

Dispersion Interaction Between an Atom and a Linear Molecule

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Abstract The Jacobi-Csanak method [Chem.Phys.Letters.30, 367 (1975)] is adapted to the calculation of the dipole-dipole, dipole-quadrupole, quadrupole-dipole, and quadrupole-quadrupole terms of the dispersion energy of an atom-linear molecule system. The angle-dependent parts of the Born amplitudes for the linear molecule are represented by real spherical harmonics. Our dispersion energy is finite at all distances and reproduces the usual expression in the asymptotic region ($R \geq 4.7 \text{ \AA}$). In the intermediary region ($2.4 \text{ \AA} \leq R < 4.7 \text{ \AA}$) our curves decrease much more slowly than the corresponding curves of the usual dispersion energy.

1. INTRODUCTION

In the last decades, the work on Van der Waals potentials was concentrated mainly in rare gases atoms¹. However, more recently, the study of systems involving interactions among small molecules has grown considerably. For He-H₂, in particular, several *ab initio* calculations involving diverse techniques have been published²⁻⁹. References 2-6 emphasize the problematical region of the Van der Waals minimum. References 7 and 8 discuss the asymptotic region, while⁹ considers the repulsive part of the potential.

The interaction between a spherically symmetric system and a rigid linear molecule depends on the distance R between the centers of mass and on the angle θ between \vec{R} and the molecular axis (See fig. 1). The knowledge of the potential anisotropy is of great importance for the understanding of some properties of several gases and liquid as well as of crystal structures⁴. Unfortunately, very little is known about the anisotropy of the interaction between an atom and a linear molecule. This is mainly because in the experimental analysis of systems such as He-H₂

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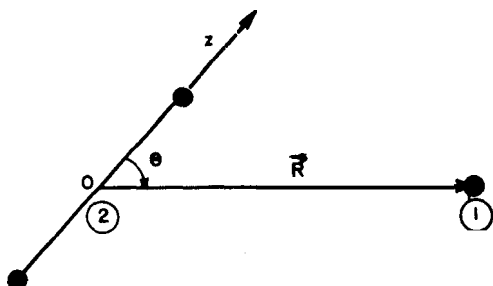


Fig.1 - Illustration of the co-ordinates used in the text.

many measurements represent an average over the angle θ . However, the results already obtained show that the total potential presents a weak anisotropy and that, when the molecule is treated as a rigid rotor, the potential is well described by an expansion in Legendre polynomials containing merely one angle dependent term⁴

$$V^{(T)}(R, \theta) = V_0^{(T)}(R) + V_2^{(T)}(R)P_2(\cos \theta), \quad (1)$$

where $V_0^{(T)}(R)$ is the spherically symmetric term and $V_2^{(T)}(R)$ describes the radial dependence of the anisotropic term.

Particularly for the dispersion potential, Meyer⁷ derived the expansion

$$V(R, \theta) = - \sum_{n \geq 3} \frac{C_{2n}}{R^{2n}} \left[1 + \Gamma_{2n} P_2(\cos \theta) \right] \quad (2)$$

obtaining also accurate values for the parameters C_6, C_8, C_{10} and Γ_6 . However, for Γ_8 the value presented in ref. 7 is about 3.3 times smaller than more recent results obtained with the inclusion of terms^{8,4}.

Since in eq. (2) $V \rightarrow -\infty$ when $R \rightarrow 0$, that potential cannot be applied for interacting systems separated by small distances. One way of avoiding this undesirable behaviour is to introduce a damping factor such that V becomes negligible for small R ^{10,11}. On the other hand, there is a possibly more rational alternative that will be adapted to the case in the present work: the analytical technique of Jacobi-Csanak¹².

2. THE METHOD

In a previous paper¹³ we have applied the Jacobi-Csanak technique¹² to the study of the dispersion interaction between two closed shell distinct atoms, separated by intermediate and long distances (compared to their linear dimensions). We have used the usual spherical harmonics to represent the angle-dependent part of the Born amplitude, written as ($\vec{n} \equiv n, \ell, m$)

$$F_{\vec{n}}(\vec{q}) = F_{n\ell}(q) Y_{\ell m}(\hat{q}) \quad (3)$$

where the radial part $F_{n\ell}(q)$ is given by eq. (7) of that paper¹³.

In this work we make an extension of the Jacobi-Csanak method in order to apply it to the study of the dispersion interaction between an atom and a linear molecule. In a molecule, the electric charge distribution does not have spherical symmetry and then eq. (3) has to be properly modified. To do this, is important to note that the real spherical harmonics form an adequate basis for the description of the group of symmetry operations in molecules having a unique principal axis¹⁴. Then, we introduce these functions to represent the angular parts of the Born amplitudes for linear molecules. They are defined in terms of the usual spherical harmonics as¹⁵

$$y_{\ell m}(\hat{q}) = \begin{cases} \frac{1}{\sqrt{2}} \left[(-)^m Y_{\ell m}(\hat{q}) + Y_{\ell, -m}(\hat{q}) \right] \equiv \bar{y}_{\ell m}(\hat{q}) \\ -\frac{i}{\sqrt{2}} \left[(-)^m Y_{\ell m}(\hat{q}) - Y_{\ell, -m}(\hat{q}) \right] \equiv \bar{\bar{y}}_{\ell m}(\hat{q}) \end{cases} \quad m > 0 \quad (4a)$$

