Chapter 3

Self-Consistent Hartree–Fock–Wigner Calculations: A Two-Electron-Density Functional Theory

Darragh P. O'Neill and Peter M. W. Gill

Department of Physical Chemistry, University of Nottingham, University Park NG7 2RD, United Kingdom

We recently presented a correlation method based on the Wigner intracule, in which correlation energies are calculated directly from a Hartree-Fock wavefunction. We now describe a self-consistent form of this approach which we term the Hartree-Fock-Wigner method. The efficacy of the new scheme is demonstrated using a simple weight function to reproduce the correlation energies of the first- and second-row atoms with a mean absolute deviation of 2.5 mE_h.

Introduction

The electron correlation problem remains a central research area for quantum chemists, as its solution would provide the exact energies for arbitrary systems. Today there exist many procedures for calculating the electron correlation energy (*1*), none of which, unfortunately, is both robust and computationally inexpensive. Configuration interaction (CI) methods provide a conceptually simple route to correlation energies and a full CI calculation will provide exact energies but only at prohibitive computational cost as it scales factorially with the number of basis functions, N. Truncated CI methods such as CISD (N^6 cost) are more computationally feasible but can still only be used for small systems and are neither size consistent nor size extensive. Coupled cluster

(CC) methods, which have largely superseded CI methods, in the limit can also be used to give exact solutions but again with same prohibitive cost as full CI. As with CI, CC methods are often truncated, most commonly to CCSD (N^6 cost), but as before these can still only be applied to systems of modest size. Finally, Møller-Plesset (MP) perturbation theory, which is usually used to second order (MP2 has a N^5 cost), is more computationally accessible but does not provide as robust results.

We have recently introduced the Wigner intracule (*2*), a two-electron phase-space distribution. The Wigner intracule, $W(u, v)$, is related to the probability of finding two electrons separated by a distance u and moving with relative momentum v. This reduced function provides a means to interpret the complexity of the wavefunction without removing all of the explicit multi-body information contained therein, as is the case in the one-electron density.

Electron correlation is inherently a multi-electron phenomenon, and we believe that the retention of explicit two-electron information in the Wigner intracule lends itself to its description (*3*). It has been well established that electron correlation is related to the inter-electronic distance, but it has also been suggested (*4*) that the relative *momentum* of two electrons should be considered which led us to suggest that the Hartree-Fock (HF) Wigner intracule contains information which can yield the electron correlation energy. The calculation of this correlation energy, like HF, formally scales as N^4.

Although the HF Wigner intracule can be used to estimate correlation energies, the resulting energy is not variational with respect to the molecular orbital (MO) coefficients, so gradients, which are needed to perform geometry optimizations and frequency calculations, are complicated. The calculation of such gradients is made more straightforward when using a set of MOs which have been self-consistently optimized taking the corrections due to the correlation energy into account. A self-consistent scheme such as this, which we term the Hartree-Fock-Wigner (HFW) method, will now be described.

Theory

We have recently proposed (*3*) that the correlation energy can be estimated from equations of the form

$$E = \int_0^\infty \int W_{\mathrm{HF}}(u,v) G_{\mathrm{HF}}(u,v) \mathrm{d}u\mathrm{d}v \qquad (1)$$

where W_{HF} *(u, v)* is the Wigner intracule derived from a HF wavefunction and G_{HF} *(u, v)* is a weight function. If the MOs are expanded within a basis set, the correlation energy becomes

$$E_C = \frac{1}{2}\sum_{\mu\nu\lambda\sigma}\left[P_{\mu\nu}P_{\lambda\sigma} - P^{\alpha}_{\mu\sigma}P^{\alpha}_{\nu\lambda} - P^{\beta}_{\mu\sigma}P^{\beta}_{\nu\lambda}\right](\mu\nu\lambda\sigma)_G \qquad (2)$$

where $P^{\alpha}_{\mu\nu}$ and $P^{\beta}_{\mu\nu}$ are elements of the α and β HF density matrices, $P_{\mu\nu}$ is an element of the total HF density matrix $P_{\mu\nu} = P^{\alpha}_{\mu\nu} + P^{\beta}_{\mu\nu}$ and $(\mu\nu\lambda\sigma)_G$ is the 10-dimensional correlation integral

