Intracule functional models. II. Analytically integrable kernels

Deborah L. Crittenden, Elise E. Dumont, and Peter M. W. Gill[a)]
Research School of Chemistry, Australian National University, Canberra ACT 0200, Australia

We present, within the framework of intracule functional theory (IFT), a class of kernels whose correlation integrals can be found in closed form. This approach affords three major advantages over other kernels that we have considered previously; ease of implementation, computational efficiency, and numerical stability. We show that even the simplest member of the class yields reasonable estimates of the correlation energies of 18 atomic and 56 molecular systems and we conclude that this kernel class will prove useful in the development of future IFT models. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2795694]

I. INTRODUCTION

Intracule functional theory (IFT) is based on the argument, first made by Rassolov[1] to explain the trend in correlation energies of the heliumlike ions, that the strength of the correlation between two electrons depends both on their relative displacement $\mathbf{u}=\mathbf{r}_1-\mathbf{r}_2$ and their relative momentum $\mathbf{v} = \mathbf{p}_1-\mathbf{p}_2$. As the Heisenberg uncertainty principle precludes the construction of a phase-space wavefunction, we have turned instead to the second-order reduced Wigner distribution $W_2(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)$,[2,3] and argued that all of the physically relevant information in this function can be condensed into the Omega intracule $\Omega(u,v,\omega)$,[4] which is a function of the three key variables $u=|\mathbf{u}|$, $v=|\mathbf{v}|$, and ω, the angle between $\mathbf{u}$ and $\mathbf{v}$. We have then postulated that the correlation energy of a system can be obtained by contracting its Hartree-Fock (HF) Omega intracule with a suitable correlation kernel.[4] In previous work, Gill and co-workers[4–6] and others[7–9] have investigated a range of kernels involving combinations of the variables u, v, and ω, but have never been able to obtain the required correlation integrals in closed form for molecular systems, and have been forced to resort to quadrature. However, in the present work, we present a class of kernels, involving general quadratic forms in $\mathbf{u}$ and $\mathbf{v}$, which yield closed-form correlation integrals. We evaluate the performance of these kernels by calculating correlation energies for the first 18 atoms in the Periodic Table and the molecules contained within Pople's G1 dataset.[10,11] Atomic units are used throughout.

II. THEORY

In calculations using one-electron basis functions $\phi_a(\mathbf{r})$, the Omega intracule is given[12] by

$$\Omega(u,v,\omega) = \sum_{abcd} \Gamma_{abcd}[abcd]_\Omega, \quad (1)$$

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

$$[abcd]_\Omega = \int \Phi_{ad}^*(\mathbf{u},\mathbf{v})\Phi_{bc}(\mathbf{u},\mathbf{v})\delta(\theta_{uv} - \omega)d\Omega_\mathbf{u}d\Omega_\mathbf{v}, \quad (2)$$

are formed from the phase functions

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

If the basis functions ϕ_a are unnormalized s-type Gaussians with exponents α, β, γ, and δ on centers A, B, C, and D, it is not difficult to show that the Omega integral is

$$[ssss]_\Omega = \frac{\exp(-\lambda^2 u^2 - \mu^2 v^2 - R)}{8(\alpha+\delta)^{3/2}(\beta+\gamma)^{3/2}}\int \exp(-i\eta\mathbf{u}\cdot\mathbf{v} - \mathbf{P}\cdot\mathbf{u} - i\mathbf{Q}\cdot\mathbf{v})\delta(\theta_{uv}-\omega)d\Omega_\mathbf{u}d\Omega_\mathbf{v}, \quad (4)$$

where λ, μ, η, $\mathbf{P}$, $\mathbf{Q}$, and R are simple functions of the exponents and centers.[12]

