

Dispersion forces between noble gas atoms

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The coefficients of the R^{-6} , R^{-8} , and R^{-10} terms in the series representation of the dispersion interaction between helium, neon, and argon at distance R are calculated using an elementary variation method.

I. INTRODUCTION

The study of dispersion forces has long been of great interest to physicists and chemists. For the leading term, which is due to the dipole-dipole interaction, a number of simple approximate expressions are available,¹ as well as accurate numerical values for a number of atoms and molecules.² For simple systems (H, He, H₂) these accurate values have been obtained from theoretical calculations, but for more complicated systems they are based on a combination of experimental and theoretical knowledge of static polarizabilities, oscillator strength sums, and excitation energies. For the calculation of higher order dispersion forces the latter method is less convenient because the necessary experimental information is difficult to obtain. Therefore it appears that for the evaluation of higher order dispersion forces one has to resort to theoretical methods. In this paper we extend a simple variation procedure first used by Karplus and Kolker³ and by Chan and Dalgarno⁴ for the calculation of the dipole-dipole dispersion interaction between hydrogen and helium, to calculate the dipole-dipole, dipole-quadrupole, quadrupole-quadrupole, and dipole-octupole dispersion forces between helium, neon, and argon.

II. THEORY

Using second order perturbation theory,² it is found that the dispersion interaction between two closed shell atoms A and B can be represented as

$$U(R) = - \sum_{l_a, l_b=1}^{\infty} \frac{C(l_a, l_b)}{R^{2(l_a+l_b+1)}}. \quad (1)$$

Here R is the interatomic distance, and $C(l_a, l_b)$ represents the contribution to the dispersion force due to the interaction of the 2^{l_a} -pole on A with the 2^{l_b} -pole on B,

$$C(l_a, l_b) = \frac{(2l_a + 2l_b)!}{4(2l_a)!(2l_b)!} \sum_{\nu, \nu'} \frac{f_{\nu_0}^{(l_a)} f_{\nu'_0}^{(l_b)}}{\omega_{\nu_0}^{(a)} \omega_{\nu'_0}^{(b)} (\omega_{\nu_0}^{(a)} + \omega_{\nu'_0}^{(b)})}, \quad (2)$$

where $\omega_{\nu_0}^{(a)}$ is the excitation energy for the transition from $\psi_0^{(a)}$ to $\psi_{\nu}^{(a)}$ and $f_{\nu_0}^{(l_a)}$ is the 2^{l_a} -pole oscillator strength for that transition:

$$f_{\nu_0}^{(l_a)} = \frac{8\pi}{(2l_a + 1)}$$

$$\times \omega_{\nu_0}^{(a)} |\langle \psi_0^{(a)} | \sum_{i=1}^N r_i^{l_a} Y_{l_a, 0}(\theta_i) | \psi_{\nu}^{(a)} \rangle|^2. \quad (3)$$

For $l_a = l_b = 1$, Eq. (2) reduces to the well-known Eisen-schitz-London expression for the dipole-dipole dispersion interaction.⁵

The starting point of most modern work on dispersion forces is provided by the Casimir-Polder⁶ formula, in which the dispersion interaction is expressed as an integral over imaginary frequencies of the appropriate dynamic polarizabilities of the interacting species. Introducing the dynamic multipole polarizability

$$\alpha_l(\omega) = \sum_{\nu} \frac{f_{\nu_0}}{\omega_{\nu_0}^2 - \omega^2} \quad (4)$$

and using the identity

$$\frac{1}{x+y} = \frac{2}{\pi} \int_0^{\infty} \frac{xy}{(x^2 + \xi^2)(y^2 + \xi^2)} d\xi,$$

one easily sees that Eq. (2) can be written as

$$C(l_a, l_b) = \frac{(2l_a + 2l_b)!}{4(2l_a)!(2l_b)!} \frac{2}{\pi} \int_0^{\infty} \alpha_{l_a}(i\xi) \alpha_{l_b}(i\xi) d\xi. \quad (5)$$

The problem of calculating dispersion interaction coefficients is thus effectively reduced to the calculation of dynamic polarizabilities.

