Theoret. chim. Acta (Berl.) 25, 130—137 (1972)

Intermolecular Interactions-Dependence on Inter- and Intra-Molecular Distances. A Configuration Interaction Study of the $H_2 \cdots H_2$ System

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Received September 9, 1971

The potential energy curves for two H_2 molecules are calculated by a SCF-MO-LCGO-CI procedure. The orientational and internal geometry dependence of the interaction energy is studied. Numerical results show: a) that repulsive interaction energy increases with increased intramolecular dimensions and b) that it has a rough additivity dependence with the number of stretched partners. The attractive interaction energies display a behavior similar to the repulsive one. A simple qualitative explanation for this fact is advanced.

Die Potentialkurven für zwei H_2-Moleküle werden mit Hilfe eines SCF-MO-LCGO-CI-Verfahrens berechnet. Die Abhängigkeit der Wechselwirkungsenergie von der Orientierung sowie der inneren Geometrie der beiden Moleküle wird untersucht. Die numersichen Ergebnisse zeigen: a) die abstoßende Wechselwirkungsenergie steigt mit wachsenden intramolekularen Dimensionen, und b) dieser Energieanteil zeigt ungefähr Additivität entsprechend der Zahl der gestreckten Wechselwirkungspartner. Die anziehenden Anteile der Wechselwirkung zeigen ähnliches Verhalten wie die abstoßenden. Eine einfache qualitative Erklärung für dieses Verhalten wird vorgeschlagen.

Les courbes d'énergie potentielle du systeme formé de deux molécules H_2 sont déterminées par la méthode SCF-MO-LCGO-CI et la dépendance de l'énergie d'interaction en fonction de l'orientation et de la géométrie est explicitée. Les résultats montrent que: a) la partie répulsive de l'énergie d'interaction croît avec les dimensions intramoléculaires du système, b) la dépendance est, grosso modo, additive en fonction du nombre de partenaires «étirés». La partie attractive de l'énergie d'interaction présente le méme comportement que dans le cas répulsif. Une tentative d'explication qualitative simplifiée de ces résultats est présentée.

1. Introduction

An increased interest in the knowledge of the internal geometry dependence of intermolecular forces has been raised, principally due to work of Bratos *et al.* [1], on vapor-solution infrared (IR) frequency shifts and band shape. They have shown that these shifts depend on the difference between the mean energies of the solute-solvent interaction in the two vibrational states implied in the IR transition. Speaking pictorially these shifts depend on the variation of the intermolecular forces with the effective size of the interacting molecules. Also, in connection with chemical reaction mechanism, a vibrational excitation mechanism has been suggested for the exchange reaction $H_2 + D_2$ in presence of argon atoms [2, 3]. These developments showed the interest to undertake a study of intermolecular

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forces and their dependence on the distance, orientation and internal geometry from a theoretical point of view. In previous papers [4, 5], Pauli repulsive interaction between two H_2 molecules in their electronic ground state has been investigated using a SCF-MO-LCGO procedure. For this type of system, repulsive forces predominate at short range distances, and the SCF-MO method is the adequate theoretical tool for the calculation of the intermolecular potential energy. At intermediate distances, however, Van der Waals forces become important. It has been shown by London [6] that these forces come out from dynamic electronic correlations. The SCF-MO scheme does not take into account this kind of correlation and a configuration interaction (CI) is needed to introduce it. The $H_2 \ldots H_2$ system is considered here as a model because it has the main features of four centers molecular interactions and nevertheless one is still able to make rather exact calculations. This system has been often considered and parallel calculations have been carried out by Magnasco *et al.* [12, 13] using a restricted basis of Slater orbitals for a different set of distances and geometries. Reference to their work and conclusions has been reported in our preceeding paper [5].

In Section 2, we present the method, models and details of the calculations. Section 3 contains the results and discussion of the dependence of the potential energy on intermolecular distance and orientation. The intramolecular distance dependence of the interaction energy is discussed in Section 4, and for reasons further discussed only the linear geometrical configuration is studied.

