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Two-electron distribution functions and intracules

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Abstract. Two-electron distribution functions and intracules are functions of electronic coordinates and occupy an important, and frequently overlooked, middle ground between the beguiling simplicity of electron densities and the bewildering complexity of wavefunctions. We survey the functions that have been considered by earlier workers and introduce two new ones, the Wigner intracule and the action intracule, that have not previously been discussed. To illustrate their usefulness, we consider the intracules of jellium, a few small atoms and the dissociating hydrogen molecule.

Keywords: Position intracule – Momentum intracule – Wigner intracule

1 Introduction

The goal of quantum chemistry, it is often said, is to be able to solve the Schrödinger equation for arbitrarily complex chemical systems. This would certainly be an achievement, for it would yield the energy of a system and all of the many observables (e.g. vibrational frequencies, NMR shifts) that can be extracted from various derivatives of the energy [1]. We could then compute the numerical value of any physical quantity of interest to chemists and we would have completed a major scientific revolution.

However, we would still not be entirely satisfied. Whereas the energy and its derivatives are just numbers, easily understood and interpreted, wavefunctions are extraordinarily complicated things and no mortal mind could assimilate the information contained in the wavefunction of even a simple molecule like ethanol. After all, it would depend on the coordinates of each of the nine nuclei and 26 electrons and would describe every pirouette of the intricate dance in which they engage.

But do we really need this level of detail? Is it necessary, in order to understand chemical phenomena, that we master every detail of the complex electronic choreography? Organic and inorganic chemists do not appear to think so and, during the last century, made astonishing progress using only the most elementary constructs of electronic structure theory: the orbital, the electron pair, and the dubious curly arrow. But how can this be? Do experimentalists and theoreticians inhabit different universes?

The truth is that we occupy the same universe but that there is more than one language and level in which a chemical system can be comprehended. The reductionist theoretician, echoing his distant forebears, believes that there are one-body problems, two-body problems and many-body problems and clings to the hope that, if he can solve the first two, the solution to the last will emerge as a straightforward corollary. The holist experimentalist observes that molecular structure is correlated with molecular reactivity and regards electrons as the glue that holds everything together. Each perspective has its uses and, since they are views of the same physical object, there must exist relationships between them. Coulson's famous aphorism, "Give me insight, not numbers!" urges us to discover these relationships but it has taken years for the connections between the bewildering complexity of the wavefunction and the comparative simplicity of the holist's molecule to emerge.

For some time, Parr and his collaborators have argued [2] that the electron density $\rho(\mathbf{r})$ is the point at which the reductionist and holist can meet and density functional theory [3] is now an entrenched paradigm within the quantum chemistry community. Nonetheless, it is clear that the simple one-electron picture is not sufficient for all purposes and there is much to learned from also studying pairs of electrons. In the following sections, we discuss the variety of one- and two-electron distributions that can be derived for an n-electron system whose position–space wavefunction is $\Psi(\mathbf{r}'_1, \mathbf{r}'_2, \ldots, \mathbf{r}'_n)$ and momentum–space wavefunction is $\Phi(\mathbf{p}'_1, \mathbf{p}'_2, \ldots, \mathbf{p}'_n)$, respectively. These lead to an important class of

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functions called intracules and we present and discuss a number of examples of these including two, the Wigner intracule and the action intracule, that have not previously been discussed. We use atomic units throughout.

2 One-electron distribution functions

The most familiar one-electron probability distribution is the electron density

$$\rho(\mathbf{r}_1) = n\langle\Psi|\delta(\mathbf{r}'_1 - \mathbf{r}_1)|\Psi\rangle \ , \tag{2.1}$$

which gives the probability that an electron will be found at the point $\mathbf{r}_1$. Similarly, the momentum density

$$\pi(\mathbf{p}_1) = n\langle\Phi|\delta(\mathbf{p}'_1 - \mathbf{p}_1)|\Phi\rangle \tag{2.2}$$

gives the probability that an electron will be found with a momentum $\mathbf{p}_1$. Furthermore, if ρ_1 is the spinless reduced first-order density matrix [4] of our system, one may loosely interpret the first-order Wigner density,

$$W_1(\mathbf{r}_1, \mathbf{p}_1) = \frac{1}{\pi^3}\int \rho_1(\mathbf{r}_1 + \mathbf{q}, \mathbf{r}_1 - \mathbf{q})e^{-2i\mathbf{p}_1\cdot\mathbf{q}}d\mathbf{q} \ , \tag{2.3}$$

as the probability that an electron will be found at $\mathbf{r}_1$ with momentum $\mathbf{p}_1$. This interpretation is dubious. In fact, $W_1(\mathbf{r}_1, \mathbf{p}_1)$ is not even positive everywhere and it is sometimes described as a "quasi-probability" density [2, 5]. Much of this overview will be concerned with such densities and we will also use the term "quasi-probability" to describe them.

The nth-order function, W_n, was defined by Wigner [6] and the introduction of reduced Wigner functions has been credited [7] to Groenewold [8]. Phase-space quantum distribution functions have been reviewed by a number of authors [5, 9]; however, explicit calculations of such functions for atoms and molecules have been relatively rare. Dahl and Springborg [10] considered $W_1(\mathbf{r}_1, \mathbf{p}_1)$ for the ground state of the hydrogen atom and found that, although they could not compute it in closed form for the exact exponential wavefunction because the integrals were too hard, one can compute $W_1(\mathbf{r}_1, \mathbf{p}_1)$ if the wavefunction is approximated by a sum of Gaussians. In this way, they showed that the function is highly oscillatory and has large negative regions.

Subsequently, Springborg [11] examined changes in the LiH molecule during bond formation and Springborg and Dahl [7] have constructed $W_1(\mathbf{r}_1, \mathbf{p}_1)$ for the He, Be, Ne, Ar and Zn atoms using Hartree–Fock (HF) wavefunctions.

