

Distributions of $r_1 \cdot r_2$ and $p_1 \cdot p_2$ in Atoms

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S Supporting Information

ABSTRACT: We consider the two-electron position and momentum dot products, $\alpha = \mathbf{r}_1 \cdot \mathbf{r}_2$ and $\beta = \mathbf{p}_1 \cdot \mathbf{p}_2$, and present a method for extracting their distributions, $A(\alpha)$ and $B(\beta)$, from molecular wave functions built on Gaussian basis functions. The characteristics of the Hartree–Fock $A_{\text{HF}}(\alpha)$ and $B_{\text{HF}}(\beta)$ for He and the first-row atoms are investigated, with particular attention to the effects of Pauli exchange. The effects of electron correlation are studied via the holes, $\Delta A(\alpha) \equiv A(\alpha) - A_{\text{HF}}(\alpha)$ and $\Delta B(\beta) \equiv B(\beta) - B_{\text{HF}}(\beta)$, and the hole structures are rationalized in terms of radial and angular correlation effects. Correlation effects are also examined through an analysis of the first moments of $A(\alpha)$, $A_{\text{HF}}(\alpha)$, $B(\beta)$, and $B_{\text{HF}}(\beta)$.

1. INTRODUCTION

Accurate quantum chemical calculations cannot ignore the effects of electron correlation. However, despite the constant evolution of existing methods^{1–3} and the development of new approaches,^{4–8} a universal and efficient solution to the correlation problem remains elusive. Density functional theory (DFT)⁹ has enjoyed years of success as an accurate and efficient computational approach, but recently many of its flaws have been exposed.^{10–18} New routes have been taken to develop improved density functionals,^{19,20} but a more promising solution may lie with the two-electron functionals of intracule functional theory (IFT).^{21–26}

Two-electron probability distribution functions, particularly intracules, are useful tools for understanding the physical details of electron correlation,^{27–35} and this is essential, not only for the development of IFT but for the development of any approach to the correlation problem. The best known are the (spherically averaged) position²⁷ $P(u)$ and momentum²⁹ $M(v)$ intracules:

$$P(u) = \frac{N(N-1)}{2} \langle \Psi | \delta(u - r_{12}) | \Psi \rangle \quad (1a)$$

$$M(v) = \frac{N(N-1)}{2} \langle \Phi | \delta(v - p_{12}) | \Phi \rangle \quad (1b)$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$, $p_{12} = |\mathbf{p}_1 - \mathbf{p}_2|$, δ is the Dirac delta function, and Ψ and Φ are the N -electron wave functions in position and momentum space, respectively. $P(u)$ and $M(v)$ give the probability distributions of the relative distance u and momentum v of pairs of electrons in the system. If desired, the effects of electron correlation can be isolated by constructing the intracule holes

$$\Delta P = P - P_{\text{HF}} \quad (2a)$$

$$\Delta M = M - M_{\text{HF}} \quad (2b)$$

which are the differences between the exact and Hartree–Fock (HF) intracules.

The prototypical hole is ΔP for the helium atom, first given by Coulson and Neilson,²⁷ which shows that correlation decreases the probability of small u and increases the

probability of large u ; i.e., it tends to push electrons apart. Banyard and Reed found²⁹ that ΔM for helium is more complicated than ΔP and that it results from the competing effects of angular and radial correlation. Recently, subtler features of intracule holes have been uncovered,^{32–35} in both position and momentum space, and these have further refined our picture of the correlation phenomenon.

Because the $P(u)$ and $M(v)$ intracules are one-dimensional projections of the six-dimensional two-electron densities $\rho(\mathbf{r}_1, \mathbf{r}_2)$ and $\Pi(\mathbf{p}_1, \mathbf{p}_2)$, it can sometimes be difficult to decipher the effects of electron correlation revealed by intracule holes. When this is the case, one may turn to objects of higher dimensionality such as the Intex distribution^{36,37} or to other one-dimensional functions.³⁸ For example, the interelectronic angles $\angle \mathbf{r}_1 \mathbf{O} \mathbf{r}_2$ and $\angle \mathbf{p}_1 \mathbf{O} \mathbf{p}_2$ (where the origin \mathbf{O} refers to the position or momentum of a nucleus) have been studied at both the Hartree–Fock³⁹ and correlated^{29,31} levels in atoms but not, as far as we know, in molecules.