2. Method, Models and Calculations

a) Wave Function

The wave function of the composite system is taken as a linear combination of a zero^th order, singly and doubly excited electronic configurations state functions

$$\psi = C_0\psi_0 + \sum_S C_S\psi_S + \sum_D C_D\psi_D . \tag{1}$$

The coefficients C_0, C_S, C_D are determined variationally. ψ_0 stands for the SCF closed shell electronic wave function of the ground state represented by a single Slater determinant. ψ_S and ψ_D stand for singly and doubly excited state functions. The virtual SCF-MO's have been used to build up the ψ_S and ψ_D functions. The total Hamiltonian, H, once diagonalized in this basis, the lowest energy eigenvalue represents the ground electronic energy, $E_{\mathrm{SCF-CI}}$. In the CI calculation, we consider only up to diexcited electronic configurations. The reason follows from a second order perturbation analysis of $E_{\mathrm{SCF-CI}}$ in terms of essentially localized MO's at long range distances. One can show that the total energy can be written approximately

$$E_{\mathrm{SCF-CI}} \approx E_{\mathrm{SCF}} - \sum_D \frac{|\langle\psi_0|H|\psi_D\rangle|^2}{E_D^0 - E_0^0}, \tag{2}$$

where $E_{\mathrm{SCF}} = \langle\psi_0|H|\psi_0\rangle$ and E_D^0 and E_0^0 are the expectation values of the hamiltonian taken over a non interacting unperturbed system. The second term of Eq. (2), $E^{(2)}$, is an approximation to the dynamic electronic correlation energy.

If the limit of our approximate basis seems to be severe, however a study of this expression, using essentially localized MO's, shows that the Van der Waals interaction energy, which behaves asymptotically like $-1/R^6$, is accounted for. Owing to the fact that the dielectronic integrals involved are exactly calculated, mainly all second order dispersion effects are implicitly contained in within the limits of our approximate basis. Of course to take a full account of the Van der Waals interaction term, a more extended basis would be required.

b) Models

The dependence of potential energy on orientational and intermolecular distance has been considered by analysing four geometrical configurations, a) rectangular configuration (D_{2h}), b) perpendicular configuration (C_{2v}), c) linear configuration ($D_{\infty h}$) and d) *T*-configuration (C_{2v}). The standard symbols are used to indicate the corresponding symmetry point group, Fig. 1. The internal geometry dependence is studied by considering one or both partner molecules at an intramolecular distance, r, greater than the equilibrium distance, $r_0 = 1.4166$ a.u. This model is a consequence of the assumption that a vibrationally excited state has a vibration amplitude greater then the fundamental one. The value $r = 1.6$ a.u. for the stretched molecule (s) is considered.

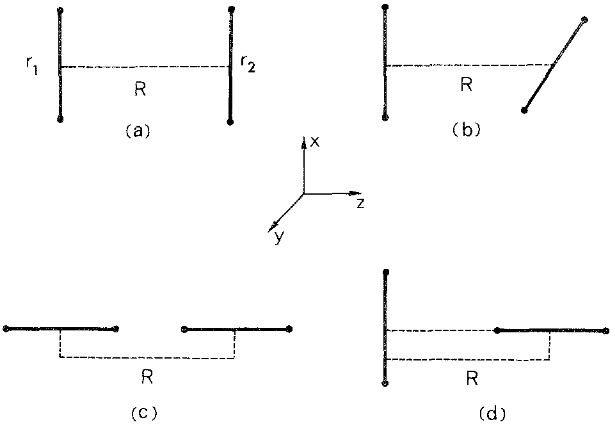

Fig. 1. Geometrical conformation, frame of reference, parameters: R intermolecular distance, r_1 and r_2 intramolecular distances

c) Calculations

A Gaussian orbital basis set has been used to expand the MO's. In this basis all the electronic many centers integrals could be calculated exactly, so that one of the most serious drawback of intermolecular calculations is taken away. We have considered twenty four Gaussian functions. Six centered on each hydrogen atom; (three of s-type and three of p-type: p_x, p_y, p_z). The rather great number of points of the energy curve to be calculated prevents any attempt to optimize the Gaussian exponents. More details concerning this basis could be found elsewhere [5]. For all geometric configurations, the same CI basis set built up from the first six supermolecule SCF-MO's is used. This number of MO's allows us to build all singly and doubly excited configurations which can be accomodated in the computer core storage; this amounts to 117 Slater determinants arranged in 45 S^2-operator eigenfunctions with $S=0$. A CI Fortran program for CDC 3600 computer has been written [7]. It needs as input, the "Basint" tape of Gaussian integrals and the SCF-MO coefficients. These inputs are directly obtained from IBMOL program [8].

