

Intracule functional models: I. Angle-corrected correlation kernels

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We explore the merits of applying a simple angle-dependent correction to the correlation kernel within the framework of Hartree–Fock–Wigner theory. Based on numerical results for the first eighteen atoms, we conclude that such a correction offers a significant improvement over the action kernel that we and others have explored previously.

I. Introduction

Hartree–Fock (HF) theory^{1–3} often yields fairly accurate predictions of molecular structure but it is much less satisfactory for many other properties. In particular, its simplistic treatment of electron motion fails to account properly for the formation of an electron pair during bond formation and it has been known for many years that quantitative predictions are possible only if the theoretical model is extended to account for electron correlation. Allowing the electrons to avoid one another stabilizes the system and the difference between its exact and HF energies is known^{4,5} as the correlation energy E_c . The difficulty of calculating E_c is known as “the correlation problem” and has been the most challenging obstacle to the progress of quantum chemistry during its eighty-year history.

A few years ago, Rassolov argued⁶ that the strength of the correlation of two electrons depends on both their separation $\mathbf{u} = \mathbf{r}_1 - \mathbf{r}_2$ in position space and their separation $\mathbf{v} = \mathbf{p}_1 - \mathbf{p}_2$ in momentum space. We believe that this insight is a profound one but, because the Heisenberg uncertainty principle precludes the construction of a phase-space wavefunction, we have turned instead to Wigner’s^{7,8} reduced second-order phase-space distribution $W(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2)$ to provide a relatively simple function, the Omega intracule $\Omega(u, v, \omega)$, that gives the joint quasi-probability density of u , v and ω , the last of these being the angle between \mathbf{u} and \mathbf{v} .^{9,10} Besley has argued¹¹ that it may be preferable to derive phase-space intracules from the rigorously non-negative Husimi distribution¹² but we do not explore this possibility here.

We have suggested that the correlation energy of a system can be found by contracting its HF Omega intracule with a suitable correlation kernel $G(u, v, \omega)$. Using arguments based on the known correlation energies of the helium-like ions, we have assumed in our work to date that the correlation kernel depends on the product $s = uv$ but is independent of ω . A number of investigations^{9,13–16} of this assumption have been published and they have concluded that, although such kernels can provide surprisingly good estimates of ground-state atom-

ic correlation energies, they seem to be less effective in describing the variations of E_c across isoelectronic molecules.

To obtain even higher accuracy, it is clear that more flexible kernels are needed. In this paper, we explore the possibility of adding a small ω -based correction and present results for a number of atoms. We define the correlation energy to be the difference between the complete-basis UHF energy and the exact eigenvalue of the non-relativistic Schrödinger equation and we use atomic units throughout.

II. Angle intracules

In calculations using one-electron basis functions $\phi_a(\mathbf{r})$, the Omega intracule is¹⁰

$$\Omega(u, v, \omega) = \sum_{abcd} \Gamma_{abcd} [abcd]_{\Omega} \quad (2.1)$$

where Γ_{abcd} is a two-particle density matrix element and the Omega integrals

$$[abcd]_{\Omega} = \int \Phi_{ad}^*(\mathbf{u}, \mathbf{v}) \Phi_{bc}(\mathbf{u}, \mathbf{v}) \delta(\theta_{uv} - \omega) d\Omega_{\mathbf{u}} d\Omega_{\mathbf{v}} \quad (2.2)$$

are formed from the phase functions

$$\Phi_{ad}(\mathbf{u}, \mathbf{v}) = (2\pi)^{-3/2} \int \phi_a(\mathbf{r}) \phi_d(\mathbf{r} + \mathbf{u}) e^{i\mathbf{v}\cdot\mathbf{r}} d\mathbf{r} \quad (2.3)$$

The Omega integrals are more difficult than the analogous $[abcd]$ Coulomb integrals but we have shown how they can be calculated efficiently over Gaussian basis functions, exploiting Boys’ approach¹⁷ in which the fundamental $[ssss]_{\Omega}$ integral is found and differentiated with respect to the coordinates of the Gaussians to yield $[abcd]_{\Omega}$ of higher angular momentum.

