Theoret. Chim. Acta (Berl.) 32, 151—159 (1973)

Ab initio SCF–CI Studies of the Intermolecular Interaction between Two Hydrogen Molecules near the Van der Waals Minimum

Elise Kochanski*, Björn Roos**, Per Siegbahn**, Melvyn H. Wood*

Institut de Chimie, 1, Rue Blaise Pascal, F-67 Strasbourg, France, and Institute of Theoretical Physics,
University of Stockholm, Vanadisvägen 9, S-11346 Stockholm, Sweden

Received June 27, 1973/September 20, 1973

SCF–CI calculations have been used to study the intermolecular energy between two hydrogen molecules in four different geometrical configurations. The CI matrix was diagonalized using perturbation techniques. The importance of the perturbation expansion order upon the intermolecular energy could therefore be studied. The wave function includes all singly and doubly excited configurations. The natural orbitals have been determined and their relative importance on the intermolecular energy is considered.

Key words: Intermolecular interactions – Two hydrogen molecules

1. Introduction

Most of the previous calculations of the intermolecular energy between two atoms or non polar molecules near the Van der Waals minimum have been based on perturbation theory. Only recently has the treatment of the correlation energy by *ab initio* methods allowed the study of the problem by the "supermolecule" approach. The first papers in this series concerned the interaction of two Helium atoms [1, 2], the two procedures used being based on the idea that the intra-molecular correlation is constant with varying distances; simultaneously the interaction of two lithium atoms has been investigated [3]. The treatment of the intermolecular interactions from computations involving both intra- and intermolecular correlation is a more difficult task. Although, using a large basis set, this procedure may be developed extensively, since that part of the correlation which it is necessary to take into account is only a very small percentage of the total correlation energy, it is relevant to investigate how this small percentage may be obtained with less computational effort. Indeed, it is possible to have a good determination of the total correlation energy and miss that part responsible for the intermolecular energy, or inversely it may be possible to obtain the inter-

---

* Strasbourg.

** Stockholm.

molecular part and neglect an important part of the intramolecular energy. Another danger of the use of a non complete basis set is the possibility of an artificially deep well [4].

The treatment of two hydrogen molecules as a supermolecule has so far been very limited, Bender and Schaefer [5] with a small basis set have considered only the linear configuration, which is the least important in the average according to Evett and Margenau [6], while Tapia and Bessis [7] obtain a qualitatively correct minimum in the linear case (1.168×10^{-4} a.u.), a much too deep minimum in the perpendicular planar case (11.589×10^{-4} a.u.) and no minimum in the two others configurations.

Recently a new method has been proposed for large scale CI calculations [8], the main feature of the method being the direct calculation of the CI-vector from a list of molecular two-electron integrals using an iterative procedure, the time consuming building of a Hamiltonian matrix is thus avoided. Thus, the only limitation to the length of the CI-vector is the available core storage. Very large CI expansions can therefore be used (calculations with as much as 50000 configurations are presently being done). The computing time is also much shorter than with conventional CI methods. The iterative procedure used in the present calculations is identical to *nth*-order RS perturbation theory, which makes it possible to study the effect of the perturbation expansion order in the interaction energy.

This method has been used here to investigate the intermolecular interaction between two hydrogen molecules. Previous calculations using a perturbative procedure have shown that the dispersion energy in H_4 can be correctly obtained from an *ab initio* wave function if one uses basis functions of $2p$-type with exponents appropriate for the polarization of the two molecules [9]. This suggests that the minimum obtained by Bender and Schaefer [5] for the linear configuration, treated as a supermolecule with a small basis set, could be improved by using a more extended basis set containing polarization functions with small exponents.

2. Details of the Calculations

Although the dispersion energy in a perturbative scheme of the intermolecular interactions can be described correctly from a small s basis set adequatly polarized [9], the SCF energy of the supermolecule is very sensitive to the s set, thus the present work has used a more extended s set than in [9], taken from the paper of Huzinaga [10], with six primitive Gaussians contracted to three functions (4, 1, 1). It was shown in [9] that in the case of the dispersion energy between two hydrogen molecules, the number of p-type functions could be limited to a few. If properly chosen, the wave function built with just one such function gives about the same result as a wave function obtained with an extended p set.

