

BOUNDS ON DISPERSION COEFFICIENTS FOR THE INTERACTION OF HELIUM ATOMS

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We use a recently developed method to obtain tight bounds on multipole dispersion coefficients for the interaction of helium atoms.

1. Introduction

The first method [1] to construct bounds on dispersion coefficients was reported independently by Langhoff and Karplus [1,2] and Gordon [3]. The fact that the original methods of Langhoff et al. [4] only involve even oscillator-strength sum rules was considered to be an advantage since even dipole oscillator-strength sum rules can be obtained from refraction data [5]. However higher-order multipole sum rules are not readily available from experiment and thus the success of these methods is essentially limited to the evaluation of bounds on dipole-dipole dispersion coefficients. In general the higher-order multipole sum rules must be obtained from theoretical calculations, which however yield both even and odd oscillator-strength sum rules [6-9].

An elegant method to construct bounds on dispersion coefficients, using both even and odd sum rules has been developed by Alexander [10]. However, the bounds provided by this method are not optimal. Further Langhoff obtained bounds on dynamic polarizabilities [11] and hence on dispersion coefficients [12] using the oscillator-strength sum rules $S(2)$, $S(1)$, $S(0)$, $S(-1)$, $S(-2)$, together with the lowest resonance frequency ω_1 . In two recent articles [13,14] we introduced a new method to obtain bounds on dispersion coefficients which uses both even and odd oscillator-strength sum rules in an optimal and general way. In

the present letter we apply this method to the calculation of bounds on dispersion coefficients for the interaction of helium atoms. The method proves to be especially efficient for the evaluation of bounds on higher-order multipole dispersion coefficients.

2. Theory

The dispersion interaction between closed-shell atoms can be represented as

$$U(R) = - \sum_{n=3}^{\infty} C_{2n}/R^{2n}. \quad (1)$$

The coefficients C_{2n} , $n = 3, 4, 5, \dots$ can be written as

$$C_{2n} = \sum_{l_1, l_2=1}^{\infty} C_{AB}(l_1, l_2) \delta_{l_1+l_2+1, n}.$$

The dispersion coefficients $C_{AB}(l_1, l_2)$, which represent the contribution to the dispersion force due to a 2^{l_1} -pole on atom A with a 2^{l_2} -pole on B, can be expressed in terms of an integral over imaginary frequencies of the dynamic polarizabilities of the interacting atoms [15]:

$$C_{AB}(l_1, l_2) = [(2l_1 + 2l_2)!/4(2l_1)!(2l_2)!] \\ \times \frac{2}{\pi} \int_0^{\infty} \alpha_{l_1}(i\xi) \alpha_{l_2}(i\xi) d\xi. \quad (2)$$

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The perturbation expression for the frequency-dependent polarizability can be expressed as

$$\alpha_l(i\xi) = \sum_{n \neq 0}^{\infty} \frac{f_{n0}^{(l)}}{\omega_n^2 + \xi^2} = \int_0^{\infty} \frac{d\psi(u)}{u^2 + \xi^2}. \quad (3)$$

Except for a few very simple systems (the harmonic oscillator, the hydrogen atom) the dynamic polarizability cannot be calculated exactly. However, the oscillator strengths $f_{n0}^{(l)}$ and excitation frequencies ω_n satisfy sum rules defined as

$$S_l(-k) = \sum_{n \neq 0}^{\infty} \frac{f_{n0}^{(l)}}{\omega_n^k} = \int_0^{\infty} u^{-k} d\psi(u), \quad (4)$$

$k = -2, -1, 0, 1, \dots$

which are more readily available, from experiment or theoretical calculations, than the dynamic polarizability itself.

Langhoff et al. [4] proved that it is possible to construct an approximate polarizability

$$\bar{\alpha}(i\xi) = \sum_{j=1}^n \bar{f}_j / (\bar{\omega}_j^2 + \xi^2), \quad (5)$$

which is an upper or lower bound to the exact dynamic polarizability at imaginary frequencies, by having the effective oscillator strengths \bar{f}_j and excitation frequencies $\bar{\omega}_j$ satisfy a sequence of $2n$ even oscillator-strength sum rules. Substituting these bounded dynamic polarizabilities (5) in the Casimir-Polder expression (2) directly leads to bounded dispersion coefficients.

