Theoret. Chim. Acta (Berl.) 39, 339–346 (1975)

Ab initio Calculation of the Intermolecular Energy between Two Hydrogen Molecules near the Van der Waals Minimum

E. Kochanski
Eq. N° 139 du CNRS, Université Louis Pasteur, Strasbourg

Received March 24, 1975

The interaction energy between two hydrogen molecules near the van der Waals minimum is computed as the sum of the SCF interaction energy of the supermolecule and the so-called "Hartree-Fock dispersion energy". The most stable configuration is the perpendicular planar one (*T* configuration), this configuration being stable through the first order term. The energy averaged over the four configurations is in agreement with the available experimental data. The perturbative polarization energy is negligible near the van der Waals minimum but it seems that the charge transfer energy must be taken into account.

Key words: Intermolecular energies – $(H_2)_2$

1. Introduction

Though the H_4 system at large and intermediate distances has often been studied, from a theoretical as well as from an experimental point of view, the difficulties encountered in such studies are far from being overcome. Two important books [1, 2] provide an exhaustive review of the work published before 1969. Further references can be found in papers [3–5] and, in the course of the last two years, other studies concerning this subject have been published [6–11]. The five last ones use *ab initio* functions with different degrees of accuracy: Ref. [9] gives the leading term of the dispersion energy computed with a large basis set; Refs. [7, 8, 11] correspond to more complete treatments using a medium size [7] and a small [8, 11] basis set respectively. Ref. [10] studies the effect of the basis set on the SCF supermolecule energy [10a] and corrects it by the use of the function counterpoise method with the view of treating such problems with small basis sets [10b].

A comparison between all these results emphasizes a rather dangerous fact: good values can often be due to cancellation of errors and offer no real guarantees of reliability. Thus the average energy is similar in Refs. [1, 2, 3, 11, 12] whereas the energy of each configuration is rather different. Such cancellation can also occur, for one configuration, between the first order electrostatic and exchange terms [13]. As shown by Urban and Hobza [10a] small basis sets underestimate the repulsive energy in the first order term (corresponding to the first iteration of the supermolecule treatment) and overestimate the attractive part corresponding to the polarization and charge-transfer energies (E^2 in Ref. [10]). This explains why the neglect of E^2 partially cancels the underestimation of E^1 in [3].

In the present paper, the total intermolecular energy between two hydrogen molecules near the van der Waals minimum is computed as the sum of the SCF interaction energy of the supermolecule and the so-called "Hartree-Fock dispersion energy". A rather large basis set is used, with 6 *s* and 4 *p* uncontracted gaussian functions. This basis set has been previously [14] determined for the treatment of $Li^+ + H_2$, one diffuse *p* function being added to Lester's basis set [15] with the view of improving the description of the dispersion energy. The SCF results published by Urban and Hobza [10a] with basis IX in the case of the linear configuration are very close to our own present values.

2. First Order Term

In the case of $Li^+ + H_2$ and $H_2 + H_2$ we have shown [13] that the first order term of the perturbation series is equivalent to the first iteration of the supermolecule treatment starting from Schmidt orthogonalized molecular vectors under two conditions:

(a) large basis sets must be used
(b) the charge-overlap effect must be included in the perturbative treatment.

We call E_1^{Δ} the difference between the first iteration of the calculations and the SCF energy of the isolated molecules. As seen in [13], E_1^{Δ} is less sensitive to the basis set than the perturbative term. Thus, we think that E_1^{Δ} computed with our basis (64) [64] (Table 1) also gives a good description of the perturbative term. We can see that the *T* configuration is stable through the first order term. We have shown in Ref. [13] that this is due to the electrostatic part, which is in good agreement with Buckingham's idea that the quadrupole-quadrupole interaction favours the stability of this configuration [16]. The most repulsive configuration is the linear one. The other two configurations are almost equivalent, the rectangular one being slightly more repulsive than the non planar one.

A comparison with the results published by Urban and Hobza [10] shows that E^1 is systematically too repulsive when small basis sets are used [10a]. The corrected energy E_c^1 is significantly improved [10b], though still too small with basis VI. The "basis set superposition error" being one of the great difficulties in the treatment of such problems [17, 18], the function counterpoise method correction could also be of help with large basis sets to determine the accuracy of the results.