Since the part of the correlation energy in H_4, treated as a supermolecule, which gives the Van der Waals minimum, is of the same nature as the dispersion energy defined from a perturbative procedure, we expect that one p function, with a small exponent is responsible for this contribution. As it is dangerous, in an SCF procedure, to use an unbalanced basis set, we have limited the *p* set to two functions, one with a fixed exponent $\zeta_1 = 1.0$, giving a contribution mainly to intramolecular energy, the other one with an exponent ζ_2, optimized in H_4, being chiefly responsible for the intermolecular energy.

This optimization was carried out in a rectangular configuration with the H_2 internuclear distance fixed at 1.4 a.u.. All singly and doubly excited configurations were taken into account. The basis set is not saturated with respect to the correlation energy for the hydrogen molecule. A straightforward optimization of the orbital exponent, minimizing the total energy, is therefore not possible. Such a procedure gives an orbital exponent of 0.3 corresponding to a correlation energy of 0.0377 a.u., and a total energy of -1.1704 a.u. for the hydrogen molecule, no Van der Waals minimum being obtained with such a large exponent. It was found that the exponent had to be smaller than 0.2 in order to obtain a minimum. The deepest minimum was found with $\zeta_2 = 0.1$ giving -1.270×10^{-4} a.u. and -2.3362 a.u. for the intermolecular and total energies respectively. This optimization of ζ_2 is equivalent to the assumption that a part of the energy which is constant at any intermolecular distance may be neglected, this part being intramolecular energy. A more involved study capable of describing both the intra- and intermolecular correlations would need three *p*-type basis functions with exponents 1.0, 0.3 and 0.1. It is quite possible that, as described in paper [4], the basis set allows a better determination of the intramolecular correlation at intermediate distances than at large distances, giving a systematically too deep potential well, the extra stability being about the same for all the geometrical configurations since it is due to intramolecular correlation. This would probably not lead to any pronounced changes in the qualitative informations obtained around the van der Waals minimum for the following reasons:

– the intermolecular energy due to the SCF part is hardly affected by the variation of ζ_2

– the intermolecular energy due to the correlation part is strongly dependant on ζ_2. The direct calculation of the dispersion energy from the perturbative procedure used in Ref. [9] gives good values when $\zeta_2 = 0.1$, in the four geometrical configurations considered.

Therefore, this value of ζ_2 was used in all subsequent calculations.

Calculations have been done for four geometric configurations, a planar rectangular configuration (1), (molecular axis *z*, intermolecular axis *y*); a linear configuration (2), (linear axis *z*); a planar orthogonal configuration (3), (molecular axes *y* and *z* for molecules A and B, respectively, intermolecular axis *y*); and a non planar orthogonal configuration (4) (molecular axes *x* and *z* for molecules A and B respectively, intermolecular axis *y*). The CI calculations included singly and doubly excited configurations. The number of such spin and space symmetrized configurations being 802, 800, 836 and 702 respectively for the four configurations. In all cases the configurations were built from canonical SCF molecular orbitals. Test calculations showed that variations of the intramolecular hydrogen bond distance have only a minor effect on the intermolecular energy at the distances of interest here. In all calculations this distance was therefore kept fixed at 1.4 a.u.

3. Results and Discussions

The intermolecular energies obtained for the different geometrical configurations are shown in Table 1. The corresponding curves are also shown in Fig. 1. Configuration (3) is found to be most stable, with a depth of 2.26×10^{-4} a.u. at the intermolecular distance 6.6 a.u. Corresponding values for the other geometries are 1.70×10^{-4} a.u. at 6.7 a.u. (4); 1.32×10^{-4} a.u. at 6.7 a.u. (1) and 1.06×10^{-4} a.u. at 6.9 a.u. for the linear configuration, (2). The exceptional stability of the orthogonal configuration has been mentioned previously by other authors [11, 12] being based on quadrupole and exchange interactions. This stability was shown in Ref. [9] to be due also to the importance of the dispersion term.

