

DISPERSION FORCES BETWEEN CLOSED SHELL ATOMS

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Using Kirkwood's variation method, simple approximate formulae for the multipole dispersion forces between closed shell atoms are derived. These expressions are tested in the case of the interaction of two hydrogen atoms and are used to calculate the dipole–dipole, dipole–quadrupole, quadrupole–quadrupole and dipole–octupole dispersion forces between helium, neon and argon. The agreement with available accurate and semi-empirical calculation is encouraging.

1. Introduction

The well-known dispersion interaction between closed shell atoms A and B can be represented by an expansion in inverse powers of the separation R of the following form

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

where the coefficients C_{2n} , $n = 3, 4, 5, \dots$ are commonly known as Van der Waals coefficients. For the leading term, which is due to the dipole–dipole interaction, a number of simple approximate expressions are available¹⁾. Using a variational method, Kirkwood²⁾ obtained‡

$$C_6 = \frac{4}{9} \frac{\langle R_A^2 \rangle^2 \langle R_B^2 \rangle^2}{N_B \langle R_A^2 \rangle + N_A \langle R_B^2 \rangle}. \quad (2)$$

In (2) N_A is the number of electrons of atom A and

$$\langle R_A^2 \rangle = \left\langle \psi_0^A \left| \sum_{i,j=1}^{N_A} \{x_i x_j + y_i y_j + z_i z_j\} \right| \psi_0^A \right\rangle, \quad (3)$$

where ψ_0^A is the ground-state wave function of atom A. In actual calculations the cross terms $\sum_{i \neq j} \langle x_i x_j \rangle$ have frequently been neglected which leads to

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‡ Equation (2) 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.

unsatisfactory results. This was first pointed out by Vinti³) and has been discussed by Salem¹). Using the same variational method as Kirkwood, Buckingham⁴) obtained a simple expression for the Van der Waals coefficient C_8 which is due to the dipole-quadrupole interaction.

$$C_8 = \frac{2(\langle R_A^2 \rangle \langle R_B^4 \rangle + \langle R_A^4 \rangle \langle R_B^2 \rangle)^2}{(3N_B \langle R_A^4 \rangle + 3N_A \langle R_B^4 \rangle + 10\langle r_A^2 \rangle \langle R_B^2 \rangle + 10\langle R_A^2 \rangle \langle r_B^2 \rangle)}, \quad (4)$$

where

$$\langle r_A^2 \rangle = \left\langle \psi_0^A \left| \sum_{i=1}^{N_A} r_i^2 \right| \psi_0^A \right\rangle \quad (5)$$

and

$$\langle R_A^4 \rangle = 5 \left\langle \psi_0^A \left| \sum_{i,j=1}^{N_A} \{x_i y_i x_j y_j + x_i z_i x_j z_j + y_i z_i y_j z_j\} \right| \psi_0^A \right\rangle. \quad (6)$$

In section 3 we shall show that expression (4) can only be expected to give reliable results for the dipole-quadrupole dispersion interaction between like atoms.

In this article we extend the Kirkwood variation method to obtain simple approximate formulae for all multipole dispersion interaction coefficients. These expressions are used to calculate the Van der Waals coefficients up to C_{10} for the interaction between hydrogen, helium, neon and argon. The agreement with highly accurate calculations on the dispersion interaction between hydrogen atoms⁵) and recent semi-empirical calculations on the noble-gas interactions⁶) is encouraging.

Van der Waals coefficients can be expressed as integrals over dynamic multipole polarizabilities at imaginary frequencies^{7,8}). Thus the problem of calculating Van der Waals coefficients can be reduced to the calculation of dynamic multipole polarizabilities.

In this article we will obtain approximate expressions for the dynamic multipole polarizabilities using the Kirkwood variation method. In order to introduce the method we first apply it to the calculation of static polarizabilities.

