Vol. A59 (1981) ACTA PHYSICA POLONICA No. 3

LONG-RANGE AND MANY-BODY NON-ADDITIVE DISPERSION INTERACTION DESCRIBED BY THE USE OF PADÉ APPROXIMANTS TO THE POLARIZABILITY*

By F. I. Suleman and G. C. Shukla

Department of Physics, College of Science, University of Basrah**

(Received June 14, 1980)

The present work deals with the evaluation of dispersion forces between two and many interacting species; excluding and including the relativistic corrections, using the Casimir-Polder formula, which requires knowledge of frequency dependent dipole polarizabilities of the interacting species. Such an expression for polarizabilities has been constructed using Padé approximants, and known Cauchy moments of the systems.

PACS numbers: 02.90.+p, 34.20.—b, 35.10.Di, 35.20.My

1. Introduction

In this work the method of Padé approximants [1–3] has been used to discuss the influence of retardation [4] on dispersion forces at large distances, in the evaluation of the leading coefficient $C_{ab}(R)$ in the interaction energy between two neutral spherical systems a and b — as given by the Casimir-Polder integral formula [5]. Such an expression $C_{ab}(R)$ involves in the integrand product of frequency dependent dipole polarizabilities of interacting species $\alpha_a(w)$ and $\alpha_b(w)$. In an earlier work, using the method of Padé approximants, convergence has been achieved in frequency dependent polarizabilities to evaluate the dispersion interactions [2, 6, 7]. The evaluation of $C_{ab}(R)$ as well as of the coefficient of the leading relativistic correction term are performed for the systems H, He and H_2 by the use of Padé approximants to the polarizability. Also the n-body non-additive dispersion interaction energy has been evaluated, and convergence in the values is obtained.

In Section 2 the formulae used to carry out the calculations are given. In Section 3 the results are discussed.

---

* This work constitutes part of the M.Sc. thesis (Basrah University) of F. I. Suleman.

** Address: Department of Physics, College of Science, University of Basrah, Basrah, Iraq.

2. *The formulae used*

The leading term in the very-long range interaction potential appropriate for two neutral, spherical systems is given in [5]

$$V(R) = -\frac{C_{ab}(R)}{R^6}, \tag{1}$$

where

$$C_{ab}(R) = \frac{1}{\pi}\int_0^\infty \alpha_a(iy)\alpha_b(iy)P(yR/c)\exp(-2yR/c)dy, \tag{2}$$

where c is the velocity of light, $P(x)$ is a fourth-degree polynomial.

$$P(x) = x^4+2x^3+5x^2+6x+3. \tag{3}$$

$\alpha_a(iy)$ and $\alpha_b(iy)$ are the dynamic dipole polarizabilities at imaginary frequency.

It is desirable to obtain approximate analytic representations valid for small and large intermolecular separation. Langhoff [8] has worked out an expansion for the general form of the Casimir-Polder formula in the limit as $R \to 0$,

$$\lim_{R\to 0} C_{ab}(R) = C_{ab}^6 - W_{ab}^4\left(\frac{R}{c}\right)^2 + \ldots \tag{4}$$

$W_{ab}^4\left(\frac{R}{c}\right)^2$ being the leading term in the relativistic correction to the energy, where

$$W_{ab}^4 = \frac{1}{\pi}\int_0^\infty y^2\alpha_a(iy)\alpha_b(iy)dy. \tag{5}$$

Using the Casimir-Polder integral formula, it is easy to discuss many body non--additive interactions for such distances where retardation effects are neglected. The leading term in the long-range non-additive interaction energy between n neutral systems (atoms or molecules) $A_1, A_2, \ldots, A_n$ depends on the coefficient γ_n (9)

$$\gamma_n = \gamma(A_1, A_2, \ldots A_n) = \frac{3}{\pi}\int_0^\infty \alpha_{A_1}(iy)\alpha_{A_2}(iy)\ldots\alpha_{A_n}(iy)dy. \tag{6}$$

The above expression is a generalization of the Casimir-Polder formula involving many centers. The n-body interaction energy can be given by

$$\Delta E_n = \theta(A_1, A_2, \ldots A_n)\gamma_n, \tag{7}$$

where θ depends on the distances between the nuclei of n systems; and γ_n depends on the type of interacting systems.

