Computation and analysis of molecular Hartree–Fock momentum intracules

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An efficient general algorithm for the computation of molecular momentum intracule densities from Hartree–Fock wavefunctions using Gaussian basis functions is described. The momentum intracules for a number of systems are examined, and comparison with their position space counterparts discussed.

1. Introduction

Since it is easier to comprehend than a many-electron wavefunction $\Psi(\mathbf{r}_i)$, the one-electron density $\rho(\mathbf{r})$, which measures the probability of finding an electron at a given point in space has been extensively studied, both theoretically and experimentally [1]. However, some important information is lost when $\Psi(\mathbf{r}_i)$ is reduced to $\rho(\mathbf{r})$. An important intermediate quantity is the intracule density $P(u)$, which measures the probability of finding two electrons separated by $u = |\mathbf{r}_1 - \mathbf{r}_2|$. Since intracule densities are two-electron functions they are well suited to studying interelectronic interactions and, in particular, the effects of electron correlation. However despite their potential usefulness, intracules have not yet been widely embraced by quantum chemists.

In 1961 Coulson and Neilson [2] derived intracules for helium from both uncorrelated and correlated wavefunctions and used these to investigate the shape of the Coulomb hole. Their work was later extended to study the dependence of the Coulomb hole on the nuclear charge of He-like ions [3, 4]. Subsequently, intracules have been reported for a number of atoms and small molecules using both uncorrelated and correlated wavefunctions [5–13], confirming the intuitive result that electron correlation increases the average separation between electrons.

Early intracule work has focused on highly accurate descriptions of small systems. However, in recent years there has been an effort towards the computation of intracules for large molecular systems [14, 15]. Very recently, the computation of the Coulomb and exchange Hartree–Fock (HF) intracules for Gaussian wavefunc-

tions within the PRISM [16, 17] approach has been reported [18] and implemented within Q-Chem [19]. This has enabled intracules for large systems, such as endothelin-1 ($C_{82}H_{121}N_{20}O_{25}S_5$) [18] and graphene ($C_{96}H_{24}$) [20], to be studied.

Both the one-electron and intracule densities are easily visualized in position space. However, analogous densities can be constructed in momentum space. Here $\hat{\rho}(\mathbf{p})$ measures the probability of an electron having a momentum $\mathbf{p}$ and the associated intracule density, $P(v)$, measures the probability of finding two electrons with relative momentum $v = |\mathbf{p}_1 - \mathbf{p}_2|$. Electron densities in momentum space are complementary to position space and yield additional information. The inter-relationships between these representations has been discussed by Thakker *et al.* [21]. Experimentally the one-electron density $\hat{\rho}(\mathbf{p})$ can be measured through Compton profile experiments [22], while the intracule density $P(v)$ can be related to scattering experiments [23] and, as we show later, the kinetic energy. Theoretical investigations of momentum intracules have been reported by a number of authors.

Both Fermi and Coulomb holes have been studied in momentum space [24–34]. These studies have included a number of atoms and diatomic molecules, exploring factors such as the Z dependence of the momentum intracules [30, 34]. Koga and Matsuyama have reported moments of intracules [35–37] and extracules [37–39] in momentum space for many atoms, based on numerical HF wavefunctions. Although there have been a number of studies of momentum intracules, these have been limited to atoms and small molecules.

The aim of this paper is to extend the study of momentum intracules to large molecular systems. We present the theory of momentum intracules for HF

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wavefunctions using Gaussian basis functions, and describe an implementation within Q-Chem [19] to evaluate these intracules. Finally, we compute and discuss momentum intracules for a number of examples.

2. Theory

Suppose we have a many-electron system whose wavefunction in position space is given by Ψ. Then its position intracule

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

gives the distribution of the interelectronic separation. If Ψ is an HF wavefunction, we can partition $P(u)$ into Coulomb and exchange parts, i.e.

$$P(u) = J(u) + K(u), \tag{2}$$

where the Coulomb intracule is defined by

$$J(u) = \frac{1}{2} \langle \rho | \delta(r_{12} - u) | \rho \rangle, \tag{3}$$

and the exchange intracule is defined by

$$K(u) = -\frac{1}{2} \langle \chi_a \chi_b | \delta(r_{12} - u) | \chi_a \chi_b \rangle. \tag{4}$$

