

The performance of the Hartree–Fock–Wigner correlation model for light diatomic molecules

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Abstract Results of the Hartree–Fock–Wigner correlation model for diatomic molecules with light atoms (H_2 , LiH , Li_2 , F_2 , He_2 , Ne_2) using two different atomic parametrizations and one molecular parametrization of the correlation kernel are presented and interpreted in terms of Wigner intracules as well as differences thereof. The molecular parametrization yields encouraging results for simple systems exhibiting covalent or ionic bonding. However, similar to the purely atomic parametrizations severe overestimations of the attractive interaction in van der Waals systems is observed. It is argued that the remaining shortcomings partly result from the restriction of the currently used correlation kernel to be symmetric in relative position and relative momentum.

1 Introduction

There is a large variety of approaches to calculate estimates of the correlation energy of many-electron systems [1–3]. Among the most widely used schemes are standard wavefunction theories (WFT) like configuration interaction, coupled cluster and many-body perturbation theory on one hand and density-functional theory based methods (DFT) on the other hand. WFT and DFT approaches both cover potential exactness by complete basis set expansions in the one- and many-electron space and the Hohenberg-Kohn theorem, respectively. However, only WFT methods provide a constructive way to the exact result. Unfortunately, aside of small

model systems for practical purposes the finally exact result cannot be reached for either of the two methods due to the high cost for WFT methods or the unknown exact functional for DFT approaches.

Traditionally quantum chemistry was dominated by WFT, whereas DFT mainly in terms of the local density approximation (LDA) was the most popular approach to electronic structure in solid state physics. During the last two decades however, DFT in its modern form applying gradient-corrected (and possibly hybrid) functionals began to conquer quantum chemistry and nowadays is almost routinely used for studying the ground state chemistry of non-van der Waals type systems [4]. A corresponding entirely successful application of WFT to the electronic structure theory of solids was not achieved so far, despite many possible benefits of such an extension and the ongoing efforts by several groups [5–8].

Despite the undoubted success of DFT, it seems to be more natural to base an electron correlation model on two-electron properties rather than on the one-electron density. In contrast to DFT methods intracule-based approaches [9] parametrize the distance between two electrons explicitly while keeping the same formal N^4 scaling as for DFT in the basis set size N . An intracule is the probability density function for the distance between two electrons in a certain space. Recently Gill et al. [10] proposed a new type of intracule defined in phase space. The new intracule results from a reduction of the second-order Wigner density [11] and was therefore called Wigner intracule. The Wigner intracule is related to the probability of two electrons being at distance u apart and moving with a relative momentum v . It has been used on one hand as a purely analytical tool to study many-electron or model systems [13–15] and on the other hand for obtaining an estimate of the correlation energy by weighting it with a correlation function $G_{HF}(u, v)$ and performing a subsequent integration over the whole range of relative positions u and

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momenta v . Initial parametrizations of the unknown function $G_{HF}(u, v)$ were performed and atomic test calculations yielded encouraging results for total correlation energies [9]. In a previous publication [16] we attempted to generate correlation kernels of He_2 and LiH on a per molecule basis by fitting to correlation contributions along the potential curves. In the present work we try to determine a universal correlation kernel by fitting both to atomic as well as to molecular data. We also discuss the first results for molecular constants of light diatomic molecules based on the Hartree–Fock–Wigner (HFw) model and outline some directions for improvement.

2 Method

Gill et al. [12] proposed that 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 the relative position u and momentum v , i.e.,

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

For a Hartree–Fock wavefunction Gill et al. [10] were able to derive a Hartree–Fock–type energy expression with modified two-electron integrals tentatively yielding the correlation energy of the system.