Table 2 allows a comparison with previous calculations of different accuracy. All these results show that it is rather difficult to obtain better than a good order of magnitude without performing a very accurate calculation and that a good agreement between the averaged energy and the experimental value can be rather fortuitous when all the approximations involved in these different cases are considered. The most striking result is, perhaps, the stability of configuration (3), which is again, as in Ref. [9], much more pronounced than in calculations *b* of Ref. [13] and *c* of Ref. [14]. Comparison with the CI study of Bender and Schaefer [5] shows the importance of the basis set, especially the diffuse $2p$ orbital which accounts for most of the intermolecular energy. The difference would be probably still more important in the other configurations since it has been shown [9] that the linear case is the least sensitive to the p exponents,

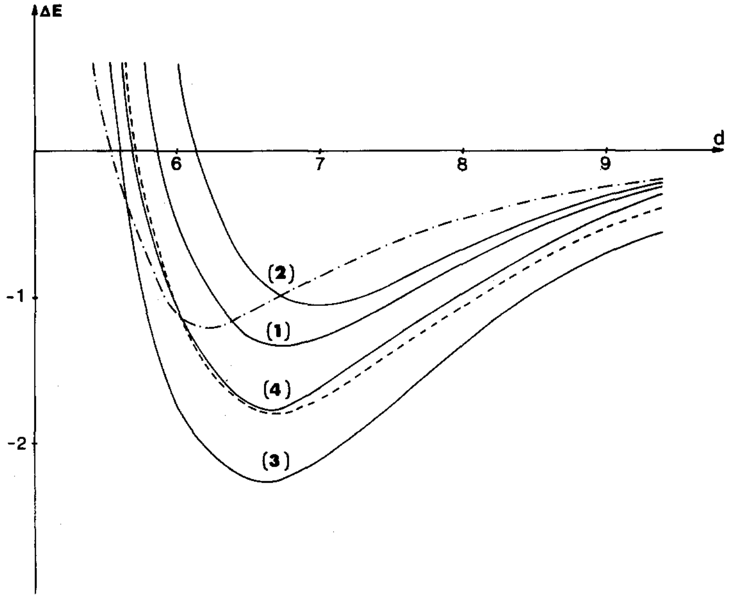

Fig. 1. Intermolecular energies in configurations (1), (2), (3), (4) (———), for the calculated average (– – –) and from experimental datas (–·–·–). ΔE is the intermolecular energy in 10^{-4} a.u., d is the intermolecular distance in a.u.

Table 1. H_4: Total energy and intermolecular energy in some geometrical configurations

Geometrical configurations	(1)		(2)		(3)		(4)		Average[d]	Experimental[e]
d[a]	E[b]	ΔE[c]	E	ΔE	E	ΔE	E	ΔE		
4	−2.328605	74.33	−2.324160	118.79	−2.327851	81.86	−2.328930	71.07		
5	−2.335063	9.75	−2.334287	17.52	−2.335136	9.01	−2.335182	8.55	9.80	7.203
5.5	−2.335813	2.25	−2.335521	5.18	−2.335953	0.84	−2.335894	1.43	1.71	0.184
6	−2.336086	− 0.48	−2.335980	0.59	−2.336212	− 1.75	−2.336145	− 1.08	−1.07	−1.110
6.5	−2.336165	− 1.27	−2.336119	− 0.80	−2.336263	− 2.25	−2.336210	− 1.73	−1.75	−1.103
7	−2.336167	− 1.29	−2.336144	− 1.05	−2.336249	− 2.12	−2.336199	− 1.62	−1.70	−0.864
7.5	−2.336142	− 1.04	−2.336131	− 0.92	−2.336210	− 1.73	−2.336165	− 1.28	−1.38	−0.634
10	−2.336045	− 0.07	−2.336051	− 0.12	−2.336072	− 0.35	−2.336048	− 0.12	−0.20	−0.130
20	−2.336038		−2.336039		−2.336038		−2.336039			
100	−2.336038		−2.336039		−2.336037		−2.336037			
∞ (full CI)	−2.337199		−2.337199		−2.337199		−2.337199			

[a] d is the intermolecular distance in "a.u.".

