Angular dependence of the two-electron intex distribution

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1. Introduction

The importance of understanding the correlated behaviour of electrons in atomic and molecular systems cannot be overstated. In fact, it is the pursuit of this goal that drives much of the current research in electronic structure theory. It is a significant challenge to predict the electronic structure of chemical systems due to the inseparability of the electronic Schrödinger equation and the application of a mean-field approach and thus we require methods to approximate its solution are required and there exists several promising methodologies [2]. Hartree–Fock molecular orbital theory (HF), which forms the starting point for most ab initio approximations to the solution of the electronic Schrödinger equation, fails to account for the correlated motion of electrons because of the application of a mean-field approach and thus we commonly refer to HF as missing the critically important “correlation energy”. Textbooks will often ascribe this error in HF theory to electronic repulsions being too large [3]. In other words, electrons tend to be too close according to HF theory and so more accurate methods predict that electrons are generally farther away from each other than in HF. Coulson and Neilson highlighted this point by calculating the spherically averaged interelectronic probability distribution (also known as the intracule) of the ground state of the helium atom at various levels of theory given by

\[ P(u) = \langle \Psi(r_1, r_2) | \delta(|r_1 - r_2|) | \Psi(r_1, r_2) \rangle, \]

where \( \Psi \) is the wave function for the system of interest, \( u = |r_1 - r_2| \) is the interelectronic distance, and \( \delta(x) \) is a one-dimensional Dirac delta function [4]. They subsequently coined the term “Coulomb hole” to describe the difference between the predicted intracules from HF and that of highly accurate wave functions \( \Delta P(u) = P^{\mathrm{exact}}(u) - P^{\mathrm{HF}}(u) \) and observed an increase in the average distance between electrons relative to HF. That is, \( \Delta P(u) \) is negative for small \( u \) and positive for larger \( u \), and similar behaviour has been observed extensively in the Coulomb holes of larger atoms and molecules [5]. This further reinforced the notion that the primary effect of electron correlation is to separate electrons.

Recently, however, a richer topology within the context of \( \Delta P(u) \) has been revealed [6–9], and demonstrates that the naïve notion that electrons in a correlated treatment of electronic structure will always increase their relative separation compared to what HF theory predicts is incomplete. Indeed, the so-called “secondary Coulomb hole” [6–9] indicates that correlation can in fact contract distant electron pairs to varying extents and seems to do so in a wide range of chemical contexts [10]. In the ground state of the helium atom, for example, correlation does reduce \( P(u) \) for small \( u \) and increase it for moderate \( u \), but it also reduces it slightly for large \( u \). In the \( H_2 \) molecule, a similar effect is observed and as the bond is lengthened the secondary Coulomb hole becomes the dominant feature of \( \Delta P(u) \) and thus a highly accurate method will actually predict larger electronic repulsion energies than HF [8]. These results are in stark contrast to the conventional wisdom of the errors in HF theory and require further study to be properly understood.

The fact that distant electrons contract toward each other in correlated methods relative to HF theory indicates that HF generally produces a more asymptotically diffuse distribution of electrons at long range than that of correlated methods. In addition, the energetic cost of bringing electrons closer together must be outweighed by favourable changes to the other components of the electronic energy, as the variational theorem ensures us that the exact solution will produce a result with a lower total energy than HF. What though, are the spatial configurations of the electron pairs that give rise to these seemingly anomalous effects? To simply say that distant electrons contract in a correlated treatment relative to HF is lacking in detail. It is critically important to
understand how electron pairs are distributed in atoms and molecules and how this distribution changes depending upon the level of accuracy of the chosen theoretical method and this is a central goal of the current work.

In a previous Letter [7], we have developed the so-called intex density to describe the spatial distribution of electron pairs in terms of the intraculear and extraculear coordinates simultaneously, where the extraculear coordinate, $\mathbf{R}$, corresponds to the position of the center-of-mass of an electron pair

$$\mathbf{R} = \frac{\mathbf{r}_1 + \mathbf{r}_2}{2}. \quad (2)$$

The intex density is therefore given by

$$X(\mathbf{R}, \mathbf{u}) = \langle \Psi(\mathbf{r}_1, \mathbf{r}_2) | \delta \left( \mathbf{R} - \frac{1}{2} (\mathbf{r}_1 + \mathbf{r}_2) \right) \delta (|\mathbf{r}_1 - \mathbf{r}_2|) | \Psi(\mathbf{r}_1, \mathbf{r}_2) \rangle \quad (3)$$

and describes the probability that a pair of electrons will be separated by a distance $\mathbf{u}$ and simultaneously have their center of mass located at a distance $\mathbf{R}$ from a reference point. For a generalized application to polyatomic systems, the vector form of $\mathbf{R}$ may be considered (vide infra).

