

This paper is published as part of a PCCP Themed Issue on: Explicit- r_{12} Correlation Methods and Local Correlation Methods

Guest Editors: Hans-Joachim Werner and Peter Gill

Editorial

Explicit- r_{12} correlation methods and local correlation methods

Phys. Chem. Chem. Phys., 2008

DOI: [10.1039/b808067b](https://doi.org/10.1039/b808067b)

Papers

Implementation of the CCSD(T)-F12 method using cusp conditions

Denis Bokhan, Seiichiro Ten-no and Jozef Noga, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b803426p](https://doi.org/10.1039/b803426p)

Analysis of non-covalent interactions in (bio)organic molecules using orbital-partitioned localized MP2

Stefan Grimme, Christian Mück-Lichtenfeld and Jens Antony, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b803508c](https://doi.org/10.1039/b803508c)

Tighter multipole-based integral estimates and parallel implementation of linear-scaling AO-MP2 theory

Bernd Doser, Daniel S. Lambrecht and Christian Ochsenfeld, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b804110e](https://doi.org/10.1039/b804110e)

Local correlation domains for coupled cluster theory: optical rotation and magnetic-field perturbations

Nicholas J. Russ and T. Daniel Crawford, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b804119a](https://doi.org/10.1039/b804119a)

Local and density fitting approximations within the short-range/long-range hybrid scheme: application to large non-bonded complexes

Erich Goll, Thierry Leininger, Frederick R. Manby, Alexander Mitrushchenkov, Hans-Joachim Werner and Hermann Stoll, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b804672q](https://doi.org/10.1039/b804672q)

Equations of explicitly-correlated coupled-cluster methods

Toru Shiozaki, Muneaki Kamiya, So Hirata and Edward F. Valeev, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b803704n](https://doi.org/10.1039/b803704n)

Vanadium oxide compounds with quantum Monte Carlo

Annika Bande and Arne Lüchow, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b803571g](https://doi.org/10.1039/b803571g)

Second-order Møller–Plesset calculations on the water molecule using Gaussian-type orbital and Gaussian-type geminal theory

Pål Dahle, Trygve Helgaker, Dan Jonsson and Peter R. Taylor, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b803577f](https://doi.org/10.1039/b803577f)

The Σ^- states of the molecular hydrogen

Jacek Komasa, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b803548b](https://doi.org/10.1039/b803548b)

Slater-type geminals in explicitly-correlated perturbation theory: application to n -alkanols and analysis of errors and basis-set requirements

Sebastian Höfener, Florian A. Bischoff, Andreas Glöß and Wim Klopper, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b803575j](https://doi.org/10.1039/b803575j)

Accurate calculations of intermolecular interaction energies using explicitly correlated wave functions

Oliver Marchetti and Hans-Joachim Werner, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b804334e](https://doi.org/10.1039/b804334e)

Variational formulation of perturbative explicitly-correlated coupled-cluster methods

Martin Torheyden and Edward F. Valeev, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b803620a](https://doi.org/10.1039/b803620a)

Resolution of the identity atomic orbital Laplace transformed second order Møller–Plesset theory for nonconducting periodic systems

Artur F. Izmaylov and Gustavo E. Scuseria, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b803274m](https://doi.org/10.1039/b803274m)

On the use of the Laplace transform in local correlation methods

Danylo Kats, Denis Usvyat and Martin Schütz, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b802993h](https://doi.org/10.1039/b802993h)

Intracule densities in the strong-interaction limit of density functional theory

Paola Gori-Giorgi, Michael Seidl and Andreas Savin, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b803709b](https://doi.org/10.1039/b803709b)

Intracule functional models

Part III. The dot intracule and its Fourier transform

Yves A. Bernard, Deborah L. Crittenden and Peter M. W. Gill, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b803919d](https://doi.org/10.1039/b803919d)

Density matrix renormalisation group Lagrangians

Garnet Kin-Lic Chan, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b805292c](https://doi.org/10.1039/b805292c)

The interaction of carbohydrates and amino acids with aromatic systems studied by density functional and semi-empirical molecular orbital calculations with dispersion corrections

Raman Sharma, Jonathan P. McNamara, Rajesh K. Raju, Mark A. Vincent, Ian H. Hillier and Claudio A. Morgado, *Phys. Chem. Chem. Phys.*, 2008, **10**, 2767

The principle-quantum-number (and the radial-quantum-number) expansion of the correlation energy of two-electron atoms

Werner Kutzelnigg, *Phys. Chem. Chem. Phys.*, 2008

DOI: [10.1039/b805284k](https://doi.org/10.1039/b805284k)

Intracule functional models

Part III. The dot intracule and its Fourier transform†

Yves A. Bernard, Deborah L. Crittenden and Peter M. W. Gill

Received 6th March 2008, Accepted 11th April 2008

First published as an Advance Article on the web 8th May 2008

DOI: 10.1039/b803919d

The dot intracule $D(x)$ of a system gives the Wigner quasi-probability of finding two of its electrons with $\mathbf{u}\cdot\mathbf{v} = x$, where \mathbf{u} and \mathbf{v} are the interelectronic distance vectors in position and momentum space, respectively. In this paper, we discuss $D(x)$ and show that its Fourier transform $d(k)$ can be obtained in closed form for any system whose wavefunction is expanded in a Gaussian basis set. We then invoke Parseval's theorem to transform our intracule-based correlation energy method into a $d(k)$ -based model that requires, at most, a one-dimensional quadrature.

I. Introduction

In principle, the Schrödinger equation¹ provides a complete description of the non-relativistic electronic structure of atoms and molecules. Unfortunately, it is almost always too complex to solve exactly and systematic approximations are necessary. In the most famous of these, the Hartree–Fock method,^{2,3} the wave function is approximated by a single determinant of one-electron functions and the difference between the resulting energy and the exact Schrödinger eigenvalue is defined⁴ as the correlation energy E_c . This quantity is very difficult to calculate, even for small systems, and a wide range of approximate methods have been devised. Wavefunction-based schemes,⁵ such as configuration interaction, perturbation theory and coupled-cluster methods, estimate E_c from the molecular orbitals and their energies; DFT methods⁶ estimate it from the electron density. More recently, however, we have proposed that it may also be possible to extract E_c from intracules.

