

A simultaneous probability density for the intracule and extracule coordinates

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We introduce the intex density $X(R,u)$, which combines both the intracule and extracule coordinates to yield a simultaneous probability density for the position of the center-of-mass radius (R) and relative separation (u) of electron pairs. One of the principle applications of the intex density is to investigate the origin of the recently observed secondary Coulomb hole. The Hartree–Fock (HF) intex densities for the helium atom and heliumlike ions are symmetric functions that may be used to prove the isomorphism $2I(2R)=E(R)$, where $I(u)$ is the intracule density and $E(R)$ is the extracule density. This is not true of the densities that we have constructed from explicitly correlated wave functions. The difference between these asymmetric functions and their symmetric HF counterparts produces a topologically rich intex correlation hole. From the intex hole distributions ($X^{\text{exact}}(R,u)-X^{\text{HF}}(R,u)$), we conclude that the probability of observing an electron pair with a very large interelectronic separation increases with the inclusion of correlation *only* when their center-of-mass radius is close to half of their separation. © 2010 American Institute of Physics. [doi:10.1063/1.3499316]

I. INTRODUCTION

In any chemical system having more than a single electron the motions of the electrons are correlated in such a way that they naturally avoid one another. The accurate nonrelativistic mathematical description of this phenomenon requires one to solve the many-electron Schrödinger equation,¹ but unfortunately this has not been achieved for chemical systems even as small as the helium atom and thus we are forced to approximate its solutions for such cases. The most common way to do this is to employ the Hartree–Fock (HF) approximation, which is a “mean-field” approximation in that it treats the repulsion of electrons in an average way and thus their motions are statistically independent and uncorrelated. The difference between the exact energy of a system and that predicted by HF theory is known as the correlation energy² and developing accurate methods of obtaining the correlation energy continues to be a central theme of research in theoretical chemistry and physics.³

The study of electron pair distributions is a useful way to gain insight into the phenomenon of electron correlation.^{4–14} The probability density for the interelectronic separation variable $u=|\mathbf{r}_1-\mathbf{r}_2|$ is known as the radial intracule density, $I(u)$. Comparison of correlated and HF intracules demonstrates how average distances between pairs of electrons change with correlation, which is important information when developing new correlation models.^{4,10}

The Coulomb hole

$$\Delta I(u) = I^{\text{exact}}(u) - I^{\text{HF}}(u) \quad (1)$$

was first described by Coulson and Neilson⁴ and in studying $\Delta I(u)$ it is generally found that correlation facilitates an in-

crease in electron repulsion and, as a consequence, electrons get further apart. However, we recently reported results for the helium atom and heliumlike ions showing that when electrons are at greater distances from one another (e.g., $u > 3.6$ for He) correlation actually brings them closer together.⁵ This so called “secondary Coulomb hole” was subsequently observed for the H₂ molecule¹⁵ and is amplified as the bond in H₂ is stretched.

It would be invaluable to know more about *where* the electrons are in the case that correlation induces a contraction of their distribution. This information is impossible to obtain from the radial intracule density alone, as it only measures *relative* distances between electrons and not their *absolute* location. The location of an electron pair however may be probed using its center-of-mass vector $\mathbf{R}=(1/2)(\mathbf{r}_1+\mathbf{r}_2)$ ^{16,17} and thus it would be advantageous to develop a simultaneous probability density for both of these coordinates. In the current work, we will be concerned with deriving such a density for the ground state of the helium atom and heliumlike ions. Thus, for simplicity, we need only consider the radial component of the extracule coordinate $R=(1/2)|\mathbf{r}_1+\mathbf{r}_2|$.

The simultaneous probability of finding two electrons at a certain distance, u , apart and with their center-of-mass located at a radius of R is described by

$$X(R,u) = \langle \Psi | \delta\left(R - \frac{1}{2}|\mathbf{r}_1 + \mathbf{r}_2|\right) \delta(u - |\mathbf{r}_1 - \mathbf{r}_2|) | \Psi \rangle, \quad (2)$$

where Ψ is the wave function and $\delta(x)$ is a one-dimensional Dirac delta function. Because this density combines both relative (intracule) and absolute (extracule) position information to more completely describe the spatial distribution of electron pairs, we refer to $X(R,u)$ as the intex density.

