

Molecular results for the Hartree-Fock-Wigner model

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Abstract

Results of the Hartree-Fock-Wigner model for He₂ and LiH using an atomic and a molecular parameterization of the correlation kernel are presented and interpreted in terms of Wigner intracules. The purely atomic parameterization turns out to be insufficient for molecules and is replaced by a fit along the potential curve on a per-molecule basis. It is argued that the remaining shortcomings partly result from the restriction of the currently used correlation function to be symmetric in relative position and relative momentum.

Key words: Hartree-Fock-Wigner, Electron-correlation, Correlation kernel, Wigner intracule, Electronic structure

1 Introduction

Today *first-principles* electronic structure theory comprises mainly the standard wavefunction theory (WFT) and density functional theory (DFT) [1]. In addition more or less unconventional approaches like Quantum Monte Carlo (QMC) are in use. Whereas the main advantage of DFT over WFT is the speed with which the computations can be carried out as well as the large size

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of the accessible systems, WFT has still the advantage to be at least in principle systematically improvable towards the exact solution of the Schrödinger equation. An attractive goal of method development in the field of quantum chemistry is the derivation of approaches which combine the advantages of WFT and DFT, i.e., schemes which generate accurate approximate solutions at low cost.

A useful introduction (so-called "road map") to one-matrices and related densities was given by Thakkar, Tannar and Smith [2]. They presented the interrelationships between the position, momentum, Wigner [3] and Moyal [4] representations of the spin-traced first-order reduced density operator, and charge densities, momentum densities, form factors and internally folded densities. Two-electron distribution functions, so-called intracules, are intermediate between the simplicity of electron densities and the complexity of the corresponding wavefunctions. The term intracule was coined by Eddington [5] and later introduced to density matrix theory by Coleman [6]. The relative motion of arbitrary two electrons in position space is embodied by the position intracule $P(u)$ (for a review see [7]). In addition to these authors Boyd et al. and Cioslowski et al. have made significant contributions to its development (e.g. [8,9]). The momentum intracule $M(v)$ which gives the probability of finding two electrons moving with a relative momentum v was initially investigated by Banyard and Reed [10] and later by Koga and Matsuyama [11]. Recently Gill et al. [12] proposed a new type of intracule defined in phase space. The new intracule results from a reduction of the second-order Wigner density [3] and was therefore called a Wigner intracule. The Wigner intracule can be interpreted as a quasi-probability of finding two electrons at a distance u with a relative momentum v . The integration of the Wigner intracule over v and u leads to the position and momentum intracule, respectively.

Wigner intracules apparently contain more information about the behaviour of electrons than the position and momentum intracules alone [13]. Aside from using them as a purely analytical tool to analyze many-electron or model systems [14–16], it is tempting to base a method for quantitative electronic structure calculations on them. It has been demonstrated by Besley et al. [13] that in case of Gaussian basis functions expressions for the evaluation of molecular Hartree-Fock-Wigner intracules $W_{HF}(u, v)$ can be derived. It was further suggested that by weighting the intracules with a correlation function $G_{HF}(u, v)$ and subsequent integration over the whole range of relative positions u and momenta v an estimate of the correlation energy could be obtained. For a special choice of the weighting function $G_{HF}(u, v)$ Gill et al. were able to derive a Hartree-Fock-type energy expression with modified two-electron integrals yielding the correlation energy of the system [17]. Initial parameterizations of the unknown function $G_{HF}(u, v)$ were performed and atomic test calculations yielded encouraging results. In the present contribution we present and analyze for the first time molecular results based on the Hartree-Fock-Wigner

model.

