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Dispersion Interaction Between Two Hydrogen Molecules

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Abstract We have adapted the theory of Boehm-Yaris [J. Chem. Phys. 55, 2620 (1971)] and Jacobi-Csanak [Chem. Phys. Lett. *30*, 367 (1975)] to the calculation of the dispersion energy of a system of two linear molecules. The angle-dependent parts of the Born amplitudes are represented by real spherical harmonics. Our results are analytical for any intermolecular distance and their asymptotic behavior reproduces the corresponding usual dispersion energy. In the intermediary region ($3.0\ a_0 \lesssim R < 8.0\ a_0$) our curves decrease much more slowly than the corresponding curves of the usual dispersion energy.

1. INTRODUCTION

A good understanding of the macroscopic characteristics of a given substance may be obtained by the knowledge of the inter-molecular potential energy, $V^{(I)}$, of the system made up by two of its molecules. This energy is given by the expression[1]

$$V^{(I)} = E^{(T)} - 2E^{(L)} , \tag{1}$$

where $E^{(T)}$ is the system's total energy when the molecules centers are separated by a finite distance R, and $2E^{(L)}$ is the system's binding energy when its molecules are infinitely separated.

For the H_2-H_2 system the interaction energy consists in three parts[2]

$$V^{(I)} = V^{(\mathrm{val})} + V^{(Q,Q)} + V , \tag{2}$$

where $V^{(\mathrm{val})}$ is the valence (or chemical) energy due to the superposition of the wave functions of the two molecules, $V^{(Q,Q)}$ the electrostatic interaction energy between the two quadrupoles formed by the molecular charges and V the dispersion energy (due to the correlation between the electrons of distinct molecules).

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The techniques most often used in the calculation of inter-molecular potentials frequently involve a perturbation theory. In particular, for H_2-H_2 system the calculation methods have been continuously improved. Dèboer[3] used the perturbation method, neglecting some multiple center integrals and was followed by Margenau and Evett[4] with an approximation including all integrals. Later, Mason and Hirschfelder[1] published more efficient methods for multi-center-integral calculations and made new developments related to H_2-H_2 interaction. Kochanski and Gouyet[5] improved the integral calculation still more, including bi-orthogonal orbital treatments.

The valence and electrostatic energies may be obtained together by first order calculations, while the dispersion energy is due to second order contributions[2].

For two linear molecules with non-overlapping charge distributions, the perturbation theory, by a multipolar expansion, supplies the following result for the dipole-dipole term of the dispersion energy[2,6]

$$W_{d,d} = -\frac{1}{R^6}\{(C_{10,10} - C_{10,11} - C_{11,10} + C_{11,11})\left[\text{sen}\,\Theta_1\,\text{sen}\,\Theta_2\cos(\phi_2-\phi_1) - 2\cos\Theta_1\cos\Theta_2\right]^2 + 3(C_{10,11} - C_{11,11})\cos^2\Theta_1$$

$$+ 3(C_{11,10} - C_{11,11})\cos^2\Theta_2 + (C_{10,11} + C_{11,10} + 4C_{11,11})\}\ , \qquad (3)$$

where Θ_i and ϕ_i $(i=1,2)$ are the angles assigned in fig. 1 and $C_{\ell_1 m_1,\ell_2 m_2}$ dispersion coefficients defined in terms of the dynamicpolarizabilities $\alpha^{(k)}_{\ell_k m_k}$ as[6]

$$C_{\ell_1 m_1,\ell_2 m_2} \equiv \frac{1}{2\pi}\int du\ \alpha^{(1)}_{\ell_1 m_1}(iu)\,\alpha^{(2)}_{\ell_2 m_2}(iu)\ . \qquad (4)$$

Using a spherical tensor formalism, Piecuch[7] recently studied long range intermolecular interactions in all perturbation orders. Stone and Tough[8], also, published general expressions for the several contributions to the dispersion energy for a pair of molecules is terms of spherical tensor components. These authors expressed the dependence of