2. Static polarizabilities

If an atom is placed in an external electric field, multipole moments are induced in the charge distribution of the atom that are in first approximation proportional to the external field. Writing the potential in the form

$$\Phi(\mathbf{r}) = \sum_{l,m} A_{l,m} r^l Y_{l,m}^*(\theta, \varphi),$$

the proportionality between the induced moment and the electric field can be expressed as

$$\langle Q_{l,m} \rangle = -\alpha_l A_{l,m} \quad (l \geq 1). \quad (7)$$

Here $\langle Q_{l,m} \rangle$ is the expectation value of the multipole operator

$$Q_{l,m} = -\frac{4\pi}{2l+1} \sum_{i=1}^N r_i^l Y_{l,m}(\theta_i, \varphi_i) \quad (8)$$

with respect to the perturbed wave function of the atom. The proportionality factor α_l is called the 2^l -pole polarizability, which for closed shell atoms only depends on l and not on m .

The starting point for the quantum-mechanical calculation of the 2^l -pole polarizability is the first-order perturbation equation.

$$(H_0 - E_0)\chi_l + V_l\psi_0 = 0. \quad (9)$$

Here H_0 is the hamiltonian of the atom in the absence of an external electric field and ψ_0 and E_0 are the ground-state wave function and energy of that hamiltonian. Further V_l represents the additional term that appears in the hamiltonian if the atom is placed in an external electric field with potential $\Phi(\mathbf{r}) = r^l Y_{l,0}(\theta)$. Thus

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

Further χ_l is the first order correction to the ground-state wave function due to the presence of the external electric field. Once χ_l has been obtained λ_l can be calculated.

$$\alpha_l = -\langle Q_{l,0} \rangle = -2\langle \psi_0 | Q_{l,0} | \chi_l \rangle. \quad (11)$$

Except for the hydrogen atom the first order perturbation equation (9) cannot be solved analytically and one has to resort to an approximation method. Now it can easily be seen that the differential equation (9) is equivalent to the variation principle that requires the functional

$$L[\chi_l] = \langle \chi_l | H_0 - E_0 | \chi_l \rangle + \langle \chi_l | V_l | \psi_0 \rangle + \langle \psi_0 | V_l | \chi_l \rangle \quad (12)$$

to be stationary with respect to variations of χ_l . Following Kirkwood²⁾ we choose as trial function

$$\chi_l = \lambda_l V_l \psi_0. \quad (13)$$

Minimizing L with respect to λ_l yields

$$\lambda_l = -\frac{\langle \psi_0 | V_l^2 | \psi_0 \rangle}{\langle \psi_0 | V_l (H_0 - E_0) V_l | \psi_0 \rangle}. \quad (14)$$

Substituting this value for λ_l in (13) one obtains an approximate expression

for χ_l , that, when used in (11), leads to the following formula for the polarizability

$$\alpha_l = \frac{2(2l+1)\{\langle\psi_0|Q_{l,0}^2|\psi_0\rangle\}^2}{4\pi\langle\psi_0|Q_{l,0}(H_0 - E_0)Q_{l,0}|\psi_0\rangle}. \quad (15)$$

This formula can be simplified considerably. One easily sees that

$$\langle\psi_0|Q_{l,0}(H_0 - E_0)Q_{l,0}|\psi_0\rangle = \frac{1}{2}\langle\psi_0|C|\psi_0\rangle, \quad (16)$$

where the operator C is given by

$$C = [Q_{l,0}[H_0, Q_{l,0}]]. \quad (17)$$

Working out this commutator leads to

$$\begin{aligned} C &= \sum_{i=1}^N (\text{grad}_i Q_{l,0})^2 \\ &= \left(\frac{4\pi}{2l+1}\right)^2 \sum_{i=1}^N r_i^{2l-2} \{l^2 Y_{l,0}^2(\theta_i) + l(l+1) |Y_{l,1}(\theta_i, \varphi_i)|^2\}. \end{aligned} \quad (18)$$

