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Ab initio Calculation of the First Order Term of the Intermolecular Energy near the Van der Waals Minimum

A Comparison between a Perturbative Method and the SCF Supermolecule Treatment in the Cases of H_2+H_2 and $Li^+ + H_2$

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The first order term of the intermolecular energies between two hydrogen molecules and between Li^+ and H_2 has been computed by three different methods: two of them are based on a perturbative procedure, including or neglecting the overlap between the orbitals of the interacting molecules or atoms in the calculation of the electrostatic and exchange terms. We can then study the effect of the overlap on each of these terms. The third method is the SCF supermolecule treatment which provides results in very good agreement with the perturbative procedure including the overlap. The T configuration in the case of two hydrogen molecules and the C_{2v} configuration for $Li^+ + H_2$ are stable with respect to the first order term.

Key words: Intermolecular interactions – $(H_2)_2$, $Li^+ + H_2$

1. Introduction

In the calculation of the intermolecular interactions between two molecules or atoms from a perturbative procedure, the first order energy is not the least of the difficulties because of its strong sensitivity to the overlap in the region of the van der Waals minimum. For such intermolecular distances, we have then to take into account both the exchange energy (Refs. 1 and 2 give most of the procedures which have been proposed to include this term in a general treatment) and the effect of the charge overlap. This last effect which is neglected in the multiple expansion has been considered in some cases for the dispersion [3, 4, 5a] or the induction energy [4a, 5] but it seems that such a treatment has been done only for the Coulomb energy when the first-order term plays an important role [5c]. Recently, we published some preliminary results concerning two hydrogen molecules, obtained from a perturbative procedure using biorthogonal orbitals [2]. For each Coulomb term of the perturbative series we can thus study the effect of the charge overlap and the effect of the corresponding exchange term. In the present work, this procedure (where the biothogonal orbitals are built from the set of occupied orbitals only) is compared with a perturbative method neglecting the charge overlap and with the first iteration of the SCF supermolecule treatment. This is done for H_2+H_2 and $Li^+ + H_2$ at large and intermediate distances using extended basis sets.

2. The Details of the Calculations

In the perturbative method based on biorthogonal orbitals, the Rayleigh-Schrödinger perturbation expansion is expressed directly in a non orthogonal basis [6]. Each molecular orbital $|i\rangle$ (occupied or virtual of the molecule A or B) is associated with an orbital $|\underline{i}\rangle$; the set of these biorthogonal orbitals $|\underline{i}\rangle$ is obtained by expanding

$$|\underline{i}\rangle = \sum_{j} |j\rangle \, (S^{-1})_{ji} \tag{1}$$

where $(S^{-1})_{ji}$ is the ji element of the inverse of the total overlap matrix built from the molecular orbitals of A and B. We have then

$$\langle \underline{i}|j\rangle = \delta_{ij} \tag{2}$$

In this work, only the occupied orbitals have been used to build the set of bi-orthogonal orbitals. Starting from an Epstein-Nesbet partition of the hamiltonian, we can write

$$H = \hat{H}_0 + \hat{V} \tag{3}$$

where

$$\hat{H}_0 = \sum_{I} \langle \underline{J}|H|I\rangle |I\rangle\langle \underline{I}|$$

and

$$\hat{H}_0|K\rangle = \varepsilon_K^0|K\rangle \quad \text{with} \quad |K\rangle = |\mathscr{A} I_A I_B\rangle$$

I_A and I_B describing configurations of A and B. The antisymmetrized zeroth-order wavefunction is an eigenfunction of the non-hermitian hamiltonian $\hat{H}_0$ and possesses the proper symmetry with respect to the intermolecular electron permutation. For closed-shell molecules, if we write

$$\begin{aligned} E^{BO}_{\text{elect}} &= 2\sum_{a_0} (\underline{a}_0|V_{NB}|a_0) + 2\sum_{b_0} (\underline{b}_0|V_{NA}|b_0) \\ &\quad + \sum_{a_0 b_0} 4(\underline{a}_0 a_0|\underline{b}_0 b_0) \end{aligned} \tag{4}$$

$$E^{BO}_{\text{exch}} = -\sum_{a_0 b_0} 2(\underline{a}_0 b_0|\underline{b}_0 a_0) \tag{5}$$

then the first-order energy is

$$E_1^{BO} = E^{BO}_{\text{elect}} + E^{BO}_{\text{exch}} \tag{6}$$

where a_0 and b_0 refer to the occupied molecular orbitals of the molecules A and B. V_{NA} and V_{NB} are the nuclear attraction hamiltonians for the molecules A and B respectively.