3. Polarization and Charge Transfer Terms

The two terms $E_{\mathrm{pol+CT}}^{\Delta}$ and $E_{\mathrm{pol}}^{\Delta}$ can be compared in Table 1. $E_{\mathrm{pol+CT}}^{\Delta}$ is the difference between the SCF energy of the supersystem and the energy of the first iteration of the calculation starting from Schmidt orthogonalized molecular vectors. It is commonly considered that this term corresponds to polarization and charge transfer energy. It is called E^2 in Ref. [10a], the corresponding corrected term being E_c^2 in Ref. [10b]. In contrast with E^2 which is very bad with basis VI,

Table 1. Intermolecular energies between two hydrogen molecules near the van der Waals minimum. Basis (64) [64][a] - energies in 10^{-4} hartree

Configuration	d (a.u.)	E_1^{Δ}	$E^{\Delta}_{\mathrm{pol+CT}}$	E_{pol}	$E^{\mathrm{HF}}_{\mathrm{disp}}$	E_{TOT}
(1)	5	18.623	−1.764	−0.099	−7.674	9.185
rectangular		(19.054)				
	5.5	7.914	−0.667	−0.022	−4.547	2.700
	6	3.405	−0.238	−0.009	−2.671	0.496
	6.5	1.523	−0.121	−0.006	−1.734	−0.332
		(1.610)				
	7	0.724	−0.062	−0.004	−1.115	−0.453
	7.5	0.388	−0.070	−0.002	−0.734	−0.416
	10	0.070	−0.037	−0.000	−0.127	−0.095
(2)	5	38.580	−9.339	−2.475	−16.534	12.706
linear		(39.316)				
	5.5	16.618	−3.504	−0.810	−9.566	3.548
	6	7.377	−1.319	−0.283	−5.660	0.398
	6.5	3.445	−0.487	−0.108	−3.428	−0.470
		(3.638)				
	7	1.731	−0.199	−0.047	−2.130	−0.598
	7.5	0.966	−0.090	−0.023	−1.358	−0.482
	10	0.167	−0.009	−0.002	−0.208	−0.050
(3)	5	21.091	−4.291	−0.650	−10.642	6.158
T conf.		(21.712)				
	5.5	8.052	−1.584	−0.205	−6.243	0.225
	6	2.844	−0.585	−0.074	−3.757	−1.498
	6.5	0.850	−0.205	−0.031	−2.320	−1.675
		(0.966)				
	7	0.138	−0.082	−0.015	−1.470	−1.414
	7.5	−0.093	−0.036	−0.008	−0.982	−1.111
	10	−0.054	−0.006	−0.001	−0.149	−0.209
(4)	5	17.477	−1.769	−0.119	−7.068	8.640
non planar		(17.911)				
	5.5	7.222	−0.685	−0.027	−4.226	2.312
	6	2.976	−0.288	−0.009	−2.596	0.092
	6.5	1.128	−0.129	−0.005	−1.636	−0.537
		(1.282)				
	7	0.525	−0.088	−0.003	−1.057	−0.620
	7.5	0.232	−0.072	−0.002	−0.700	−0.540
	10	0.033	−0.038	−0.000	−0.123	−0.118

[a] Basis (64) [64] has 6 *s* and 4 *p* uncontracted gaussian functions. The values in parentheses are the first order energies computed from a perturbative procedure including the charge overlap effect [11, 13].

E_c^2 is very close to our own values, though slightly smaller in magnitude. As with E_c^1, E_c^2 is probably not totally corrected. But because larger basis sets tend to decrease $E^{\Delta}_{\mathrm{pol+CT}}$ it is not possible to determine if E_c^2 is underestimated. Nevertheless E_c^2 and $E^{\Delta}_{\mathrm{pol+CT}}$ are close enough to allow interpretation. Table 1 shows that this term $E^{\Delta}_{\mathrm{pol+CT}}$ is not negligible at the average van der Waals minimum distance (around $d=6.5$ a.u.). At slightly shorter distances it can even be larger than the total energy ($d=6$ a.u. in configurations (2) and (4); $d=5.5$ a.u. in configuration (3)), but at still smaller distances it becomes less important. So we can see that an accurate determination of the van der Waals minimum needs an accurate evaluation of this term in this region. A comparison of the four configurations shows that, as with E_1^{Δ}, configuration (1) and (4) have a similar behaviour. The polarization and charge-transfer energy in these cases is less important than in the T configuration, the largest contribution occurring in the linear case. As with the dispersion energy [3], the relative importance of $E_{\mathrm{pol+CT}}^{\Delta}$ in the four configurations varies in the same way as the separation between the two nearest atoms.