2 Method

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.,

$$E_{corr} = \int_0^\infty \int_0^\infty W(u, v) G(u, v) du dv. \quad (1)$$

For a finite basis set expansion of the orbitals a HF-energy-like expression for the correlation energy E_{corr} can be derived from (1)

$$E_{corr} = -\frac{1}{2} \sum_{\mu\nu\lambda\sigma} [P_{\mu\nu}P_{\lambda\sigma} - P_{\mu\sigma}^\alpha P_{\nu\lambda}^\alpha - P_{\mu\sigma}^\beta P_{\nu\lambda}^\beta](\mu\nu\lambda\sigma)_G \quad (2)$$

Here $P_{\mu\nu}$ denotes the density matrix element of the basis function pair μ, ν and $(\mu\nu\lambda\sigma)_G$ are a new type of two-electron integrals

$$(\mu\nu\lambda\sigma)_G = \frac{1}{2\pi^2} \int \varphi_\mu(\mathbf{r})\varphi_\nu(\mathbf{r} + \mathbf{q})\varphi_\lambda(\mathbf{r} + \mathbf{q} + \mathbf{u})\varphi_\sigma(\mathbf{r} + \mathbf{u}) \times \quad (3)$$

$$v^2 j_0(qv) G_{HF}(u, v) d\mathbf{r} d\mathbf{q} d\mathbf{u} dv.$$

j_0 reflects the zeroth-order spherical Bessel function entering through the angular integration over \mathbf{v} . Since an evaluation of (3) for general $G_{HF}(u, v)$ is a rather sophisticated task, Gill and coworkers [17] expanded $G_{HF}(u, v)$ into Gaussian functions according to

$$G_{HF}^G(u, v) = \sum_i c_i \exp(-\zeta_i u^2 v^2). \quad (4)$$

Using $G_{HF}^G(u, v)$ the multi-center integrals for Gaussian s-functions φ (Gaussian lobe functions) can be carried out analytically and one is left with the radial integration over u , which has to be carried out numerically. Unfortunately, for actual calculations this remaining numeric integration turns out to be still challenging. We implemented an integration scheme based on cubic spline functions which proved to be numerically sufficiently stable and still not prohibitively time-consuming. Nevertheless, the numeric integration currently constitutes the main bottleneck in actual calculations and has to be improved for real world applications.

Interestingly, various attempts to obtain the weighting function $G_{HF}(u, v)$ by fitting the correlation energy along various atoms always resulted in a highly oscillatory function. According to Gill [18] the fit of $G_{HF}^G(u, v)$ roughly resembles a zeroth-order Bessel function

$$G_{HF}^B(u, v) = aj_0(\omega uv) \quad (5)$$

with a and ω optimized to 0.10093 and 0.90447 respectively.

However, as it will turn out in the results section the ansatz $G_{HF}^B(u, v)$ originating from atomic fits may yield unsatisfactory results for molecular applications. Therefore we kept the ansatz $G_{HF}^G(u, v)$ but performed the fit along the potential energy curve for individual molecules. This will provide us with information about the applicability of the ansatz $G_{HF}^B(u, v)$ and will result in a deeper understanding of the deficiencies of it.

The full configuration interaction (full CI) reference calculations were performed with the MOLPRO ab initio program package [19] using Dunning’s correlation-consistent polarized valence quintuple-zeta basis sets (cc-pV5Z) for He and Dunning’s correlation-consistent polarized valence triple-zeta basis sets (cc-pVTZ) for Li and H [20]. The corresponding Hartree-Fock-Wigner (HFW) calculations were performed using Wigner intracules derived from the HF wavefunction expanded in a Gaussian lobe basis sets, i.e., 6-311++G for He and 6-311++G** and 6-31++G* for H and Li, respectively. The HF calculations were carried out with the Bochum suite of ab initio programs [21] and the HFW correlation calculation with a C++ code developed in our group.

3 Results and discussion

For test applications we selected the two isoelectronic molecules He₂ and LiH reflecting a van der Waals interaction and an ionic/polar covalent bonding respectively. Figure 1 shows the resulting correlation energies obtained by various methods for He₂ and LiH, respectively. Analyzing the shape of the full CI correlation energies we note that the correlation energies of He₂ and LiH show a different character. For both molecules we see an increase of the correlation energy for $R \rightarrow 0$ which may be easily explained by an accumulating number of electrons within a limited space. Additionally, for LiH there is another increase in the correlation energy for $R \rightarrow \infty$ which may be drawn to static correlation effects from the multi-configurational dissociation within a closed shell one-particle basis. Since most likely ansatz (2) cannot account for non-dynamical correlation effects, we eliminated the branch of the ground state potential curve for larger R than the approximate position of the crossing of the ionic and neutral asymptotic limits.