Contraction of this Omega integral with a correlation kernel $G(u,v,\omega)$ yields the correlation integral

$$[ssss]_G = \frac{1}{8(\alpha+\delta)^{3/2}(\beta+\gamma)^{3/2}}\int \exp(-\lambda^2 u^2 - \mu^2 v^2 - i\eta\mathbf{u}\cdot\mathbf{v} - \mathbf{P}\cdot\mathbf{u} - i\mathbf{Q}\cdot\mathbf{v} - R)G(u,v,\omega)d\mathbf{u}d\mathbf{v}, \quad (5)$$

but, unfortunately, we have not been able to evaluate this integral in closed form for kernels such as $G(u,v,\omega) = j_0(\zeta uv)$ or $G(u,v,\omega)=\sin(2n+1)\omega$, unless the four Gaussian centers are identical. This has allowed us to explore the accuracy of such kernels for atoms,[4,6] but analogous molecular investigations have been plagued by numerical issues.[7,8]

However, there is one class of kernels for which the integral (5) is almost trivial. If, like the rest of the integrand, the kernel is of the generalized Gaussian form

$$G(v,v,\omega) = \sum_{k=1}^{n} C_k \exp(-\lambda_k^2 u^2 - \mu_k^2 v^2 - i\eta_k\mathbf{u}\cdot\mathbf{v}), \quad (6)$$

then, it is easy to show that

TABLE I. Exact atomic and molecular correlation energies (mE_h) and errors of the two-parameter kernel (ΔE_c^2), the three-parameter kernel (ΔE_c^3) and the LYP density functional (ΔE_c^{LYP}).

Molecule	E_c^{exact}	ΔE_c^2	ΔE_c^3	ΔE_c^{LYP}	Molecule	E_c^{exact}	ΔE_c^2	ΔE_c^3	ΔE_c^{LYP}
H	0	0	0	0	HCO	553	−26	−21	−46
He	42	1	20	2	S	597	1	11	33
H_2	41	−1	1	−3	SiH_2 ($^3B_1$)	540	27	17	36
Li	45	0	31	9	SiH_2 ($^1A_1$)	567	6	8	29
Be	94	−12	3	1	O_2	636	−54	−33	−67
LiH	83	7	23	6	H_2CO	586	−12	−17	−46
B	121	−9	7	5	C_2H_4	518	53	4	−21
BeH	93	5	28	15	Cl	658	8	22	34
C	151	0	13	9	PH_2	611	−34	−9	8
Li_2	124	4	36	10	SiH_3	575	44	23	40
N	185	14	17	7	Ar	723	17	33	28
CH	194	−3	10	3	HCl	707	23	14	19
O	249	5	23	9	H_2S	683	31	6	17
NH	236	13	15	0	PH_3	652	41	6	22
CH_2 ($^3B_1$)	208	31	16	4	SiH_4	606	61	28	42
CH_2 ($^1A_1$)	239	−4	2	−7	F_2	757	−75	−49	−82
F	318	−1	22	4	H_2O_2	711	−31	−38	−75
OH	309	4	11	−8	N_2H_4	641	33	−10	−45
NH_2	287	20	10	−9	CH_3OH	629	38	2	−34
CH_3	254	45	19	3	C_2H_6	561	96	23	−10
Ne	391	−2	11	−7	CO_2	876	−52	−41	−87
HF	389	−4	−5	−27	CS	867	−33	−30	−21
H_2O	371	9	−8	−31	Na_2	819	−9	29	23
NH_3	340	32	−1	−23	SiO	879	−48	−32	−27
CH_4	299	60	14	−5	SO	957	−33	−20	−18
Na	396	−8	25	13	ClO	1002	−28	−4	−12
Mg	438	−15	10	22	FCl	1063	−35	−10	−17
LiF	441	−3	17	−23	HOCl	1045	−14	−11	−20
Al	465	−12	11	30	CH_3Cl	968	58	23	14
CN	483	−63	−60	−73	CH_3SH	946	68	13	11
Si	500	−9	7	31	NaCl	1101	30	36	32
N_2	549	−59	−39	−67	Si_2	1077	−30	−34	23
CO	535	−46	−25	−52	P_2	1205	−22	−41	6
HCN	515	−23	−29	−52	S_2	1275	2	−6	30
HCCH	480	14	−19	−36	SO_2	1334	−76	−61	−81
P	540	−2	2	27	Si_2H_6	1183	113	43	77
NO	596	−64	−42	−71	Cl_2	1380	9	16	32