When the overlap is neglected, $\underline{a}_0$ is identical to a_0, and $\underline{b}_0$ to b_0 in expressions (4) and (5). We shall call these terms $E^{\mathrm{AM}}_{\mathrm{elect}}$, $E^{\mathrm{AM}}_{\mathrm{exch}}$ and E^{AM}_1. They correspond to the term $\varepsilon^{\mathrm{HF}}_1$ given in expression (16) of Ref. [7] based on the Amos and Musher procedure [8]. The comparison of these terms with $E^{\mathrm{BO}}_{\mathrm{elect}}$, $E^{\mathrm{BO}}_{\mathrm{exch}}$ and E^{BO}_1 respectively shows the effect of the charge overlap. We must notice that, if none of these two procedures is based on the multipole expansion (since we do not use the R^{-1} expansion which allows the decomposition in terms of multipoles) the second one has the common property with the multipole expansion that the charge overlap is not taken into account.

These perturbative approaches are compared with the first iteration of the supermolecule treatment. We call E^{d}_1 the difference between the SCF energies of the isolated molecules and the energy of the first iteration of the calculation where starting vectors are Schmidt orthogonalized vectors of these isolated molecules.[1]

Basis Sets

In the system $\mathrm{Li}^+ + \mathrm{H}_2$, we have used the same basis as in Ref. 9. In this basis, some polarisation functions have been added to the initial basis used by Lester [10] in view to improving the description of the dispersion energy. We have then:

Li^+ (94) [54]
s 921.271(0.001366); 138.730(0.010413); 31.9415(0.049827);
9.35330(0.160586); 3.15790(0.344478); 1.15690;
0.44460; 0.07670; 0.02860;
p 0.775; 0.33700; 0.07980;
0.02460.

H_2 (64) [64]
s 68.16; 10.2465; 2.34648; 0.67332; 0.22466; 0.082217
p 1.021269; 0.866381; 0.342309; 0.1275

In the notation (m_1m_2) $[n_1n_2]$, m_1 gaussian *s* functions are contracted into n_1 functions and m_2 gaussian *p* functions are contracted into n_2 functions. For Li^+, the 5 first *s* gaussian functions are contracted into one function. The contraction coefficients are given in parentheses. All the other functions are kept uncontracted. These basis sets give respectively $E_{\mathrm{SCF}}(\mathrm{Li}^+) = -7.2359875$ hartree and $E_{\mathrm{SCF}}(\mathrm{H}_2) = -1.1332821$ hartree.

In the case of two hydrogen molecules, some points have been computed with this basis (64) [64], but a smaller basis set (62) [32] is used for the general study in which the four first *s* gaussian functions are contracted into one function.

H_2 (62) [32]
s 68.16(.00255); 10.2465(0.1938); 2.34648(.09280); .673320(.29430); .22466;
.082217
p 1.; 0.1.

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[1] The SCF calculations have been performed with "Asterix", a system of programs for the Univac 1110 developed in Strasbourg (A. Dedieu, J. Demuynck, M. M. Rohmer, A. Strich and A. Veillard, unpublished work).

This basis set gives $E_{SCF}(H_2) = -1.132676$ hartree. We know that this basis set does not provide very good results in the treatment of the super-system including the total correlation energy because of a bad saturation with respect to the intramolecular correlation [11]. But we have checked that around the van der Waals minimum the first order energy is very close to the results obtained from basis (64) [64], the largest difference (0.15×10^{-4} hartree) being obtained for the linear configuration. Bases (64) [64] and (62) [32] seem comparable to bases IX [4*s*, 3*p*] and VII [4*s*, 2*p*] respectively, used by Urban and Hobza [12] in the SCF treatment of the supersystem. For the configurations that they have studied, the discrepancy for E_1^{Δ} is less important than for E_{SCF}^{Δ}.