The intex density has proven quite useful in providing a clearer picture of the effects of electron correlation and the spatial distribution of electron pairs owing to the fact that it contains information regarding the relative separation of electrons and their absolute position in space. In the current work, we aim to expand the development of the intex density by studying its dependence on the angle between the coordinate vectors $\mathbf{R}$ and $\mathbf{u}$. Figure 1 illustrates these coordinates along with the more traditional coordinates $\mathbf{r}_1$, $\mathbf{r}_2$, and $\theta_{12}$ to describe electronic positions. In spherically symmetric systems such as the ground states of two-electron atoms, the set of scalar coordinates $\mathbf{r}_1$, $\mathbf{r}_2$, $\theta_{12}$ is essentially complete. Analogously, the scalar intraculear coordinate, $\mathbf{u}$, extraculear coordinate, $\mathbf{R}$, and angle $\theta_{12}$ also represent a complete set. As such, we will focus on the ground states of the helium isoelectronic sequence in this work for the purposes of simplifying our initial implementation.

Two-electron atoms have been the focus of a wide range of theoretical research. There is value in understanding the pair-wise interactions of electrons in such simple systems as this can usually be extrapolated to better understand even the most subtle correlation effects in arbitrarily large systems [10]. Even the electronic structure and correlation energy of the helium atom still garners attention from the theoretical physics community [11–15]. Furthermore, the subtle (and counterintuitive) correlation effects that have been observed within the context of the Coulomb hole [6-9] have still not been satisfactorily explained.

Probability densities of interelectronic angles have been studied extensively [11,16–34] and are intimately related to angular correlation. These densities describe the probability of finding two electrons with an angle of $\theta_{12}$ separating their respective position vectors and are usually of the form

$$A(\theta_{12}) = \iint \rho(\mathbf{r}_1, \mathbf{r}_2) \frac{d\mathbf{r}_1 d\mathbf{r}_2}{\sin(\theta_{12})} \quad (4)$$

where $\rho(\mathbf{r}_1, \mathbf{r}_2)$ is the spinless two-electron density function for an $n$-electron system given by

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \frac{n(n-1)}{2} \iint \left| \Psi(x_1, \ldots, x_n) \right|^2 dx_1 dx_2 \cdots dx_n \quad (5)$$

In this expression, $x_i = (r_i, s_i)$ denotes the combined position and spin coordinates of electron $i$. In an alternative approach to studying angular correlation phenomena, we calculate the contributions of the angle $\theta_{12}$ to the intex probability distribution and observe the effects correlation has on the optimal angle between the $\mathbf{R}$ and $\mathbf{u}$ vectors. This probability distribution may also be obtained from the two-electron density by

$$X(\mathbf{R}, \mathbf{u}, \theta_{10n}) = \iint \iint \rho(\mathbf{r}_1, \mathbf{r}_2) \left| \mathbf{R} - \frac{1}{2} (\mathbf{r}_1 + \mathbf{r}_2) \right| \delta (|\mathbf{r}_1 - \mathbf{r}_2|) \frac{d\Omega_1 d\Omega_2}{d\theta_{12}} \quad (6)$$

where $\theta_{10n}$ is an angular component of the vector $\mathbf{u}$ with the $\mathbf{R}$ vector acting as the principal axis and $d\Omega_1 d\Omega_2/d\theta_{10n}$ denotes integration over all angular components of the $\mathbf{R}$ and $\mathbf{u}$ vectors except $\theta_{10n}$. The angular component may then be isolated by

$$A(\theta_{10n}) = \int X(\mathbf{R}, \mathbf{u}, \theta_{10n}) d\mathbf{R} d\mathbf{u} \quad (7)$$

and throughout this work we refer to $X(\mathbf{R}, \mathbf{u}, \theta_{10n})$ as the angular-dependent intex density and to $A(\theta_{10n})$ simply as the angular intex density. The form of our expression differs slightly from that in Eq. (4) in that we retain the $\sin(\theta)$ component within the expression so that we may maintain the normalization of the probability distribution, which in the case of such two-electron densities is the number of electron pairs, or $n(n-1)/2$. This resembles the approach of Boyd and coworkers for interelectronic angle densities [20–22] and may be interpreted as the probability distribution for the variable $\theta_{10n}$.