(The χ are spin orbitals and we have used the summation convention.) If the molecular orbitals ψ_a are expanded in a basis set $\{\phi_\mu\}$

$$\psi_a = \sum_\mu c_{\mu a} \phi_\mu, \tag{5}$$

then the $J(u)$ and $K(u)$ intracules can be written in terms of density matrices as

$$J(u) = \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} (\mu\nu|\lambda\sigma)_u, \tag{6}$$

$$K(u) = -\frac{1}{2} \sum_{\mu\nu\lambda\sigma} (P_{\mu\lambda}^\alpha P_{\nu\sigma}^\alpha + P_{\mu\lambda}^\beta P_{\nu\sigma}^\beta)(\mu\nu|\lambda\sigma)_u, \tag{7}$$

where $(\mu\nu|\lambda\sigma)_u$ are integrals of the form

$$(\mu\nu|\lambda\sigma)_u = \int\int \phi_\mu(\mathbf{r}_1)\phi_\nu^*(\mathbf{r}_1)\delta(r_{12} - u)$$
$$\times \phi_\lambda(\mathbf{r}_2)\phi_\sigma^*(\mathbf{r}_2)\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\,\mathrm{d}\Omega_u. \tag{8}$$

Some of the moments of these intracules are physically-significant and can be generated readily [40]. For example, we have

$$\int_0^\infty u^0 P(u)\,\mathrm{d}u = \frac{n(n-1)}{2}, \tag{9}$$

$$\int_0^\infty u^0 J(u)\,\mathrm{d}u = \frac{n^2}{2}, \tag{10}$$

$$\int_0^\infty u^2 J(u)\,\mathrm{d}u = nQ - \mu^2, \tag{11}$$

$$\int_0^\infty u^0 K(u)\,\mathrm{d}u = -\frac{n}{2}, \tag{12}$$

where n is the number of electrons, μ is the electronic dipole moment and Q is the trace of the electronic quadrupole moment tensor.

The momentum intracule can be defined in a similar way:

$$P(v) = \frac{n(n-1)}{2} \langle \hat{\Psi} | \delta(p_{12} - v) | \hat{\Psi} \rangle, \tag{13}$$

where $\hat{\Psi}$ represents the wavefunction in momentum space. For an HF wavefunction, the corresponding Coulomb and exchange intracules are given by

$$J(v) = \frac{1}{2} \langle \hat{\rho} | \delta(p_{12} - v) | \hat{\rho} \rangle, \tag{14}$$

$$K(v) = -\frac{1}{2} \langle \hat{\chi}_a \hat{\chi}_b | \delta(p_{12} - v) | \hat{\chi}_a \hat{\chi}_b \rangle, \tag{15}$$

where the $\hat{\chi}$ are the HF momentum spin orbitals. The momentum intracules $J(v)$ and $K(v)$ can be constructed through

$$J(v) = \frac{1}{2} \sum_{\mu\nu\lambda\sigma} P_{\mu\nu} P_{\lambda\sigma} (\mu\nu|\lambda\sigma)_v, \tag{16}$$

$$K(v) = -\frac{1}{2} \sum_{\mu\nu\lambda\sigma} (P_{\mu\lambda}^\alpha P_{\nu\sigma}^\alpha + P_{\mu\lambda}^\beta P_{\nu\sigma}^\beta)(\mu\nu|\lambda\sigma)_v. \tag{17}$$

The two-electron integrals are defined by

$$(\mu\nu|\lambda\sigma)_v = \int\int \hat{\phi}_\mu(\mathbf{p}_1)\hat{\phi}_\nu^*(\mathbf{p}_1)\delta(p_{12} - v)$$
$$\times \hat{\phi}_\lambda(\mathbf{p}_2)\hat{\phi}_\sigma^*(\mathbf{p}_2)\,\mathrm{d}\mathbf{p}_1\,\mathrm{d}\mathbf{p}_2\,\mathrm{d}\Omega_v, \tag{18}$$

where $\hat{\phi}_\mu(\mathbf{p})$ is the Fourier transform of the basis function $\phi_\mu(\mathbf{r})$, but this can be simplified to

$$(\mu\nu|\lambda\sigma)_v = \frac{v^2}{2\pi^2} \int \phi_\mu(\mathbf{r})\phi_\nu^*(\mathbf{r} + \mathbf{q})\phi_\lambda(\mathbf{r} + \mathbf{q} + \mathbf{u})$$
$$\times \phi_\sigma^*(\mathbf{r} + \mathbf{u})j_0(vq)\,\mathrm{d}\mathbf{q}\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{u}. \tag{19}$$