3 Two-electron distribution functions

The most familiar two-electron probability distribution is the two-electron density

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \frac{n(n-1)}{2}\langle\Psi|\delta(\mathbf{r}'_1 - \mathbf{r}_1)\delta(\mathbf{r}'_2 - \mathbf{r}_2)|\Psi\rangle \ , \tag{3.1}$$

which gives the probability that one electron will be found at $\mathbf{r}_1$ and another at $\mathbf{r}_2$. Similarly, the two-electron momentum density

$$\pi(\mathbf{p}_1, \mathbf{p}_2) = \frac{n(n-1)}{2}\langle\Phi|\delta(\mathbf{p}'_1 - \mathbf{p}_1)\delta(\mathbf{p}'_2 - \mathbf{p}_2)|\Phi\rangle \tag{3.2}$$

gives the probability that one electron will be found with a momentum $\mathbf{p}_1$ and another with momentum $\mathbf{p}_2$. Furthermore, as previously, if ρ_2 is the spinless reduced second-order density matrix of a system, one may interpret the second-order Wigner density,

$$\begin{aligned} &W_2(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2) \\ &\quad = \frac{1}{\pi^6}\int \rho_2(\mathbf{r}_1 + \mathbf{q}_1, \mathbf{r}_1 - \mathbf{q}_1, \mathbf{r}_2 + \mathbf{q}_2, \mathbf{r}_2 - \mathbf{q}_2) \\ &\qquad \times e^{-2i(\mathbf{p}_1\cdot\mathbf{q}_1 + \mathbf{p}_2\cdot\mathbf{q}_2)}d\mathbf{q}_1 d\mathbf{q}_2 \ , \end{aligned} \tag{3.3}$$

as the quasi-probability of finding one electron at $\mathbf{r}_1$ with momentum $\mathbf{p}_1$ and another at $\mathbf{r}_2$ with momentum $\mathbf{p}_2$. We note that, like $W_1(\mathbf{r},\mathbf{p})$, the second-order function $W_2(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2)$ is not positive everywhere.

For a detailed discussion, we refer the interested reader to the helpful paper by Thakkar et al. [12] which examines the relationship between all of the distributions (Eqs. 2.1, 2.2, 2.3, 3.1, 3.2, 3.3).

4 Intracules

For some purposes, the relative position of two electrons is more important than their absolute positions and it proves useful to reduce the two-electron density (Eq. 3.1) further. This leads to the position intracule

$$\begin{aligned} P(u) &= \int \rho(\mathbf{r}_1, \mathbf{r}_2)\delta(\mathbf{r}_{12} - \mathbf{u})d\mathbf{r}_1 d\mathbf{r}_2 d\Omega_{\mathbf{u}} \\ &= \frac{n(n-1)}{2}\langle\Psi|\delta(r_{12} - u)|\Psi\rangle \ , \end{aligned} \tag{4.1}$$

where Ω_u is the angular part of $\mathbf{u}$, which gives the probability of finding two electrons separated by a distance u and is the generating kernel for expectations [13, 14] of functions of r_{12}, i.e.

$$\int_0^\infty f(u)P(u)du = \frac{n(n-1)}{2}\langle f(r_{12})\rangle \ . \tag{4.2}$$

The $P(u)$ intracule has been widely discussed in the literature. It appeared in the work of Eddington [15], was introduced into chemistry by Coulson and Neilson [16] and was advocated by Coleman [17]. It has been particularly popular among Canadian theoreticians and their collaborators and Smith, Boyd, Thakkar, Cioslowski and Ugalde have each made significant contributions to its development [13, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32]. Much of the earlier work sought to compare the intracules generated from correlated wavefunctions with those from uncorrelated calculations, for the differences between these yield information about the effects of electron correlation. Our own work has concentrated on the extraction of $P(u)$ from uncorrelated (i.e. HF) wavefunctions and we have shown that these can be computed efficiently, even for large molecules.

We note that the $P(u)$ intracule, which is the distribution of the interelectronic distance u, has a cousin called the extracule, which gives the distribution of the centre of mass $(\mathbf{r}_1+\mathbf{r}_2)/2$. In practice, this function is less useful than the intracule and we do not discuss it further here.

In the same way as the two-electron density (Eq. 3.1) yields the position intracule $P(u)$, the two-electron momentum density (Eq. 3.2) yields the momentum intracule,

$$M(v) = \int \pi(\mathbf{p}_1,\mathbf{p}_2)\delta(\mathbf{p}_{12}-\mathbf{v})\mathrm{d}\mathbf{p}_1\mathrm{d}\mathbf{p}_2\mathrm{d}\Omega_{\mathbf{v}} \\ = \frac{n(n-1)}{2}\langle\Phi|\delta(p_{12}-v)|\Phi\rangle \ , \qquad (4.3)$$

which gives the probability of finding two electrons moving with a relative momentum v. It is the generating kernel for expectations of functions of p_{12}, i.e.

$$\int_0^\infty f(v)M(v)\mathrm{d}v = \frac{n(n-1)}{2}\langle f(p_{12})\rangle \ , \qquad (4.4)$$

and has been investigated by a number of authors [14, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53], led initially by Banyard and, more recently, by Koga. Again, whereas most of this work compares correlated and uncorrelated momentum intracules, our work [14] has focused on the efficient extraction of $M(v)$ from HF wavefunctions in large molecules.

The second-order Wigner density (Eq. 3.3) can be reduced in an analogous way to yield

$$W(u,v) = \int W_2(\mathbf{r}_1\mathbf{p}_1\mathbf{r}_2\mathbf{p}_2)\delta(\mathbf{r}_{12}-\mathbf{u}) \\ \times \delta(\mathbf{p}_{12}-\mathbf{v})\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2\mathrm{d}\mathbf{p}_1\mathrm{d}\mathbf{p}_2\mathrm{d}\Omega_{\mathbf{u}}\mathrm{d}\Omega_{\mathbf{v}} \ , \qquad (4.5)$$

which we call the Wigner intracule. This function gives the quasi-probability of finding two electrons at a distance u and moving with relative momentum v and is thus the generating kernel for expectation values of functions of r_{12} and p_{12}. Thus,

$$\int_0^\infty\int_0^\infty f(u,v)P(u,v)\mathrm{d}u\,\mathrm{d}v = \frac{n(n-1)}{2}\langle f(r_{12},p_{12})\rangle. \qquad (4.6)$$

Although the Wigner intracule is not strictly a joint probability distribution for u and v, it does yield the position and momentum intracules when integrated appropriately, i.e.

$$\int_0^\infty W(u,v)\mathrm{d}v = P(u) \ , \qquad (4.7)$$

$$\int_0^\infty W(u,v)\mathrm{d}u = M(v) \ . \qquad (4.8)$$

As far as we know, Wigner intracules have not previously been discussed in the literature.

Finally, we can obtain the distribution of the variable $w=uv$ by appropriately integrating the Wigner intracule to give

$$A(w) = \int_0^\infty W\left(u,\frac{w}{u}\right)\frac{\mathrm{d}u}{u} \ , \qquad (4.9)$$

which we call the action intracule. The function $A(w)$ gives the quasi-probability of finding two electrons with $r_{12}p_{12}=w$ and is therefore the generating kernel for expectation values of functions of $r_{12}p_{12}$. Thus,

$$\int_0^\infty f(w)A(w)\mathrm{d}w = \frac{n(n-1)}{2}\langle f(r_{12}p_{12})\rangle \ . \qquad (4.10)$$

Action intracules have not previously appeared in the literature.