and

$$y_{\ell 0}(\hat{q}) = Y_{\ell 0}(\hat{q}) \quad (4b)$$

Thus, by choosing the coordinate system as shown in fig. 1, and using for the Born amplitudes in systems 1 and 2, respectively, the fac-

torization of eq. (3) and

$$F_{\vec{n}}(q) = F_{n\ell}(q) y_{\ell m}(\hat{q}), \quad (5)$$

we can write the dispersion potential as

$$V(\vec{R}) = -\frac{8}{\pi^3} \sum_{\substack{L', L \\ n_1, n_2, \ell_1, \ell_2}} (-)^{\ell_1 + \ell_2} i^{L+L'} g_{n_1 \ell_1, n_2 \ell_2} I_{n_1 \ell_1, n_2 \ell_2}^{(L, L')} (R) \\ \times \sum_{\substack{M, M' \\ m_1, m_2}} Y_{LM}^*(R) Y_{L'M'}(R) \int d\hat{q} y_{\ell_1 m_1} y_{\ell_2 m_2}^* Y_{L'M'}^* \int d\hat{q}' Y_{\ell_1 m_1}^* y_{\ell_2 m_2} Y_{LM} \quad (6)$$

where

$$g_{n_1 \ell_1, n_2 \ell_2} = \int_0^\infty du \left[\frac{W_{n_1 \ell_1}}{W_{n_1 \ell_1}^2 + u^2} \frac{W_{n_2 \ell_2}}{W_{n_2 \ell_2}^2 + u^2} \right] \quad (7)$$

and

$$I_{n_1 \ell_1, n_2 \ell_2}^{(L, L')} (R) = \int dq' j_L(q'R) F_{n_1 \ell_1}^{(L)}(q') F_{n_2 \ell_2}^{(L')} (q') \int dq j_{L'}(qR) F_{n_1 \ell_1}^*(q) F_{n_2 \ell_2}^*(q) \quad (8)$$

In eq. (7), $W_{n\ell}$ is the excitation energy for the transition from the ground to the $(n\ell)$ excited state of each part of the system.

By inserting eqs. (4a) and (4b) in eq. (6) and using well known method from angular momentum analysis¹⁷, we get

$$V_{m_2=0}^{(R)} = -\frac{1}{2\pi^5} \sum_{\substack{L, L', \ell' \\ n_1, n_2, \ell_1, \ell_2}} (-)^{L+\ell_1} i^{L+L'} g_{n_1 \ell_1, n_2 \ell_2} I_{n_1 \ell_1, n_2 \ell_2}^{(L, L')} (R) \\ \times (2\ell_1+1)(2\ell_2+1) \sqrt{(2L+1)(2L'+1)} (\ell_1 \ell_2 L; 000) (\ell_1 \ell_2 L'; 000) (\ell_2 \ell_2 \ell'; 000) \\ \times (L L' \ell'; 0 0 0) \begin{Bmatrix} \ell_2 & \ell_2 & \ell' \\ L & L' & \ell_1 \end{Bmatrix} \times P_{\ell'}(\cos \theta) \quad (9)$$

and

$$\begin{aligned}
 V_{m_2 > 0}(\vec{R}) = & -\frac{1}{\pi^5} \sum_{\substack{\ell_1, \ell_2 \\ n_1, n_2}} \sum_{\substack{L', L \\ \ell', m_2}} (-)^{L+\ell_1+m} z^{L+L'} P_{\ell'}(\cos \theta) g_{n_1 \ell_1, n_2 \ell_2} \\
 & \times I_{n_1 \ell_1, n_2 \ell_2}^{(R)}(L, L') (2\ell_1+1)(2\ell_2+1) \sqrt{(2L+1)(2L'+1)} (\ell_1 \ell_2 L; 0 0 0) \\
 & \times (\ell_1 \ell_2 L'; 0 0 0) (L L' \ell'; 0 0 0) (\ell_2 \ell_2 \ell'; m_2, -m_2, 0) \left\{ \begin{matrix} \ell_2 & \ell_2 & \ell' \\ L & L' & \ell_1 \end{matrix} \right\}.
 \end{aligned}
 \tag{10}$$

In eqs. (9) and (10), R' is an even integer, $(j_1 j_2 J; m_1 m_2 M)$

and

$$\left\{ \begin{matrix} j_1 & j_2 & j_3 \\ J_1 & J_2 & J_3 \end{matrix} \right\}$$

are the usual Clebsch-Gordan coefficients and $6-j$ Wigner symbols respectively, and $P_{\ell'}(\cos \theta) = \sqrt{4\pi/(2\ell'+1)} Y_{\ell' 0}(\vec{R})$ is a Legendre polynomial of degree R'.

3. CALCULATION

Let us now use eqs. (9) and (10) for the study of the dispersion interaction between an atom and a linear molecule, including dipole-dipole, dipole-quadrupole, quadrupole-dipole and quadrupole-quadrupole contributions. We can write the dispersion potential as a sum in the form

$$V(\vec{R}) = V_{d,d}(\vec{R}) + V_{d,q}(\vec{R}) + V_{q,d}(\vec{R}) + V_{q,q}(\vec{R}) \tag{11}$$

and then we can calculate each one of these contributions as a sum of terms that are labeled as $V_{\ell_1, \ell_2 m_2}(\vec{R})$.

We use the approximation that the radial part of the Born amplitude $F_{n\ell}(q)$ can be replaced by the leading term of the corresponding Csanak-Taylor series¹⁸.