In the present work, we focus on the dot products, $\alpha = \mathbf{r}_1 \cdot \mathbf{r}_2$ and $\beta = \mathbf{p}_1 \cdot \mathbf{p}_2$. Their distributions $A(\alpha)$ and $B(\beta)$, which we call the position-dot and momentum-dot distributions, reveal *orientational* information about the positions and momenta of the electrons and this can help to resolve ambiguities in $P(u)$ and $M(v)$. For example, although a large value of v could pertain either to a situation in which the two electrons are moving in the same direction at very different speeds or to one in which they are moving in opposite directions at similar speeds, knowledge of $B(\beta)$ helps to distinguish these possibilities and, indeed, it did so in our recent work on the motion of the electrons in the H_2 molecule.³⁵

Instead of calculating $A(\alpha)$ and $B(\beta)$, one could extract orientational information from a combination of the intracule and the extracule, where the latter is the distribution of the mean coordinate $(\mathbf{r}_1 + \mathbf{r}_2)/2$ or $(\mathbf{p}_1 + \mathbf{p}_2)/2$. However, $A(\alpha)$ and $B(\beta)$ yield this information more directly.

It should be noted that, unlike intracules but like extracules, $A(\alpha)$ and $B(\beta)$ depend on the choices of origins, \mathbf{O}_r and \mathbf{O}_p , in position and momentum space, respectively. For atoms, it is

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natural to choose \mathbf{O}_r to be the nucleus, and we have done so throughout this study: for molecules, the choice is less obvious. For any stationary system, it is natural to choose $\mathbf{O}_p = (0,0,0)$.

In the next section, we introduce a method for calculating $A(\alpha)$ and $B(\beta)$ for an arbitrary molecular system whose wave function is expanded in a Gaussian basis set. After discussing computational details in section 3, we examine $A_{\text{HF}}(\alpha)$ and $B_{\text{HF}}(\beta)$ for small atoms in section 4 and conclude with a study of correlation effects in section 5. Atomic units are used throughout.

2. THEORY

We define the two new distributions by the expectation values

$$A(\alpha) = \frac{N(N-1)}{2} \langle \Psi | \delta(\alpha - \mathbf{r}_1 \cdot \mathbf{r}_2) | \Psi \rangle \quad (3a)$$

$$B(\beta) = \frac{N(N-1)}{2} \langle \Phi | \delta(\beta - \mathbf{p}_1 \cdot \mathbf{p}_2) | \Phi \rangle \quad (3b)$$

When devising methods to construct the distributions of the dot product variables $\mathbf{r} \cdot \mathbf{p}$ and $\mathbf{r}_{12} \cdot \mathbf{p}_{12}$, Bernard et al. discovered^{24,40,41} that it is straightforward to compute the Fourier transform of the desired distribution and then to back-transform this. We have found that this strategy is also effective for the generation of $A(\alpha)$ and $B(\beta)$.

For the Fourier transforms $\hat{A}(k)$ and $\hat{B}(k)$, the fundamental integrals^{42,43} over s -type Gaussians with exponents $\zeta_a, \zeta_b, \zeta_c$ and ζ_d and centers $\mathbf{A}, \mathbf{B}, \mathbf{C}$, and \mathbf{D} are given by

$$[\mathbf{0000}]_{\hat{A}} = \frac{8\pi^3 e^{-\mu|\mathbf{A}-\mathbf{B}|^2 - \lambda|\mathbf{C}-\mathbf{D}|^2}}{[4\nu\sigma + k^2]^{3/2}} \times \exp\left[-\frac{k^2[\nu P^2 + \sigma Q^2] + 4ik\nu\sigma\mathbf{P} \cdot \mathbf{Q}}{4\nu\sigma + k^2}\right] \quad (4a)$$