The purpose of this article is to introduce the intex density and subsequently determine the intex correlation holes

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of the ground states of the helium atom and heliumlike ions, defined as the difference between the exact and HF intex densities. This provides the opportunity to obtain a deeper understanding of the phenomenon of electron correlation; more specifically, it will allow for a more complete description of the secondary Coulomb hole,^{5,15} which demonstrates the high utility of this novel probability density. Atomic units are used throughout.

II. HARTREE–FOCK INTEX DENSITY

For an n -electron ($n \geq 2$) system, the two-electron density

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \frac{n(n-1)}{2} \langle \Psi | \delta(\mathbf{r}'_1 - \mathbf{r}_1) \delta(\mathbf{r}'_2 - \mathbf{r}_2) | \Psi \rangle \quad (3)$$

gives the probability that one electron will be found at \mathbf{r}_1 and another at \mathbf{r}_2 simultaneously. The radial intracule and extracule densities may be obtained from $\rho(\mathbf{r}_1, \mathbf{r}_2)$ by

$$I(u) = \int \int \int \rho(\mathbf{r}_1, \mathbf{r}_2) \delta(u - [\mathbf{r}_1 - \mathbf{r}_2]) d\mathbf{r}_1 d\mathbf{r}_2 d\Omega_{\mathbf{u}} \quad (4)$$

and

$$E(R) = \int \int \int \rho(\mathbf{r}_1, \mathbf{r}_2) \delta\left(\mathbf{R} - \frac{1}{2}[\mathbf{r}_1 + \mathbf{r}_2]\right) d\mathbf{r}_1 d\mathbf{r}_2 d\Omega_{\mathbf{R}}, \quad (5)$$

respectively, where $d\Omega_i$ denotes integration over the angular components of vector \mathbf{i} .

In a similar fashion, the intex density may be obtained from the two-electron density by

$$X(R, u) = \int \int \int \int \rho(\mathbf{r}_1, \mathbf{r}_2) \delta\left(\mathbf{R} - \frac{1}{2}[\mathbf{r}_1 + \mathbf{r}_2]\right) \times \delta(u - [\mathbf{r}_1 - \mathbf{r}_2]) d\mathbf{r}_1 d\mathbf{r}_2 d\Omega_{\mathbf{u}} d\Omega_{\mathbf{R}}. \quad (6)$$

This intex distribution leads naturally to the intracule and extracule densities by

$$\int_0^\infty X(R, u) dR = I(u), \quad (7)$$

$$\int_0^\infty X(R, u) du = E(R). \quad (8)$$

If the two-particle density is obtained from a HF wave function, the intex density may be expanded as

$$X^{\text{HF}}(R, u) = \sum_{\mu\nu\lambda\sigma}^K \Gamma_{\mu\nu\lambda\sigma}^{\text{HF}} (\mu\nu\lambda\sigma)_X, \quad (9)$$

where $\Gamma_{\mu\nu\lambda\sigma}^{\text{HF}}$ represents the usual HF two-particle density matrix element and $(\mu\nu\lambda\sigma)_X$ are the intex integrals over atomic orbital basis functions denoted by μ , ν , λ , and σ . These integrals are given by

$$(\mu\nu\lambda\sigma)_X = \int \int \phi_\mu^*\left(\mathbf{R} - \frac{\mathbf{u}}{2}\right) \phi_\nu\left(\mathbf{R} - \frac{\mathbf{u}}{2}\right) \times \phi_\lambda^*\left(\mathbf{R} + \frac{\mathbf{u}}{2}\right) \phi_\sigma\left(\mathbf{R} + \frac{\mathbf{u}}{2}\right) d\Omega_{\mathbf{u}} d\Omega_{\mathbf{R}}. \quad (10)$$

