

UNIVERSIDADE DE SÃO PAULO

INSTITUTO DE FÍSICA
CAIXA POSTAL 20516
01498 - SÃO PAULO - SP
BRASIL

PUBLICAÇÕES

IFUSP/P-529

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

by

J.C. Antônio

Instituto de Física, Universidade de São Paulo

Maio/1985

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

J.C. Antônio*

Instituto de Física da Universidade de São Paulo,
C.P. 20516, São Paulo, Brazil

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.

*On leave from Departamento de Física, Universidade do Amazonas, 69000, Manaus - AM, Brazil

1. INTRODUCTION

The London⁽¹⁾ dispersion force theory for large distances has been treated, in details, by Longuet-Higgins⁽²⁾ 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⁽³⁾ suggested to apply this method to calculate the interatomic electrostatic potential between neutral atoms. Following Lassette's⁽³⁾ suggestion Csanak and Taylor⁽⁴⁾ 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⁽⁵⁾ were the first to calculate⁽⁶⁾ 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⁽⁵⁾.

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⁽⁵⁾, we can easily show that the second order dipole-quadrupole interaction energy between two neutral atoms in the ground state is given by⁽⁷⁾

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

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⁽⁵⁾.

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

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

where D_n is the electric dipole matrix of element transition and α , the reciprocal average radius of the ground and excited states, is practically independent of n ⁽³⁾.

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⁽⁵⁾

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

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,

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

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

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

For large interatomic distances R Eq. (4) becomes⁽⁷⁾

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

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⁽⁷⁾ 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⁽⁷⁾ 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⁽⁴⁾ it will appear a term proportional to R^{-8} . This possibility is presently being considered and will be published shortly⁽⁸⁾.

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⁽⁷⁾

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

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

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

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,

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

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

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

ACKNOWLEDGMENTS

The author is greatly indebted to Dr. György Csanak for helpful discussions on the problem.

REFERENCES

- (1) F. London, Zeits. F. Physik 63, 245 (1930).
- (2) H.C. Longuet-Higgins, Proc. Roy. Soc. A235, 537 (1956).
- (3) E.N. Lassettre, J. Chem. Phys. 43, 4479 (1965).
- (4) G. Csanak and A.S. Taylor, Phys. Rev. A6, 5 (1972).
- (5) Jacobi and Csanak, Chem. Phys. Letters 30,3 (1975).
- (6) R. Feltgen, Potential Model for Atom-Atom Interactions Involving Symmetry, Max-Planck-Institut Fur Stromungsforschung, 1980.
- (7) J.C. Antônio, Masters Thesis, Instituto de Física e Química de São Carlos - USP, 1981.
- (8) J.C. Antônio and S. Ragusa, to be published.
- (9) L. Pauling and E.B. Wilson, Jr., Introduction to Quantum Mechanics, McGraw-Hill, New York (1935).