$$[\mathbf{0000}]_{\hat{B}} = \frac{\pi^3}{[\nu\sigma(1 + 4\mu\lambda k^2)]^{3/2}} \times \exp\left[-\frac{\mu R^2 + \lambda S^2 + 4ik\mu\lambda\mathbf{R} \cdot \mathbf{S}}{1 + 4\mu\lambda k^2}\right] \quad (4b)$$

where

$$\mathbf{P} = \frac{\zeta_a\mathbf{A} + \zeta_b\mathbf{B}}{\zeta_a + \zeta_b}, \quad \mathbf{Q} = \frac{\zeta_c\mathbf{C} + \zeta_d\mathbf{D}}{\zeta_c + \zeta_d} \quad (5)$$

$$\mathbf{R} = \mathbf{B} - \mathbf{A}, \quad \mathbf{S} = \mathbf{C} - \mathbf{D} \quad (6)$$

$$\mu = \frac{\zeta_a\zeta_b}{\zeta_a + \zeta_b}, \quad \lambda = \frac{\zeta_c\zeta_d}{\zeta_c + \zeta_d} \quad (7)$$

$$\nu = \zeta_a + \zeta_b, \quad \sigma = \zeta_c + \zeta_d \quad (8)$$

Integrals of higher angular momentum can be constructed using a five-term recurrence relation (RR) similar to the one we have recently derived for Dot and Posmom intracule integrals.²⁶ The RRs for augmenting the angular momentum of the Gaussian with center \mathbf{A} in the i direction ($i = x, y, z$) are given by

$$\begin{aligned} [(\mathbf{a} + \mathbf{1}_i)\mathbf{bcd}]_{\hat{A}} &= \left(\frac{\zeta_b}{\nu} (B_i - A_i) - \frac{k^2 P_i + 2gk\sigma Q_i}{4\nu\sigma + k^2} \right) \\ &\times [abcd]_{\hat{A}} + \frac{1}{2\nu} \left(1 - \frac{k^2}{4\nu\sigma + k^2} \right) \\ &\times (a_i [(\mathbf{a} - \mathbf{1}_i)\mathbf{bcd}]_{\hat{A}} \\ &+ b_i [a(\mathbf{b} - \mathbf{1}_i)\mathbf{cd}]_{\hat{A}}) - g \frac{k}{4\nu\sigma + k^2} \\ &\times (c_i [ab(\mathbf{c} - \mathbf{1}_i)\mathbf{d}]_{\hat{A}} \\ &+ d_i [abc(\mathbf{d} - \mathbf{1}_i)]_{\hat{A}}) \end{aligned} \quad (9a)$$

$$\begin{aligned} [(\mathbf{a} + \mathbf{1}_i)\mathbf{bcd}]_{\hat{B}} &= \frac{1}{\zeta_a(1 + 4\mu\lambda k^2)} (\mu R_i + 2gk\mu\lambda S_i) [abcd]_{\hat{B}} \\ &+ \frac{a_i}{2\zeta_a} \left(1 - \frac{\mu}{\zeta_a(1 + 4\mu\lambda k^2)} \right) \\ &\times [(\mathbf{a} - \mathbf{1}_i)\mathbf{bcd}]_{\hat{B}} + \frac{b_i}{2\nu(1 + 4\mu\lambda k^2)} \\ &\times [a(\mathbf{b} - \mathbf{1}_i)\mathbf{cd}]_{\hat{B}} + g \frac{k\mu\lambda}{\zeta_a(1 + 4\mu\lambda k^2)} \\ &\times \left(\frac{c_i}{\zeta_c} [ab(\mathbf{c} - \mathbf{1}_i)\mathbf{d}]_{\hat{B}} \right. \\ &\left. - \frac{d_i}{\zeta_d} [abc(\mathbf{d} - \mathbf{1}_i)]_{\hat{B}} \right) \end{aligned} \quad (9b)$$

where $\mathbf{a} = (a_x, a_y, a_z)$ is a vector of angular momentum quantum numbers and $g = \sqrt{-1}$. The RRs for augmenting the angular momentum on centers \mathbf{B}, \mathbf{C} , and \mathbf{D} are provided in the Supporting Information. For atomic systems, we have $\mathbf{P} = \mathbf{Q} = \mathbf{R} = \mathbf{S} = \mathbf{0}$, and the first term of each RR vanishes.

