E_h$) is significantly lower than that reported by Kais *et al.* [4] ($2.039325E_h$) but the reason for this discrepancy is not clear [30]. Using an expansion of eight Gaussian basis functions [31] an energy of $2.038\,439\,0E_h$ can be achieved. This is slightly lower than the energy of $2.038\,51E_h$ achieved by Amovilli *et al.* [22] using ten Gaussians.

By subtracting our lowest HF energy from the exact energy ($E=2$), we deduce that the exact correlation energy of hookium is $-38.438\,873\,3\mathrm{m}E_h$. This is a little smaller than the correlation energy of helium ($-42.044\mathrm{m}E_h$) and supports the assertion by Kestner and Sinanoglu that the correlation energies of two-electron systems are remarkably insensitive to the nature or magnitude of the external field [1].

Although it is straightforward to calculate the position and momentum intracules using the basis set in Eq. (19), the Wigner intracule proves more difficult. For this reason, we use the eight-Gaussian basis set mentioned above to calculate all of the intracules. The quality of this Gaussian basis set is such that we do not see any differences in the intracules derived from it as compared to those derived using the Hermite basis set.

B. Helium

We expand the HF wave function for helium as a linear combination of ten s-type Gaussians. In particular, the exponents are taken from the s functions used in Dunning's correlation consistent polarized valence sextuple zeta (cc-pV6Z) basis set [32] for helium, uncontracting the contracted basis function. This basis yields an energy of $-2.861\,673E_h$, almost reaching the HF limit ($-2.861\,68E_h$). Subtracting this from the energy resulting from the near-exact wave function gives a correlation energy of $29.45\mathrm{m}E_h$, which is 70% of the true correlation energy for helium.

IV. EFFECT OF CORRELATION ON THE INTRACULES

To examine the effect that the inclusion of electron correlation has on the intracules for hookium and helium, each of the position, momentum, and Wigner intracules will be examined for both the (near-)exact and HF cases and also the Coulomb hole [33], ΔZ, where

$$\Delta Z = Z_{Exact} - Z_{HF}, \tag{20}$$

where Z is $P(u)$, $M(v)$, or $W(u,v)$.

A. Hookium

1. Position intracule

Figure 1(a) shows the exact position intracule for hookium. At $u=0$ the intracule vanishes, indicating that there is no probability of finding the two electrons at the same point in space. Near the origin it grows quadratically

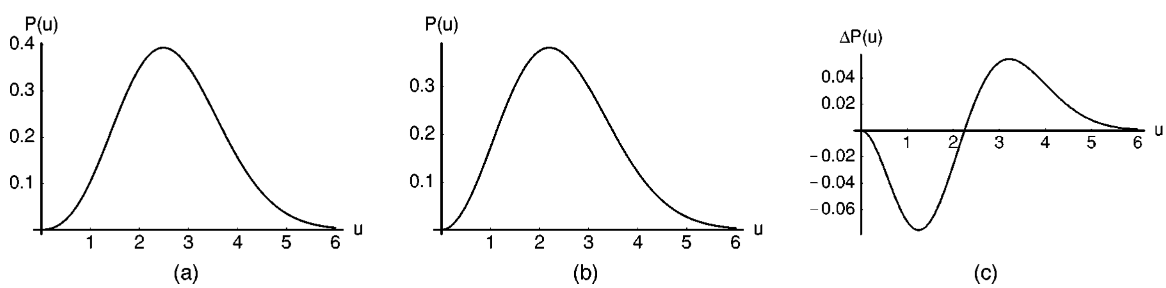

FIG. 1. The exact and HF position intracules and the corresponding Coulomb hole for hookium.

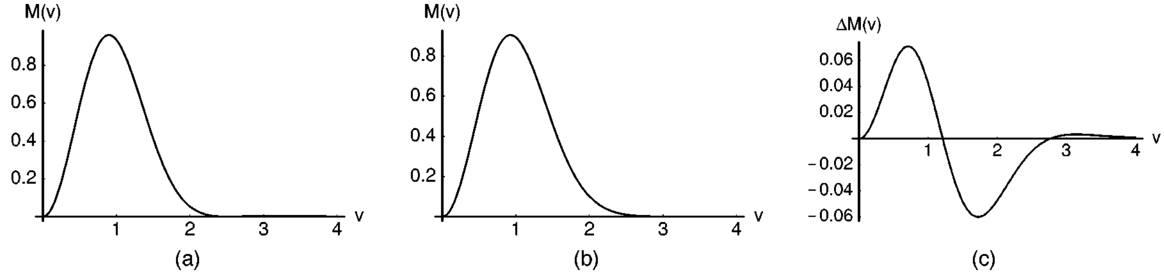

FIG. 2. The exact and HF momentum intracules and the corresponding Coulomb hole for hookium.