We have reported intracules for various atoms and molecules, in ground and excited states (see ref. 9 and references therein) and, most recently, we have studied the Angle intracule

$$\Upsilon(\omega) = \int_0^{\infty} \int_0^{\infty} \Omega(u, v, \omega) du dv \quad (2.4)$$

which gives the (quasi-)probability density of ω . In a system where the directions of \mathbf{u} and \mathbf{v} are statistically independent, such as two identical harmonic oscillators,¹⁸ the Angle intracule is determined entirely by the appropriate geometric

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Table 1 Fourier coefficients, exact correlation energies, LYP errors and kernel-based errors^{a-f}

	$\frac{n(n-1)}{4}$	d_1	$-d_3$	d_5	$-d_7$	E_c	ΔE_c^{LYP}	ΔE_c^2	ΔE_c^3
C_s								0.1060	0.1008
C_ω								0	0.0075
ζ								0.9163	0.9101
H	0.0	0.0000	0.0000	0.0000	0.0000	0.0	0.0	0.0	0.0
He	0.5	0.0237	0.0804	0.0183	0.0054	42.1	1.7	1.3	0.5
Li	1.5	0.0213	0.0698	0.0114	0.0029	45.4	8.1	2.3	1.3
Be	3.0	0.0194	0.0630	0.0125	0.0104	94.4	0.2	-3.3	-5.9
B	5.0	0.0466	0.1447	0.0112	0.0072	120.8	5.5	0.2	-2.2
C	7.5	0.0950	0.3019	0.0211	0.0057	151.3	8.2	3.3	2.2
N	10.5	0.1723	0.5412	0.0440	0.0065	184.7	7.5	7.3	8.6
O	14.0	0.2495	0.7868	0.0682	0.0070	248.5	9.8	2.5	5.2
F	18.0	0.3408	1.0763	0.0955	0.0082	317.8	4.4	-4.3	0.5
Ne	22.5	0.4657	1.4792	0.1474	0.0153	390.8	-7.2	-11.3	-3.0
Na	27.5	0.4199	1.3141	0.0927	0.0018	395.9	12.5	-7.8	-1.5
Mg	33.0	0.3644	1.1269	0.0591	0.0066	438.4	21.1	-3.3	-0.7
Al	39.0	0.3341	1.0226	0.0379	0.0104	465.2	29.6	0.8	1.5
Si	45.5	0.3303	1.0046	0.0281	0.0143	500.2	30.6	-2.5	-2.5
P	52.5	0.3195	0.9631	0.0191	0.0281	539.8	26.5	-1.9	-2.8
S	60.0	0.3216	0.9701	0.0277	0.0431	596.8	33.1	1.5	-0.8
Cl	68.0	0.3200	0.9652	0.0361	0.0621	658.3	33.0	4.1	0.4
Ar	76.5	0.3139	0.9434	0.0400	0.0826	722.7	28.1	7.6	2.3
RMSD							19.0	4.7	3.2
MAD							14.8	3.6	2.3

^a All energies in millihartrees. Correlation energies are taken to be positive numbers. ^b E_c = exact value taken from ref. 21. ^c ΔE_c^{LYP} = error of the LYP density functional. ^d ΔE_c^2 = error of the two-parameter kernel, eqn (3.15). ^e ΔE_c^3 = error of the three-parameter kernel, eqn (3.17). ^f LYP and kernel calculations used UHF/6-311G wavefunctions.

Jacobian and it is easy to show that

$$Y_0(\omega) = \frac{n(n-1)}{2} \frac{\sin \omega}{2} \quad (2.5)$$

In more interesting systems, it is useful to take this as a baseline and write

$$Y(\omega) = Y_0(\omega) + \Delta Y(\omega) \quad (2.6)$$

Because both $Y(\omega)$ and $Y_0(\omega)$ are normalized to $n(n-1)/2$, the differential intracule $\Delta Y(\omega)$ has no net content. However, its subtle features provide a lens through which one can perceive important changes in the mutual orbital motion of electrons.

For example, we found that $\Delta Y(\omega)$ for a helium atom is positive around $\omega = \pi/2$ and correspondingly negative around $\omega = 0$ and $\omega = \pi$. This is significant because, at $\omega = \pi/2$, the electrons' relative momentum vector is perpendicular to their relative position vector, indicating a circular orbit. In the H_2 molecule, $\Delta Y(\omega)$ is also positive in this region, but less so than in the helium atom, indicating that the tendency for the electrons to orbit one another is weaker in the molecule than in the atom. Moreover, as the molecule is stretched, $\Delta Y(\omega)$ flattens even further until, in the dissociated limit, it vanishes completely. (See Fig. 4 in ref. 10.)

A similar trend is observed as a neon atom is transmuted successively into HF, H_2O , NH_3 and CH_4 , indicating that the localization of the neon lone-pair electrons into the σ bonds of the molecules increases the ellipticity of their orbits. (See Fig. 8 in ref. 10)