Although the $P(u)$, $M(v)$, $W(u,v)$ and $A(w)$ intracules are quite different, they share many of the same global properties and we will use the symbol Z to represent a general intracule. For example, each of the four can be partitioned into spin intracules and so we can write

$$Z = Z^{\alpha\beta} + Z^{\alpha\alpha} + Z^{\beta\beta} \\ = Z^{\alpha\beta} + Z'' \ , \qquad (4.11)$$

where $Z^{\alpha\beta}$ pertains to opposite-spin electrons and Z'' to same-spin electrons. In the same way, it can be shown that the integral of an intracule or its spin component is given by

$$\int Z = \frac{n(n-1)}{2} \ , \qquad (4.12)$$

$$\int Z^{\alpha\beta} = n^\alpha n^\beta \ , \qquad (4.13)$$

$$\int Z'' = \frac{n^\alpha(n^\alpha-1)}{2} + \frac{n^\beta(n^\beta-1)}{2} \ , \qquad (4.14)$$

where n^α and n^β are the numbers of α and β electrons, respectively.

5 Intracules from single-determinant wavefunctions

If we confine our attention to determinantal wavefunctions (such as those from HF theory), it can be shown that the general intracule can be written as

$$Z^{\alpha\beta} = \sum_{ij}(\psi_i^\alpha\psi_i^\alpha\psi_j^\beta\psi_j^\beta)_{\mathrm{Z}} \\ = \sum_{\mu\nu\lambda\sigma} D_{\mu\nu}^\alpha D_{\lambda\sigma}^\beta(\mu\nu\lambda\sigma)_{\mathrm{Z}} \ , \qquad (5.1)$$

$$Z^{\alpha\alpha} = \frac{1}{2}\sum_{ij}\left[(\psi_i^\alpha\psi_i^\alpha\psi_j^\alpha\psi_j^\alpha)_{\mathrm{Z}} - (\psi_i^\alpha\psi_j^\alpha\psi_j^\alpha\psi_i^\alpha)_{\mathrm{Z}}\right] \\ = \frac{1}{2}\sum_{\mu\nu\lambda\sigma}\left(D_{\mu\nu}^\alpha D_{\lambda\sigma}^\alpha - D_{\mu\sigma}^\alpha D_{\nu\lambda}^\alpha\right)(\mu\nu\lambda\sigma)_{\mathrm{Z}} \ , \qquad (5.2)$$

$$Z^{\beta\beta} = \frac{1}{2}\sum_{ij}\left[(\psi_i^\beta\psi_i^\beta\psi_j^\beta\psi_j^\beta)_{\mathrm{Z}} - (\psi_i^\beta\psi_j^\beta\psi_j^\beta\psi_i^\beta)_{\mathrm{Z}}\right]$$
$$= \frac{1}{2}\sum_{\mu\nu\lambda\sigma}\left(D_{\mu\nu}^\beta D_{\lambda\sigma}^\beta - D_{\mu\sigma}^\beta D_{\nu\lambda}^\beta\right)(\mu\nu\lambda\sigma)_{\mathrm{Z}} \ , \tag{5.3}$$

where $\mathbf{D}^\alpha$ and $\mathbf{D}^\beta$ are the usual spin density matrices. The $(\psi_{\mathrm{i}}\psi_{\mathrm{j}}\psi_{\mathrm{k}}\psi_{\mathrm{l}})_{\mathrm{Z}}$ are appropriate two-electron integrals in the molecular orbital basis and the $(\mu\nu\lambda\sigma)_{\mathrm{Z}}$ are the corresponding integrals in the atomic orbital basis. Some of these integrals have been discussed previously.

The position integral is

$$(\mu\nu\lambda\sigma)_{\mathrm{P}} = \iint \phi_\mu^*(\mathbf{r})\phi_\nu(\mathbf{r})\phi_\lambda^*(\mathbf{r}+\mathbf{u})\phi_\sigma(\mathbf{r}+\mathbf{u})\mathrm{d}\mathbf{r}\mathrm{d}\Omega_{\mathbf{u}} \ . \tag{5.4}$$

If the basis functions are Gaussian, the integral can be reduced [30] to elementary functions. If $\phi_\mu(\mathbf{r})$, $\phi_\nu(\mathbf{r})$, $\phi_\lambda(\mathbf{r})$ and $\phi_\sigma(\mathbf{r})$ are concentric s-type Gaussians with exponents α, β, γ and δ, respectively, the integral is

$$(ssss)_{\mathrm{P}} = \left(\frac{\pi}{\alpha+\beta}\right)^{3/2}\left(\frac{\pi}{\gamma+\delta}\right)^{3/2}\left(\frac{\theta}{\pi}\right)^{3/2} \times 4\pi u^2 \exp(-\theta u^2) \ , \tag{5.5}$$

$$\theta = \left(\frac{1}{\alpha+\beta} + \frac{1}{\gamma+\delta}\right)^{-1} \ . \tag{5.6}$$

The $(ssss)_{\mathrm{P}}$ integral is always positive.

The momentum integral is

$$(\mu\nu\lambda\sigma)_{\mathrm{M}} = \frac{v^2}{2\pi^2}\iiint \phi_\mu^*(\mathbf{r})\phi_\nu(\mathbf{r}+\mathbf{q})\phi_\lambda^*(\mathbf{u}+\mathbf{q}) \times \phi_\sigma(\mathbf{u})j_0(qv)\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{q}\mathrm{d}\mathbf{u} \ . \tag{5.7}$$

If the basis functions are Gaussian, the integral can be reduced [14] to elementary functions. If $\phi_\mu(\mathbf{r})$, $\phi_\nu(\mathbf{r})$, $\phi_\lambda(\mathbf{r})$ and $\phi_\sigma(\mathbf{r})$ are concentric s-type Gaussians with exponents α, β, γ and δ, respectively, the integral is

$$(ssss)_{\mathrm{M}} = \left(\frac{\pi}{\alpha+\beta}\right)^{3/2}\left(\frac{\pi}{\gamma+\delta}\right)^{3/2}\left(\frac{\hat{\theta}}{\pi}\right)^{3/2} 4\pi v^2 \exp(-\hat{\theta}v^2) \ , \tag{5.8}$$

$$\hat{\theta} = \left(\frac{1}{\hat{\alpha}+\hat{\beta}} + \frac{1}{\hat{\gamma}+\hat{\delta}}\right)^{-1} \ , \tag{5.9}$$

where the Fourier exponents $\hat{\alpha}$, $\hat{\beta}$, $\hat{\gamma}$ and $\hat{\delta}$ are given by $1/(4\alpha)$, $1/(4\beta)$, $1/(4\gamma)$ and $1/(4\delta)$, respectively. The $(ssss)_{\mathrm{M}}$ integral is always positive.