$$(\mu\nu\lambda\sigma)_G = \frac{1}{2\pi^2}\int \phi_\mu(\mathbf{r})\phi_\nu(\mathbf{r}+\mathbf{q})\phi_\lambda(\mathbf{r}+\mathbf{q}+\mathbf{u})\phi_\sigma(\mathbf{r}+\mathbf{u}) \times v^2 j_0(qv)G(u,v)\,\mathbf{dr}\,\mathbf{dq}\,\mathbf{du}\,dv \qquad (3)$$

where $\phi_i(\mathbf{r})$ is a basis function and $j_0(x)$ is the zeroth-order spherical Bessel function (*5*).

The HF energy is given by

$$E_{HF} = \sum_{\mu\nu} P_{\mu\nu}H_{\mu\nu} + \frac{1}{2}\sum_{\mu\nu\lambda\sigma}\left[P_{\mu\nu}P_{\lambda\sigma} - P^{\alpha}_{\mu\sigma}P^{\alpha}_{\nu\lambda} - P^{\beta}_{\mu\sigma}P^{\beta}_{\nu\lambda}\right](\mu\nu|\lambda\sigma) \qquad (4)$$

where $(\mu\nu|\lambda\sigma)$ are the usual Coulomb integrals. This expression may trivially be combined with equation 2 to yield the HFW energy

$$E_{HFW} = \sum_{\mu\nu} P_{\mu\nu}H_{\mu\nu} + \frac{1}{2}\sum_{\mu\nu\lambda\sigma}\left[P_{\mu\nu}P_{\lambda\sigma} - P^{\alpha}_{\mu\sigma}P^{\alpha}_{\nu\lambda} - P^{\beta}_{\mu\sigma}P^{\beta}_{\nu\lambda}\right](\mu\nu\lambda\sigma)_{HFW} \qquad (5)$$

where $(\mu\nu|\lambda\sigma)_{HFW} = (\mu\nu|\lambda\sigma) + (\mu\nu\lambda\sigma)_G$ and $P_{\mu\nu}$ is no longer a HF density matrix element but rather a density matrix element obtained when a self-consistent calculation is performed with the inclusion of the Wigner perturbation.

When implementing the HFW method the extra computational cost incurred is that of evaluating and digesting the correlation integrals. The details (*6*) of calculating the $(\mu\nu\lambda\sigma)_G$ integrals depends on the choice of *G(u, v)*, and in this work gaussian weight functions in uv and u, $G(u,v) = Ae^{-\zeta u^2 v^2}$ and $G(u,v) = Be^{-\eta u^2}$, were chosen as these permit the 10-dimensional correlation integral (equation 3) to be reduced to a one-dimensional integral in u. The remaining integration is then performed by quadrature (*6*). Several quadrature

schemes have been explored to approximate this final integral and it has been found that the recently introduced MultiExp grid (*7*) is particularly efficient. The form of the integrand is suitable for use with this grid as it is the product of a power, a gaussian and a modified spherical Bessel function (*5*) in u, and can be approximated well by a sum of exponentials which MultiExp integrates exactly.

The digestion of the HFW integrals differs from that of HF integrals as the $(\mu\nu\lambda\sigma)_G$ integrals possess lower permutational symmetry than their HF counterparts. Correlation integrals, like the Wigner integrals which make up the Wigner intracule and unlike the conventional Coulomb integrals, have only four-fold permutational symmetry (*8*)

$$\begin{aligned}(\mu\nu\lambda\sigma)_G &= (\nu\mu\sigma\lambda)_G = (\sigma\lambda\nu\mu)_G = (\lambda\sigma\mu\nu)_G \\ (\mu\nu\sigma\lambda)_G &= (\nu\mu\lambda\sigma)_G = (\sigma\lambda\mu\nu)_G = (\lambda\sigma\nu\mu)_G\end{aligned} \tag{6}$$

and hence an HFW calculation is roughly twice as expensive as the same HF calculation. When the HFW integrals are being assembled, clearly we do not wish to compute the Coulomb integrals twice, so care must be taken to combine the correct Coulomb and correlation integrals. It should also be pointed out that a negligibly small Coulomb integral does not imply that the corresponding correlation integral is negligibly small, so we currently evaluate all of the HFW integrals. A cutoff criterion for discarding correlation integrals, analogous to the Schwarz inequality for Coulomb integrals, would be a desirable tool and is being investigated (*9*).