Substituting this result in the r.h.s. of (16) and using the fact that closed shell atoms have a spherically symmetric charge distribution one obtains

$$\langle\psi_0|Q_{l,0}(H_0 - E_0)Q_{l,0}|\psi_0\rangle = \frac{(2\pi)l}{2l+1} \langle r^{2l-2} \rangle. \quad (19)$$

The polarizability can now be written as

$$\alpha_l = \frac{4\langle(R^{2l})\rangle^2}{(2l+1)^2 l \langle r^{2l-2} \rangle}. \quad (20)$$

The quantity $\langle R^{2l} \rangle$, is defined by

$$\langle R^{2l} \rangle = 4\pi \left\langle \psi_0 \left| \sum_{i,j=1}^N r_i^l Y_{l,0}(\theta_i) r_j^l Y_{l,0}(\theta_j) \right| \psi_0^A \right\rangle. \quad (21)$$

It is easily seen that the quantities $\langle R^2 \rangle$ and $\langle R^4 \rangle$ given by (3) and (6) respectively are special cases of the general expression above. The expression (20) for the multipole polarizability was first obtained by De Wette⁹ neglecting exchange effects in which case $\langle R^{2l} \rangle = \langle r^{2l} \rangle$.

It is of interest to compare the results of the variation method with the results of a standard second order perturbation method, in which case one obtains⁸)

$$\alpha_l = \frac{8\pi}{2l+1} \sum_{\nu \neq 0} \frac{\left| \left\langle \psi_0 \left| \sum_{i=1}^N r_i^l Y_{l,0}(\theta_i) \right| \psi_\nu \right\rangle \right|^2}{E_\nu - E_0}. \quad (22)$$

Replacing in the denominator of (22) the energy differences $E_\nu - E_0$ by an effective 2^l -pole excitation energy Δ_l (Unsöld approximation) and using the

closure relation one obtains the following approximate expression for the static 2^l -pole polarizability

$$\alpha_l = \frac{2\langle R^{2l} \rangle}{(2l+1)\Delta_l} \quad (23)$$

Comparing expressions (20) and (23) it follows that the simple variation method and the Unsöld approximation yield the same result if one uses for the effective 2^l -pole excitation energy

$$\Delta_l = \frac{(2l+1)l\langle r^{2l-2} \rangle}{2\langle R^{2l} \rangle} \quad (24)$$

Notice that with this expression for Δ_l the variation parameter λ_l given by (14) can be written as

$$\lambda_l = -1/\Delta_l$$

3. Van der Waals coefficients

As mentioned in the introduction the Van der Waals coefficients can be expressed as integrals over dynamic multipole polarizabilities at imaginary frequencies. Expanding the electrostatic potential of two interacting atoms A and B in inverse powers of the separation R and applying perturbation theory to second order one finds that the Van der Waals coefficients C_{2n} , $n = 3, 4, 5, \dots$, can be written as⁸⁾

$$C_{2n} = \sum_{l_1, l_2=1} C_{AB}(l_1, l_2) \delta_{l_1+l_2+1, n} \quad (25)$$

where

$$C_{AB}(l_1, l_2) = \frac{(2l_1+2l_2)!}{4(2l_1)!(2l_2)!} \frac{2}{\pi} \int_0^\infty \alpha_l^A(i\xi) \alpha_l^B(i\xi) d\xi \quad (26)$$

The coefficient $C_{AB}(l_1, l_2)$ represents the contribution to the dispersion force of the 2^{l_1} -pole on A with the 2^{l_2} -pole on B.