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

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

$$(\mu\nu\lambda\sigma)_G = \frac{1}{2\pi^2} \int \varphi_\mu(\mathbf{r}) \varphi_\nu(\mathbf{r} + \mathbf{q}) \varphi_\lambda(\mathbf{r} + \mathbf{q} + \mathbf{u}) \varphi_\sigma(\mathbf{r} + \mathbf{u}) \times v^2 j_0(qv) G_{HF}(u, v) d\mathbf{r} d\mathbf{q} d\mathbf{u} dv. \quad (3)$$

j_0 denotes the zeroth-order spherical Bessel function. In order to determine approximations for the correlation kernel Gill et al. fitted linear combinations of elementary functions in the product $u \cdot v$ to exact atomic correlation energies. The dependency as the product $u \cdot v$ was motivated by the finding of Rassolov, that the correlation energy of He-like ions approaches a constant for increasing nuclear charge [17], as does the product of the expectation values $\langle u \rangle \cdot \langle v \rangle$ [9]. Various attempts to obtain the weighting function always resulted in a highly oscillatory function, resembling roughly a zeroth-order Bessel function:

$$G_{HF}(u, v) = a \cdot j_0(\omega uv). \quad (4)$$

It should be noted that when using the ansatz (4) two distinct Bessel functions enter the modified two-electron integrals (3): $j_0(qv)$ originating from the angular integration and $j_0(\omega uv)$ from the assumption Eq. 4.

Unfortunately, the new two-electron integrals cannot be evaluated in closed form for G_{HF} containing a Bessel function. Therefore $G_{HF}(u, v)$ is expanded in terms of Gaussian functions

$$G_{HF}(u, v) = \sum_{i=1}^n c_i \exp(-\zeta_i u^2 v^2). \quad (5)$$

The resulting multi-center integrals for Gaussian s-functions (Gaussian lobes) can be carried out analytically, except for the radial integration in u , which still has to be performed numerically. For a single Gaussian $\exp(-\zeta u^2 v^2)$ one obtains [12]

$$(ssss)_G = \frac{\pi^{5/2} e^{-R}}{2(\alpha + \delta)^{3/2} (\beta + \gamma)^{3/2}} \int_0^\infty \frac{u^2}{(u^2 \zeta + \mu^2)^{3/2}} \times \exp\left(-\lambda^2 u^2 - \frac{\eta^2 u^2 + Q^2}{4(u^2 \zeta + \mu^2)}\right) \times i_0\left(\left|\mathbf{P} + \frac{\eta \mathbf{Q}}{2(u^2 \zeta + \mu^2)}\right| u\right) du \quad (6)$$

with $i_0(z) = \sinh(z)/z$. The quantities η, μ, R, \mathbf{P} and \mathbf{Q} are determined by the four lobe exponents $\alpha, \beta, \gamma, \delta$ and the four lobe center position vectors. In our present program we used a 14-term ($n = 14$ in Eq. 5) Gaussian expansion of $G_{HF}(u, v)$ and applied an integration scheme based on cubic spline functions on an adaptive grid, which proved to be numerically sufficiently stable and still not prohibitively time-consuming.

In the ansatz (4) the two parameters a and ω were adjusted by Gill and coworkers to reproduce the pair energies of the Ne atom in a 6-311G basis set (Fit A). In a second scheme (Fit B) the parameters are optimized by a least-squares-fit to the correlation energies of all atoms from H to Ar based on UHF/6-311G wave functions [9]. In addition to these atomic parametrizations we will discuss in this work a combined fit to molecules and atoms (Fit C). In this case we fitted simultaneously to the spectroscopic constants of $\text{H}_2, \text{LiH}, \text{Li}_2$ and F_2 and to the correlation energies of the He-like-ions $\text{He}-\text{Ne}^{8+}$. For this purpose the sum of the absolute values of relative errors in bond lengths, binding energies and vibrational frequencies of $\text{H}_2, \text{LiH}, \text{Li}_2$ and F_2 as well as total correlation energies of He-like ions was minimized with equal weights for each category. All fit parameters are listed in Table 1.

