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Intracule functional models

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After introducing the electron correlation problem, we discuss a variety of two-electron probability distributions (intracules), showing how these are interrelated and how they can be constructed from the results of standard molecular orbital calculations. We then consider how these intracules may be used to estimate molecular correlation energies.

1. Introduction

1926 marked the beginning of a radically new chapter in the history of chemistry, for the advent of the Schrödinger equation¹ finally transformed chemistry into a calculable science. The problem, of course, was the inordinate complexity of the equation for all but the simplest of atomic and molecular systems and the discipline of Quantum Chemistry may be usefully characterised as the development and application of methods for reducing that complexity to tractable levels.

Soon after Schrödinger's seminal publications, Hartree recognized that most of the difficulties associated with the Schrödinger equation for a general many-electron system can be avoided if its wavefunction is approximated by a product

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\dots\phi_n(\mathbf{r}_n) \quad (1)$$

of molecular orbitals (MOs).² It is easy to show that such wavefunctions imply statistically independent motion of the electrons and, although interelectronic repulsion makes this an implausible assumption, it turns out to be satisfactory for many qualitative purposes. Shortly thereafter, both Slater³ and Fock⁴ pointed out that Hartree's wavefunction fails to satisfy the Pauli Principle,⁵ but that this can be rectified by the antisymmetrization of (1) to form a determinant.

Unfortunately, although a well-defined and practicable scheme, the resulting Hartree-Fock (HF) model completely neglects the statistical correlation between the motions of opposite-spin electrons and these were found to be essential for a quantitative treatment of such chemically important phenomena as bond making and breaking. In the homolytic fission of a single bond, for example, the two formerly paired electrons migrate in opposite directions and it is well known that this cannot be correctly described by a single determinant.

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The difference between a molecule's HF energy and its exact energy is the correlation energy E_c and the challenge of calculating it is known as the "electron correlation problem". Historically, approaches have fallen into two broad classes.

Wavefunction-based methods construct an improved wavefunction by linearly combining "substituted" determinants (in which previously empty orbitals become occupied) with the HF determinant. Such methods are guaranteed eventually to approach the exact solution of the Schrödinger equation, but their convergence is slow because a linear combination of determinants struggles to approximate the interelectronic cusps in the true wavefunction.⁶ As a consequence, wavefunction-based methods are feasible (on the desktop computers of 2011) only for systems with a few dozen non-hydrogen atoms.

Density-based methods are a popular low-cost alternative. They are based upon the Hohenberg-Kohn theorem,⁷ which states that the energy of the ground state of a system is a universal functional of its electron density $\rho(\mathbf{r})$. Unfortunately, the theorem is non-constructive and, despite the efforts of many researchers over many years, the form of the functional remains unknown. Many approximate functionals have been devised, each with its own strengths and weaknesses, but none yet has proven accurate for all types of chemical problem. The major systematic weaknesses⁸ of density functional theory (DFT) stem from its inability to deal with intrinsically two-electron phenomena such as bond cleavage and static correlation.

Between the complexity of wavefunction schemes (which depend explicitly on the coordinates of *every* electron) and the simplicity of density schemes (which depend only on the *one*-electron density), one can perceive an intermediate regime wherein *two*-electron information becomes the key ingredient. This idea, which springs naturally from the observation that the Schrödinger equation contains only one- and two-body terms, is the avenue explored in this article. Atomic units are used throughout.

2. Intracules

2.1 The Position intracule

A plausible starting point for the development of a two-electron analogue of DFT is the two-electron density

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \int |\Psi(\mathbf{r}_1, \dots, \mathbf{r}_n)|^2 d\mathbf{r}_3 \dots d\mathbf{r}_n \quad (2)$$

which gives the joint probability of finding one electron at \mathbf{r}_1 and another at \mathbf{r}_2 . How might one extract the correlation energy from this function of six variables? Intuitively, one may expect the statistical correlation between the motions of two electrons to depend strongly on their separation $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ and this leads naturally to the position intracule⁹

$$P(u) = \int \rho_2(\mathbf{r}_1, \mathbf{r}_2) \delta(r_{12} - u) d\mathbf{r}_1 d\mathbf{r}_2 \quad (3)$$

(where δ is the Dirac delta distribution) which gives the probability density of finding two electrons separated by a distance u .

Unfortunately, although it is straightforward¹⁰ to compute $P(u)$, it turns out that this is not an effective starting point for a simple electron correlation model. This can be demonstrated by considering the two-electron helium-like ions (*i.e.* H^- , He, Li^+ , ...), which are parameterized by the nuclear charge Z . It is known^{11,12} that, as Z increases, the correlation energy $E_c = E_{\text{exact}} - E_{\text{HF}}$ approaches a limiting value (-46.66 mE_h). Similar behaviour is found in other two-electron systems^{13,14} and,

indeed, Loos has proven that their correlation energies always approach a limiting value as they are compressed toward the high-density limit.¹⁵ In sharp contrast, as Z increases, the position intracule $P(u)$ approaches $\delta(u)$ (see section 4), indicating that $P(u)$ does not possess the qualitative behaviour required to capture E_c in these simple systems.