The problem of calculating Van der Waals coefficients is thus effectively reduced to the calculation of dynamic polarizabilities. The latter can be obtained by the same variation method as was used in previous section for the calculation of static polarizabilities. The dynamic polarizability can be written as⁸⁾

$$\alpha_l(\omega) = -\langle \psi_0 | Q_{l,0} | \chi_l^+(\omega) + \chi_l^-(\omega) \rangle \quad (27)$$

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

$$(H_0 - E_0 \pm \omega) \chi_l^{\pm}(\omega) + V_l \psi_0 = 0 \quad (28)$$

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

$$L[\chi_i^\pm] = \langle \chi_i^\pm | H_0 - E_0 \pm \omega | \chi_i^\pm \rangle + \langle \chi_i^\pm | V_i | \psi_0 \rangle + \langle \psi_0 | V_i | \chi_i^\pm \rangle \quad (29)$$

to be stationary with respect to variations of $\chi_i^\pm(\omega)$. As trial function we use again a function of the form (13) where now the variation parameter is a function of ω

$$\chi_i^\pm(\omega) = \lambda_i^\pm(\omega) V_i \psi_0. \quad (30)$$

Minimizing L with respect to $\lambda_i^\pm(\omega)$ yields

$$\lambda_i^\pm(\omega) = -\frac{1}{\Delta_i \pm \omega} \quad (31)$$

where Δ_i is the effective 2^l -pole excitation energy given by (24). Substituting this value for $\lambda_i^\pm(\omega)$ in (30) one obtains an approximate expression for $\chi_i^\pm(\omega)$, that when used in (27) leads to the following formula for the dynamic polarizability

$$\alpha_i(\omega) = \frac{l \langle r^{2l-2} \rangle}{\Delta_i^2 - \omega^2}. \quad (32)$$

Using the approximate expression (32) for the dynamic polarizability in (26) and carrying out the integration one obtains

$$C_{AB}(l_1, l_2) = \frac{2(2l_1 + 2l_2)!}{(2l_1 + 1)!(2l_2 + 1)!} \times \frac{(\langle R_A^{2l_1} \rangle)^2 (\langle R_B^{2l_2} \rangle)^2}{[(2l_2 + 1)l_2 \langle r_B^{2l_2-2} \rangle \langle R_A^{2l_1} \rangle + (2l_1 + 1)l_1 \langle r_A^{2l_1-2} \rangle \langle R_B^{2l_2} \rangle]}. \quad (33)$$

The advantage of (33) is that it only requires the knowledge of quantum-mechanical averages over the ground-state wave functions of the interacting systems. The expression for the Van der Waals coefficient $C_6 = C_{AB}(1, 1)$ that follows from the general formula (33) is identical with the Kirkwood expression for the dipole dispersion interaction [eq. (2)]. For the Van der Waals coefficient C_8 one obtains from (25) and (33)

$$C_8 = C_{AB}(1, 2) + C_{AB}(2, 1) \\ = \frac{2(\langle R_A^2 \rangle)^2 (\langle R_B^4 \rangle)^2}{10 \langle r_B^2 \rangle \langle R_A^2 \rangle + 3 N_A \langle R_B^2 \rangle} + \frac{2(\langle R_A^4 \rangle)^2 (\langle R_B^2 \rangle)^2}{10 \langle r_A^2 \rangle \langle R_B^2 \rangle + 3 N_B \langle R_A^2 \rangle}. \quad (34)$$

This formula only reduces to Buckingham's expression for C_8 [eq. (4)] in case A and B are like atoms. For the case of unlike atoms it can easily be shown that the values of C_8 obtained by (34) are higher than or equal to the values for C_8 given by (4). The origin of the difference between expressions (4) and (34) lies in the fact that Buckingham uses the same variation parameter for the dipole (A)–quadrupole (B) interaction and the quadrupole (A)–dipole (B) interaction which is only justified in the case A and B are like atoms.

Notice that using expression (20) for the static polarizability in (33) the multipole dispersion coefficients $C_{AB}(l_1, l_2)$ can be written in the form

$$C_{AB}(l_1, l_2) = \frac{(2l_1 + 2l_2)!}{4(2l_1)!(2l_2)!} \frac{\alpha_{l_1}^A \alpha_{l_2}^B}{\left(\frac{\alpha_{l_1}^A}{l_1 \langle r_A^{2l_1-2} \rangle}\right)^{1/2} + \left(\frac{\alpha_{l_2}^B}{l_2 \langle r_B^{2l_2-2} \rangle}\right)^{1/2}}. \quad (35)$$

For $l_1 = l_2 = 1$ this expression also reduces to a formula derived by Kirkwood²⁾ for the dipole dispersion interaction.