and reaches a maximum at $u \approx 2.494$ and then decays away as u increases. Figure 1(b) shows the corresponding HF intracule. Again, it vanishes at the origin and grows to a maximum, this time at $u \approx 2.204$, before decaying away. As expected, the effect of correlation is to keep the two electrons further apart, and this is clearly shown in the Coulomb hole in Fig. 1(c). The radius of the Coulomb hole, as defined by Coulson and Nielson [33], for hookium is ≈ 2.25.

2. Momentum intracule

Figure 2(a) shows the exact momentum intracule for hookium. Like the position intracule, it vanishes at the origin indicating that there is no probability of finding the two electrons with zero relative momentum. It then grows quadratically to a maximum at $v \approx 0.897$ followed by a rapid decay back to zero at $v \approx 2.506$, indicating that there is no probability of the two electrons having this relative momentum. Another much smaller maximum then occurs at $v \approx 3.086$. Figure 2(b) shows the HF momentum intracule. Again, it vanishes at the origin and grows to maximum at $v \approx 0.926$, before decaying away. The second peak does not appear on the HF intracule indicating that correlation also favors electrons moving with high relative momentum. Figure 2(c) shows the Coulomb hole for hookium in momentum space. It is considerably more complex than its position-space counterpart, with correlation favoring both lower and higher relative momenta.

3. Wigner intracule

Figure 3(a) shows the exact Wigner intracule for hookium. The intracule vanishes along the axes $u=0$ and $v=0$ indicating that there is no probability of finding two electrons at the same point in either position or momentum space. From the origin it grows quadratically in both u and v and reaches a maximum at $(u,v) \approx (2.378, 0.899)$. We also note the presence of a shallow negative region at $(u,v) \approx (1.109, 2.048)$. Whereas the position and momentum intracules are everywhere positive, this is not the case for the Wigner intracule which reflects its interpretation as a quasiprobability. Figure 3(b) shows the HF Wigner intracule. Again, it vanishes at the origin and along the axes, and it grows to a maximum at $(u,v) \approx (2.187, 0.923)$. The negative region present in the exact intracule is no longer present. Figure 3(c) shows the Coulomb hole in phase space. It combines the results of the two previous sections and shows that, in hookium, correlation favors a larger interelectronic separation and lower relative momentum and to a much lesser extent higher relative momentum.

B. Helium

1. Position intracule

Figure 4(a) shows the near-exact position intracule for helium. At $u=0$ the intracule vanishes, indicating that there is no probability of finding the two electrons at the same point in space. Near the origin it grows quadratically and reaches a maximum at $u \approx 1.0765$ and then decays away as u increases. Figure 4(b) shows the corresponding HF intracule. Again, it vanishes at the origin and grows to a maximum, this time at $u \approx 0.995$, before decaying away. As expected, the effect of correlation is to keep the two electrons further apart, and this is clearly shown in the Coulomb hole in Fig.

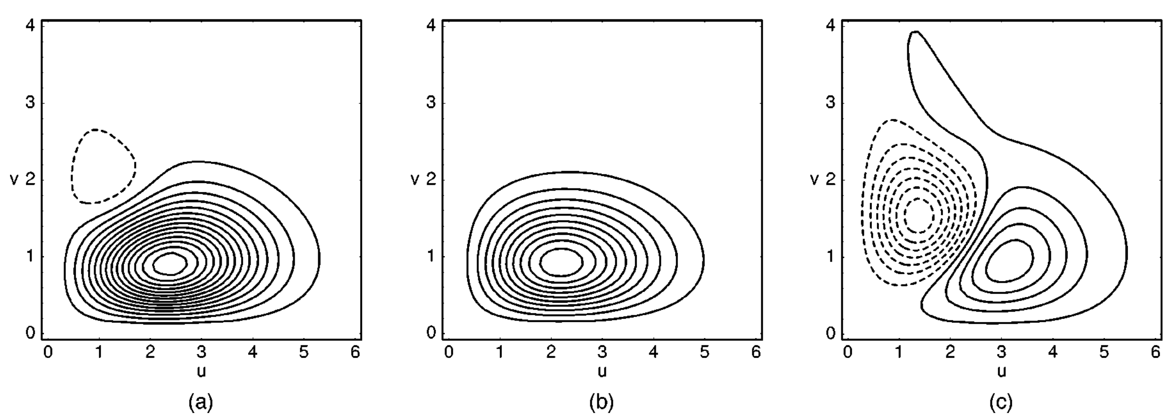

FIG. 3. The exact and HF Wigner intracules and the corresponding Coulomb hole for hookium.