In the concentric case for two-electron systems where all basis functions are Gaussians of s-type symmetry, Eq. (10) may be integrated analytically as

$$(ssss)_X = 16\pi^2 R^2 u^2 e^{[(\alpha+\beta+\gamma+\delta)(R^2+u^2/4)]} \frac{\sinh[Ru(\alpha+\beta-\gamma-\delta)]}{Ru(\alpha+\beta-\gamma-\delta)}, \quad (11)$$

where α , β , γ , and δ represent the Gaussian exponents. Alternatively, one may pursue other forms for ϕ such as Slater functions to enforce the nuclear-electronic cusp conditions. However these are significantly more difficult to implement and have been shown to have a minimal effect on intracules when compared to an appropriately chosen set of Gaussians.^{18,19}

In order to construct accurate HF intex distributions, we employed a series of even-tempered basis sets proposed by Schmidt and Ruedenberg²⁰ which utilize Gaussian primitives with exponents given by

$$\zeta_k = \alpha \beta^k \quad (k = 1, 2, \dots, K), \quad (12)$$

where

$$\ln \ln \beta = b \ln K + b' \quad (13)$$

and

$$\ln \alpha = a \ln(\beta - 1) + a'. \quad (14)$$

The coefficients (a, a', b, b') for all atoms from helium through argon are available in the literature,²⁰ thus, it is straightforward to construct a basis set containing any number of Gaussian functions, K . Atomic orbital coefficients were then determined using the Q-CHEM package.²¹

We have calculated $X^{\text{HF}}(R, u)$ with basis sets up to $K=40$ and find that the largest of these is satisfactorily converged for the purposes of our investigation. This is demonstrated by comparing the $K=39$ and $K=40$ intex densities and calculating the maximum difference between the two as $\max_{u>0, R>0} |X_{40}^{\text{HF}}(R, u) - X_{39}^{\text{HF}}(R, u)| = 1.0 \times 10^{-7}$, which we interpret as a measure of the maximum basis set incompleteness error in the $K=40$ intex density and this level of accuracy is more than sufficient to study fine correlation effects at large u .⁵

The HF intex density for the ground state of the helium atom is shown in Fig. 1(a). The distribution has a global maximum at $u=0.891$ and $R=0.446$ and monotonically decays in all directions away from it. Interestingly, one can see that the distribution is symmetric about the $u=2R$ line.

Inspection of Eq. (11) reveals that $X^{\text{HF}}(R, u) = X^{\text{HF}}(u/2, 2R)$, confirming that the distribution is *exactly* symmetric. This demonstrates a rigorous relationship between the HF intracule and extracule densities for spherically symmetric systems in accordance with the isomorphisms for