We wish to point out that the results obtained here for multipole polarizabilities and dispersion forces using the Kirkwood variation method can also be obtained by a completely different method which is based on oscillator strength sum rules. This was first demonstrated by Vinti³⁾ for the case of dipole polarizabilities and dispersion forces. The generalization to higher multipole polarizabilities and dispersion forces is straightforward. According to second order perturbation theory the dynamic 2^l -pole polarizability is given by⁸⁾

$$\alpha_l(\omega) = \frac{8\pi}{2l+1} \sum_{\nu \neq 0} \frac{(E_\nu - E_0) \left| \langle \psi_0 \left| \sum_{i=1}^N r_i^l Y_{l,0}(\theta_i) \right| \psi_\nu \rangle \right|^2}{(E_\nu - E_0)^2 - \omega^2}. \quad (36)$$

In the denominator of (36) we replace the energy differences $(E_\nu - E_0)$ by an effective 2^l -pole excitation energy \bar{E}_l . This leads to the following approximate expression for the dynamic 2^l -pole polarizability

$$\alpha_l(\omega) = \frac{Z_l}{\bar{E}_l^2 - \omega^2}, \quad (37)$$

where

$$Z_l = \frac{8\pi}{2l+1} \sum_{\nu \neq 0} (E_\nu - E_0) \left| \langle \psi_0 \left| \sum_{i=1}^N r_i^l Y_{l,0}(\theta_i) \right| \psi_\nu \rangle \right|^2.$$

One easily sees that Z_l can be written as

$$Z_l = \frac{2l+1}{4\pi} \langle \psi_0 | C | \psi_0 \rangle,$$

where the operator C is given by (17). Using the form (18) of this operator one finds

$$Z_l = l \langle r^{2l-2} \rangle. \quad (38)$$

Setting $\omega = 0$ in (37) and taking into account (38) one obtains for the static polarizability

$$\alpha_l = \frac{l \langle r^{2l-2} \rangle}{\bar{E}_l^2}. \quad (39)$$

On the other hand by directly applying the Unsöld approximation the second

order perturbation expression leads to expression (23). If we now set $\Delta_l = \bar{E}_l$ one obtains by combining (23) and (39)

$$\bar{E}_l = \frac{(2l+1)l\langle r^{2l-2} \rangle}{2\langle R^{2l} \rangle}. \quad (40)$$

This is precisely the same expression for the effective 2^l -pole excitation energy as is found by using the simple variation method. Substituting (38) and (40) in (37) leads to the same expression for the dynamic polarizability as is obtained by using the variation method [eq. (32)]. The reason that both methods yield the same result is due to the fact that the trial function (30) leads to a dynamic multipole polarizability for which the oscillator strength sum rule (38) is automatically satisfied.

4. Results and discussion

In order to check whether the simple closed formula (33) for the multipole dispersion interaction constants yields satisfactory results we first apply to the case of atomic hydrogen for which case accurate calculations are available for comparison. Substituting the expression for the moments of the charge distribution of the hydrogen atom

$$\langle R^{2l} \rangle = \langle r^{2l} \rangle = \frac{(2l+2)!}{2^{2l+1}}. \quad (41)$$

in (34) one obtains an approximate analytic expression for the Van der Waals coefficients

$$C_{\text{HH}}(l_1, l_2) = \frac{(2l_1 + 2l_2)!(l_1 + 1)^2(l_2 + 1)^2}{2^{2l_1 + 2l_2} [l_1(l_2 + 1) + l_2(l_1 + 1)]}. \quad (42)$$

In table I we compare the multipole dispersion interaction constants calculated using (42) with the results of accurate calculations⁵. Notice that the relative error decreases for the higher multipole dispersion interaction constants. Thus one may hope that the approximate expressions for the higher order Van der Waals coefficients that follow from (33) will turn out to be equally useful as the well-known Kirkwood expression for the dipole dispersion interaction [eq. (2)].