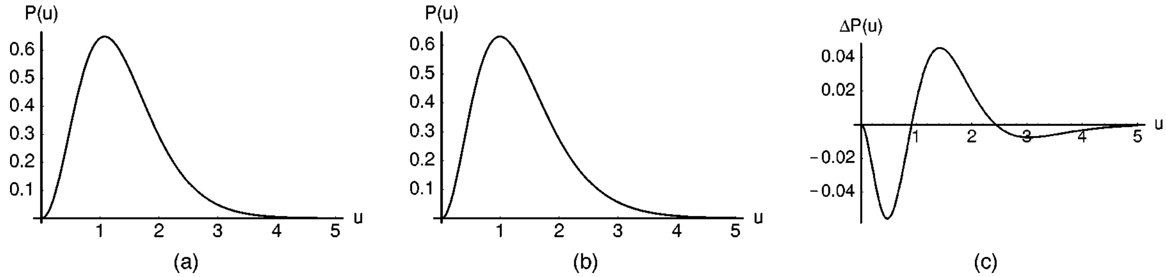

FIG. 4. The near-exact and HF position intracules and the corresponding Coulomb hole for helium.

4(c). The radius of the Coulomb hole for helium is ≈ 0.95. This is significantly less than 1.1 quoted by Coulson and Nielson and we attribute this difference to the inferior quality of our correlated wave function. We also note the presence of a second node in the Coulomb hole and again believe that this is due to our choice of wave function rather than having physical significance. Comparing these results with those of hookium, we see qualitatively the same features but quantitatively hookium's Coulomb hole is much larger reflecting its diffuseness relative to helium.

2. Momentum intracule

Figure 5(a) shows the near-exact momentum intracule for helium. Like the position intracule, it vanishes at the origin indicating that there is no probability of finding the two electrons with zero relative momentum. It then grows quadratically to a maximum at $v \approx 1.498$ and decays away with v. Figure 5(b) shows the HF momentum intracule. Again, it vanishes at the origin and grows to maximum at $v \approx 1.447$, before decaying away. The shifting of this maximum shows that correlation favors electrons moving with lower relative momentum. Figure 5(c) shows the Coulomb hole for helium in momentum space. It is considerably more complex than its position-space counterpart, with correlation disfavoring both lower and higher relative momenta. The Coulomb hole in momentum space has been studied previously [34–38] using configuration interaction, multiconfiguration Hartree-Fock and explicitly correlated position wave functions to derive the correlated intracule. We are not aware of any studies using a wave function linear in r_{12}. Comparing our results with those of Gálvez *et al.* [37], we obtain qualitatively the same result although quantitatively the magnitude of our peaks are too large. Again this reflects the relatively poor quality of our choice of wave function.

The Coulomb hole for helium is very different to that of hookium. Whereas in helium (and the hydride ion [34]) correlation disfavors both low and high relative momenta, in hookium the opposite is true. The physical significance for this is not clear, though it does reflect the fact that although hookium is often used as a model for helium in some respects they are very different.

3. Wigner intracule

Figure 6(a) shows the near-exact Wigner intracule for helium. The intracule vanishes at the origin and along the axes $u=0$ and $v=0$ indicating that there is no probability of finding two electrons with either or both the same position in space and zero relative momentum. From the origin it grows quadratically in both u and v and reaches a maximum at $(u,v) \approx (1.170,1.589)$. Figure 6(b) shows the HF Wigner intracule. Again, it vanishes at the origin and along the axes and it grows to a maximum at $(u,v) \approx (1.316,1.589)$. Figure 6(c) shows the Coulomb hole in phase space. It combines the results of the two previous sections and shows that, in helium, correlation favors a larger interelectronic separation and lower relative momentum.