2.2 The momentum intracule

Several years ago, Rassolov argued that the relative momentum $p_{12} = |\mathbf{p}_1 - \mathbf{p}_2|$ of two electrons also plays a role in their correlation.¹⁶ This undoubtedly makes sense in a classical picture, where a high relative velocity would reduce the interaction time for a pair of electrons, but it is less intuitively obvious in a quantum mechanical setting.

The Fourier transform of $|\Psi(\mathbf{r}_1, \dots, \mathbf{r}_n)|$ is the momentum wavefunction

$$\Phi(\mathbf{p}_1, \dots, \mathbf{p}_n) = (2\pi)^{-3n/2} \int \Psi(\mathbf{r}_1, \dots, \mathbf{r}_n) e^{-i(\mathbf{p}_1 \cdot \mathbf{r}_1 + \dots + \mathbf{p}_n \cdot \mathbf{r}_n)} d\mathbf{r}_1 \dots d\mathbf{r}_n \quad (4)$$

which can be integrated to produce the two-electron momentum density

$$\pi_2(\mathbf{p}_1, \mathbf{p}_2) = \int |\Phi(\mathbf{p}_1, \dots, \mathbf{p}_n)|^2 d\mathbf{p}_3 \dots d\mathbf{p}_n \quad (5)$$

and integrated further to yield the momentum intracule^{17,18}

$$M(v) = \int \Pi_2(\mathbf{p}_1, \mathbf{p}_2) \delta(p_{12} - v) d\mathbf{p}_1 d\mathbf{p}_2 \quad (6)$$

Unfortunately, although it is straightforward¹⁹ to compute $M(v)$, it turns out that, like $P(u)$, it is an ineffective starting point for a simple electron correlation model. As before, this can be illustrated by the helium-like ions (see section 4), whose $M(v)$ become flatter and flatter as Z increases.

The position and momentum intracules of the helium-like ions become infinitely sharp and infinitely flat, respectively, in the $Z \rightarrow \infty$ limit. As a result, neither appears to be a natural ingredient for the two-electron DFT analogue that we seek. However, one might speculate that the correlation in these ions could be modelled *via* a *product* variable involving both r_{12} and p_{12} . In order to explore this possibility, we must move into phase space and attempt to utilise *both* the relative position and relative momentum of the electrons.

2.3 Phase-space quasi-intracules

The reader may well view the goal of this subsection as hopeless because, although one can form a momentum-space wavefunction from its position-space counterpart using a Fourier transform, the Uncertainty Principle forbids the construction of a phase-space wavefunction. Likewise, although $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$ and $\pi_2(\mathbf{p}_1, \mathbf{p}_2)$ can be easily obtained, there exists no comparable joint probability density $P(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2)$.

Nevertheless, though a genuine density in phase-space is prohibited, it is possible to concoct *quasi*-densities with some of the properties that the genuine article would possess. The most famous of these are the Wigner quasi-density²⁰

$$W_n(\mathbf{r}_1, \dots, \mathbf{r}_n, \mathbf{p}_1, \dots, \mathbf{p}_n) = \pi^{-3n} \int \Psi(\mathbf{r}_1 + \mathbf{q}_1, \dots, \mathbf{r}_n + \mathbf{q}_n)^* \times \Psi(\mathbf{r}_1 - \mathbf{q}_1, \dots, \mathbf{r}_n - \mathbf{q}_n) e^{2i(\mathbf{p}_1 \cdot \mathbf{q}_1 + \dots + \mathbf{p}_n \cdot \mathbf{q}_n)} d\mathbf{q}_1 \dots d\mathbf{q}_n \quad (7)$$

and the Husimi quasi-density^{21,22} We will confine our attention to the former.

Being a function of $6n$ coordinates, the Wigner quasi-density is even more complicated than the wavefunction. However, because we are primarily interested

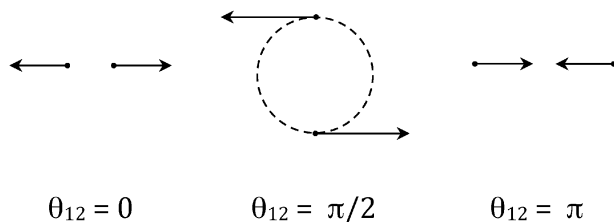


Fig. 1 Physical interpretation of the dynamical angle θ_{12} .