A. Dipole-dipole contribution

In this case, $R_1 = R_2 = 1$. Then

$$V_{\vec{d},\vec{d}}(\vec{R}) = V_{1,10}(\vec{R}) + V_{1,11}(\vec{R}) \quad (12)$$

and the *radial part* of the Born amplitude takes the form

$$F_{n_k 1}(q) = \alpha_k^6 D_{n_k} \frac{q}{(\alpha_k^2 + q^2)^3} \quad (k = 1, 2) \quad (13)$$

where (in atomic units)

$$\alpha_k = \sqrt{2I_k} + \sqrt{2(I_k - W_k)}, \quad (14)$$

I_k being the ionization energy of the k -th system and W_k being one of its excitation energies.

In eq. (13) D_{n_k} are parameters which are directly related to the corresponding oscillator strength $f_{n_k 1m}$ by¹³.

$$|D_{n_k}|^2 = \frac{2\pi}{3} \frac{f_{n_k 10}}{W_{n_k 1}}. \quad (15)$$

By considering some angular-momentum properties of the coefficients in eq. (9), inserting there the actual values of the Clebsch-Gordan coefficients and Wigner 6-j symbols^{19,20}, and using eqs. (8),(13) and (15) we get

$$V_{1,10}(\vec{R}) = -\frac{1}{9\pi} (\alpha_1 \alpha_2)^{12} \int_0^\infty du \left[\sum_n \frac{f_{n10}}{W_{n1}^2 + u^2} \sum_s \frac{f_{s10}}{W_{s1}^2 + u^2} \right] \left\{ \left[\frac{1}{2} (Z_{33}^{02}(R))^2 + (Z_{33}^{22}(R))^2 \right] + \left[-2 Z_{33}^{02}(R) Z_{33}^{22}(R) + (Z_{33}^{22}(R))^2 \right] P_2(\cos \theta) \right\} \quad (16)$$

where the $Z_{mn}^{rs}(R)$ are integrals defined by eq. (16) of reference 13, and $P_2(\cos \theta)$ is a Legendre polynomial of degree two.

Now, defining the frequency-dependent polarizabilities as⁷

$$\alpha_{\ell_1 \ell_2 m_2}^{(\ell_1 \ell_2 m_2)}(\omega) = \sum_{n_1 n_2} \frac{f_{n_1 \ell_1 m_1} f_{n_2 \ell_2 m_2}}{n_1^2 n_2^2 - \omega^2} \tag{17}$$

and introducing the dispersion coefficients of the interaction between an atom and a linear molecule by the expression

$$C_{\ell_1, \ell_2 m_2} = \frac{(2\ell_1 + 2\ell_2)!}{4(2\ell_1)! (2\ell_2)!} \frac{2}{\pi} \int_0^\infty du \alpha_{\ell_1}^{(1)}(iu) \alpha_{\ell_2 m_2}^{(2)}(iu), \tag{18}$$

eq. (16) takes the form

$$V_{1,10}(\vec{R}) = - \frac{C_{1,10}}{27} (\alpha_1 \alpha_2)^{12} \{ [0.5 (Z_{33}^{02}(R))^2 + (Z_{33}^{22}(R))^2] + [-2 Z_{33}^{02}(R) Z_{33}^{22}(R) + (Z_{33}^{22}(R))^2] P_2(\cos \theta) \}, \tag{19}$$

where the functions $Z_{33}^{02}(R)$ and $Z_{33}^{22}(R)$ are given respectively by eqs. (A9) and (A10) of reference 13.

Analogously we obtain

$$V_{1,11}(\vec{R}) = - \frac{C_{1,11}}{27} (\alpha_1 \alpha_2)^2 \{ [(Z_{33}^{02}(R))^2 + 2(Z_{33}^{22}(R))^2] + [2 Z_{33}^{02}(R) Z_{33}^{22}(R) - (Z_{33}^{22}(R))^2] P_2(\cos \theta) \}. \tag{20}$$

In eqs. (19) and (20) above the coefficients C_{ℓ_1, ℓ_2, m_2} are given by eq. (18).

B. Dipole-quadrupole contribution

In this case $\ell_1 = 1$, $\ell_2 = 2$ and one has to calculate the equation

$$V_{d,q}(\vec{R}) = V_{1,20}(\vec{R}) + V_{1,21}(\vec{R}) + V_{1,22}(\vec{R}) \tag{21}$$

with the term $V_{1,20}$ being calculated from eq. (9) and the terms $V_{1,21}$ and $V_{1,22}$ being calculated from eq. (10).

For the radial part of the Born amplitudes we are going to use

eq.(13) for dipole transitions and

$$F_{n_k^2}(q) = \frac{1}{2} \alpha_k^8 Q_{n_k} \frac{q^2}{(q^2 + \alpha_k^2)^4} \quad (k = 1, 2) \quad (22)$$

for quadrupole transitions. In eq. (22), the Q_{n_k} are parameters directly related to the corresponding values of the oscillator strength through¹³

$$|Q_{n_k}|^2 = \frac{8\pi}{45} \frac{A_{n_k^{20}}}{W_{n_k^2}} \quad (23)$$

Again, considering some angular-momentum properties of the coefficients and taking the numerical values of the Clebsch-Gordan coefficients and Wigner 6- j symbols (as we did in subsection A), and using eqs. (8), (13), (22), (15) and (23), we get

