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Computation of molecular Hartree–Fock Wigner intracules

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The computation of molecular Wigner intracules from Hartree–Fock wave functions using Gaussian basis functions is described. The Wigner intracule is a new type of intracule that contains information about both the relative position and momentum of the electrons. Two methods for evaluating the required integrals are presented. The first approach uses quadrature while the second requires summation of an infinite series. © *2003 American Institute of Physics.*
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I. INTRODUCTION

The many dimensions of an electronic wave function make it difficult to analyze and interpret and it is therefore desirable to extract low-dimensional functions that can readily provide chemical insight. The most familiar of these ''reduced'' functions is the one-electron density, where $\rho(\mathbf{r})d\mathbf{r}$ gives the probability of finding an electron at a given point in space. The one-electron density can be easily visualized and assists in the understanding and prediction of the chemical behavior of molecules.[1,2] However, many chemical phenomena, for example electron correlation, depend on the interaction between pairs of electrons. Such phenomena are more readily studied using reduced functions that retain explicit two-electron information. The position intracule, $P(u)$, measures the probability that two electrons will be found a distance $u=|\mathbf{r}_1\text{-}\mathbf{r}_2|$ apart. Analogously, the momentum intracule, $M(v)$, gives the probability that two electrons have relative momentum $v=|\mathbf{p}_1\text{-}\mathbf{p}_2|$.[3] Over many years, a number of authors have reported work on both position[4–32] and momentum[33–53] intracules. Recently, the development and implementation of efficient algorithms within a modified version of the Q-CHEM[54] software package have been described for both position[28] and momentum[53] intracules. Consequently, $P(u)$ and $M(v)$ for large molecular systems can be computed from Hartree–Fock (HF) wave functions.[22,28,30,53]

$P(u)$ and $M(v)$ provide a representation of an electron distribution in either position *or* momentum space but neither alone provides a complete description and it is desirable to have a *combined* position and momentum description. This new function could potentially play an important role in the study of electron correlation.[55] Recently,[56] we introduced a new phase space intracule called the Wigner intracule, $W(u,v)$, which is related to the probability of two electrons being a distance u apart and moving with a relative momentum v. The aim of the present paper is to describe the computation of Wigner intracules for molecular systems. First, the Wigner intracule will be described followed by details of an implementation within Q-CHEM.

II. WIGNER INTRACULE

The natural starting point for deriving a combined position and momentum intracule would be a wave function in phase space but, due to Heisenberg's uncertainty principle, such a function does not exist. However, a number of phase space quantum distribution functions have been defined,[57–59] the best known of which is the Wigner distribution[57,59,60]

$$W(\mathbf{r}_1,\ldots,\mathbf{r}_n;\mathbf{p}_1,\ldots,\mathbf{p}_n) = \frac{1}{\pi^{3n}}\int \Psi(\mathbf{r}_1+\mathbf{q}_1,\ldots,\mathbf{r}_n+\mathbf{q}_n;\sigma_1,\ldots,\sigma_n) \times\Psi^*(\mathbf{r}_1-\mathbf{q}_1,\ldots,\mathbf{r}_n-\mathbf{q}_n;\sigma_1,\ldots,\sigma_n) \times e^{-2i(\mathbf{p}_1\cdot\mathbf{q}_1+\cdots+\mathbf{p}_n\cdot\mathbf{q}_n)}\mathrm{d}\mathbf{q}_1\cdots\mathrm{d}\mathbf{q}_n\mathrm{d}\sigma_1\cdots\mathrm{d}\sigma_n, \tag{2.1}$$

which is a joint probability function for the coordinates $\mathbf{r}_1,\ldots,\mathbf{r}_n$ and associated momenta $\mathbf{p}_1,\ldots,\mathbf{p}_n$. Springborg and Dahl have reported Wigner distributions for atomic and small molecular systems including H, He, Be, Ne, Ar, Zn, and LiH.[60–62] These show that typically the Wigner distributions are complicated with positive and negative regions. Since the Wigner distribution is not everywhere positive it is often termed a ''quasiprobability'' distribution function.