in two-electron information, it is natural to integrate over all but two of the electrons and to use instead the second-order reduced Wigner quasi-density

$$W_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2) = \pi^{-6} \int \rho_2(\mathbf{r}_1 + \mathbf{q}_1, \mathbf{r}_2 + \mathbf{q}_2, \mathbf{r}_1 - \mathbf{q}_1, \mathbf{r}_2 - \mathbf{q}_2) \times e^{2i(\mathbf{p}_1 \cdot \mathbf{q}_1 + \dots + \mathbf{p}_2 \cdot \mathbf{q}_2)} d\mathbf{q}_1 \dots d\mathbf{q}_2 \quad (8)$$

where ρ_2 is the reduced second-order density matrix.²³

W_2 is a simpler object than W_n but it is nonetheless a function of 12 variables and it is desirable to extract from it only the information that is relevant to our correlation model. Because it contains information about the relative position \mathbf{r}_{12} and momentum \mathbf{p}_{12} vectors, it also gives insight into the angle θ_{12} between them, and this, in turn, reveals the nature of the electrons' mutual orbit (Fig. 1).

Following the pattern of eqn (3) and (6), we can extract the joint quasi-density for r_{12} , p_{12} and θ_{12} , and we call this the Omega quasi-intracule²⁴

$$\begin{aligned} \Omega(u, v, \omega) &= \int W_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2) \delta(r_{12} - u) \delta(p_{12} - v) \delta(\theta_{12} - \omega) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{p}_1 d\mathbf{p}_2 \\ &= \frac{1}{8\pi^3} \int \rho_2(\mathbf{r}, \mathbf{r} + \mathbf{q} + \mathbf{u}, \mathbf{r} + \mathbf{q}, \mathbf{r} + \mathbf{u}) e^{i\mathbf{v} \cdot \mathbf{q}} \delta(\theta_{uv} - \omega) d\mathbf{r} d\mathbf{q} d\Omega_u d\Omega_v \end{aligned} \quad (9)$$

Here, \mathbf{u} and \mathbf{v} are vectors of length u and v , and θ_{uv} is the angle between them.

Because the Wigner quasi-density is not a *bona fide* probability density,²⁰ the Omega quasi-intracule is similarly afflicted. Nonetheless, following Wigner, we will often ignore this inconvenient truth.

2.4 Lower (quasi-)intracules

The Omega quasi-intracule is the antecedent of a family (Fig. 2) of lower-dimensional intracules, each of which is obtained by appropriate integration, *viz.*

$$\text{(Wigner)}^{25} \quad W(u, v) = \int_0^\pi \Omega(u, v, \omega) d\omega \quad (10)$$

$$\text{(Lambda)}^{24} \quad \Lambda(s, \omega) = \int_0^\infty \Omega(u, s/u, \omega) u^{-1} du \quad (11)$$

$$\text{(Position)}^9 \quad P(u) = \int_0^\infty W(u, v) dv \quad (12)$$

$$\text{(Momentum)}^{17} \quad M(v) = \int_0^\infty W(u, v) du \quad (13)$$

$$\text{(Angle)}^{24} \quad \Upsilon(\omega) = \int_0^\infty \Lambda(s, \omega) ds \quad (14)$$

$$\text{(Action)}^{25} \quad A(s) = \int_0^\pi \Lambda(s, \omega) d\omega \quad (15)$$

$$\text{(Dot)}^{24} \quad D(x) = \int_x^\infty \Lambda(s, \omega) (s \sin \omega)^{-1} ds \quad (16)$$

where we have introduced the new product variables $s = r_{12}p_{12}$ and $x = \mathbf{r}_{12} \cdot \mathbf{p}_{12}$, which have dimensions of angular momentum and units of Planck's constant \hbar .

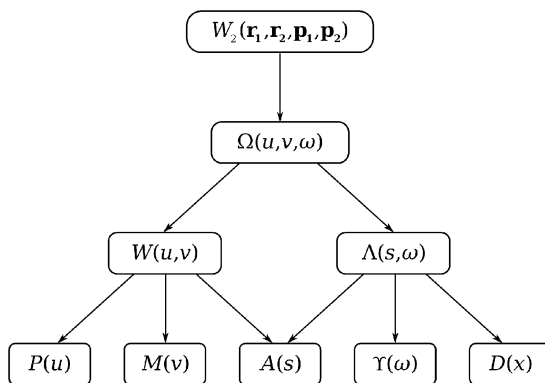


Fig. 2 Genealogical relationships between intracules derived from the Wigner density.

Most of the descendants of $\Omega(u, v, \omega)$ are quasi-intracules but we see that the genuine intracules, $P(u)$ and $M(v)$, also emerge as its offspring.