In the present work the HF solutions were obtained using Gaussian lobe basis functions [18, 19] and the correlation contributions were evaluated using the HF density matrix. The integral code applied here [20] originates from work of Driesler and Ahlrichs [21, 22]. The use of Gaussian lobe

Table 1 Correlation kernels $G_{HF}(u, v)$: optimized parameters (cf. Eq. 4) and mean relative error for atoms (Table 2) and molecules (Table 3) ($s_{\text{total}}/21$) as well as for molecules ($s_{\text{mol}}/12$) and atoms ($s_{\text{atm}}/9$) individually

	Fit A ^a	Fit B ^b	Fit C ^c	LYP
	Ne	H-Ar	H ₂ , LiH, Li ₂ , F ₂ , He-like ions	
a	−0.10093	−0.0925	−0.10428	
ω	0.90447	0.88	0.88	
$s_{\text{total}}/21$	0.128	0.146	0.103	0.140
$s_{\text{mol}}/12$	0.185	0.180	0.167	0.172
$s_{\text{atm}}/9$	0.053	0.100	0.018	0.098

^a [27]^b [9]^c this work

functions has the advantage that only formulas for ssss-two-electron integrals are required, since higher angular momentum functions are approximated by linear combinations of off-center Gaussian lobe functions. Standard 6-31++G** basis sets were applied for the HFW calculations. In addition we performed calculations using the correlation density functional of Lee, Yang and Parr (LYP) [23,24] applying the uncontracted primitive basis sets of the aug-cc-pV6Z (H,F,Ne,He) and cc-pV5Z (Li) basis sets of Dunning and coworkers [25,26] Bond lengths and vibrational constants were determined by fitting a fourth degree polynomial in the bond length R times a factor of R^{-1} to six points near the equilibrium distance. The binding energies were calculated with respect to individual calculations for the atoms based on the restricted HF ground state wavefunction.

3 Results and discussion

As a measure of the quality of a fit we calculated the sums of the absolute values of the relative errors in the correlation energies of the He-like ions s_{atm} (for He to Ne⁸⁺ with respect to the exact values listed in Table 2; 9 values) as well as the relative errors in the spectroscopic constants of the

covalent and ionic molecules s_{mol} (with respect to the experimental values listed in Table 3; 12 values). In order to balance the importance of atomic and molecular data the sums were weighted depending on the fitted values and the function $s(a, \omega) = s_{\text{atm}}/9 + s_{\text{mol}}/12$ was minimized with respect to a and ω . As can be seen from $s_{\text{total}} = (s_{\text{atm}} + s_{\text{mol}})/21$ in Table 1 Fit C performs overall best as expected, but it also leads individually to the best results for the He-like ions and the molecules. Table 2 summarizes the correlation energies for He and the He-like ions. Assuming the same kernel our data agrees within 0.02 mH with the values provided by Gill and collaborators [9], proving the numerical accuracy of our code. The increase of the exact correlation energies from He to Ne⁸⁺ (3.65 mH) is not well described by all three fits (0.27, 0.26 and 0.29 mH for Fit A, B and C, respectively), but the order of magnitude of the correlation energies is correct in all three cases. As pointed out by Gill and coworkers [9] the popular Lee–Yang–Parr (LYP) correlation functional [23,24] does not perform better than Fit A or B, i.e. mean relative errors of 9.8, 5.3, 10.0 and 1.8% were found for LYP, Fits A, B and C, respectively.

The bond lengths, binding energies and vibrational constants for a number of selected diatomic molecules containing light atoms are listed in Table 3. For the covalent and ionic bonded systems all three parametrizations of the correlation kernel yield too large force constants. Whereas the errors remain below $\approx 3.5\%$ for H₂, LiH and Li₂, they amount to up to $\approx 20\%$ for F₂. The bond distances of the covalent and ionic dimers, with exception of Li₂ in all three parametrizations, tend to be too short (by up to 6.5% for F₂). The results for the binding energies of covalent and ionic bonded systems with exception of F₂ appear to be overall acceptable. Here Fit C provides, except for H₂, by far the best results. Severe errors, i.e., a $\approx 0.1 \text{ \AA}$ too short bond length, a by almost 50% overestimated vibrational frequency and a near to zero binding energy, are observed in case of F₂ for all fits. We attribute this to a too slow decay of the correlation function $G_{HF}(u, v)$ with increasing u , i.e., a too strong attractive interaction between electrons in spatially well separated orbitals localized on different nuclei. The results of all three fits for the van der Waals systems He₂