The Fourier transforms are formed by contracting these integrals with the two-electron reduced density matrix, i.e.,

$$\hat{A}(k) = \sum_{abcd} \Gamma_{abcd} [abcd]_{\hat{A}} \quad (10a)$$

$$\hat{B}(k) = \sum_{abcd} \Gamma_{abcd} [abcd]_{\hat{B}} \quad (10b)$$

Finally, the desired distributions are found as the inverse Fourier transforms

$$A(\alpha) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \hat{A}(k) e^{i\alpha k} dk \quad (11a)$$

$$B(\beta) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \hat{B}(k) e^{i\beta k} dk \quad (11b)$$

and, if these are constructed using both correlated and uncorrelated wave functions, the resulting holes are given by

$$\Delta A = A - A_{\text{HF}} \quad (12a)$$

$$\Delta B = B - B_{\text{HF}} \quad (12b)$$

It follows from the identities

$$\langle r^2 \rangle \equiv \frac{\langle (\mathbf{r}_1 - \mathbf{r}_2) \cdot (\mathbf{r}_1 - \mathbf{r}_2) \rangle}{2} + \langle \mathbf{r}_1 \cdot \mathbf{r}_2 \rangle \quad (13a)$$

Table 1. Decomposition of $\langle r^2 \rangle$ and T into Two-Electron Components, eq 14

atom	$\langle r^2 \rangle$	P_2	A_1	T	M_2	B_1
He ($1s^2$)	2.370	2.370	0	2.861	5.722	0
He (triplet $1s2s$)	18.406	18.406	0	2.215	4.429	0
He (triplet $1s2p$)	6.925	7.272	-0.173	2.436	5.404	-0.266
He (triplet $1s3d$)	4.715	4.715	0	3.514	7.028	0
Li	18.632	18.632	0	7.433	14.865	0
Be	17.320	17.320	0	14.573	29.146	0
B	15.862	16.571	-0.354	24.529	49.258	-0.101
C	13.803	14.512	-0.354	37.688	75.931	-0.278
N	12.093	12.703	-0.305	54.399	109.857	-0.530
O	11.215	11.731	-0.258	74.808	151.285	-0.835
F	10.259	10.693	-0.217	99.405	201.235	-1.213
Ne	9.385	9.751	-0.183	128.539	260.403	-1.663

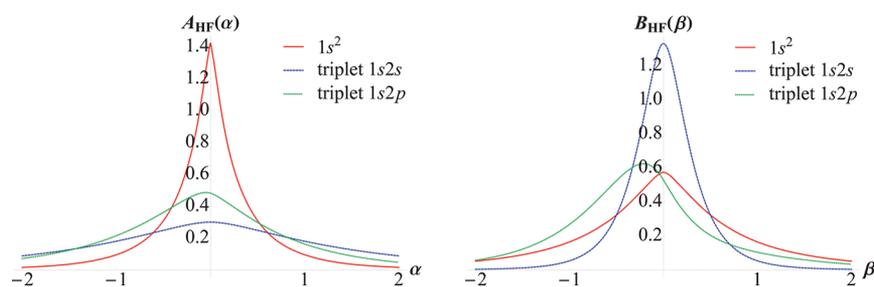


Figure 1. Position-dot (left) and momentum-dot (right) distributions for low-lying states of He.

$$\langle p^2 \rangle \equiv \frac{\langle (\mathbf{p}_1 - \mathbf{p}_2) \cdot (\mathbf{p}_1 - \mathbf{p}_2) \rangle}{2} + \langle \mathbf{p}_1 \cdot \mathbf{p}_2 \rangle \quad (13b)$$

that the second radial moment⁴⁴ $\langle r^2 \rangle$ and the kinetic energy T are related to moments of the two-electron distributions by

$$\begin{aligned} \langle r^2 \rangle &= \frac{1}{N-1} \left(\int_0^\infty u^2 P(u) du + 2 \int_{-\infty}^\infty \alpha A(\alpha) d\alpha \right) \\ &= P_2 + 2A_1 \end{aligned} \quad (14a)$$

$$\begin{aligned} 2T &= \frac{1}{N-1} \left(\int_0^\infty v^2 M(v) dv + 2 \int_{-\infty}^\infty \beta B(\beta) d\beta \right) \\ &= M_2 + 2B_1 \end{aligned} \quad (14b)$$