2.5 The Dot quasi-intracule

Two years after the introduction²⁴ of the Dot intracule, Bernard and Crittenden showed²⁶ that it is mathematically equivalent, but much simpler, to find the dot intracule as the Fourier transform

$$D(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \hat{D}(k) \exp(ikx) dk \quad (17)$$

of the two-particle autocorrelation function

$$\hat{D}(k) = \int \rho_2(\mathbf{r}, \mathbf{r} + (1 + k)\mathbf{u}, \mathbf{r} + k\mathbf{u}, \mathbf{r} + \mathbf{u}) d\mathbf{r} d\mathbf{u} \quad (18)$$

In this way, the Dot intracule is formed directly from the second-order density matrix, without the need to use the Wigner quasi-density (8) as an intermediate. Of course, it is still a quasi-intracule and is not guaranteed to be non-negative.

2.6 The Posmom intracule

Following his work on the Dot intracule, Bernard showed that the “posmom” $s = \mathbf{r} \cdot \mathbf{p}$ of a quantum mechanical particle is an observable whose probability density $S(s)$ can be computed relatively easily from its position wavefunction.²⁷ Subsequently, he computed $S(s)$ for a variety of atomic systems²⁸ and proposed that posmometry is a potentially valuable new spectroscopic technique.²⁹

Recently, we have shown³⁰ that $\mathbf{x} = \mathbf{r}_{12} \cdot \mathbf{p}_{12}$ is also a quantum mechanical observable with a probability density that can be found as the Fourier transform

$$X(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \hat{X}(k) \exp(ikx) dk \quad (19)$$

of the two-particle hyperbolic autocorrelation function

$$\hat{X}(k) = \int \rho_2(\mathbf{r}, \mathbf{r} + \exp(k)\mathbf{u}, \mathbf{r} + \sinh(k)\mathbf{u}, \mathbf{r} + \cosh(k)\mathbf{u}) d\mathbf{r} d\mathbf{u} \quad (20)$$

It is interesting to compare the true intracule $X(x)$ with the quasi-intracule $D(x)$ derived from the Wigner density. The comparison is easy in Fourier space and, by comparing eqn (18) and (20), one sees that $\hat{D}(k)$ is a small- k approximation to $\hat{X}(k)$,

and the difference between them is $O(\hbar^2)$. As we will see in Section 4, this apparently small difference is significant.

3. Introduction of a basis

If we expand the MOs in a basis set $\{\phi_i\}$, the second-order density matrix is

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}'_1, \mathbf{r}'_2) = \sum_{abcd} \Gamma_{abcd} \phi_a(\mathbf{r}_1) \phi_b(\mathbf{r}_2) \phi_c(\mathbf{r}'_1) \phi_d(\mathbf{r}'_2) \quad (21)$$

where the Γ_{abcd} are two-particle density matrix (2PDM) elements. Thus, from eqn (9), the Omega intracule is

$$\Omega(u, v, \omega) = \sum_{abcd} \Gamma_{abcd} [abcd]_{\Omega} \quad (22)$$

where the Omega integrals are

$$[abcd]_{\Omega} = \frac{1}{8\pi^3} \int \phi_a(\mathbf{r}) \phi_b(\mathbf{r} + \mathbf{q} + \mathbf{u}) \phi_c(\mathbf{r} + \mathbf{q}) \phi_d(\mathbf{r} + \mathbf{u}) \times e^{i\mathbf{v}\cdot\mathbf{q}} \delta(\theta_{uv} - \omega) d\mathbf{r} d\mathbf{q} d\mathbf{u} d\mathbf{v} \quad (23)$$

If the ϕ_i are s Gaussians centred at \mathbf{A} , \mathbf{B} , \mathbf{C} , \mathbf{D} , with exponents α , β , γ , δ , it can be shown³¹ that

$$[ssss]_{\Omega} = K \exp(-R) \frac{1}{\pi} \int_0^{\pi} i_0(\sqrt{x + y \cos t}) dt \quad (24)$$

where

$$K = \frac{\pi^2 u^2 v^2 \sin \omega}{(\alpha + \delta)^{3/2} (\beta + \gamma)^{3/2}} \exp(-\lambda^2 u^2 - \mu^2 v^2 - i\eta uv \cos \omega) \quad (25)$$

$$R = \frac{\alpha\delta}{\alpha + \delta} |\mathbf{A} - \mathbf{D}|^2 + \frac{\beta\gamma}{\beta + \gamma} |\mathbf{B} - \mathbf{C}|^2 \quad (26)$$

$$x = (Pu)^2 + (iQv)^2 + 2(Pu)(iQv) \cos \chi \cos \omega \quad (27)$$

$$y = 2(Pu)(iQv) \sin \chi \sin \omega \quad (28)$$

and

$$\lambda^2 = \frac{\alpha\delta}{\alpha + \delta} + \frac{\beta\gamma}{\beta + \gamma} \quad (29)$$

$$4\mu^2 = \frac{1}{\alpha + \delta} + \frac{1}{\beta + \gamma} \quad (30)$$

$$\eta = \frac{\alpha}{\alpha + \delta} - \frac{\beta}{\beta + \gamma} \quad (31)$$