Table 2 Correlation Energies (mH) of He-like systems

	H [−]	He	Li ⁺	Be ²⁺	B ³⁺	C ⁴⁺	N ⁵⁺	O ⁶⁺	F ⁷⁺	Ne ⁸⁺
-Exact	39.82	42.04	43.50	44.27	44.74	45.05	45.28	45.45	45.59	45.69
-LYP	31.01	43.78	47.55	49.05	49.72	50.03	50.17	50.22	50.23	50.21
-Fit A ^a	40.96	42.02	42.16	42.22	42.25	42.26	42.27	42.28	42.28	42.29
-Fit A ^b	40.94	42.00	42.15	42.21	42.24	42.25	42.27	42.28	42.48	42.49
-Fit B ^a	38.90	39.92	40.06	40.11	40.14	40.16	40.17	40.17	40.17	40.18
-Fit B ^b	38.91	39.92	40.06	40.12	40.14	40.16	40.17	40.18	40.19	40.19
-Fit C ^c	44.84	45.01	45.16	45.22	45.25	45.27	45.28	45.29	45.29	45.30

^a data recalculated in this work^b data taken from Gill and coworkers [9]^c Fit and calculation in this work

Table 3 Bond lengths R_e (Å), binding energies D_e (eV) and vibrational constants ω_e (cm^{-1}) of selected diatomic molecules from Hartree–Fock and Hartree–Fock–Wigner (HFW) calculations in comparison to results obtained with the Lee–Yang–Parr (LYP) correlation density functional and experimental data (exp)

Molecule		HF ^a	FitA ^a	FitB ^a	FitC ^a	exp	HF ^b	LYP
H ₂	R_e	0.736	0.734	0.734	0.734	0.741	0.734	0.728
	D_e	3.62	4.75	4.70	4.83	4.48	3.64	4.68
	ω_e	4,610	4,633	4,633	4,638	4,401	4,584	4,660
LiH	R_e	1.622	1.596	1.578	1.574	1.596	1.606	1.572
	D_e	1.41	2.33	2.36	2.48	2.52	1.49	2.45
	ω_e	1,394	1,436	1,492	1,499	1,406	1,430	1,497
Li ₂	R_e	2.818	2.750	2.729	2.722	2.673	2.784	2.697
	D_e	0.12	0.70	0.73	0.80	1.06	0.18	0.88
	ω_e	337	357	359	362	351	339	366
F ₂	R_e	1.347	1.320	1.318	1.315	1.412	1.326	1.308
	D_e	−1.41	−0.14	−0.03	0.14	1.66	−1.12	−0.17
	ω_e	1,229	1,340	1,346	1,361	917	1,267	1,323
He ₂	R_e		2.099	2.06	2.013	2.97 ^{c,d}		2.384
	D_e	*	−0.12	0.05	0.06	0.0009 ^{c,d}	*	0.007
	ω_e		225	270	301	33 ^c		126
Ne ₂	R_e		2.288	2.301	2.261	3.09 ^e		2.663
	D_e	*	−0.30	−0.26	−0.29	0.0036 ^e	*	0.01
	ω_e		197	184	201	29 ^c		72

All data refers to the $^1 \Sigma_g^+$ (H₂, Li₂, F₂, He₂, Ne₂) and $^1 \Sigma^+$ (LiH) ground states

^a HFW: 6-31++G** basis sets

^b uncontracted spdfg primitive set of the aug-cc-pV6Z (H, F, Ne, He) and cc-pV5Z (Li) basis sets of Dunning and coworkers [25,26]

^c Mourik et al. [29] CCSD(T) t-aug-cc-pVnZ basis set limit

^d Aziz et al. [30] “exact” potential curve based on QMC and FCI results

^e Aziz and Slaman [31] semiempirical potential curve, exp. [32]

* repulsive

and Ne₂ show a dramatic overbinding and appear to support this point of view. Summing up, none of the three fits yields molecular results which are equally acceptable for all molecules and spectroscopic constants investigated here.

As for He and the He-like ions we included the LYP functional in the comparison for molecules. It can be seen from Table 3 that the LYP data for molecules is slightly better than Fit A and B, but somewhat worse than Fit C. The mean relative errors are 17.2, 18.5, 18.0 and 16.7% for LYP, Fits A, B and C, respectively. The corresponding values for atoms and molecules are 14.0, 12.8, 14.6 and 10.3%. We conclude that as for the He-like systems Fit C performs better than LYP for the molecules studied here.