A primary and immediate application of these angular densities is to better understand the spatial distributions of electron pairs and how this gives rise to the anomalous secondary Coulomb hole. These quantities are also important for the fundamental understanding of electron-electron interactions in our test systems because for probable configurations of $\mathbf{u}$ and $\mathbf{R}$, there exists two extremes whereby $\theta_{10n} = \pi/2$ or $\theta_{10n} = (0, \pi)$ and these represent cases where the electrons are equidistant from the nucleus and where the pair of electrons and the nucleus are colinear, respectively. Therefore the influence of the nuclear potential may be probed using this technique. Also, $X(\mathbf{R}, \mathbf{u}, \theta_{10n})$ allows one to understand the distribution of $\theta_{10n}$ for specific values of $\mathbf{u}$ and $\mathbf{R}$. For a more general application to larger atoms and molecules, the vectorized extraculear coordinate may be considered, $\mathbf{R}$, which will allow for the localization of such an analysis by affording the determination of the probability density of interelectronic separation (the intracule) for electron pairs whose center of mass is at a specific location in three-dimensional space.

In the present work, we study the features of these probability distributions and consequently learn about the restrictions that correlation imposes upon the spatial distribution of electron pairs. Along with the intex density, it is shown that this novel density provides a clearer picture of the effects of electron correlation and more details concerning the nature of the secondary Coulomb hole. Atomic units are used throughout.

![Figure 1. Schematic representation of a two-electron atom with electronic coordinate vectors $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{R}$, $\mathbf{u}$, and the angular coordinates $\theta_{10n}$, and $\theta_{12}$. $\mathbf{Z}$ indicates the nuclear charge at the origin.](image-url)
2. Theory

2.1. Hartree–Fock wave function

The angular and angular-dependent inteX densities may be obtained from Eqs. (7) and (6), respectively. If one uses a HF wave function to generate the two-particle density, the angular dependence function may be expressed as an expansion

\[ \Xi(R, u, \theta_{b_a}) = \sum_{\mu, \sigma} \Gamma^\text{HF}_{\mu, \sigma}(\mu \nu \sigma \tau) \chi_{\mu, \sigma}, \]

where \( \Gamma^\text{HF}_{\mu, \sigma} \) is the usual HF two-particle density matrix while \( \langle \mu \nu \sigma \tau \rangle \chi_{\mu, \sigma} \) are the angular inteX integrals over the set of K atomic orbital basis functions denoted by \( \mu, \nu, \sigma, \) and \( \tau \). These integrals are given by

\[ \langle \mu \nu \sigma \tau \rangle \chi_{\mu, \sigma} = \int \phi^*_\nu(R - \frac{u}{2}) \phi^*_\sigma(R - \frac{u}{2}) \phi_{\sigma}(R + \frac{u}{2}) \frac{d\Omega}{d\theta_{b_a}}, \]

and for spherically concentric systems utilizing Gaussian basis functions of s-type symmetry, these integrals may be expressed analytically as

\[ \langle sss \rangle \chi_{a} = 8\pi^2 R^2 u^2 \sin(\theta_{b_a}) e^{-R^2 + u^2/4} \delta(x+k \cos \theta_{b_a}), \]

where \( k = 1, 2, \ldots, C \), \( x \) and \( \beta \) are parameters defined as

\[ \ln x = b \ln K + b', \quad \ln \beta = a \ln(b - 1) + a'. \]

The coefficients in these equations \( a, a', b, b' \) have been determined for all atoms from hydrogen through argon [38], therefore constructing a basis set of any size for these atoms is straightforward. For a given expansion size, K, atomic orbital coefficients were subsequently determined using the Q-CHEM package [39].

