NOTE ON THE CALCULATION OF van der WAALS FORCES[1]

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Abstract

The general expression for the van der Waals energy arising from dipole inter-action between atoms involves a summation over transition probabilities. These are in most cases difficult to calculate. It is here pointed out that since these transition probabilities obey the sum rule of Thomas and Kuhn, they may be evaluated in a manner which permits van der Waals' forces to be calculated with good approxima-tion, provided that the polarizability is known. The method is outlined and illus-trated by application to two examples: Na and He. The result in the case of He is in very good agreement with that obtained by the variational method.

THE methods proposed so far for a calculation of intermolecular forces depend on an (exact or approximate) knowledge either of the molecular wave functions[2] or of the oscillator strengths (dispersion f-values) associated with transitions from the ground state of the molecules in question.[3] Occa-sionally, useful approximations were obtained in terms of polarizabilities and other known characteristics. In this note we wish to suggest a method, semi-empirical in character and not involving the use of wave functions, which in general, enables a calculation of van der Waals forces between atoms with greater accuracy than others of equal simplicity permit. It consists in expres-sing the perturbational energy of the second order as a sum over f-values, as was first done by London, and then determining these f-values by means of the sum rule of Thomas and Kuhn, and the relative intensities of spectral lines.

Suppose that the two interacting atoms, A_1 and A_2, are similar and a dis-tance R apart, R being so large that electron interchange does not take place. Let both A_1 and A_2 be in their lowest energy state which we take to be spheri-cally symmetrical (s-state). α and β denumerate the various excited states of A_1 and A_2 respectively. If we restrict our consideration to the effects of the classical dipole interaction

$$V = \frac{e^2}{R^3}(y_1 y_2 + z_1 z_2 - 2 x_1 x_2) \tag{1}$$

[1] Part of the considerations here presented have been reported at the meeting of the Amer. Phys. Soc., Feb. 26–28. Hitherto we did not feel that they were of sufficient interest to be pub-lished more fully. Recently, however, Slater and Kirkwood (see ref. 2) have calculated a value for the attractive forces between He atoms differing widely from London's result. They at-tribute this discrepancy to the neglect of double electron jumps in London's theory. Aside from being applicable to many cases not of immediate interest at present, the method here outlined shows the correctness of the latter supposition.

[2] Eisenschitz and London, Zeits. f. Physik 60, 491 (1930); Slater and Kirkwood, Phys. Rev. 37, 682 (1931); Hassé, Proc. Camb. Phil. Soc. 27, 66 (1931).

[3] F. London, Zeits. f. phys. Chemie, B, 11, 222 (1930).

which is proper for large separations only, the second order perturbation energy of $A_1 + A_2$ becomes

$$\Delta_2 E = - \sum_{\alpha\beta}{}' \frac{|V_{11,\alpha\beta}|^2}{E_\alpha + E_\beta - 2E_1}, \tag{2}$$

where

$$|V_{11,\alpha\beta}|^2 = \frac{e^4}{R^6}(y_{1\alpha}^2 y_{1\beta}^2 + z_{1\alpha}^2 z_{1\beta}^2 + 4x_{1\alpha}^2 x_{1\beta}^2 + 2y_{1\alpha}z_{1\alpha}y_{1\beta}z_{1\beta}$$
$$- 4x_{1\alpha}y_{1\alpha}x_{1\beta}y_{1\beta} - 4x_{1\alpha}z_{1\alpha}x_{1\beta}z_{1\beta}) \tag{3}$$

$q_{1\alpha}$ is the coordinate matrix associated with a transition of A from the lowest state (1) to the state α, e.g. $x_{1\alpha} = \int R_{10}(r)xR_{nl}(r)P_l^m e^{im\phi}r^2\sin\theta dr d\theta d\phi$; n, l, and m being the quantum numbers with their usual significance. (We are writing R_{10} for the radial function of the lowest state without meaning to imply that $n = 1$ for this state.) It follows directly that

$$\sum_m x_{1\alpha}y_{1\alpha} = \sum_m x_{1\alpha}z_{1\alpha} = \sum_m y_{1\alpha}z_{1\alpha} = 0,$$

and that

$$\sum_m x_{1\alpha}^2 = \sum_m y_{1\alpha}^2 = \sum_m z_{1\alpha}^2 = \tfrac{1}{3}\delta_1{}' r_{1\alpha}^2.$$