As in previous papers [7, 11], (1) is the rectangular planar configuration, (2) the linear one, (3) the planar perpendicular one or *T* configuration, and (4) the non planar perpendicular configuration.

3. Results

3.1. *Effect of the Overlap on the First Order Energies*

Tables 1 and 2 allow us to study the effect of the overlap on the first order energies. It is obvious that the neglect of the overlap (E_1^{AM}) involves a bad description of the first order term. In the best case (Table 1, linear configuration of $Li^+ + H_2$) E_1^{AM} is not repulsive enough at large and intermediate distances and

Table 1. $Li^+ + H_2$–First order energies in 10^{-4} Hartree.
Basis Li^+ (94) [54]
H_2 (64) [64]

θ	*d* a.u.	E_1			E_{elect}			$E_{exch.}$	
		E_1^{Δ}	E_1^{BO}	E_1^{AM}	E_{elect}^{BO}	E_{elect}^{AM}	E_{coul} (Ref. [13])	E_{exch}^{BO}	E_{exch}^{AM}
90°	3	163.8	163.55	−196.32	123.93	−75.42	−85.2	39.62	−120.90
C_{2v}	3.5	32.9	32.66	−93.41	18.87	−50.91		13.79	−42.50
	3.75	7.2	6.73		−1.34			8.07	
	4	−6.6	−6.77	−49.70	−11.48	−35.02	−35.9	4.71	−14.68
	4.5	−15.7	−15.73	−29.87	−17.34	−24.81		1.61	−5.05
	5	−15.6	−15.56	−19.84	−16.13	−18.08	−18.4	0.56	−1.75
	6	−10.8	−10.79	−10.52	−10.86	−10.30	−10.7	0.07	−0.22
	7	−7.0	−7.07	−6.32	−7.08	−6.29	−6.7	0.01	−0.03
	10	−2.4	−2.46	−1.87	−2.46	−1.87	−2.3	0.0	0.0
0°	2.5		1527.65	−126.67	1360.50	421.12		167.15	−547.79
linear	3.5	249.4	261.71	61.82	240.67	128.93		21.03	−67.11
	4	129.2	129.11	60.69	121.81	83.81	71.9	7.29	−23.12
	4.5	72.8	72.93	50.04	70.42	58.02		2.51	−7.99
	4.7	60.0	60.12	45.55	58.47	50.77		1.64	−5.22
	5	46.4	46.47	39.30	45.60	42.07	36.8	0.87	−2.76
	6	24.0	24.00	24.04	23.89	24.38	21.3	0.11	−0.34
	7	14.7	14.66	15.46	14.65	15.50	13.4	0.01	−0.04
	10	5	4.96	5.59	4.96	5.59	4.6	0.0	

Table 2. H_2+H_2–First order energies in 10^{-4} hartree. wasis (62) [32]. The values in parenthesis correspond to basis (64) [64]