Whereas $E_{\mathrm{pol+CT}}^{\Delta}$ includes both polarization and charge-transfer terms, E_{pol} allows us to study the polarization energy alone. This term is computed using a double perturbation scheme and an Epstein-Nesbet partition of the molecular hamiltonians [14]. The charge-overlap effect is not taken into account. The influence of this on the induction energy has been studied only for H_2^+ [19a] or two hydrogen atoms [20]. The case of two hydrogen atoms is probably of no help in our present studies because the atoms have no permanent dipole or quadrupole moment. They provide no induction energy in the multipole expansion approximation while the calculations of Chałasinski and Jesiorski [20] exhibit an attractive induction energy. In H_2^+ the multipole expansion approximation provides an overestimation of the induction energy [19a]. This repulsive charge overlap effect is also seen in the first order term [13] and the dispersion energy [11, 19, 20a, 21]. In $\mathrm{Li}^+ + \mathrm{H}_2$, the comparison between $E_{\mathrm{pol+CT}}^{\Delta}$ and E_{pol} had led us to conclude that the charge transfer energy was negligible and E_{pol} overestimated at intermediate distances [14]. From all these results, we think that E_{pol} is also overestimated at intermediate distances in the present studies. In these conditions, even if $E_{\mathrm{pol+CT}}^{\Delta}$ is somewhat overestimated by an effect of the basis set, Table 1 shows that $E_{\mathrm{pol+CT}}^{\Delta}$ is mainly due to the charge transfer energy. As with $E_{\mathrm{pol+CT}}^{\Delta}$, the largest values of E_{pol} occur for the linear configuration, then for the T shape, and finally for the configurations (1) and (4) which are equivalent.

A more detailed study of the polarization energy shows that only two kinds of orbitals in the polarized molecule can provide some contribution: either the σ_g orbitals, or some orbitals oriented along the intermolecular axes. Thus, with an intermolecular axis along y, a polarized molecule oriented in this direction provides some polarization energy through its σ_g and σ_u orbitals, while a molecule perpendicular to this axis provides some contribution through its σ_g and πy_u orbitals. All these orbitals have a non zero electronic density along the intermolecular axis and can contribute to the component of the polarizability along this axis. These same groups of orbitals σ_g, σ_u or σ_g, π_u are also components of the SCF orbitals of the supermolecule treatment where both the polarization and the charge transfer energies are taken into account.

An analysis of E_{pol} for the T configuration shows that the orientation of the polarizing molecule is more important than the orientation of the polarized molecule. Thus, at $d=6.5$ a.u., the molecule along the intermolecular axes polarized by the molecule perpendicular to this axis provides $E_{\mathrm{pol},1} = -0.0068 \times 10^{-4}$ hartree, whereas the molecule perpendicular to this axis polarized by the molecule along this axis provides $E_{\mathrm{pol},2} = -0.0242 \times 10^{-4}$ hartree. More generally, the polarization energy is larger when the polarizing molecule lies along the intermolecular axis.

4. Dispersion Energy

The "Hartree-Fock dispersion energy" $E_{\mathrm{disp}}^{\mathrm{HF}}$ has previously been studied in the four configurations using a double perturbation scheme and an Epstein-Nesbet partition of the molecular hamiltonians [3]. Our present work differs only by the use of a larger basis set. This involves a quantitative increase of 5–10% with respect to the results obtained with basis B3 in Ref. [3] (10% is reached near the van der Waals minimum in configurations (1), (3) and (4)). The small basis A3 (a double zeta *s* plus one diffuse *p* function [3]) provides at least 85% of the present results obtained with uncontracted 6 *s* and 4 *p* functions. Apart from this quantitative difference, the other conclusions are identical. We briefly recall them:

(a) The most attractive energy occurs in the linear configuration, then in the *T* shape and finally in configuration (1) and (4) which are almost equivalent ((1) being slightly more attractive than (4)). As we said previously, this behaviour could be related to the distance between the two nearest atoms.