The Wigner integral is

$$(\mu\nu\lambda\sigma)_{\mathrm{W}} = \frac{v^2}{2\pi^2}\iiint \phi_\mu^*(\mathbf{r})\phi_\nu(\mathbf{r}+\mathbf{q})\phi_\lambda^*(\mathbf{r}+\mathbf{q}+\mathbf{u}) \times \phi_\sigma(\mathbf{r}+\mathbf{u})j_0(qv)\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{q}\mathrm{d}\Omega_{\mathbf{u}} \ . \tag{5.10}$$

If the basis functions are Gaussian and collinear, the integral can be expressed [54] in terms of elementary functions and error functions [55]. In the noncollinear case, we have reduced Eq. (5.10) to a 1D integral [54] which can be evaluated either by series expansion or by quadrature. If $\phi_\mu(\mathbf{r})$, $\phi_\nu(\mathbf{r})$, $\phi_\lambda(\mathbf{r})$ and $\phi_\sigma(\mathbf{r})$ are concentric s-type gaussians with exponents α, β, γ and δ, respectively, the integral is

$$(ssss)_{\mathrm{W}} = \frac{2\pi^2u^2v^2}{(\alpha+\delta)^{3/2}(\beta+\gamma)^{3/2}}\exp(-\kappa u^2)\exp(-\hat{\kappa}v^2)j_0(\eta uv) \ , \tag{5.11}$$

$$\kappa = \frac{\alpha\delta}{\alpha+\delta} + \frac{\beta\gamma}{\beta+\gamma} \ , \tag{5.12}$$

$$\hat{\kappa} = \frac{\hat{\alpha}\hat{\delta}}{\hat{\alpha}+\hat{\delta}} + \frac{\hat{\beta}\hat{\gamma}}{\hat{\beta}+\hat{\gamma}} \ , \tag{5.13}$$

$$\eta = \frac{\alpha}{\alpha+\delta} - \frac{\beta}{\beta+\gamma} = \frac{\hat{\beta}}{\hat{\beta}+\hat{\gamma}} - \frac{\hat{\alpha}}{\hat{\alpha}+\hat{\delta}} \ . \tag{5.14}$$

The $(ssss)_{\mathrm{W}}$ integral is not always positive. Its sign is determined by the sign of $j_0(\eta \mathrm{uv})$.

The action integral is

$$(\mu\nu\lambda\sigma)_{\mathrm{A}} = \frac{w^2}{2\pi^2}\iiint \phi_\mu^*(\mathbf{r})\phi_\nu(\mathbf{r}+\mathbf{q})\phi_\lambda^*(\mathbf{r}+\mathbf{q}+\mathbf{u}) \times \phi_\sigma(\mathbf{r}+\mathbf{u})j_0\left(\frac{qw}{u}\right)\left(\frac{1}{u}\right)\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{q}\mathrm{d}\mathbf{u} \ . \tag{5.15}$$

If the basis functions are Gaussian and concentric, the integral can be expressed in terms of elementary functions and modified Bessel functions of the second kind $K_{\mathrm{m}}(x)$ [55]. In the nonconcentric case, we have reduced the action integral to a 2D integral that can be evaluated by quadrature. If $\phi_\mu(\mathbf{r})$, $\phi_\nu(\mathbf{r})$, $\phi_\lambda(\mathbf{r})$ and $\phi_\sigma(\mathbf{r})$ are concentric s-type Gaussians with exponents α, β, γ and δ, respectively, the integral is

$$(ssss)_{\mathrm{A}} = \frac{2\pi^2w^2}{(\alpha+\delta)^{3/2}(\beta+\gamma)^{3/2}}K_0(2\kappa\hat{\kappa}w)j_0(\eta w) \ . \tag{5.16}$$

The sign of the $(ssss)_{\mathrm{A}}$ integral is determined by the sign of $j_0(\eta \mathrm{w})$.

All four of these intracule integrals have the same total content

$$\int_0^\infty (ssss)_{\mathrm{P}}\mathrm{d}u = \int_0^\infty (ssss)_{\mathrm{M}}\mathrm{d}v = \int_0^\infty\int_0^\infty (ssss)_{\mathrm{W}}\mathrm{d}v\mathrm{d}u = \int_0^\infty (ssss)_{\mathrm{A}}\mathrm{d}w = \left(\frac{\pi}{\alpha+\beta}\right)^{3/2}\left(\frac{\pi}{\gamma+\delta}\right)^{3/2} \ . \tag{5.17}$$

The position integrals, being invariant to the permutations $\{\mu \leftrightarrow \nu,\ \lambda \leftrightarrow \sigma,\ \mu\nu \leftrightarrow \lambda\sigma\}$, exhibit eightfold symmetry. The momentum, Wigner and action integrals, being invariant only to the permutations $\{\mu\sigma \leftrightarrow \nu\lambda, \mu\nu \leftrightarrow \lambda\sigma\}$, exhibit only fourfold symmetry.

We have implemented the calculation of intracule integrals $(\mu\nu\lambda\sigma)_Z$, for *s*- and *p*-type basis functions, within the Mathematica [56] and Q-Chem [57] packages and have used these to obtain the numerical results that we discuss later.

Because each intracule is a two-electron distribution, it can be decomposed into a sum of contributions from each pair of occupied orbitals in the system. Thus,

$$Z(u,v) = \sum_{i \leq j}^{n} Z_{ij}(u,v) \ . \tag{5.18}$$

6 Intracules for the uniform electron gas

Although our ultimate interest lies in molecular intracules, the uniform electron gas (or jellium) is the basis for a variety of density functionals for exchange and correlation [2] and is a system of fundamental interest in solid-state physics. It is also an admirably simple but qualitatively accurate model of electronic structure in large molecules. Its intracules are likely to share some the important characteristics of the intracules of more chemically interesting many-electron systems, while retaining a simplicity that allows us to manipulate them easily.

The one-electron density $\rho(\mathbf{r})$ of jellium is constant everywhere, i.e. $\rho(\mathbf{r}) = \rho = n/V$, but the antisymmetry of the determinantal wavefunction induces variations in the two-electron density $\rho(\mathbf{r}_1, \mathbf{r}_2)$ and leads, therefore, to nontrivial intracules. Fortunately, because of the structural simplicity of jellium, these intracules can be evaluated in closed form using Eqs. (5.4), (5.7), (5.10) and (5.15).