After the HFW integrals have been assembled, we then move on to the self-consistent field (SCF) procedure. For the most part this is the same as the HF version (*10*), with the exception of constructing the Fock matrix. The Fock matrix elements for an unrestricted HFW calculation are analogous to their HF counterparts and are given by

$$F^{\alpha}_{\mu\nu} = H^{\text{core}}_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma}(\mu\nu\lambda\sigma)_{\text{HFW}} - P^{\alpha}_{\lambda\sigma}(\mu\lambda\nu\sigma)_{\text{HFW}} \tag{7}$$

$$F^{\beta}_{\mu\nu} = H^{\text{core}}_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma}(\mu\nu\lambda\sigma)_{\text{HFW}} - P^{\beta}_{\lambda\sigma}(\mu\lambda\nu\sigma)_{\text{HFW}} \tag{8}$$

The method usually employed to build the Fock matrix is an integral-driven algorithm in which each integral contributes to six elements of the Fock matrix. Due to the lower symmetry of the HFW integrals, each one contributes to only four elements of the Fock matrix. For a given integral $(\mu\nu\lambda\sigma)_{\text{HFW}}$ the upper or lower diagonal of the α Fock matrix is built up as follows

$$\begin{aligned}F^{\alpha}_{\mu\nu} &= F^{\alpha}_{\mu\nu} + P_{\lambda\sigma}(\mu\nu\lambda\sigma)'_{\text{HFW}} \\ F^{\alpha}_{\lambda\sigma} &= F^{\alpha}_{\lambda\sigma} + P_{\mu\nu}(\mu\nu\lambda\sigma)'_{\text{HFW}} \\ F^{\alpha}_{\mu\sigma} &= F^{\alpha}_{\mu\sigma} + P^{\alpha}_{\nu\lambda}(\mu\nu\lambda\sigma)'_{\text{HFW}} \\ F^{\alpha}_{\nu\lambda} &= F^{\alpha}_{\nu\lambda} + P^{\alpha}_{\mu\sigma}(\mu\nu\lambda\sigma)'_{\text{HFW}}\end{aligned} \tag{9}$$

where the prime indicates that the integrals have been scaled by the number of permutationally equivalent integrals and then by $\frac{1}{4}$. After this Fock matrix is calculated it must be corrected by multiplying the diagonal elements by a factor of two. The β Fock matrix is constructed analogously.

Results

Currently the Hartree-Fock-Wigner method is implemented as a standalone program, but work is underway to integrate this method into the Q-Chem (*11*) package. Using a gaussian weight function, $(\mu\nu\lambda\sigma)_G$ has been formulated for all *s*- and *p*-type basis functions, and is readily extensible to functions of higher angular momentum. The results that will be considered are those for a $G(u,v)$ which aims to reproduce the energies of the atoms of the first and second rows. To accomplish this, the four parameters, A, B, ζ and η, in the gaussian weight function $G(u,v) = Ae^{-\zeta u^2 v^2} + Be^{-\eta u^2}$ will be fitted.

We have found that the Wigner intracule is quite insensitive to basis set size and we expect the derived correlation energies to be similarly insensitive. In stark contrast to the post-HF methods mentioned in the introduction, we expect similar Wigner correlation energies from both moderate and large basis sets and thus estimates (made using accurate experimental and theoretical data) to the exact non-relativistic correlation energies (*12*) are used in the fitting routine. The Hartree-Fock energy, however, is much more sensitive to basis set so the target of the HFW method will be to calculate the sum of the Hartree-Fock energy for a given basis set and the "exact" correlation energy.