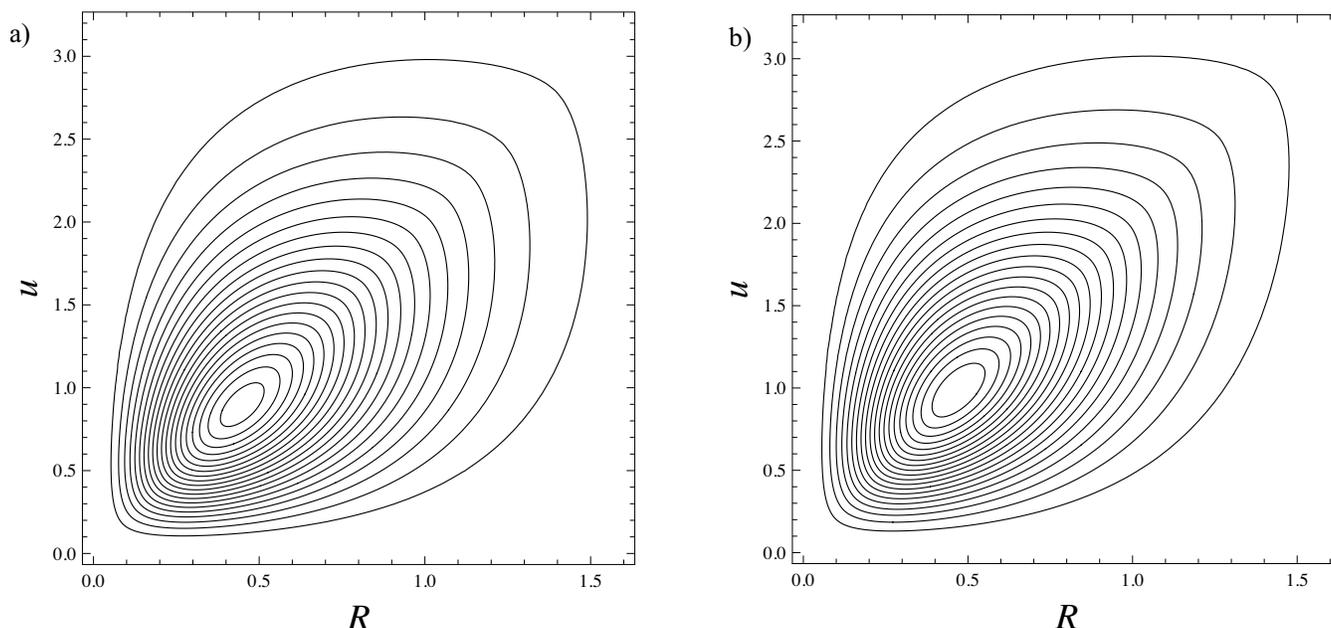


FIG. 1. (a) HF intex density of the helium atom. (b) Correlated intex density of the helium atom. Contours have magnitudes of $5n \times 10^{-2}$, where $n=1, 2, 3, \dots, 20$.

intracule and extracule densities reported elsewhere.^{22–27}

From an empirical relation, Koga found the approximate isomorphism $d(R) \cong 8h(2R)$ for the spherically averaged extracule and intracule densities,^{22–26} where $d(R) = E^{\text{HF}}(R) \times (4\pi R^2)^{-1}$ and $h(u) = I^{\text{HF}}(u) (4\pi u^2)^{-1}$. Romera later confirmed that this expression was exact for systems with two-electron densities of even parity.²⁷ Integrating our intex distribution (11) appropriately [Eqs. (7) and (8)] provides a simple alternative derivation for this isomorphism.

In addition to the ground state of the helium atom, we have computed the HF intex densities for the ground states of the heliumlike ions with atomic numbers $Z=3$ to 10. As in several previous studies of this series,^{5,28} the hydride ion, H^- , was omitted due to the difficulty in obtaining adequately converged results. As expected, the maxima in the intex densities shift to lower u and R with increasing charge on the ions. The coordinates and magnitude of the maxima in the intex densities are listed in Table I. Despite the contraction toward the origin, the intex density for each ion of the He isoelectronic series is qualitatively similar.

III. CORRELATED WAVE FUNCTION AND INTEX DISTRIBUTION

In a previous paper,⁵ we employed explicitly correlated wave functions of the Hylleraas type²⁹ to produce correlated intracules and the corresponding Coulomb holes. Unfortunately, however, variationally optimized exponents and coefficients of the Hylleraas expansions are not available in the literature⁹ for all of the ions in the isoelectronic series presented here and thus we have also explored a series of explicitly correlated wave functions based on those first described by Kinoshita.³⁰

$$\Psi^{\text{Kin}}(\mathbf{r}_1, \mathbf{r}_2) = e^{-\zeta s} \sum_{i=1}^N c_i s^{l_i/2} \left(\frac{t}{u}\right)^{m_i} \left(\frac{u}{s}\right)^{n_i/2}, \quad (15)$$

where s , t , and u are the Hylleraas coordinates defined as $s = |\mathbf{r}_1| + |\mathbf{r}_2|$, $t = |\mathbf{r}_1| - |\mathbf{r}_2|$ and $u = |\mathbf{r}_1 - \mathbf{r}_2|$. The exponents l_i , m_i , and n_i are non-negative integers. These exponents, along with the nonlinear parameter ζ , and the linear parameters c_i may be variationally optimized and this has been reported previously³¹ for a variety of expansion sizes, N . The Ki-

TABLE I. Coordinates $(R_{\text{max}}, u_{\text{max}})$ and magnitude of the maxima in the HF and correlated intex densities for the helium isoelectronic series.