Recently we [13] showed that an approximate dispersion coefficient

$$\bar{C}_{AB}(l_1, l_2) = [(2l_1 + 2l_2)! / 4(2l_1)!(2l_2)!] \times \int_0^{\infty} d\bar{\psi}_A(u) \int_0^{\infty} \frac{d\bar{\psi}_B(v)}{uv(u+v)} \quad (6)$$

is a lower bound to the exact dispersion coefficient $C_{AB}(l_1, l_2)$ if the approximate distributions $d\bar{\psi}(u)$

$$d\bar{\psi}(u) = \sum_{j=1}^n \bar{f}_j \delta(u - \bar{\omega}_j) \quad (7)$$

satisfy sequences of $2n$ sum rules

$$S(-k) = \int_0^{\infty} d\psi(u)u^{-k} = \int_0^{\infty} d\bar{\psi}(u)u^{-k}, \quad (8)$$

$k = q, q+1, \dots, q+2n-1,$

with

$$q = -2, 0, 2, 3, 4, \dots, \quad n = 1, 2, 3, 4, \dots, \quad (9)$$

$q = -1, \quad n = 1.$

For the remaining q and n values

$$q = 1, \quad n = 1, 2, 3, 4, \dots, \quad (10)$$

$q = -1, \quad n = 2, 3, 4, \dots,$

the approximate dispersion coefficient $\bar{C}_{AB}(l_1, l_2)$ given by (6) will be an upper bound for the exact coefficient. An important distinction with the work of Langhoff et al. [4] is that the approximate dynamic polarizabilities

$$\bar{\alpha}(i\xi) = \int_0^{\infty} d\bar{\psi}(u)/(u^2 + \xi^2) \quad (11)$$

are neither upper, nor lower bounds to the exact dynamic polarizability.

It is possible to express the bounded dispersion coefficients (6) directly in terms of the sum rules $S_l(-k)$, $k = q, q+1, \dots, q+2n-1$ as [14]

$$\bar{C}_{AB}(l_1, l_2) = [(2l_1 + 2l_2)! / 4(2l_1)!(2l_2)!] \times \{[(\mathbf{N}_{l_1}^{-1} \mathbf{M}_{l_1})^{1-q} \mathbf{N}_{l_1}^{-1} \otimes (\mathbf{N}_{l_2}^{-1} \mathbf{M}_{l_2})^{-p} \mathbf{N}_{l_2}^{-1} + (\mathbf{N}_{l_1}^{-1} \mathbf{M}_{l_1})^{-q} \mathbf{N}_{l_1}^{-1} \otimes (\mathbf{N}_{l_2}^{-1} \mathbf{M}_{l_2})^{1-p} \mathbf{N}_{l_2}^{-1}]^{-1}\}_{11} \quad (12)$$

The matrices \mathbf{M} and \mathbf{N} occurring in (12) are defined in terms of the sum rules as

$$M_{ij} = S(-i-j-q+2), \quad N_{ij} = S(-i-j-q+1).$$

3. Results

In this letter we obtain bounds on the dipole-dipole, dipole-quadrupole, quadrupole-quadrupole and dipole-octupole dispersion coefficients for the interaction of helium atoms. The necessary dipole, quadru-

Table 1
Oscillator-strength sum rules for the helium atom

		Luyckx et al. [16]	Langhoff et al. [7]	Chan and Dalgarno [8]	Dalgarno [9]
dipole oscillator	$S_1(0)$	2.0000	2.0000	2.0000	
	$S_1(-1)$	1.5048	1.5050	1.5047	
	$S_1(-2)$	1.3786	1.3816	1.3786	
	$S_1(-3)$	1.4031	1.4136	1.4032	
	$S_1(-4)$	1.5196	1.5413	1.5197	
quadrupole oscillator	$S_2(0)$	4.7733			4.776
	$S_2(-1)$	3.1645			3.150
	$S_2(-2)$	2.4303			2.436
	$S_2(-3)$	2.0452			2.070
	$S_2(-4)$	1.8303			1.868
octupole oscillator	$S_3(0)$	23.812			
	$S_3(-1)$	14.932			
	$S_3(-2)$	10.479			
	$S_3(-3)$	7.9526			
	$S_3(-4)$	6.3954			

pole and octupole sum rules can be obtained using a variational method [16]. In table 1 we give numerical values for the sequence of sum rules

$$S_l(-k), \quad k = 0, 1, 2, 3, 4, \quad l = 1, 2, 3, \quad (13)$$

evaluated with a properly correlated 20-parameter Hylleraas wavefunction [17] for the description of the ground state of the helium atom and compare them with accurate theoretical values for oscillator-strength sum rules [6-9]. The sequence of sum rules presented is sufficient to evaluate the lower bounds $q = 0, n = 1, 2$ for which the general matrix expression (12) reduces to

$$\begin{aligned} \bar{C}_{AB}(l_1, l_2) = & [(2l_1 + 2l_2)/4(2l_1)!(2l_2)!] \\ & \times [(\mathbf{N}_{l_1}^{-1} \mathbf{M}_{l_1} \mathbf{N}_{l_1}^{-1} \otimes \mathbf{N}_{l_2}^{-1} \\ & + \mathbf{N}_{l_1}^{-1} \otimes \mathbf{N}_{l_2}^{-1} \mathbf{M}_{l_2} \mathbf{N}_{l_2}^{-1})^{-1}]_{11}, \end{aligned} \quad (14)$$

and the upper bound $q = 1, n = 1, 2$ for which the specific matrix expression reads

$$\begin{aligned} \bar{C}_{AB}(l_1, l_2) = & [(2l_1 + 2l_2)/4(2l_1)!(2l_2)!] \\ & \times [(\mathbf{N}_{l_1}^{-1} \otimes \mathbf{M}_{l_2}^{-1} + \mathbf{M}_{l_1}^{-1} \otimes \mathbf{N}_{l_2}^{-1})^{-1}]_{11}. \end{aligned} \quad (15)$$