We will now examine the results obtained when the parameters of $G(u,v)$ are optimized for both non-SCF Wigner correlation and HFW using the 6-311G basis set. The parameters were optimized using the BFGS quasi-Newton method given in ref (*13*). The two resulting weight functions are as follows

$$G_{\mathrm{HF}}(u,v) = -0.135433e^{-0.303089u^2v^2} + 0.004183e^{-0.325456u^2} \qquad (10)$$

$$G_{\mathrm{HFW}}(u,v) = -0.135410e^{-0.303715u^2v^2} + 0.004232e^{-0.344968u^2} \qquad (11)$$

Table I shows the energies obtained when non-SCF and HFW calculations are performed using each of the functions given in equations 10 and 11. Excellent agreement is seen between the exact and calculated values when using the appropriate function for a given calculation type, with mean absolute deviations of 2.6 mE_h and 2.5 mE_h and the maximum absolute deviations being 6.8 mE_h and 7.1 mE_h in the case of the nitrogen atom.

Table I: Errors in Non-SCF and HFW Energies [a]

Calc. Type		*Non-SCF*		*HFW*	
Function Type[b]	*Total*[c]	G_{HF}	G_{HFW}	G_{HF}	G_{HFW}
He	–2.9019	–0.8	–0.8	–0.8	–0.8
Li	–7.4096	0.8	0.7	1.0	0.9
Be	–14.6662	–0.7	–0.7	–0.6	–0.6
B	–24.6519	0.6	0.6	0.6	0.7
C	–37.8424	3.1	3.3	3.2	3.3
N	–54.5863	6.8	7.0	6.9	7.1
O	–75.0604	–0.6	–0.4	–0.5	–0.3
F	–99.7186	–4.0	–3.9	–3.9	–3.9
Ne	–128.9130	–6.2	–6.3	–6.1	–6.2
Na	–162.2416	–3.7	–4.1	–3.0	–3.4
Mg	–200.0448	2.6	2.1	2.9	2.4
Al	–242.3396	3.0	2.5	3.3	2.8
Si	–289.3528	2.1	1.8	2.3	2.0
P	–341.2476	2.1	2.1	2.3	2.3
S	–398.0999	–2.3	–2.0	–2.1	–1.8
Cl	–460.1355	–3.3	–2.7	–3.2	–2.5
Ar	–527.5287	1.0	1.9	1.2	2.1
Mean[d]		2.6	2.5	2.6	2.5
Max[e]		6.8	7.0	6.9	7.1

[a] Total energies in Eh and errors in mE_h
[b] From equations 10 and 11
[c] Sum of HF/6-311G and exact correlation energies
[d] Mean Absolute Deviation
[e] Maximum Absolute Deviation

Table II: Errors in HFW/STO-3G Energies[a]

	Total[b]	*HFW*
He	−2.8498	−0.6
Li	−7.3609	5.3
Be	−14.4462	−0.2
B	−24.2738	0.5
C	−37.3548	1.9
N	−53.9073	5.0
O	−74.0621	−1.3
F	−98.311	−3.1
Ne	−126.995	−3.3
Na	−160.064	20.2
Mg	−197.4456	17.4
Al	−239.328	11.8
Si	−285.9712	4.1
P	−337.409	−0.2
S	−393.735	−7.7
Cl	−455.2082	−9.1
Ar	−521.945	−6.9
Mean[c]		5.8
Max[d]		20.2

[a] Total energies in E_h and errors in mE_h

[b] Sum of HF/STO-3G and exact correlation energies

[c] Mean Absolute Deviation

[d] Maximum Absolute Deviation

As expected only minor differences are seen between the results obtained when the correct and incorrect fits are used for each calculation type and this is reflected in the similarity of the weight functions.

We predicted above that the Wigner correlation energies should not be very sensitive to the basis set used. The validity of this will now be examined. Table II shows the result of using the HFW weight function optimized for the 6-311G basis set applied to the STO-3G basis set. Again, we cannot expect to reproduce the HF/6-311G energy at the STO-3G level so the total energies now use the HF/STO-3G energy add to the exact correlation energy. Good agreement is seen with the mean absolute deviation increasing to 5.8 mE_h and the maximum absolute deviation being 20.2 mE_h, in the case of the sodium atom.