3. Distance and Orientation Dependence of the Potential Energy. Results and Discussion

For all geometrical configurations the SCF energy, E_{SCF}, and the configuration interaction energy, E_{SCF-CI}, are collected in Table 1 as a function of intermolecular distance, R. This distance is expressed in units of the H_2 equilibrium distance as $L=R/r_0$. The point $L=20.0$ is calculated in order to check the behavior of the composite system at very long range distance. We remark that E_{SCF} at this distance corresponds to almost two non interacting H_2 molecules. E_{SCF} for the two isolated H_2 molecules is 2.2510089 a.u. which compares fairly well with E_{SCF} $(L=20)$ from Table 1, and it is quite independent of the different orientations. For the geometries considered: rectangular and linear, the CI calculation leads to nearly the same value of E_{SCF-CI} $(L=20)$. The imposition to MO's of a lower overall symmetry seems to play an important role in the calculation of the total energy: $2\,E_{SCF-CI}(H_2)=2.2703348$ a.u. Nevertheless the orientational independent value of E_{SCF-CI} $(L=20)$ suggests that one still have a meaningful shape for the intermolecular potential. In this calculation, this later value is taken as the energy of two almost independent molecules.

A glance at the columns of E_{SCF-CI} (Table 1) shows a very different behavior of the potential energy for the molecules orientations considered. The rectangular and perpendicular configurations do not display a characteristic minimum in the experimental Van der Waals region [9]. Our results, for the linear configuration, compare fairly well with experimental ones [9]. For the same case, Wilson *et al.* [10] do not succeded to get any minimum. The potential energy curve has a minimum located at about 3.45 Å. Gordon *et al.*, quote an experimental determined value of 3.34 Å. The dissociation energy in our scheme is equal to $E_{min}=50.5\times 10^{-23}\,J$, matching rather well the experimental value of $51.5\times 10^{-23}\,J$ [9]. The T-configuration energy curve shows a lesser depth at a larger distance $R=3.75$ Å.

These very different results, when orientation is varied, could be understood if one consider the MO's involved in the calculations. In Fig. 2, we present a MO diagram of these orbitals which shows schematically the nodal planes. For sake of simplicity two geometries are discussed: the linear and the rectangular one. In spite of the total σ-character of all MO's involved in calculations, to each one a different local symmetry can be assigned. This is indicated in the Fig. 2 using a reference frame as defined on Fig. 1. Incidentally one can see that at very

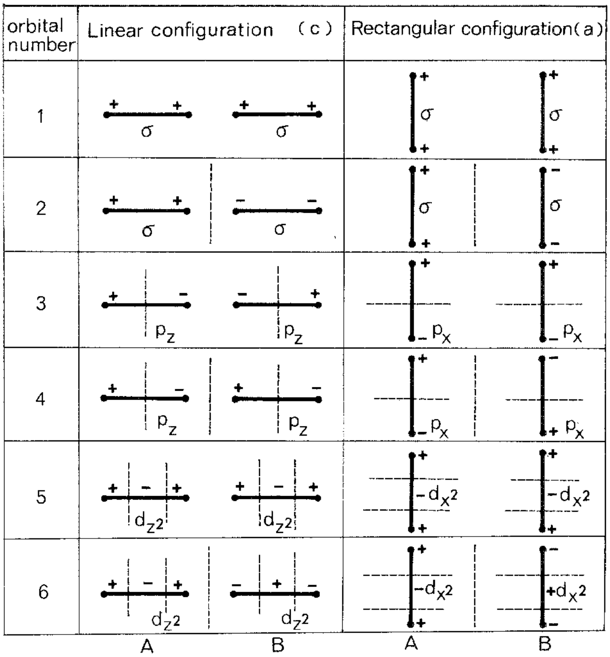

Fig. 2. Molecular orbitals diagram. For each molecular orbital local symmetry is indicated, and the nodal plane is represented by broken lines. Sign variations are indicated

long distances, where intermolecular overlaps are negligible, the linear combination of molecular orbitals taken by pairs, (1 ± 2), (3 ± 4), (5 ± 6) would give the localized MO's with local symmetry indicated on Fig. 2. Now, if we consider in $E^{(2)}$ the terms corresponding to the Van der Waals attraction between molecules, it contains, associated with the appropriate denominators, for the linear configuration, two electrons integrals of the type

$$\left\langle \sigma_A(1)\, p_{Z_A}(1) \left| \frac{1}{r_{12}} \right| \sigma_B(2)\, p_{Z_B}(2) \right\rangle$$

and

$$\left\langle \sigma_A(1)\, d_{Z_A^2}(1) \left| \frac{1}{r_{12}} \right| \sigma_B(2)\, d_{Z_B^2}(2) \right\rangle ,$$

and for the rectangular configuration

$$\left\langle \sigma_A(1)\, p_{X_A}(1) \left| \frac{1}{r_{12}} \right| \sigma_B(2)\, p_{X_B}(2) \right\rangle$$

and

$$\left\langle \sigma_A(1)\, d_{X_A^2}(1) \left| \frac{1}{r_{12}} \right| \sigma_B(2)\, d_{X_B^2}(2) \right\rangle .$$

In the region where the multipolar expansion of $1/r_{12}$ is valid, we can retain the leading dipole-dipole interaction operator $V_{dd} = \frac{1}{R^3}(X_1 X_2 + Y_1 Y_2 - 2Z_1 Z_2)$. It follows, for the second order interaction energy, that $E^{(2)}_{\text{linear}} \approx 4E^{(2)}_{\text{rectangular}}$ when we use our MO's basis set. The contributions coming from MO's, whose local symmetry allows the interaction along the direction of the intermolecular axis, and which have a higher energy than that used by us, are fundamental in order to get a Van der Waals minimum. Work is in progress to test numerically this contention.