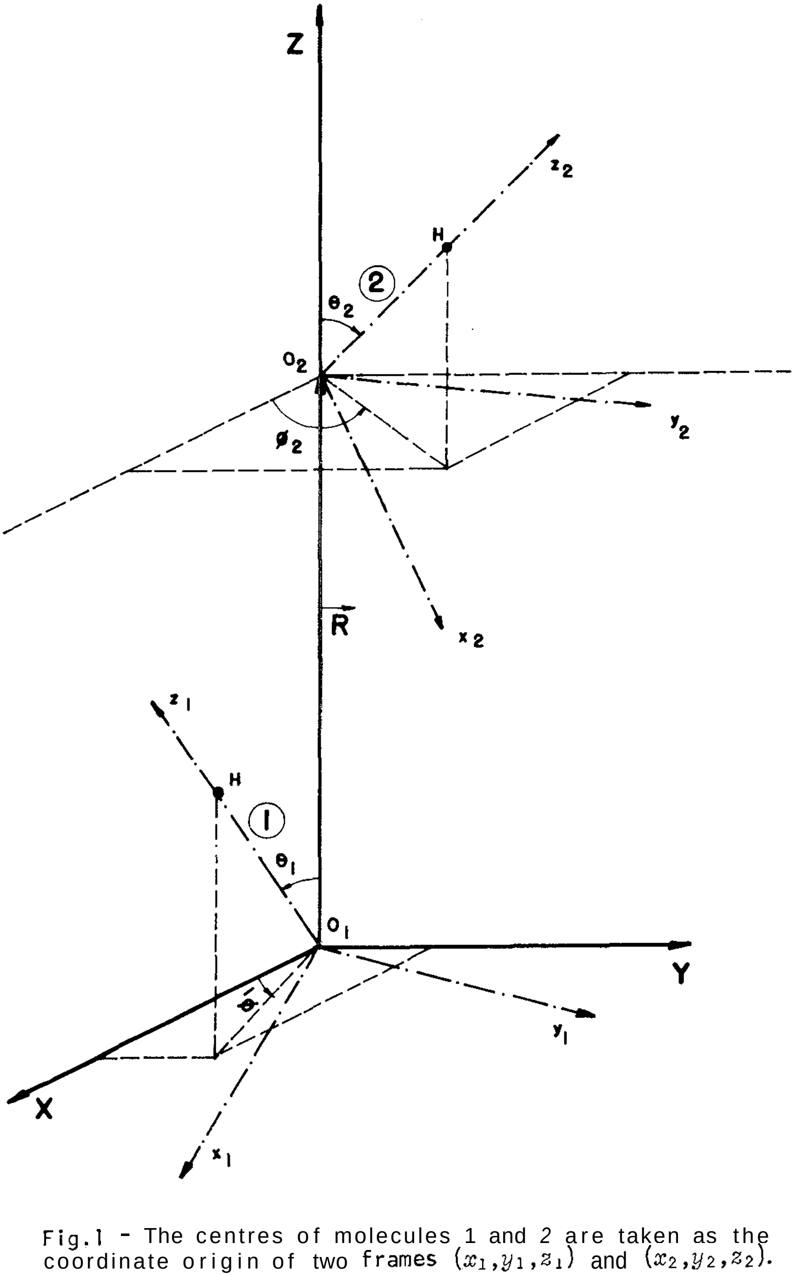

Fig.1 - The centres of molecules 1 and 2 are taken as the coordinate origin of two frames (x_1,y_1,z_1) and (x_2,y_2,z_2). (XYZ) is a fixed laboratory frame. Two rotations described by the Euler angles $(\phi_1,\theta_1,0)$ and $(\phi_2,\theta_2,0)$ align these molecule-attached frames to the fixed one.

the interaction with the molecular orientation in terms of scalar expansion functions, denoted by $S^{k_1k_2}_{\ell_1\ell_2 j}$. For the principal dispersion energy term, of a system formed by two linear molecules, the Stone-Tough formalism furnishes a result equivalent to eq. (3).

In eq. (3) $V \to -\infty$ when $R \to 0$. Then, that potential cannot be applied for interacting molecules separated by small distances. This undesirable behaviour can be avoided by introduction a damping factor such that the potential becomes negligible for small R[9,10]. There is, also, a possibly more rational alternative, that will be adapted to the case in our work: the analytical technique of Jacobi-Csanak[11].

2. THE METHOD

The Jacobi-Csanak technique deals with the dispersion interaction between two closed-shell atoms and was used by its authors in analysing the principal term of the dispersion potential of two identical atoms (He-He). Through an immediate generalization of this technique, we recently studied the dispersion interaction between two different closed-shell atoms (He-Ne)[12] and between an atom and a linear molecule (He-H_2)[13].

The purpose of this paper is to extend the Jacobi-Csanak technique to the dispersion energy study in the system made up by two linear molecules. That energy will be obtained through the equation[11,14]

$$V = -\frac{1}{2\pi^5}\int d\vec{q}\,d\vec{q}\,'\,\frac{e^{i\vec{q}\cdot\vec{R}}}{q^2}\,\frac{e^{i\vec{q}\,'\cdot\vec{R}}}{q'^2}\sum_{\bar{n}_1\neq\bar{0}_1}\sum_{\bar{n}_2\neq\bar{0}_2}\Big[g_{\bar{n}_1,\bar{n}_2}F^*_{\bar{n}_1}(-\vec{q})F_{\bar{n}_1}(\vec{q}\,')F^*_{\bar{n}_2}(\vec{q})F_{\bar{n}_2}(-\vec{q}\,')\Big] \qquad (5)$$

with

$$g_{\bar{n}_1,\bar{n}_2} = \int_0^\infty du\,\frac{W_{\bar{n}_1}}{W^2_{\bar{n}_1}+u^2}\cdot\frac{W_{\bar{n}_2}}{W^2_{\bar{n}_2}+u^2} \qquad (6)$$

($W_{\bar{n}_j} = E_{\bar{n}_j} - \varepsilon_{\bar{0}}$ are excitation energies), where $F_{\bar{n}_1}(\vec{q})$ and $F_{\bar{n}_2}(\vec{q})$ are Born amplitudes, referring respectively to the axis-systems (x_1, y_1, z_1)

and (x_2,y_2,z_2) of fig. 1. Here $\bar{n} \equiv (n,\ell,m)$.

Since it is convenient to make the calculation in the laboratory frame (where $\vec{R}$ is a fixed vector) it is necessary to transform the coordenates of $F_{\bar{n}_1}(\vec{q})$ and $F_{\bar{n}_2}(\vec{q})$ of references frames (x_1,y_1,z_1) and (x_2,y_2,z_2) to (XYZ) by suitable rotation operations.