Mean absolute deviations				
Atoms only		6	15	15
Molecules only		33	21	30
Atoms and molecules		27	20	27

$$[ssss]_G = \sum_{k=1}^{n} C_k \left[\frac{\pi^2}{(\alpha + \delta)(\beta + \gamma)(4l^2m^2 + h^2)} \right]^{3/2}$$

$$\times \exp\left[\frac{m^2P^2 + h\mathbf{P}\cdot\mathbf{Q} - l^2Q^2}{4l^2m^2 + h^2} - R \right], \quad (7)$$

where $l^2 = \lambda^2 + \lambda_k^2$, $m^2 = \mu^2 + \mu_k^2$, and $h = \eta + \eta_k$. (We note that Dolg has examined the effectiveness of gaussian kernels with $\mu_k = \eta_k = 0$ to distinguish the relatively similar correlation energies of the He-like ions.[13])

Following Boys,[14] integrals of higher angular momentum can then be formed by differentiating Eq. (7) with respect to the Cartesian coordinates of the basis function centers and we have used this approach to generate explicit formulas for all integrals up to $[pppp]$. These have been implemented in a development version of the Q-CHEM 3.1 software package,[15] allowing us to compute the correlation energy

$$E_c = \sum_{abcd} \Gamma_{abcd}[abcd]_G, \quad (8)$$

for an arbitrary molecular system with an arbitrary Gaussian sp basis set.

All of the results presented below are based on UHF/6-311G wavefunctions. Once we have the capability, it will be important to assess the impact of polarization functions on the numerical results that we have obtained. However, we have decided to defer this investigation until we have discov-
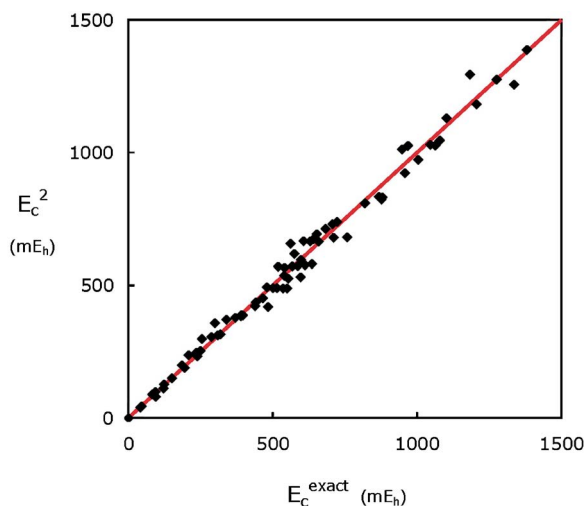
FIG. 1. Exact vs G_2 correlation energies for H–Ar and the G1 molecules.

FIG. 2. Exact vs G_3 correlation energies for H–Ar and the G1 molecules.

ered a recurrence relation[16] for the systematic and efficient construction of correlation integrals of high angular momentum.

III. RESULTS AND DISCUSSION

For the purposes of this Communication, we have confined our attention to the simple one-term kernel

$$G(u,v,\omega) = C_1 \exp(- \lambda_1^2 u^2 - \mu_1^2 v^2 - i \eta_1 \mathbf{u} \cdot \mathbf{v}) \qquad (9)$$

and optimized the parameters in Eq. (9) by least-squares fits to exact atomic and molecular correlation energies.[17]

In the first optimization, we fitted the correlation energies of the atoms He to Ar and were surprised to discover that the optimal values of both λ_1 and μ_1 were essentially zero. This produced the two-parameter kernel

$$G_2(u,v,\omega) = C_1 \exp(- i \eta_1 \mathbf{u} \cdot \mathbf{v}), \qquad (10)$$

where $C_1 = 0.076\,95$ and $\eta_1 = 0.8474$. This may be compared with another two-parameter kernel that we have recently developed[6] in which uv and ω occur in separate terms.