The main point is that this kind of "frozen CI basis", which does not take into account the change of symmetry, cannot reproduce the orientational dependence of attractive intermolecular forces.

4. Internal Geometry Dependence of Intermolecular Interactions

a) Numerical Results

The success in getting a significant contribution to the interaction correlation energy for the linear configuration, allows us to undertake the study of internal geometry dependence of attractive and Pauli repulsion interaction energy. In Table 2, the values of E_{SCF} and $E_{\text{SCF-CI}}$ are given for different intermolecular distances R and the following cases: a) both molecules at equilibrium distance $r_1 = r_2 = r_0$, b) one stretched molecule $r_1 = 1.6$ a.u., for the other $r_2 = r_0$ and c) both molecules stretched $r_1 = r_2 = 1.6$ a.u. Also E_{SCF} for two isolated H_2 molecules in the three cases is indicated. The E_{SCF} for the stretched systems (b) and (c) at the distance $L = 20$ represents rather well two non interacting molecules. The three total energy curves present a minimum nearly at the same intermolecular distance. The depth of the potential is independent of the variation of the internal parameters. The SCF potential energy curve corresponds to a repulsive state between the two H_2 molecules.

The variation of interaction energy with respect to case (a) is presented in Table 3. The total interaction energy, $U_{\text{SCF-CI}}(L, r_1, r_2)$, is defined as:

$$U_{\text{SCF-CI}}(L, r_1, r_2) = E_{\text{SCF-CI}}(L, r_1, r_2) - E_{\text{SCF-CI}}(20.0, r_1, r_2). \tag{3}$$

The correlation interaction energy, $U_{\text{corr}}(L, r_1, r_2)$ is defined to be:

$$U_{\text{corr}}(L, r_1, r_2) = U_{\text{SCF-CI}}(L, r_1, r_2) - U_{\text{SCF}}(L, r_1, r_2),$$

where U_{SCF} comes from formula (3) with SCF instead of SCF-CI energies. Finally, the variation of the interaction energy $\varDelta U(L, r_1, r_2)$ is defined by the formula:

$$\varDelta U(L, r_1, r_2) = U(L, r_1, r_2) - U(L, r_0, r_0). \tag{4}$$

The comparison of $\varDelta U_{\text{SCF}}$, at a given distance L, for the cases (b) and (c) shows us that this quantity is rather additive with the number of stretched molecules. This same result was found for the rectangular and perpendicular configurations [5]. The repulsive energy increases with increased internal dimension in accordance with our previous results [5]. It is worth to note that, the additivity of repulsive energy with the number of stretched molecules is more accurately reproduced for the rectangular and perpendicular configuration than it is for the linear one. This result seems not surprising because one could expect a great electronic cloud deformation in the linear case, this obviously could shade any kind of additivity.

The new results concern the correlation interaction energy: the attractive $U_{\text{corr}}(L, r_1, r_2)$ increases with increasing values of r_1 and or r_2. A glance at Table 3 shows us that ΔU_{corr}, at a given distance, is also a roughly additive function over all the ranges studied. It seems that molecules retain a certain identity inside the composite system.

Table 1. E_{SCF} and $E_{\text{SCF-CI}}$ values for the geometrical configurations: a) rectangular, b) perpendicular, c) linear, d) T, as a function of intermolecular distance L in R/r_0 units