The wavefunction for jellium of density ρ is a determinant of plane-wave orbitals,

$$\psi_{\mathbf{k}}(\mathbf{r}) = \pi^{-3/2} \exp(i\,\mathbf{k}\cdot\mathbf{r}) \ , \tag{6.1}$$

whose momenta $\mathbf{k}$ are uniformly distributed in the first octant of the Fermi ball with radius

$$k_{\mathrm{F}} = (3\pi^2\rho)^{1/3} \ . \tag{6.2}$$

A sum over these orbitals can be achieved through an appropriate integration, for example,

$$\sum_{\mathbf{k}} \psi_{\mathbf{k}}^* \psi_{\mathbf{k}} = \frac{1}{8\pi^3} \int_0^{k_{\mathrm{F}}} 4\pi k^2 \mathrm{d}k = \frac{1}{8\pi^3} \frac{4\pi k_{\mathrm{F}}^3}{3} = \frac{\rho}{2} \ . \tag{6.3}$$

Because jellium contains an infinite number of electrons in an infinite volume, its intracules are also infinite. For this reason, specific intracules (i.e. intracules per unit volume), which we will indicate using an overbar, are more convenient.

The specific position intracules are [29]

$$\bar{P}^{\alpha\beta}(u) = 4\pi u^2 \left(\frac{\rho^2}{4}\right) \ , \tag{6.4}$$

$$\bar{P}^{\parallel}(u) = 4\pi u^2 \left[1 - \left(\frac{3 j_1(k_{\mathrm{F}} u)}{k_{\mathrm{F}} u}\right)^2\right] \left(\frac{\rho^2}{4}\right) \tag{6.5}$$

and

$$\bar{P}(u) = 4\pi u^2 \left[1 - \frac{9}{2}\left(\frac{j_1(k_{\mathrm{F}} u)}{k_{\mathrm{F}} u}\right)^2\right] \left(\frac{\rho^2}{2}\right) \ , \tag{6.6}$$

where $j_1(x)$ is the first-order spherical Bessel function [55]. The antiparallel intracule shows that electrons of opposite spin are completely uncorrelated in jellium and therefore the probability of finding two at a distance u depends only on the Jacobian factor. The parallel intracule shows, as originally found by Dirac [58], that electrons of parallel spin are locally correlated in jellium and are unlikely to be found at a separation less than $O(1/k_{\mathrm{F}})$. The ratio of the parallel and antiparallel intracules is shown in Fig. 1 and illustrates the Fermi hole, an exclusion zone around an electron that is respected only by other electrons of the same spin. The

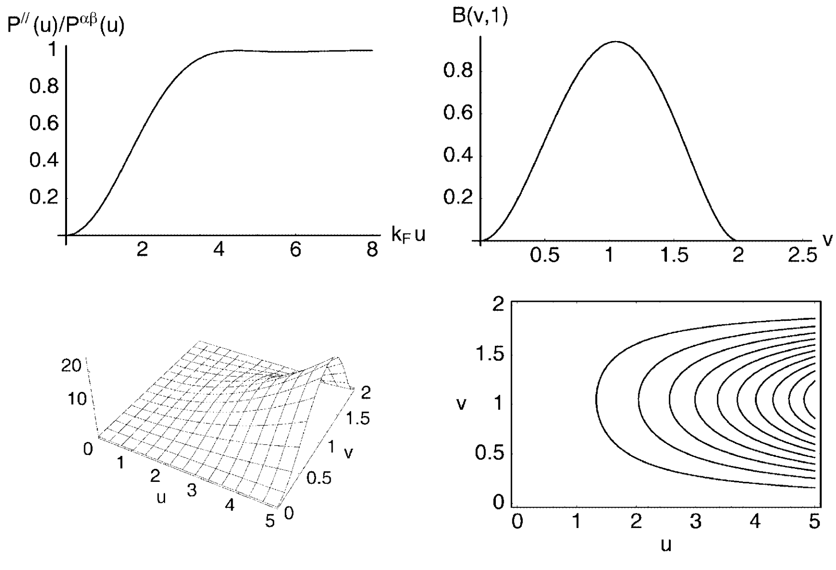

Fig. 1. *Top left*: ratio of the parallel to the antiparallel position intracule in jellium. *Top right*: ball function for the momentum intracule in jellium, see Eq. (6.11). *Bottom left*: specific Wigner intracule for jellium. *Bottom right*: contour plot of specific Wigner intracule for jellium

Dirac exchange functional can be obtained from the Fermi hole through

$$\bar{E}_{\mathrm{X}} = \int_0^\infty u^{-1}\left[\bar{P}''(u) - \bar{P}^{\alpha\beta}(u)\right]\mathrm{d}u = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\rho^{4/3} \ . \tag{6.7}$$

The specific momentum intracules are

$$\bar{M}^{\alpha\beta}(v) = B(v,k_{\mathrm{F}})\left(\frac{n\rho}{4}\right) \ , \tag{6.8}$$

$$\bar{M}''(v) = B(v,k_{\mathrm{F}})\left(\frac{n\rho}{4}\right) - \delta(v)\frac{\rho}{2} \tag{6.9}$$

and

$$\bar{M}(v) = B(v,k_{\mathrm{F}})\left(\frac{n\rho}{2}\right) - \delta(v)\frac{\rho}{2} \tag{6.10}$$

for $0 \le v \le 2k_{\mathrm{F}}$ and, because electrons in jellium have momenta $|\mathbf{k}| \le k_{\mathrm{F}}$, the intracules vanish for $v > 2k_{\mathrm{F}}$. The function

$$B(v,R) = \frac{3v^2(2R-v)^2(4R+v)}{16R^6} \tag{6.11}$$

gives the probability [13] that two points in a sphere of radius R (i.e. two momenta in the Fermi ball) are separated by a distance v. It is shown in Fig. 1. The Thomas–Fermi kinetic energy functional [59, 60] can be found from the second moment of the momentum intracule

$$\bar{E}_{\mathrm{T}} = \frac{1}{2n}\int_0^\infty v^2\bar{M}(v)\mathrm{d}v = \frac{3}{10}(3\pi^2)^{2/3}\rho^{5/3} \ . \tag{6.12}$$

The specific Wigner intracules are

$$\bar{W}^{\alpha\beta}(u,v) = 4\pi u^2 B(v,k_{\mathrm{F}})\left(\frac{\rho^2}{4}\right) \ , \tag{6.13}$$

$$\bar{W}''(u,v) = 4\pi u^2\left[B(v,k_{\mathrm{F}}) - \left(\frac{3j_1(k_{\mathrm{F}}u)}{k_{\mathrm{F}}u}\right)^2\delta(v)\right]\left(\frac{\rho^2}{4}\right) \tag{6.14}$$

and

$$\bar{W}(u,v) = 4\pi u^2\left[B(v,k_{\mathrm{F}}) - \frac{9}{2}\left(\frac{j_1(k_{\mathrm{F}}u)}{k_{\mathrm{F}}u}\right)^2\delta(v)\right]\left(\frac{\rho^2}{2}\right) \tag{6.15}$$

and this is shown as a 3D plot and as a contour plot in Fig. 1. The 3D plot reveals that whereas the Wigner intracule vanishes beyond $v = 2k_{\mathrm{F}}$, it grows rapidly as u increases. This reflects the fact that the number of electrons at a distance u from a reference electron in jellium increases as u^2 for simple geometric reasons.