$$\begin{aligned} V_{1,20}(\vec{R}) = & -\frac{\alpha_1^{12} \alpha_2^{16}}{225\pi} \int_0^\infty du \left\{ \sum_n \frac{f_{n10}}{W_{n1}^2 + u^2} \sum_s \frac{f_{s20}}{W_{s2}^2 + u^2} \right\} \left\{ \left[(Z_{34}^{13}(R))^2 \right. \right. \\ & + 1.5 (Z_{34}^{33}(R))^2 \left. \right] + \left[(Z_{34}^{13}(R))^2 - \frac{6}{7} Z_{34}^{13}(R) Z_{34}^{33}(R) + \frac{12}{7} (Z_{34}^{33}(R))^2 \right] \\ & \times P_2(\cos \theta) + \left[-\frac{36}{7} Z_{34}^{13}(R) Z_{34}^{33}(R) + \frac{9}{7} ((Z_{34}^{33}(R))^2) \right] P_4(\cos \theta) \left. \right\}, \quad (24) \end{aligned}$$

where $Z_{34}^{13}(R)$ and $Z_{34}^{33}(R)$ are given respectively by eqs. (A11) and (A12) of reference 13.

Finally, using eqs. (17) and (18) we get

$$\begin{aligned} V_{1,20}(\vec{R}) = & -\frac{2C_{1,20}}{3375} \alpha_1^{12} \alpha_2^{16} \left\{ \left[(Z_{34}^{13}(R))^2 + 1.5 (Z_{34}^{33}(R))^2 \right] \right. \\ & + \left[(Z_{34}^{13}(R))^2 - \frac{6}{7} Z_{34}^{13}(R) Z_{34}^{33}(R) + \frac{12}{7} (Z_{34}^{33}(R))^2 \right] P_2(\cos \theta) \\ & \left. + \left[-\frac{36}{7} Z_{34}^{13}(R) Z_{34}^{33}(R) + \frac{9}{7} (Z_{34}^{33}(R))^2 \right] P_4(\cos \theta) \right\}. \quad (25) \end{aligned}$$

Analogously, from eq. (10) we get

$$\begin{aligned}
 V_{1,21}(\vec{R}) = & -\frac{2C_{1,21}}{3375} \alpha_1^{12} \alpha_2^{16} \{ [2(Z_{34}^{13}(R))^2 + 3(Z_{34}^{33}(R))^2] \\
 & + [(Z_{34}^{13}(R))^2 - \frac{6}{7} Z_{34}^{13}(R) Z_{34}^{33}(R) + \frac{12}{7} (Z_{34}^{33}(R))^2] P_2(\cos \theta) \\
 & + [\frac{48}{7} Z_{34}^{13}(R) Z_{34}^{33}(R) - \frac{12}{7} (Z_{34}^{33}(R))^2] P_4(\cos \theta) \} \quad (26)
 \end{aligned}$$

and

$$\begin{aligned}
 V_{1,22}(\vec{R}) = & -\frac{2C_{1,22}}{3375} \alpha_1^{12} \alpha_2^{16} \{ [2(Z_{34}^{13}(R))^2 + 3(Z_{34}^{33}(R))^2] \\
 & + [-2(Z_{34}^{13}(R))^2 + \frac{12}{7} Z_{34}^{13}(R) Z_{34}^{33}(R) - \frac{24}{7} (Z_{34}^{33}(R))^2] P_2(\cos \theta) \\
 & + [-\frac{12}{7} Z_{34}^{13}(R) Z_{34}^{33}(R) + \frac{3}{7} (Z_{34}^{33}(R))^2] P_4(\cos \theta) \} \quad (27)
 \end{aligned}$$

In eqs. (26) and (27) the dispersion coefficients $C_{1,21}$ and $C_{1,22}$ are obtained from eq. (18).

C. Quadrupole-dipole contribution

For this contribution we take $\ell_1 = 2$ and $\ell_2 = 1$ to calculate'

$$V_{q,d}(\vec{R}) = V_{2,10}(\vec{R}) + V_{2,11}(\vec{R}) \quad (28)$$

where the terms $V_{2,10}$ and $V_{2,11}$ are obtained from eqs. (9) and (10) respectively. Working in the same way as we did in the previous case, we get

$$\begin{aligned}
 V_{2,10}(\vec{R}) = & -\frac{2C_{2,10}}{2025} \alpha_1^{16} \alpha_2^{12} \{ [(Z_{43}^{13}(R))^2 + 1.5 (Z_{43}^{33}(R))^2] \\
 & + [\frac{1}{5} (Z_{43}^{13}(R))^2 - \frac{18}{5} Z_{43}^{13}(R) Z_{43}^{33}(R) + \frac{6}{5} (Z_{43}^{33}(R))^2] P_2(\cos \theta) \} \quad (29)
 \end{aligned}$$

and

$$V_{2,11}(\vec{R}) = -\frac{2C_{2,11}}{2025} \alpha_1^{16} \alpha_2^{12} \left\{ \left[2(Z_{43}^{13}(R))^2 + 3(Z_{43}^{33}(R))^2 \right] \right. \\ \left. + \left[-\frac{1}{5} (Z_{43}^{13}(R))^2 + \frac{18}{5} Z_{43}^{13}(R) Z_{43}^{33}(R) - \frac{6}{5} (Z_{43}^{33}(R))^2 \right] P_2(\cos \theta) \right\}. \quad (30)$$

The dispersion coefficients in eqs. (29) and (30) are both given by eq. (18) and the functions $Z_{43}^{13}(R)$ and $Z_{43}^{33}(R)$ are given respectively, by eqs. (A13) and (A14) of reference 13.

