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INVITED ARTICLE

Can correlation bring electrons closer together?

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We discuss the exact Coulomb hole for the ground state of the helium atom and helium-like ions. We find that the correlated wavefunction yields a smaller probability of finding the electrons at large separations than does the Hartree–Fock wavefunction, leading to the counterintuitive conclusion that correlation brings distant electrons closer together. This effect becomes less pronounced as the nuclear charge increases.

Keywords: Coulomb hole; intracule; electron correlation; helium atom

1. Introduction

Coulomb's Law states that particles of the same charge repel and opposites attract. In atoms and molecules, this causes the electrons to try to be close to the nuclei while remaining far from each other. This gives rise to the phenomenon of electron correlation and its exact mathematical description requires that the manyelectron Schrödinger equation [1] be solved. This has not been accomplished exactly—even for the helium atom—but there exist a variety of approximations that have yielded valuable insight into electron correlation and its effects.

The antisymmetry of an electronic wavefunction ensures that same-spin electrons are kept apart and creates the Fermi hole, a region around each electron wherein another electron of the same spin is unlikely to be found. For electrons of opposite spin, antisymmetry has no effect but Coulomb repulsion creates a similar, though smaller, 'exclusion zone' around each electron and this is intimately associated with the correlation phenomenon, as first discussed by Coulson and Neilson [2].

The singlet ground state of the helium atom is a relatively simple correlated system and the probability density of finding its two electrons at a separation $u = |\mathbf{r}_1 - \mathbf{r}_2|$ is given by the exact position intracule

$$P(u) = \langle \Psi | \delta(r_{12} - u) | \Psi \rangle, \tag{1}$$

where $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ is the exact wavefunction.

In the Hartree–Fock (HF) approximation, each electron moves in the *mean* field generated by the

other electron, and their motions are therefore statistically independent and uncorrelated. This generates the HF position intracule

$$P^{\rm HF}(u) = \langle \Psi^{\rm HF} | \delta(r_{12} - u) | \Psi^{\rm HF} \rangle, \qquad (2)$$

where $\Psi^{\text{HF}}(\mathbf{r}_1, \mathbf{r}_2)$ is the HF wavefunction and the difference,

$$\Delta P(u) = P(u) - P^{\rm HF}(u), \qquad (3)$$

is known as the Coulomb hole.

Coulson and Nielson showed [2] that correlation decreases the likelihood of finding the electrons close together and increases the probability of their being far apart. As a consequence, the hole is negative for small u and positive for larger u, a pattern that has subsequently been observed in a wide range of systems [3]. To quantify this, one may seek the critical points of the hole and, in particular, we define \check{u}_1 , \bar{u}_1 and \hat{u}_1 to be the minimum, the root and the maximum of the hole. Because each intracule is normalized, i.e.

$$\int_0^\infty P(u)\mathrm{d}u = \int_0^\infty P^{\mathrm{HF}}(u)\mathrm{d}u = 1, \qquad (4)$$

the hole has no net content but we can define its strength as

$$S_1 = Z \int_0^{\bar{u}_1} |\Delta P(u)| \,\mathrm{d}u, \tag{5}$$

where Z is the nuclear charge.

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There have, however, been occasional reports of Coulomb holes (in the helium atom and other systems) with somewhat richer behaviour [4–8]. Although these calculations agree that $\Delta P(u)$ is negative for small uand positive for larger u, they predict that there is a second root \bar{u}_2 and a second minimum at \check{u}_2 , giving a secondary hole whose strength we will define as

$$S_2 = Z \int_{\bar{u}_2}^{\infty} |\Delta P(u)| \,\mathrm{d}u. \tag{6}$$

The existence of a secondary hole would imply that correlation *reduces* the probability that electrons will be found at large separations $(u > \bar{u}_2)$ but this prediction is sufficiently counterintuitive that secondary holes have usually been dismissed as artefacts arising from inaccurate estimates of P(u) or $P^{\text{HF}}(u)$.

In this paper, we use highly accurate calculations to hunt for secondary holes in helium-like ions and to attempt to find the definitive answer to the question: *Does correlation ever draw electrons closer together?* Atomic units are used throughout.