The Position intracule $P(u)$ ^{7,8} and Momentum intracule $M(v)$ ^{9,10} were introduced long ago and give the probability density for finding two electrons with separation $u = |\mathbf{r}_1 - \mathbf{r}_2|$ in position space or $v = |\mathbf{p}_1 - \mathbf{p}_2|$ in momentum space. However, neither is well suited to the estimation of correlation energies and the reason for this, first clearly enunciated by Rassolov,¹¹ is that the correlation contribution from a pair of electrons depends on both their relative position *and* their relative momentum.

In an attempt to obtain such “phase-space” information, we turned to the reduced Wigner distribution^{12,13} and we showed how this can be manipulated to form the Omega intracule $\Omega(u,v,\omega)$,¹⁴ which can be interpreted as the *joint* quasi-probability density for u , v and ω , the angle between the vectors \mathbf{u} and \mathbf{v} . Appropriate integration of $\Omega(u,v,\omega)$ yields the lower intracules,¹⁵ including the bivariate Wigner intracule $W(u,v)$ and Lambda intracule $A(s,\omega)$, and the univariate $P(u)$, $M(v)$

and $\lambda(\omega)$ intracules, as well as the Action intracule $A(s)$ and the Dot intracule $D(x)$, where $s = uv$ and $x = \mathbf{u}\cdot\mathbf{v}$.

Each intracule is normalized¹⁶ to the number of pairs of electrons and so, for example,

$$\int_{-\infty}^{\infty} D(x)dx = \frac{n(n-1)}{2} \quad (1.1)$$

where n is the number of electrons in the system. Moreover, if the underlying wavefunction is expanded in a basis of one-electron functions, the Dot intracule is given by¹⁶

$$D(x) = \sum_{abcd} \Gamma_{abcd} [abcd]_D \quad (1.2)$$

where Γ_{abcd} is a two-particle density matrix element and $[abcd]_D$ is the Dot integral over the four basis functions with indices a , b , c and d . In section II of this paper, we show how $D(x)$ and its Fourier transform can be computed efficiently and, in section III, we discuss their physical interpretation using several simple examples.

We have conjectured¹⁵ that the correlation energy E_c is a universal functional of the Omega intracule and, in particular, that one can write

$$E_c = \int_0^\infty \int_0^\infty \int_0^\pi \Omega(u,v,\omega) G(u,v,\omega) d\omega dv du \quad (1.3)$$

where $G(u,v,\omega)$ is a correlation kernel. By extending this conjecture, each of the lower intracules can be combined with a suitable kernel to yield a correlation model. Of these, the Wigner intracule ansatz

$$E_c = \int_0^\infty \int_0^\infty W(u,v) G(u,v) du dv \quad (1.4)$$

has been the most popular to date and has been studied numerically in several papers.^{15,17–22} In sections IV and V of the present paper, however, the Dot intracule ansatz

$$E_c = \int_{-\infty}^{\infty} D(x) G(x) dx \quad (1.5)$$

and related approaches will be our primary concern. All of our numerical results are based on UHF/6-311G wavefunctions and we use atomic units throughout.

Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia. E-mail: peter.gill@anu.edu.au
† For Part II see ref. 22.

II. The Dot intracule and its Fourier transform

The Omega intracule is formed¹⁵ from the reduced two-particle density matrix by

$$\begin{aligned} \Omega(u, v, \omega) = & \frac{1}{(2\pi)^3} \int \rho_2(\mathbf{r}, \mathbf{r} + \mathbf{q}, \mathbf{r} + \mathbf{u} + \mathbf{q}, \mathbf{r} + \mathbf{u}) \\ & \times e^{i\mathbf{q}\cdot\mathbf{v}} \delta(u - |\mathbf{u}|) \delta(v - |\mathbf{v}|) \delta(\omega - \theta_{uv}) \, d\mathbf{r} \, d\mathbf{q} \, d\mathbf{v} \, d\mathbf{u} \end{aligned} \quad (2.6)$$

and the Dot intracule is given similarly by

$$\begin{aligned} D(x) = & \frac{1}{(2\pi)^3} \int \rho_2(\mathbf{r}, \mathbf{r} + \mathbf{q}, \mathbf{r} + \mathbf{u} + \mathbf{q}, \mathbf{r} + \mathbf{u}) \\ & e^{i\mathbf{q}\cdot\mathbf{v}} \delta(x - \mathbf{u} \cdot \mathbf{v}) \, d\mathbf{r} \, d\mathbf{q} \, d\mathbf{v} \, d\mathbf{u} \end{aligned} \quad (2.7)$$

This 12-dimensional integral can be simplified by substituting the Dirac identity

$$\delta(z) \equiv \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{izk} \, dk \quad (2.8)$$

and integrating over \mathbf{v} and \mathbf{q} to obtain

$$\begin{aligned} D(x) = & \frac{1}{2\pi} \int \rho_2(\mathbf{r}, \mathbf{r} + k\mathbf{u}, \mathbf{r} + \mathbf{u} + k\mathbf{u}, \mathbf{r} + \mathbf{u}) \\ & e^{ikx} \, dk \, d\mathbf{r} \, d\mathbf{u} \end{aligned} \quad (2.9)$$

Thus, we can obtain the Dot intracule as the Fourier transform

$$D(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d(k) e^{ikx} \, dk \quad (2.10)$$

of the f -Dot function

$$d(k) = \int \rho_2(\mathbf{r}, \mathbf{r} + k\mathbf{u}, \mathbf{r} + \mathbf{u} + k\mathbf{u}, \mathbf{r} + \mathbf{u}) \, d\mathbf{r} \, d\mathbf{u} \quad (2.11)$$

We note that the normalization of $D(x)$ implies that $d(0) = n(n-1)/2$. If the wavefunction is expanded in a one-electron basis, eqn (2.11) becomes

$$d(k) = \sum_{abcd} \Gamma_{abcd} [abcd]_d \quad (2.12)$$

where the f -Dot integrals $[abcd]_d$ are four-centre overlap integrals that can, in some cases, be found in closed form. For example, if the basis functions are s -type Gaussians, we obtain

$$\begin{aligned} [ssss]_d = & \int e^{-\alpha|r-A|^2} e^{-\beta|r+ku-B|^2} e^{-\gamma|r+u+ku-C|^2} e^{-\delta|r+u-D|^2} \, d\mathbf{r} \, d\mathbf{u} \\ = & \frac{\pi^3}{[(\alpha + \delta)(\beta + \gamma)]^{3/2}} \frac{\exp\left[\frac{\mu^2 P^2 + (\eta+k) \mathbf{P} \cdot \mathbf{Q} - \lambda^2 Q^2}{4\lambda^2 \mu^2 + (\eta+k)^2} - R\right]}{[4\lambda^2 \mu^2 + (\eta+k)^2]^{3/2}} \end{aligned} \quad (2.13)$$

where λ , μ , η , \mathbf{P} , \mathbf{Q} and R are the usual functions of the exponents and centers.²³ Integrals of higher angular momentum can be generated by differentiating $[ssss]_d$ with respect to the Cartesian coordinates of the basis function centres, as first suggested by Boys.²⁴

We have modified a development version of the Q-CHEM 3.1 package²⁵ to use (2.12), together with (2.13) and its higher analogues up to $[pppp]_d$, to construct the f -Dot function for

arbitrary molecules with s and p basis functions. We are currently extending our implementation to include d and f functions and this will allow us to explore the effects of polarization functions. We will report a systematic investigation of basis set effects elsewhere²⁶ but we do not expect that the neglect of polarization functions in the present work will alter our qualitative conclusions.