The even-order moments of the momentum intracules are also physically significant

$$\int_0^\infty v^0 P(v)\,\mathrm{d}v = \frac{n(n-1)}{2}, \tag{20}$$

$$\int_0^\infty v^0 J(v)\,\mathrm{d}v = \frac{n^2}{2}, \tag{21}$$

$$\int_0^\infty v^2 J(v)\,\mathrm{d}v = 2nE_{\mathrm{T}}, \tag{22}$$

$$\int_0^\infty v^o K(v)\,\mathrm{d}v = -\frac{n}{2}, \tag{23}$$

where n is the number of electrons and E_{T} is the total electronic kinetic energy.

The position space integrals $(\mu\nu|\lambda\sigma)_u$ exhibit eightfold permutational symmetry, i.e.

$$(\mu\nu|\lambda\sigma)_u = (\nu\mu|\sigma\lambda)_u = (\sigma\lambda|\nu\mu)_u = (\lambda\sigma|\mu\nu)_u$$
$$= (\nu\mu|\lambda\sigma)_u = (\mu\nu|\sigma\lambda)_u = (\lambda\sigma|\nu\mu)_u = (\sigma\lambda|\mu\nu)_u. \tag{24}$$

The momentum space integrals $(\mu\nu|\lambda\sigma)_v$ possess only fourfold permutational symmetry, i.e.

$$(\mu\nu|\lambda\sigma)_v = (\nu\mu|\sigma\lambda)_v = (\sigma\lambda|\nu\mu)_v = (\lambda\sigma|\mu\nu)_v, \tag{25}$$

$$(\nu\mu|\lambda\sigma)_v = (\mu\nu|\sigma\lambda)_v = (\lambda\sigma|\nu\mu)_v = (\sigma\lambda|\mu\nu)_v, \tag{26}$$

and therefore the generation of momentum intracules is roughly twice as expensive as that of position intracules.

3. Implementation

Following the recent implementation [18] to compute $P(u)$, we have employed the PRISM algorithm [16, 17] to evaluate the $(\mu\nu|\lambda\sigma)_u$ integrals. For four s functions on centres **A**, **B**, **C** and **D** with exponents $\alpha, \beta, \gamma, \delta$ and contraction coefficients D_a, D_b, D_c, D_d, respectively, it can be shown that the fundamental integrals [16] are given by

$$[m]_v = U_P U_Q (2\hat{\theta}^2)^{m+3/2}\,\mathrm{e}^{R^2} v^2\,\mathrm{e}^{-v^2\hat{\theta}^2}$$
$$\times \sqrt{\frac{2}{\pi}} \sum_{k=1}^m \binom{m}{k}(-2\hat{\theta}^2 v^2)^k \frac{j_k[2\hat{\theta}Rv]}{(2\hat{\theta}Rv)^k}, \tag{27}$$

where

$$\mathbf{R} = \frac{\lambda}{(\kappa+\lambda)^{1/2}}(\mathbf{C}-\mathbf{D}) - \frac{\kappa}{(\kappa+\lambda)^{1/2}}(\mathbf{A}-\mathbf{B}), \tag{28}$$

$$U_P = D_a D_b \left(\frac{\pi}{\zeta}\right)^{3/2} \mathrm{e}^{-\kappa|\mathbf{A}-\mathbf{B}|^2}, \tag{29}$$

$$U_Q = D_c D_d \left(\frac{\pi}{\eta}\right)^{3/2} \mathrm{e}^{-\lambda|\mathbf{C}-\mathbf{D}|^2}, \tag{30}$$

$$\hat{\theta}^2 = \frac{1}{4(\kappa+\lambda)}, \tag{31}$$

$$\kappa = \frac{\alpha\beta}{\zeta}, \tag{32}$$

$$\lambda = \frac{\gamma\delta}{\eta}, \tag{33}$$

$$\zeta = \alpha + \beta, \tag{34}$$

$$\eta = \gamma + \delta, \tag{35}$$

and j_n are spherical Bessel functions

$$j_n(x) = x^n \left(-\frac{1}{x}\frac{\mathrm{d}}{\mathrm{d}x}\right)^n \frac{\sin(x)}{x}. \tag{36}$$