In order to get a clearer picture of the correlation effects we listed the correlation contributions to the molecular parameters R_e , D_e , ω_e as well as the total correlation energy E_C and its derivative with respect to the bond distance $(dE_C/dR)_{R_e}$ at the HF equilibrium distance in Table 4. It is obvious that the correlation corrections of the binding energies are of the right direction and with exception of F₂ also roughly of the right magnitude. Since the relative errors of the HF binding ener-

gies are much larger than those of the HF bond lengths and vibrational frequencies, the Fit C always improves the former but not in all cases the latter. Since in all cases the HFW similar to the LYP correlation contributions $|E_C|$ decrease with increasing bond distance, there is no possibility to obtain bond length increases by adding HFW correlation to the HF energies. Due to the anharmonicity of the potential curves the correlation induced bond length contractions result in an increase of the vibrational frequencies, which only leads to a change in the right direction for Li₂.

We note here, that using the present symmetric ansatz for the correlation kernel it is possible to chose a combination of the two parameters ($a = -0.002107$, $\omega = 0.90447$) which yields very good results for He₂ ($R_e = 3.036 \text{ \AA}$, $D_e = 0.0009 \text{ eV}$, $\omega_e = 40 \text{ cm}^{-1}$) and also describes Ne₂ without further fitting reasonably well ($R_e = 2.871 \text{ \AA}$, $D_e = 0.002 \text{ eV}$, $\omega_e = 51 \text{ cm}^{-1}$). However, such a fit to the He₂ spectroscopic constants emphasizes only the interatomic correlation contributions of the van der Waals interaction and leads to more than an order of magnitude too small values of the total correlation energies as well as to almost negligible correlation

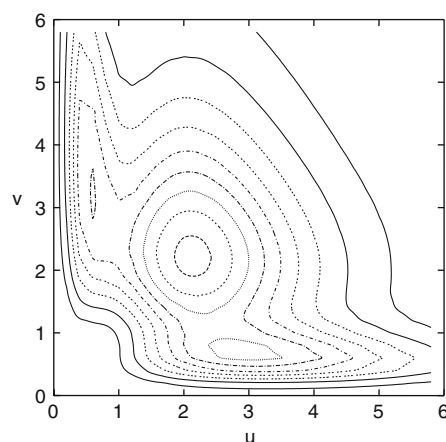
Table 4 Correlation contributions to bond lengths ΔR_e (Å), binding energies ΔD_e (eV) and vibrational frequencies $\Delta \omega_e$ (cm^{-1}) as well as correlation energies E_C (mH) and their derivatives with respect to thebond length dE_C/dR (mH/Bohr) at the HF equilibrium distance for the covalently and ionically bound diatomic molecules from Table 3

Molecule		FitA	FitB	FitC	LYP	exp ^a
H ₂	ΔR_e	-0.002	-0.002	-0.002	-0.006	0.007
	ΔD_e	1.13	1.08	1.21	1.04	0.84
	$\Delta \omega_e$	23	23	28	76	-183
	$-E_C$	41.8	39.7	44.8	38.4	40.8
	$-dE_C/dR$	-1.4	-1.3	-1.5	-4.3	5.9
LiH	ΔR_e	-0.026	-0.044	-0.048	-0.034	-0.010
	ΔD_e	0.92	0.95	1.07	0.96	1.03
	$\Delta \omega_e$	42	98	105	67	-24
	$-E_C$	89.5	86.2	97.1	88.8	82.5
	$-dE_C/dR$	-3.3	-3.9	-4.4	-4.4	-0.6
Li ₂	ΔR_e	-0.068	-0.089	-0.096	-0.087	-0.111
	ΔD_e	0.58	0.61	0.68	0.70	0.88
	$\Delta \omega_e$	20	22	25	27	12
	$-E_C$	132.8	127.2	143.4	132.5	124.41
	$-dE_C/dR$	-2.1	-1.7	-1.9	-2.6	-3.2
F ₂	ΔR_e	-0.027	-0.029	-0.032	-0.018	-0.086
	ΔD_e	1.27	1.38	1.55	0.95	2.78
	$\Delta \omega_e$	111	117	132	56	-350
	$-E_C$	676.8	686.4	773.8	678.2	720.1
	$-dE_C/dR$	-30.4	-32.8	-37.0	-20.5	94.0

^a The experimental (exp.) correlation contributions ΔR_e , ΔD_e and $\Delta \omega_e$ were obtained as the difference between the experimental values and the best Hartree-Fock results of Table 3. $-E_C$ and $-dE_C/dR$ were obtained from the difference of exact potential curves of Lie and Clementi [33,34] and the best HF curves of this work

corrections to the HF values of spectroscopic constants of the ionic and covalent diatomics.