We have formally defined[56] the Wigner intracule as

$$W(u,v)=\int W_2(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2)\,\delta(\mathbf{r}_{12}-\mathbf{u})\,\delta(\mathbf{p}_{12}-\mathbf{v}) \times \mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\,\mathrm{d}\mathbf{p}_1\,\mathrm{d}\mathbf{p}_2\,\mathrm{d}\Omega_u\,\mathrm{d}\Omega_v \tag{2.2}$$

where Ω_u and Ω_v are the angular parts of $\mathbf{u}$ and $\mathbf{v}$, δ is the Dirac delta function and W_2 is the second-order reduced Wigner function[59]

$$W_2(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2)=\frac{1}{\pi^6}\int \rho_2(\mathbf{r}_1+\mathbf{q}_1,\mathbf{r}_1-\mathbf{q}_1,\mathbf{r}_2+\mathbf{q}_2,\mathbf{r}_2-\mathbf{q}_2)e^{-2i(\mathbf{p}_1\cdot\mathbf{q}_1+\mathbf{p}_2\cdot\mathbf{q}_2)}\mathrm{d}\mathbf{q}_1\mathrm{d}\mathbf{q}_2 \tag{2.3}$$

and ρ_2 is the spinless reduced second-order density matrix[1] of the wave function. Substituting Eq. (2.3) into Eq. (2.2) and using the identity,

$$\int e^{-2i(\mathbf{p}_1\cdot\mathbf{q}_1+\mathbf{p}_2\cdot\mathbf{q}_2)}\delta(\mathbf{p}_{12}-\mathbf{v})d\mathbf{p}_1\,d\mathbf{p}_2\,d\Omega_v \equiv 4\pi^4v^2j_0(2q_1v)\,\delta(\mathbf{q}_1+\mathbf{q}_2) \tag{2.4}$$

to integrate over $\mathbf{p}_1$, $\mathbf{p}_2$, and Ω_v yields the simpler expression,

$$W(u,v)=\frac{v^2}{2\pi^2}\int \rho_2(\mathbf{r},\mathbf{r}+\mathbf{q},\mathbf{r}+\mathbf{q}+\mathbf{u},\mathbf{r}+\mathbf{u}) \times j_0(qv)\,d\mathbf{r}\,d\mathbf{q}\,d\Omega_u, \tag{2.5}$$

where $j_0(x)$ is the zeroth-order spherical Bessel function. For HF wave functions, the Wigner intracule becomes

$$W(u,v)=\frac{1}{2}\left[\sum_a^n\sum_b^n(\psi_a\psi_a\psi_b\psi_b)_W - \sum_a^{n^\alpha}\sum_b^{n^\alpha}(\psi_a^\alpha\psi_b^\alpha\psi_b^\alpha\psi_a^\alpha)_W - \sum_a^{n^\beta}\sum_b^{n^\beta}(\psi_a^\beta\psi_b^\beta\psi_b^\beta\psi_a^\beta)_W\right], \tag{2.6}$$

where n_α and n_β are the number of alpha and beta electrons, respectively, $n=n_\alpha+n_\beta$ and $\psi_a(\mathbf{r})$ are molecular orbitals. The molecular orbital integrals are defined by

$$(\psi_a\psi_b\psi_c\psi_d)_W=\frac{v^2}{2\pi^2}\int \psi_a(\mathbf{r})\psi_b(\mathbf{r}+\mathbf{q})\psi_c(\mathbf{r}+\mathbf{q}+\mathbf{u}) \times \psi_d(\mathbf{r}+\mathbf{u})j_0(qv)\,d\mathbf{r}\,d\mathbf{q}\,d\Omega_u. \tag{2.7}$$