Unfortunately, because the specific Wigner intracule grows without bound as u increases, the integral Eq. (4.9) diverges and the specific action intracule $A(w)$ is infinite in jellium.

7 Intracules for atoms and molecules

7.1 He atom using HF/[1s]

It is illuminating to begin our survey by examining a system of transparent simplicity, for which all of the intracules can be written in compact form. The HF wavefunction for the ground state of the helium atom places both electrons in a spherical orbital. If the orbital is approximated by a single Gaussian function (for example, using the STO-1G basis), one obtains the crude position and momentum wavefunctions

$$\Psi(\mathbf{r}_1,\mathbf{r}_2) = \left(\frac{2\alpha}{\pi}\right)^{3/2}\exp\left[-\alpha\left(r_1^2 + r_2^2\right)\right] \tag{7.1}$$

and

$$\Phi(\mathbf{p}_1,\mathbf{p}_2) = \left(\frac{1}{2\pi\alpha}\right)^{3/2}\exp\left(-\frac{p_1^2+p_2^2}{4\alpha}\right) \ . \tag{7.2}$$

Note that these are also the exact wavefunctions of a pair of uncoupled, 3D harmonic oscillators. The corresponding intracules are then found to be

$$P(u) = \left(\frac{\alpha}{\pi}\right)^{3/2}4\pi u^2\exp\left(-\alpha u^2\right) \ , \tag{7.3}$$

$$M(v) = \left(\frac{1}{4\pi\alpha}\right)^{3/2}4\pi v^2\exp\left(-\frac{v^2}{4\alpha}\right) \ , \tag{7.4}$$

$$W(u,v) = \frac{2u^2v^2}{\pi}\exp\left(-\alpha u^2 - \frac{v^2}{4\alpha}\right) \tag{7.5}$$

and

$$A(w) = \frac{2w^2}{\pi}K_0(w) \ . \tag{7.6}$$

The value of the exponent that minimises the HF energy of the helium atom is $\alpha = \left(33 - 8\sqrt{2}\right)/(9\pi) \sim 0.767$ and Fig. 2 shows the intracules of Eqs. (7.3), (7.4), (7.5) and (7.6) for this value of the exponent.

The position intracule vanishes at $u = 0$, indicating that there is no chance of finding the two electrons at the same point in space. Initially, it grows quadratically with u but it reaches a maximum at $u = \alpha^{-1/2} \approx 1.14$ au and then decays quickly as u increases further. The probability of finding the electrons more than 3 au apart is only 0.003.

The momentum intracule vanishes at $v = 0$, indicating that there is no chance of finding the two electrons with identical momenta. Initially, it grows quadratically with v but it reaches a maximum at $v = 2\alpha^{1/2} \approx 1.75$ au. The momentum intracule decays as v increases further, but does so more slowly than the position intracule, implying that a large relative momentum is more likely than a large separation. The probability of the relative momentum exceeding 3 au is more than 0.118.

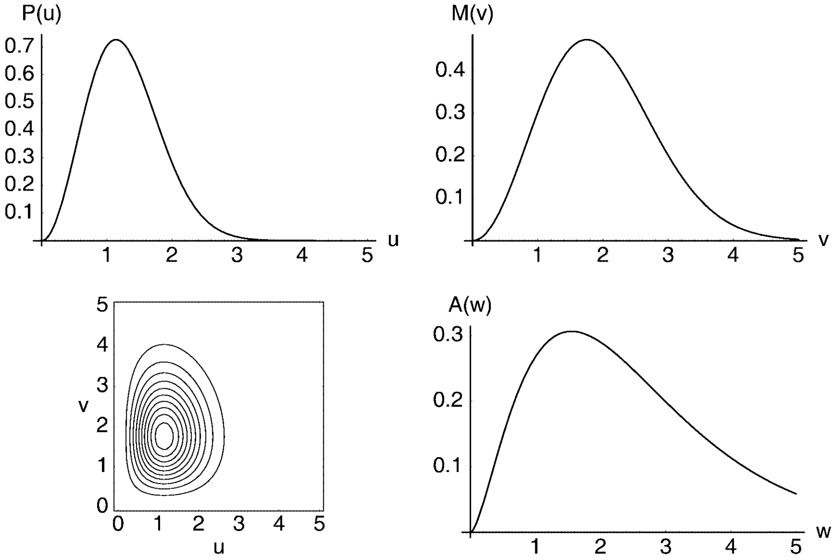

Fig. 2. Position (*top left*), momentum (*top right*), Wigner (*bottom left*) and action (*bottom right*) intracules for the helium atom using a restricted Hartree–Fock (*RHF*)/[1s] wavefunction

The Wigner intracule in this very simple system is exactly the product of the position and momentum intracules: this is rare and, in more complex systems, such a factorisation is not observed. The contour plot in Fig. 2 reveals that $W(u, v)$ is everywhere positive and possesses a single maximum at $(\alpha^{-1/2}, 2\alpha^{1/2})$. It follows that, if the exponent α were varied, the maximum would move along the hyperbola $uv = 2$ au.

The action intracule is independent of the exponent α, reflecting the complementary responses of the position and momentum wavefunctions to changes in the exponent. Our $A(w)$ thus applies not only to the helium atom, but to any helium-like ion (H^-, Li^+, Be^{2+}, etc.) in a single-Gaussian basis. The intracule vanishes at $w = 0$, confirming that there is no chance of finding the two electrons either at the same point or moving with identical momenta and, because of the logarithmic singularity of $K_0(w)$, the intracule initially behaves as $w^2 \log w$. It reaches a maximum at $w \approx 1.55$ au and thereafter decays exponentially with w.

7.2 He atom using HF/6-311G

The foregoing example was chosen for its simplicity, not its realism, and one may suspect that a more accurate wavefunction would yield very different intracules for the helium atom. To explore this, we constructed the four intracules again using the HF/6-311G wavefunction and these are shown in Fig. 3. Comparing this with Fig. 2 allows us to assess the effects of improving the basis set but not, of course, of incorporating electron correlation [16].