On the other hand, since in linear molecules the electrical charge distribution is not spherically symmetric, we must conveniently change the factorization[15,11]

$$F_{\bar{n}}(\vec{q}) = F_{n\ell}(q)\; Y_{\ell m}(\hat{q}) \;, \tag{7}$$

which is applicable only to spherical symmetric systems. Here $Y_{\ell m}(\hat{q})$ is an usual spherical harmonic. The *radial part* of the Born amplitude $F_{n\ell}(q)$ is given by[15]

$$F_{n\ell}(q) = 4\pi\, i^{\ell} \sum_{j=1}^{N} \int \psi_{\bar{n}}^{*}(x) j_{\ell}(q\hat{r}_j) Y_{\ell m}(\hat{r}_j) \psi_{\bar{0}}(x)\, d\tau \quad . \tag{8}$$

In eq. (8) $\psi_{\bar{n}}$ and $\psi_{\bar{0}}$ are, respectively, the wave functions of the excited and ground states of a molecule with N electrons and j_ℓ is a spherical Bessel function of order ℓ.

Since real spherical harmonics form an adequate basis for symmetrical operation groups in molecules with only one principal axis[16], we introduce those functions to represent the angular part of the Born amplitudes in linear molecules**. In terms of usual spherical harmonics they are defined as

$$y_{\ell m}(\hat{q}) = \begin{cases} \frac{1}{2}\left[(-)^m Y_{\ell m}(\hat{q}) + Y_{\ell,-m}(\hat{q})\right] \equiv \bar{y}_{\ell m}(\hat{q}) \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{for } m>0 \\ -\frac{i}{\sqrt{2}}\left[(-)^m Y_{\ell m}(\hat{q}) - Y_{\ell,-m}(\hat{q})\right] \equiv \bar{\bar{y}}_{\ell m}(\hat{q}) \end{cases} \tag{9a}$$

and

$$y_{\ell 0}(\hat{q}) = Y_{\ell 0}(\hat{q}) \; . \tag{9b}$$

So, choosing coordinates in accordance with the geometry indicated in fig. 1 and using, for the Born amplitudes, the factorization[13,17]

$$F_{\bar{n}}(\vec{q}) = F_{n\ell}(q)\, y_{\ell m}(\hat{q}) \ , \tag{10}$$

it follows from eq. (5) that

$$V = -\frac{1}{2\pi^5}\int d\vec{q}\, d\vec{q}\,'\, \frac{e^{i\vec{q}.\vec{R}}}{q^2}\,\frac{e^{i\vec{q}\,'.\vec{R}}}{q'^2} \sum_{\bar{n}_1\neq\bar{0}_1}\ \sum_{\bar{n}_2\neq\bar{0}_2} \Big[(-)^{\ell_1+\ell_2}\, g_{\bar{n}_1,\bar{n}_2}$$

$$\times\ F^*_{n_1\ell_1}(q)F^*_{n_2\ell_2}(q)F_{n_1\ell_1}(q')F_{n_2\ell_2}(q')\,y^{(1)}_{\ell_1 m_1}(\hat{q})\,y^{(2)}_{\ell_2 m_2}(\hat{q})\,y^{(1)}_{\ell_1 m_1}(\hat{q}')\,y^{(2)}_{\ell_2 m_2}(\hat{q}')\Big] \tag{11}$$

where the upper indices 1 and 2 are used to denote that, referring to the coordinate system (XYZ), it is necessary to express the angular parts of the Born amplitudes for the molecules ① and ② (affected as they are by the rotation operations) in terms of angles measured in this reference frame. This can be accomplished by the following rotations[19]

$$Y^{(1)}_{\ell_1 m_1} = \sum_{m_1'} D^{\ell_1}_{m_1' m_1}(\phi_1,\Theta_1,0)\,Y_{\ell_1 m_1'}$$

and

$$Y^{(2)}_{\ell_2 m_2} = \sum_{m_2'} D^{\ell_2}_{m_2' m_2}(\phi_2,\Theta_2,0)\,Y_{\ell_2 m_2'} \tag{12}$$

with the angles of $Y_{\ell_1 m_1'}(\hat{q})$ and $Y_{\ell_2 m_2'}(\hat{q})$ measured in the (XYZ) reference frame. In this equation $D^{\ell}_{m'm}$ are elements of the Wigner finite rotation matrices. In this paper the Euler angles ϕ_1 and Θ_1 (ϕ_2 and Θ_2) establish the direction of the axis $o_1\, z_1$ ($o_2\, z_2$) with respect to the vector $\vec{R}$ (see fig.1).