If one requires the Dot intracule, there are two ways to proceed. The first method is to use (1.2) and obtain the required Dot integrals from the Fourier transforms

$$\begin{aligned} [ssss]_D = & \frac{\pi^3}{[(\alpha + \delta)(\beta + \gamma)]^{3/2}} \\ & \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{\exp\left[\frac{\mu^2 P^2 + (\eta+k) \mathbf{P} \cdot \mathbf{Q} - \lambda^2 Q^2}{4\lambda^2 \mu^2 + (\eta+k)^2} - R + ikx\right]}{[4\lambda^2 \mu^2 + (\eta+k)^2]^{3/2}} \, dk \end{aligned} \quad (2.14)$$

In the concentric special case (*i.e.* $P = Q = R = 0$), the integral (2.14) is

$$[ssss]_D = \frac{\pi^2 e^{-\eta x}}{4\lambda^2 \mu^2 [(\alpha + \delta)(\beta + \gamma)]^{3/2}} c K_1(c) \quad (2.15)$$

where K_1 is a modified Bessel function of the second kind²⁷ and $c = 2\lambda\mu|x|$. However, in the general case, we have not been able to solve it in closed form and have turned instead to numerical methods. For large x , the evaluation of (2.14) by standard quadrature becomes problematic because the integrand oscillates rapidly but we found that the Evans-Chung method of optimal contour integration²⁸ can be employed to overcome this obstacle. For very large x , it should be possible to use the asymptotic form²⁹ of (2.14).

A second, more efficient method for forming the Dot intracule is to form the f -Dot function and then perform the Fourier transform (2.10). To obtain the results in the next section, we used Q-CHEM to compute $d(k)$ on a grid of k points and then performed the inverse transform using the NINTEGRATE module in the MATHEMATICA package.³⁰

Table 1 summarizes some of the properties of the $[ssss]_d$ integral that follow from (2.13) and the properties of the $[ssss]_D$ integral that then follow by the Fourier transform theory.³¹

III. Interpretation of $D(x)$ and $d(k)$

In a system with n_α spin-up electrons and n_β spin-down electrons, the Dot intracule $D(x)$ and f -Dot function $d(k)$ contain $n_\alpha n_\beta$ contributions from electrons with antiparallel spins and $\frac{1}{2}n_\alpha(n_\alpha - 1) + \frac{1}{2}n_\beta(n_\beta - 1)$ contributions from electrons with parallel spins. These two types of contribution are conveniently isolated and illustrated by the helium atom in its lowest singlet (1S , antiparallel spins) and triplet (3S , parallel spins) states.

Table 1 Properties of the $[ssss]_d$ and $[ssss]_D$ integrals

$f_d(k) = [ssss]_d$	$f_D(x) = [ssss]_D$
$f_d(k)$ is a real function	$f_D(x)$ is a hermitian function
$f_d(k) = O(k ^{-3})$ as $ k \rightarrow \infty$	$f''_D(x)$ is discontinuous at $x = 0$
$f_d(k)$ is smooth for all real k	$f_D(x) = O(e^{-2\lambda\mu x })$ as $ x \rightarrow \infty$

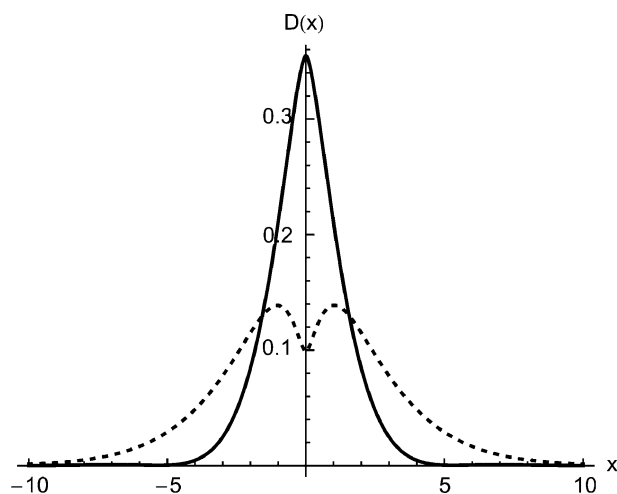


Fig. 1 $D(x)$ for 1S (—) and 3S (···) states of He atom.

Fig. 1 shows $D(x)$ for both states. The intracules are even functions and the discontinuity of $D''(x)$ at $x = 0$ is visible. In the singlet state, the most likely value of x is zero. Because x is the dot product of $\mathbf{u} = \mathbf{r}_1 - \mathbf{r}_2$ and $\mathbf{v} = \mathbf{p}_1 - \mathbf{p}_2$, this shows that the electrons are likely to be close together or moving relatively slowly or orbiting each other.¹⁴ In the triplet state, however, we observe a marked reduction around $x = 0$ and a significant broadening of the intracule. We attribute this to the effects of antisymmetry, which creates a Fermi hole around each electron and substantially reduces the probability of small u values compared with the singlet. Consequently, small values of x are also less likely.

Fig. 2 shows $d(k)$ for both states. The functions are even and their k^{-3} decay is slower than the exponential decay of their respective intracules. As one would expect, the f -Dot function, which is narrower for the triplet than for the singlet, provides a complementary perspective to the Dot intracule. The dip in the triplet's intracule causes $d(k)$ to become negative for $k \gtrsim 1$.