Ion	Z	$(R_{\text{max}}, u_{\text{max}})_{\text{HF}}$	$X^{\text{HF}}(R_{\text{max}}, u_{\text{max}})$	$(R_{\text{max}}, u_{\text{max}})_{\text{Exact}}$	$X^{\text{Exact}}(R_{\text{max}}, u_{\text{max}})$
He	2	(0.446, 0.891)	1.031	(0.468, 0.978)	1.045
Li^+	3	(0.282, 0.564)	2.680	(0.290, 0.598)	2.711
Be^{2+}	4	(0.206, 0.413)	5.099	(0.210, 0.430)	5.147
B^{3+}	5	(0.163, 0.325)	8.291	(0.165, 0.336)	8.355
C^{4+}	6	(0.134, 0.268)	12.253	(0.136, 0.275)	12.334
N^{5+}	7	(0.114, 0.228)	16.987	(0.115, 0.234)	17.084
O^{6+}	8	(0.099, 0.199)	22.492	(0.100, 0.203)	22.605
F^{7+}	9	(0.088, 0.176)	28.769	(0.089, 0.179)	28.898
Ne^{8+}	10	(0.079, 0.158)	35.817	(0.079, 0.160)	35.962

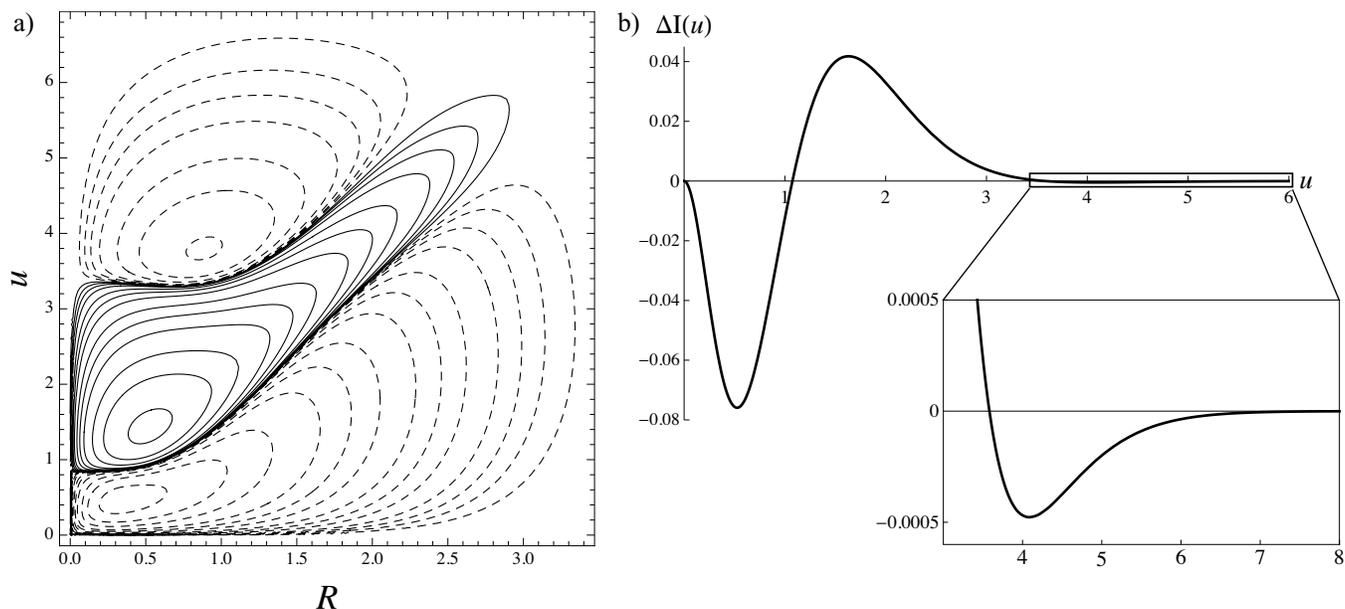


FIG. 2. (a) The intex correlation hole, $\Delta X(R, u)$, for the ground state of the helium atom. Contours have values of $\pm 2 \times 10^{-n}$, $\pm 4 \times 10^{-n}$, and $\pm 8 \times 10^{-m}$, where $n=2, 3, 4, 5$ and $m=2, 3, 4, 5, 6$. Positive contours are denoted by solid lines whereas negative contours are denoted by dashed lines. (b) The Coulomb hole, $\Delta I(u)$, for the ground state of the helium atom.