Integrals of higher angular momentum are generated through the differentiation of $[0]_v$ with respect to the coordinates of **A**, **B**, **C** and **D** [41]. Alternatively, they can be generated using recursion relations of the form

$$[(\mathbf{a}+\mathbf{1}_i)\mathbf{b}|\mathbf{cd}]^{(m)}$$
$$= \left(\frac{2\beta}{2\zeta}\right)\Bigg\{ (B_i - A_i)[\mathbf{ab}|\mathbf{cd}]^{(m)} - \left(\frac{R_i}{\hat{\theta}}\right)[\mathbf{ab}|\mathbf{cd}]^{(m+1)}$$
$$- a_i \left[\left(\frac{1}{2\alpha}\right)[(\mathbf{a}-\mathbf{1}_i)\mathbf{b}|\mathbf{cd}]^{(m)}\right.$$
$$\left.- \left(\frac{2\beta}{2\zeta}\right)[(\mathbf{a}-\mathbf{1}_i)\mathbf{b}|\mathbf{cd}]^{(m+1)}\right]$$
$$+ b_i \left[\left(\frac{1}{2\beta}\right)[\mathbf{a}(\mathbf{b}-\mathbf{1}_i)|\mathbf{cd}]^{(m)}\right.$$
$$\left.- \left(\frac{2\alpha}{2\zeta}\right)[\mathbf{a}(\mathbf{b}-\mathbf{1}_i)|\mathbf{cd}]^{(m+1)}\right]$$
$$- c_i \left(\frac{2\delta}{2\eta}\right)[\mathbf{ab}|(\mathbf{c}-\mathbf{1}_i)\,\mathbf{d}]^{(m+1)}$$
$$+ d_i \left(\frac{2\gamma}{2\eta}\right)[\mathbf{ab}|\mathbf{c}(\mathbf{d}-\mathbf{1}_i)]^{(m+1)}\Bigg\}. \tag{37}$$

In the current implementation, the loop over the points v is located within the loop over shell-quartets. Within the loop over v, both $(\mu\nu|\lambda\sigma)_v$ and $(\mu\nu|\sigma\lambda)_v$ integrals are computed. These represent the two fourfold sets of integrals that would correspond to one eightfold set in position space. For small x the $j_n(x)/x^n$ in expression (27) are evaluated through a power series expansion. Subsequently, $P(v)$ is evaluated by the appropriate contraction with the HF density matrix elements. For checking purposes, we have used quadrature to confirm the moment equations (20)–(23) are satisfied.

Before studying complex systems using Gaussian wavefunctions, we shall examine some simple systems for which position and momentum intracules can be derived in closed form.

4. Intracules for the helium atom

The He atom provides a simple system in which HF intracules can be studied. If we take the simple position wavefunction

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{a^3}{\pi} e^{-a(r_1+r_2)}, \qquad (38)$$

it can be shown [20] that

$$P(u) = \frac{a^3 u^2}{6}(3 + 6au + 4a^2u^2) e^{-2au}. \qquad (39)$$

Taking the Fourier transform of equation (38) yields the momentum wavefunction

$$\Psi(\mathbf{p}_1, \mathbf{p}_2) = \frac{8a^5}{\pi^2(a^2 + p_1^2)^2(a^2 + p_2^2)^2}, \qquad (40)$$

from which it can be shown that

$$P(v) = \frac{64a^5(1584a^4v^2 + 88a^2v^4 + 3v^6)}{3\pi(4a^2 + v^2)^6}. \qquad (41)$$