Fig. 3 shows how $D(x)$ evolves in larger atoms. As we move from helium to neon, the intracule broadens and develops a small dip around $x = 0$. The broadening arises principally from the higher v (and therefore x) values that occur in heavier

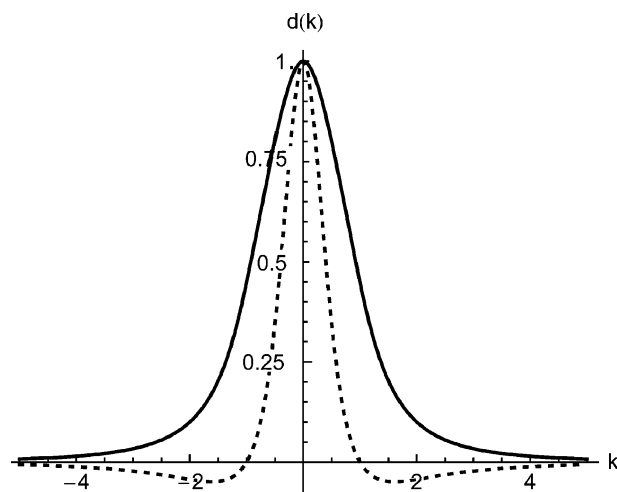


Fig. 2 $d(k)$ for 1S (—) and 3S (···) states of He atom.

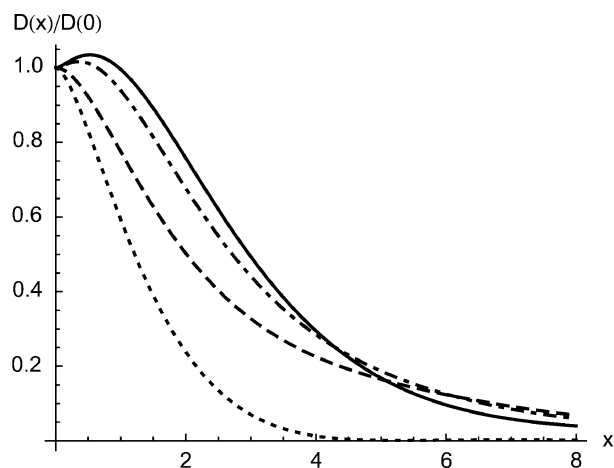


Fig. 3 $D(x)/D(0)$ for He (···), Be (---), C (-·-) and Ne (—).

atoms and the dip reflects the increasing importance of parallel-spin contributions to the intracule (*cf.* triplet helium).

Fig. 4, in which we have defined $\Delta D(x) = D(x) - D_{\text{Ne}}(x)$, shows the way in which $D(x)$ is perturbed as the neon atom is progressively transmuted into HF, H₂O, NH₃ and CH₄. During this alchemy, the four lone pairs are successively converted into σ bonds and the intracule decreases slightly for $x \lesssim 4$ and increases slightly for larger values of x . This is consistent with our previous conclusion¹⁴ that, whereas electrons in lone pairs tend to move orbitally (*i.e.* $\omega \approx \pi/2$ and so $|x|$ is small), those in σ bonds tend to move collinearly (*i.e.* $\omega \approx 0$ or $\omega \approx \pi$ and so $|x|$ is large).

Fig. 5 and 6 show the parallel and antiparallel components of $D(x)$ and $d(k)$ for the He···He dimer at the experimental internuclear separation of 5.6 a.u. The system has $n_\alpha = n_\beta = 2$ and therefore two parallel and four antiparallel contributions. Both of the parallel contributions and two of the antiparallel contributions arise from distant (*i.e.* $u \approx 5.6$) electrons; the other antiparallel contributions arise from electrons on the same atom.

Because the parallel electrons are far apart and $\mathbf{u} \cdot \mathbf{v}$ can therefore take a wide range of values, the parallel component of $D(x)$ (the dashed curve in Fig. 5) is very flat. We note, however, the slight dip near $x = 0$ that arises from the Fermi

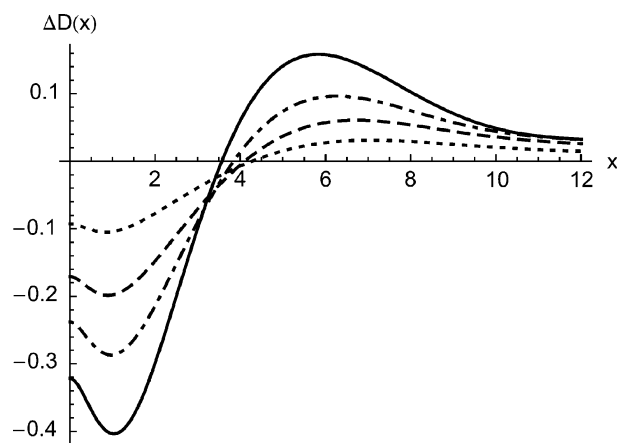


Fig. 4 $\Delta D(x)$ for HF (···), H₂O (---), NH₃ (-·-) and CH₄ (—).

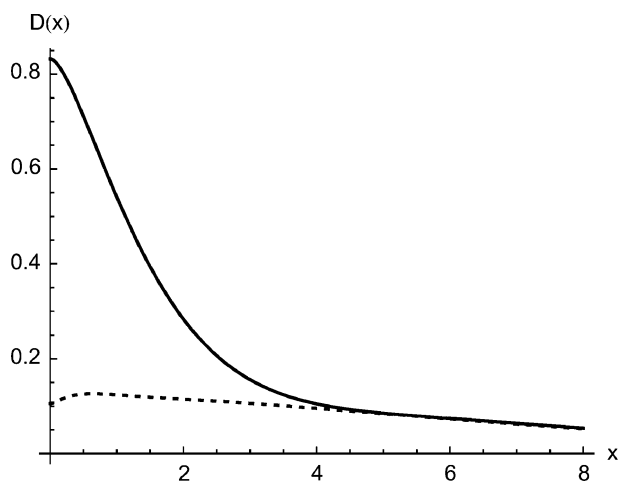


Fig. 5 Parallel (---) and antiparallel (—) components of $D(x)$ for He...He.

hole. Because the parallel component of $D(x)$ is flat, the parallel component of $d(k)$ (the dashed curve in Fig. 6) is correspondingly sharp. The antiparallel component of $D(x)$ (the solid curve in Fig. 5) is a sum of a contribution from distant electrons (which produces the tail of the intracule and which is almost identical to the parallel component) and close electrons (which govern its behaviour at small x). The two contributions that produce the antiparallel component of $d(k)$ are also clear in the solid curve in Fig. 6.