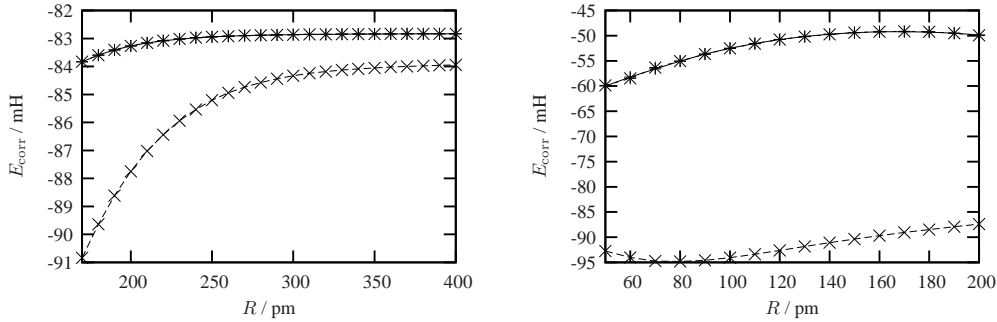


Fig. 1. Correlation energies along the potential curve (left: He₂, right: LiH) (+: E(FCI), basis: cartesian Gaussians, counter-poise corrected, He₂:cc-pV5Z, LiH:cc-pVTZ; ×: E(HFW) kernel G_{HF}^B , basis: Gaussian Lobes, He:6-311++G, H:6-311++G**, Li:6-31++G**, *: E(HFW) per molecule fit, basis: Gaussian Lobes, He:6-311++G, H:6-311++G**, Li:6-31++G**)

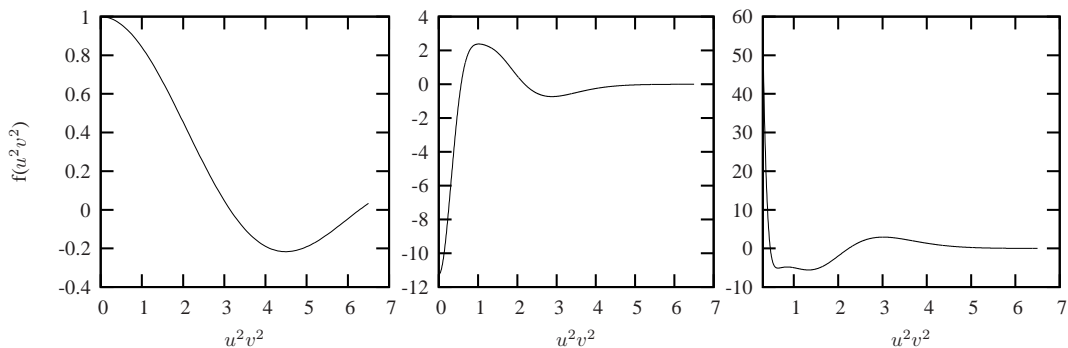


Fig. 2. The correlation kernel $G_{HF}(u, v)$ of the form $G_{HF}^G(u, v)$. (left: kernel (5) fitted to atoms, middle: kernel fitted to He₂, right: kernel fitted to LiH)

The HFW energies based on the kernel $G_{HF}^B(u, v)$ fitted to atoms show a significant overestimation of the correlation for both molecules. Although, it seems to be qualitatively correct in the case of He₂ it obviously fails for LiH where it predicts a maximum of the correlation energy close to the equilibrium distance. This is reflected by the non-parallelity error (NPE), i.e., the difference between the maximum and minimum deviations to full-CI results, which amounts 0.0059 for He₂ and 0.0091 for LiH.

The correlation kernels fitted to individual molecules on the other hand perform very well in both cases. However, this is no surprise since the correlation functionals were optimized for this special case and are no longer "universal". In this case the NPE amounts 0.00001 for He₂ and 0.00052 for LiH.