(b) Some virtual orbitals are of special importance: the occupied σ_g orbital in H_2 can be associated with virtual orbitals of the type σ_u or π_u, which provide an important contribution to the dispersion energy if they have a large coefficient corresponding to diffuse functions.

(c) Each pair of such orbitals in one molecule (σ_g, σ_u or σ_g, π_u) interacts with similar pairs in the other molecule, the interaction being stronger when these orbitals have some of their direction along the intermolecular axis. The analysis of these contributions has been given for the four configurations at $d=5$ a.u. using basis A3 (Table IV in Ref. [3] and Figs. 3 and 4 in Ref. [22]). In order to recall the main contributions, we define $\pi_{u\perp}$ and $\pi_{u\|}$ as the π_u orbitals perpendicular or parallel to the intermolecular axis and (*ab*, *cd*) as molecular orbitals *a* and *b* on the first molecule, *c* and *d* on the second one.

In the rectangular configuration the total dispersion energy is -7.108×10^{-4} hartree; -2.891×10^{-4} is due to $(\sigma_g\pi_{u\|}, \sigma_g\pi_{\|})$; -1.960×10^{-4} to $(\sigma_g\sigma_u, \sigma_g\sigma_u)$ and -0.876×10^{-4} to $(\sigma_g\pi_{u\perp}, \sigma_g\pi_{u\perp})$.

In the linear configuration, the total dispersion energy is -15.038×10^{-4} hartree, with -8.844×10^{-4} due to $(\sigma_g\sigma_u, \sigma_g\sigma_u)$ and -1.109×10^{-4} to each of the two groups $(\sigma_g\pi_{u\perp}, \sigma_g\pi_{u\perp})$, the $\pi_{u\perp}$ being parallel in molecules 1 and 2.

In the *T* configuration where the first molecule is along the intermolecular axis the total dispersion energy is -9.622×10^{-4} hartree; -4.306×10^{-4} is due to $(\sigma_g\sigma_u, \sigma_g\pi_{u\|})$, -1.423×10^{-4} to $(\sigma_g\pi_{u\perp}, \sigma_g\sigma_u)$ this $\pi_{u\perp}$ being in the plane of the molecules, and -0.983×10^{-4} to $(\sigma_g\pi_{u\perp}, \sigma_g\pi_{u\perp})$ these two $\pi_{u\perp}$ being perpendicular to the plane of the molecules.

In the non planar configuration the total dispersion is -6.448×10^{-4} hartree, -2.883×10^{-4} being due to $(\sigma_g\pi_{u\|}, \sigma_g\pi_{u\|})$, -1.268×10^{-4} to $(\sigma_g\sigma_u, \sigma_g\pi_{u\perp})$ and -1.268×10^{-4} to $(\sigma_g\pi_{u\perp}, \sigma_g\sigma_u)$.

The present work shows that the energy of the virtual orbitals providing a significant contribution to the dispersion energy is lower than 5.70 hartree.

5. Total Energy

The total energy E_{TOT} is computed as the sum of E_1^{Δ}, $E_{\mathrm{pol+CT}}^{\Delta}$ and $E_{\mathrm{disp}}^{\mathrm{HF}}$. The stability of the configurations decreases in the order (3), (4), (2), (1) as in Ref. [3], the depth of the minimum in the T configuration (-1.675×10^{-4} hartree at $d=6.5$ a.u.) being much more attractive than in the others (-0.620, -0.598 and -0.439×10^{-4} at $d=7$ a.u.). We can ask the question: is there one component of the total energy which particularly favours the T configuration? We have seen that this configuration is stable through the first order term, the stability being due to the electrostatic energy [13, 16]. But the study of the first order term alone does not explain why the minima of the other three configurations lie in the same range of energies when $d=7$ a.u. whereas the depth of the minimum of the T shape reaches -1.675×10^{-4} hartree at $d=6.5$ a.u. A quantitative analysis of the results (Table 1) shows that, around the van der Waals minima, E_1^{Δ} and $E_{\mathrm{disp}}^{\mathrm{HF}}$ are of the same order of magnitude but with opposite sign in configurations (1), (2) and (4). On the contrary, in configuration (3), the dispersion energy does not need to compensate an important repulsive term. Thus we can say that it is the first order term which favours the T shape.