V. CONCLUSIONS

Although there has been interest in the position-space properties of hookium over the last four decades, its momentum-space properties have not been considered. Here, we have presented the momentum-space wave function, the corresponding momentum intracule, and also the Wigner intracule for hookium. The momentum intracule exhibits two maxima and a value $v \approx 2.506$ of the relative momentum p_{12} that can never occur. We have not observed such nodes in $M(v)$ before. The Wigner intracule allows us to look at the position- and momentum-space properties of hookium simultaneously.

The position- and momentum-space properties of helium

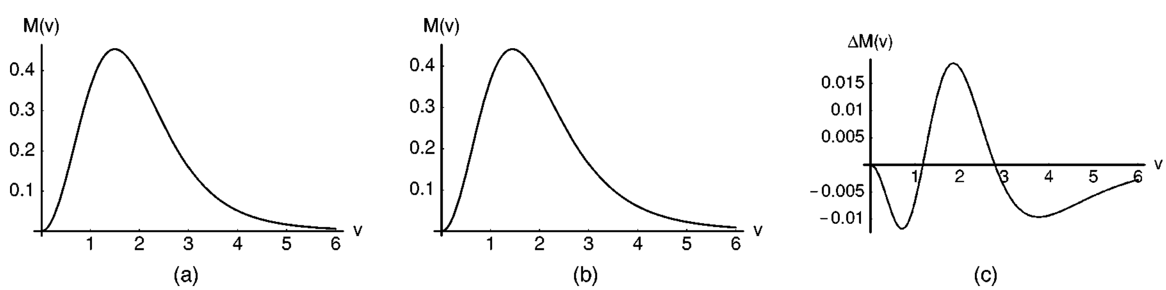

FIG. 5. The near-exact and HF momentum intracules and the corresponding Coulomb hole for helium.

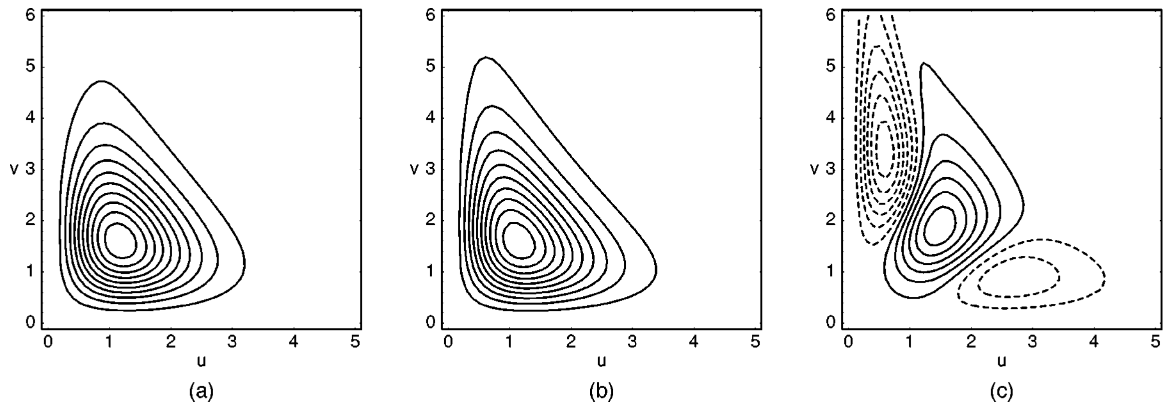

FIG. 6. The near-exact and HF Wigner intracules and the corresponding Coulomb hole for helium.

have been studied extensively. In this paper, we use a simple explicitly correlated wave function, which is linear in r_{12} to look at the effects of correlation in helium. Qualitatively, we reproduce the results of previous work, such as Coulson and Nielson, and Gálvez *et al.*, although quantitatively our results are not as accurate. These could be improved by the use of a more sophisticated wave function. By expanding the Slater functions in our wave function in terms of Gaussians, we were able to look at the momentum intracule for a wave function which depended explicitly on r_{12}, and this approach could easily be extended to more accurate wave functions.

In both hookium and helium, the effect of correlation is to keep the electrons further apart. They differ, however, in the effect that correlation has on their momentum distributions. Correlation favors lower relative momentum and, to a much lesser extent, higher relative momentum in hookium, whereas the analogous Coulomb hole in helium shows the opposite preferences, disfavoring both lower and higher relative momentum. Looking at the Coulomb hole in phase space again shows us both the similarities and differences between hookium and helium.