In all of our numerical studies, the computed $D(x)$ is a strictly positive function. On the basis of this empirical evidence, we conjecture that $D(x)$ is positive (or, equivalently, that $d(k)$ is a positive-definite function³²) in all systems.

IV. A correlation model based on $D(x)$

Given that we can compute $D(x)$ for an arbitrary molecule, how can we then extract an estimate of the correlation energy from it? In previous work, we have taken eqn (1.5) as our starting point and explored various $G(x)$ kernels. A simpler approach is to base an estimate on the value of the intracule at

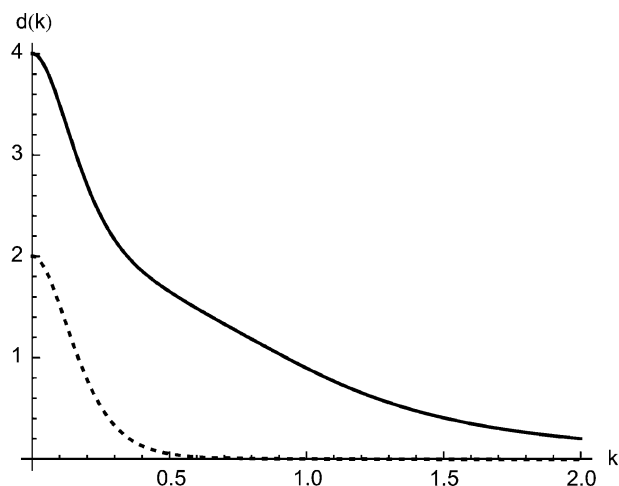


Fig. 6 Parallel (---) and antiparallel (—) components of $d(k)$ for He...He.

a selected point x . For example, it can be shown¹⁵ that $x = 0$ corresponds to either $u = 0$, $v = 0$ or $du/dt = 0$. Each of these is a physical situation in which one might expect the electrons to be strongly correlated and one could guess that $D(0)$, the quasi-probability density for $x=0$, may therefore be a useful indicator of E_c .

At $x = 0$, the $[ssss]_D$ integral (2.14) takes the simpler form

$$[ssss]_D = \frac{\pi^3}{[(\alpha + \delta)(\beta + \gamma)]^{3/2}} \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{\exp\left[\frac{\mu^2 P^2 + kP \cdot Q - \lambda^2 Q^2}{4\lambda^2 \mu^2 + k^2} - R\right]}{(4\lambda^2 \mu^2 + k^2)^{3/2}} dk \quad (4.16)$$

However, we have not been able to solve this in closed form and we have therefore obtained $D(0)$ from eqn (2.10) by integrating $d(k)$ numerically.

We have investigated the simple ansatz

$$E_c^D = c_D D(0)^\alpha \quad (4.17)$$

where c_D and α are parameters and, by approximate fitting to the known correlation energies of the first 18 atoms, we obtained $c_D = -90 mE_h$ and $\alpha = 3/4$. Table 2 summarizes the performance of this model for each of the atoms and molecules in the G1 dataset.³³ The second column gives the exact correlation energy³⁴ of each species. The differences $\Delta E_c^D = E_c^{\text{exact}} - E_c^D$ between the exact correlation energies and the energies from eqn (4.17) are given in the fifth column and, for comparison, the differences $\Delta E_c^{\text{MP2}} = E_c^{\text{exact}} - E_c^{\text{MP2}}$ between the exact and MP2/6-311G correlation energies are given in the third column.

The scatterplot of E_c^{exact} against E_c^D is shown in Fig. 7 and the mean absolute error (MAE) over the G1 set is 28 mE_h . Examination of the errors in Table 2 reveals that, although the ansatz performs well for most atoms (Ne, with $\Delta E_c^D = -33 mE_h$, is the worst) and for many of the smallest molecules, it performs poorly for the larger systems and disilane ($\Delta E_c^D = 169 mE_h$) and ethane ($\Delta E_c^D = 138 mE_h$) are the extreme examples of this.

The reason for such failures can be understood by examining the variation of $D(0)$ in the H_2 molecule with the bond length R . Table 3 shows that $D(0)$, and therefore E_c^D , decays too slowly at large R . In fact, whereas London dispersion produces $E_c^{\text{exact}} \sim O(R^{-6})$, it can be shown that $D(0) \sim O(R^{-1})$. As a result, in large molecules, $D(0)$ includes spuriously large contributions from well-separated electrons.

V. A correlation model based on $d(k)$

In section II, we showed that it is useful, both theoretically and numerically, to regard the Dot intracule as the Fourier transform of a more fundamental (and more easily computed) object (2.11) that we have called the f -Dot function. In view of this, it is interesting to explore the use of the General Parseval Relation³⁵ to re-cast (1.5) as

$$E_c = \int_{-\infty}^{\infty} d(k)g(k)dk \quad (5.18)$$

where $g(k)$ is the Fourier transform of $G(x)$. This leads us to consider a new class of kernel, in k space rather than x space, and allows us to exploit the fact that we can compute $d(k)$ analytically and thereby obtain an expression for the

Table 2 The exact correlation energy (E_c^{exact}), the MP2 error (ΔE_c^{MP2}), the E_c^d error (ΔE_c^d), and the E_c^D error (ΔE_c^D), for the atoms and molecules in the G1 dataset. All values in mE_h