The present treatment is limited to the calculation of a few terms: E_1^{Δ} is equivalent to the first order term of a perturbation series including the charge-overlap effect [13]; $E_{\mathrm{pol+CT}}^{\Delta}$ should correspond to the second-order charge-transfer and polarization terms; in $E_{\mathrm{disp}}^{\mathrm{HF}}$ the charge-overlap effect and the exchange terms are neglected.

A previous study performed with a small basis set [11] gave qualitative information about these two last points (accurate results would need a large basis set). The effect of the overlap being more sensitive in (3) than in (4) the relative stability of (3) may slightly decrease but probably not significantly. For the same reason, configuration (1) may become slightly more stable than configuration (2).

Up to now, no accurate information is available about the effect of the intramolecular electronic correlation on the dispersion terms and of the higher order terms for the case of two hydrogen molecules. It is reasonable to think that these effects are small [8, 23]. More accurate determination would be necessary in the region of the van der Waals minimum. Nevertheless, as the experimental results provide only an average energy, theoretical calculations, even approximate, are needed to study each configuration and to give a good picture of the phenomena.

6. Average Energy

As in Ref. [3] the energy is averaged over the four configurations using Evett and Margenau's procedure [12]. Table 2 shows the contribution of each configuration to the average energy. Both the depth of the minimum and the value of the coefficient in the average lead to the T configuration providing the main part of the energy (-0.695×10^{-4} hartree for an average energy of -0.952×10^{-4} hartree). On the contrary the linear configuration only improves the accuracy of the calculation near the van der Waals minimum but becomes more important in the repulsive part.

Table 2. Intermolecular energies between two hydrogen molecules near the van der Waals minimum: average of the energy over the four configurations (in 10^{-4} hartree)

d	Contribution to the average configuration				Average over the four configurations	exp[a]	exp[b]	exp[c]
	(1)	(2)	(3)	(4)				
5	2.30	1.08	2.55	2.16	8.09	7.203	(10.8)	(15.0)
5.5	0.68	0.30	0.09	0.58	1.65	0.184	1.78	(3.0)
6	0.12	0.03	−0.62	0.02	−0.44	−1.110	−0.65	−0.41
6.5	−0.08	−0.04	−0.69	−0.13	−0.95	−1.103	−1.08	−1.10
7	−0.11	−0.05	−0.59	−0.15	−0.90	−0.864	−0.93	−0.98
7.5	−0.10	−0.04	−0.46	−0.13	−0.64	−0.634	−0.70	−0.75
10	−0.02	−0.00	−0.09	−0.03		−0.130	−0.125	−0.125

[a] from Refs. [2] and [24].
[b] from Ref. [25].
[c] from Ref. [5].

The values given in the two last columns (cases *b* and *c*) have been interpolated from the results published in Refs. [25] and [5]; the values in parenthesis can be strongly in error.

Our averaged values are compared with some experimental data (Table 2). Besides the earliest work [2, 24] which gives a depth minimum of 1.110×10^{-4} hartree around $d=6$ a.u., three other recent papers provide -1.064×10^{-4} hartree at $d=6.614$ a.u. [25], -1.101×10^{-4} hartree at $d=6.595$ a.u. [5] and -1.139×10^{-4} hartree at 6.463 a.u. [4]. Our minimum is somewhat smaller than all these results, whereas our curve is less repulsive than the last three determinations at short distances. Near the van der Waals minimum, the curve obtained by Toennies *et al.* is the most repulsive one, as can be seen from their diagrams [4]. To complement their comparison, Table 2 provides some values interpolated from the results of Dondi *et al.* [25] and of Farrar *et al.* [5] (such numerical results are not available for the work of Toennies *et al.*).