On the other hand, taking

$$V = \sum_{\substack{\ell_2,m_2\\ \ell_1,m_1}} V_{\ell_1 m_1,\ell_2 m_2} \qquad (m_1 \geqslant 0,\ m_2 \geqslant 0) \tag{13}$$

and considering that in the (XYZ) reference frame

$$e^{i\vec{q}.\vec{R}}\, e^{i\vec{q}\,'.\vec{R}} = \sum_{L,L'} i^{L+L'}\,(4\pi)\sqrt{(2L+1)\,(2L'+1)}\,j_L(q'R)\,j_{L'}(qR)\,Y_{L0}(\hat{q}')\,Y_{L'0}(\hat{q})$$

we have

$$V_{\ell_1 m_1,\ell_2 m_2} = -\sum_{n_1,n_2,L,L'} H^{L,L'}_{n_1 n_2}(R)\int d\hat{q}'\, y^{(1)}_{\ell_1 m_1} y^{(2)}_{\ell_2 m_2}\, Y_{LO}\int d\hat{q}\, y^{(1)}_{\ell_1 m_1}\, y^{(2)}_{\ell_2 m_2} Y_{L'O} \tag{14}$$

where

$$H^{L,L'}_{n_1,n_2}(R) = \frac{1}{2\pi^5}\left\{(-)^{\ell_1+\ell_2} i^{L+L'}\, g_{n_1\ell_1,n_2\ell_2}\ (4\pi)\ \sqrt{(2L+1)(2L'+1)}\ I^{(L,L')}_{n_1\ell_1,n_2\ell_2}(R)\right. \tag{15}$$

with

$$I^{(L,L')}_{n_1\ell_1,n_2\ell_2}(R) = \int dq'\, j_L(q'R)\, F_{n_1\ell_1}(q')F_{n_2\ell_2}(q')\int dq\, j_{L'}(qR)F^*_{n_1\ell_1}(q)F^*_{n_2\ell_2}(q) \tag{16}$$

In the present paper, we will calculate only the principal term of the dispersion interaction, However, eqs. (13-(16) can also be applied to other contributions.

Our calculations are performed in atomic units: a.u. of length (bohr) = $a_0 = 4\pi\varepsilon_0\hbar^2/(m_e e^2) = 5.2917\times10^{-11}$m; a.u. of energy (hartree) $E_h = \hbar^2/(m_e a_0^2) \approx 4.35981\times10^{-18}\ J$.

3. CALCULATION

The principal term (dipole-dipole) is obtained by taking in eq. (13) $\ell_1 = \ell_2 = 1$

$$V_{d,d} = V_{10,10} + V_{10,11} + V_{11,10} + V_{11,11} \tag{17}$$

A) Calculation of $V_{10,10}$

From eqs. (14), (9b) and (15) we obtain

$$V_{10,10} = -\frac{1}{2\pi^5}\sum_{\substack{L,L'\\ s_1 s_2}} i^{L+L'}\, g_{s_1 1,s_2 1}\ I^{(L,L')}_{s_1 1,s_2 1}\, f^{(L,L')}_{10,10} \tag{18}$$

where

$$f^{(L,L')}_{10,10} = (4\pi)\sqrt{(2L+1)(2L'+1)}\int d\hat{q}'\, Y^{(1)}_{10}\, Y^{(2)}_{10}\, Y_{L0}\int d\hat{q}\, Y^{(1)}_{10}\, Y^{(2)}_{10}\, Y_{L'0}\,. \quad (19)$$

On the other hand, from eq. (12) we have

$$\begin{aligned} Y^{(k)}_{10} = {} & \left[-\frac{\sqrt{2}}{2}\,\mathrm{sen}\,\Theta_k\, e^{-i\phi_k}\right] Y_{1,1}(\hat{q}) + (\cos\Theta_k)\, Y_{10}(\hat{q}) \\ & + \left[\frac{\sqrt{2}}{2}\,\mathrm{sen}\,\Theta_k\, e^{i\phi_k}\right] Y_{1,-1}(\hat{q}) \end{aligned} \quad (20)$$

where k = 1, 2 and $\hat{q}$ represent the angles that specify the direction of the vector $\vec{q}$ in the XYZ axis system. Moreover, using eqs. (20) and (19) and the relation (4.34) of reference 19, we conclude that $f^{(L,L')}_{10,10} \neq 0$ only for $L = 0, 2$ and L' = 0, 2. Then, weobtain the results (B2), (B3) and (B4) (see appendix B).

Moreover, from eq. (18) it follows that

$$\begin{aligned} V_{10,10} = -\frac{1}{2\pi^5}\sum_{s_1,s_2} g_{s_1 1,s_2 1}\Big[& I^{(0,0)}_{s_1 1,s_2 1}\, f^{(0,0)}_{10,10} - \Big\{ I^{(0,2)}_{s_1 1,s_2 1} \\ & + I^{(2,0)}_{s_1 1,s_2 1}\Big\} f^{(0,2)}_{10,10} + I^{(2,2)}_{s_1 1,s_2 1}(R)\, f^{(2,2)}_{10,10}\Big] \end{aligned} \quad (21)$$

Now, we will make use of the approxirnation where the *radial part* of the Born amplitude [eq. (8)] is replaced (for $\ell=1$) by the principal term of the corresponding series of Csanak-Taylor[15]

$$F_{s1}(q) = \alpha^6\, D_s\, \frac{q}{(a' + q^2)^3}\,, \quad (22)$$

where (in a.u.)