In the second optimization, we fitted the correlation energies of the atoms *and* all of the molecules in the G1 dataset. As before, μ_1 was found to be unimportant, but λ_1 was now significant and this yielded the three-parameter kernel

$$G_3(u,v,\omega) = C_1 \exp(- \lambda_1^2 u^2 - i \eta_1 \mathbf{u} \cdot \mathbf{v}), \qquad (11)$$

where $C_1 = 0.2113$, $\lambda_1 = 0.5578$, and $\eta_1 = 1.0374$.

Differences between the exact and calculated correlation energies for each of the atoms and molecules in the full data set are presented in Table I and illustrated in Figs. 1 and 2. For comparison, we have computed the correlation energies using the popular four-parameter Lee-Yang-parr (LYP) density functional,[18] and these results are also presented in Table I. Mean absolute deviations for the two- and three-parameter kernels, as well as LYP, are also given.

From Fig. 1, we observe that the two-parameter kernel yields reasonable correlation energies, particularly for atoms and small systems. However, as the molecules increase in size and correlation energy, the performance of this kernel
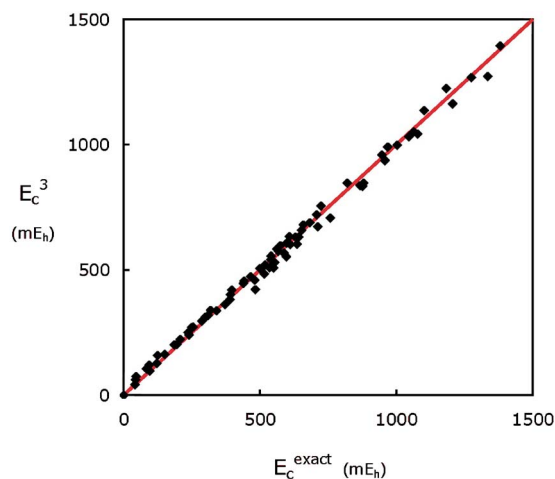
degrades and we observe an increase in scatter about the diagonal $E_c^2 = E_c^{\text{exact}}$ line. Inspection of Table I reveals that the largest errors come from molecules with the largest numbers of atoms and σ bonds, namely, C_2H_6 (+96 mE_h) and Si_2H_6 (+113 mE_h). The correlation energies of the other molecules with four or more σ bonds are also significantly overestimated, with ΔE_c^2 values ranging between +33 and +68 mE_h. In contrast, the energies of molecules with significant multireference character are underestimated, the largest such errors arising for SO_2 (−76 mE_h) and F_2 (−75 mE_h). Errors in the correlation energies of di- and triatomics with several π bonds fall in the range from −22 to −63 mE_h.

From Fig. 1, we also notice that a pattern of horizontally scattered points appears at a series of discrete energies, around 250, 300, 380, 490, 580, 680, 830, and 1000 mE_h. From Table I, we see that the data points that form these patterns correspond to molecules that belong to an isoelectronic series. For example, the horizontally scattered points near 380 mE_h correspond to the isoelectronic series comprised of CH_4, NH_3, H_2O, HF, and Ne. In this case, the predicted correlation energies of Ne and HF are almost exact, but the error gets progressively worse as one moves along the isoelectronic series to CH_4, whose correlation energy is overestimated by 60 mE_h. This is consistent with the previous observation that the two-parameter kernel overestimates the correlation energy of molecules with several σ bonds. Finally, we note that this kernel has the same overall accuracy as the LYP functional, although it performs significantly better for atoms and slightly worse for molecules.