$$\mathbf{P} = \frac{2\alpha\delta}{\alpha + \delta} (\mathbf{A} - \mathbf{D}) + \frac{2\beta\gamma}{\beta + \gamma} (\mathbf{B} - \mathbf{C}) \quad (32)$$

$$\mathbf{Q} = \frac{\alpha\mathbf{A} + \delta\mathbf{D}}{\alpha + \delta} - \frac{\beta\mathbf{B} + \gamma\mathbf{C}}{\beta + \gamma} \quad (33)$$

$$\mathbf{P}\cdot\mathbf{Q} = PQ \cos \chi \quad (34)$$

and $i_0(z) = z^{-1} \sinh z$. The integral in (24) can be evaluated by quadrature or series expansion.³¹ However, if the Gaussian centres are collinear, it can be found in closed form and, if they are concentric, it reduces to

$$[\text{ssss}]_{\Omega} = K \quad (35)$$

Integrals over p, d, \dots Gaussians can be found by Boys differentiation³² of the $[\text{ssss}]_{\Omega}$ integral. However, Hollett has very recently constructed an 18-term recurrence relation¹⁹ to generate such integrals more efficiently.

4. Intracules in He-like ions

If we model the $1s$ orbital in a He-like ion by the single Gaussian $\exp(-\alpha r^2)$, the HF position and momentum wavefunctions are

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = 2(\alpha\pi)^{3/2} \exp[-\alpha(r_1^2 + r_2^2)] \quad (36)$$

$$\Phi(\mathbf{p}_1, \mathbf{p}_2) = (2\pi\alpha)^{-3/2} \exp[-(p_1^2 + p_2^2)/4\alpha] \quad (37)$$

and the reduced second-order density matrix is

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}'_1, \mathbf{r}'_2) = (2\alpha/\pi)^3 \exp[-\alpha(r_1^2 + r_2^2 + r'^2_1 + r'^2_2)] \quad (38)$$

Using (9), one finds that the Omega intracule is

$$\Omega(u, v, \omega) = (1/\pi)u^2 \exp(-\alpha u^2)v^2 \exp(-v^2/4\alpha) \sin \omega \quad (39)$$

and eqn (10)–(20) then yield

$$W(u, v) = (2/\pi)u^2 \exp(-\alpha u^2)v^2 \exp(-v^2/4\alpha) \quad (40)$$

$$\Lambda(s, \omega) = (1/\pi)s^2 K_0(s) \sin \omega \quad (41)$$

$$P(u) = (\alpha/\pi)^{3/2} 4\pi u^2 \exp(-\alpha u^2) \quad (42)$$

$$M(v) = (4\pi\alpha)^{-3/2} 4\pi v^2 \exp(-v^2/4\alpha) \quad (43)$$

$$Y(\omega) = (1/2) \sin \omega \quad (44)$$

$$A(s) = (2/\pi)s^2 K_0(s) \quad (45)$$

$$D(x) = (1/\pi)x K_1(x) \quad (46)$$

$$X(x) = (2\pi^3)^{-1/2} |\Gamma[(3 + ix)/4]|^2 \quad (47)$$

where K_ν is a modified Bessel function of the second kind and Γ is the gamma function.³³

The exponent that minimizes the HF energy of the He atom is

$$\alpha_0 = \frac{33 - 8\sqrt{2}}{9\pi} \quad (48)$$

and using this yields the position and momentum intracules shown in Fig. 3.

$P(u)$ is a Maxwell distribution whose maximum occurs at $u = 1/\sqrt{\alpha}$. Thus, as the exponent α increases and the orbital shrinks, the probability of small interelectronic distances increases, and the intracule contracts toward the origin.

$M(v)$ is also a Maxwell distribution whose maximum occurs at $v = 2\sqrt{\alpha}$. Thus, as the exponent α increases and the orbital shrinks, the probability of high relative momenta increases, and the intracule broadens away from the origin.

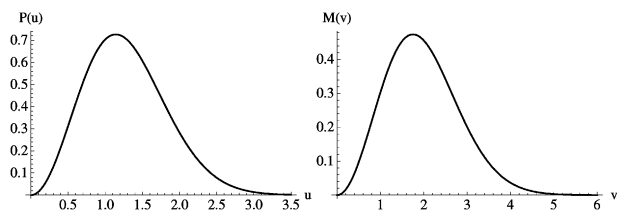


Fig. 3 Position intracule (left) and momentum intracule (right) for the helium atom.

$Y(\omega)$ is trivial in this system and reflects the “Jacobian” effect that, as r_{12} and p_{12} range independently over their respective domains, the angle θ_{12} between them is close to $\pi/2$ much more often than it is close to 0 or π .