$$\alpha = \sqrt{2I} + \sqrt{2(I-W)} \quad (23)$$

(I being the ionization energy of the molecule and W one of its excitation energies) and D_s is the transition dipolar coefficient, directly related to the corresponding oscillator strength $f_{s\ell m}$ (for $\ell=1$ and $m=0$)

by[17]

$$|D_s|^2 = \frac{2\pi}{3}\,\frac{f_{s10}}{W_{s1}} \; . \qquad (24)$$

Introducing eq.(22) in eq.(16) (with L = L' = 0, L = 0 and L'= = 2 and L = 2 and L' = 0, L = L' = 2) and substituting the results into eq.(21) we have

$$V_{10,10} = -\frac{\alpha^{24}}{8\pi^3}\left(\sum_{s_1,s_2} g_{s_11,s_21}\,|D_{s_1}|^2\,|D_{s_2}|^2\right)\Big[(K^{(0)}(R))^2 f^{(0,0)}_{10,10}$$

$$- 2K^{(0)}(R)\,K^{(2)}(R)\,f^{(0,2)}_{10.10} + (K^{(2)}(R))^2\,f^{(2,2)}_{10,10}\Big] \; , \qquad (25)$$

where

$$K^{(L)}(R) = \frac{2}{\pi}\int_0^\infty dq \;\; j_L(qR)\,\frac{q^2}{(\alpha^2+q^2)^6} \qquad (L = 0,\ 2)\; . \qquad (26)$$

On the other hand, using eqs. (6) and (24), defining the frequency-dependent polarizabities as[20]

$$\alpha_{\ell m} = \sum_n \frac{f_{n\ell m}}{W^2_{n\ell} - \omega^2} \qquad (27)$$

and introducing the dispersion coefficients by eq.(4), we have

$$\sum_{s_1,s_2} g_{s_11,s_21}\;|D_{s_1}|^2|D_{s_2}|^2 = \frac{8\pi^3}{9}\,C_{10,10} \; . \qquad (28)$$

Then, eq.(25) takes the final form (B1).

B) Calculation of V,,,,,

In this case, we take in eq.(14) $m_1 = 0$ and R, = $\ell_2 = m_2 = 1$. Then, using the procedures and definitions of the preceding sub- section and the relations''

$$\bar{y}_{11}^{(k)} = \left(-\frac{\sqrt{2}}{2}\cos\Theta_k\, e^{-i\phi_k}\right) Y_{11}(\hat{q}) + (-\text{sen}\,\Theta_k)\, Y_{10}(\hat{q})$$
$$+\left(\frac{\sqrt{2}}{2}\cos\Theta_k\, e^{i\phi_k}\right) Y_{1,-1}(\hat{q}) \qquad (29)$$

and

$$\bar{\bar{y}}_{11}^{(k)} = \left(i\,\frac{\sqrt{2}}{2}\, e^{-i\phi_k}\right) Y_{11}(\hat{q}) + \left(i\,\frac{\sqrt{2}}{2}\, e^{i\phi_k}\right) Y_{1,-1}(\hat{q}) \qquad (30)$$

we obtain eq. (B5).

Calculation of $V_{11,10}$ and $V_{11,11}$

Starting from eq. (14) and working in the same way as we did in the previous cases, eqs. (B9)-(B16) result.

It is worth noting that the coefficients $C_{\ell_1 m_1, \ell_2 m_2}$ in eqs. (B1), (B5), (B9) and (813) are obtained from eq. (4) and that the functions $K^{(L)}(R)$ (L = 0,2) are given by eqs. (A1) and (A2).

D) Application to the H_2-H_2 system

For sufficiently large values of R, it results from eqs.(A1) and (A2) that

$$K^{(0)}(R) \to 0 \quad \text{and} \quad K^{(2)}(R) \to 3/(\alpha^{12} R^3) \ .$$

Introducing these limits into eqs. (B1), (B5), (B9) and (B13) and substituting the results thus obtained into eq. (17) we have

$$W_{d,d} = -\frac{1}{R^6}\left[C_{10,10}\, f_{10,10}^{(2,2)} + C_{10,11}\, f_{10,11}^{(2,2)} + C_{11,10}\, f_{11,10}^{(2,2)} + C_{11,11}\, f_{11,11}^{(2,2)}\right] \qquad (31)$$

where we have used the letter W to indicate the form of our energy in the asymptotic region.

We note that the usual form of the dispersion energy of a system of two linear molecules can be reproduced by substituting in eq. (31) the results contained in eqs. (B4), (B8), (812) and (B16).

In figures 2, 3, 4 and 5 we show a summary of our results for four different relative orientations from two hydrogen molecules. We have selected two different values for the a parameter: 1.370 a.u. (corresponding with the $X \rightarrow D$ transition) and 1.549 a.u. (referring to the average excitation energy, calculated by Victor and Dalgarno[21]). As dispersion coefficients we use those of Meyer[20]: $C_{10,10} =$ $= 2.972$ a.u., $C_{10,11} = C_{11,10} = 2.189$ a.u. and $C_{11,11} = 1.620$ a.u.. In the same figures we also show the corresponding values of the usual dispersion energy [eq.(3)].