D. Quadrupole-quadrupole contribution

For this contribution we have $\ell_1 = \ell_2 = 2$, and we calculate all terms on the right-hand side of the expression

$$V_{q,q}(\vec{R}) = V_{2,20}(\vec{R}) + V_{2,21}(\vec{R}) + V_{2,22}(\vec{R}) \quad (31)$$

from eqs. (9) and (10).

The same procedure we have used in sub-sections A and B gives us

$$V_{2,20}(\vec{R}) = -\frac{C_{2,20}}{70875} (\alpha_1 \alpha_2)^{16} \left\{ \left[0.5 (Z_{44}^{04}(R))^2 + \frac{5}{7} (Z_{44}^{24}(R))^2 + \frac{9}{7} (Z_{44}^{44}(R))^2 \right] \right. \\ \left. + \left[-\frac{75}{343} (Z_{44}^{24}(R))^2 - \frac{10}{7} Z_{44}^{04}(R) Z_{44}^{24}(R) - \frac{360}{343} Z_{44}^{24}(R) Z_{44}^{44}(R) \right. \right. \\ \left. \left. + \frac{450}{343} (Z_{44}^{44}(R))^2 \right] P_2(\cos \theta) + \left[\frac{180}{343} (Z_{44}^{24}(R))^2 - \frac{900}{343} Z_{44}^{24}(R) Z_{44}^{44}(R) \right. \right. \\ \left. \left. + \frac{18}{7} Z_{44}^{04}(R) Z_{44}^{44}(R) + \frac{243}{343} (Z_{44}^{44}(R))^2 \right] P_4(\cos \theta) \right\}, \quad (32)$$

$$\begin{aligned}
 V_{2,21}(\vec{R}) = & -\frac{C_{2,21}}{70875} (\alpha_1 \alpha_2)^{16} \left\{ \left[(Z_{44}^{04}(R))^2 + \frac{10}{7} (Z_{44}^{24}(R))^2 + \frac{18}{7} (Z_{44}^{44}(R))^2 \right] \right. \\
 & + \left[-\frac{75}{343} (Z_{44}^{24}(R))^2 - \frac{10}{7} Z_{44}^{04}(R) Z_{44}^{24}(R) - \frac{360}{343} Z_{44}^{24}(R) Z_{44}^{44}(R) \right. \\
 & + \left. \left. \frac{450}{343} (Z_{44}^{44}(R))^2 \right] P_2(\cos \theta) + \left[-\frac{240}{343} (Z_{44}^{24}(R))^2 + \right. \right. \\
 & \left. \left. + \frac{1200}{343} Z_{44}^{24}(R) Z_{44}^{44}(R) - \frac{24}{7} Z_{44}^{04}(R) Z_{44}^{44}(R) - \frac{324}{343} (Z_{44}^{44}(R))^2 \right] P_4(\cos \theta) \right\}
 \end{aligned}
 \tag{33}$$

and

$$\begin{aligned}
 V_{2,22}(\vec{R}) = & -\frac{C_{2,22}}{70875} (\alpha_1 \alpha_2)^{16} \left\{ \left[(Z_{44}^{04}(R))^2 + \frac{10}{7} (Z_{44}^{24}(R))^2 + \frac{18}{7} (Z_{44}^{44}(R))^2 \right] \right. \\
 & + \left[\frac{150}{343} (Z_{44}^{24}(R))^2 + \frac{20}{7} Z_{44}^{04}(R) Z_{44}^{24}(R) + \frac{720}{343} Z_{44}^{24}(R) Z_{44}^{44}(R) \right. \\
 & - \left. \left. \frac{900}{343} (Z_{44}^{44}(R))^2 \right] P_2(\cos \theta) + \left[\frac{60}{343} (Z_{44}^{24}(R))^2 - \frac{300}{343} Z_{44}^{24}(R) Z_{44}^{44}(R) \right. \right. \\
 & \left. \left. + \frac{6}{7} Z_{44}^{04}(R) Z_{44}^{44}(R) + \frac{81}{343} (Z_{44}^{44}(R))^2 \right] P_4(\cos \theta) \right\}.
 \end{aligned}
 \tag{34}$$

In the three equations above, the dispersion coefficients $C_{2,21}$ and $C_{2,22}$ are calculated from eq. (18), and the functions $Z_{44}^{04}(R)$, $Z_{44}^{24}(R)$ and $Z_{44}^{44}(R)$ are found in eqs. (A15), (A16) and (A17) of reference 13.

E. Dispersion energy in the asymptotic region. Dispersion coefficients

For sufficiently large values of R , we can introduce the limits given by eq. (A18) of reference 13 into eqs. (19), (20), (25), (26), (27),

(29), (30), (32), (33) and (34). From this, we obtain:

$$V_{1,10} \xrightarrow{R \rightarrow \infty} -\frac{C_{1,10}}{3} \frac{1}{R^6} \left[1 + P_2(\cos \theta) \right] = W_{1,10}$$

$$V_{1,11} \xrightarrow{R \rightarrow \infty} -\frac{C_{1,11}}{3} \frac{1}{R^6} \left[2 - P_2(\cos \theta) \right] = W_{1,11}$$

$$V_{1,20} \xrightarrow{R \rightarrow \infty} -\frac{C_{1,20}}{5} \frac{1}{R^8} \left[1 + \frac{8}{7} P_2(\cos \theta) + \frac{6}{7} P_4(\cos \theta) \right] = W_{1,20}$$

$$V_{1,21} \xrightarrow{R \rightarrow \infty} -\frac{C_{1,21}}{5} \frac{1}{R^8} \left[2 + \frac{8}{7} P_2(\cos \theta) - \frac{8}{7} P_4(\cos \theta) \right] = W_{1,21}$$