In these simple systems, the multidimensional intracules are simple products of the one-dimensional ones and we therefore find $\Omega(u,v,\omega) \equiv P(u)M(v)Y(\omega)$, $W(u,v) \equiv P(u)M(v)$ and $\Lambda(s,\omega) \equiv A(s)Y(\omega)$. Such products imply that u , v and ω are statistically independent in these systems. This is highly exceptional.

The four one-dimensional intracules, $Y(\omega)$, $A(s)$, $D(x)$ and $X(x)$ are all independent of the exponent α and the plots in Fig. 4 and 5 therefore apply, not only to the helium atom, but to any helium-like ion. Their invariance to dilation suggests that, unlike $P(u)$ and $M(v)$, these intracules may naturally yield correlation models that behave correctly for two electrons in the high-density limit (see section 2.1). We will return to this in section 5.

$A(s)$ appears Maxwellian but is not, decaying only exponentially at large s . Like $P(u)$ and $M(v)$, it possesses a single maximum and this occurs at $s \approx 1.55$

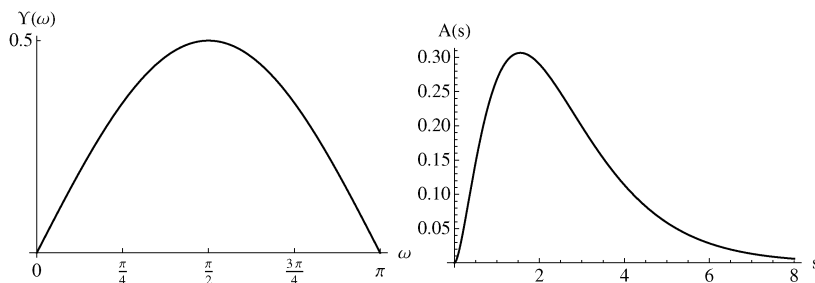


Fig. 4 Angle intracule (left) and action intracule (right) for the helium-like ions.

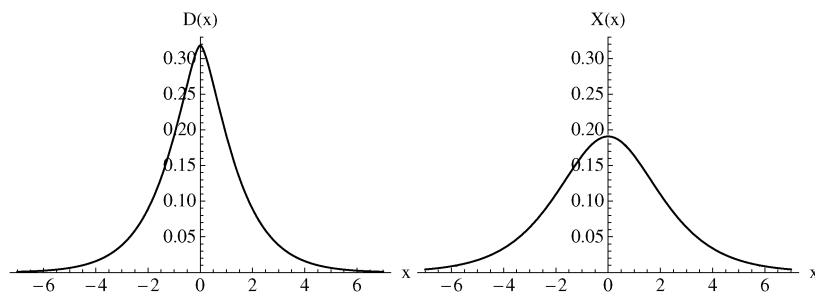


Fig. 5 Dot intracule (left) and posmom intracule (right) for the helium-like ions.

(the root of $2K_0(s) = sK_1(s)$), implying that this is the most likely value of $r_{12}p_{12}$. It also has a weak logarithmic singularity at $s = 0$.

$D(x)$ is a bell curve with infinite curvature at $x = 0$ and inflection points at $x \approx \pm 0.595$ (the root of $K_0(x) = xK_1(x)$). The variance of $D(x)$ is $\sigma_D^2 = 3$ and, for large x , one finds $D(x) = O(x^{1/2}e^{-x})$.

$X(x)$ is a bell curve, confirming that the most likely value of $r_{12}p_{12}$ is zero, *i.e.* the vectors are orthogonal. However, with points of inflection at $x \approx \pm 1.61$, a variance $\sigma_X^2 = 6$, and a large- x decay $X(x) = O(x^{1/2}e^{-\pi x/4})$, it is clear the true intracule is much broader than the quasi-intracule.

The comparison between $X(x)$ and $D(x)$ is sobering: the Wigner quasi-density (8) is a convenient source of phase-space information, but it is not quantitatively reliable and should be eschewed whenever a rigorous alternative is available.

5. Electron correlation models

The Omega intracule for a molecular system offers an impressively detailed picture of the dynamical behaviour of its electrons. We know, for any given values of u , v and ω , the quasi-probability of finding two of its electrons at a distance u , moving with a relative speed v at a dynamical angle ω . In addition, the posmom intracule $X(x)$ reveals the true distribution of the posmom variable $x = r_{12}p_{12}$. Can we use this information to construct an electron correlation model?

