

Quadrupole Contributions to London's Dispersion Forces

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signs. With these bipolar coacervates, if V_1 is to remain unchanged for particles of both kinds, the electric fields and the charges on the micelles increase when the concentration increases, whereas with unipolar coacervates the fields decrease. The fact that the particles in the bipolar coacervates remain separated by considerable distances and do not come into contact proves the presence of some other kind of repulsive force than that given by Eq. (48). Hydration seems to be the most reasonable explanation.

The very intense fields that develop when the particles come close together are apparently able to draw water in between the particles and so hold them apart.

It seems, therefore, that Bungenberg de Jong's working hypothesis for this type of coacervation should be accepted. It should be noted that in bipolar coacervates the particles are far closer together than they are in such unipolar coacervates as bentonite, tobacco virus and iron oxide sols.

Quadrupole Contributions to London's Dispersion Forces

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The contribution of terms in R^{-8} and R^{-10} to the dispersion forces is expressed by a simple, approximate formula (Eq. (7)) involving only measurable quantities (polarizability, absorption frequency, oscillator strength). The formula is applicable when the dispersion curve of the substance can be represented with the use of a single resonant frequency. Numerical values of the terms in question are calculated for a number of molecules (Table II). Except in the case of the alkalis, where the convergence of the sequence in inverse powers of R fails at distances around 6A, the R^{-10} term is generally negligible, while the R^{-8} term contributes appreciably in the region of the van der Waals minimum.

FOR large distances of separation (R), the interaction energy of two neutral molecules is given with good approximation by C_1/R^6 , where C_1 is a coefficient which may be calculated with considerable precision for simpler molecules and atoms. For the case where the dispersion curve of the substance in question is given with sufficient accuracy by an expression involving but a single resonant frequency, ν , London¹ has derived the particularly simple and beautiful formula:

$$C_1 = -\frac{3}{4}h\nu\alpha^2, \quad (1)$$

which, in applications, has proved fairly successful.

On the other hand, it is known that C_1/R^6 is only the first term of an expansion to which multipoles contribute higher powers in $1/R$. In detailed investigations, and especially when

attention is given to values of the intermolecular distance in the neighborhood of the van der Waals minimum, these higher power terms are important. I wish to point out in this note that, under the conditions for which (1) is valid, equally simple formulas are available for the coefficients of the higher terms.

Expression (1) is derived most directly with the use of a model which possesses only a single frequency, the simple harmonic oscillator.¹ The state function for two three-dimensional isotropic oscillators, infinitely far apart, and vibrating in quantum states n_1, n_2, n_3 , and n_4, n_5, n_6 , respectively, is given by

$$\psi(n_1 \cdots n_6) = \prod_1^6 H_{n_i}(\beta^{\frac{1}{2}} x_i) \exp [-(\beta/2)x_i^2], \quad (2)$$

where the x_i stand for the 6 coordinates of the two oscillators, each referred to the center of mass of its molecule. The parameter β measures

¹ F. London, *Zeits. f. physik. Chemie* **B11**, 222 (1930); *Trans. Faraday Soc.* **33**, 8 (1937).

the stiffness of the oscillators; elementary theory shows it to be related to the polarizability α and the classical frequency ν as follows:

$$\beta = e^2 / \alpha h \nu. \quad (3)$$

As the two molecules approach, a perturbation $V = V_1 + V_2 + V_3 + \dots$ is called into play, where²

$$\begin{aligned} V_1 &= -(e^2/R^3)(2z_1z_2 - x_1x_2 - y_1y_2), \\ V_2 &= (3e^2/2R^4)[(x_1^2 + y_1^2 - 2z_1^2 - 2x_1x_2 - 2y_1y_2)z_2 \\ &\quad - (x_2^2 + y_2^2 - 2z_2^2 - 2x_1x_2 - 2y_1y_2)z_1], \\ V_3 &= \frac{3}{4}(e^2/R^5)[3x_1^2x_2^2 + 3y_1^2y_2^2 + x_1^2y_2^2 + y_1^2x_2^2 \\ &\quad - 4(x_1^2 + y_1^2)z_2^2 - (4x_2^2 + y_2^2)z_1^2 + 8z_1^2z_2^2 \\ &\quad + 4(x_1x_2y_1y_2 + 4x_1x_2z_1z_2 + 4y_1y_2z_1z_2)]. \end{aligned}$$

The z axis of both molecules is here chosen parallel to R .

