

DISPERSION INTERACTION BETWEEN HELIUM ATOMS

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Accurate values for the coefficients of the R^{-6} , R^{-8} and R^{-10} in the series representation of the dispersion interaction between two helium atoms at distance R are obtained by a simple variation method.

1. Introduction

About ten years ago Chan and Dalgarno [1] obtained with a simple variation procedure an analytic representation for the dynamic dipole polarizability of helium. From this they calculated an accurate value for the coefficient C_6 of the R^{-6} term in the dispersion interaction between helium atoms. Later the coefficients C_8 and C_{10} of the R^{-8} and R^{-10} terms in the series representation of the dispersion energy were also calculated from first principles. However these calculations are either more complicated [2,3] or less accurate [4] than those of Chan and Dalgarno.

Surprisingly the original method of Chan and Dalgarno has, as far as we know, not been extended to calculate C_8 and C_{10} . It is the purpose of this paper to fill this gap. Actually using an operator identity the calculations are materially simplified. Further it is shown that the variational procedure automatically ensures that the 2^l -pole oscillator strength sum rule is satisfied. This was first observed for the dipole polarizability by Chan and Dalgarno [1].

2. Theory

The dispersion interaction between closed shell atoms can be represented as

$$U(R) = -C_6/R^6 - C_8/R^8 - C_{10}/R^{10} - \dots \quad (1)$$

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

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

Here $C_{AB}(l_1, l_2)$ represents the contribution to the dispersion force due to the interaction of the 2^{l_1} -pole on A with the 2^{l_2} -pole on B. These coefficients can be expressed as integrals of products of dynamic polarizabilities evaluated at imaginary frequencies [5]**

$$C_{AB}(l_1, l_2) = [(2l_1 + 2l_2)!/4(2l_1)!(2l_2)!] (2/\pi) \times \int_0^\infty \alpha_{l_1}^A(i\xi) \alpha_{l_2}^B(i\xi) d\xi \quad (3)$$

The problem of calculating van der Waals coefficients is thus effectively reduced to the calculation of the dynamic polarizabilities.

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

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

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

** Eq. (3) is expressed in atomic units, which are used throughout this paper. The atomic unit of length is 0.529×10^{-10} m and the unit of energy is 4.36×10^{-18} J.

$$(H_0 - E_0 \pm \omega) \chi_l^\pm(\omega) - \sum_{i=1}^N r_i^l Y_{l,0}(\theta_i) \psi_0 = 0. \quad (5)$$

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

$$L[\chi_l^\pm(\omega)] = \langle \chi_l^\pm(\omega) | H_0 - E_0 \pm \omega | \chi_l^\pm(\omega) \rangle - 2 \langle \psi_0 | \sum_{i=1}^N r_i^l Y_{l,0}(\theta_i) | \chi_l^\pm(\omega) \rangle, \quad (6)$$

to be stationary with respect to variations of $\chi_l^\pm(\omega)$.

Following Chan and Dalgarno [1] we adopt for the ground state wavefunction of helium the 20-parameter representation of Hart and Herzberg [6] and a trial function of the form

$$\chi_l^\pm(\omega) = \sum_{p=1}^m c_p^\pm(\omega) A_p^{(l)} \psi_0, \quad (7)$$

the coefficients $c_p^\pm(\omega)$ being variational parameters, one set for each l . The operators $A_p^{(l)}$ are defined as

$$A_p^{(l)} = \sum_{i=1}^N r_i^{l+p-1} Y_{l,0}(\theta_i). \quad (8)$$

Minimizing the variation functional L with respect to the variation parameters $c_p^\pm(\omega)$ one obtains

$$c_p^\pm(\omega) = [\mathbf{N}^{-1} \mathbf{M} \pm \omega \mathbf{I}]^{-1}, \quad (9)$$

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

$$M_{pq} = \langle \psi_0 | A_p^{(l)} (H_0 - E_0) A_q^{(l)} | \psi_0 \rangle + \langle \psi_0 | A_q^{(l)} (H_0 - E_0) A_p^{(l)} | \psi_0 \rangle, \quad (10)$$

$$N_{pq} = 2 \langle \psi_0 | A_p^{(l)} A_q^{(l)} | \psi_0 \rangle. \quad (11)$$

The form of the coefficients $c_p^\pm(\omega)$ given by (9) is not very convenient for further calculations and analysis. Using elementary matrix theory [7] it can be shown that the coefficients $c_p^\pm(\omega)$ can be written in the form

$$c_p^\pm(\omega) = \sum_{\mu=1}^m R_{p1}^{(\mu)} / (\Delta_\mu \pm \omega). \quad (12)$$

Here $\Delta_1, \Delta_2, \dots, \Delta_m$ are the eigenvalues of the matrix $\mathbf{N}^{-1} \mathbf{M}$ and $\mathbf{R}^{(\mu)}$ is the residue matrix corresponding to

the eigenvalue Δ_μ . These residue matrices can be expressed in terms of the left and right eigenvectors of $\mathbf{N}^{-1} \mathbf{M}$ and they obey the relation

$$\sum_{\mu=1}^m \Delta_\mu \mathbf{R}^{(\mu)} = \mathbf{N}^{-1} \mathbf{M}. \quad (13)$$