[b] $E = E_{\mathrm{SCF}} + E_{\mathrm{correl}}$ in a.u.

[c] $\Delta E = E(d) - E(d = 100)$ in 10^{-4} a.u.

[d] Average = 0.25(1) + 0.085(2) + 0.415(3) + 0.25(4) according to Ref. [14].

[e] From compressibility datas; Ref. [13, 15].

Table 2. Comparison of the intermolecular energies for four geometrical configurations (in 10^{-4} a.u.)

Configurations	Distance	a	b	c	d	Present work
(1)	5.5	1.816	−1.101	0.698		2.25
	6	−0.103	−1.076	−0.735		−0.48
	6.5	−0.545	−0.803	−0.955		−1.27 (−1.08)[e]
	7	−0.532	−0.557	−0.845		−1.29
	7.5	−0.407	−0.380	−0.625		−1.04
	10	−0.064	−0.061			−0.07
(2)	5.5	3.983	13.993	2.940	6.300	5.18
	6	0.289	3.498	0.367	1.450	0.59
	6.5	−0.634	0.780	−0.441	−0.190	−0.80
	7	−0.694	0.071	−0.551	−0.580	−1.05
	7.5	−0.539	−0.092	−0.441	−0.530	−0.92
	10	−0.065	−0.025		−0.001	−0.12
(3)	5.5	0.221	0.665	0.882		0.84
	6	−1.453	−1.330	−0.808		−1.75
	6.5	−1.691	−1.399	−1.139		−2.25
	7	−1.372	−1.110	−0.992		−2.12
	7.5	−1.024	−0.820	−0.771		−1.73
	10	−0.202	−0.177			−0.35
(4)	5.5	1.572	−1.652	0.367		1.43
	6	−0.305	−1.422	−0.845		−1.08
	6.5	−0.704	−1.030	−1.066		−1.73
	7	−0.643	−0.714	−0.919		−1.62
	7.5	−0.492	−0.491	−0.698		−1.28
	10	−0.093	−0.088			−0.12

[a] From a perturbation procedure, using basis B3 in Ref. [9].
[b] From Hirschfelder and Cow. [13].
[c] From Evett and Margenau (from the diagram) [14].
[d] From Bender and Schaefer [5], considering singly and doubly excited configurations.
[e] Uncontracted basis set.

the larger contribution in this case arising from a σ_u orbital. The contraction of the *s* primitive functions seems to be useful since it decreases considerably the computing time and introduces only a rather small error (1.27 instead of 1.08×10^{-4} a.u. near the Van der Waals minimum in the rectangular configuration).

Although, according to Ref. [5], the use of a full CI does not change appreciably the intermolecular energy, there is no evidence that this is also the case in configurations (3), (1) and (4), which are the most important in the average. Preliminary calculations have indicated that the contribution of some quadruple excitations is of the same order of magnitude as the intermolecular energy. A full CI treatment might therefore modify the numerical values. Work in this direction is in progress. The overall effect of the higher excitations seems to be to diminish the depths of the energy minima. This agrees well with the present results for which the average energy curve falls below the experimental values.

The results discussed so far are concerned with the converged values. Since a perturbation procedure was used for the diagonalization of the CI-matrix

Table 3. Importance of the order of the perturbation series for the intermolecular energies (energies in 10^{-4} a.u.)