In order to carry out the above mentioned calculations, we have chosen some analytical expression to the polarizabilities $\alpha(w)$; Padé approximants which give a suitable expression for the polarizability. They are used to construct upper and lower limits to the polarizability [1–3, 6, 7]. The $[n, n-1]$ Padé approximant is a ratio of two polynomials. The coefficients of those polynomials can be evaluated by solving a set of coupled equations (for details see Ref. [7]).

3. *Results*

Using the [6, 5] Padé approximants for the polarizability of the hydrogen atom, we have evaluated the leading coefficient in the interaction energy taking the retardation effect into account; $C_{ab}(R)$ which is given by Eq. (2). Weddle's method of numerical integra-

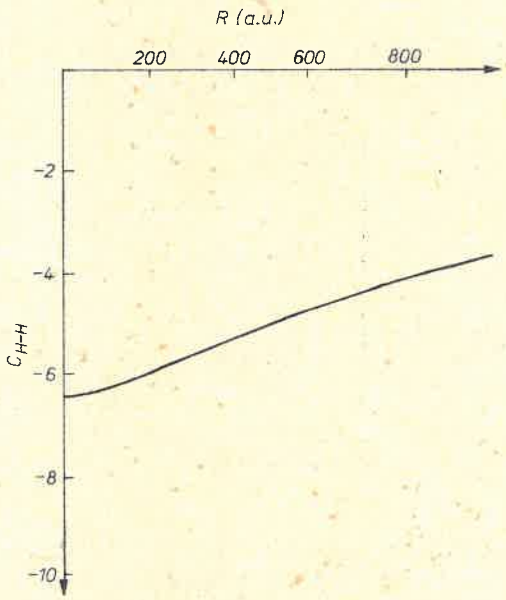

Fig. 1

tion has been performed. $C_{ab}(R)$ has been evaluated for different values of the atomic separation (R) and plotted in Fig. 1 against (R).

Upper and lower bounds on the leading coefficient in the relativistic correction to the energy W_{ab}^4 have been evaluated for different combinations of H, He an H_2 by using up to [6, 5] and [5, 4] Padé approximants to the polarizability. Good agreement between present values and previous calculations as shown on Table I, are achieved.

The non-additive interaction coefficient γ_n defined by Eq. (6), has been evaluated, for atomic and molecular hydrogen and atomic helium. Such calculations have been carried

TABLE I

Bounds on the leading Relativistic Interaction coefficient W^4_{ab} obtained from Padé approximant $[n, n-1]$, $n = 1-5,6$

n	H–H	H–He	H–H_2	He–He	He–H_2	H_2–H_2
1	0.5298/0.3523[a]	0.5867/0.3454	0.9163/0.6033	0.8109/0.4060	1.0797/0.6251	1.6144/1.0516
2	0.4764/0.4303	0.5187/0.4444	0.8268/0.7444	0.6969/0.5565	0.9533/0.8137	1.4590/1.3106
3	0.4670/0.4497	0.5051/0.4736	0.8104/0.7804	0.6711/0.6074	0.9273/0.8703	1.4298/1.3783
4	0.4643/0.4563	0.5007/0.4847	0.8062/0.7921	0.6623/0.6282	0.9196/0.8907	1.4233/1.3992
5	0.4633/0.4590	0.4986/0.4878	0.8048/0.7371	0.6575/0.6311	0.9163/0.7888	1.4218/1.2138
6	0.4629/0.4603					
others[b]	0.4628	0.503		0.6643		

[a] Calculated values are written as a/b, where a is the upper bound and b the lower bound.
[b] Given by Ref. [11].

TABLE II

$\gamma_3, \gamma_4, \gamma_5$ and γ_6^* for interacting hydrogen atoms as given by [1, 0], [2, 1], [3, 2], [4, 3], [5, 4] and [6, 5] Padé approximants to the polarizability. Calculated values are written as a/b where a is the upper bound and b the lower bound

n^{**}	γ_3	γ_4	γ_5	γ_6
1	21.16/21.09	90.61/79.08	356.78/311.40	1444.98/1261.15
2	21.72/21.61	80.80/80.56	316.67/316.06	1278.57/1276.88
3	21.65/21.64	80.63/80.61	316.20/316.17	1277.21/1277.16
4	21.64/21.64	80.62/80.62	316.18/316.18	1277.17/1277.17
5	21.64/21.64	80.62/80.62	316.18/316.18	1277.17/1277.17
6	21.64/21.64	80.62/80.62	316.18/316.18	1277.17/1277.17

* γ_n refers to the interaction coeffiicent between n systems.
** n refers to the order of Padé a approximant.