We have determined that basis sets consisting of \( K = 30 \) Gaussians produce inteX densities that are more than adequately converged for the current work. This determination is based on the calculation of a maximum basis set incompleteness error (BSIE) for the \( K = 30 \) Gaussian helium-like ion basis set as \n
\[ \max_{u=0:K=30}(R, u) - X^\text{BSIE}_{u=29}(R, u) \] \n
where \( s, t, \) and \( u \) are the so-called Hylleraas coordinates [44] defined by

\[ s = |r_1| + |r_2|, \quad t = |r_1| - |r_2|, \quad u = |r_1 - r_2|. \]

The exponents \( l, m, \) and \( n \) are all non-negative integers which, along with the linear parameters \( c \) and the nonlinear parameter \( \zeta \), may be variationally optimized. This optimization has been reported for the helium isoelectronic series from He up to Ne^{18+} by Koga for a variety of expansion sizes, N [43]. The Kinoshita wave functions employed here consist of expansions of \( N = 100 \) terms and have been shown to reproduce the ground state energy for the helium atom to within 1 picohartree of the exact value [43] and are thus sufficiently converged for our purposes [7].

To obtain the angular-dependent inteX density, \( \chi(R, u, \theta_{b_a}) \), a function solely dependent on \( \theta_{b_a}, s, \) and \( t \) was substituted by their equivalent expressions containing \( r_1 \) and \( r_2 \) after which these variables were replaced by the identities

\[ r_1 = \sqrt{R^2 + u^2/4 - Ru \cos(\theta_{b_a})}, \quad r_2 = \sqrt{R^2 + u^2/4 + Ru \cos(\theta_{b_a})}. \]

The angular-dependent inteX density may then be obtained directly from the resultant wave function, dependent on \( R, u, \) and \( \theta_{b_a} \) while the angular inteX density, \( \chi(\theta_{b_a}) \), is then obtained through the numerical integration of \( \chi(R, u, \theta_{b_a}) \) over the \( R \) and \( u \) components.

3. Results and discussion

The HF and Kinoshita angular inteX densities for the ground state of the helium atom are shown in Figure 2a. The figure demonstrates that the dependence on the angle between the vectors \( R \) and \( u \) is minimal over most of the range from 0 to \( \pi \). Due to the inherent symmetry in the definition of \( \theta_{b_a} \), \( A(\theta_{b_a}) \) is symmetric about \( \pi/2 \). The density displays maxima at \( \theta_{b_a} = 0.749 \) and 2.393 for HF whereas the maxima occur at \( \theta_{b_a} = 0.574 \) and 2.568 for the correlated treatment. The minima for both methods occur at \( \theta_{b_a} = \pi/2 \). Figure 2b displays the angular inteX correlation hole, \( \Delta A(\theta_{b_a}) \), which is given by

\[ \Delta A(\theta_{b_a}) = A^{\text{Kin}}(\theta_{b_a}) - A^{\text{HF}}(\theta_{b_a}) \]

We observe a minimum at \( \pi/2 \) radians in \( \Delta A(\theta_{b_a}) \), indicating, as expected, that HF has a preference for configurations where the electrons are equidistant from the nucleus in comparison to exact treatments. The maxima are much closer to 0 and \( \pi \), which signifies a preference in correlated systems for configurations where one electron is closer to the nucleus than the other.

Due to the spherical symmetry of the systems in the helium iso-electronic series, one might expect that the most probable configuration would be that of the electrons being equidistant from the nucleus (i.e., \( \theta_{b_a} = \pi/2 \)). However, with local minima occurring where the \( R \) and \( u \) vectors are perpendicular to one another (i.e., electrons equidistant from the nucleus), the plot of \( A(\theta_{b_a}) \) confirms that this is not the case and the angular-dependent inteX density may be used to explore this further (vide infra).

The angular inteX densities were determined for the series of helium-like ions from He to Ne^{18+} and the coordinates of the maxima are indicated in Table 1. Also included in the table is a measure of the relative angular dependence of \( A(\theta_{b_a}) \) for each of the ions defined by

\[ \Delta = \frac{A^{\text{max}}(\theta_{b_a}) - A^{\text{min}}(\theta_{b_a})}{A^{\text{max}}(\theta_{b_a})} \]

where \( A^{\text{max}}(\theta_{b_a}) \) and \( A^{\text{min}}(\theta_{b_a}) \) correspond to the value of \( A(\theta_{b_a}) \) at the local minimum and maximum, respectively. The value of \( \Delta \) demonstrates the relative difference in probabilities of the local
minima and maxima in densities where a local minimum is observed and thus provides a measure of how greatly the density of the system is affected by changes in this angle. Although \( \Delta \alpha \) is defined only when \( A^{\text{ext}}(\theta_{\text{a}}) \) exists, we note that it is well-defined in all cases presented here and is a useful quantitative measure of \( \theta_{\text{a}} \) dependence.

