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THE DIPOLE-QUADRUPOLE VAN DER WAALS POTENTIAL  
FOR INTERMEDIATE AND LARGE DISTANCES

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ABSTRACT

We study the dipole-quadrupole interaction energy between two neutral systems for intermediate and large distances compared with their linear dimensions.

RESUMO

Estudamos a parte dipolo-quadrupolo da energia de interação entre dois sistemas neutros, para distâncias intermediárias e grandes em relação as dimensões lineares dos mesmos.

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1. INTRODUCTION

The London<sup>(1)</sup> dispersion force theory for large distances has been treated, in details, by Longuet-Higgins<sup>(2)</sup> for intermediate and large distances. Since the usual multipole expansion fails for intermediate distances, he has written the interaction matrix elements without expanding the interatomic potential in multipoles. Lassette<sup>(3)</sup> suggested to apply this method to calculate the interatomic electrostatic potential between neutral atoms. Following Lassette's<sup>(3)</sup> suggestion Csanak and Taylor<sup>(4)</sup> have applied this method to calculate the first terms of the transition matrix element of the charge density operator  $X_{nL}^-(q)$ , also called polarization potential. They have also successfully obtained expressions for the polarization potential for the electron-atoms scattering.

Jacobi and Csanak<sup>(5)</sup> were the first to calculate<sup>(6)</sup> the dipole-dipole term of the London dispersion force for intermediate and large distances. Their results are very useful in electron-atoms scattering problems or in virial coefficient calculations<sup>(5)</sup>.

In section 2 we show, using the same formalism, how to estimate the dipole-quadrupole term of the interaction energy between two neutral atoms in the ground state. These calculations can be considered as the departure point to construct a more reliable model for the interaction potential between atoms.

In the appendix we estimate an upper and lower limit for the dipole-quadrupole term of the London dispersion potential between two neutral systems. We verify that the values for the dipole-quadrupole interaction energy are inside these limits, as expected.

In section 3, we make some comments about our results obtained in section 2 and about future works.

## 2. THE DIPOLE-QUADRUPOLE TERM

Following Jacobi and Csanak<sup>(5)</sup>, we can easily show that the second order dipole-quadrupole interaction energy between two neutral atoms in the ground state is given by<sup>(7)</sup>

$$\begin{aligned}
 W(R) = & \frac{-2}{\pi^3} \int_0^\infty du \int_0^\infty dq \int_0^\infty dq' \sum_{LL'\ell} \begin{bmatrix} L & L' & \ell \\ 0 & 0 & 0 \end{bmatrix}^2 \\
 & \cdot j_L(qR) j_{L'}(q'R) \left[ \frac{(2L+1)(2L'+1)(2\ell+1)}{4} \right] \\
 & \sum_{n \neq 0} \frac{\left[ E_{nL}^{(1)} - E_0^{(1)} \right] X_{nL}(q) X_{nL'}^*(q')}{\left[ E_{nL}^{(1)} - E_0^{(1)} \right]^2 + u^2} \\
 & \sum_{m \neq 0} \frac{\left[ E_{mL}^{(2)} - E_0^{(2)} \right] X_{mL}(q) X_{mL'}^*(q')}{\left[ E_{mL}^{(2)} - E_0^{(2)} \right]^2 + u^2} \quad (1)
 \end{aligned}$$

where  $R$  is the distance between the centre of mass of the two systems,  $E_{nL}$  refers to the unperturbed excited state energy of the atom with energy in the ground state  $E_0$ ,  $X_n(q)$  corresponds to the Fourier Transform of the excited state and  $j_L(qR)$  is the Bessel spherical function. Finally,  $u$  is an integral variable that appears when we convert all spatial integrals to  $q$ -integrals, to obtain the dispersion force<sup>(5)</sup>.

The leading term of  $X_{nL}(q)$  for the dipole-dipole case,  $L=1$  is<sup>(5)</sup>

$$X_{nL}(q) = D_n \frac{\alpha^6 q}{(q^2 + \alpha^2)^3} \quad (2)$$

where  $D_n$  is the electric dipole matrix of element transition and  $\alpha$ , the reciprocal average radius of the ground and excited states, is practically independent of  $n$ <sup>(3)</sup>.

Substituting Eq. (2) into Eq. (1), for  $L=L'=1$ , Jacobi and Csanak obtained an expression for the dipole-dipole interaction energy for intermediate and large distances  $R$ , which reduces to the London dipole-dipole interaction energy for large distances.