4. ANALYSIS OF THE RESULTS

From figures 2, 3, 4 and 5 we deduce that:

a) In the asymptotic region ($R \geqslant 8.0\ a_0$) the dependence of our results relative to the parameter a is negligible.

b) In the intermediate region ($3.0\ a_0 \lesssim R < 8.0\ a_0$) our curves decrease in value far more slowly than the corresponding graphs for the usual dispersion energy and the dependence of our results on the parameter a is no longer negligible. This dependence grows continuously with decreasing values of R.

c) The dependence of our results on the angles (θ_1,ϕ_1) and (θ_2,ϕ_2) which establish the relative orientation of the two molecules is fairly accentuated. For example, from the comparison of the figures 2 and 5 for a = 1.370 a.u. and $R = 6.0\ a_0$, we have

$$\frac{V_{d,d}\ (\text{fig.2})}{V_{d,d}\ (\text{fig.5})} = 1.2\ .$$

On the other hand, it is easy to verify that eqs. (17), (B1), (B5), (B9) and (B13) are analytical for all R-values and that they reduce to the usual values in the asymptotic region. In this way, our results may be useful in the study of problems such as molecule-molecule scattering and equations of state of compressed solid hydrogen

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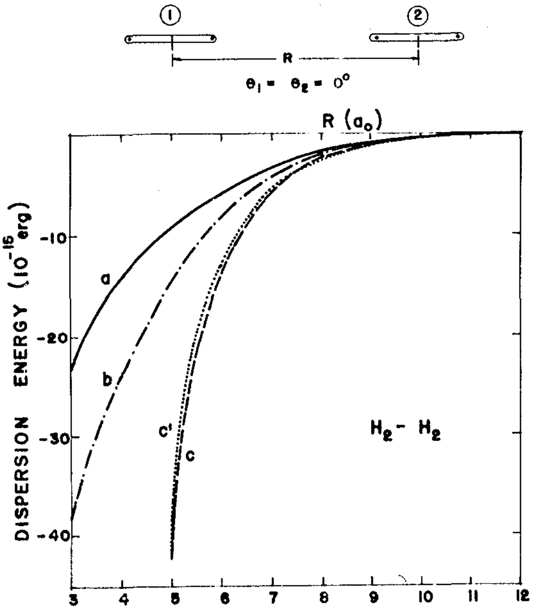

Fig.2 - **(a)** Values of $V_{d,d}(\vec{R})$ [eq.(17)] for α=1.370 a.u. and $\theta_1=\theta_2=0^0$. (b) The same as item (a) a =1.549 a.u.. (c) Values of $W_{d,d}(\vec{R})$ [eq.(3)] for $\theta_1=\theta_2 = 0^0$. (c') The same as item (c) but with those coefficients calculated in ref.6.

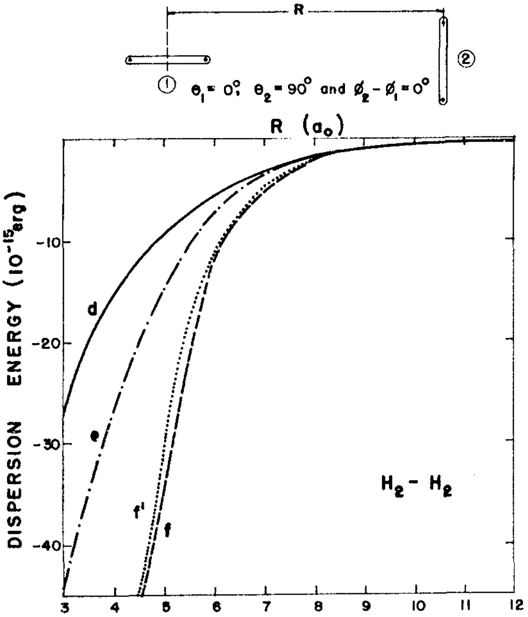

Fig.3 - (d) Values of $V_{d,d}(\vec{R})$ [eq.(17)] for a = 1.370 a.u., $\theta_1=0^0$, $\theta_2=90^0$ and $\phi_2-\phi_1 = 0^0$. (e) The same as item (d) for a = 1.549 a.u.. (f) Values of $W_{d,d}(\vec{R})$ [eq. (3)] for $\theta_1 = 0^0$, $\theta_2 = 90^0$ and $\phi_2-\phi_1= 0^0$. (f') The same as item (f) but with those coefficients calculated in ref. 6.

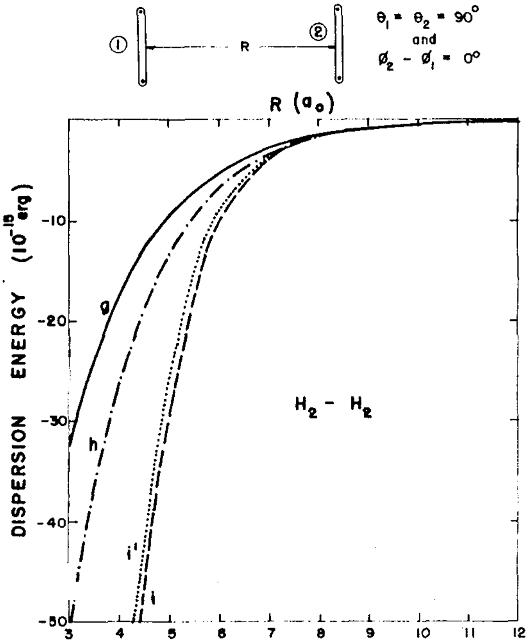

Fig.4 - (g) Values of $V_{d,d}(\vec{R})$ [eq.(17)] for a=1.370 a.u., $\theta_1=\theta_2=90^0$ and $\phi_2-\phi_1=0^0$. (h) The same as item (g) for α = = 1.549 a.u.. (i) Values of $W_{d,d}(\vec{R})$ [eq.(3)] for $\theta_1=\theta_2$ = = 90^0 and $\phi_2-\phi_1=0^0$. (i') The same as item (i) but with those coefficients calculated in ref.6.

