Hartree - Fock - Wigner theory

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Introduction

The Wigner Intracule[1,2]

With the spinless reduced second-order density matrix ρ_2 the second-order Wigner density is given by

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

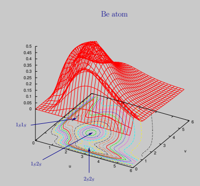
which could be interpreted as the quasi-probability of finding one eletcron at $\mathbf{r}_1$ with momentum $\mathbf{p}_1$ and another at $\mathbf{r}_2$ with momentum $\mathbf{p}_2$. Reducing the second-order Wigner density [1] yields

$$W(u,v) = \int W_2(\mathbf{r}_1\mathbf{p}_1\mathbf{r}_2\mathbf{p}_2)\delta(\mathbf{r}_{12}-\mathbf{u})\delta(\mathbf{p}_{12}-\mathbf{v})\, d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{p}_1 d\mathbf{p}_2 d\Omega_u d\Omega_v \qquad (2)$$

which is called the Wigner intracule. This function is the quasi-probability of finding two electrons at a distance u and moving with a relative momentum v. Although the Wigner Intracule is not strictly a joint probability distibution for u and v, it does yield the following marginal densities (the position and momentum intracules)

$$\int_0^\infty W(u,v)dv = P(u) \qquad (3)$$

$$\int_0^\infty W(u,v)du = M(v). \qquad (4)$$



Calculation of the correlation energy[3]

The correlation energy of a many electron system may be derived from the Wigner Intracule $W(u,v)$ by multiplication with a weighting function $G(u,v)$ and integration over all relative positions u and momenta v, i.e.,

$$E_{corr} = \int\int_0^\infty W(u,v)G(u,v)dudv \qquad (5)$$

Orbital representation based correlation kernel fitting

For a finite basis set expansion of the orbitals a HF-energy-like expression for the correlation energy E_{corr} can be derived from (5)

$$E_{corr} = -\frac{1}{2}\sum_{\mu\nu\lambda\sigma}[P_{\mu\nu}P_{\lambda\sigma} - P^\alpha_{\mu\sigma}P^\alpha_{\nu\lambda} - P^\beta_{\mu\sigma}P^\beta_{\nu\lambda}](\mu\nu\lambda\sigma)_G \qquad (6)$$

$$(\mu\nu\lambda\sigma)_G = (2\pi)^{-3}\int \phi_\mu(\mathbf{r})\phi_\nu(\mathbf{r}+\mathbf{q})\phi_\lambda(\mathbf{r}+\mathbf{q}+\mathbf{u}) \cdot \phi_\sigma(\mathbf{r}+\mathbf{u})\cdot G(u,v) j_0(qv) d\mathbf{r}d\mathbf{q}d\mathbf{u}d\mathbf{v} \qquad (7)$$

Since an evaluation of (7) for general $G_{HF}(u,v)$ is a rather sophisticated task, Gill and coworkers expanded $G_{HF}(u,v)$ into Gaussian functions according to

$$G^G_{HF}(u,v) = \sum_i c_i \exp(-\zeta_i u^2 v^2). \qquad (8)$$

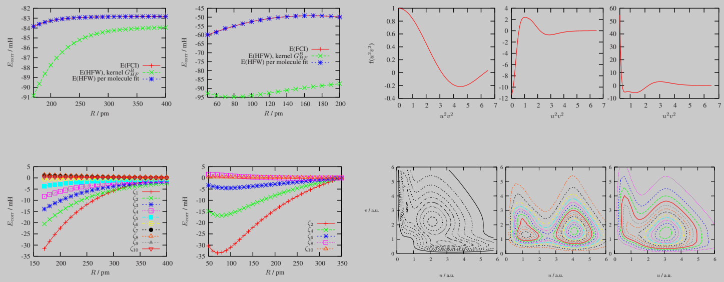
Substituting (8) in (7) yields

$$E_{corr} = \sum_i c_i \frac{1}{2}\sum_{\mu\nu\lambda\sigma}[P_{\mu\nu}P_{\lambda\sigma} - P^\alpha_{\mu\sigma}P^\alpha_{\nu\lambda} - P^\beta_{\mu\sigma}P^\beta_{\nu\lambda}] \cdot \frac{1}{2\pi^2}\int \phi_\mu(\mathbf{r})\phi_\nu(\mathbf{r}+\mathbf{q})\phi_\lambda(\mathbf{r}+\mathbf{q}+\mathbf{u}) \cdot \phi_\sigma(\mathbf{r}+\mathbf{u})\cdot \exp(-\zeta_i u^2 v^2)\cdot j_0(qv) d\mathbf{r}d\mathbf{q}d\mathbf{u}d\mathbf{v} \qquad (9)$$

The fit of $G^G_{HF}(u,v)$ roughly resembles a zeroth-order Bessel function

$$G^B_{HF}(u,v) = a j_0(\omega u v) \qquad (10)$$

with a and ω optimized to 0.10093 and 0.90447 respectively.