In table 2 we give numerical values for bounds on dis-

Table 2
Dispersion coefficients for the interaction of helium atoms

	D-D ^{a)}	D-Q	Q-Q	D-O
this work ^{b)}	1.45-1.46	6.99-7.05	63.5-63.9	58.9-59.3
this work ^{c)}	1.45-1.46	6.98-7.03	63.0-63.6	-
this work ^{d)}	1.45-1.46	-	-	-
Langhoff ^{e)}	1.43-1.49	-	-	-
Tang et al. [19]	1.46-1.48	6.91-7.11	61.6-64.4	45.4-6.16
previous work [18]	1.4579	7.034	63.82	59.31

a) D: dipole, Q: quadrupole, O: octupole.

b) The first value the lower bound, the second the upper bound obtained using the sum rules of ref. [16].

c) Dipole sum rules of ref. [8] and quadrupole sum rules of ref. [9] have been used.

d) Dipole sum rules of ref. [7] have been used.

e) The lower bound of Langhoff [12] using the sequence of sum rules $S(2), S(1), S(0), S(-1)$ is included as $q = -2, n = 2$ in eq. (12) of this work.

persion coefficients, obtained using the sequences of sum rules $S(0)$, $S(1)$, ..., $S(-4)$ presented in table 1. For the dipole-dipole interaction three different sequences of sum rules [7,8,17] have been used. For the dipole-quadrupole and quadrupole-quadrupole coefficients two sets of sum rules were available [9,17]. For the octupole sum rules of helium only one accurate calculation [17] seems to be available in literature.

The present method leads to theoretical bounds on dispersion coefficients for the interaction of helium atoms which are only slightly dependent on the specific methods used to calculate the required sum rules, provided that an accurate correlated ground-state wavefunction was used in the calculation. In addition the present bounds are in close agreement with accurate theoretical calculations [18]. For the sake of comparison we have also included bounds obtained by Langhoff [12] and Tang [19].

References

- [1] P.W. Langhoff and M. Karplus, *Phys Rev Letters* 19 (1967) 1461.
- [2] P.W. Langhoff and M. Karplus, *J. Chem. Phys.* 53 (1970) 233.
- [3] R.G. Gordon, *J. Chem. Phys.* 48 (1968) 3929.
- [4] P.W. Langhoff, R.G. Gordon and M. Karplus, *J. Chem. Phys.* 55 (1971) 2126.
- [5] P.W. Langhoff and M. Karplus, *J. Opt. Soc. Am.* 59 (1969) 863.
- [6] P.W. Langhoff, J. Sims and C.T. Corcoran, *Phys. Rev.* A10 (1974) 829.
- [7] P.W. Langhoff, C.T. Corcoran, J. Sims, F. Weinhold and R.M. Glover, *Phys. Rev.* A14 (1976) 1043.
- [8] Y.M. Chan and D. Dalgarno, *Proc. Phys. Soc. (London)* 80 (1965) 777.
- [9] A. Dalgarno, private communication.
- [10] M.H. Alexander, *Phys. Rev.* A1 (1970) 1397.
- [11] P.W. Langhoff, *Chem Phys Letters* 9 (1971) 89.
- [12] P.W. Langhoff, *Chem Phys Letters* 12 (1971) 217.
- [13] R. Luyckx, F. Delbaen, Ph. Coulon and H.N.W. Lekkerkerker, *Phys Rev* A19 (1979) 324.
- [14] R. Luyckx, Ph. Coulon and H.N.W. Lekkerkerker, *J. Chem Phys* 71 (1979) 3462.
- [15] H.B.G. Casimir and D. Polder, *Phys. Rev.* 73 (1948) 455
- [16] R. Luyckx, Ph. Coulon and H.N.W. Lekkerkerker, *Chem Phys. Letters* 48 (1977) 187.
- [17] J.F. Hart and G. Herzberg, *Phys Rev.* 106 (1959) 79.
- [18] L.J. Bartolotti and J. Tyrrehl, *Chem Phys Letters* 39 (1976) 19.
- [19] K.T. Tang, J.M. Norbeck and P.R. Certain, *J. Chem. Phys.* 64 (1976) 3063