It is convenient to characterize the differential intracule *via* its Fourier expansion

$$\Delta Y(\omega) = d_1 \sin \omega + d_3 \sin 3\omega + d_5 \sin 5\omega + \dots \quad (2.7)$$

$$d_k = \frac{2}{\pi} \int_0^\pi \Delta Y(\omega) \sin k\omega \, d\omega \quad (2.8)$$

and we note that the integration of (2.7) yields the sum rule

$$0 = d_1 + \frac{d_3}{3} + \frac{d_5}{5} + \dots \quad (2.9)$$

We have evaluated d_1 , d_3 , d_5 and d_7 for the UHF/6-311G wavefunctions of the first 18 atoms in the periodic table and they are listed in columns 3–6 of Table 1. By comparing the d_k with $n(n-1)/4$, we see that $\Delta Y(\omega)$ is never more than a small component of $Y(\omega)$ and that its contribution falls from roughly 20% in the helium atom, to 10% in neon, and to less than 2% in argon. Further examination reveals that the Fourier expansion (2.7) seems to converge rapidly and d_3 is always the largest coefficient. Moreover, we find $d_3 \approx -3d_1$ in all cases, as the sum rule (2.9) would predict for a rapidly converging series. From these observations, we conclude that the d_3 values capture most of the information in the $\Delta Y(\omega)$.

The d_3 values are plotted as a function of the atomic number Z in Fig. 1 and it is immediately clear that they reflect the atomic shell structure. The detailed variations can be rationalized by recognizing that d_3 is a sum of contributions from all $n(n-1)/2$ pairs of electrons in the atom and that, whereas two electrons in the same shell give a negative contribution, two electrons in different shells give a smaller positive contribution.¹⁰

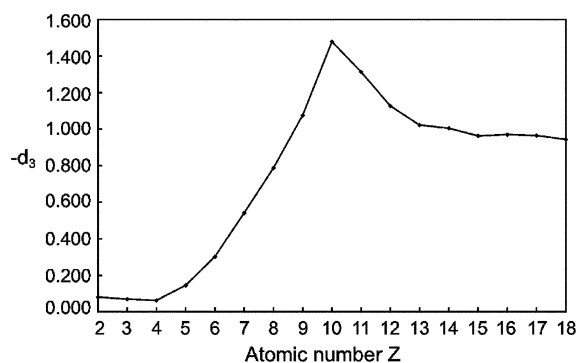


Fig. 1 The d_3 Fourier coefficients for the first 18 atoms. Based on UHF/6-311G wavefunctions.

The d_3 value in helium is -0.0804 and, as described above, this reflects the fact that the two electrons are often found orbiting each other. When a third electron is added (Li), it goes into the 2s subshell. Through its interaction with the two 1s electrons, this electron introduces two new positive contributions and, as a result, d_3 becomes slightly smaller. The addition of a fourth electron (Be) creates two positive contributions and one larger negative contribution and the value of d_3 remains almost unchanged. However, as the next six electrons (B to Ne) are successively added to the 2p subshell, the additional negative contributions significantly outweigh the positive contributions and d_3 grows quadratically.

As we move to sodium, an electron is added to the 3s subshell, leading to ten new positive contributions and a precipitous drop in d_3 . The addition of the twelfth electron (Mg) has a similar effect but the subsequent six additions (Al to Ar) reduce d_3 much less, as the new positive and negative contributions almost balance.

3. Intracule-based correlation models

We have conjectured⁹ that an Omega correlation energy functional exists, *i.e.*

$$E_c = F[\Omega(u, v, \omega)] \quad (3.10)$$

and we have additionally speculated that it can be written

$$E_c = \int_0^\infty \int_0^\infty \int_0^\pi \Omega(u, v, \omega) G(u, v, \omega) d\omega dv du \quad (3.11)$$

where $G(u, v, \omega)$ is a universal correlation kernel. Substituting eqn (2.1) into eqn (3.11) yields

$$E_c = \sum_{abcd} \Gamma_{abcd} [abcd]_G \quad (3.12)$$

where we have introduced the correlation integral

$$[abcd]_G = \int \Phi_{ad}^*(\mathbf{u}, \mathbf{v}) \Phi_{bc}(\mathbf{u}, \mathbf{v}) G(u, v, \omega) d\mathbf{u} d\mathbf{v} \quad (3.13)$$

In the case where each of the basis functions is an s-type Gaussian, this becomes

$$[ssss]_G = \frac{1}{[4(\alpha + \delta)(\beta + \gamma)]^{3/2}} \int \int e^{-\lambda^2 u^2 - \mu^2 v^2 - i\eta \mathbf{u} \cdot \mathbf{v} - \mathbf{P} \cdot \mathbf{u} - i\mathbf{Q} \cdot \mathbf{v} - R} \times G(u, v, \omega) d\mathbf{u} d\mathbf{v} \quad (3.14)$$

and the various constants depend on the Gaussian exponents and centers.⁹

We and others have explored the two-parameter correlation kernel

$$G(u, v, \omega) = C_s j_0(\zeta s) \quad (3.15)$$

where $s = uv$, and this produces the concentric fundamental integral

$$[ssss]_{j_0} = \frac{\pi^3}{[(\alpha + \delta)(\beta + \gamma)]^{3/2}} \frac{[4\lambda^2 \mu^2 + (\zeta - \eta)^2]^{-1/2} - [4\lambda^2 \mu^2 + (\zeta + \eta)^2]^{-1/2}}{2\zeta\eta} \quad (3.16)$$