If the molecular orbitals are expanded within a basis set

$$\psi_a(\mathbf{r})=\sum_\mu^N c_{\mu a}\phi_\mu(\mathbf{r}), \tag{2.8}$$

the Wigner intracule becomes

$$W(u,v)=\tfrac{1}{2}\sum_{\mu\nu\lambda\sigma}[P_{\mu\nu}P_{\lambda\sigma}-P_{\mu\sigma}^\alpha P_{\nu\lambda}^\alpha-P_{\mu\sigma}^\beta P_{\nu\lambda}^\beta] \times(\mu\nu\lambda\sigma)_W, \tag{2.9}$$

where $P_{\mu\nu}$ etc. are the usual density matrix elements. More generally for arbitrary wavefunctions $W(u,v)$ can be expressed as

$$W(u,v)=\sum_{\mu\nu\lambda\sigma}\Gamma_{\mu\nu\lambda\sigma}(\mu\nu\lambda\sigma)_W, \tag{2.10}$$

where $\Gamma_{\mu\nu\lambda\sigma}$ is the two particle density matrix. $(\mu\nu\lambda\sigma)_W$ are the eight-dimensional Wigner integrals,

$$(\mu\nu\lambda\sigma)_W=\frac{v^2}{2\pi^2}\int \phi_\mu(\mathbf{r})\phi_\nu(\mathbf{r}+\mathbf{q})\phi_\lambda(\mathbf{r}+\mathbf{q}+\mathbf{u}) \times\phi_\sigma(\mathbf{r}+\mathbf{u})j_0(qv)\,d\mathbf{r}\,d\mathbf{q}\,d\Omega_u. \tag{2.11}$$

These integrals are analogous[53] to the position and momentum integrals

$$(\mu\nu\lambda\sigma)_P=\int \phi_\mu(\mathbf{r})\phi_\nu(\mathbf{r})\phi_\lambda(\mathbf{r}+\mathbf{u})\phi_\sigma(\mathbf{r}+\mathbf{u})\,d\mathbf{r}\,d\Omega_u, \tag{2.12}$$

$$(\mu\nu\lambda\sigma)_M=\frac{v^2}{2\pi^2}\int \phi_\mu(\mathbf{r})\phi_\nu(\mathbf{r}+\mathbf{q})\phi_\lambda(\mathbf{q}+\mathbf{u}) \times\phi_\sigma(\mathbf{u})j_0(qv)\,d\mathbf{r}\,d\mathbf{q}\,d\mathbf{u}. \tag{2.13}$$

However, whereas position integrals exhibit eightfold permutational symmetry,

$$\begin{aligned}(\mu\nu\lambda\sigma)_P&=(\nu\mu\sigma\lambda)_P=(\sigma\lambda\nu\mu)_P=(\lambda\sigma\mu\nu)_P\\&=(\nu\mu\lambda\sigma)_P=(\mu\nu\sigma\lambda)_P=(\lambda\sigma\nu\mu)_P\\&=(\sigma\lambda\mu\nu)_P,\end{aligned} \tag{2.14}$$

the momentum and Wigner integrals possess only fourfold symmetry,

$$\begin{aligned}(\mu\nu\lambda\sigma)_{M\text{ or }W}&=(\nu\mu\sigma\lambda)_{M\text{ or }W}\\&=(\sigma\lambda\nu\mu)_{M\text{ or }W}\\&=(\lambda\sigma\mu\nu)_{M\text{ or }W}.\end{aligned} \tag{2.15}$$

The loss of eightfold permutational symmetry for the integrals required for the computation of nonspherically averaged position intracules, $I(\mathbf{u})$, has been noted by Thakkar *et al.*[16] Once the integrals have been generated, $W(u,v)$ can be evaluated through the simple contraction (2.9) with the appropriate HF density matrix elements. The difficulty arises in the evaluation of the Wigner integrals (2.11) and we now describe two approaches to this.

III. THE [*ssss*] WIGNER INTEGRAL

In the present work, we are concerned only with the use of Gaussian basis functions. Consequently, integrals involving basis functions of arbitrary angular momentum can be generated through differentiation of the $[ssss]_W$ integral.[63] Given four unnormalized s-functions on centers **A**, **B**, **C**, and **D** with exponents α, β, γ, and δ, respectively, the $[ssss]_W$ integral is

$$[ssss]_W=\frac{v^2}{2\pi^2}\int\int\int \exp[-\alpha|\mathbf{r}-\mathbf{A}|^2-\beta|\mathbf{r}+\mathbf{q}-\mathbf{B}|^2 -\gamma|\mathbf{r}+\mathbf{q}+\mathbf{u}-\mathbf{C}|^2-\delta|\mathbf{r}+\mathbf{u}-\mathbf{D}|^2] \times j_0(qv)\,d\mathbf{r}\,d\mathbf{q}\,d\Omega_u. \tag{3.1}$$