The dynamic 2^l -pole polarizability can be written as

$$\alpha_l(\omega) = \frac{4\pi}{2l+1} \langle \psi_0 | \sum_{i=1}^N r_i^l Y_{l, 0}(\theta_i) | \chi_l^+(\omega) + \chi_l^-(\omega) \rangle, \quad (6)$$

where the function $\chi_l^+(\omega)$ is a solution of the perturbation equation

$$(H_0 - E_0 \pm \omega) \chi_l^{\pm}(\omega) - \sum_{i=1}^N r_i^l Y_{l, 0}(\theta_i) \psi_0 = 0. \quad (7)$$

This differential equation is equivalent to the variation principle that requires the functional

$$L[\chi_l^{\pm}(\omega)] = \langle \chi_l^{\pm}(\omega) | H_0 - E_0 \pm \omega | \chi_l^{\pm}(\omega) \rangle - 2 \langle \psi_0 | \sum_{i=1}^N r_i^l Y_{l, 0}(\theta_i) | \chi_l^{\pm}(\omega) \rangle \quad (8)$$

to be stationary with respect to variations of $\chi_l^{\pm}(\omega)$. We use for the variation function the following ansatz:

$$\chi_l^{\pm}(\omega) = \sum_{p=1}^m c_p^{(l)\pm}(\omega) A_p^{(l)} \psi_0, \quad (9)$$

where the coefficients $c_p^{(l)\pm}(\omega)$ are variation parameters and the operators $A_p^{(l)}$ are defined as

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TABLE I. Strength factors and effective excitation energies for $\alpha_l(\omega)$.

	l=1		l=2		l=3	
	(dipole)		(quadrupole)		(octupole)	
	$Z_\mu^{(1)}$	$\Delta_\mu^{(1)}$	$Z_\mu^{(2)}$	$\Delta_\mu^{(2)}$	$Z_\mu^{(3)}$	$\Delta_\mu^{(3)}$
He	0.4422	0.8048	0.6301	0.9154	2.057	0.9706
	0.6576	1.113	1.873	1.222	10.24	1.300
	0.6818	2.065	1.790	2.095	9.423	2.098
	0.2185	6.325	0.4800	5.388	2.092	4.716
Ne	0.4881	0.8054	1.027	0.9181	6.310	0.9181
	2.274	1.276	4.900	1.279	26.54	1.275
	4.210	2.880	8.099	2.500	38.57	2.198
	3.028	14.59	4.716	12.21	10.26	5.016
Ar	3.089	0.5996	14.35	0.7371	165.1	0.8424
	2.969	0.9260	13.95	1.018	142.4	1.067
	3.866	1.852	17.75	1.757	104.2	1.589
	8.076	17.41	5.906	7.581	14.78	3.084

$$A_p^{(l)} = \sum_{i=1}^N r_i^{l+p-1} Y_{l,0}(\theta_i). \quad (10)$$

For the dipole case the variation function given by Eq. (9) reduces to the one used by Karplus and Kolker³ and Chan and Dalgarno.⁴ Minimizing the variation functional L with respect to the variation parameters $c_p^{(l)\pm}(\omega)$, one obtains

$$c_p^{(l)\pm}(\omega) = [\mathbf{N}_l^{-1} \mathbf{M}_l \pm \omega \mathbf{I}]_{pl}^{-1}, \quad (11)$$

where the matrices \mathbf{M}_l and \mathbf{N}_l are given by

$$[M_l]_{pq} = \langle \psi_0 | A_p^{(l)} (H_0 - E_0) A_q^{(l)} | \psi_0 \rangle + \langle \psi_0 | A_q^{(l)} (H_0 - E_0) A_p^{(l)} | \psi_0 \rangle, \quad (12)$$

$$[N_l]_{pq} = 2 \langle \psi_0 | A_p^{(l)} A_q^{(l)} | \psi_0 \rangle. \quad (13)$$