Mole- cule	$-E_c^{\text{exact}}$	ΔE_c^{MP2}	ΔE_c^d	ΔE_c^D	Mole- cule	$-E_c^{\text{exact}}$	ΔE_c^{MP2}	ΔE_c^d	ΔE_c^D
H	0	0	0	0	HCO	553	-298	-26	-8
He	42	-29	1	-1	S	597	-458	1	5
H ₂	41	-23	-1	-1	SiH ₂ (³ B ₁)	540	-382	27	44
Li	45	-32	0	10	SiH ₂ (¹ A ₁)	567	-400	6	20
Be	94	-56	-12	-5	O ₂	636	-349	-54	-42
LiH	83	-57	7	10	H ₂ CO	586	-319	-12	10
B	121	-80	-9	1	C ₂ H ₄	518	-293	53	80
BeH	93	-62	5	24	Cl	658	-579	8	0
C	151	-108	0	7	PH ₂	611	-440	29	30
Li ₂	124	-82	4	13	SiH ₃	575	-403	44	58
N	185	-137	14	13	Ar	723	-628	17	-6
CH	194	-128	-3	7	HCl	707	-605	23	2
O	249	-174	5	1	H ₂ S	683	-503	31	17
NH	236	-158	13	10	PH ₃	652	-464	41	39
CH ₂ (³ B ₁)	208	-135	31	34	SiH ₄	606	-420	61	76
CH ₂ (¹ A ₁)	239	-152	-4	6	F ₂	757	-433	-75	-69
F	318	-210	-1	-15	H ₂ O ₂	711	-403	-31	-17
OH	309	-194	4	-10	N ₂ H ₄	641	-368	33	60
NH ₂	287	-177	20	8	CH ₃ OH	629	-364	38	67
CH ₃	254	-156	45	39	C ₂ H ₆	561	-327	96	138
Ne	391	-243	-2	-33	CO ₂	876	-451	-52	-23
HF	389	-230	-4	-35	CS	867	-575	-33	-18
H ₂ O	371	-215	9	-20	Na ₂	819	-543	-9	-59
NH ₃	340	-198	32	8	SiO	879	-530	-48	-36
CH ₄	299	-178	60	45	SO	957	-635	-33	-9
Na	396	-265	-8	-13	ClO	1002	-787	-28	-3
Mg	438	-292	-15	-15	FCI	1063	-806	-35	-18
LiF	441	-260	-3	-21	HOCl	1045	-792	-14	3
Al	465	-324	-12	-5	CH ₃ Cl	968	-757	58	82
CN	483	-290	-63	-39	CH ₃ SH	946	-654	68	100
Si	500	-363	-9	2	NaCl	1101	-872	30	-21
N ₂	549	-264	-59	-48	Si ₂	1077	-761	-30	-30
CO	535	-275	-46	-35	P ₂	1205	-816	-22	-26
HCN	515	-257	-23	-15	S ₂	1275	-933	2	10
HCCH	480	-254	14	21	SO ₂	1334	-791	-76	-7
P	540	-405	-2	8	Si ₂ H ₆	1183	-821	113	169
NO	596	-335	-64	-49	Cl ₂	1380	-1186	9	10
Mean absolute errors (MAEs)									
Atoms only						244	6	8	
Molecules only						421	33	34	
Atoms and molecules						378	27	28	

correlation energy E_c that requires at most a one-dimensional quadrature.

One of the simplest possible k -space kernels is

$$g(k) = c_d \delta(k - k_0), \quad (5.19)$$

where c_d and k_0 are parameters. In this case, eqn (5.18) takes the simple closed form

$$E_c^d = c_d d(k_0) \quad (5.20)$$

This expression is equivalent to the two-parameter formula given in eqn (10) of ref. 22 where, by fitting to the known correlation energies of the first 18 atoms, it was found that the optimal values of the parameters are $c_d = -76.95 mE_h$ and $k_0 = 0.8474$. The differences $\Delta E_c^d = E_c^{\text{exact}} - E_c^d$ between the energies from eqn (5.20) and the exact correlation energies for the atoms and molecules in the G1 dataset are given in the fourth column of Table 2.

The scatterplot of E_c against E_c^d is shown in Fig. 8 and the MAE over the G1 set is $27 mE_h$. Examination of the errors in Table 2 reveals that, like (4.17), the ansatz (5.20) performs well

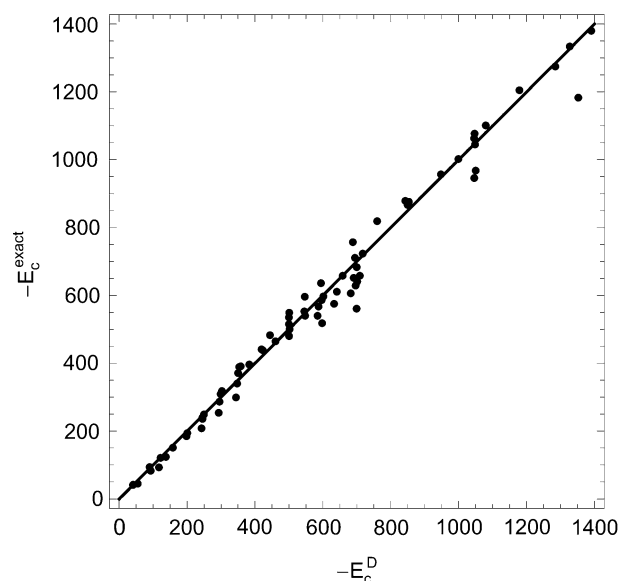


Fig. 7 E_c^{exact} vs. E_c^D for the systems in the G1 dataset (mE_h).

for atoms (Ar, with $\Delta E_c^d = 17 mE_h$, is worst) and small molecules, but is less effective in the larger systems. As before, disilane ($\Delta E_c^d = 113 mE_h$) and ethane ($\Delta E_c^d = 96 mE_h$) produce the largest errors.

As with the first ansatz, part of the reason for such failures can be traced to the variation of $d(k_0)$ in the H₂ molecule. The results in Table 3 show that, unlike $D(0)$, $d(k_0)$ decays too rapidly with R . In fact, it can be shown that $d(k_0) \sim O(e^{-\zeta R^2})$, where ζ depends on the exponents of the Gaussian basis functions, and this means that E_c^d is incapable of describing long-range correlation (e.g. dispersion). Nonetheless, although $d(k_0)$ behaves incorrectly, it seems to approximate R^{-6} somewhat better than $D(0)$ does.

Finally, we note that while the R -dependent decay behaviour of $D(0)$ and $d(k_0)$ is very different, the models based upon these two quantities produce very similar estimates of the correlation energy. Their overall errors are almost indistinguishable and, moreover, there are strong statistical similarities between their errors for individual molecules. Given that a single point in x space embodies information from all k values (and *vice versa*), it is particularly surprising that these two different models seem to capture the same electron correlation effects.