In this work we are interested in the interaction term that is proportional to  $R^{-8}$  which corresponds to the dipole-quadrupole case. To obtain this we put  $L=1, L'=2$  and  $L=2, L'=1$  in Eq. (1). In this case, the leading term of  $X_{n2}(q)$  is<sup>(5)</sup>

$$X_{n2}(q) = Q_n \frac{\alpha^8 q^2}{2(\alpha^2 + q^2)^4} \quad (3)$$

where  $Q_n$  is the quadrupole momentum transition.

Substituting equations (2) and (3) into Eq. (1), for  $L=1, L'=2$  and  $L=2, L'=1$ , the following result is obtained

$$W^{(1,2)}(R) = \frac{-3\alpha^{28} A}{4\pi^5} \left[ I_1^2(R) + \frac{3}{2} I_3^2(R) \right] \quad (4)$$

where

$$A = \int_0^\infty d\omega \alpha(i\omega) \beta(i\omega) \quad (5)$$

$\alpha(i\omega)$  is the frequency-dependent dipole polarizability,  $\beta(i\omega)$

is the frequency-dependent quadrupole polarizability,

$$I_1(R) = \frac{\pi e^{-\alpha R}}{2 \alpha^{10}} \left[ \frac{7\alpha R}{128} + \frac{7\alpha^2 R^2}{512} + \frac{\alpha^3 R^3}{512} + \frac{\alpha^4 R^4}{4608} + \frac{\alpha^5 R^5}{45080} \right], \quad (6)$$

$$I_3(R) = \frac{7,5}{\alpha^{10}} \frac{1}{(\alpha R)^4} \left[ 1 - e^{-\alpha R} P_9(\alpha R) \right], \quad \text{and} \quad (7)$$

$$P_9(\alpha R)^2 = 1 + \alpha R + \frac{1}{46080} \left[ 23040(\alpha R)^2 + 7680(\alpha R)^3 + 1920(\alpha R)^4 + \frac{887}{6}(\alpha R)^5 + 64(\alpha R)^6 + 9(\alpha R)^7 + \frac{49}{48}(\alpha R)^8 + \frac{2}{15}(\alpha R)^9 \right]. \quad (8)$$

For large interatomic distances  $R$  Eq. (4) becomes<sup>(7)</sup>

$$W^{(1,2)}(R) = \frac{-A}{\pi^3 R^8}.$$

As can be seen in the appendix, the interaction energy  $W^{(1,2)}(R)$  obeys the following relation

$$135 \frac{e^2 a_0^7}{R^8} \leq -W^{(1,2)}(R) \leq 180 \frac{e^2 a_0^7}{R^8}.$$

This value has been obtained<sup>(7)</sup> using the perturbation theory and variational method, respectively, following the usual development that has been applied to the dipole-dipole term of the London dispersion force.

### 3. COMMENTS AND CONCLUSIONS

In this paper we have analysed only the interaction between two hydrogen atoms. We must note, however, that this simple case, studied here, will be taken as a departure point to calculate the interaction between any kind of atoms that we intend to analyse in a following work.

We have shown<sup>(7)</sup> that for large  $R$  we recover the Van der Waals interaction of dipole-quadrupole induced between two atoms of hydrogen and that this calculation is valid for intermediate distances.

In this paper we have considered only the leading term  $X_{n2}(q)$ , putting  $L=1, L'=2$  and  $L=2, L'=1$  in Eq. (1). If we take  $X_{n1}$  as is given by Csanak and Taylor<sup>(4)</sup> it will appear a term proportional to  $R^{-8}$ . This possibility is presently being considered and will be published shortly<sup>(8)</sup>.

## APPENDIX

CALCULATION OF AN UPPER AND A LOWER LIMIT FOR THE DIPOLE-  
QUADRUPOLE TERM OF THE INTERACTION ENERGY BETWEEN TWO NEUTRAL  
SYSTEMS

The usual perturbed expression of the interaction energy of the system is (7):

$$H' = -\frac{e^2}{R^3} (2X_1X_2 - Y_1Y_2 - Z_1Z_2) + \frac{3e^2}{2R^4} \left[ r_1^2X_2 - r_2^2X_1 + (2Y_1Y_2 + 2Z_1Z_2 - 3X_1X_2)(X_1 - X_2) \right] + \dots \quad (1)$$

The interaction energy of the two hydrogen atoms in second-order perturbation is given by:

$$W(R) = \sum_n' \frac{|\langle 0 | H' | n \rangle|^2}{E_0 - E_n} \quad (2)$$

Denoting the quantum numbers of each system separately Eq. (2) is written as (7):

$$-W(R) = \sum_{n_1, n_2}' \frac{|\langle 0_1, 0_2 | H' | n_1, n_2 \rangle|^2}{(E_{n_1} - E_{01}) + (E_{n_2} - E_{02})} \quad (3)$$

where  $|0_1, 0_2\rangle$  refers to the quantum numbers of the ground state and  $|n_1, n_2\rangle$  refers to the quantum numbers of the one excited state.