Using some simple operator algebra⁷ it can be shown that the elements of the matrix \mathbf{M}_l can be written as

$$[M_l]_{pq} = \frac{[(l+p-1)(l+q-1) + l(l+1)]}{4\pi} \langle \psi_0 | \sum_{i=1}^N r_i^{2l+p+q-4} | \psi_0 \rangle. \quad (14)$$

The use of this relation rather simplifies the actual calculations. Substituting the variationally determined functions $\chi_l^{\pm}(\omega)$ in Eq. (6) and using elementary matrix theory, one obtains⁷

$$\alpha_l(\omega) = \sum_{\mu=1}^m \frac{Z_\mu^{(l)}}{(\Delta_\mu^{(l)})^2 - \omega^2}. \quad (15)$$

The effective excitation energies $\Delta_1^{(l)}, \Delta_2^{(l)}, \dots, \Delta_m^{(l)}$ are the eigenvalues of the matrix $\mathbf{N}_l^{-1} \mathbf{M}_l$ and the corresponding strength factors $Z_1^{(l)}, Z_2^{(l)}, \dots, Z_m^{(l)}$ are given by

$$Z_\mu^{(l)} = \frac{4\pi}{2l+1} \Delta_\mu^{(l)} [\mathbf{N}_l \mathbf{R}_\mu^{(l)}]_{11}, \quad (16)$$

where $\mathbf{R}_\mu^{(l)}$ is the residue matrix of $\mathbf{N}_l^{-1} \mathbf{M}_l$ corresponding to the eigenvalue $\Delta_\mu^{(l)}$. The residue matrices can be expressed in terms of the left and right eigenvectors of $\mathbf{N}_l^{-1} \mathbf{M}_l$, and they have the following important property:⁸

$$\sum_{\mu=1}^m (\Delta_\mu^{(l)})^n \mathbf{R}_\mu^{(l)} = (\mathbf{N}_l^{-1} \mathbf{M}_l)^n, \quad (17)$$

where n is a positive or negative integer or zero. For the dipole case Karplus and Kolker³ and Chan and Dalgarno⁴ noticed that the variation procedure they used automatically ensures that the f -sum rule is satisfied. This also holds for the higher order polarizabilities.^{7,9} Indeed, using Eqs. (17) and (14) one easily sees that

$$\sum_{\mu=1}^m Z_\mu^{(l)} = l \langle \psi_0 | \sum_{i=1}^N r_i^{2l-2} | \psi_0 \rangle = \sum_{\nu} f_{\nu 0}^{(l)}. \quad (18)$$

Substituting the dynamic polarizabilities given by Eq. (15) in Eq. (5) and carrying out the integration one obtains

$$C(l_a, l_b) = \frac{(2l_a + 2l_b)!}{4(2l_a)!(2l_b)!} \times \sum_{\mu=1}^m \sum_{\mu'=1}^{m'} \frac{Z_\mu^{(l_a)} Z_{\mu'}^{(l_b)}}{\Delta_\mu^{(l_a)} \Delta_{\mu'}^{(l_b)} (\Delta_\mu^{(l_a)} + \Delta_{\mu'}^{(l_b)})}. \quad (19)$$

This equation is the variation analog of the generalized Eisenschitz-London expression (2).