If we introduce

$$\lambda^2=\left(\frac{\alpha\delta}{\alpha+\delta}+\frac{\beta\gamma}{\beta+\gamma}\right), \tag{3.2}$$

$$\mu^2=\frac{1}{4}\left(\frac{1}{\alpha+\delta}+\frac{1}{\beta+\gamma}\right), \tag{3.3}$$

$$\eta=\left(\frac{\alpha}{\alpha+\delta}-\frac{\beta}{\beta+\gamma}\right), \tag{3.4}$$

$$\mathbf{P}=\frac{2\alpha\delta}{\alpha+\delta}(\mathbf{A}-\mathbf{D})+\frac{2\beta\gamma}{\beta+\gamma}(\mathbf{B}-\mathbf{C}), \tag{3.5}$$

$$\mathbf{Q}=\frac{\alpha\mathbf{A}+\delta\mathbf{D}}{\alpha+\delta}-\frac{\beta\mathbf{B}+\gamma\mathbf{C}}{\beta+\gamma}, \tag{3.6}$$

$$R=\frac{\alpha\delta}{\alpha+\delta}|\mathbf{A}-\mathbf{D}|^2+\frac{\beta\gamma}{\beta+\gamma}|\mathbf{B}-\mathbf{C}|^2, \tag{3.7}$$

$$\mathbf{V}=\frac{(\gamma+\delta)\mathbf{u}+(\beta+\gamma)\mathbf{q}-(\alpha\mathbf{A}+\beta\mathbf{B}+\gamma\mathbf{C}+\delta\mathbf{D})}{\alpha+\beta+\gamma+\delta}, \tag{3.8}$$

it is straightforward to show that

$$[ssss]_W = \frac{v^2}{2\pi^2} e^{-(R+\lambda^2 u^2)} \int e^{-\mathbf{P}\cdot\mathbf{u}} \times \exp\left[-\frac{|\mathbf{q}-(\mathbf{Q}+\eta\mathbf{u})|^2}{4\mu^2} \right] \times \exp[-(\alpha+\beta+\gamma+\delta)|\mathbf{r}+\mathbf{V}|^2] \times j_0(qv)\, d\mathbf{r}\, d\mathbf{q}\, d\Omega_u \tag{3.9}$$

and integrating over $\mathbf{r}$ and $\mathbf{q}$ gives

$$[ssss]_W = \frac{\pi v^2 e^{-(R+\lambda^2u^2+\mu^2v^2)}}{2(\alpha+\delta)^{3/2}(\beta+\gamma)^{3/2}} \times \int e^{-\mathbf{P}\cdot\mathbf{u}} j_0(|\mathbf{Q}+\eta\mathbf{u}|v)\, d\Omega_u . \tag{3.10}$$

This integral can be evaluated using an Addition Theorem (p. 440 of Ref. 64) yielding

$$[ssss]_W = \frac{2\pi^2 u^2 v^2 e^{-(R+\lambda^2u^2+\mu^2v^2)}}{(\alpha+\delta)^{3/2}(\beta+\gamma)^{3/2}} \sum_{n=0}^{\infty} (2n+1) \times i_n(Pu) j_n(\eta uv) j_n(Qv) P_n\left(\frac{\mathbf{P}\cdot\mathbf{Q}}{PQ} \right), \tag{3.11}$$

where $i_n(x)$ is a modified spherical Bessel function, $j_n(x)$ is a spherical Bessel function, and $P_n(x)$ is a Legendre polynomial. It can be convenient to rearrange Eq. (3.11) to give

$$[ssss]_W = \frac{2\pi^2 u^2 v^2 e^{-(R+\lambda^2u^2+\mu^2v^2)}}{(\alpha+\delta)^{3/2}(\beta+\gamma)^{3/2}} \sum_{n=0}^{\infty} (2n+1) u^n v^n \times \frac{i_n(Pu)}{(Pu)^n} j_n(\eta uv) \frac{j_n(Qv)}{(Qv)^n} \left[(PQ)^n P_n\left(\frac{\mathbf{P}\cdot\mathbf{Q}}{PQ} \right) \right]. \tag{3.12}$$