noshita wave function employed here uses half-integer powers, which was demonstrated to significantly improve the accuracy of the expansion.³¹ Using an expansion of only $N=100$ terms, the wave function reproduces an energy for the ground state of the helium atom to within 1 phartree of the exact value³¹ which exceeds the accuracy of the previously reported Hylleraas wave functions.⁹

With the u variable already incorporated into the wave function, the extracule variable, R , may be related to these expressions by the equality

$$4R^2 = s^2 + t^2 - u^2. \quad (16)$$

Changing to Hylleraas coordinates and integrating over the three external angles gives

$$d\mathbf{r}_1 d\mathbf{r}_2 \rightarrow \frac{4\pi^2 R u (4R^2 + u^2 - 2t^2)}{\sqrt{4R^2 + u^2 - t^2}} dt dR du \quad (17)$$

and integration of the resultant expression over t affords the intex density. These expressions were integrated numerically using the built-in numerical integrator in the MATHEMATICA package.³²

Figure 1(b) illustrates the intex density obtained using the 100-term Kinoshita wave function. Although, like in the case of HF, the correlated intex density appears symmetric about the $u=2R$ line, close inspection of Eq. (15) shows that the intex density obtained from these correlated functions will not possess such exact symmetry. This asymmetry is more clearly evident in the intex correlation hole (*vide infra*) and in the data provided in Table I. From this data, it is clearly seen that, in addition to other effects, correlation causes a deviation in the maxima from this line of symmetry.

IV. INTEX CORRELATION HOLE

The intex density is a valuable quantity to describe correlation effects in atomic and molecular systems due to its

inherent relative (intracule density) and absolute (extracule density) position information. Figure 2 displays the intex correlation hole for the ground state of the helium atom, $\Delta X(R, u)$, which is given by

$$\Delta X(R, u) = X^{\text{exact}}(R, u) - X^{\text{HF}}(R, u), \quad (18)$$

as well as the usual Coulomb hole⁵ calculated by

$$\int_0^\infty \Delta X(R, u) dR = \Delta I(u). \quad (19)$$

From Fig. 2 we observe two negative regions bisected by a positive region in the correlation hole. A negative value of $\Delta X(R, u)$ indicates a *decrease* in probability due to the effects of electron correlation whereas a positive value of $\Delta X(R, u)$ indicates an *increase* in probability. Because each intex density is normalized to the number of electron pairs, the integral

$$\iint \Delta X(R, u) dR du = 0 \quad (20)$$

vanishes and thus the size of both negative regions is exactly proportional to that of the positive one. The positive region reaches a maximum value of 0.092 at $R=0.520$ and $u=1.417$ and this area extends along the $u=2R$ line, creating a ridge. The first negative region, which mainly occurs at small u , reaches a minimum value of 0.109 at $R=0.344$ and $u=0.562$ (min I). The second negative region is far more shallow than the first and reaches a minimum value of 0.0008 at $R=0.886$ and $u=3.786$ (min II).

The Coulomb hole for the helium atom⁵ (see Fig. 2) is equal to zero at $u=1.1$ and $u=3.6$ and the conclusion is that the effects of correlation make it less favorable for electrons to be closer than 1.1 a.u. or farther apart than 3.6 a.u. While the former is more intuitive than the latter, the results are

TABLE II. Coordinates (R, u) of the extrema in intex correlation holes and secondary hole strength for the helium isoelectronic series.

Ion	Z	Min I (R, u)	Max (R, u)	Min II (R, u)	S
He	2	(0.344, 0.562)	(0.520, 1.417)	(0.886, 3.786)	6.30×10^{-4}
Li ⁺	3	(0.227, 0.286)	(0.316, 0.873)	(0.570, 2.399)	3.54×10^{-4}
Be ²⁺	4	(0.170, 0.207)	(0.227, 0.632)	(0.421, 1.759)	2.33×10^{-4}
B ³⁺	5	(0.136, 0.162)	(0.177, 0.495)	(0.333, 1.389)	1.71×10^{-4}
C ⁴⁺	6	(0.113, 0.134)	(0.146, 0.407)	(0.276, 1.149)	1.34×10^{-4}
N ⁵⁺	7	(0.097, 0.114)	(0.123, 0.346)	(0.235, 0.979)	1.09×10^{-4}
O ⁶⁺	8	(0.085, 0.099)	(0.107, 0.300)	(0.205, 0.852)	9.20×10^{-5}
F ⁷⁺	9	(0.076, 0.087)	(0.095, 0.265)	(0.182, 0.756)	7.94×10^{-5}
Ne ⁸⁺	10	(0.068, 0.078)	(0.085, 0.238)	(0.163, 0.677)	6.97×10^{-5}