It is possible to write Eq. (19) in a form that does not require the calculation of eigenvalues and eigenvectors. Indeed, realizing that $\Delta_\mu^{(l_a)} + \Delta_{\mu'}^{(l_b)}$ ($\mu = 1, 2, \dots, m; \mu' = 1, 2, \dots, m'$) are the eigenvalues of the Kronecker sum of $\mathbf{N}_{l_a}^{-1} \mathbf{M}_{l_a}$ and $\mathbf{N}_{l_b}^{-1} \mathbf{M}_{l_b}$,

$$\mathbf{N}_{l_a}^{-1} \mathbf{M}_{l_a} \otimes \mathbf{I} + \mathbf{I} \otimes \mathbf{N}_{l_b}^{-1} \mathbf{M}_{l_b},$$

and that the corresponding residue matrices are given by

$$\mathbf{R}_\mu^{(l_a)} \otimes \mathbf{R}_{\mu'}^{(l_b)} \quad \mu = 1, 2, \dots, m; \mu' = 1, 2, \dots, m',$$

one obtains

$$C(l_a, l_b) = \frac{4\pi^2 (2l_a + 2l_b)!}{(2l_a + 1)!(2l_b + 1)!} \times [(\mathbf{N}_{l_a}^{-1} \mathbf{M}_{l_a} \mathbf{N}_{l_a}^{-1}) \otimes \mathbf{N}_{l_b}^{-1} + \mathbf{N}_{l_a}^{-1} \otimes (\mathbf{N}_{l_b}^{-1} \mathbf{M}_{l_b} \mathbf{N}_{l_b}^{-1})]_{11}^{-1}. \quad (20)$$

The advantage of this formula is that it expresses the van der Waals coefficients directly in terms of the moments of the charge distributions of the interacting

TABLE II. Static dipole, quadrupole, and octupole polarizabilities. (For the sake of comparison we have added representative literature values.)

	α_1	α_2	α_3
He	1.379	2.430	10.48
	1.3838 ^a	2.3263 ^b	10.011 ^b
Ne	2.67	5.71	32.2
	2.6680 ^a	6.416 ^c	30.367 ^c
Ar	13.2	45.7	401
	11.091 ^a	48.237 ^c	449.720 ^c

^aP. W. Langhoff and M. Karplus, J. Opt. Soc. Am. 59, 863 (1969).

^bA. Dalgarno and G. A. Victor, Proc. Phys. Soc. London 90, 605 (1967).

^cM. B. Doran, J. Phys. B 7, 558 (1974).

TABLE III. Moments of the oscillator strength distribution of the dynamic dipole polarizability.

	$S_1(-2)$	$S_1(-4)$	$S_1(-6)$
He	1.379	1.519	1.981
	1.3838	1.550	2.066
Ne	2.67	2.08	2.32
	2.6680	2.863	5.682
Ar	13.2	28.3	71.3
	11.091	28.16	96.78

^aThe first line for each atom contains the result of the present work. The second line gives the result of Langhoff and Karplus, *J. Opt. Soc. Am.* **59**, 863 (1969) obtained from optical refractivity data.

atoms. For example, in the case where we work with one variation parameter (generalized Kirkwood method) we obtain

$$C(l_a, l_b) = \frac{2(2l_a + 2l_b)!}{(2l_a + 1)!(2l_b + 1)!} \times \frac{\langle R^{2l_a} \rangle^2 \langle R^{2l_b} \rangle^2}{(2l_b + 1)l_b \langle r^{2l_b-2} \rangle \langle R^{2l_a} \rangle + (2l_a + 1)l_a \langle r^{2l_a-2} \rangle \langle R^{2l_b} \rangle}, \quad (21)$$

where

$$\langle r^{2l-2} \rangle = \langle \psi_0 | \sum_{i=1}^N r_i^{2l-2} | \psi_0 \rangle$$

and

$$\langle R^{2l} \rangle = 4\pi \langle \psi_0 | \sum_{i,j=1}^N r_i^l Y_{l,0}(\theta_i) r_j^l Y_{l,0}(\theta_j) | \psi_0 \rangle.$$

In a previous publication¹⁰ we have used the simple expression (21) for the calculation of the dipole-dipole,

dipole-quadrupole, quadrupole-quadrupole, and dipole-octupole dispersion forces between noble gas atoms and obtained quite satisfactory results.