Especially with respect to universality it is illuminating to look at the shape of the two molecularly fitted correlation kernels. They are shown in figure 2. Naturally, for $u^2 v^2 \rightarrow \infty$ all three kernels converge to zero. Besides this, the oscillating behaviour as well as the degree of the oscillations are very different. Anyway, the occurrence of an oscillation looks a bit curious and might be a

i	ζ_i	$c_i(\text{He}_2)$	$c_i(\text{LiH})$
1	0.173 287	-3.527 903	—
2	0.213 934	8.813 418	54.630 656
3	0.270 761	-36.733 798	—
4	0.353 647	46.741 100	-125.447 836
5	0.481 352	2.145 166	—
6	0.693 147	-8.042 320	84.849 500
7	1.083 042	-17.897 183	—
8	1.925 409	16.732 270	-23.634 035
9	4.332 170	-19.223 525	—
10	17.328 680	-0.262 351	298.128 268

Table 1

Expansion coefficients optimized for a per-molecule fit for He₂ and LiH

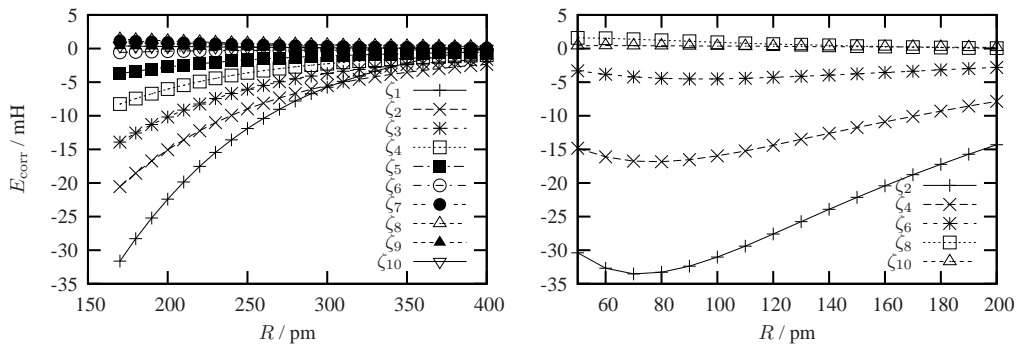


Fig. 3. Basis functions to span the exact correlation energy. (left: He₂, right: LiH, for ζ_i see table 1)

hint that the correlation kernel in its current form is not optimal.

In order to get a deeper understanding of the problem we shall look at the linear fit resulting from $G_{HF}^G(u, v)$ as a basis set expansion of the exact correlation energy along the potential curve. Calculating the correlation energy for each exponent in $G_{HF}^G(u, v)$ individually we arrive at a correlation energy curve in R per exponent. This is plotted in figure 3. As each function contributes to the basis approximately spanning the correlation energy curve along R it will be called a basis function. The fit tries to combine the basis functions to resemble the exact correlation energy obtained from full CI calculations. Analyzing figure 3 we encounter two different situations: For He₂, which was fitted with 10 Gaussian functions, on the left hand side the basis functions reflect the shape of the exact correlation energy rather well. This is confirmed by the structure of the fitting coefficients which are of modest size. In contrast to this the basis functions for LiH, where the fit contains 5 Gaussian functions, on the right hand side do not qualitatively reflect the shape of the exact correlation curve. Consequently the fitting coefficients become large and the sign changes frequently (cf. table 1). Finally, as may be seen from the larger NPE the overall quality of the fit is poorer than for He₂.

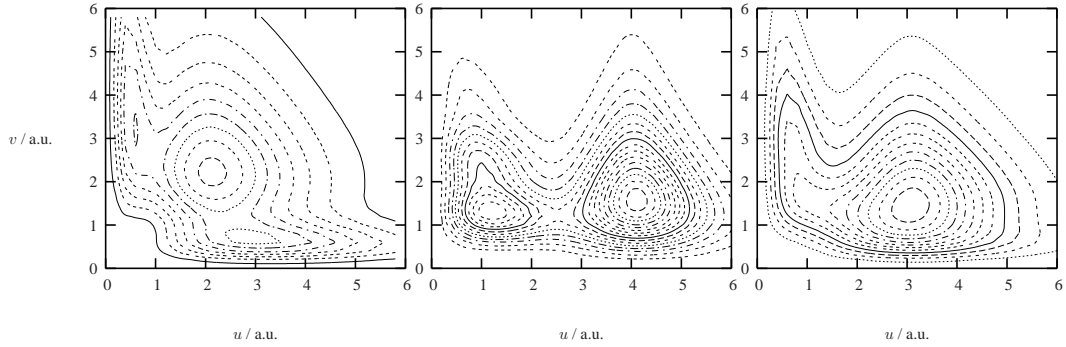


Fig. 4. Wigner intracules for Be, He₂ and LiH (from left to right, at equilibrium distance for the molecules)