Table 1 demonstrates that as the nuclear charge increases, the angle of the global maxima steadily increases in addition to an apparent decrease in the relative angular dependence, \( \Delta \alpha \). With the only difference in these systems being that of the differing nuclear charges, these trends can be attributed to the electrons being drawn closer to the nucleus in the systems containing more protons. Consequently, when the electrons are closer to the nucleus, the positions of the electrons are more limited.

In addition to these trends, which are common to both HF and correlated cases, there are some significant differences between the two approaches. From the tabulated data, it can be noted that \( \theta_{\text{max}}^{\text{HF}} \) is lower in correlated systems suggesting a preference for angles closer to 0 (or \( \pi \)), as discussed previously. Furthermore, the relative angular dependence is significantly greater in correlated systems, especially for the ions with lower nuclear charges. Therefore the data demonstrates that correlated treatments favor configurations where one electron is closer to the nucleus more so than HF.

To investigate the properties of the intex correlation hole [7] we may take slices of the angular-dependent intex distribution, \( X(R, u, \theta_{\text{a}}) \), at fixed values of \( R \) and \( u \). This will afford an analysis of the probability distribution of \( \theta_{\text{a}} \) for configurations of the electron pair relevant to the Coulomb and secondary Coulomb holes. Appropriate values of \( R \) and \( u \) may then be chosen from the extrema of the intex correlation hole \( \Delta X(R, u) = X^{\text{Kin}}(R, u) - X^{\text{HF}}(R, u) \) and these are shown in Figure 3. There are two minima occurring at \( (R_1, u_1) = (0.344, 0.562) \) and \( (R_2, u_2) = (0.886, 3.786) \) and a maximum at \( (R, u) = (0.520, 1.417) \).

The HF and Kinoshita angular-dependent intex densities at the coordinates of the extrema of the intex correlation hole are displayed in Figure 4a–c while their respective angular-dependent intex correlation holes, \( \Delta X(R, u, \theta_{\text{a}}) \), are represented in Figure 4d–f. Due to the fact that the densities are slices of the overall angular-dependent intex density, they are not normalized and comparisons of probabilities at specific angles are not possible. However, as expected the probability for HF systems is greater in a and c which represent the two minima in the intex correlation hole. Conversely, correlated systems are favoured in the system described in b which is taken from the coordinates of the maximum in the intex correlation hole. From the plots of \( \Delta X(R, u, \theta_{\text{a}}) \), we see that a minimum occurs at \( \theta_{\text{a}} = \pi/2 \) in all cases. This again confirms that this configuration represents a greater portion of the density for HF systems regardless of the value of \( R \) and \( u \).

The main point of interest here is the trend that is observed when we progress from a to c. As we progress from the coordinates of a to the coordinates of c, the values of \( R \) and \( u \) are both increasing. From Figure 4, we see that in a, the density reaches a maximum at...
for both HF and correlated systems, whereas in b and c, \( \pi/2 \) represents a minimum and the level of dependence on \( \theta_{Ru} \) is increasing. This reveals the explanation behind the overall form of the angular intex density in Figure 2. In the case where both \( R \) and \( u \) are very large values, two extremes would be possible: the first case being that where both electrons are far from the nucleus (and each other) with \( h_{Ru} = \pi/2 \) and the second case being the configuration where one electron is approaching the nucleus while the other is very far away corresponding to \( h_{Ru} = 0 \) or \( \pi \). In the first case, we effectively have three separate one particle systems where neither electron has significant interaction with the nucleus nor each other, whereas in the second case, one electron is interacting favourably with the nucleus while the other is far enough away to be considered an isolated system. It is obvious that the latter is the more favourable configuration and thus it is expected that as we increase \( R \) and \( u \), the level of angular dependence will increase and the optimal angle will approach 0 and \( \pi \) with the angular intex density consisting of two sharp peaks in these regions.