In order to gain additional understanding of the trends in the results we discuss the Wigner intracules of Be (Fig. 1), He₂ (Fig. 2a) and LiH (Fig. 2c). The plots for the molecules refer to the HFW equilibrium distances obtained with Fit A. Although these systems are entirely different, all of them possess two electron pairs. The Wigner intracule for Be has already been discussed by Gill et al. [10]. 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 $u \approx v$). 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 [10]. In He₂ two maxima are clearly visible, the larger one again 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-

**Fig. 1** Hartree-Fock Wigner intracule of the Be atom [10]

shell contributions. The latter appears roughly at the position of the maximum of the He Wigner intracule [10].

It is obvious that in contrast to Be the Wigner intracules of LiH and He₂ are not approximately symmetric in relative position u and relative momentum v , whereas the currently used correlation function $G_{HF}(u, v)$ is symmetric. In case of Be this leads to roughly equal contributions of 1s–1s

(36.6 mH) and 2s–2s (42.2 mH) to the total correlation energy in agreement with pair correlation energies obtained previously by Kutzelnigg and Ahlrichs, i.e., 41.7 and 45.2 mH [28]. We note however, that upon dissociation of He₂ 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., whereas terms dependent solely on u are possible, 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.

We propose to study differences of molecular and atomic Wigner intracules in order to analyze the behaviour of electrons in the formation of chemical bonds. Assuming Eq. 1 to hold, it is clear that weighting an intracule difference and integrating over u and v directly yields the correlation contribution to the binding energy. As a reference one might consider the Wigner intracule of the separated atoms at a large distance, i.e.,

$$W_{AB;R_e}(u, v) - W_{AB;R \rightarrow \infty}(u, v) \quad (7)$$

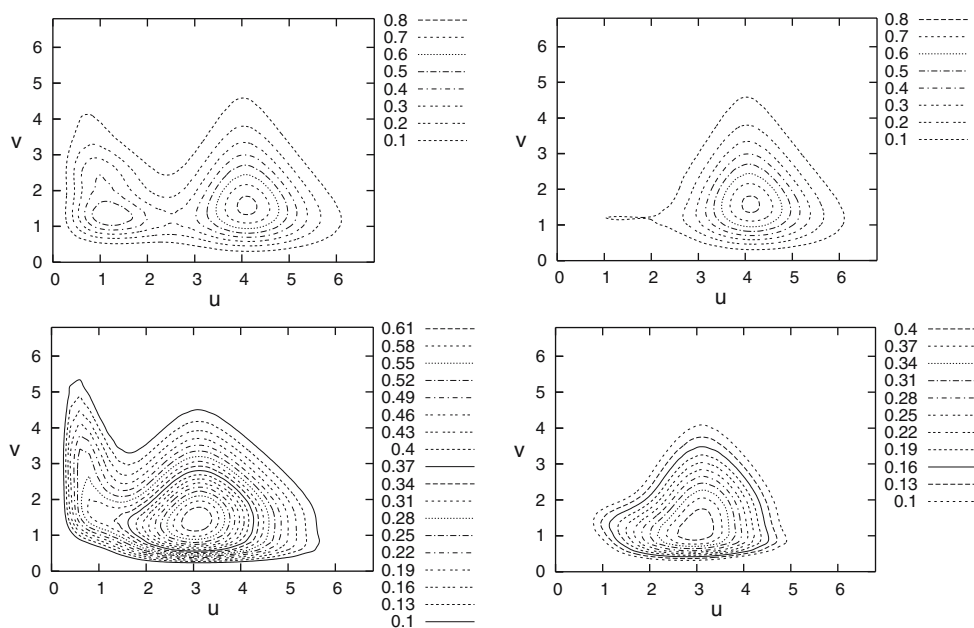
or the sum of individual atomic intracules, i.e.,

$$W_{AB;R_e}(u, v) - W_A(u, v) - W_B(u, v) \quad (8)$$

The two cases differ by minima at large u caused by the intra-shell contributions between the two atoms, which are present in the first case, but not in the second. However, since size-extensivity requires that these regions of (u, v) -space do not contribute to the correlation energy, one can limit the discussion of the difference maps to those regions where