clear and the intex density offers additional insight into such a phenomenon. Perhaps not surprisingly, it would appear as though the relative separation of an electron pair does not *universally* indicate whether correlation will act to separate or contract the pair. The absolute position of the electron pair is an important quantity, as is evidenced by the rich topology of the intex density in both the u and R dimensions. Evidently, correlation *can* increase the probability of finding electrons separated by large distances ($u > 3.6$) so long as their center-of-mass is close to $(1/2)u$. However this is outweighed by the secondary Coulomb hole behavior exhibited by electrons where $u \approx 4R$ and $u \approx R$. Additionally, when $u < R$, which implies that the electron pair is on the same side of the nucleus, the intex correlation hole is always negative. This feature indicates that in such cases correlation will always act to either separate the electrons or move their center-of-mass closer to the origin (or both).

The intex correlation holes were also determined for the helium isoelectronic series up to Ne⁸⁺ and as expected, the features of $\Delta X(R, u)$ contract toward the origin as the atomic number and nuclear charge increase. As with the case of the Coulomb holes of this series,⁵ the intex correlation holes are all qualitatively similar and each system bears the same topological features. Table II summarizes the extrema of the correlation holes and lists the strengths of the secondary Coulomb holes defined by

$$S = \int_{\bar{u}_2}^{\infty} |\Delta I(u)| du, \quad (21)$$

where \bar{u}_2 is the second root of $\Delta I(u)$. S is well defined for all of the systems under investigation in the current work because all exhibit a second root \bar{u}_2 and it appears as though such secondary Coulomb holes may be ubiquitous in two-electron systems.^{5,15,33} S has been reported previously for Z -scaled intracules⁵ for He, Li⁺, Be²⁺, B³⁺, and Ne⁸⁺ and all are in exact agreement with those in Table II upon introduction of the scaling factor, Z . The additional data for C⁴⁺, N⁵⁺, O⁶⁺, and F⁷⁺ confirm the trend that the proportion of the secondary Coulomb hole diminishes with increasing Z .

V. CONCLUDING REMARKS

We have introduced a novel electron pair distribution, the intex density, which is defined by Eq. (2). This new density employs both the intracular and extracular coordinates to

more completely describe the probability distributions of electron pairs in position space. Using even-tempered basis sets of 40 s-type Gaussians, we have calculated the HF intex distribution of the ground state heliumlike ions from He to Ne⁸⁺. In all of these cases we note that the intex distribution is identically symmetrical about the line $u=2R$, implying the previously described²²⁻²⁷ relation $2I(2R)=E(R)$.

A correlated treatment of the intex density was performed using Kinoshita type wave functions. Unlike the HF intex density, the correlated intex density is not symmetric about the $u=2R$ line. Using the correlated intex densities, we were able to determine the intex correlation hole for the ground state of the helium atom and the helium isoelectronic series. The intex correlation hole provides us with a more complete picture of the effects of electron correlation on the spatial distribution of electron pairs in an atomic system. Specifically, we observe that the secondary Coulomb hole is not universal; it does not occur at all large values of u , but instead is dependent on the center-of-mass of the electron pair. We conclude that the probability of observing an electron pair with a very large interelectronic separation increases with the inclusion of correlation *only* when their center-of-mass radius is close to half of their separation. It would be reasonable to conjecture that in such cases, one electron remains close to the nucleus while the second is far away and this may be elucidated further by considering the probability distribution of the angle between the interelectronic separation and center-of-mass vectors. Additionally, it has been shown that part of the effects of correlation in these systems is to decrease the probability of observing $u < R$ (i.e., both electrons on the same side of the nucleus).

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