A perturbation calculation leads to the results desired. The first-order energy is zero because the average of V over the normal state vanishes. To compute

$$E^{(2)} = \sum_{\lambda} \frac{|V_{0\lambda}|^2}{E_0 - E_{\lambda}},$$

we only require the following formulas for the elements of the individual coordinate matrices:

$$\begin{aligned} x_{01} &= (2\beta)^{-\frac{1}{2}}; \quad (x^2)_{00} = (2\beta)^{-1}; \\ (x^2)_{02} &= 2^{-\frac{1}{2}}\beta^{-1}. \end{aligned}$$

Elements not listed here either do not appear or are zero. Distinction between the coordinates is unnecessary because the oscillators are taken to be isotropic. The unperturbed energies, E_{λ} , are given by

$$E_{\lambda} = h\nu \sum_{i=1}^6 (n_i + \frac{1}{2}).$$

In Table I we show (1) the excited states $\psi(n_1 \dots n_6)$ for which $V_{0\lambda}$ is different from zero, (2) the corresponding energy difference $E_{\lambda} - E_0$, (3) the value of $V_{0\lambda}$. It will be noticed that V_1 causes the ground state to combine only with doubly excited states, V_2 with triply, and V_3 with

quadruply excited states. This means that there is no collusion between the three terms in V ; each produces cleanly its own order of approximation, and there are no terms with powers of $1/R$ intermediate between those appearing in the result. The parentheses in the first column contain the quantum numbers of the functions in question; they refer to $x_1y_1 \dots z_2$, in that order. Finally, we are using the abbreviations $p_1 = -e^2/R^3$, $p_2 = 3e^2/2R^4$, $p_3 = \frac{3}{4}e^2/R^5$.

Adding up the squares of the elements and dividing by $(E_0 - E_{\lambda})$ we obtain

$$E^{(2)} = -\frac{3/2 p_1^2}{2h\nu \beta^2} - \frac{5 p_2^2}{3h\nu \beta^3} - \frac{70 p_3^2}{4h\nu \beta^4},$$

which, on inserting the values of the p 's and of β (Eq. (3)), becomes

$$E^{(2)} = -\frac{3 \alpha^2 h \nu}{4 R^6} - \frac{15 \alpha^3 (h \nu)^2}{4 e^2 R^8} - \frac{315 \alpha^4 (h \nu)^3}{32 e^4 R^{10}}. \quad (4)$$

The division of elements in Table I shows, of course, that the same result could have been obtained by squaring V_1 , V_2 and V_3 , computing 0-0-elements, and dividing by $2h\nu$, $3h\nu$ and $4h\nu$, respectively.

The next step is to generalize this expression so as to make it valid for the case where each

TABLE I.

FUNCTIONS	$(E_{\lambda} - E_0)/h\nu$	$V_{0\lambda}$	
(100,100)	2	$-(2\beta)^{-1}p_1$	Elements of V_1
(010,010)	2	$-(2\beta)^{-1}p_1$	
(001,001)	2	$2(2\beta)^{-1}p_1$	
(200,001)	3	$\frac{1}{2}\beta^{-\frac{1}{2}}p_2$	Elements of V_2
(020,001)	3	$\frac{1}{2}\beta^{-\frac{1}{2}}p_2$	
(002,001)	3	$-\beta^{-\frac{1}{2}}p_2$	
(100,101)	3	$-2(2\beta)^{-\frac{1}{2}}p_2$	
(010,011)	3	$-2(2\beta)^{-\frac{1}{2}}p_2$	
(001,200)	3	$\frac{1}{2}\beta^{-\frac{1}{2}}p_2$	
(001,020)	3	$\frac{1}{2}\beta^{-\frac{1}{2}}p_2$	Elements of V_3
(001,002)	3	$-\beta^{-\frac{1}{2}}p_2$	
(101,100)	3	$-2(2\beta)^{-\frac{1}{2}}p_2$	
(011,010)	3	$-2(2\beta)^{-\frac{1}{2}}p_2$	
(200,200)	4	$3 \cdot \frac{1}{2}\beta^{-2}p_3$	
(020,020)	4	$3 \cdot \frac{1}{2}\beta^{-2}p_3$	
(200,020)	4	$\frac{1}{2}\beta^{-2}p_3$	
(020,200)	4	$\frac{1}{2}\beta^{-2}p_3$	
(002,200)	4	$-4 \cdot \frac{1}{2}\beta^{-2}p_3$	
(002,020)	4	$-4 \cdot \frac{1}{2}\beta^{-2}p_3$	
(200,002)	4	$-4 \cdot \frac{1}{2}\beta^{-2}p_3$	
(020,002)	4	$-4 \cdot \frac{1}{2}\beta^{-2}p_3$	
(002,002)	4	$8 \cdot \frac{1}{2}\beta^{-2}p_3$	
(110,110)	4	$4 \cdot (2\beta)^{-2}p_3$	
(101,101)	4	$16 \cdot (2\beta)^{-2}p_3$	
(011,011)	4	$16 \cdot (2\beta)^{-2}p_3$	