Likewise, the correlation contributions to $\langle r^2 \rangle$ and T can be related to hole moments by

$$\begin{aligned} \langle r^2 \rangle_c &= \frac{1}{N-1} \left(\int_0^\infty u^2 \Delta P(u) du + 2 \int_{-\infty}^\infty \alpha \Delta A(\alpha) d\alpha \right) \\ &= \Delta P_2 + 2\Delta A_1 \end{aligned} \quad (15a)$$

$$\begin{aligned} 2T_c &= \frac{1}{N-1} \left(\int_0^\infty v^2 \Delta M(v) dv + 2 \int_{-\infty}^\infty \beta \Delta B(\beta) d\beta \right) \\ &= \Delta M_2 + 2\Delta B_1 \end{aligned} \quad (15b)$$

In these relations, we have introduced quantities such as the reduced second moment of the position intracule, which is defined as

$$P_2 = \frac{1}{N-1} \int_0^\infty u^2 P(u) du \quad (16)$$

3. COMPUTATIONAL DETAILS

ROHF and CISD wave functions were computed using the aug-cc-pVTZ basis set for He and the aug-cc-pCVQZ(-fg) basis set for Li to F. (All calculations used six Cartesian, rather than five

pure, d functions.) Excited-state HF wave functions for helium were found using the Maximum Overlap Method (MOM)^{45,46} within the Q-Chem software package.⁴⁷ The ROHF and CISD wave functions were computed using the GAMESS⁴⁸ software package, and the two-electron distributions were extracted from the resulting wave functions using in-house software.

In section 4, we study the effects of Pauli exchange by restricting our attention to the distributions $A_{\text{HF}}(\alpha)$ and $B_{\text{HF}}(\beta)$ obtained from HF wave functions. In section 5, we examine the effects of correlation and contrast these with those of exchange.

4. HARTREE-FOCK CALCULATIONS

4.1. $A_{\text{HF}}(\alpha)$ and $B_{\text{HF}}(\beta)$ in Small Atoms. The ground, or singlet $1s^2$, state of the He atom is more compact than the triplet $1s2s$ and $1s2p$ states, and this is reflected in the $\langle r^2 \rangle$ values in Table 1. It is therefore unsurprising to find that the distribution of $\alpha = \mathbf{r}_1 \cdot \mathbf{r}_2$ in the $1s^2$ state is much narrower than those in the triplet $1s2s$ and $1s2p$ states (Figure 1, left).

The electrons move more rapidly in the $1s^2$ state than in the triplet $1s2s$ and $1s2p$ states, and this is reflected in the T values in Table 1. It is therefore unsurprising to find that the distribution of $\beta = \mathbf{p}_1 \cdot \mathbf{p}_2$ in the $1s^2$ state is much broader than those in the triplet $1s2s$ and $1s2p$ states (Figure 1, right).

The distributions in Figure 1 also differ in their symmetry about the origin. The symmetry of $A_{\text{HF}}(\alpha)$ in the $1s^2$ and triplet $1s2s$ states means that the two electrons are equally likely to be found on the same, or opposite, sides of the nucleus. The symmetry of $B_{\text{HF}}(\beta)$ in the $1s^2$ and triplet $1s2s$ states means the electrons are equally likely to be found traveling with aligned, or opposed, momenta. In contrast, $A_{\text{HF}}(\alpha)$ and $B_{\text{HF}}(\beta)$ are asymmetric in the triplet $1s2p$ state, implying that the electrons are more likely to be found on opposite sides of the nucleus (where $\alpha < 0$) than on the same side (where $\alpha > 0$) and that they are more likely to be found with opposed ($\beta < 0$) rather