Direct fit of the correlation kernel

The symmetric anstaz in u and v of the correlation kernel according to (8) is too restrictive to be molecule universal. For this reason we expanded the correlation kernel $G(u,v)$ into a set of Gaussian functions on a two dimensional grid.

$$\tilde{G}(u,v) = \sum_{ij} g_{ij} f^G_{ij}(u,v) \qquad (11)$$

with

$$f^G_{ij}(u,v) = \exp\left(-\xi^{Gu}_i(u-u^G_i)^2 - \xi^{Gv}_j(v-v^G_j)^2\right) \qquad (12)$$

Doing so, we still encounter the integration bottleneck of (7). Fortunately the problem simplifies significantly if we do not use the deviation via the density matrix representation of (6) and (7) to evaluate the correlation energy but expand the intracule $W(u,v)$ into a set of Gaussian functions themselves similar to $G(u,v)$:

$$\tilde{W}(u,v) = \sum_{ij} w_{ij} f^W_{ij}(u,v) \qquad (13)$$

with

$$f^W_{ij}(u,v) = \exp\left(-\xi^{Wu}_i(u-u^W_i)^2 - \xi^{Wv}_j(v-v^W_j)^2\right) \qquad (14)$$

The parameters ξ^{Wu}_i, ξ^{Wv}_i, ξ^{Gu}_i, ξ^{Gv}_i and u^W_i, v^W_i, u^G_i, v^G_i of (12) and (14) constitute exponents and centers of the basis set expansion respectively and must be suitably chosen to meet the shape of the intracule $W(u,v)$ and correlation kernel $G(u,v)$.

Inserting (13) and (11) into (5) we arrive at

$$\begin{aligned}\tilde{E}_{corr} &= \sum_{ijkl} w_{ij}g_{kl}\int_0^\infty\int_0^\infty \exp\Big[-\xi^{Wu}_i(u-u^W_i)^2 - \xi^{Wv}_j(v-v^W_j)^2 \\ &\qquad -\xi^{Gu}_k(u-u^G_k)^2 - \xi^{Gv}_l(v-v^G_l)^2 \Big] du\, dv \\ &= \sum_{ijkl} w_{ij}g_{kl}U_{ik}V_{jl}\end{aligned} \qquad (15)$$

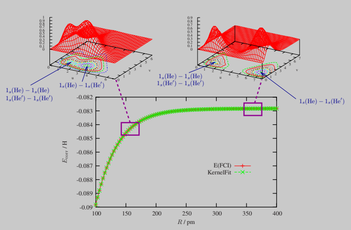
with

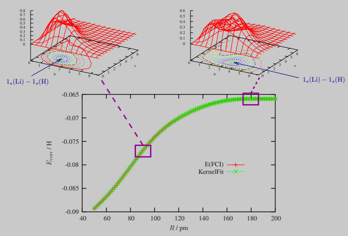
$$U_{ij} = \int_0^\infty \exp\left(-\xi^{Wu}_i(u-u^W_i)^2 - \xi^{Gu}_j(u-u^G_j)^2\right) du \qquad (16)$$

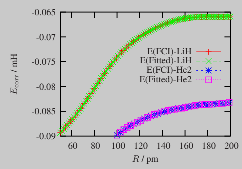
and

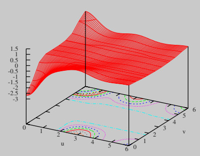
$$V_{ij} = \int_0^\infty \exp\left(-\xi^{Wv}_i(v-v^W_i)^2 - \xi^{Gv}_j(v-v^G_j)^2\right) dv \qquad (17)$$

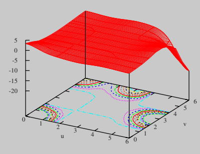
which may be easily evaluated using the addition theorems for Gaussian functions.

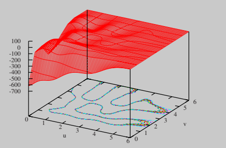












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References

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