Figure 2 reveals that including an extra parameter (λ_1) in the kernel and reoptimizing with respect to the full data set results in a significant improvement in the predicted correlation energies, particularly for larger molecules. This is also evident from the mean absolute deviation data presented in Table I, which show that the three-parameter kernel performs substantially better overall than either the two-parameter kernel or the LYP functional. However, the data presented in Table I show that this improvement comes at the expense of the atoms, all of which are now overestimated, particularly helium and lithium. We also notice that the majority of the improvement in the performance of this kernel comes from

TABLE II. D1 diagnostics from CCSD/6-311G calculations on 18-electron systems.

Molecule	D1	Molecule	D1
Ar	0.0089	F_2	0.0302
HCl	0.0119	H_2O_2	0.0232
H_2S	0.0158	CH_3OH	0.0173
PH_3	0.0184	N_2H_4	0.0151
SiH_4	0.0128	C_2H_6	0.0104

molecules with several σ bonds, whose errors are typically decreased by a factor of 3. For molecules with significant multireference character, including the majority of molecules with π bonds, the predicted correlation energies improve only slightly.

The relationship between multireference character and the error in the correlation energy (ΔE_c^3) is clearly illustrated by, for example, the 18-electron systems. The multireference character of each of these can be quantified by the D1 diagnostic[19] obtained from CCSD/6-311G calculations carried out within MOLPRO.[20] These results are presented in Table II and the linear relationship (Fig. 3) between the D1 diagnostic and ΔE_c^3 indicates that the kernel increasingly fails to recover the full correlation energy as the multireference character of the system increases. We infer from this that the G_2 and G_3 correlation kernels recover primarily the dynamic correlation energy and the considerable similarity between E_c^3 and E_c^{LYP} (Fig. 4) also supports this conclusion.

Taken together, these observations suggest that the three-parameter kernel estimates the dynamic component of the correlation energy more accurately than the two-parameter kernel, but that both kernels struggle to recover the static component, which is particularly significant for systems with several π bonds and/or radical character. In this way, our results are similar to correlation energies obtained using density functional theory, whose correlation functionals also fail to recover the static component of the correlation energy. It has been suggested that this deficiency may be remedied by using a multiconfiguration reference wavefunction, then calculating the dynamic correlation correction using an appropriate correlation functional.[21,22] Analogously, we are also
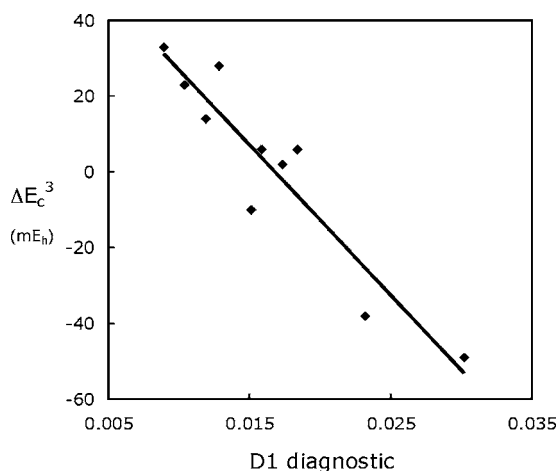
FIG. 3. D1 diagnostic vs G_3 correlation energy error in 18-electron systems.
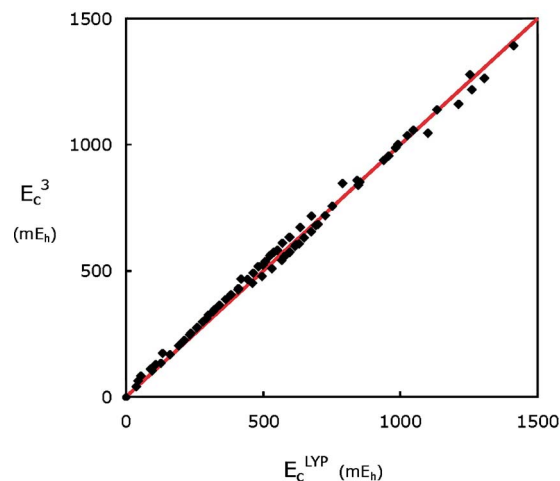
FIG. 4. LYP vs G_3 correlation energies for H–Ar and the G1 molecules.

currently investigating the possibility of recovering the static correlation energy using a low-cost multireference method, then using IFT to recover the dynamic component of the correlation energy.