In Eqs. (3.11) and (3.12), the $[ssss]_W$ integral is expressed in terms of an infinite series. In the special case that $\mathbf{P}$ and $\mathbf{Q}$ are collinear, this infinite series can be summed to give

$$[ssss]_W = \frac{\pi^2 u^2 v^2 e^{-(R+\lambda^2u^2+\mu^2v^2)}}{(\alpha+\delta)^{3/2}(\beta+\gamma)^{3/2}} \times \left(\frac{e^{Pu}}{Pu} \mathrm{f}\left[\frac{PQ-\eta Pu+i\eta Qv}{\sqrt{2\eta PQ}} \right] - \frac{e^{-Pu}}{Pu} \mathrm{f}\left[\frac{PQ+\eta Pu+i\eta Qv}{\sqrt{2\eta PQ}} \right] \right), \tag{3.13}$$

where

$$f[x+iy] = \frac{\sqrt{\pi}}{4} \exp(x^2-y^2) \frac{\mathrm{erf}(x+iy)-\mathrm{erf}(x-iy)}{iy}, \tag{3.14}$$

and erf is the error function. In the noncollinear case, we have not yet been able to sum the series. However, this is not a major concern in practice because the differentiation[64] of Bessel functions and Legendre polynomials produces only more Bessel functions and Legendre polynomials.

TABLE I. Convergence of the HF/6-311G Wigner intracule for ethene using the Lebedev quadrature (atomic units).

Grid	*W(1,1)*	*W(1,4)*	*W(4,1)*	*W(4,4)*
6	1.428210792	2.315903870	12.050144049	3.330809610
74	1.415070359	2.644503481	7.940815642	2.024274600
194	1.415070336	2.264503426	7.952388673	1.847231337
302	1.415070336	2.264503426	7.951761663	1.839467059
590	1.415070336	2.264503426	7.952573144	1.849946553
974	1.415070336	2.264503426	7.952532473	1.849439804
1454	1.415070336	2.264503426	7.952521929	1.849294392
2030	1.415070336	2.264503426	7.952529619	1.849395320
5294	1.415070336	2.264503426	7.952527680	1.849370626
Exact	1.415070336	2.264503426	7.952527682	1.849370666

IV. IMPLEMENTATION USING QUADRATURE

One approach to evaluating the Wigner integrals is to adopt the form of $[ssss]_W$ given in Eq. (3.10) and use the quadrature to approximate the integral over Ω_u. This is an integral across the surface of a sphere, for which a variety of quadrature schemes are available, for example Gauss–Legendre and Lebedev. We have chosen the Lebedev quadrature,[65–67] which exactly integrates all spherical harmonics, $Y_{lm}(\theta,\phi)$, up to a certain degree L. This method of treating the Wigner integrals has been implemented within Q-CHEM for integrals involving s and p basis functions and we have employed grids[68] with as many as 5294 points ($L=125$).

Table I shows values of $W(u,v)$ for ethene (HF/6-311G, geometry: $r_{\mathrm{CC}}=1.336\,460$ Å, $r_{\mathrm{CH}}=1.091\,353$ Å, and $\theta_{\mathrm{CCH}}=121.907\,128°$ and default Q-CHEM SCF convergence criteria[69]) at different points on the intracule using various grids. These results show that at the point *(1,1)* convergence to ten significant figures is achieved using a 194-point grid. However, at the points *(4,1)* and *(4,4)*, the largest grid (5294-point) available gives convergence to nine and eight significant figures, respectively. The source of this problem is the $e^{-\mathbf{P}\cdot\mathbf{u}}$ factor in Eq. (3.10), which can be rewritten as $e^{-Pu\cos\theta}$ to show its angular dependence. As either P or u becomes large, the integrand can no longer be represented accurately by spherical harmonics of low degree and hence very large grids are required perform the quadrature. Since the integrals that require larger grids can be identified *a priori*, it is possible to devise a scheme that selects an appropriate grid for each integral. This is currently being explored.