To summarize: In the case of LiH the basis functions resulting from the ansatz $G_{HF}^G(u, v)$ do not span the exact correlation energy along the potential energy curve appropriately. Increasing the number of expansion coefficients could of course improve the overall accuracy of the fit. However, this would fail to be molecule universal and would only conceal that there is a principle deficiency in the ansatz $G_{HF}^G(u, v)$.

Obviously, ansatz $G_{HF}^G(u, v)$ misses a certain degree of freedom to distinguish between the two molecules. In order to analyze this lack of flexibility we plotted the Wigner intracules for He₂ and LiH and additionally Be in figure 4. The plots for the molecules refer to the HFW equilibrium distances. Although these systems are entirely different, all three of them possess two electron pairs. The Wigner intracule for Be has already been discussed by Gill et al. [12] and is reprinted here for convenience and completeness. The three maxima visible in the contour line plot correspond to intra-shell contributions of 1s-1s (smaller u , larger v) and 2s-2s (larger u , smaller v) as well as a larger 1s-2s inter-shell contribution (intermediate $u \approx v$). In He₂ two maxima are clearly visible, the larger one from the 1s_{He}-1s_{He'} inter-shell contribution and the smaller one from the superposition of the 1s_{He}-1s_{He} and 1s_{He'}-1s_{He'} intra-shell contributions. The latter appear roughly at the position of the maximum of the He Wigner intracule [12]. The Wigner intracule of LiH exhibits only a single maximum about as high as the 1s-2s inter-shell contribution of Be. This maximum can be associated mainly to the 1s_{Li}-1s_H inter-shell contribution, whereas the 1s_{Li}-1s_{Li} and 1s_H-1s_H intra-shell contributions only cause a shoulder extending to smaller u and large v values. The position of the shoulder indeed corresponds to the 1s_{Li}-1s_{Li} intra-shell maximum in the Li Wigner intracule [12].

Analyzing the structure of ansatz $G_{HF}^G(u, v)$ we find trivially $G_{HF}^G(u, v) = G_{HF}^G(v, u)$. Naturally, this discards any information asymmetric in u and v . However, from figure 4 it is obvious that this asymmetry should be of increasing importance when calculating the correlation energy along the sequence Be – He₂ – LiH.

The asymmetry in u and v may additionally be rationalized from the following thoughts: Upon dissociation of He_2 the inter-shell maximum is shifted to larger values of u corresponding roughly to the interatomic distance R , whereas the intra-shell contributions approximately remain at their positions. Whereas the latter should yield twice the atomic correlation energy of He, the former should not contribute at all, i.e., terms dependent solely on u are possible, but a dependence of terms solely on v has to be avoided.

These findings suggest the construction of new correlation functions $G_{HF}(u, v)$ which do not treat u and v symmetrically. Work along these lines is subject to current investigations in our research group.

4 Conclusions

We presented the first molecular results for correlated calculations within the framework of the Hartree-Fock-Wigner model. Whereas a correlation kernel fitted to atomic data yielded results of only limited accuracy for He_2 and LiH an improved kernel based on a per-molecule fit provided better results. An analysis of the Wigner intracules of simple systems suggests to abandon the symmetric role of the relative position u and relative momentum v in order to arrive at a more accurate correlation kernel. Due to the currently limited flexibility in G_{HF}^G the results should be seen as intermediate and should significantly improve for a more general kernel.

5 Acknowledgement

The financial support of the German Science Council (Deutsche Forschungsgemeinschaft) through the priority program (Schwerpunktprogramm) 1145 is gratefully acknowledged. We thank Prof. V. Staemmler, Bochum, for a copy of his Hartree-Fock code and Prof. P. Gill, Canberra, for valuable discussions.

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