² H. Margenau, Phys. Rev. **38**, 747 (1931). The three terms here retained are known as dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole energies.

molecule contains several oscillating charges, all having the same frequency. Let the number of electrons be f . The modification of (2) is obvious; instead of (3) we have

$$\beta = fe^2/\alpha h\nu.$$

V_1 , V_2 and V_3 must be modified by attaching to all coordinates labeled 1, another subscript i , to those labeled 2 another subscript j , and then summing over both i and j independently from 1 to f . There will then be many more functions in Table I, and the matrix elements there listed will be repeated f^2 times. On adding them up as before, there emerges a factor f^{-1} in the second, and f^{-2} in the third term on the right-hand side of (4), the first term being unaltered. The final formula therefore reads

$$E^{(2)} = -\frac{3}{4} \frac{\alpha^2 h\nu}{R^6} - \frac{15}{4} \frac{\alpha^3 (h\nu)^2}{fe^2 R^8} - \frac{315}{32} \frac{\alpha^4 (h\nu)^3}{f^2 e^4 R^{10}}. \quad (7)$$

The meaning of f here is perfectly clear; it is the oscillator strength of the transition of energy $h\nu$. As a concession to the structure difference between real molecules and our simple model we must permit f to be nonintegral. Moreover, this quantity is always known from the dispersion formula whenever $h\nu$ is known. This is an advantage not shared by the results of variational calculations, which often involve the number of electrons in the outer shell in a rather ambiguous way.

Equation (7) may, of course, be written in a way such that $h\nu$ does not appear, because of an elementary relation between α , $h\nu$ and f , holding for a molecule with a single absorption frequency. In fact, for a collection of simple oscillators, as well as an ideal molecule with single ν ,

$$\nu = (e/2\pi)(f/\alpha m)^{\frac{1}{2}}.$$

When this is introduced in (7) that equation becomes

$$E^{(2)} = -\frac{3}{4R^6} \hbar e \left(\frac{f\alpha^3}{m} \right)^{\frac{1}{2}} - \frac{15}{4R^8} \frac{\hbar^2}{m} \alpha^2 - \frac{315}{32R^{10}} \frac{\hbar^3}{e} \left(\frac{\alpha^5}{fm^3} \right)^{\frac{1}{2}}. \quad (7')$$

The first term on the right represents the

formula of Slater and Kirkwood,³ except that the oscillator strength appears in place of their parameter N , the number of electrons in the outer shell. It is thus apparent that for molecules having a single ν , N should really be replaced by f .

The manner in which we have derived formula (7) shows clearly its limit of validity: it arises from the fact that it contains only a single frequency. One must also remember that the error committed in approximating the dispersion curve with the use of a single frequency is magnified in each succeeding term of (7), because these terms involve increasingly higher moments of the total spectral intensity distribution. But it seems that one may trust this formula as a guide somewhat beyond the limitations implied in its derivation, since it contains only measurable quantities not peculiar to the simple oscillator model. Remarks by Van Vleck⁴ on the use of the oscillator model in deriving corrections to the Clausius-Mosotti law are illuminating in this connection.

To test it, we refer to the case of He, where the dispersion curve can be represented with sufficient accuracy if the single quantum $h\nu = 24.4$ e-volts is employed, and where the dipole-quadrupole term is known from other calculations.^{2, 5} The f value associated with ν is 1.1. We write Eq. (7) in the form $E^{(2)} = C_1 R^{-6} + C_2 R^{-8} + C_3 R^{-10}$. Of primary interest is C_2/C_1 , which has the value $1.53 \times 10^{-16} \text{ cm}^2$. The most accurate calculation of this quantity is probably the one by Page, who finds $1.75 \times 10^{-16} \text{ cm}^2$. This agreement is to be regarded as satisfactory.

In Table II may be found the calculated values of C_1 , C_2 and C_3 for a number of molecules, together with the data used for $h\nu$, α and f .⁶ The numerical results are based on Eq. (7), not (7'). The two forms often give slightly different results because the experimental value of α does not agree exactly with that extrapolated from

³ J. C. Slater and J. G. Kirkwood, *Phys. Rev.* **37**, 682 (1931).

⁴ J. H. Van Vleck, *J. Chem. Phys.* **5**, 556 (1937). See especially p. 564.