We now apply (33) to the calculation of the dipole-dipole, dipole-quadrupole, quadrupole-dipole and dipole-octupole dispersion forces between helium, neon and argon. The required moments were calculated from the accurate Self Consistent Field wave functions obtained by Clementi¹⁰ (see table II).

Using these moments in (33) one obtains the Van der Waals coefficients given in table III. For the sake of comparison we have included in table III the recent calculations of Tang, Norbeck and Certain⁶ on upper and lower bounds for the higher multipole dispersion interactions. These calculations are

Table I
Van der Waals coefficients for the interaction of two hydrogen atoms (in a.u.)

	One-parameter variation method [eq. (42)]	Accurate calculation (ref. 4)
$C(1, 1)$	6.00	6.499
$C(1, 2)$	57.9	62.2
$C(2, 2)$	1063	1135
$C(1, 3)$	1008	1075

Table II
Values of $\langle r^2 \rangle$, $\langle R^2 \rangle$, $\langle r^4 \rangle$, $\langle R^4 \rangle$ and $\langle R^6 \rangle$ (in a.u.) for helium, neon and argon from accurate SCF-wave functions (ref. 10)

	$\langle r^2 \rangle$	$\langle R^2 \rangle$	$\langle r^4 \rangle$	$\langle R^4 \rangle$	$\langle R^6 \rangle$
He	2.370	2.370	7.775	7.775	50.56
Ne	9.371	6.086	27.23	21.63	165.5
Ar	25.98	16.36	142.2	110.1	1399

Table III
Van der Waals coefficients for the interaction of He, Ne and Ar (a.u.)

Interacting pair	Dip-dip.	Dip-quad.	Quad-dip.	Oct-quad.	Dip-oct	Oct-dip.
He-He	1.48 1.47 ± 0.01	6.60 7.01 ± 0.10	6.60 7.01 ± 0.10	55.5 63.0 ± 1.4	55.5 53.4 ± 8.0	55.5 53.4 ± 8.0
He-Ni	2.58 3.13 ± 0.08	14.9 17.5 ± 3.9	11.9 15.2 ± 0.6	128 157 ± 38	175 156 ± 31	101 116 ± 22
He-Ar	8.86 9.82 ± 0.35	106.7 107 ± 25	40.1 46.5 ± 2.1	886 949 ± 244	1895 1940 ± 450	338 358 ± 58
Ne-Ne	5.01 6.87 ± 0.40	28.4 38.0 ± 10.2	28.4 38.0 ± 10.2	302 424 ± 177	320 338 ± 81	320 338 ± 81
Ne-Ar	16.1 20.7 ± 1.3	184 226 ± 62	92.7 118 ± 27	1993 2560 ± 1020	3214 4120 ± 1110	1069 1050 ± 210
Ar-Ar	54.1 67.2 ± 3.6	636 740 ± 171	636 740 ± 171	14384 16100 ± 6200	11229 13300 ± 3000	11229 13300 ± 3000

The first line for each interacting pair contains the results of the present work [eq. (33)]. The second line gives bounds on the Van der Waals coefficients obtained by Tang, Norbeck and Certain (ref. 6).

based on a combination of theoretical and experimental knowledge on static polarizabilities, oscillator strength sums and excitation energies.

For the data presented in table III it appears that the results obtained with (33) are generally in satisfactory agreement with the bounds obtained by Tang, Norbeck and Certain⁶). Whenever deviations occur from these bounds the values given by (33) are too low as is to be expected from a simple one-parameter variation method.

The extension of the method used in this paper to the calculation of higher order Van der Waals coefficients for molecules is straightforward. These higher order coefficients are especially interesting for highly symmetric molecules (e.g. CH₄). Here the lowest-order dispersion forces are isotropic whereas the higher order dispersion interactions are anisotropic as was first emphasized by Buckingham¹¹).

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