Substituting the variationally obtained $\chi_l^\pm(\omega)$ in (4) one gets

$$\alpha_l(\omega) = \sum_{\mu=1}^m Z_\mu / (\Delta_\mu^2 - \omega^2), \quad (14)$$

where the strength factors Z_μ are given by

$$Z_\mu = [4\pi/(2l+1)] \Delta_\mu [\mathbf{N} \mathbf{R}^{(\mu)}]_{11}. \quad (15)$$

We wish to point out that the elements of the matrix \mathbf{M} given by (10), can be written as

$$M_{pq} = \{[(l+p-1)(l+q-1) + l(l+1)]/4\pi\} \times \langle \psi_0 | \sum_{i=1}^N r_i^{2l+p+q-4} | \psi_0 \rangle. \quad (16)$$

Indeed one easily verifies that

$$M_{pq} = \frac{1}{2} \langle \psi_0 | C_{p+q} - C_p - C_q | \psi_0 \rangle, \quad (17)$$

where the operator C_{p+q} is given by

$$C_{p+q} = [A_p^{(l)} + A_q^{(l)}, [H_0, A_p^{(l)} + A_q^{(l)}]] \quad (18)$$

and the operators C_p and C_q are given by similar expressions. Working out these commutators leads to

$$C_{p+q} - C_p - C_q = 2 \sum_{i=1}^N (\text{grad}_i A_p^{(l)}) \cdot (\text{grad}_i A_q^{(l)}). \quad (19)$$

Substituting (19) in (17) and making use of the spherical symmetry of the charge distribution of closed shell atoms one obtains (16).

We also want to point out that $\alpha_l(\omega)$ given by (14) satisfies the 2^l -pole oscillator strength sum rule. Perturbation theory gives for the dynamic polarizability

$$\alpha_l(\omega) = \sum_{\nu} f_{\nu}^{(l)} / [(E_{\nu} - E_0)^2 - \omega^2], \quad (20)$$

where $f_{\nu}^{(l)}$ is the 2^l -pole oscillator strength for the transition to the ν th excited state ψ_{ν} .

Table 1
Strength factors and effective excitation energies for $\alpha_l(\omega)$ [eq. (14)]

| $l = 1$ (dipole) | | $l = 2$ (quadrupole) | | $l = 3$ (octupole) | |
|-----------------------|-------------|-----------------------|-------------|-----------------------|-------------|
| Z_μ | $\Delta\mu$ | Z_μ | $\Delta\mu$ | Z_μ | $\Delta\mu$ |
| 0.44215 | 0.80484 | 0.63007 | 0.91538 | 2.0574 | 0.97059 |
| 0.65762 | 1.1132 | 1.8734 | 1.2223 | 10.240 | 1.2999 |
| 0.68175 | 2.0651 | 1.7899 | 2.0951 | 9.4228 | 2.0980 |
| 0.21848 | 6.3253 | 0.48000 | 5.3880 | 2.0917 | 4.7165 |
| $\alpha_1(0) = 1.379$ | | $\alpha_2(0) = 2.430$ | | $\alpha_3(0) = 10.48$ | |

$$f_\nu^{(l)} = [8\pi/(2l+1)] (E_\nu - E_0) \times \left| \langle \psi_0 | \sum_{i=1}^N r_i^l Y_{l,0}(\theta_i) | \psi_\nu \rangle \right|^2. \quad (21)$$

One easily sees that

$$S_l = \sum_\nu f_\nu^{(l)} = l \langle \psi_0 | \sum_{i=1}^N r_i^{2l-2} | \psi_0 \rangle, \quad (22)$$

which for $l = 1$ reduces to the well known Thomas-Reiche-Kuhn sum rule $S_1 = N$, where N is the number of electrons. The sum of strength factors in the variationally obtained expression for the dynamic polarizability yields using (13) and (16)

$$\begin{aligned} \sum_{\mu=1}^m Z_\mu &= [4\pi/(2l+1)] \sum_{\mu=1}^m \Delta\mu [N R^{(\mu)}]_{11} \\ &= [4\pi/(2l+1)] M_{11} \\ &= l \langle \psi_0 | \sum_{i=1}^N r_i^{2l-2} | \psi_0 \rangle. \end{aligned} \quad (23)$$

We thus see that the 2^l -pole oscillator strength sum rule (22) is satisfied by the variational expression for $\alpha_l(\omega)$. As mentioned this was first observed by Chan and Dalgarno [1] for the dipole case. However as far as we know a general proof has not been given before.

3. Results and discussion

It was already noticed by Chan and Dalgarno [1] that the convergence of the variational procedure is very rapid and with four parameters accurate values for the dynamic polarizabilities and consequently for the interaction coefficients can be obtained. In table 1 we present the values for the strength factors Z_μ and the

effective excitation energies $\Delta\mu$ for a four term representation of the dipole, quadrupole and octupole dynamic polarizabilities of helium.

Using the variationally determined polarizabilities given in table 1 we obtain for the dispersion energy

$$U(R) = - \left[\frac{1.458}{R^6} + \frac{14.06}{R^8} + \frac{118.4 + 63.76}{R^{10}} \right], \quad (24)$$

where the dipole-octupole interaction contributes 118.4 and the quadrupole-quadrupole interaction contributes 63.76 to the R^{-10} term. The results are in close agreement with the best estimate of Dalgarno and Victor [4] and the elaborate calculations of Davison [2] and Bartolotti and Tyrrell [3].

The advantage of the method used in this letter is its simplicity which allows it to be extended to more complicated systems. Results of such calculations will be published elsewhere.

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