$W_{AB;R_e}(u, v)$ is noticeably different from zero. The corresponding difference maps for He₂ (Fig. 2b) and LiH (Fig. 2d) differ mainly in their height as well as the different extent of the shoulder at small u, v . When going from two separated He atoms to He₂ a total of four (distant) new electron pairs is formed, whereas for the formation of LiH from Li and H only three (distant) new electron pairs arise. Thus explaining the lower height observed in Fig. 2c compared to Fig. 2a. Furthermore since the 1s–2s intracule for Li is located at $r_e = 3$ a.u. and it is subtracted according to Eq. 8 the height of the difference plot 2d is lower than for 2b. In addition, the strong admixture of ionic character in LiH decreases the contribution of distant pairs and creates a new pair, thus resulting in the shoulder at small u, v observed in Fig. 2d. In view of the not too large differences in shape and the slightly different position of the maxima, it appears to be a quite difficult task for a correlation function $G_{HF}(u, v)$ to “distinguish” between a quite strong covalent bond with high ionic character in LiH and a very weak van der Waals interaction in He₂. Since the difference intracule of He₂ approximately retains its shape for increasing bond distances R exhibiting a maximum near $u = R$, and the correlation energy E_{corr} should decrease as $1/R^6$, we suppose that the long-range behaviour of an improved $G_{HF}(u, v)$ should be $1/u^6$. A similar conclusion has been obtained by studying the interaction between two coupled London oscillators (O’Neill and Gill, in preparation). We think that only by abandoning the symmetry in u and v of the correlation kernel $G_{HF}(u, v)$ it is possible to construct an approximation which has correct long range behavior for u (van der Waals interaction) and v (size-extensivity). It remains to be seen if such a more flexible ansatz can convert the subtle differences in e.g. the difference

Fig. 2 First row Hartree–Fock Wigner intracule of **a** the He₂ dimer (left) at a bond distance of 2.099 Å and of **b** the difference between the He₂ and two He intracules (right). Second row Hartree–Fock Wigner intracule of **c** the LiH molecule (left) at a bond distance of 1.596 Å and of **d** the difference between the LiH and Li and H intracules (right)



maps of the Wigner intracules into the correct correlation contributions to bonding. The group of Gill takes another direction and includes in their new proposal besides u and v also the angle between the relative position and relative momentum [9] (Crittenden and Gill, in preparation). Our findings also imply that most likely a simple parametrization to atomic data will not be sufficiently accurate and not generally transferable to molecular situations covering different types of bonding. Molecular Wigner intracules allow to probe a wider area in the (u, v) -plane than atomic ones and thus add important information when fitting $G(u, v)$ in Eq. 1, especially in the long u range.

4 Conclusions

We presented the first results for molecular constants of light diatomic molecules for correlated calculations within the framework of the Hartree–Fock–Wigner model. Whereas two different correlation kernels fitted to atomic data yielded results of only limited accuracy for simple covalent and ionic systems as well as far too attractive Van der Waals interactions, it was demonstrated that a mixed atomic and molecular adjustment to the spectroscopic constants of H_2 , LiH , Li_2 , F_2 and the correlation energies of He-like-ions ($He-Ne^{8+}$) leads to an improvement of the binding energies, but like the two atomic fitted kernels fails to describe van der Waals bonded systems properly. It is argued that the present two-parameter ansatz cannot yield simultaneously accurate results for all types of bonding and is thus in its present form not molecule universal. In addition an analysis of the Wigner intracules of simple systems suggests, that the symmetric role of the relative position u and relative momentum v has to be abandoned in order to arrive at a more accurate correlation kernel.

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