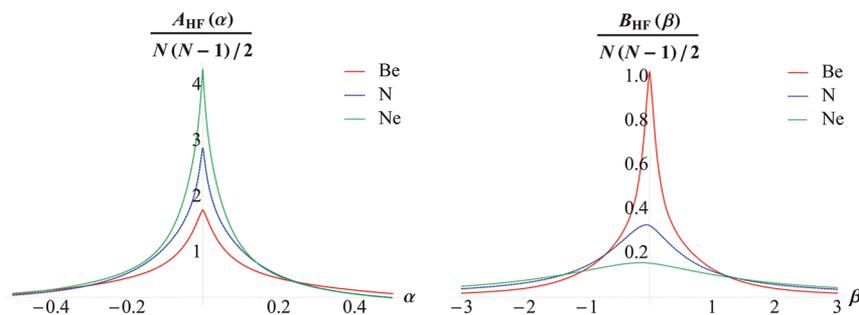


Figure 2. Position-dot (left) and momentum-dot (right) distributions for Be, N, and Ne.

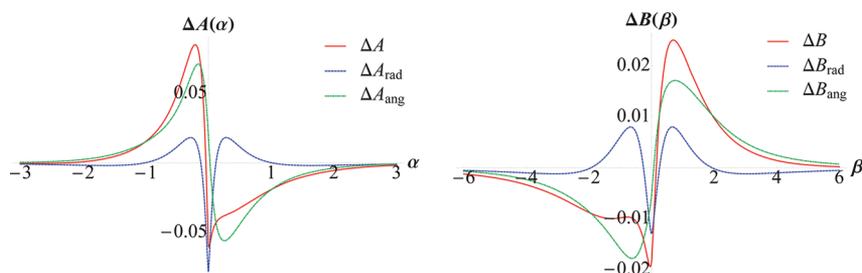


Figure 3. Position-dot (left) and momentum-dot (right) holes in the ground state of He.

than aligned ($\beta > 0$) momenta. Surprisingly, however, higher excited states (e.g. triplet $1s3d$) have symmetric distributions.

This curious anomaly was first explained by Koga.³⁹ In cases such as the triplet $1s2p$ state, where the electrons occupy orbitals whose angular momenta differ by unity, the exchange effect increases their angular separation, leading to an increase in the probability of $\alpha < 0$ and breaking the symmetry of $A_{\text{HF}}(\alpha)$. A similar effect is observed in momentum space, where the exchange interaction leads to an increased probability of opposed momenta, $\beta < 0$.

The current analysis of the effects of Pauli exchange on the low-lying states of helium complement the analysis of singly excited states of two-electron ions by Cann et al.,^{49,50} wherein the effects of exchange are revealed through comparison of both one and two-electron distributions of singlet and triplet states with the same electronic configuration.

Understanding $A_{\text{HF}}(\alpha)$ and $B_{\text{HF}}(\beta)$ for the low-lying states of helium enables us to rationalize the corresponding distributions in many-electron atoms such as Be, N, and Ne (Figure 2). As the nuclear charge increases, the atoms become more compact; small r_1 , r_2 , and $\alpha = \mathbf{r}_1 \cdot \mathbf{r}_2$ values become more likely; and the $A_{\text{HF}}(\alpha)$ distribution becomes narrower. At the same time, large p_1 , p_2 , and $\beta = \mathbf{p}_1 \cdot \mathbf{p}_2$ values become more likely, and the $B_{\text{HF}}(\beta)$ distribution becomes broader.

As before, exchange effects play a subtle role. In Be, which has only $1s$ and $2s$ electrons, $A_{\text{HF}}(\alpha)$ and $B_{\text{HF}}(\beta)$ are symmetric. This means that a given pair of electrons in Be are equally likely to be found on the same, or opposite, sides of the nucleus and to have aligned, or opposing, momenta. However, in N and Ne, exchange between the $2p$ and ns electrons skews both $A_{\text{HF}}(\alpha)$ and $B_{\text{HF}}(\beta)$ to the left. These effects are visible upon careful inspection of Figure 2.