Equations (39) and (41) show that the intracules in position and momentum space behave differently. Both decrease quadratically near the origin but, whereas the position intracule eventually decays exponentially, the momentum intracule decays only as v^{-6}. This is illustrated in figure 1, which depicts $P(u)$ and $P(v)$ for the variationally optimal exponent $a = 27/16$. The momentum intracule is more diffuse, indicating that a high relative momentum is more likely than a high relative separation. Figure 2 shows how $P(u)$ and $P(v)$ vary as the exponent is changed. The top panel depicts the intracules for a diffuse orbital ($a = 27/32$) where there is
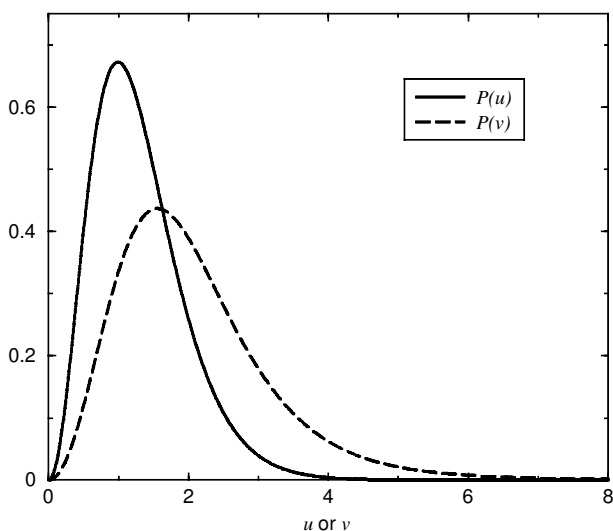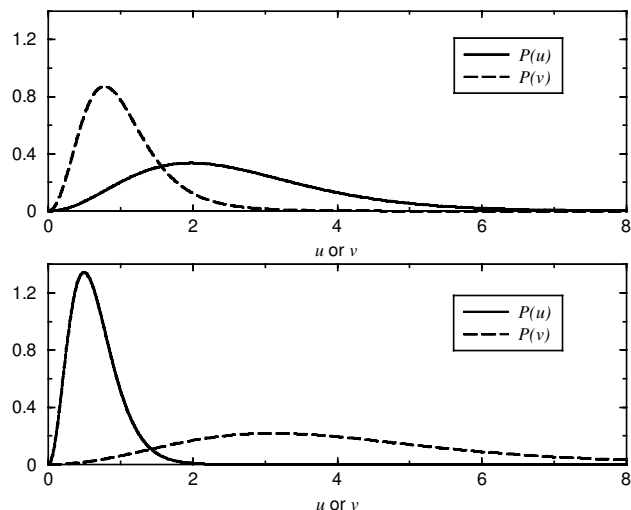

Figure 2. $P(u)$ and $P(v)$ for the He atom using $a = 27/32$ (upper panel) and $a = 27/8$ (lower panel).

a broad distribution of the relative separation of the electrons. The corresponding momentum intracule is relatively narrow because when the electrons are further from the nucleus their momenta decrease and, consequently, the probability of large relative momentum decreases. For a compact orbital ($a = 27/8$) the properties of $P(u)$ and $P(v)$ are interchanged. There is a narrow distribution of relative separation and a broad distribution of the relative momentum. This demonstrates the complementary behaviour of the position and momentum intracules.

The effect of correlation can be illustrated by the Coulomb hole, which is defined [2] as

$$\Delta P(u) = P(u)^{\text{Correlated}} - P(u)^{\text{HF}}, \qquad (42)$$

and similarly for $P(v)$. Both position and momentum intracules can be generated for correlated wavefunctions and their respective Coulomb holes studied. In position space the shape of the ground state Coulomb hole of He is well known [2]. Electron correlation results in a more diffuse intracule with greater intracule density for large u. In momentum space, the effect of correlation is more complex [24]. If the relative separation is small, both electrons moving in the same direction (low v) and electrons moving towards each other (high v) will be disfavoured when electron correlation is introduced.

5. Larger systems

Figure 3 shows HF intracules for the He atom computed using STO-3G and 6-311G basis sets. Both intracules show some sensitivity to the basis set used. The HF/6-311G intracules are almost identical to those derived from the HF-limit wavefunction of Roothaan
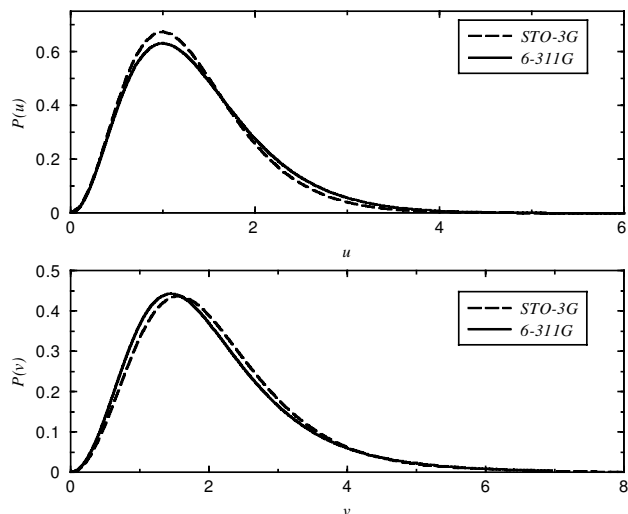

Figure 1.   Position and momentum intracules for the He atom, $a = 27/16$.

Figure 3. $P(u)$ and $P(v)$ for the He atom using different basis sets.