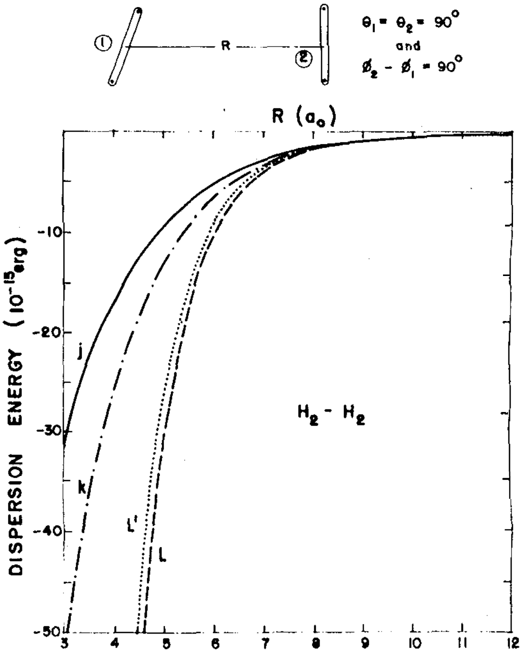

Fig.5 - (j) Values of $V_{d,d}(\vec{R})$ [eq. (17)] for α = 1.370 a.u., $\theta_1=\theta_2=90^0$ and $\phi_2-\phi_1=90^0$. (k) The same as item (j) for a = = 1.549 a.u.. (L) Values of $W_{d,d}(\vec{R})$ [eq.(3)] for $\theta_1=\theta_2$ = = 90^0 and $\phi_2-\phi_1=90^0$. (L') The same as item (L) butwith those coefficients calculates in ref. 6.

APPENDIX A – Integrals $K^{(L)}(R)$

From the calculation of integrals defined in eq. (26), the following expressions result[11,17]

$$K^{(0)}(R) = \frac{e^{-\alpha R}}{\alpha^9} P_4(\alpha R) , \tag{A1}$$

where

$$P_4(\alpha R) = \frac{1}{256}\left[7 + 7 (\alpha R) + 3 (\alpha R)^2 + \frac{2}{3} (\alpha R)^3 + \frac{1}{15} (\alpha R)^4\right] ,$$

and

$$K^{(2)}(R) = \frac{3}{\alpha^{12} R^3}\left[1 - e^{-\alpha R} P_7(\alpha R)\right] \tag{A2}$$

with

$$P_7(\alpha R) = 1 + (\alpha R) + \frac{1}{2} (\alpha R)^2 + \frac{1}{6} (\alpha R)^3 + \frac{1}{24} (\alpha R)^4 + \frac{31}{3840} (\alpha R)^5 + \frac{13}{11520} (\alpha R)^6 + \frac{1}{11520} (\alpha R)^7 .$$

APPENDIX B – Summary of our results

We obtain the following results for the $V_{\ell_1 m_1, \ell_2 m_2}$ terms indicated in eq. (17). We have

$$V_{10,10} = -\frac{C_{10,10}}{9} \alpha^{24}\Big[(K^{(0)}(R))^2 f^{(0,0)}_{10,10} - (2K^{(0)}(R)K^{(2)}(R)) f^{(0,2)}_{10,10} + (K^{(2)}(R)^2 f^{(2,2)}_{10,10}\Big] \tag{B1}$$

where

$$f^{(0,0)}_{10,10} = (\cos\Theta_1 \cos\Theta_2 + \text{sen}\,\Theta_1\, \text{sen}\,\Theta_2 \cos(\phi_2 - \phi_1))^2 , \tag{B2}$$

$$f^{(0,2)}_{10,10} = f^{(2,0)}_{10,10} = - \Big[(\cos\Theta_1 \cos\Theta_2 + \text{sen}\,\Theta_1\, \text{sen}\,\Theta_2 \cos(\phi_2 - \phi_1)) \times (-2 \cos\Theta_1 \cos\Theta_2 + \text{sen}\,\Theta_1\, \text{sen}\,\Theta_2 \cos(\$2\ \phi_1))\Big] \tag{B3}$$

and

$$f^{(2,2)}_{10,10} = (-2\cos\Theta_1 \cos\Theta_2 + \text{sen}\,\Theta_1\, \text{sen}\,\Theta_2 \cos(\phi_2-\phi_1))^2 . \qquad \text{(B4)}$$

Also,

$$V_{10,11} = -\frac{C_{10,11}}{9}\,\alpha^{24}\Big[(K^{(0)}(R))^2 f^{(0,0)}_{10,11} - (2K^{(0)}(R)K^{(2)}(R))f^{(0,2)}_{10,11}$$

$$+ (K^{(2)}(R))^2 f^{(2,2)}_{10,11}\Big] , \qquad \text{(B5)}$$

with

$$f^{(0,0)}_{10'11} = \Big[(\text{sen}\,\Theta_1 \cos\Theta_2 \cos(\phi_2-\phi_1) - \cos\Theta_1\, \text{sen}\,\Theta_2)^2 + (\text{sen}\,\Theta_1\, \text{sen}(\phi_2-\phi_1))^2\Big], \qquad \text{(B6)}$$