4.2. Two-Electron Decompositions of Atomic Size and Kinetic Energy. The size $\langle r^2 \rangle$ and kinetic energy T of a system are one-electron quantities. Nonetheless, eq 14 shows that they can be exactly decomposed into an intracuclear contribution from the second moment of $P(u)$ or $M(v)$ and an orientational contribution from the first moment of $A(\alpha)$ or $B(\beta)$. Table 1

illustrates this for various states of helium and the ground-state first-row atoms.

The first moment of a symmetric distribution is identically zero, and therefore the orientational contributions to $\langle r^2 \rangle$ and T vanish in the $1s^2$ and triplet $1s2s$ states of He. For the same reasons, the orientational contributions to $\langle r^2 \rangle$ and T vanish in the ground-state Li and Be atoms.

In the heavier atoms, the orientational contribution A_1 to the atomic size is always negative, indicating that the contraction of atomic radii across the periodic table is aided by Pauli exchange. This interaction tends to keep s and p electrons in opposite hemispheres, thus reducing their mutual repulsion and facilitating a more compact electron density. As we proceed from B to Ne, the atomic radii become smaller, and the magnitude of the orientational contribution decreases.

In these same atoms, because exchange increases the probability that s and p electrons move in opposite directions, the relative-motion component overestimates the kinetic energy and has to be corrected by a negative orientational contribution B_1 . As we proceed from B to Ne, the electrons move more quickly, and the magnitude of this orientational correction increases.

5. CORRELATED CALCULATIONS

5.1. $A(\alpha)$ and $B(\beta)$ in the He Atom. The position-dot hole $\Delta A(\alpha)$ and the momentum-dot hole $\Delta B(\beta)$ of helium are shown in Figure 3. Like $\Delta M(v)$, these holes can be understood in terms of angular and radial correlation effects,²⁹ and we define the radial components by

$$\Delta A_{\text{rad}} = A^s - A_{\text{HF}}^s \quad (17a)$$

$$\Delta B_{\text{rad}} = B^s - A_{\text{HF}}^s \quad (17b)$$

(the superscript indicates that only s basis functions are used) and the angular components by

$$\Delta A_{\text{ang}} = \Delta A - \Delta A_{\text{rad}} \quad (18a)$$

$$\Delta B_{\text{ang}} = \Delta B - \Delta B_{\text{rad}} \quad (18b)$$

ΔA_{rad} is symmetric because, by definition, radial correlation cannot affect the interelectronic angle θ_{12} . It favors moderate $r_1 r_2$ values, at the expense of small and large ones, for it reduces the probability of both electrons being close to, or far from, the nucleus, while increasing the probability that one is close and the other is far. In contrast, angular correlation favors negative α ($\theta_{12} > 90^\circ$) over positive α ($\theta_{12} < 90^\circ$). The relative magnitude of the radial and angular correlation effects on two-electron distributions have been the subject of previous studies.^{51,52}

ΔB_{rad} is symmetric and favors moderate $p_1 p_2$ values, presumably because the electron that is close to the nucleus is moving fast and the distant one is moving slowly. Angular correlation increases the probability of aligned momenta²⁹ and therefore favors positive β over negative β .

Angular correlation works in the same direction as exchange in position space, but in the opposite direction in momentum space. Thus, whereas both exchange and correlation tend to keep the electrons in opposite hemispheres of the atom ($\alpha < 0$), exchange increases the likelihood that electrons travel in opposite directions ($\beta < 0$) and correlation increases the likelihood that they travel in the same direction ($\beta > 0$).

5.2. Correlation Effects in First-Row Atoms. Table 2 shows how electron correlation affects the size $\langle r^2 \rangle$ and kinetic

Table 2. Decomposition of $\langle r^2 \rangle_c$ and T_c into Two-Electron Components, eq 15

atom	$\langle r^2 \rangle_c$	ΔP_2	ΔA_1	T_c	ΔM_2	ΔB_1
He	0.023	0.155	-0.066	0.037	-0.250	0.162
Li	-0.209	-0.141	-0.034	0.002	-0.302	0.153
Be	-0.915	0.337	-0.626	0.085	-0.118	0.144
B	-0.360	0.154	-0.257	0.112	-0.086	0.155
C	-0.033	0.182	-0.108	0.134	-0.079	0.174
N	0.129	0.207	-0.039	0.149	-0.100	0.199
O	0.220	0.301	-0.040	0.199	-0.109	0.253
F	0.212	0.284	-0.036	0.252	-0.140	0.322
Ne	0.192	0.253	-0.031	0.308	-0.193	0.405