$$V_{1,22} \xrightarrow{R \rightarrow \infty} -\frac{C_{1,22}}{5} \frac{1}{R^8} \left[2 - \frac{16}{7} P_2(\cos \theta) + \frac{2}{7} P_4(\cos \theta) \right] = W_{1,22}$$

$$V_{2,10} \xrightarrow{R \rightarrow m} -\frac{C_{2,10}}{3} \frac{1}{R^8} \left[1 + \frac{4}{5} P_2(\cos \theta) \right] = W_{2,10}$$

$$V_{2,11} \xrightarrow{R \rightarrow \infty} -\frac{C_{2,11}}{3} \frac{1}{R^8} \left[2 - \frac{4}{5} P_2(\cos \theta) \right] = W_{2,11}$$

$$V_{2,20} \xrightarrow{R \rightarrow \infty} -\frac{C_{2,20}}{5} \frac{1}{R^{10}} \left[1 + \frac{350}{343} P_2(\cos \theta) + \frac{189}{343} P_4(\cos \theta) \right] = W_{2,20}$$

$$V_{2,21} \xrightarrow{R \rightarrow \infty} -\frac{C_{2,21}}{5} \frac{1}{R^{10}} \left[2 + \frac{350}{343} P_2(\cos \theta) - \frac{252}{343} P_4(\cos \theta) \right] = W_{2,21}$$

and

$$V_{2,22} \xrightarrow{R \rightarrow \infty} -\frac{C_{2,22}}{5} \frac{1}{R^{10}} \left[2 - \frac{700}{343} P_2(\cos \theta) + \frac{63}{343} P_4(\cos \theta) \right] = W_{2,22}$$

where we use the letter W instead of V to indicate that we are taking the asymptotic part of the potential.

Then, it follows from eqs. (12), (21), (28) and (31), respectively:

$$1) W_{d,d}(\vec{R}) = -\frac{1}{R^6} \left[C_{1,1}^{(0)} + C_{1,1}^{(2)} P_2(\cos \theta) \right] \quad (35)$$

where

$$C_{1,1}^{(0)} = \frac{C_{1,10} + 2C_{1,11}}{3} \quad \text{and} \quad C_{1,1}^{(2)} = \frac{C_{1,10} - C_{1,11}}{3}$$

$$2) W_{d,q}(\vec{R}) = -\frac{1}{R^8} \left[C_{1,2}^{(0)} + C_{1,2}^{(2)} P_2(\cos \theta) + C_{1,2}^{(4)} P_4(\cos \theta) \right] \quad (36)$$

where

$$C_{1,2}^{(0)} = \frac{0.5 C_{1,20} + C_{1,21} + C_{1,22}}{2.5}, \quad C_{1,2}^{(2)} = \frac{4C_{1,20} + 4C_{1,21} - 8C_{1,22}}{17.5}$$

and

$$C_{1,2}^{(4)} = \frac{3C_{1,20} - 4C_{1,21} + C_{1,22}}{17.5}$$

$$3) W_{q,d}(\vec{R}) = -\frac{1}{R^8} \left[C_{2,1}^{(0)} + C_{2,1}^{(2)} P_2(\cos \theta) \right] \quad (37)$$

where

$$C_{2,1}^{(0)} = \frac{C_{2,10} + 2C_{2,11}}{3} \quad \text{and} \quad C_{2,1}^{(2)} = \frac{4C_{2,10} - 4C_{2,11}}{15}$$

$$4) W_{q,q}(\vec{R}) = -\frac{1}{R^{10}} \left[C_{2,2}^{(0)} + C_{2,2}^{(2)} P_2(\cos \theta) + C_{2,2}^{(4)} P_4(\cos \theta) \right] \quad (38)$$

where

$$C_{2,2}^{(0)} = \frac{C_{2,20} + 2C_{2,21} + 2C_{2,22}}{5}, \quad C_{2,2}^{(2)} = \frac{10C_{2,20} + 10C_{2,21} - 20C_{2,22}}{49}$$

and

$$C_{2,2}^{(4)} = \frac{27C_{2,20} - 36C_{2,21} + 9C_{2,22}}{245}$$

In table I we present the dispersion coefficients which we used in our numerical calculation for the He-H₂ system. From this table and from eqs. (36) and (38) we can expect that the contribution of terms in $P_4(\cos \theta)$ should be very small for large values of R. In fact, our numerical results have shown that this happens even for intermediate distances (in comparison to the sum of the linear dimensions of the atom and of the molecule). This fact enables us to neglect the contribution coming from the terms in $P_4(\cos \theta)$ and we can write our final result in the form:

$$V(\vec{R}) = V_0(R) + V_2(R) P_2(\cos \theta) \quad (39)$$

where $V_0(R)$ is the spherically symmetric term and $V_2(R)$ is a function that describes the radial dependence of the anisotropic term. Moreover, we can write the asymptotic part of $V(\vec{R})$, which coincides with the usual dispersion energy, in the form

$$W(\vec{R}) = W_0(R) + W_2(R) P_2(\cos \theta) \quad (40)$$

where

$$W_0(R) = -\frac{C_{1,1}^{(0)}}{R^6} - \frac{(C_{1,2}^{(0)} + C_{2,1}^{(0)})}{R^8} - \frac{C_{2,2}^{(0)}}{R^{10}} \quad (41)$$

and

$$W_2(R) = -\frac{C_{1,1}^{(2)}}{R^6} - \frac{(C_{1,2}^{(2)} + C_{2,1}^{(2)})}{R^8} - \frac{C_{2,2}^{(2)}}{R^{10}} \quad (42)$$

Table 1 - He-H₂ dispersion coefficients (in atomic units). The calculation used the data from Meyer⁷.