$$f^{(0,2)}_{10,11} = f^{(2,0)}_{10,11} = -\Big[(-\cos\Theta_1\, \text{sen}\,\Theta_2 + \text{sen}\,\Theta_1 \cos\Theta_2 \cos(\phi_2-\phi_1))(2\cos\Theta_1\, \text{sen}\,\Theta_2$$

$$+ \text{sen}\,\Theta_1 \cos\Theta_2 \cos(\phi_2-\phi_1)) + (\text{sen}\,\Theta_1\, \text{sen}(\phi_2-\phi_1))^2\Big] \qquad \text{(B7)}$$

and

$$f^{(2,2)}_{10,11} = -(\text{sen}\,O,\ \text{sen}\,O,\ \cos(\phi_2-\phi_1) - 2\cos 0,\ \cos\Theta_2)^2 + 3\cos^2 0_1 + 1 , \qquad \text{(B8)}$$

We also have

$$V_{11,10} = -\frac{C_{11,10}}{9}\,\alpha^{24}\Big[(K^{(0)}(R))^2 f^{(0,0)}_{11,10} - (2K^{(0)}(R)K^{(2)}(R))f^{(0,2)}_{11,10}$$

$$+ (K^{(2)}(R))^2 f^{(2,2)}_{11,10}\Big] , \qquad \text{(B9)}$$

where

$$f^{(0,0)}_{11,10} = (\cos\Theta_1\, \text{sen}\,\Theta_2 \cos(\phi_2-\phi_1) - \text{sen}\,\Theta_1 \cos\Theta_2)^2 + (\text{sen}\,\Theta_2\, \text{sen}(\phi_2-\phi_1))^2 , \qquad \text{(B10)}$$

$$f^{(0,2)}_{11,10} = -\Big[(\cos\Theta_1 \operatorname{sen}\Theta_2 \cos(\phi_2-\phi_1) - \operatorname{sen}\Theta_1 \cos\Theta_2)$$

$$\times (\cos\Theta_1 \operatorname{sen}\Theta_2 \cos(\phi_2-\phi_1) + 2 \operatorname{sen}\Theta_1 \cos\Theta_2) \qquad \text{(B11)}$$

$$+ (\operatorname{sen}\Theta_2 \operatorname{sen}(\phi_2-\phi_1))^2\Big]$$

and

$$f^{(2,2)}_{11,10} = -(\operatorname{sen}\Theta_1 \operatorname{sen}\Theta_2 \cos(\phi_2-\phi_1) - 2\cos\Theta_1 \cos\Theta_2)^2 + 3\cos^2\Theta_2 + 1. \qquad \text{(B12)}$$

Finally we have

$$V_{11,11} = -\frac{C_{11,11}}{9}\alpha^{24}\Big[(K^{(0)}(R))^2 f^{(0,0)}_{11,11} - (2K^{(0)}(R)K^{(2)}(R)) f^{(0,2)}_{11,11}$$

$$+ (K^{(2)}(R))^2 f^{(2,2)}_{11,11}\Big], \qquad \text{(B13)}$$

$$f^{(0,0)}_{11,11} = (\cos\Theta_1 \cos\Theta_2 \cos(\phi_2-\phi_1) + \operatorname{sen}\Theta_1 \operatorname{sen}\Theta_2)^2 + (\cos\Theta_1 \operatorname{sen}(\phi_2-\phi_1))^2$$

$$+ (\cos\Theta_2 \operatorname{sen}(\phi_2-\phi_1))^2 + \cos^2(\phi_2-\phi_1), \qquad \text{(B14)}$$

$$f^{(0,2)}_{11,11} = -\Big[(\cos\Theta_1 \cos\Theta_2 \cos(\phi_2-\phi_1) + \operatorname{sen}\Theta_1 \operatorname{sen}\Theta_2)$$

$$\times (\cos\Theta_1 \cos\Theta_2 \cos(\phi_2-\phi_1) - 2 \operatorname{sen}\Theta_1 \operatorname{sen}\Theta_2) \qquad \text{(B15)}$$

$$+ (\cos\Theta_1 \operatorname{sen}(\phi_2-\phi_1))^2 + (\cos\Theta_2 \operatorname{sen}(\phi_2-\phi_1))^2 + \cos^2(\phi_2-\phi_1)\Big]$$

and

$$f^{(2,2)}_{11,11} = (\operatorname{sen}\Theta_1 \operatorname{sen}\Theta_2 \cos(\phi_2-\phi_1) - 2\cos\Theta_1 \cos\Theta_2)^2$$

$$- 3\cos^2\Theta_1 - 3\cos^2\Theta_2 + 4. \qquad \text{(B16)}$$

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Resumo

A teoria de Boehm-Yaris [J.Chem.Phys. 55, 2620 (1971)] e Jacobi-Csanak [Chem.Phys.Lett. 30, 367 (1975)] é adaptada ao cálculo da energia de dispersão em um sistema contendo duas moléculas lineares. As partes angulares das amplitudes de Born são representadas por funções denominadas harmônicos esféricos reais. Os resultados obtidos são analíticos para todas as distâncias e, na região assintótica, reproduzem a energia de dispersão usual. Na região intermediária $(3.0\,a, \leqslant R < 8.0\,a,)$, nossas curvas decrescem bem mais lentamente que as correspondentes curvas da energia de dispersão usual.