III. RESULTS

In our calculations we have used for the ground state wavefunction of helium the 20-parameter Hylleraas-type representation of Hart and Herzberg¹¹ and for neon and argon the self-consistent-field wavefunctions of Clementi.¹² As noticed by Karplus and Kolker³ and by Chan and Dalgarno,⁴ the convergence of the employed variational procedure is very rapid and with four parameters one obtains dynamic polarizabilities that are accurate over a sufficient frequency range for a four significant figures convergence of the van der Waals coefficients $C(l_a, l_b)$. Using Eq. (20) for the calculation of the van der Waals coefficients one does not need the dynamic polarizabilities in the spectral decomposed form (15). However, since they may be useful in other connections, the values of the effective oscillator strengths $Z_\mu^{(l)}$ and the corresponding effective excitation energies $\Delta_\mu^{(l)}$ for the dynamic dipole, quadrupole, and octupole polarizabilities of helium neon, and argon are listed in Table I. In Table II we compare the static polarizabilities that follow from the data presented in Table I to experimental values (for the dipole polarizability) and theoretical values (for the quadrupole and octupole polarizabilities), and in Table III we compare the moments of the dynamic dipole polarizabilities

$$S_1(k) = \sum_{\mu=1}^m (\Delta_\mu^{(1)})^k Z_\mu^{(1)}$$

with the values obtained by Langhoff and Karplus from optical refractivity data. We see that the values for the static polarizabilities and oscillator strength sums for helium are in close agreement with the literature values. The agreement for neon and argon, although fair, is not as good. We feel that the main reason for this is the inadequacy of the use of self-consistent wavefunctions as zeroth order wavefunctions.

TABLE IV. Van der Waals coefficients for the interaction of He, Ne, and Ar.

Interacting pair ^a	D-D ^b	D-Q	Q-D	Q-Q	D-O	O-D
He-He	1.458	7.029	7.029	63.76	59.18	59.18
	1.47 ± 0.01	7.01 ± 0.10	7.01 ± 0.10	63.0 ± 1.4	53.4 ± 8.0	53.4 ± 8.0
He-Ne	3.18	17.0	15.5	154	182	131
	3.13 ± 0.08	17.5 ± 3.9	15.2 ± 0.6	157 ± 38	156 ± 31	116 ± 22
He-Ar	11.8	114	56.0	1017	1925	469
	9.82 ± 0.35	107 ± 25	46.5 ± 2.1	949 ± 244	1940 ± 450	358 ± 58
Ne-Ne	7.07	37.8	37.8	378	406	406
	6.87 ± 0.40	38.0 ± 10.2	38.0 ± 10.2	424 ± 177	338 ± 81	338 ± 81
Ne-Ar	25.2	246	134	2444	4171	1443
	20.7 ± 1.3	226 ± 62	118 ± 27	2560 ± 1020	4120 ± 1110	1050 ± 210
Ar-Ar	97.0	924	924	16 578	15 611	15 611
	67.2 ± 3.6	740 ± 171	740 ± 171	16 100 ± 6200	13 300 ± 3000	13 300 ± 3000

^aThe first line for each interacting pair contains the results of the present work. The second line gives bounds on the van der Waals coefficients obtained by Tang, Norbeck, and Certain (Ref. 13).

^bD: dipole; Q: quadrupole; O: octupole.

In Table IV we present the results of the van der Waals coefficients for the dipole-dipole, dipole-quadrupole, quadrupole-quadrupole, and dipole-octupole dispersion forces between helium, neon, and argon. For the sake of comparison we have included in Table IV the recent calculations of Tang, Norbeck, and Certain¹³ on upper and lower bounds for the higher order van der Waals coefficients. These calculations are based on a combination of theoretical and experimental knowledge of static polarizabilities, oscillator strength sums, and excitation energies. From the data presented in Table IV it appears that the results obtained here are generally in satisfactory agreement with the bounds obtained by Tang, Norbeck, and Certain.¹³ All deviations that occur from these bounds involve the dipole polarizability of argon, for which we obtain too high a value.

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