Figure 5. $K(u)$ and $K(v)$ for the Be atom using different basis sets.

et al. [42], leading us to conclude that the STO-3G basis introduces some error but that increasing the size of the basis set beyond 6-311G does not result in significant change.

Analogous intracules for the Be atom are shown in figure 4. Because the $1s$ electrons are close together and move relatively quickly, they are responsible for the inner peak in $P(u)$ and the outer peak in $P(v)$. Conversely, because the $2s$ electrons occupy a relatively large orbital and move more slowly, the $1s$–$2s$ and $2s$–$2s$ interactions provide the outer peak in $P(u)$ and the inner one in $P(v)$. Thus, although both $P(u)$ and $P(v)$ are bimodal, we see that their peaks anti-correspond. This observa-
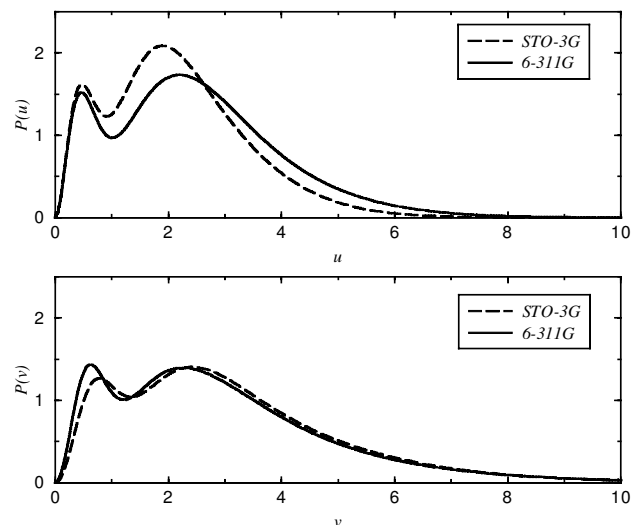
tion also rationalizes the behaviour of the intracules as the basis set is changed: because the STO-3G basis describes the $1s$ orbital better than the $2s$ orbital, the STO-3G and 6-311G intracules agree best for small u and large v. The corresponding exchange intracules (figure 5) show similar trends. In position space, the large peak for low u arises from the inner $1s$ electrons and the outer $2s$ electrons give rise to a broad peak that is described poorly by the STO-3G basis set. In momentum space, the inner $1s$ electrons result in a broad peak with a long tail, while the narrow peak for low v arises from the $2s$ electrons.

Figure 6 shows position and momentum intracules for H_2 as the bond length is increased, for both RHF and UHF wavefunctions. In the RHF case, two distinct peaks develop in the position intracule because the wavefunction contains both ionic ($H^+ + H^-$) contributions, in which the electrons are close together, and covalent ($H\cdot + H\cdot$) contributions, in which they are far apart. By contrast, because the UHF wavefunction dissociates correctly to two neutral H atoms, the UHF intracule lacks the spurious peak for low u. The difference between the RHF and UHF momentum intracules is less stark. The RHF intracule becomes narrower when the bondlength is extended, reflecting the contribution of the H^- ions which will have a diffuse, low momentum, orbital. As the bond length is increased the UHF intracule broadens because of the loss of low momentum electron density between the hydrogen atoms.

Figure 7 shows scaled intracule densities for a variety of organic molecules. Whereas $P(u)$ contain several peaks that reflect the geometrical structure of the molecules [20], $P(v)$ intracules are smooth almost
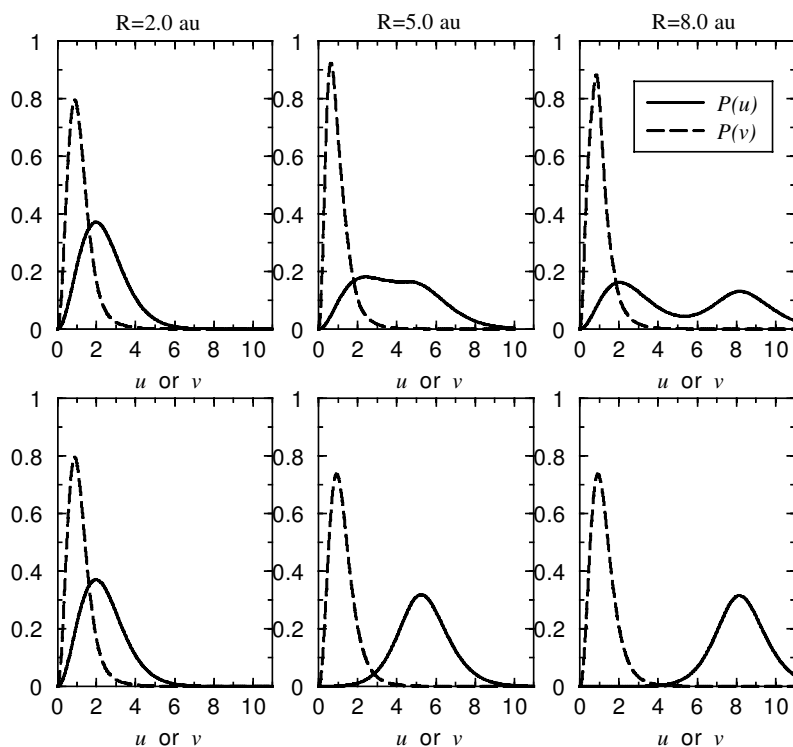