Configurations	d	2nd order	3rd order	4th order	5th order	13th order (converged)
(1)	5.5	2.80	1.98	2.05	2.18	2.25
	6	−0.07	−0.68	−0.62	−0.52	−0.48
	6.5	−0.96	−1.43	−1.39	−1.31	−1.27
	7	−1.07	−1.41	−1.37	−1.31	−1.29
	7.5	−0.89	−1.14	−1.10	−1.06	−1.04
	10	−0.09	−0.12	−0.09	−0.07	−0.07
(2)	5.5	5.33	4.50	4.83	5.08	5.18
	6.	0.74	0.18	0.38	0.54	0.59
	6.5	−0.72	−1.06	−0.92	−0.82	−0.80
	7	−1.01	−1.22	−1.12	−1.06	−1.05
	7.5	−0.92	−1.03	−0.96	−0.92	−0.92
	10	−0.13	−0.13	−0.12	−0.11	−0.12
(3)	5.5	1.20	0.37	0.56	0.75	0.84
	6	−1.49	−2.10	−1.96	−1.82	−1.75
	6.5	−2.08	−2.53	−2.42	−2.30	−2.25
	7	−1.97	−2.31	−2.23	−2.15	−2.12
	7.5	−1.65	−1.91	−1.83	−1.76	−1.73
	10	−0.32	−0.37	−0.36	−0.35	−0.35
(4)	5.5	2.07	1.17	1.22	1.35	1.43
	6	−0.57	−1.27	−1.24	−1.14	−1.08
	6.5	−1.33	−1.88	−1.85	−1.77	−1.73
	7	−1.34	−1.75	−1.72	−1.65	−1.62
	7.5	−1.09	−1.38	−1.36	−1.31	−1.28
	10	−0.12	−0.16	−0.13	−0.11	−0.12

we can analyse the effect of the different orders of perturbation on the intermolecular energy. At the equilibrium distance, between 80 and 95 per cent of the interaction energy is obtained in second order.

Values especially close to the converged ones are obtained for the linear case. As expected the convergence gets slower with decreasing intermolecular distance. As an example only 53% of the converged value is obtained in configuration (4) at the distance 6.0 a.u. while 82% is obtained in second order at 6.5 a.u. Third order contributions are in general of the order of 20–30%. The energies will therefore in most cases converge towards the final values from below. Convergence to all significant figures is obtained in order thirteen, but the values at the fifth order are already very close to the final ones.

Also of interest is a study of the effect of the natural orbitals on the inter and intramolecular energy. When the molecules are well separated, the natural orbitals are localized on each molecule, with occupation numbers 1.9685 ($1\sigma_g$), 0.0197 ($1\sigma_u$), 0.0059 ($2\sigma_g$) and 0.0027 ($1\pi_{ux}$ and $1\pi_{uy}$ when the molecular axis is along z) for the five most important orbitals. All these orbitals have a rather small coefficient (<0.2) corresponding to $\zeta_{2p}=0.1$. These orbitals provide an important contribution to the intramolecular correlation energy. The next orbital is a σ_u orbital, with an occupation number 0.00020 and a large coefficient for $\zeta_{2p}=0.1$ followed by σ_g (0.00019), π_{gx} and π_{gy} (0.00013), π_{uy} and π_{ux} (0.000066), the latter two having larger coefficients for $\zeta_{2p}=0.1$ than for $\zeta_{2p}=1.0$. The remaining orbitals are of the type σ_g, σ_u, π_{gx}, π_{gy}. When the molecules interact with each other, each orbital of one molecule can be perturbed by orbitals of the other molecules. Depending upon symmetry, two arrangements are possible. Either the orbital will be still localized to one of the molecules and is only perturbed by the interaction, or delocalized orbitals of the types $a+b$ and $a-b$ are formed; thus it is possible to study the evolution of pairs of orbitals. Two calculations have been performed on the perpendicular configuration using the natural orbitals obtained at 100 a.u. and 6.5 a.u. While all the natural orbitals provide an intermolecular energy of 2.3×10^{-4} a.u., the limitation of the orbitals whose occupation number is $\geqq 0.00013$ gives an energy of 0.94×10^{-4} a.u. If, from amongst these orbitals we delete the two σ_u orbitals whose occupation numbers are 0.00020, we have only 0.34×10^{-4} a.u. The corresponding change in the correlation energy being -2.67, -1.26 and -0.68×10^{-4} a.u. respectively for the three groups of natural orbitals when d varies from 100 a.u. to 6.5 a.u.