Table 3 Variation of the correlation energy E_c^{exact} (mE_h , from ref. 36), $D(0)$ and $d(k_0)$, with the bond length R (a.u.) in the H₂ molecule

R	$-E_c^{\text{exact}}$	$D(0)$	$d(k_0)$
0	42.05	0.3548	0.5549
1	39.40	0.3493	0.5338
2	46.51	0.3367	0.4996
3	40.11	0.2138	0.2404
4	13.50	0.1453	0.0978
5	3.30	0.1127	0.0417
6	0.76	0.0931	0.0181
7	0.19	0.0796	0.0078
8	0.05	0.0696	0.0033
9	0.02	0.0619	0.0014
10	0.01	0.0557	0.0005
Large	$O(R^{-6})$	$O(R^{-1})$	$O(e^{-\zeta R^2})$

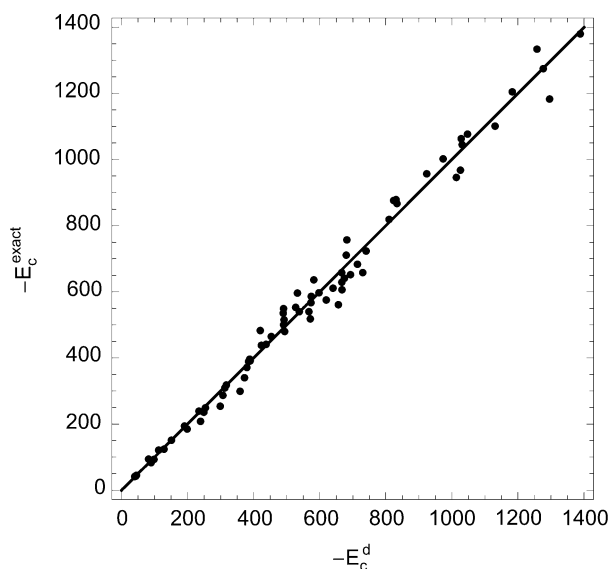


Fig. 8 E_c^{exact} vs. E_c^d for the systems in the G1 dataset (mE_h).

VI. Reaction energy errors

It is clear from Table 2 that the MAEs of the popular MP2 method are at least an order of magnitude larger than those of the E_c^d and E_c^D models. However, MP2 is a valuable tool in quantum chemistry because its errors are generally systematic and tend to cancel between reactants and products in chemical reactions, particularly for those that are isodesmic (same number and type of bonds in the reactants and products) and isogyric (same number of unpaired electrons in the reactants and products).

In Table 4, we consider a variety of reactions whose MP2, E_c^d and E_c^D correlation energy errors can be derived from the data in Table 2. Each of the first 47 reactions involves a homolytic bond fission and is therefore neither isodesmic nor isogyric. Overall, the accuracies of the three methods are comparable, with MAEs close to $20 mE_h$, but MP2 tends to be least accurate for the smallest systems. The remaining 24 reactions are both isodesmic and isogyric and, as such, are significantly easier to model accurately. Both MP2 and the intracule-based approaches are more accurate for these reactions and, on average, the MP2 errors are roughly half as large as those of the E_c^d and E_c^D models.

Table 4 Reaction correlation energy errors ΔE (mE_h) of the MP2, E_c^d and E_c^D models

Reaction	ΔE^{MP2}	ΔE^d	ΔE^D	Reaction	ΔE^{MP2}	ΔE^d	ΔE^D
H ₂ → H + H	23	1	1	O ₂ → 2O	0	64	44
LiH → Li + H	25	-6	0	F ₂ → 2F	13	73	39
BeH → Be + H	7	-17	-29	HOOH → 2OH	15	38	-3
Li ₂ → Li + Li	18	-4	7	CO ₂ → CO + O	1	12	-11
CH → C + H	21	3	0	CS → C + S	9	34	30
NH → N + H	20	0	3	SiO → Si + O	-7	44	39
CH ₂ (¹ A ₁) → CH + H	24	1	1	SO → S + O	3	39	15
OH → O + H	19	1	11	ClO → Cl + O	33	42	4
NH ₂ → NH + H	19	-7	2	FCl → F + Cl	17	42	3
CH ₃ → CH ₂ (³ B ₁) + H	22	-14	-5	HOCl → OH + Cl	19	26	-13
HF → F + H	20	4	20	SO ₂ → SO + O	-18	48	-1
H ₂ O → OH + H	21	-5	10				
NH ₃ → NH ₂ + H	22	-12	0	CH ₄ + OH → CH ₃ + H ₂ O	1	-10	-16
CH ₄ → CH ₃ + H	22	-15	-6	CH ₄ + NH ₂ → CH ₃ + NH ₃	0	-3	-6
LiF → Li + F	18	3	16	PH ₃ + OH → PH ₂ + H ₂ O	3	-7	-19
HCO → CO + H	23	-20	-27	PH ₃ + NH ₂ → PH ₂ + NH ₃	3	0	-9
H ₂ CO → HCO + H	21	-14	-18	PH ₃ + CH ₃ → PH ₂ + CH ₄	3	3	-3
C ₂ H ₄ → 2CH ₂ (³ B ₁)	24	9	-12	SiH ₄ + OH → SiH ₃ + H ₂ O	3	-12	-28
SiH ₃ → SiH ₂ (³ B ₁) + H	21	-17	-14	SiH ₄ + NH ₂ → SiH ₃ + NH ₃	-4	-5	-18
HCl → Cl + H	26	-15	-2	SiH ₄ + CH ₃ → SiH ₃ + CH ₄	-4	-2	-12
PH ₃ → PH ₂ + H	24	-12	-9	SiH ₄ + PH ₂ → SiH ₃ + PH ₃	-7	-5	-9
SiH ₄ → SiH ₃ + H	17	-17	-18	CH ₃ Cl + OH → CH ₃ OH + Cl	8	-16	-5
N ₂ H ₄ → 2NH ₂	15	6	-44	CH ₃ Cl + H ₂ O → CH ₃ OH + HCl	2	-5	7
CH ₃ OH → CH ₃ + OH	14	11	-38	C ₂ H ₆ + OH → CH ₃ OH + CH ₃	1	-17	-22
C ₂ H ₆ → 2CH ₃	15	-5	-60	C ₂ H ₆ + H ₂ O → CH ₃ OH + CH ₄	0	-7	-6
Na ₂ → 2Na	12	-7	33	CH ₃ SH + H ₂ O → CH ₃ OH + H ₂ S	1	-8	4
CH ₃ Cl → CH ₃ + Cl	22	-5	-43	CH ₃ SH + HCl → CH ₃ Cl + H ₂ S	-1	-2	-3
Si ₂ → 2Si	35	11	34	C ₂ H ₆ + Cl ₂ → 2CH ₃ Cl	0	12	16
P ₂ → 2P	6	19	42	C ₂ H ₆ + HOOH → 2CH ₃ OH	3	11	13
S ₂ → 2S	17	0	0	CH ₄ + HOCl → CH ₃ Cl + H ₂ O	-2	21	14
Si ₂ H ₆ → 2SiH ₃	15	-24	-53	CH ₄ + HOCl → CH ₃ OH + HCl	1	15	21
Cl ₂ → 2Cl	28	8	-10	HOCl + HF → ClF + H ₂ O	1	-8	-6
CN → C + N	45	77	59	HOCl + OH → ClO + H ₂ O	-16	-10	-16
N ₂ → 2N	-11	86	74	H ₂ CO + CH ₃ → HCO + CH ₄	0	1	-12
CO → C + O	-7	51	43	HCN + CH ₃ → CN + CH ₄	-55	-25	-18
HCN → CH + N	-9	33	35	CO ₂ + CH ₃ → H ₂ CO + HCO	-10	-31	-14
Mean absolute errors (MAEs)							
Dissociation reactions					18	21	21
Isodesmic and isogyric reactions					5	10	12

Overall, the reaction errors of the intracule-based models are somewhat larger and significantly less systematic than those of MP2. On the other hand, the cost of computing the E_c^d correlation energies from eqn (5.20)—roughly the same as a single Hartree–Fock SCF iteration—is small compared with MP2.