The position intracule does not change qualitatively but becomes flatter and more diffuse. The larger basis set gives an improved description of the wavefunction at small r and large r and evidently increases both the probability of finding the electrons far apart and the probability of finding them close together.

The momentum intracule also becomes more diffuse when the larger basis set is used, implying that large relative momenta are more likely. This follows from the improved description of the wavefunction near to the nucleus.

The Wigner intracule yields significantly more information. Both figures reveal that the intracule is everywhere positive, with a single maximum indicating that the two electrons are most likely to be found at a separation $u = 1.1$ and moving with relative momentum $v = 1.6$. However, the use of a better basis set leads to elongation in both the u and v dimensions and the resulting intracule has a more interesting shape.

Surprisingly, the action intracule is less sensitive to basis set than any of the other intracules, including the Wigner intracule from which it is derived. Indeed, to the naked eye, the action intracules in Figs. 2 and 3 appear identical. This curious discovery suggests that the distribution of the product $r_{12}p_{12}$ can be obtained with unexpected accuracy, even using modest wavefunctions. Comparisons for larger atoms seem to confirm this.

7.3 Li atom using HF/6-311G

We next consider the lithium atom, the intracules of which are shown in Fig. 4. To facilitate comparisons with the helium intracules in Fig. 3, we used the 6-311G basis set and restricted (open-shell) HF (RHF) theory.

The position intracule for lithium, unlike that for helium, is bimodal. The first maximum (at $u = 0.6$) shows that two of lithium's electrons are frequently found close together. This arises from the two 1*s* electrons. The second maximum (at $u = 3.2$) shows that one is also likely to find two of the atom's electrons quite distantly separated. This originates from one of the 1*s* electrons (which are generally close to the nucleus) and the 2*s* electron (which is usually far from the nucleus).

The momentum intracule for lithium has only a single maximum. This is surprising for one might have expected two peaks, just as in the position intracule. In

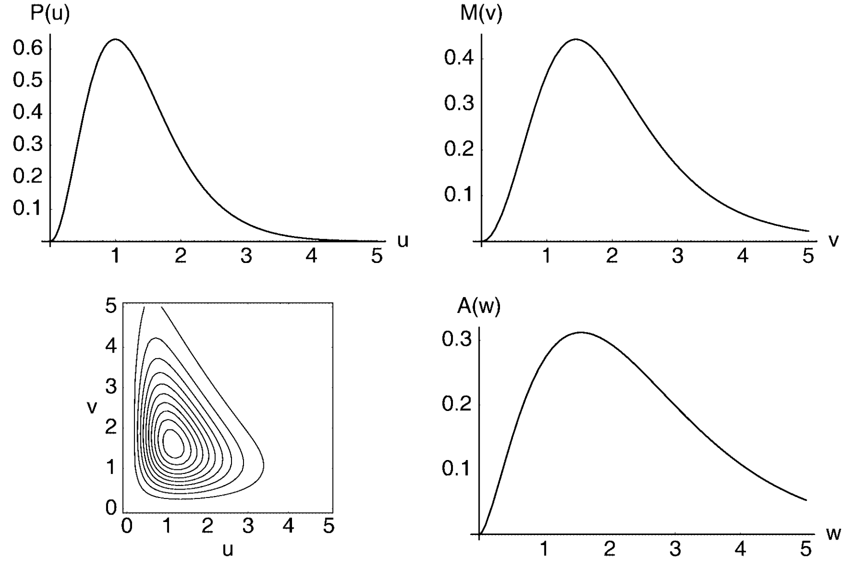

Fig. 3. Position (*top left*), momentum (*top right*), Wigner (*bottom left*) and action (*bottom right*) intracules for the helium atom using an RHF/6-311G wavefunction

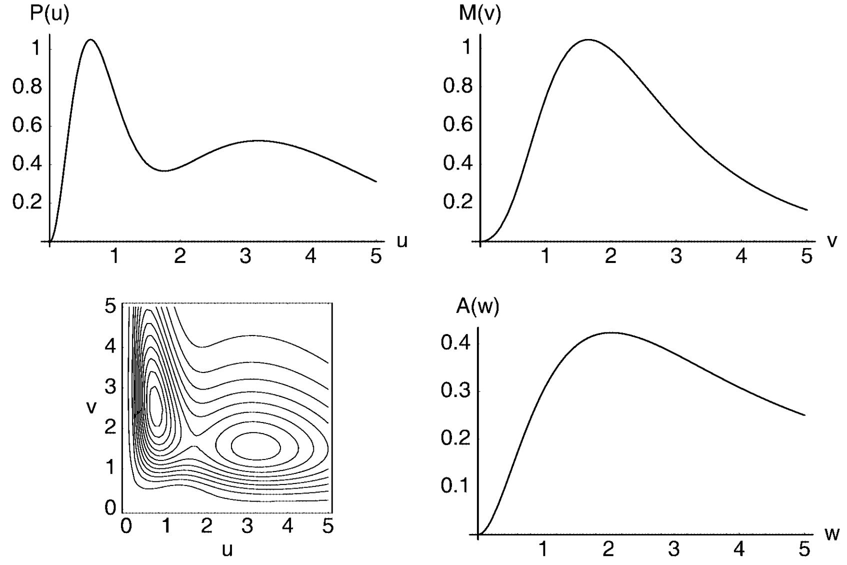

Fig. 4. Position (*top left*), momentum (*top right*), Wigner (*bottom left*) and action (*bottom right*) intracules for the lithium atom using a restricted open-shell HF/6-311G wavefunction

fact, there are two contributors to the momentum intracule, but they are sufficiently broad that they merge. This is an example of the general observation [14] that momentum intracules are usually blander, and their information content is less accessible, than their position analogues.

The Wigner intracule is more interesting. It contains two well-separated peaks, one at (0.7, 2.5) that arises from the 1*s*/1*s* pair and the other at (3.2, 1.6) that arises from 1*s*/2*s* pairs. If one mentally projects the Wigner intracule onto the *u*-axis, as in Eq. (4.7), one can see how the bimodal position intracule arises. Similarly, if one projects the Wigner intracule onto the *v*-axis, as in Eq. (4.8), one can see how the overlap of the two peaks leads to a solitary maximum in the momentum intracule.

The action intracule fails to inherit any of the interesting structure of the Wigner intracule and is characteristically dull. It has a much fatter tail than its helium analogue (Fig. 3).

7.4 Be atom using HF/6-311G

The largest atom that we consider here is beryllium and its RHF/6-311G intracules are shown in Fig. 5. These can be compared directly with the intracules in Figs. 3 and 4.