Figure 4. $P(u)$ and $P(v)$ for the Be atom using different basis sets.

Figure 6. $P(u)$ and $P(v)$ for H_2 at various bond lengths, using RHF/6-311G (upper panels) and UHF/6-311G (lower panels) wavefunctions.
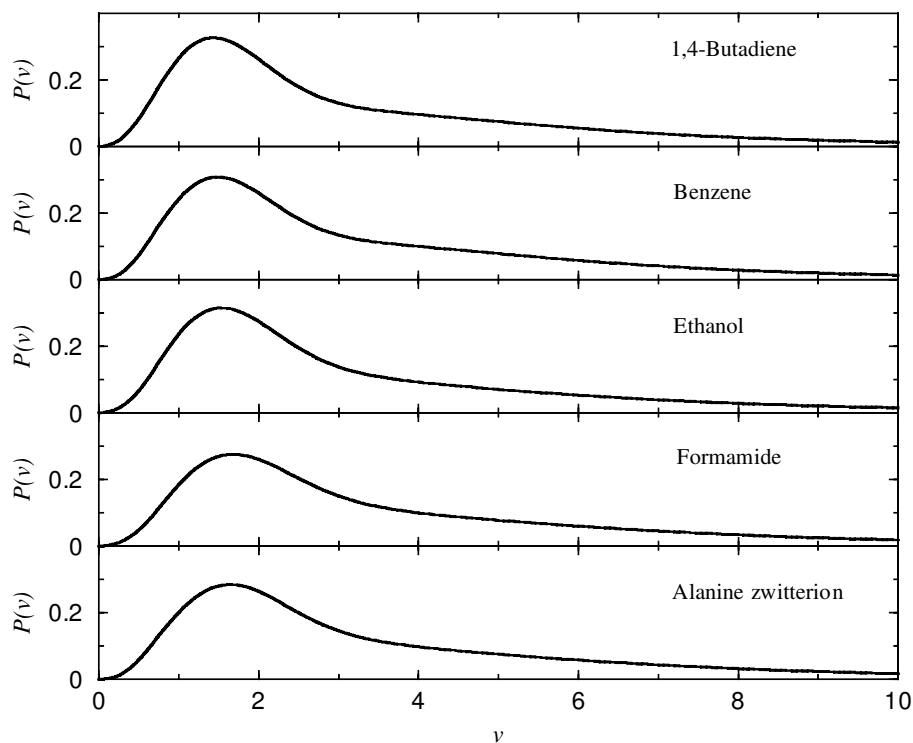

Figure 7. Normalized HF/6-311G intracules for a variety of organic molecules.