To investigate the magnitude of the effect that the inclusion of the correlation integrals has, we will look at the change in the density matrix. It is

expected that the change induced on going from HF to HFW will be small so the ratio of a HF density matrix element to its HFW counterpart should be close to unity. Because the maximum deviation in energy occurs in the case of the N atom, it has been chosen to exemplify the change in the density matrix. Our prediction that the induced change will be small is correct with the largest deviation from unity being 0.9854 in the case of the most diffuse *p*-functions.

Conclusions

We have described a self-consistent field method for calculating correlation energies based on the Wigner intracule. This method involves a perturbation to the usual two-electron integrals. The implementation of this method is very similar to the HF method and complications arise only from the calculation of the new correlation integrals and from the low permutational symmetry of the HFW integrals. It has been shown that HFW, using a simple weight function, can accurately estimate the correlation energies of the first- and second-row atoms with a mean absolute deviation of 2.5 mE_h. This weight function is used only to highlight some of the features of this new method and we are investing much effort into findings forms of $G(u,v)$ which work more generally. We are considering spin-separated weight functions as it is known that the majority of the correlation energy arises from pairs of electrons with opposite spins. Hence, we use one weight function for the parallel-spin intracule and another for the antiparallel-spin intracule. This a straightforward extension of the method described above. Work is also underway to see how derivatives from the HFW method perform when used to optimize geometries and calculate vibrational frequencies (*14*).

Acknowledgements

We would like to thank Dr. Nick Besley for useful discussions. This research was partly supported by the Engineering and Physical Sciences Research Council through a project studentship (GR/R81121) to D.P.O.

References

1. Jensen, F. *Introduction to Computational Chemistry.* John Wiley & Sons, 1999.
2. Gill, P.M.W.; O'Neill, D.P.; Besley, N.A. *Theor. Chem. Acc.*, **2003**, *109*, 241.

3. Gill, P.M.W.; O'Neill, D.P.; Besley, N.A., to be submitted.
4. Rassolov, V.A. *J. Chem. Phys.*, **1999**, *110*, 3672.
5. Abramowitz, M.; Stegun, I.A., editors. *Handbook of Mathematical Functions.* Dover, 1972.
6. O'Neill, D.P.; Gill, P.M.W., to be submitted.
7. Gill, P.M.W.; Chien, S.H. *J. Comput. Chem.*, **2003**, *24*, 732.
8. Besley, N.A.; O'Neill, D.P.; Gill, P.M.W. *J. Chem. Phys.*, **2003**, *118*, 2033.
9. O'Neill, D.P.; Gill, P.M.W. to be submitted.
10. Szabo, A.; Ostlund, N.S. *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory.* Dover, 1989.
11. Kong, J.; White, C. A.; Krylov, A. I.; Sherrill, C. D.; Adamson, R. D.; Furlani, T. R.; Lee, M. S.; Lee, A. M.; Gwaltney, S. R.; Adams, T. R.; Ochsenfeld, C.; Gilbert, A. T. B.; Kedziora, G. S.; Rassolov, V. A.; Maurice, D. R.; Nair, N.; Shao, Y.; Besley, N. A.; Maslen, P. E.; Dombroski, J. P.; Daschel, H.; Zhang, W.; Korambath, P. P.; Baker, J.; Byrd, E. F. C.; Voorhis, T. Van; Oumi, M.; Hirata, S.; Hsu, C-P.; Ishikawa, N.; Florian, J.; Warshel, A.; Johnson, B. G.; Gill, P. M. W.; Head-Gordon, M.; Pople, J. A. *J. Comput. Chem,* **2000**, *21*, 1532.
12. Chakravorty, S.J.; Gwaltney, S.R.; Davidson, E.R.; Parpia, F.A.; Froese Fischer, C. *Phys. Rev. A,* **1993**, *47*, 3649.
13. Press, W.H.; Teukolsky, S.A.; Vetterling, W.T.; Flannery, B.P. *Numerical Recipes in Fortran.* Cambridge University Press UK, second edition, 1992.
14. Dolg, M.; O'Neill, D.P.; Gill, P.M.W. to be submitted.