IV. CONCLUSIONS

We have introduced a new class of correlation kernels [Eq. (6)] whose correlation integrals can be obtained in closed form. We have found a two-parameter kernel [Eq. (10)] that depends only on $\mathbf{u} \cdot \mathbf{v}$ and provides useful correlation energy estimates for a range of atomic and molecular systems, although it systematically overestimates the energies of systems with several σ bonds and underestimates the energies of systems with significant multireference character. Including a u-dependent factor yields a three-parameter kernel [Eq. (11)] that improves the σ-bond error, but not the multireference error. Numerical evidence suggests that this is due to the inability of either kernel to recover the static component of the correlation energy and we propose using a low-cost multireference method in place of Hartree-Fock theory to obtain more accurate correlation energy estimates.

We anticipate that future progress in recovering dynamic correlation energy will involve using the kernels presented here as a basis for the construction of a superclass of more general, flexible correlation kernels. In particular, the systematic overestimation of atomic correlation energies can probably be improved by adding extra terms in the kernel expansion [i.e., using $n > 1$ in Eq. (6)].

[1] V. A. Rassolov, J. Chem. Phys. **110**, 3672 (1999).
[2] E. Wigner, Phys. Rev. **40**, 749 (1932).
[3] H. J. Groenewald, Physica (Utrecht) **12**, 405 (1946).
[4] P. M. W. Gill, D. L. Crittenden, D. P. O'Neill, and N. A. Besley, Phys. Chem. Chem. Phys. **8**, 15 (2006).

[5] P. M. W. Gill and D. P. O'Neill, J. Chem. Phys. **122**, 094110 (2005).

[6] E. E. Dumont, D. L. Crittenden, and P. M. W. Gill, Phys. Chem. Chem. Phys. **9**, 5340 (2007).

[7] R. Fondermann, M. Hanrath, M. Dolg, and D. P. O'Neill, Chem. Phys. Lett. **413**, 237 (2005).

[8] R. Fondermann, M. Hanrath, and M. Dolg, ″The performance of the Hartree-Fock-Wigner correlation model for light diatomic molecules″ Theor. Chem. Acc. (to be published).

[9] N. A. Besley, J. Chem. Phys. **125**, 074104 (2006).

[10] J. A. Pople, M. Head-Gordon, D. J. Fox, K. Raghavachari, and L. A. Curtiss, J. Chem. Phys. **90**, 5622 (1989).

[11] L. A. Curtiss, C. Jones, G. W. Trucks, K. Raghavachari, and J. A. Pople, J. Chem. Phys. **93**, 2537 (1990).

[12] D. L. Crittenden and P. M. W. Gill, J. Chem. Phys. **127**, 014101 (2007).

[13] M. Dolg (unpublished).

[14] S. F. Boys, Proc. R. Soc. London **A200**, 542 (1950).

[15] Y. Shao, L. Fusti-Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld *et al.*, Phys. Chem. Chem. Phys. **8**, 3172 (2006).

[16] P. M. W. Gill, Adv. Quantum Chem. **25**, 141 (1994).

[17] D. P. O'Neill and P. M. W. Gill, Mol. Phys. **103**, 763 (2005).

[18] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).

[19] C. L. Janssen and I. M. B. Neilsen, Chem. Phys. Lett. **290**, 423 (1998).

[20] H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz *et al.*, MOLPRO, version 2006.1, a package of *ab initio* programs, 2006, see http://www.molpro.net.

[21] J. J. W. McDouall, Mol. Phys. **101**, 361 (2003).

[22] P. Gori-Giorgi and A. Savin, Philos. Mag. **86**, 2643 (2006).