The relevant question then becomes, how large must \( R \) and \( u \) become before we observe such an inflection in the curvature of the angular-dependent intex density with respect to \( h_{Ru} \)? From Figure 4, we know that a maximum in \( X(R, u, \theta_{Ru}) \) at values of \( R \) and \( u \) corresponding to the extrema of the intex correlation hole for the ground state of the helium atom shown in Figure 3. The coordinates \((R, u)\) are as follows: (a) and (d) \( (R, u) = (0.344, 0.562), \) (b) and (e) \( (R, u) = (0.520, 1.417), \) (c) and (f) \( (R, u) = (0.886, 3.786). \)
fixed $R$ and $u$ is a minimum or a maximum with respect to $\theta_R$ at $\pi/2$. The region below this line (low $R$ and $u$) are the sets of coordinates where a maximum occurs at $\pi/2$, whereas the majority of the density which lies above the line represents the coordinates where a minimum is observed. Figure 5a demonstrates that the critical coordinate line for the HF system is symmetric about the $u = 2R$ line as expected from the known symmetry of the inflex density for two-electron systems consisting solely of s-type orbitals of even parity [7]. The differences in this critical coordinate line for the HF and Kinoshita densities are fairly minimal but the region corresponding to configurations where the angular-dependent inflex density reaches a maximum at $\theta_R = \pi/2$ is larger in HF systems.

This is more evident in Figure 6 which displays the critical coordinate lines for both treatments overlaid. Approximate numerical integrations were performed to determine the percentage of the density which lies below this critical coordinate line. It was determined that for HF densities, configurations where $\theta_R = \pi/2$ represent a maximum in probability is roughly 31% of the density whereas this percentage decreases to approximately 23% for Kinoshita densities. This figure highlights some key differences about correlated systems. The critical line for the correlated system is extended towards both the $R$ and $u$ axes. Furthermore the correlated critical line deviates from the HF line to a greater extent with respect to the $u$ values than for the $R$ values. This result is intuitive as one would expect correlation to have a greater effect on the interelectronic separation variable, $u$, than on the centre-of-mass variable, $R$.

In terms of the secondary Coulomb hole, it has been reported that the effects of correlation on the inflex density are to increase the probability that electron pairs will be found with $R \approx u/2$ [7] and thus at large $u$ the center-of-mass of the electron pair is likely to be half of the distance of their separation away from the nucleus. There exists two extremes in this scenario: one where $\theta_R = (0, \pi)$ and thus the electrons and nucleus adopt a colinear arrangement or one where $\theta_R = \pi/2$ and the electrons become equidistant from the nucleus. Our development of the angular-dependent inflex density confirms that regimes near $\theta_R = (0, \pi)$ are the most probable alternative, which is an intuitive result and indicates that it is this configuration that allows for correlated electrons to contract.

**4. Conclusion**

We have introduced the angular-dependent inflex density $X(R, u, \theta_R)$ and isolated the angular component of this distribution, $A(\theta_R)$, and used it to explore correlation effects in two-electron atoms. We have determined that exact treatments of these quantities favour angles closer to 0 or $\pi$ between the $R$ and $u$ vectors while a HF treatment favours orientations where the angle is closer to $\pi/2$. Using the angular-dependent inflex density to explore areas of interest in the inflex correlation hole, it was noted that as $R$ and $u$ grow, the favoured angles for both HF and exact densities approach 0 and $\pi$. This reflects the fact that as $R$ and $u$ grow, the electrons and the
nucleus can behave like three independent particles and thus $\theta_{\text{nu}}$ will approach 0 or $\pi$ to allow for one of the electrons to approach the nucleus and create a lower-energy configuration. In terms of the secondary Coulomb hole (which exists at large $u$), given that correlation favours orientations where $R/u^2$ [7] (see Figure 3) we may conclude that it is also likely that the intex angle ($\theta_{\text{nu}}$) approaches 0 and $\pi$ for these configurations and thus one electron remains relatively close to the nucleus while the other is far. We have demonstrated that the most probable angles can depend significantly on the values of $R$ and $u$. Both the HF and near-exact Kinoshita densities predict that electrons will generally be equidistant from the nucleus at small $R$ and/or $u$ values. The angular intex density has proven to provide a more complete picture of electron–electron interactions and the effects of electron correlation.

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References