ACKNOWLEDGMENTS

This research was partly supported by the Engineering and Physical Sciences Research Council (Grant No. GR/R81121) to D.P.O. We would also like to thank EPSRC for JREI funding for computer resources.

[1] N.R. Kestner and O. Sinanoglu, Phys. Rev. **128**, 2687 (1962).
[2] S. Kais, D.R. Herschbach, and R.D. Levine, J. Chem. Phys. **91**, 7791 (1989).
[3] U. Merkt, J. Huser, and M. Wagner, Phys. Rev. B **43**, 7320 (1991).
[4] S. Kais, D.R. Herschbach, N.C. Handy, C.W. Murray, and G.J. Laming, J. Chem. Phys. **99**, 417 (1993).
[5] M. Taut, Phys. Rev. A **48**, 3561 (1993).
[6] M. Taut, J. Phys. A **27**, 1045 (1994).
[7] C. Filippi, C.J. Umrigar, and M. Taut, J. Chem. Phys. **100**, 1290 (1994).
[8] H.F. King, Theor. Chim. Acta **94**, 345 (1996).
[9] C.J. Huang and C.J. Umrigar, Phys. Rev. A **56**, 290 (1997).
[10] M. Taut, A. Ernst, and H. Eschrig, J. Phys. B **31**, 2689 (1998).
[11] Z. Qian and V. Sahni, Phys. Rev. A **57**, 2527 (1998).
[12] N.H. March, T. Gál, and Á. Nagy, Chem. Phys. Lett. **292**, 384 (1998).
[13] P. Ziesche, V.H. Smith, Jr., M. Hô, S.P. Rudin, P. Gersdorf, and M. Taut, J. Chem. Phys. **110**, 6135 (1999).
[14] K. Ivanov, K. Burke, and M. Levy, J. Chem. Phys. **110**, 10262 (1999).
[15] P. Hessler, J. Park, and K. Burke, Phys. Rev. Lett. **82**, 378 (1999).
[16] N.H. March, C. Amovilli, and D.J. Klein, Chem. Phys. Lett. **325**, 645 (2000).
[17] J. Cioslowski and K. Pernal, J. Chem. Phys. **113**, 8434 (2000).
[18] A. Artemyev, E.V. Ludena, and V. Karasiev, J. Mol. Struct.: THEOCHEM **580**, 47 (2002).
[19] E. Romera, J. Phys. B **35**, L309 (2002).
[20] R.J. White and W. Byers Brown, J. Chem. Phys. **53**, 3869 (1970).
[21] J.M. Benson and W. Byers Brown, J. Chem. Phys. **53**, 3880 (1970).
[22] C. Amovilli and N.H. March, Phys. Rev. A **67**, 022509 (2003).
[23] E.A. Hylleraas, Z. Phys. **54**, 347 (1929).
[24] P.M.W. Gill, A.M. Lee, N. Nair, and R.D. Adamson, J. Mol. Struct.: THEOCHEM **506**, 303 (2000).
[25] N.A. Besley, A.M. Lee, and P.M.W. Gill, Mol. Phys. **100**, 1763 (2002).
[26] P.M.W. Gill, D.P. O'Neill, and N.A. Besley, Theor. Chem. Acc. **109**, 241 (2003).
[27] *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (Dover, New York, 1965).
[28] http://www.netlib.org/quadpack/
[29] C.W. Murray, N.C. Handy, and G.W. Laming, Mol. Phys. **78**, 997 (1993).
[30] N.C. Handy (private communication).
[31] The exponents used were 0.0375, 0.0750, 0.23185, 0.30241, 0.37297, 0.6000, 1.2000, 2.4000.

[32] K.A. Peterson, W.D.E., and T.H. Dunning, J. Chem. Phys. **100**, 7410 (1994).
[33] C.A. Coulson and A.H. Neilson, Proc. Phys. Soc. London **78**, 831 (1961).
[34] K.E. Banyard and C.E. Reed, J. Phys. B **11**, 2957 (1978).
[35] F. Arias de Saavedra, E. Buendía, and F.J. Gálvez, Z. Phys. D: At., Mol. Clusters **38**, 25 (1996).
[36] A. Sarsa, F.J. Gálvez, and E. Buendía, J. Chem. Phys. **110**, 5721 (1999).
[37] F.J. Gálvez, E. Buendía, and A. Sarsa, Chem. Phys. Lett. **370**, 327 (2003).
[38] T. Koga, Chem. Phys. Lett. **350**, 135 (2001).