V. IMPLEMENTATION USING SERIES EXPANSION

The large grids required to achieve converged results mean that using quadrature to produce a Wigner intracule $W(u,v)$ at a large number of (u,v) points can be a time-consuming process. In the approach adopted[28,53] for evaluating the integrals required to generate $P(u)$ and $M(v)$, expressions for integrals of higher angular momentum were generated using a recursion relation and a set of fundamental integrals. However, the expression for the fundamental Wigner integral Eq. (3.11) is much more complex than the analogous position or momentum integrals and depends on the coordinates of **A**, **B**, **C**, and **D** in a number of terms. This results in a much larger set of higher-order fundamental integrals that arise from differentiating i_n, j_n or P_n. Consequently, differentiation of Eq. (3.11) with respect to the coordinates of **A**, **B**, **C**, or **D** soon leads to cumbersome expressions. This is illustrated by considering a specific example,

$$[p_x sss]_W = \frac{1}{2\alpha}\left\{ -\frac{2\alpha\delta}{\alpha+\delta}(A_x - D_x)[0] - u\frac{2\alpha\delta}{\alpha+\delta}\frac{P_x}{P}[1]_i - v\frac{\alpha}{\alpha+\delta}\frac{Q_x}{Q}[1]_j + \frac{\alpha}{\alpha+\delta}\frac{1}{PQ}\left(2\delta Q_x + P_x - \frac{Q_x(\mathbf{P}\cdot\mathbf{Q})}{Q^2} - \frac{2\delta P_x(\mathbf{P}\cdot\mathbf{Q})}{P^2}\right)[1]_p \right\}, \tag{5.1}$$

where

$$[ssss]_W = [0] = \frac{2\pi^2 u^2 v^2 e^{-(R+\lambda^2u^2+\mu^2v^2)}}{(\alpha+\delta)^{3/2}(\beta+\gamma)^{3/2}} \sum_{n=0}^{\infty}(2n+1) \times i_n(Pu) j_n(\eta uv) j_n(Qv) P_n\left(\frac{\mathbf{P}\cdot\mathbf{Q}}{PQ}\right), \tag{5.2}$$

$$[1]_i = \frac{2\pi^2 u^2 v^2 e^{-(R+\lambda^2u^2+\mu^2v^2)}}{(\alpha+\delta)^{3/2}(\beta+\gamma)^{3/2}} \sum_{n=0}^{\infty}(2n+1) \times\left[(n+1)\frac{i_n(Pu)}{Pu} - i_{n-1}(Pu)\right] j_n(\eta uv) \times j_n(Qv) P_n\left(\frac{\mathbf{P}\cdot\mathbf{Q}}{PQ}\right), \tag{5.3}$$

$$[1]_j = \frac{2\pi^2 u^2 v^2 e^{-(R+\lambda^2u^2+\mu^2v^2)}}{(\alpha+\delta)^{3/2}(\beta+\gamma)^{3/2}} \sum_{n=0}^{\infty}(2n+1) \times i_n(Pu) j_n(\eta uv)\left[(n+1)\frac{j_n(Qv)}{Qv} - j_{n-1}(Qv)\right] P_n\left(\frac{\mathbf{P}\cdot\mathbf{Q}}{PQ}\right), \tag{5.4}$$

$$[1]_p = \frac{2\pi^2 u^2 v^2 e^{-(R+\lambda^2u^2+\mu^2v^2)}}{(\alpha+\delta)^{3/2}(\beta+\gamma)^{3/2}} \frac{(PQ)^2}{(\mathbf{P}\cdot\mathbf{Q})^2 - (PQ)^2} \times \sum_{n=0}^{\infty} n(2n+1) i_n(Pu) j_n(\eta uv) j_n(Qv) \times\left[\frac{\mathbf{P}\cdot\mathbf{Q}}{PQ} P_n\left(\frac{\mathbf{P}\cdot\mathbf{Q}}{PQ}\right) - P_{n-1}\left(\frac{\mathbf{P}\cdot\mathbf{Q}}{PQ}\right)\right]. \tag{5.5}$$