2. Correlated wavefunction and intracule

Some of the most accurate wavefunctions available for the helium atom are of the explicitly correlated form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = e^{-\zeta(r_1 + r_2)} \sum_{i=1}^N c_i (r_1 + r_2)^{l_i} (r_1 - r_2)^{2m_i} u^{n_i}, \quad (7)$$

pioneered by Hylleraas [9] in the early days of quantum mechanics. The exponents l_i , m_i , and n_i are nonnegative integers and, along with the nonlinear parameter ζ and the linear parameters c_i , these are optimized using the Variation Theorem. The wavefunction that we have used has N=204 and was developed by Koga *et al.* [10], who showed that it reproduces the exact ground-state energy of the helium atom [11] to within 3 nanohartrees.

The intracule of the 204-term Hylleraas wavefunction (7) reduces [12] to

$$P(u) = 4\pi u^2 \exp\left(-2\zeta u\right) \sum_{i=0}^{30} d_i u^i,$$
(8)

and Koga *et al.* have tabulated the coefficients d_i . By comparing this intracule with the analogous one from an N = 168 term Hylleraas wavefunction, Koga found that

$$\left(\int_0^\infty [P_{204}(u) - P_{168}(u)]^2 \,\mathrm{d}u\right)^{1/2} < 10^{-6}, \qquad (9)$$

which we interpret as an estimate of the maximum error in the N=204 intracule. Koga also showed

subsequently that $P_{204}(u)$ is almost identical to those derived from even more accurate wavefunctions [13].

3. Hartree-Fock wavefunction and intracule

Given the accurate exact intracule (8), the next step is to construct a comparably accurate exact HF intracule $P^{HF}(u)$. To achieve this, we have used the Q-CHEM package [14] to calculate the intracule from the HF wavefunction of the helium atom using a series of even-tempered basis sets devised by Schmidt and Ruedenberg [15]. These basis sets employ Gaussian primitives with exponents

$$\zeta_k = \alpha \beta^k, \quad k = 1, 2, \dots, K, \tag{10}$$

where

$$\ln \alpha = a \ln(\beta - 1) + a', \tag{11}$$

$$\ln \ln \beta = b \ln K + b', \tag{12}$$

and, having adopted the Schmidt–Ruedenberg values for *a*, *a'*, *b* and *b'*, one needs then only to choose *K*. We have explored basis sets with up to K = 60 primitives and the largest of these reproduces the exact HF energy of the helium atom [16] to within 4 nanohartrees.

It is straightforward to construct the HF intracule from our even-tempered HF wavefunctions and, by comparing the K=60 and K=50 intracules, we find that

$$\max_{u>0} |P_{60}^{\rm HF}(u) - P_{50}^{\rm HF}(u)| = 3.5 \times 10^{-6}, \qquad (13)$$

which we interpret as an estimate of the maximum error in the K = 60 intracule.

4. Coulomb holes

4.1. Helium atom

Figure 1 shows the Coulomb hole (3) derived from the 204-term Hylleraas wavefunction (7) and our 60-term HF wavefunction. Its gross features (a minimum at $\tilde{u}_1 = 0.52$, a root at $\bar{u}_1 = 1.1$ and a maximum at $\hat{u}_1 = 1.6$) are similar to those reported by Coulson and Neilson [2] but, in addition, we confirm the existence of a second root at $\bar{u}_2 = 3.6$ and a second minimum at $\tilde{u}_2 = 4.1$ which is clearer in the magnified inset plot. Evidently, we should speak of two holes, the primary associated with the decrease in probability of finding the electrons close together, and the secondary with the decrease in probability of finding the electrons far apart.

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Figure 1. The Coulomb hole in the ground-state helium atom. The inset plot compares this hole (solid line) with one computed using a [7s6p5d] basis set (dashed line).



Figure 2. Approximate Coulomb holes in the helium atom calculated from an accurate correlated wavefunction and approximate HF wavefunctions employing bases of four $(-\cdot-\cdot-)$, five $(\cdot\cdot\cdot\cdot\cdot)$, six (---), seven (--), and 60 (---) *s*-type Gaussians.

The existence of the secondary hole deepens our understanding of the effects of correlation. The simple picture in which correlation acts to push electrons slightly further apart than in the mean-field description is found to be incomplete and, although correlation does reduce P(u) for small u and increase it for moderate u, it also reduces it slightly for large u.