⁵ C. H. Page, *Phys. Rev.* **53**, 426 (1938).

⁶ The frequencies and f values used here and in Table II are taken chiefly from C. and M. Cuthbertson's investigations. Tabulations and a good survey of matters relating to the dispersion curve may be found in the article by K. L. Wolf and K. F. Herzfeld, *Handbuch der Physik*, Vol. 20 (1928).

TABLE II.

	$h\nu$ e-volts	$\alpha \times 10^{24}$	f	$C_1 \times 10^{60}$	$C_2 \times 10^{78}$	$C_3 \times 10^{92}$	$C_2/C_1 \times 10^{16}$	$C_3/C_1 \times 10^{16}$ *
Ne	25.7	.39	2.37	4.67	6.9	5.3	1.47	1.46
A	17.5	1.63	4.58	55.4	120	136	2.17	3.0
Kr	14.7	2.46	4.90	107	275	370	2.55	3.08
Xe	12.2	4.00	5.61	233	710	1120	3.04	
H ₂	(14.5)	.81	(1.5)	11.4	31	45	2.7	
N ₂	15.8	1.74	4.61	57.2	120	130	2.08	
O ₂	13.6	1.57	3.11	39.8	96	120	2.41	
CO ₂	15.5	2.86	5.70	152	410	590	2.72	
CH ₄	14.1	2.58	4.60	112	310	440	2.77	
NH ₃	11.7	2.24	2.72	70	236	410	3.37	
Cl ₂	12.7	4.60	6.55	321	1000	1630	3.10	
HCl	13.4	2.63	4.25	111	320	480	2.89	
HBr	12.1	3.58	4.71	185	600	1000	3.24	
HI	10.5	5.4	5.30	370	1360	2700	3.7	
Na	2.08	29.7	1	2190	47600	530000	21.7	
¹ K	1.60	(49)	(1)	4600	127000	1800000	28	

* Values according to Buckingham, reference 7.
Numbers in parentheses are uncertain.

the dispersion formulas here employed. Absolute units are implied throughout (energy expressed in ergs). The numbers appearing under $C_2/C_1 \times 10^{16}$ may be defined as the ratio of dipole-quadrupole to dipole-dipole energy at a hypothetical distance of separation equal to 1A (where, of course, they are physically meaningless because of other overpowering interactions).

Very refined variational calculations of van der Waals forces including the coefficient C_2 have recently been made by Buckingham.⁷ The last column contains his values of C_2/C_1 for the rare gases he considered. In judging the agreement one should recall that the range of uncertainty even in C_1 is still fairly large. (Thus, London¹ obtains for He, $C_1 = 1.22 \times 10^{-60}$ against Buckingham's $C_1 = 1.63 \times 10^{-60}$.) Also, if Buckingham's method is applied to the oscillator model, it gives a value of C_2/C_1 which is 28 percent too great. In view of these facts the agreement seems good.⁸

Two general conclusions of some interest may be drawn from Table II. First, the term in R^{-8} is always of appreciable magnitude in the region

of the van der Waals minimum, while the term in R^{-10} is quite generally negligible. Second, for the alkalis, Na and K, the quadrupole forces are particularly strong in relation to the R^{-6} forces. Indeed the indication is that the R^{-8} term is equal to the R^{-6} term at an intermolecular distance of about 5A. Here, the last term in (7) also gains importance; it contributes about half as much as the first. This means that the series expansion for V has little significance for these atoms, except at larger distances of separation.

Unfortunately, no simple formula is available for expressing the first-order forces which are of prime importance in the critical region. The approximation of infinite forces at the gas kinetic collision distance is most inadequate. It gives the appearance of success if, as a compensating error, the dipole-quadrupole forces are neglected. In general, then, if formula (7) is to be used, the first-order forces must be introduced either from detailed calculation⁹ or by a method such as that adopted by Born and Mayer,¹⁰ and by Spomer and Bruch-Willstätter.¹¹

⁷ R. A. Buckingham, Proc. Roy. Soc. **A160**, 94 (1937).

⁸ It is quite possible that our values of C_2/C_1 are a little low because of our choice of $h\nu$. For consistency, this was taken wherever possible from the same authors (Cuthbertson); their values have a tendency to be smaller than those listed by other investigators.

⁹ P. Gombar, Zeits. f. Physik **93**, 378 (1935). H. Jensen, Zeits. f. Physik **101**, 164 (1936).

¹⁰ M. Born and J. E. Mayer, Zeits. f. Physik **75**, 1 (1932).

¹¹ H. Spomer and M. Bruch-Willstätter, J. Chem. Phys. **5**, 745 (1937).