		E_1			E_{elect}		E_{exch}	
Configuration	d a.u.	E_1^A	E_1^{BO}	E_1^{AM}	$E_{\text{elect}}^{\text{BO}}$	$E_{\text{elect}}^{\text{AM}}$	$E_{\text{exch}}^{\text{BO}}$	$E_{\text{exch}}^{\text{AM}}$
1	5	18.50	21.27	−38.30	9.50	−3.74	11.77	−34.55
rectangular		(18.62)	(19.05)	(−35.46)	(8.62)	(−3.37)	(10.44)	(−32.09)
	5.5	7.80	9.45	−16.34	4.24	−1.21	5.21	−15.13
	6	3.33	4.20	−6.79	1.96	−0.27	2.24	−6.53
	6.5	1.48	1.89	−2.72	0.96	−0.04	0.93	−2.77
		(1.52)	(1.61)	(−2.49)	(0.81)	(−0.08)	(0.80)	(−2.41)
	7	0.69	0.87	−1.02	0.50	0.13	0.37	−1.15
	7.5	0.36	0.42	−0.34	0.28	0.12	0.14	−0.47
	10	0.05	0.03	−0.02	0.03	0.03	0.00	−0.00
2	5	36.44	31.61	−55.055	19.43	−2.39	12.18	−52.66
linear		(38.58)	(39.32)	(−59.64)	(23.36)	(−2.38)	(15.95)	(−57.26)
	5.5	15.74	14.92	−19.09	10.17	2.30	4.75	−21.39
	6	7.03	5.51	−7.52	3.71	0.93	1.80	−8.44
	6.5	3.31	2.57	−2.33	1.90	0.92	0.67	−3.25
		(3.44)	(3.64)	(−3.79)	(2.36)	(0.67)	(1.27)	(−4.46)
	7	1.67	1.34	−0.49	1.09	0.74	0.25	−1.23
	7.5	0.93	0.78	0.10	0.69	0.55	0.09	−0.46
	10	0.14	0.13	0.13	0.13	0.13	0.00	−0.00
3	5	21.03	20.06	−49.91	8.10	−8.15	11.96	−41.76
T conf.		(21.09)	(21.71)	(−51.55)	(8.76)	(−8.73)	(12.95)	(−42.82)
	5.5	8.000	7.52	−21.34	2.54	−3.73	4.97	−17.61
	6	2.81	2.61	−9.12	0.60	−1.83	2.01	−7.29
	6.5	0.85	0.76	−3.96	−0.03	−0.99	0.80	−2.97
		(0.85)	(0.97)	(−4.54)	(−0.04)	(−1.26)	(1.01)	(−3.28)
	7	0.13	0.10	−1.78	−0.21	−0.59	0.31	−1.19
	7.5	−0.09	−0.11	−0.86	−0.23	−0.39	0.11	−0.47
	10	−0.07	−0.09	−0.10	−0.09	−0.09	0.00	0.00
4	5	17.45	20.33	−39.27	8.55	−4.74	11.77	−34.53
non planar		(17.48)	(17.91)	(−36.38)	(7.52)	(−4.40)	(10.40)	(−31.98)
	5.5	7.15	8.85	−16.98	3.63	−1.85	5.21	−15.13
	6	2.91	3.81	−11.03	1.56	−4.51	2.24	−6.53
	6.5	1.19	1.61	−3.02	0.68	−0.25	0.93	−2.77
		(1.13)	(1.28)	(−2.82)	(0.49)	(−0.41)	(0.79)	(−2.41)
	7	0.50	0.67	−1.24	0.30	−0.09	0.37	−1.15
	7.5	0.22	0.27	−0.50	0.13	−0.04	0.14	−0.47
	10	0.01	−0.01	−0.02	−0.01	−0.02	0.00	−0.00