The dash in the sum symbol indicates that it is valid for all  $n \neq 0$ ;  $E_0$  refers to the ground state energy and

$E_n$  is the excited state energy. Since in Eq. (2),  $E_0 < E_n$ , and each numerator term of this equation is positive,  $W(R)$  is negative. Then, we conclude that the interaction potential is attractive.

To calculate an upper limit we put into Eq. (2)  $E_{n^*} = -2(e^2/8a_0)$  which is the energy of the first excited state, instead of  $E_n$ :

$$-W(R) \leq \sum_n' \frac{|\langle 0 | H' | n \rangle|^2}{E_{n^*} - E_0} \quad (4)$$

In the dipole-quadrupole interaction an upper limit for the interaction energy is obtained (7) substituting the second term of  $H'$  in Eq. (1) into Eq. (4):

$$-W(R) \leq \frac{9e^4}{4R^8} \frac{\langle 0 | [r_1^2X_2 - r_2^2X_1 + (2Y_1Y_2 + 2Z_1Z_2 - 3X_1X_2)(X_1 - X_2)]^2 | 0 \rangle}{E_{n^*} - E_0} \quad (5)$$

Calculating the numerator of Eq. (5) and substituting the value  $(E_{n^*} - E_0) = 3e^2/4a_0$  (7) we have:

$$-W(R) \leq 180 \frac{e^2 a_0^7}{R^8} \quad (6)$$

It is possible to determine a lower limit of the interaction energy applying the variational method. The trial function is selected in the following way (9)

$$\psi(\vec{r}_1, \vec{r}_2) = U_{100}(\vec{r}_1) U_{100}(\vec{r}_2) (1 + AH') \quad (7)$$

As the  $\psi(\vec{r}_1, \vec{r}_2)$  function is not normalized, a

lower limit of the interaction energy is given by:

$$E_0 + W(R) \leq \frac{\iint U_0 (1+AH') (H_0+H') U_0 (1+AH') d^3r_1 d^3r_2}{\iint U_0^2 (1+AH')^2 d^3r_1 d^3r_2} \quad (8)$$

Calculating the average value of  $H'$ ,  $H'^3$  and  $H'H_0H'$  Eq. (8) becomes<sup>(7)</sup>

$$\frac{E_0 + 2A\langle H'^2 | 0 \rangle}{(1 + A^2\langle H'^2 | 0 \rangle)} \quad (9)$$

Expanding the denominator of the Eq. (9) and taking only the second order terms of  $H'^2$ , we have

$$\frac{(E_0 + 2A\langle H'^2 | 0 \rangle)}{(1 + A^2\langle H'^2 | 0 \rangle)} \approx E_0 + (2A - E_0 A^2)\langle H'^2 | 0 \rangle \quad (10)$$

That has only one minimum for  $A=1/E_0$ . Remembering that  $E_0$  is negative and substituting  $A=1/E_0$  into Eq. (10) we obtain a lower limit of the interaction energy,

$$E_0 + W(R) \leq E_0 + \frac{\langle H'^2 | 0 \rangle}{E_0} \quad (11)$$

The lower limit for the dipole-quadrupole interaction energy is given by

$$-W(R) \leq \frac{9e^4}{4R^8} \cdot \frac{\langle 0 | [r_1^2 x_2 - r_2^2 x_1 + (2y_1 y_2 + 2z_1 z_2 - 3x_1 x_2)(x_1 - x_2)]^2 | 0 \rangle}{E_0} \quad (12)$$

where we have put  $H' = [r_1^2 x_2 - r_2^2 x_1 + (2y_1 y_2 + 2z_1 z_2 - 3x_1 x_2)(x_1 - x_2)]$  in Eq. (11).

Calculating the nominator of Eq. (12) and replacing the value  $E_0 = -2e^2/2a_0$  we obtain

$$-W(R) \geq 135 \frac{e^2 a_0^7}{R^8}$$

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