However, in the light of the discussion in the preceding section, we expect that the correlation energy of a pair of electrons will be influenced by the ellipticity of their orbit, and we are now led to consider the three-parameter angle-corrected correlation kernel

$$G(u, v, \omega) = C_s j_0(\zeta s) + C_\omega \sin 3\omega \quad (3.17)$$

The term $\sin(2k + 1)\omega$ gives rise to the concentric fundamental integral

$$[ssss]_{\sin} = \frac{\pi^3 (1 + z^2)^{3/2} (-z^2)^k \Gamma(k + \frac{3}{2})^2}{[(\alpha + \beta)(\gamma + \delta)]^{3/2} (2k)!} F\left(k + \frac{3}{2}, k + \frac{3}{2}, 2k + 2, -z^2\right) \quad (3.18)$$

where $z = \eta/(2\lambda\mu)$ and $F(a, b, c, x)$ is the hypergeometric function.¹⁹ Concentric integrals of higher angular momentum are similar to (3.16) and (3.18) but contain several such terms. Because these correlation integrals have only four-fold permutational symmetry,²⁰ the cost of computing each set of them is approximately double that of the two-electron repulsion integrals required for the preceding HF calculation. Thus, the total cost of computing the HFW correlation energy using the two-parameter kernel is roughly equivalent to two SCF iterations, and the total cost of computing the HFW correlation energy using the three-parameter kernel is similar to performing four SCF iterations.

We have optimized the values of C_s , C_ω and ζ by a least-squares fit to the exact unrestricted correlation energies²¹ of the first 18 atoms in the periodic table. In Table 1, we report both the root-mean-square deviation (RMSD), which is the quantity that was minimized, and the mean absolute deviation (MAD). All of our intracule functional calculations are based on UHF/6-311G wavefunctions.

The optimized values of C_s and ζ in the two-parameter kernel (3.15) are 0.1060 and 0.9163, respectively. When the additional $\sin 3\omega$ term is included, the coefficient C_s diminishes by 5% but ζ , which is more robust,⁹ changes by less than 1%.

Table 1 compares the exact correlation energies with the estimates obtained using the popular LYP density functional,²² the two-parameter kernel and the three-parameter kernel. The errors ΔE_c^2 and ΔE_c^3 from the two kernels are shown in Fig. 2. The inclusion of the $\sin 3\omega$ term reduces the mean absolute deviation by 36%, from 3.6 to 2.3 mE_h, but its

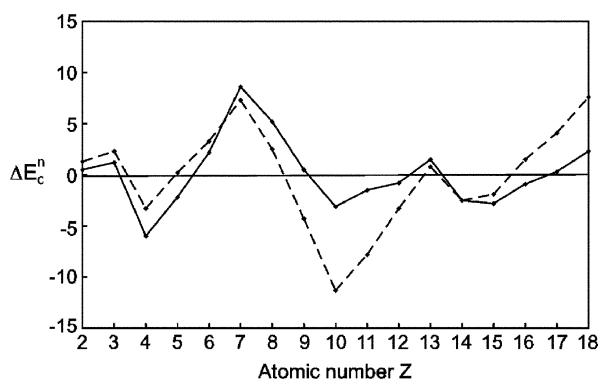


Fig. 2 Correlation energies errors (mE_h) for the first 18 atoms from the two-parameter kernel (3.15) (dashed line) and three-parameter kernel (3.17) (solid line). Based on UHF/6-311G wavefunctions.

benefits are felt primarily by the heavier atoms (F to Ar) whose MAD is reduced by almost a factor of three. Both kernels are much more accurate than the LYP functional and we have found that other commonly used correlation functionals (such as PW91) perform even worse.

Although the three-parameter kernel is significantly more accurate than its two-parameter predecessor, there is still room for improvement. The largest error ($8.6 mE_h$) occurs for the nitrogen atom, which is also the most spin-polarized system in our set, and we are encouraged by the fact that the errors across the 2p block (*i.e.* from Be to Ne) appear to be very systematic. We are currently investigating the reason for this.

4. Concluding remarks

In this paper, we have sought to improve the accuracy of intracule-based electron correlation treatments through the explicit inclusion of a term that depends on the angle ω between the interelectronic position and momentum vectors, \mathbf{u} and \mathbf{v} . We have argued that extracting the $\sin 3\omega$ component of the intracule captures the majority of the chemically

relevant correlation between \mathbf{u} and \mathbf{v} and we have explored the merits of using this as a small additive correction to the usual action-based scheme. In tests on the first eighteen atoms in the periodic table, we have shown that this correction can be applied through the introduction of a single empirical parameter and that this leads to an accuracy improvement of more than 30%.

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