becomes negative at short distances (2.5 a.u.). In all the other configurations, E_1^{AM} is negative while we expect repulsive curves at least at short distances. It is interesting to study separately the behaviour of the electrostatic and exchange parts. We can see that $E_{\text{exch}}^{\text{AM}}$ is systematically negative and falls at short distances while E_1^{BO} is repulsive, with decreasing energies at large distances. So, $E_{\text{exch}}^{\text{AM}}$ is not able to describe the exchange energy, even qualitatively. The behaviour of $E_{\text{elect}}^{\text{AM}}$ is more confusing. In the linear configuration of $\text{Li}^+ + \text{H}_2$, $E_{\text{elect}}^{\text{AM}}$ is not repulsive enough but qualitatively correct even at short distances (Table 1). We must notice that, in this configuration, $E_{\text{elect}}^{\text{BO}}$ is strongly repulsive at any distance. On the contrary, in the C_{2v} configuration of $\text{Li}^+ + \text{H}_2$ (Table 1) and the T configuration of $\text{H}_2 + \text{H}_2$ (Table 2) $E_{\text{elect}}^{\text{BO}}$ exhibits an attractive minimum while $E_{\text{elect}}^{\text{AM}}$ stays always attractive. Of the other three configurations of $\text{H}_2 + \text{H}_2$ where $E_{\text{elect}}^{\text{BO}}$ is repulsive, $E_{\text{elect}}^{\text{AM}}$ is repulsive at intermediate distance but becomes attractive at $d = 5$ a.u., for the most repulsive one (linear case) while the other two curves are completely attractive. So the neglect of the charge overlap clearly prevents the repulsion between the molecules. Ref. [5c] also exhibits an orientation-dependent charge-overlap-effect in the Coulomb energy of the system $\text{NH}_3\text{–H}^+$ and shows the role of each term of the multipole expansion. This effect has important consequences for the calculations based on the multipole expansion. As we have said previously the calculations based on this expansion have the common property with $E_{\text{elect}}^{\text{AM}}$ that the charge overlap is neglected. Then we expect that $E_{\text{elect}}^{\text{AM}}$ and the electrostatic energy computed in this way should have a similar behaviour. We can check that this is so for both configurations of $\text{Li}^+ + \text{H}_2$ (Table 1, compare $E_{\text{elect}}^{\text{AM}}$ and E^{coul} given by Kutżelnigg *et al.* [13] from the interaction between the monopole in Li^+ and the permanent quadrupole in H_2). If we consider that the van der Waals minimum is around 3.75 a.u. and 4.7 a.u. for the C_{2v} and the linear configuration respectively, we see that the discrepancy with $E_{\text{elect}}^{\text{BO}}$ becomes significant precisely at this distance. Then such methods should not be able to provide a good depth of the van der Waals minimum unless this effect is artificially taken into account (for instance through a repulsive term in the semi-empirical methods.)

3.2. Comparison between the Perturbative Procedure and the Supermolecule Treatment

The first two columns of Tables 1 and 2 provide a direct numerical comparison between the perturbative method using biorthogonal orbitals and the supermolecule treatment where a Schmidt orthogonalization is performed. With the large basis set the agreement is very good (Table 1 and values in parenthesis of Table 2). This means that the two procedures of orthogonalization are equivalent if the overlap is correctly described. Calculations with different basis sets show that the biorthogonal orbitals procedure is much more sensitive to the basis set (especially to the extension of the s set) than the Schmidt orthogonalization. For example, in the case of the rectangular configuration at $d = 6$ a.u. we obtain respectively 0.664, 0.695, 2.866, 4.20×10^{-4} hartree from the biorthogonal orbitals procedure and 2.329, 2.455, 3.069, 3.33×10^{-4} hartree from the Schmidt orthogonalization with the corresponding bases (41) [21], (43) [23], 10 s (which are bases $A3$, $B3$ and II in Ref. [7]) and (62) [32]. With basis (64) [64] we have only computed $E_1^A = 3.405 \times 10^{-4}$ hartree but the results obtained for 5 and 6.5 a.u. lead us to think that E_1^{BO} should be very close to this value.

3.3. Comparison of our Results with Previous Semi-Empirical Works

As seen previously, our E_1^{AM} term is comparable with E^{coul} in the case of $\text{Li}^+ + \text{H}_2$ (Table 1), E^{coul} being still more attractive than E_1^{AM} at short distances.

This energy E^{coul} corresponds to the interaction between the monopole in Li^+ and the quadrupole in H_2, the values of the quadrupole moment (0.460 a.u.) being taken from the calculation of McLean and Yoshimine [14]. For two hydrogen molecules, our work is compared with Refs. [15–17]. Curiously, the exchange energy provides a better agreement than the electrostatic part. As this last term in Refs. [15–17] is computed from the multipole expansion, we could expect that its behaviour would be similar to $E^{\text{AM}}_{\text{elect}}$. But Table 14-4-1 in Ref. [17], Table 1 in Ref. [16] and expression (5) in Ref. [15a] give an attractive energy for the T configuration and a repulsive energy in the three other cases and even when the sign is the same as for $E^{\text{AM}}_{\text{elect}}$ the numerical values are seriously different. A comparison with $E^{\text{BO}}_{\text{elect}}$ does not improve the agreement.