TABLE III

$\gamma_3, \gamma_4, \gamma_5$, and γ_6^* for interacting helium atoms as given by [1, 0], [2, 1], [3, 2], [4, 3] and [5, 4] Padé approximants to the polarizability. Calculated values are written as a/b where a is the upper bound and b the lower bound

n^{**}	γ_3	γ_4	γ_5	γ_6
1	1.598/1.269	1.760/1.398	2.036/1.617	2.422/1.923
2	1.345/1.325	1.458/1.446	1.671/1.662	1.976/1.969
3	1.333/1.330	1.450/1.449	1.665/1.664	1.970/1.970
4	1.332/1.331	1.449/1.449	1.664/1.664	1.970/1.970
5	1.332/1.331	1.449/1.449	1.664/1.664	1.970/1.970

* The same as in Table II.
** The same as in Table II.

TABLE IV

$\gamma_3, \gamma_4, \gamma_5$ and γ_6^* for interacting hydrogen molecules as given by [1, 0], [2, 1], [3, 2], [4, 3] and [5, 4] Padé approximants to the polarizability. Calculated values are written as a/b where a is the upper bound and b the lower bound

n^{**}	γ_3	γ_4	γ_5	γ_6
1	49.67/43.05	216.30/187.49	989.08/857.34	4652.04/4032.42
2	44.58/44.30	192.39/191.67	874.95/872.80	4100.38/4093.37
3	44.41/44.38	191.88/191.84	873.33/873.24	4094.83/4094.61
4	44.39/44.39	191.86/191.85	873.27/873.26	4094.68/4094.66
5	44.39/44.36	191.86/191.81	873.27/873.19	4094.67/4094.49

* The same as in Table II.
** The same as in Table II.

out with the use of [1, 0], [2, 1], [3, 2], [4, 3], [5, 4], and [6, 5] Padé approximants. Only the interaction energy that arises from the interaction between the dipoles in the systems has been considered. Lower and upper bounds to γ_n for the three systems (H, H_2 and He) are presented in Tables II–IV. Amos and Yoffe [10] have obtained γ_4 as 171 for the hydrogen molecule. Our estimate by [5, 4] Padé approximant is 191.86/191.81. Convergence is achieved in γ_n by proceeding to [5, 4] and [6, 5] Padé approximants.

REFERENCES

[1] G. A. Baker, Jr., *Adv. Theor. Phys.* **1**, 1 (1965).
[2] P. W. Langhoff, M. Karplus, *J. Chem. Phys.* **53**, 233 (1970).
[3] P. W. Langhoff, M. Karplus, *Application of Padé Approximants to Dispersion Force and Optical Polarizability Computations* in the *Padé Approximants in Theoretical Physics*, Edited by G. A. Baker, Jr., J. L. Gammel, Academic Press, New York 1970.
[4] J. O. Hirschfelder, C. F. Curtiss, R. B. Bird, *Molecular Theory of Gases and Liquids*, John Wiley and Sons, Inc., 1964.
[5] H. B. G. Casimir, D. Polder, *Phys. Rev.* **73**, 360 (1948).
[6] F. N. Yousif, G. C. Shukla, *J. Chem. Phys.* **70**, 314 (1979).
[7] F. I. Suleman, F. N. Yousif, G. C. Shukla, *J. Chem. Phys.* **71**, 5246 (1979).
[8] P. W. Langhoff, *Chem. Phys. Lett.* **12**, 223 (1971).
[9] A. D. McLachlan, *Mol. Phys.* **6**, 423 (1963).
[10] A. T. Amos, J. A. Yoffe, *Theor. Chim. Acta* **42**, 247 (1976).
[11] R. E. Johnson, S. T. Epstein, W. J. Meath, *J. Chem. Phys.* **47**, 1271 (1967).