VII. Conclusions

We have presented an efficient method for computing the Dot intracule $D(x)$ of an atomic or molecular system and for computing its Fourier transform, the f -Dot function $d(k)$. We have shown that the latter can be formed from the reduced two-particle density matrix and that this can be accomplished in closed form when the parent wavefunction is expanded in a Gaussian one-electron basis.

We have argued that both $D(x)$ and $d(k)$ can be used as starting points in intracule functional models of the electron correlation energy and we have discussed the numerical results of two such models. In one of these, the correlation energy estimate E_c^d is available in closed-form and can be computed very rapidly.

Acknowledgements

Y.A.B. thanks the Research School of Chemistry for a PhD scholarship. D.L.C. thanks the ARC (Grant DP0771978) and the Australian National University for financial support. P.M.W.G. thanks the APAC Merit Allocation Scheme for a grant of supercomputer time.

References

- 1 E. Schrödinger, *Ann. Phys.*, 1926, **79**, 361.
- 2 D. R. Hartree, *Proc. Cam. Phil. Soc.*, 1928, **24**, 89.
- 3 V. Fock, *Z. Phys.*, 1930, **61**, 126.
- 4 E. Wigner, *Phys. Rev.*, 1934, **46**, 1002.
- 5 A. Szabo and N. S. Ostlund, *Modern quantum chemistry*, McGraw-Hill, New York, 1989.
- 6 R. G. Parr and W. Yang, *Density-functional theory of atoms and molecules*, Oxford University Press, Oxford, 1989.
- 7 C. A. Coulson and A. H. Neilson, *Proc. Phys. Soc.*, 1961, **78**, 831.
- 8 A. M. Lee and P. M. W. Gill, *Chem. Phys. Lett.*, 1999, **313**, 271.
- 9 K. E. Banyard and C. E. Reed, *J. Phys. B*, 1978, **11**, 2957.
- 10 N. A. Besley, A. M. Lee and P. M. W. Gill, *Mol. Phys.*, 2002, **100**, 1763.
- 11 V. A. Rassolov, *J. Chem. Phys.*, 1999, **110**, 3672.
- 12 E. Wigner, *Phys. Rev.*, 1932, **40**, 749.
- 13 H. J. Groenewold, *Physica*, 1946, **12**, 405.
- 14 D. L. Crittenden and P. M. W. Gill, *J. Chem. Phys.*, 2007, **127**, 014101.
- 15 P. M. W. Gill, D. L. Crittenden, D. P. O'Neill and N. A. Besley, *Phys. Chem. Chem. Phys.*, 2006, **8**, 15.
- 16 P. M. W. Gill, D. P. O'Neill and N. A. Besley, *Theor. Chem. Acc.*, 2003, **109**, 241.
- 17 P. M. W. Gill and D. P. O'Neill, *J. Chem. Phys.*, 2005, **122**, 094110.
- 18 R. Fondermann, M. Hanrath, M. Dolg and D. P. O'Neill, *Chem. Phys. Lett.*, 2005, **413**, 237.
- 19 N. A. Besley, *J. Chem. Phys.*, 2006, **125**, 074101.
- 20 R. Fondermann, M. Hanrath and M. Dolg, *Theor. Chem. Acc.*, 2007, **118**, 777.
- 21 E. E. Dumont, D. L. Crittenden and P. M. W. Gill, *Phys. Chem. Chem. Phys.*, 2007, **9**, 5340.
- 22 D. L. Crittenden, E. E. Dumont and P. M. W. Gill, *J. Chem. Phys.*, 2007, **127**, 141103.
- 23 N. A. Besley, D. P. O'Neill and P. M. W. Gill, *J. Chem. Phys.*, 2003, **118**, 2033.
- 24 S. F. Boys, *Proc. R. Soc. (London)*, 1950, **A200**, 542.
- 25 Y. Shao, L. Fusti-Molnar, Y. Jung, J. Kusmann, C. Ochsenfeld, S. T. Brown, A. T. B. Gilbert, L. V. Slipchenko, S. V. Levchenko and D. P. O'Neill, *et al.*, *Phys. Chem. Chem. Phys.*, 2006, **8**, 3172.
- 26 J. K. Pearson, D. L. Crittenden and P. M. W. Gill, *Chem. Phys.*, to be submitted.
- 27 M. Abramowitz and I. E. Stegun, *Handbook of mathematical functions*, Dover, New York, 1972.
- 28 G. A. Evans and K. C. Chung, *Int. J. Comput. Math.*, 1998, **66**, 39.
- 29 R. Wong, *Asymptotic approximations of integrals*, SIAM, Philadelphia, 2001.
- 30 Wolfram Research, Inc., *Mathematica*, Champaign, Illinois, version 6.0 ed., 2007.
- 31 J. P. Boyd, *Chebyshev and Fourier spectral methods*, Dover, New York, 2nd edn., 2000.
- 32 M. Reed and B. Simon, *Methods of modern mathematical physics*, Academic Press, New York, 1975, vol. 2.
- 33 J. A. Pople, M. Head-Gordon, D. J. Fox, K. Raghavachari and L. A. Curtiss, *J. Chem. Phys.*, 1989, **90**, 5622.
- 34 D. P. O'Neill and P. M. W. Gill, *Mol. Phys.*, 2005, **103**, 763.
- 35 L. Debnath and D. Bhatta, *Integral transforms and their applications*, Chapman and Hall, 2nd edn, 2007.
- 36 W. Kolos, K. Szalewicz and H. J. Monkhorst, *J. Chem. Phys.*, 1986, **84**, 3278.