To conclude this work we should consider two main points of interest:

(a) concerning the problem of H_2+H_2, only a theoretical treatment can provide information about each configuration. Our present work is more rigorous than Ref. [3] since a larger basis set is used and the charge-transfer and polarization energies added. Though the basis set could be still larger and other terms taken into account, we have good hope that our results are reliable.

(b) concerning the perturbative method, there is no doubt that this procedure provides a good understanding of the phenomena. It has been commonly assumed that a perturbative treatment limited to lower order terms can give a good description of intermolecular interactions. Many approximate procedures are based on this idea and it can be very useful to perform *ab initio* calculations to test the validity of such approximations.

References

1. Margenau,H., Kestner,N.R.: Theory of intermolecular forces. New York: Pergamon Press 1969
2. Hirschfelder,J.O., Curtiss,C.F., Bird,R.B.: Molecular theory of gases and liquids. New York: Wiley 1964

3. Kochanski,E.: J. Chem. Phys. **58**, 5823 (1973)
4. Gengenbach,R., Christian,H., Schrader,W., Toennies,J.P.: Theoret. Chim. Acta (Berl) **34**, 199 (1974)
5. Farrar,J.M., Lee,Y.T.: J. Chem. Phys. **57**, 5492 (1972)
6. McKellar,A.R.W., Welsh,H.L.: Canad. J. Phys. **52**, 1082 (1974)
7. Kochanski,E., Roos,B., Siegbahn,P., Wood,M.H.: Theoret. Chim. Acta (Berl.) **32**, 151 (1973)
8. Basilevski,M.V., Berenfeld,M.M.: Intern. J. Quantum Chem. **8**, 467 (1974)
9. Martin,P.H.S., Henneker,W.H., McKoy,V.: Chem. Phys. Letters **27**, 52 (1974)
10. a) Urban,M., Hobza,P.: Theoret. Chim. Acta (Berl.) **36**, 207 (1975)
    b) ibid, **36**, 215 (1975)
11. Kochanski,E., Gouyet,J.F.: Mol. Phys. **29**, 693 (1975)
12. Evett,A.A., Margenau,H.: Phys. Rev. **90**, 1021 (1953)
13. Kochanski,E., Gouyet,J.F.: Theoret. Chim. Acta (Berl.) preceding paper
14. Kochanski,E.: Chem. Phys. Letters **28**, 471 (1974)
15. Lester,Jr,W.A.: J. Chem. Phys. **54**, 3171 (1971); J. Chem. Phys. **53**, 1511 (1970)
16. Buckingham,A.D.: Quart. Rev. **13**, 183 (1959)
17. Liu,B., McLean,A.D.: J. Chem. Phys. **59**, 4557 (1974)
18. Steven,W.J., Wahl,A.C., Gardner,M.A., Karo,A.M.: J. Chem. Phys. **60**, 2195 (1974)
19. a) Kreek,H., Meath,W.J.: J. Chem. Phys. **50**, 2289 (1969)
    b) Bukta,J.F., Meath,W.J.: Intern. J. Quantum Chem. **6**, 1045 (1972)
20. a) Kołos,W.: Intern. J. Quantum Chem. **8S**, 241 (1974)
    b) Chałasinski,B., Jesiorski: Mol. Phys. **27**, 649 (1974)
21. Murrell,J.N., Shaw,G.: J. Chem. Phys. **49**, 4731 (1968); Brigg,M.P., Murrell,J.N., Salahub,D.R.: Mol. Phys. **22**, 907 (1971)
22. Kochanski,E.: Intern. J. Quantum Chem. **8S**, 219 (1974)
23. Malrieu,J.P.: Intern. J. Quantum Chem. **5**, 455 (1971); **5**, 435 (1971)
24. De Boer,J.: Physica (Utr.) **14**, 139 (1948); Lunbeck,R.J.: Doctorat dissertation, University of Amsterdam, Amsterdam, Holland (1951)
25. Dondi,M.G., Valbusa,U., Scoles,G.: Chem. Phys. Letters **17**, 137 (1972)

Dr. E. Kochanski
Equipe n° 139 du C.N.R.S.
Institut Le Bel
Université Louis Pasteur
F-67008 Strasbourg
France