energy T of the ground-state first-row atoms, and eq 15 relates these changes to the correlation effects on the two-electron moments P_2 , A_1 , M_2 , and B_1 . Correlation consistently decreases A_1 (because it increases the angular separation of the electrons) and increases B_1 (because it aligns their momenta), but whereas the ΔB_1 are fairly uniform, the ΔA_1 are particularly large for Be, B, and C. These anomalies reflect the strong static correlation in these atoms, which arises because of the near-degeneracy of their occupied 2s and unoccupied 2p orbitals and which leads to pronounced angular correlation between the L shell electrons.^{53–55}

In most of the atoms, the decrease in A_1 is offset by an increase in P_2 (the mean squared interelectronic distance). However, in the Li atom, ΔP_2 is negative, implying that correlation decreases $\langle u^2 \rangle$. The fact that correlation also decreases $\langle u^{-1} \rangle$ (the two-electron energy) means that, in this atom, correlation increases the likelihood of moderate u values, at the expense of both large and small ones. The Li atom is therefore another simple system with a secondary position hole (see Figure 4).^{32–35}

Correlation almost always reduces the electrostatic energy between electrons, and by the virial theorem, the kinetic energy

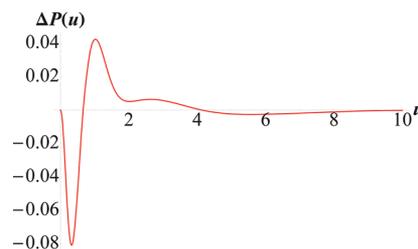


Figure 4. Position hole for Li.

therefore increases. However, although the total change T_c is positive, the results in Table 2 reveal that it comes from a relative-motion component $\Delta M_2/2$, which is negative, and a momentum-alignment component ΔB_1 , which is strongly positive. In other words, when correlation is introduced, whereas the other electrons seem to move more slowly from the perspective of a given electron, they are actually all moving faster.

6. CONCLUSIONS

The intracules $P(u)$ and $M(v)$ are useful for examining details of electronic structure including the effects of electron correlation. However, ambiguities may arise due to the dependence of u (or v) on both the magnitudes and relative orientation of \mathbf{r}_1 and \mathbf{r}_2 (or \mathbf{p}_1 and \mathbf{p}_2). The position-dot, $A(\alpha)$, and momentum-dot, $B(\beta)$, distributions introduced here offer both a tool for resolving such ambiguities and a new perspective on the relative motion of electrons. They also provide a direct connection between $P(u)$ and $M(v)$ and their associated one-electron properties, $\langle r^2 \rangle$ and T .

Exchange effects between electrons in orbitals whose angular momenta differ by unity breaks the symmetry of the $A(\alpha)$ and $B(\beta)$ distributions, skewing them to the left. In position space, this leads to an increase in the angular separation of the electrons. In momentum space, it increases the probability of opposing electron momenta. This exchange effect plays a role in the well-known decrease in atomic radii from left to right across the periodic table. As the 2p orbitals are filled from B to Ne, the exchange between s and p electrons increases their angular separation and mitigates the increase in electron repulsion as the atomic radii decrease.

Correlation effects on $A(\alpha)$ and $B(\beta)$ can be decomposed into radial and angular contributions. The radial effects are symmetric and increase the probability of moderate α and β values. The angular effects are asymmetric, increasing the probability of $\alpha < 0$ (i.e., the electrons are on opposite sides of the nucleus) and $\beta > 0$ (i.e., they travel in the same direction).

Overall, exchange and correlation have similar effects on $A(\alpha)$ but opposing effects on $B(\beta)$.

■ ASSOCIATED CONTENT

📄 Supporting Information

The recurrence relations (RRs) for augmenting the angular momentum on Gaussian centers **B**, **C**, and **D** of the fundamental $\hat{A}(k)$ and $\hat{B}(k)$ integrals are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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