The position and momentum intracules are bimodal and appear superficially similar but determining the origin of these peaks is difficult until we examine the Wigner intracule. The latter has three well-separated maxima, at (0.5, 3.4), (2.1, 2.3) and (2.9, 0.8), and, since the electron configuration is $1s^2\ 2s^2$, we can immediately assign these to 1*s*/1*s*, 1*s*/2*s* and 2*s*/2*s* pairs, respectively. If we mentally project the Wigner intracule onto the *u*-axis, we see that the inner peak of the position intracule comes from the 1*s*/1*s* pair and the outer peak from a combination of the 1*s*/2*s* and 2*s*/2*s* pairs. If we project the Wigner intracule onto the *v*-axis, we learn that the inner peak of the momentum intracule comes from the

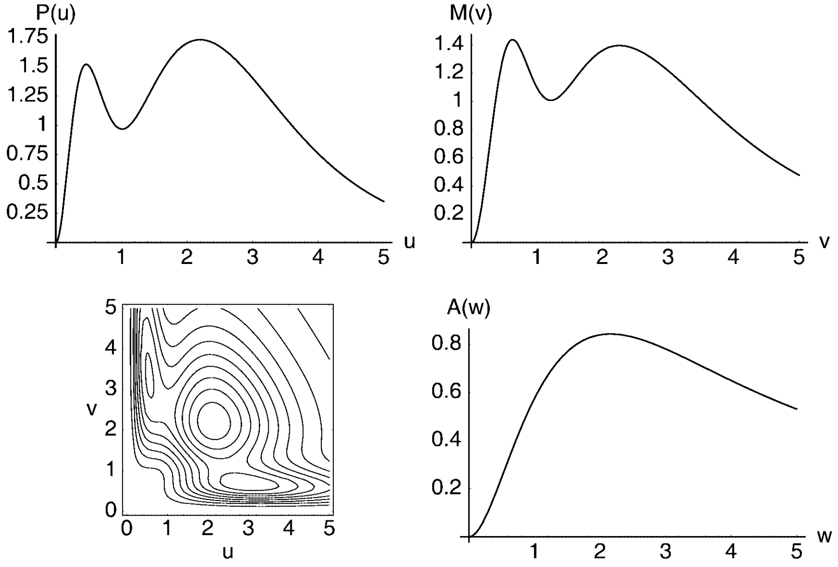

Fig. 5. Position (*top left*), momentum (*top right*), Wigner (*bottom left*) and action (*bottom right*) intracules for the beryllium atom using an RHF/6-311G wavefunction

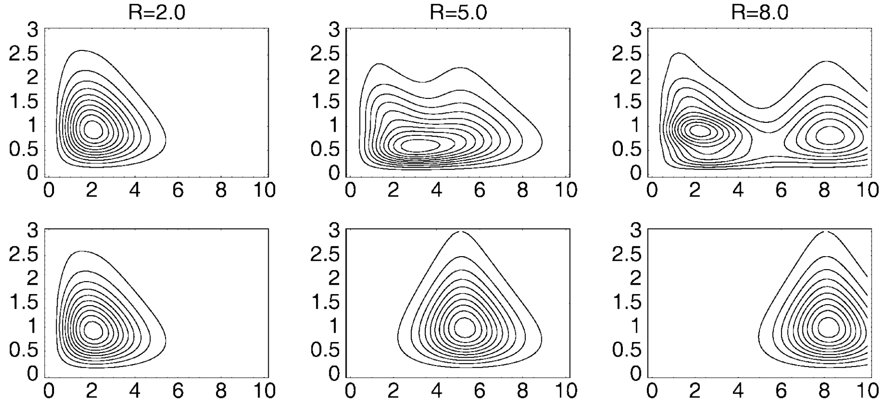

Fig. 6. Wigner intracules for H_2 at various bond lengths, *R*, using HF/6-311G wavefunctions. RHF (*top row*) and unrestricted HF (*bottom row*)

$2s/2s$ pair and the outer peak from a combination of the $1s/1s$ and $1s/2s$ pairs. This interpretation is similar, but not identical, to the slightly incorrect one presented in our recent paper [14] on momentum intracules.

Finally, for completeness, we observe that none of the interesting structure of the Wigner intracule survives into the action intracule, which is dull and fat-tailed, as it is in lithium.

7.5 Dissociation of the H_2 molecule

We conclude this overview with a simple but interesting example of the Wigner intracule of a molecule. The HF/6-311G Wigner intracule for the H_2 molecule as it dissociates is shown in Fig. 6. The upper and lower rows of the figure show the RHF and unrestricted HF (UHF) intracules, respectively.

At a bond length $R = 2$ bohr (the leftmost plots in Fig. 6), the RHF and UHF wavefunctions are identical and so, therefore, are the corresponding Wigner intracules. The intracule has a single maximum at (2.0, 0.9) and is reminiscent of that for the helium atom.

At a slightly longer bond length, it becomes energetically advantageous for the molecular orbitals to break symmetry and the RHF and UHF descriptions become distinct. At a bond length $R = 5$ bohr, the RHF intracule is strongly elongated in the u dimension but is relatively unchanged in the v dimension. In contrast, the UHF intracule is translated to larger u values but remains compact.

At $R = 8$ bohr, the dissociation is almost complete and the restricted and unrestricted intracules are even more different. Whereas the RHF intracule is strongly delocalized and has developed one maximum near (2, 1) and another near (8, 1), the UHF intracule retains its compact shape and has simply translated further in the u dimension.

These strikingly different Wigner intracules can be easily understood. As is well known, the RHF description of dissociated H_2 involves an equal mixture of the ionic and covalent resonance contributions. In the ionic contributions, both electrons reside on one atom and are therefore close together. In the covalent contributions, one electron resides on each atom and the electrons are thus far apart. This explains the two peaks in the RHF Wigner intracule. In contrast, the UHF description has only covalent contributions and, hence, there is only a single peak in the UHF Wigner intracule.

The position and momentum intracules of dissociating H_2 are shown in Fig. 6 of Ref. [14]. The Wigner intracules presented here thus complete the portrait initiated in our earlier work.

8 Closing remarks

We believe that two-electron distribution functions and, especially, the Wigner intracule have a bright future in quantum chemistry. They carry the explicit two-electron information that conventional density functional theory lacks and, if sufficiently efficient algorithms can be developed for their computation, they offer a powerful and systematic route to enhanced accuracy in the theoretical modelling of chemical systems. We encourage chemists to avail themselves of the insights that intracules can provide and we hope that this overview will stimulate interest in these simple but powerful functions.

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