featureless functions with similar shapes, that show little sensitivity to molecular structure. It is interesting that two molecules may have strikingly different position intracules and nearly indistinguishable momentum intracules. Closer inspection reveals small differences between the $P(v)$. In particular, when heavier elements are present the position of the maximum moves to higher v. This is illustrated by figure 8 which shows HF/6-311G intracules for fluorobenzene and the iso-
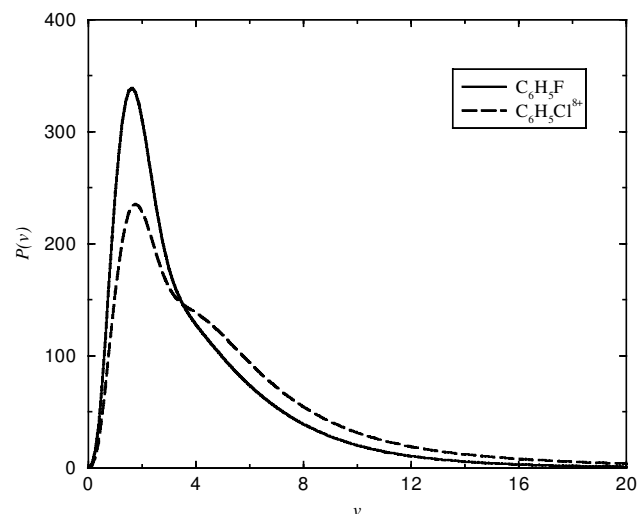
electronic chlorobenzene 8^+ ion. As expected, when heavy nuclei are present $P(v)$ is more diffuse, but also a distinct shoulder appears. However, there is no sharp structure, this is a consequence of the more continuous distribution of velocities within the molecules. Figure 9 shows scaled exchange momentum intracules for the set of organic molecules. These intracules are more sensitive to molecular structure, showing significant variations between the different molecules, but we have not been able to develop a simple physical interpretation of the structure of the $K(v)$ plots.

6. Conclusions

Understanding the interactions between pairs of electrons is crucial to the accurate modelling of the electronic structure of molecules, and intracule densities provide an excellent means for studying these interactions. In order to have a complete picture of the electron distribution it is necessary to consider both position space and momentum space representations. In this paper, the computation of intracule densities for Gaussian wavefunctions in momentum space has been described. An implementation within Q-Chem has enabled momentum intracule densities to be computed for molecular systems with a number of heavy atoms. Through studying some simple systems it has been shown that position and momentum intracules are closely coupled, and that often their behaviour is complementary. Although the position intracules for larger
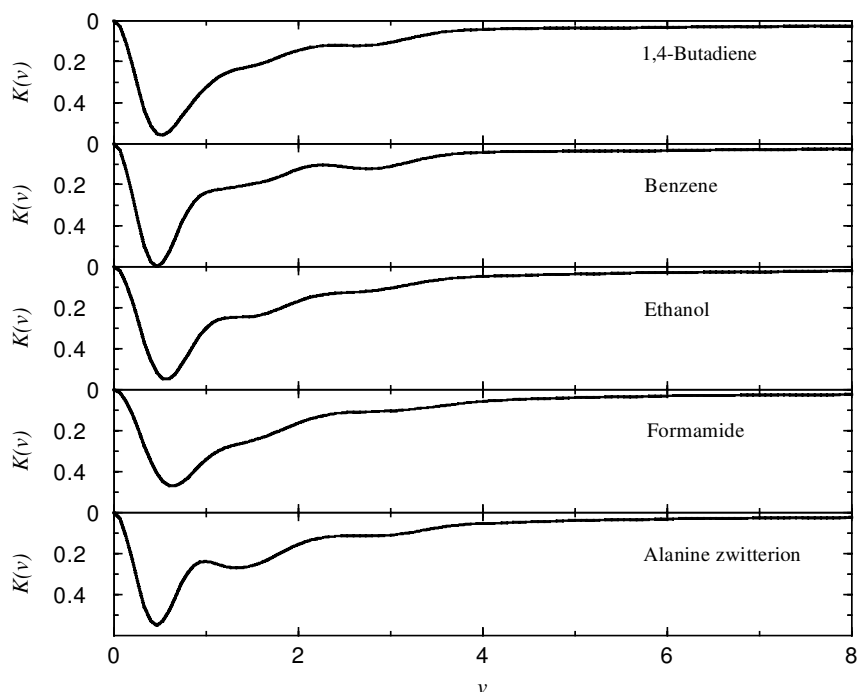

Figure 8. HF/6-311G intracules for C_6H_5F and $C_6H_5Cl^{8+}$.

Figure 9. HF/6-311G exchange intracules for a variety of organic molecules, normalized to -1.

systems become more complex, the corresponding momentum intracules remain smooth functions, which are insensitive to the molecular structure. However, these intracules are sensitive to the nuclear charge of the constituent atoms. When large differences in nuclear charge occur, distinct peaks can develop. Consequently, when expressing the intracule density in momentum space much of the information with which we are familiar in chemistry, such as chemical bonds, is lost. The resulting intracules reflect the broad distribution of momenta in molecules. The exchange component of the intracule density behaves differently, with $K(v)$ sensitive to changes in molecular structure.

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