From these results we can conclude that:

a) the natural orbitals with largest occupation number, which provide most of the intra-molecular correlation energy, have only a small contribution to the interatomic energy

b) the σ_u orbitals with a large coefficient for $\zeta_{2p}=0.1$ are of great importance since their suppression involves a change of 0.60×10^{-4} a.u.

c) the most part of the intermolecular energy is obtained when we include the natural orbitals with small occupation numbers.

This is in good agreement with the conclusion from paper [9], which stated that the strongest interaction comes from excitations of the types $1\sigma_g^a 1\sigma_g^b \rightarrow 1\sigma_u^a 1\pi_u^b$, since some of these excitations are suppressed when we delete the σ_u orbitals. Nevertheless some such contributions can still arise from other σ_u orbitals with smaller occupation numbers which have also a large coefficient corresponding to $\zeta_{2p}=0.1$. It is quite probable that the suppression of the π_u^b orbital with occupation number 0.000066 would decrease still more strongly the intermolecular energy because it seems that there is only one such convenient π_u^b orbital.

In conclusion, the present work has shown that it is now possible to give a reliable qualitative description of weak intermolecular interactions between two hydrogen molecules treated as a supermolecule, with a rather limited basis set. The basis set used overestimates the numerical values somewhat. Calculations with a larger basis set are in progress to improve the quantitative results. Our results have confirmed the stability of the perpendicular planar configuration. The use of natural orbitals shows clearly the respective importance of some orbitals on the intra and intermolecular energy, as well as the role of the small exponent $\zeta_2=0.1$. It also allows a determination of the importance of certain types of excitation, as in configuration (3).

Acknowledgements. The computations have been performed on the Univac 1108 computer of the Centre de Recherches Nucléaires de Strasbourg-Cronenbourg (Centre National de la Recherche Scientifique) and on the CDC 3600 at the computing center of the University of Stockholm (UDAC-S). Dr. A. Dedieu and Dr. M. M. Rohmer (Strasbourg) are acknowledged for their help in adapting the program to the Univac computer.

The authors thank the referee for drawing their attention to the existence of Ref.[4 b].

References

1. Schaefer, H. F., McLaughlin, D. R., Harris, F. E., Alder, B. J.: Phys. Rev. Letters **25**, 988 (1970). – McLaughlin, D. R., Schaefer, H. F.: Chem. Phys. Letters **12**, 244 (1971)
2. Bertoncini, P., Wahl, A. C.: Phys. Rev. L **25**, 991 (1970)
3. Kutzelnigg, W., Gelus, M.: Chem. Phys. Letters **7**, 296 (1970)

4a. Liu, B., McLean, A. D.: Submitted to J. Chem. Phys.

4b. Liu, B. McLean, A. D.: In: Papers, International conference on computers in chemical research and education 1973

5. Bender, C. F., Schaefer III, H. F.: J. Chem. Phys. **57**, 217 (1972)
6. Evett, A. A., Margenau, H.: Phys. Rev. **90**, 1021 (1953)
7. Tapia, O.: Chem. Phys. Letters **10**, 613 (1971). – Tapia, O., Bessis, G.: Theoret. Chim. Acta (Berl.) **25**, 130 (1972)
8. Roos, B.: Chem. Phys. Letters **15**, 153 (1972)
9. Kochanski, E.: Chem. Phys. Letters **15**, 254 (1972); J. Chem. Phys. **58**, 5823 (1973)
10. Huzinaga, S.: J. Chem. Phys. **42**, 1297 (1965)
11. Girardet, C., Robert, D., Galatry, L.: J. of Molecular Structure **11**, 305 (1972)
12. Buckingham, A. D.: Quart. Rev. **13**, 183 (1959)
13. Hirschfelder, J. O., Curtiss, C. F., Bird, R. B.: Molecular theory of gases and liquids, p. 1088 ff. New York: Wiley: 1954
14. Evett, A. A., Margenau, H.: Phys. Rev. **90**, 1021 (1953)
15. de Boer, J.: Physica **14**, 139 (1948). – Lunbeck, R. J.: Doctorate Dissertation, University of Amsterdam (1951)

Dr. E. Kochanski
Institut de Chimie
1, rue Blaise Pascal
F-67008 Strasbourg Cedex, France