Expressions for integrals of higher angular momentum are too long to reproduce here. However, they can be derived by further differentiation of Eq. (5.1), which gives rise to further fundamental integrals, for example,

$$[2]_{ij} = \frac{2\pi^2 u^2 v^2 e^{-(R+\lambda^2u^2+\mu^2v^2)}}{(\alpha+\delta)^{3/2}(\beta+\gamma)^{3/2}} \sum_{n=0}^{\infty}(2n+1) \times\left[(n+1)\frac{i_n(Pu)}{Pu} - i_{n-1}(Pu)\right] j_n(\eta uv) \times\left[(n+1)\frac{j_n(Qv)}{Qv} - j_{n-1}(Qv)\right] P_n\left(\frac{\mathbf{P}\cdot\mathbf{Q}}{PQ}\right), \tag{5.6}$$

$$[2]_{ii} = \frac{2\pi^2 u^2 v^2 e^{-(R+\lambda^2u^2+\mu^2v^2)}}{(\alpha+\delta)^{3/2}(\beta+\gamma)^{3/2}} \sum_{n=0}^{\infty}(2n+1) \times\left[(n+1)(n+2)\frac{i_n(Pu)}{(Pu)^2} - (2n+1)\frac{i_{n-1}(Pu)}{Pu} + i_{n-2}(Pu)\right] j_n(\eta uv) j_n(Qv) P_n\left(\frac{\mathbf{P}\cdot\mathbf{Q}}{PQ}\right). \tag{5.7}$$

Integrals in which **P** and/or **Q** are zero can more easily be evaluated through differentiation of Eq. (3.11) since this form leads to expressions for the integrals of higher angular momentum in which the limits as **P** and/or **Q** approach zero are well defined. In these cases the infinite series truncates after at most five terms in the $[pppp]_W$ instance. Again this is illustrated with a specific example,

$$[p_x sss]_W = \frac{1}{2\alpha}\left\{ -\frac{2\alpha\delta}{\alpha+\delta}(A_x - D_x)[0] + u^2\frac{2\alpha\delta}{\alpha+\delta}P_x[1]_i - v^2\frac{\alpha}{\alpha+\delta}Q_x[1]_j + \left(\frac{\alpha}{\alpha+\delta}P_x + \frac{2\alpha\delta}{\alpha+\delta}Q_x\right)[1]_P \right\}, \tag{5.8}$$

where

$$[0] = \frac{2\pi^2 u^2 v^2 e^{-(R+\lambda^2u^2+\mu^2v^2)}}{(\alpha+\delta)^{3/2}(\beta+\gamma)^{3/2}} i_0(Pu) j_0(Qv) j_0(\eta uv), \tag{5.9}$$

$$[1]_i = \frac{2\pi^2 u^2 v^2 e^{-(R+\lambda^2u^2+\mu^2v^2)}}{(\alpha+\delta)^{3/2}(\beta+\gamma)^{3/2}} \frac{i_1(Pu)}{Pu} j_0(Qv) j_0(\eta uv), \tag{5.10}$$

$$[1]_j = \frac{2\pi^2 u^2 v^2 e^{-(R+\lambda^2u^2+\mu^2v^2)}}{(\alpha+\delta)^{3/2}(\beta+\gamma)^{3/2}} i_0(Pu) \frac{j_1(Qv)}{Qv} j_0(\eta uv), \tag{5.11}$$

$$[1]_P = \frac{2\pi^2 u^2 v^2 e^{-(R+\lambda^2u^2+\mu^2v^2)}}{(\alpha+\delta)^{3/2}(\beta+\gamma)^{3/2}} \frac{i_1(Pu)}{Pu} \frac{j_1(Qv)}{Qv} \times 3uv\, j_1(\eta uv). \tag{5.12}$$

Evaluation of expressions (5.2)–(5.7) requires accurate determination of $j_n(x)$ for arbitrary n and x, and $i_n(x)$ for arbitrary n and positive x. To evaluate $j_n(x)$ we have followed the procedure described by Jablonski.[70] This scheme uses three separate techniques, a series expansion, ascending recurrence, and descending recurrence, depending on the value of the argument x. Modified spherical Bessel functions are evaluated using a series expansion for $x<10$. For larger