DFT methods are founded on the Hohenberg-Kohn theorem,⁷ which states that the correlation energy E_c is a functional of the one-electron density $\rho(\mathbf{r})$. We now make an analogous conjecture:²⁴ that the correlation energy is a functional of the Omega intracule, *i.e.*

$$E_c = F[\Omega(u,v,\omega)] \quad (49)$$

There are probably many possible ways to prove (or disprove) the conjecture and this remains an interesting open challenge. Our earliest attempts sought to show that the Hamiltonian can be reconstructed (apart from unimportant translations and rotations) from $\Omega(u,v,\omega)$. If this can be shown, it proves the conjecture, for E_c is certainly a functional of the Hamiltonian. However, even in the absence of a proof, we feel that the correlation-relevant information in the Omega intracule is much more *accessible* than that in the one-electron density and, therefore, it should be easier to recover E_c from $\Omega(u,v,\omega)$ than from $\rho(\mathbf{r})$. We call such schemes Intracule Functional Models.

Although one can imagine many ways to extract E_c from $\Omega(u,v,\omega)$, one of the simplest is to contract the intracule with an appropriate kernel, writing

$$E_c = \int_0^\infty \int_0^\infty \int_0^\pi \Omega(u,v,\omega) G(u,v,\omega) d\omega dv du \quad (50)$$

In such a formulation, the correlation kernel $G(u,v,\omega)$ is a weight function that assigns high priority to regions of (u,v,ω) -space where the electrons are strongly correlated, and low priority to regions where correlation is weak. As Fig. 6 shows, in situations where both u and v are small, the electrons are close together and moving relatively slowly and so we expect a large correlation contribution. Conversely, correlation effects should be small when the electrons are far apart and moving quickly. In intermediate cases, where one of u and v is large and the other is small, we expect moderate correlation effects. This picture is also consistent with the suggestion (section 2.1) that correlation in the helium-like ions is related to the product $r_{12}p_{12}$.

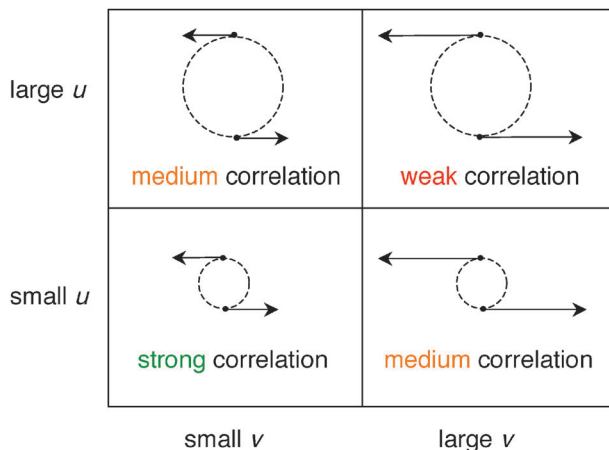


Fig. 6 Strongly, moderately and weakly correlated arrangements of two electrons.

If we expand the MOs in a basis, then eqn (22) and (50) yield

$$E_c = \sum_{abcd} \Gamma_{abcd} [abcd]_G \quad (51)$$

and one finds that the fundamental Gaussian correlation integral³⁴ is given by

$$[ssss]_G = \frac{1}{8(\alpha + \delta)^{3/2}(\beta + \gamma)^{3/2}} \times \int \exp(-\lambda^2 u^2 - \mu^2 v^2 - i\eta \mathbf{u} \cdot \mathbf{v} - \mathbf{P} \cdot \mathbf{u} - i\mathbf{Q} \cdot \mathbf{v} - R) G(u, v, \omega) d\mathbf{u} d\mathbf{v} \quad (52)$$

Of the many kernels that we have explored, the four-parameter kernel³⁵

$$G_4(u, v, \omega) = c \exp(-\lambda_0^2 u^2 - \mu_0^2 v^2 - i\eta_0 uv \cos \omega) \quad (53)$$

is particularly attractive because it leads to correlation integrals that can be found in closed form. For example,

$$[ssss]_G = c \frac{\pi^3}{(\alpha + \delta)^{3/2}(\beta + \gamma)^{3/2} (4l^2 m^2 + h^2)^{3/2}} \times \exp \left[\frac{m^2 P^2 + hPQ \cos \chi - l^2 Q^2}{4l^2 m^2 + h^2} - R \right] \quad (54)$$

where $l^2 = \lambda^2 + \lambda_0^2$, $m^2 = \mu^2 + \mu_0^2$ and $h = \eta + \eta_0$.

A recent study³⁶ by Pearson and Crittenden revealed that intracules tend to be fairly insensitive to basis set improvements. For this reason, and because the main focus of this article is conceptual rather than quantitative, the numerical results below use two-particle density matrices Γ_{abcd} from UHF/6-311G wavefunctions.

Optimization of the c , λ_0 , μ_0 and η_0 parameters in the G_4 kernel against the exact correlation energies³⁷ of the ground states of the first 18 atoms^{38,39} and the 56 small molecules in Pople's G1 data set⁴⁰ reveals that, whereas η_0 plays a critical role in capturing E_c in these systems, μ_0 is unimportant and can be set to zero without affecting the results significantly.