$C_{1,10}$	4.800	$C_{1,1}^{(0)}$	4.016
$C_{1,11}$	3.624	$C_{1,1}^{(2)}$	3.920×10^{-1}
$C_{1,20}$	4.212×10^1	$C_{1,2}^{(0)}$	3.696×10^1
$C_{1,21}$	3.947×10^1	$C_{1,2}^{(2)}$	4.085
$C_{1,22}$	3.186×10^1	$C_{1,2}^{(4)}$	1.943×10^{-2}
$C_{2,10}$	2.226×10^1	$C_{2,1}^{(0)}$	1.869×10^1
$C_{2,11}$	1.691×10^1	$C_{2,1}^{(2)}$	1.427
$C_{2,20}$	3.696×10^2	$C_{2,2}^{(0)}$	3.244×10^2
$C_{2,21}$	3.463×10^2	$C_{2,2}^{(2)}$	3.190×10^1
$C_{2,22}$	2.798×10^2	$C_{2,2}^{(4)}$	1.250×10^{-1}

F. Application: numerical results for the He-H₂ system

We used our method to calculate the dispersion energy in the Helium atom-Hydrogen molecule system. The results we got for $V_0(R)$, $W_0(R)$, $V_2(R)$ and $W_2(R)$ are shown in figs 2 and 3. In figures 4 and 5 we show our results for $V(\vec{R})$ and $W(\vec{R})$ as given by eqs. (39) and (40) respec-

tively and taken at angles $\theta = 0^\circ$ (linear geometry) and $\theta = 90^\circ$ (perpendicular geometry).

For the Helium atom we taken $\alpha_1 = 2.48535$ a.u., referring to the *average excitation energy* calculated by Victor et al.²¹, $\alpha_1 = 1.67508$ a.u., corresponding to the $1^1S \rightarrow 3^1P$ transition and $\alpha_1 = 1.84102$ a.u., corresponding to the $1^1S \rightarrow 2^1P$ transition. For the Hydrogen molecule we used $\alpha_2 = 1.54888$ a.u., corresponding to the *average excitation energy*²² and $\alpha_2 = 1.53284$ a.u. corresponding to the $X \rightarrow C$ transition.

4. ANALYSIS OF THE RESULTS

a) Naturally, one should expect that the atom-molecule interaction include the atom-atom interaction as a particular case. To verify that, we can imagine an approximation in which we neglect the anisotropy of the intra-molecular potential. Then the dispersion energy would be independent of the magnetic quantum number m and we could take $C_{1,11} = C_{1,10} = C_{1,1}, C_{1,22} = C_{1,21} = C_{1,20} = C_{1,2}, C_{2,11} = C_{2,10} = C_{2,1}$ and $C_{2,22} = C_{2,21} = C_{2,20} = C_{2,2}$. In this way, we can reobtain eqs. (21), (26), (27) and (28) of reference 13 by substituting, respectively, the following equations of the present work:

- (19) and (20) into (12)
- (25), (26) and (27) into (21)
- (29) and (30) into (28)
- (32), (33) and (34) into (31).

b) The ratio V_0/V_2 of the coefficients in the expansion of eq. (39) has a typical value of about 10^1 , as can be seen from figures 2 and 3.

c) In the long distance region our calculations for V_0 and V_2 reproduce the corresponding values W_0 and W_2 for the usual dispersion energy given by eq. (40). This can be seen by looking at the region $R \geq 4.7 \text{ \AA}$ in figs. 2 and 3. For this same region of R , these figures show that the functions $V_0(R)$ and $V_2(R)$ are roughly independent of the parameters α_1 and a .

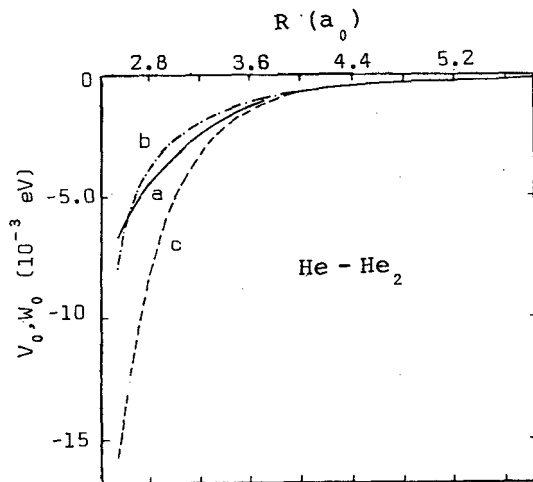


Fig.2 - (a) Values of $V_0(R)$ for $\alpha_1 = 2.48535$ a.u. and $\alpha_2 = 1.54888$ a.u.; (b) Values of $V_0(R)$ for $\alpha_1 = 1.67508$ a.u. and $\alpha_2 = 1.54888$ a.u.; (c) Values of $W_0(R)$.