TABLE II. Convergence of the HF/6-311G Wigner intracule for ethene using the series expansion (atomic units).

n	*W(1,1)*	*W(1,4)*	*W(4,1)*	*W(4,4)*
0	0.434783191	1.163162925	5.563505283	1.206842534
2	1.397225905	2.263657056	7.906692389	1.680799415
4	1.415070335	2.264502081	7.952416400	1.790157095
6	1.415070336	2.264503427	7.952527375	1.831258577
8	1.415070336	2.264503426	7.952527682	1.843955779
10	1.415070336	2.264503426	7.952527682	1.848012755
12	1.415070336	2.264503426	7.952527682	1.849136612
14	1.415070336	2.264503426	7.952527682	1.849347209
16	1.415070336	2.264503426	7.952527682	1.849369411
18	1.415070336	2.264503426	7.952527682	1.849370629
20	1.415070336	2.264503426	7.952527682	1.849370666
30	1.415070336	2.264503426	7.952527682	1.849370666

x, $\exp(-x)i_n(x)$ is determined using a procedure described in detail elesewhere.[71] Previous implementations to compute $P(u)$[28] and $M(v)$[53] follow Cioslowski[22] and locate the loop over u or v points within the loop over shell-quartets. However, when computing $W(u,v)$ for a system of only moderate size, this arrangement requires large amounts of memory to store all the integrals arising from each (u,v) point. To overcome this, we have implemented an additional scheme in which the u and v loops are outside the shell-quartet loop.

Table II shows the values of $W(u,v)$ for ethene. In these calculations, the limits in the series expansion evaluation of $i_n(x)$ and $j_n(x)$ were set to 70. A similar pattern is observed as when using quadrature. The points *(1,1)* and *(1,4)* converge rapidly, while the convergence of the points *(4,1)* and *(4,4)* is slower. The origin of this slower convergence is again large *Pu* for which terms of high n make a significant contribution to the integral. However, even in the case of the *(4,4)* point, summation of $n=20$ terms suffices to achieve ten significant figures. Investigation of the convergence of other points showed that typically all have converged with $n \leqslant 20$. For larger molecules, summation to higher n may be necessary.

Figure 1 shows $W(u,v)$ for ethene. In the Wigner intracules presented previously[56] for atomic systems and H_2, distinct peaks were observed that could be attributed to particular electron–electron interactions. For larger molecular systems, the peaks tend to merge into one. The ethene intracule is dominated by one peak and falls away rapidly in the u direction and more slowly in the v direction.

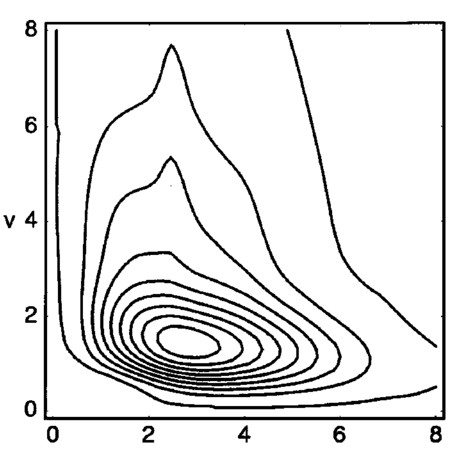

FIG. 1. HF/6-311G Wigner intracule for ethene (atomic units).

VI. CONCLUSIONS

In this paper, the computation of molecular Wigner intracules for HF wave functions using Gaussian basis functions has been described. Wigner intracules describe both the relative position and momentum of electrons and can play an important role in the study of electron correlation.[55] No simple closed form expression could be found for the required integrals and two numerical approaches to evaluating the integrals have been described. The first approach employs Lebedev quadrature while the second expresses each integral as an infinite series. These two approaches have been implemented within Q-CHEM for s and p basis functions. Very large quadrature grids are required to achieve converged results, particularly if *Pu* is large. Evaluating Wigner intracules using the approach based on an infinite series yields results that do converge rapidly. However, the greater simplicity of the quadrature scheme allows it to be extended much more readily to basis functions of higher angular momentum. We are currently exploring the summation of the series to generate a simple closed form expression for the Wigner integrals.

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