In contrast, as can be seen in Table 3, the exchange energy exhibits the same behaviour in the four series of calculations. The best agreement occurs between

Table 3. H_2+H_2 exchange energies in 10^{-4} hartree

Configuration	d a.u.	$E^{\text{BO}}_{\text{exch}}$	Ref. [15]	E_{steric} Ref. [16]	ϕ_{II} Ref. [17]
1	4	56.06	—	—	—
rectangular	4.289	—	51.78	57.64	—
	5	11.77	—	—	8.26
	5.140	—	11.39	11.39	—
	6	2.24	—	—	1.16
	6.009	—	2.358	2.08	—
	6.859	—	0.45	0.36	—
	7	0.37	—	—	0.22
2	4	70.32	—	—	—
linear	4.289	—	57.67	212.39	—
	5	12.18	—	—	65.49
	5.140	—	14.24	37.53	—
	6	1.80	—	—	5.66
	6.009	—	3.13	6.07	—
	6.859	—	0.63	0.89	—
	7	0.25	—	—	0.76
3	4	62.85	—	—	—
T conf.	4.289	—	56.36	105.80	—
	5	11.96	—	—	23.44
	5.140	—	12.79	20.41	—
	6	2.02	—	—	2.54
	6.009	—	2.73	3.54	—
	6.859	—	0.52	0.57	—
	7	0.31	—	—	0.40
4	4	55.90	—	—	—
non planar	4.289	—	52.32	54.37	—
	5	11.77	—	—	7.98
	5.140	—	11.36	10.90	—
	6	2.24	—	—	1.14
	6.009	—	2.34	2.02	—
	6.859	—	0.43	0.35	—
	7	0.37	—	—	0.22

E^{BO}_{exch} and Evett and Margenau's values, the most important difference being for the linear configuration. We must notice that it is this linear configuration which presents the largest range of values.

In summary we can see what information is provided by this work:

(*a*) The systematic agreement between E_1^A and E_1^{BO} shows that these two procedures are equivalent when large basis sets are used, the first one being less sensitive to a good description of the overlap. The neglect of the charge overlap leads to an unacceptable exchange term while the electrostatic term, good at large distances, becomes unvalid around the van der Waals minimum. The limit of the validity of the multipole expansion should be comparable to that of E^{AM}_{elect}.

(*b*) For H_2+H_2 our calculations confirm the stability of the T configuration through the electrostatic interaction as suggested by Buckingham [18]. But as seen in Ref. [7] [11], the electrostatic energy is not the only element of stabilization of these configurations: while the exchange energy is comparable in configurations (1), (3) and (4), the dispersion energy is more attractive in (3) than in (1) and (4). We can notice that for each of these three components of the energy, (1) and (4) exhibit a rather comparable behaviour. For $Li^+ + H_2$, the stability of the C_{2v} configuration is clearly due to the electrostatic energy, the exchange term and the dispersion term being almost negligible.

(*c*) As discussed by Urban and Hobza [12], the first order energy of H_2+H_2 obtained with large basis sets is somewhat more repulsive than the results given in paper [7] from smaller basis sets. We have the same phenomena near the van der Waals minimum for $Li^+ + H_2$. They also show [12] that the polarization and the charge transfer energies, neglected in paper [7], are small but not negligible so that these attractive energies should partly compensate the error due to the use of small basis set on the first order term. Further calculations performed on the dispersion energy with basis (64) [64] increase slightly the attractive dispersion energy with respect to basis $B3$ given in Ref. [7]. This explains why a treatment where the dispersion energy is added to the SCF supermolecule energy, provides (at least in the case of the T configuration which is the more important in the average over the form configurations [15a]) values which are very close to the total energies given in Table VII of Ref. [7] with basis $B3$. Values for the four configurations will be available very soon.

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