Accordingly, we optimized and explored the three-parameter kernel

$$G_3(u, v, \omega) = c \exp(-\lambda_0^2 u^2 - i\eta_0 uv \cos \omega) \quad (55)$$

($c = 0.2113$, $\eta_0 = 1.0374$, $\lambda_0 = 0.5578$) and the two-parameter kernel

$$G_2(u, v, \omega) = c \exp(-i\eta_0 uv \cos \omega) \quad (56)$$

($c = 0.07695$ and $\eta_0 = 0.8474$).

Fig. 7 and 8 plot the correlation energies predicted by the G_2 and G_3 kernels (denoted E_c^2 and E_c^3 , respectively) against the exact correlation energies of the 18 atoms and 56 molecules described above.

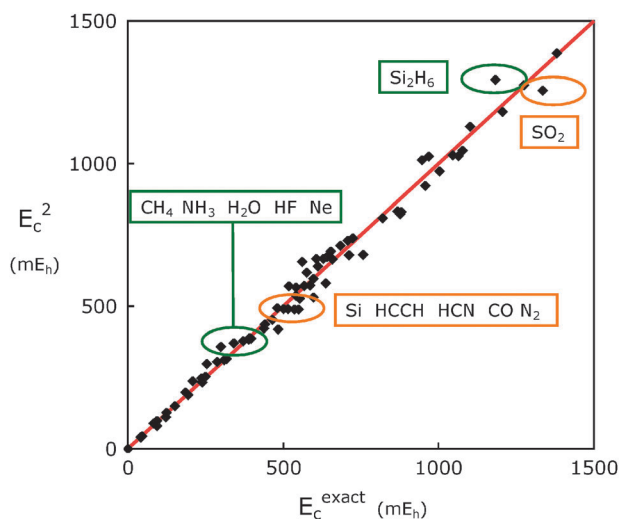


Fig. 7 Accuracy of correlation energies from the G_2 kernel for atoms and molecules.

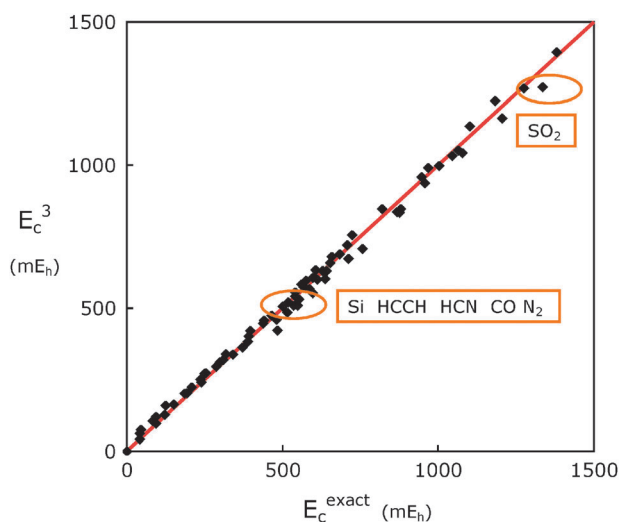


Fig. 8 Accuracy of correlation energies from the G_3 kernel for atoms and molecules.

The first thing that one learns from these scatterplots is that these simple kernels are surprisingly successful at capturing the principal correlation effects in these 74 systems. It is particularly encouraging to find that the G_2 kernel—which is simply an exponential in $x = \mathbf{r}_{12} \cdot \mathbf{p}_{12}$ —performs so well. On closer inspection, we see that the G_2 kernel tends to overestimate E_c in σ -bonded molecules such as CH_4 and Si_2H_6 and to underestimate in π -bonded molecules such as N_2 and HCCH . The overestimation in the σ -bonded systems is substantially reduced by the G_3 kernel, whose extra $\exp(-\lambda_0^2 u^2)$ factor decreases the predicted correlation energies in spatially extended systems. However, even the G_3 kernel still underestimates E_c in compact, π -bonded molecules.

Why are the unsaturated molecules problematic? It appears that it is because a significant fraction of E_c in these systems is “static”, rather than “dynamic”, in nature. Though precise definitions are elusive,⁴¹ static correlation is associated with the presence of low-lying excited states and the resulting inadequacy of a single determinant wavefunction, whereas dynamic correlation results from the intricate dance of the electrons as they strive to avoid close encounters with one another. Evidently, our G_2 and G_3 correlation models are effective at modelling dynamical correlation but struggle to capture the static component. Future work to address this shortcoming will be important.⁴¹

6. Conclusions

There is a fertile, but largely unexplored, middle ground between the simplicity of DFT and the complexity of many-electron wavefunction theories. In this region, inexpensive uncorrelated calculations are used to construct explicit two-electron probability density functions called intracules and the latter are then used to estimate correlation energies. We have described the construction of nine distinct intracules and have discussed some of the possible ways in which these may be used. Such intracule functional models, although still in their infancy, appear to have a bright future.

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