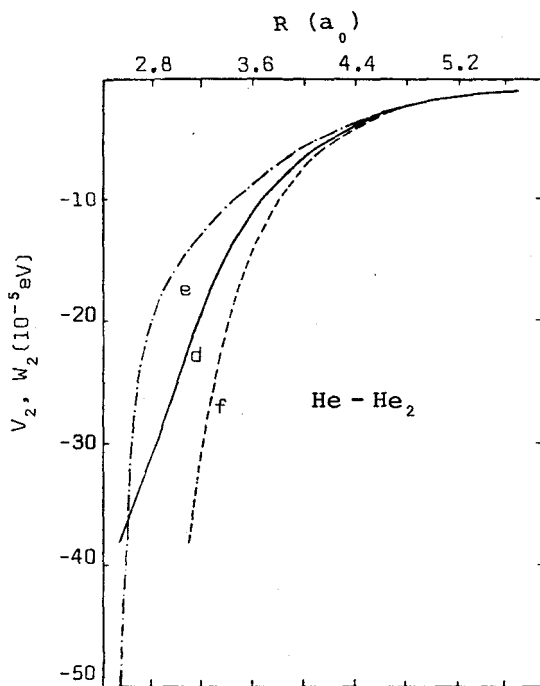


Fig.3 - (d) Values of $V_2(R)$ for $\alpha_1 = 2.48535$ a.u. and $\alpha_2 = 1.54888$ a.u.; (e) Values of $V_2(R)$ for $\alpha_1 = 1.67508$ a.u. and $\alpha_2 = 1.54888$ a.u.; (f) Values of $W_2(R)$.

d) In the intermediate region ($2.4 \text{ \AA} \leq R < 4.7 \text{ \AA}$), figs. 2,3,4 and 5 show that our curves decrease in value far more slowly than the corresponding curves for the usual dispersion energies. Moreover, in this region these figures show that the dependence of our results on the parameters α_1 and α_2 is no longer negligible. This dependence on a , and α_2 grows continuously for decreasing values of R .

e) For the regions we have considered in this work, we note that for every value of R the ratio $V(\theta=0^\circ)/V(\theta=90^\circ)$ is a number that is about unity. This fact is repeated for any pair of values of the angle θ . This means that the asymmetry for the dispersion energy of the He-H₂ system is not high.

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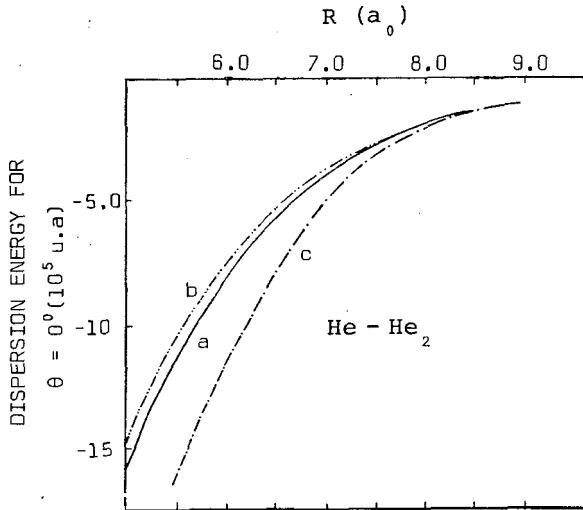


Fig.4 - (a) Values of $V(\vec{R})$ as given by eq.(39) for $\theta = 0^\circ$, $\alpha_1 = 1.84102$ a.u. and $\alpha_2 = 1.53284$ a.u.; (b) The same as (a) but for $\alpha_1 = 1.67508$ a.u. and $\alpha_2 = 1.53284$ a.u.; (c) Values of $W(\vec{R})$ as given by eq. (40) for $\theta = 0^\circ$.

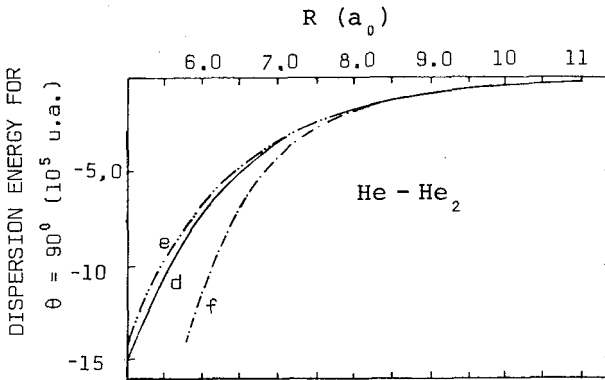


Fig.5 - (d) The same as item (a) of fig. 4, for $\theta = 90^\circ$, $\alpha_1 = 1.84102$ a.u. and $\alpha_2 = 1.53284$ a.u.; (e) The same as item (a) of fig. 4, for $\theta = 90^\circ$, $\alpha_1 = 1.67408$ a.u. and $\alpha_2 = 1.53284$ a.u.; (f) The same as item (c) of fig. 4, for $\theta = 90^\circ$.

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Resumo

O método de Jacobi-Csanak [*Chem.Phys.Letters* 30, 367 (1975)] é adaptado ao cálculo dos termos dipolo-dipolo, dipolo-quadrupolo, quadrupolo-dipolo e quadrupolo-quadrupolo da energia de dispersão em um sistema átomo-molécula linear. As partes angulares das amplitudes de Born referentes à molécula linear são representadas por harmônicos esféricos reais. Nossa energia de dispersão é finita para todas as distâncias na região assintótica ($R \geq 4,7 \text{ \AA}$) reproduz a energia de dispersão usual. Na região intermediária ($2,4 \text{ \AA} \leq R < 4,7 \text{ \AA}$) nossos gráficos decrescem bem mais lentamente que as correspondentes curvas da energia de dispersão usual.