Because the secondary hole is small, it has either been missed in previous studies [2] or has been dismissed as a finite-basis artefact [4–8] that will disappear as the basis set approaches completeness. In contradiction of this expectation, Figure 2 (which uses the same scale as the inset plot of Figure 1) shows that the secondary hole *emerges* as the quality of the Schmidt–Ruedenberg basis for the HF calculation is improved and, indeed, does not appear until at least six Gaussians are used. We are obliged to conclude that the presence of the secondary hole is the signature of a good basis, not a poor one.



Figure 3. Approximate Coulomb holes in the helium atom calculated from an accurate HF wavefunction and the MP2/6-31G (\cdots), MP2/6-311G (- – –), MP2/6-311G(d, p) (- –), and exact (-) correlated wavefunctions.



Figure 4. Coulomb holes in the ground-state helium-like ions.

We have also explored the extent to which the secondary hole is affected by imperfections in the correlation treatment underlying the exact P(u). Figure 3 shows that, if the exact intracule P(u) is approximated by various small-basis MP2 intracules, the secondary hole is significantly overestimated. This suggests that a reliable description of the secondary hole requires a *balanced* treatment of the exact and HF intracules.

This is supported by the inset plot of Figure 1, which compares the exact secondary hole with that derived from HF and Full Configuration Interaction (FCI) calculations using a [7s6p5d] basis set [17]. Although the FCI/[7s6p5d] treatment is modest in comparison with the Hylleraas one, and a treatment using only seven *s*-type Gaussians fails to reach the HF limit, the fact that they use the same basis set yields a secondary hole that agrees surprisingly well with the exact one.

Ion	Ζ	Z ŭ $_1$	$Z \bar{u}_1$	$Z\hat{\mathfrak{u}}_1$	$Z\bar{u}_2$	Z ŭ $_2$	S_1	S_2
He	2	1.05	2.15	3.26	7.17	8.17	0.0924	0.00122
Li ⁺	3	0.98	1.99	3.02	6.64	7.55	0.0898	0.00106
Be^{2+}	4	0.94	1.92	2.92	6.45	7.31	0.0889	0.00094
B^{3+}	5	0.92	1.88	2.86	6.35	7.19	0.0884	0.00086
Ne ⁸⁺	10	0.89	1.81	2.75	6.18	6.97	0.0875	0.00071

Table 1. Scaled minima, roots and maxima, and strengths, of the Coulomb holes in the helium-like ions.

4.2. Helium-like ions

Is the secondary Coulomb hole peculiar to the helium atom? To answer this, we have explored the effect of varying the nuclear charge from its value (Z=2) in the helium atom. The Coulomb holes of the resulting helium-like ions were constructed in the same way as that of helium, using Hylleraas wavefunctions from Koga *et al.* [10] and HF wavefunctions with eventempered Schmidt-Ruedenberg basis sets (10). Like Cioslowski and Liu [18], we found that it is hard to obtain satisfactorily converged results for the hydride ion H⁻ and we therefore excluded it from our study.

Figure 4 shows the Coulomb holes for He, Li⁺, Be^{2+} , B^{3+} , and Ne^{8+} . As Z increases, the electrons are drawn closer to the nucleus and their intracules and Coulomb holes contract toward the origin. The inset plot magnifies the region $6 \le Zu \le 14$ and, in this scaled representation, the secondary holes are similar.

Table 1 lists the minima, roots, maxima and strengths of the Coulomb holes in the helium-like ions. As Z increases, the holes contract and the locations of the minima, roots and maxima scale as $O(Z^{-1})$. The strengths of the primary and secondary holes decrease monotonically but, whereas S_1 appears to approach a non-zero limit, S_2 decays more rapidly and may vanish completely in the $Z = \infty$ limit. This question could be addressed through 1/Z perturbation theory.

5. Concluding remarks

We have calculated the Coulomb hole in the helium atom and several helium-like ions using a 204-term Hylleraas wavefunction and a [60s] HF wavefunction. These Coulomb holes, which are among the most accurate published to date, exhibit a primary hole at small u and a secondary hole at larger u. The existence of the latter reveals that electron correlation reduces the probability that the two electrons will be found at large separations, thus contradicting the naïve idea that correlation always acts to increase interelectronic separation. We have also demonstrated that, as the nuclear charge Z increases, the secondary hole diminishes.

It is possible that additional holes may exist at even larger values of *u*. However, to investigate this possibility with confidence, one would need to employ even more accurate exact and HF wavefunctions than those used in the present study.

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