L	a		b		c		d	
	$-E_{\text{SCF}}$	$-E_{\text{SCF CI}}$	$-E_{\text{SCF}}$	$-E_{\text{SCF CI}}$	$-E_{\text{SCF}}$	$-E_{\text{SCF CI}}$	$-E_{\text{SCF}}$	$-E_{\text{SCF CI}}$
1.5	2.0784015	2.1007100	2.0892859	2.1059093	1.7473396	1.7869960	2.0652882	2.0837133
2.0	2.1910301	2.2114234	2.1934048	2.2121826	2.1440852	2.1732333	2.1862722	2.204925
3.0	2.2449125	2.2644072	2.2451236	2.2639088	2.2413293	2.2620255	2.2442769	2.2636663
4.0	2.2504927	2.2698157	2.2505365	2.2696830	2.2501745	2.2713600	2.2505509	2.2699905
5.0	2.2509628	2.2701892	2.2509771	2.2701715	2.2509032	2.2708407	2.2510103	2.2703179
6.0	2.2510009	2.2702014	2.2510066	2.2701994	2.2509880	2.2703126	2.2510263	2.2702342
20.0	2.2510088	2.2702012	2.2510080	—	2.2510086	2.2702011	2.2510085	—

Table 2. SCF and SCF CI energies in a.u. Variation with both, intermolecular L and intramolecular distances r_1, r_2. For comparison, E_{SCF} for two isolated H_2 molecules is indicated in the last row

L	Normal molecules $r_1 = r_2 = r_0$		One stretched molecule $r_1 = 1.6$ a.u., $r_2 = r_0$		Two stretched molecules $r_1 = r_2 = 1.6$ a.u.	
	$-E_{\text{SCF}}$	$-E_{\text{SCF-CI}}$	$-E_{\text{SCF}}$	$-E_{\text{SCF-CI}}$	$-E_{\text{SCF}}$	$-E_{\text{SCF-CI}}$
3.5	2.2481432	2.2695262	2.2414195	2.2649886	2.2346822	2.2604253
4.0	2.2501745	2.2713600	2.2437478	2.2670295	2.2373082	2.2626580
4.5	—	—	2.2444251	2.2669503	2.2381021	2.2625769
5.0	2.2509032	2.2708907	2.2446272	2.2664151	2.2383473	2.2619743
6.0	2.2509880	2.2703126	2.2447315	2.2657678	2.2384739	2.2612156
20.0	2.2510086	2.2702011	2.2447569	2.2656275	2.2385041	2.2610468
$2H_2$	2.2510089	—	2.2447561	—	2.2385043	—

Table 3. ΔU_{SCF} and correlation interaction energy ΔU_{corr}. Variation of interaction energy, with respect to the intermolecular distance L and the intramolecular distances r_1, r_2 in a.u.

L	One stretched molecule $r_1 = 1.6$ a.u., $r_2 = r_0$		Two stretched molecules $r_1 = r_2 = 1.6$ a.u.	
	ΔU_{SCF}	$-\Delta U_{\text{corr}}$	ΔU_{SCF}	$-\Delta U_{\text{corr}}$
3.5	0.01283	0.01379	0.02603	0.02746
4.0	0.00475	0.01136	0.00985	0.02215
5.0	0.00069	0.00467	0.00140	0.00923
6.0	0.00012	0.00089	0.00026	0.00181

b) Discussion

The increase of attractive intermolecular energy with the internal dimensions can be understood in terms of molecular properties of the partners, particularly their dipolar polarizabilities. Since our numerical results on the variation of attractive interaction energy with the number of stretched molecules seems to support the idea of a certain independence of the partners, and with the hypothesis that, roughly, the main contribution to the correlation interaction energy is of a second order dispersion type, U_{corr} can be represented by the London term $U_{\text{corr}} \approx -C^{(6)}_{H_2-H_2}/R^6$. The $C^{(6)}$ coefficient being intimately connected with dipolar-polarizabilities. Proceeding with the Slater-Kirkwood formula, one gets the expression

$$-U_{\text{corr}}R^6 \approx \tfrac{3}{4}\bar{E}\alpha_{H_2} \cdot \alpha_{H_2}, \tag{5}$$

where $\bar{E}$ is an average excitation energy and α the polarizability of isolated molecules. Ishiguro *et al.*, studied the variation of polarizabilities with interatomic distance for the H_2 molecule [11]. They found that α_{H_2} is an increasing function of interatomic distance. Formula (5) shows that, at a given distance, U_{corr} must increase with internal dimensions. This behavior prompts a qualitative picture. When bonds are formed, electrons flow to the interatomic region and become tightly bound, exactly the opposite is going on when atoms are stretched from their equilibrium positions. The molecule become larger and more easily polarizable. But if this is so, in a given point of space, between the interacting molecules, the electron density increases when one (or both) molecule (*s*) is stretched, then, the Pauli repulsion energy increases. This picture seems to be in agreement with the numerical results obtained on calculations of this type of forces [4, 5].

Acknowledgements. The authors would like to thank Professor S. Bratos for several suggestions and helpful discussions. The computer time for this work was supported by the C.M.O.A. of Paris, and Professor R. Daudel, Director of this Laboratory, is much acknowledged.

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