Hence in summing (3) over the magnetic quantum numbers of both A_1 and A_2 we obtain $\tfrac{2}{3}\delta_1{}^{l\alpha}\delta_1{}^{l\beta}e^4/R^6\, r_{1\alpha}^2 r_{1\beta}^2$ so that (2) becomes

$$\Delta_2 E = - \frac{2}{3}\frac{e^4}{R^6}\sum_{\alpha\beta}{}' \frac{r_{1\alpha}^2 r_{1\beta}^2}{E_\alpha + E_\beta - 2E_1}, \tag{4}$$

where now the summation is no longer over magnetic quantum numbers and includes only states connected with the ground state by dipole radiation ($l_\alpha = l_\beta = 1$). But $r_{1\alpha}$ is related to the f-values appearing in the dispersion formula

$$n^2 - 1 = \frac{e^2 N}{\pi m}\sum_\alpha \frac{f_{1\alpha}}{\nu_\alpha^2 - \nu^2}$$

by the relation

$$r_{1\alpha}^2 = \frac{3}{2m}\left(\frac{h}{2\pi}\right)^2 \frac{f_{1\alpha}}{E_\alpha - E_1}. \tag{5}$$

Substituting this in (4) there results a formula meanwhile already obtained by London and used by him to compute intermolecular forces by means of a knowledge of a limited number of empirical f-values. We wish to propose a scheme permitting the f-values to be determined independently of spectroscopic dispersion formulae, which necessarily emphasize unduly the f's in the vicinity of the spectral region for which the formulae were calculated.

Combining (5) and (4) and realizing that $\Sigma_{\alpha\beta}{}'$ includes an integration over the continuous region of the spectrum we may write

$$\Delta_2 E = -F\left\{ {\sum_{\alpha\beta}}' \frac{f_{1\alpha}f_{1\beta}}{v_\alpha v_\beta(v_\alpha + v_\beta)} + 2{\sum_\alpha}' \int_0^\infty \frac{f_{1\alpha}(df_{1E}/dE)dE}{v_\alpha(1 + E)(v_\alpha + 1 + E)} \right.$$

$$\left. + \int_0^\infty \int_0^\infty \frac{(df_{1E'}/dE')(df_{1E''}/dE'')dE'dE''}{(1 + E')(1 + E'')(2 + E' + E'')} \right\}. \tag{6}$$

We are here using the abbreviations:

$$\epsilon_\alpha = -E_\alpha; \quad v_\alpha = 1 - \frac{\epsilon_\alpha}{\epsilon_1}; \quad F = \frac{1}{R^6} \frac{3}{2m^2\epsilon_1^3}\left(\frac{he}{2\pi}\right)^4$$

E is the energy of any state beyond the series limit, measured in units equal to the energy of the series limit, ϵ_1. (6) does not take explicit account of possible multiple electron transitions to discrete states beyond the series limit, the energy of which is frequently not known. They may be considered included in the integration, however, since the f-values will be adjusted in such a manner that their sum obeys the theorem of Kuhn and Reiche,[4] which postulates:

$${\sum_\alpha}' f_{1\alpha} + \int_0^\infty \frac{df_{1E}}{dE} dE = Z_0 \tag{7}$$

Z_0 being the number of dispersion electrons.

It becomes necessary to make some assumption about the distribution of the f_{1E}'s. Fortunately, the calculation of $\Delta_2 E$ is not very sensitive to this choice, provided that (7) is satisfied. We shall suppose, in conformity with what is known about H and x-ray spectra, that

$$\frac{df_{1E}}{dE} = \frac{\gamma}{(1 + E)^3}, \tag{8}$$

γ being at present undetermined. Moreover, we shall consider that the relative intensities of the first few emission lines of the principal series are known. The accuracy of the calculation is not seriously impaired if this is not the case. Suppose these relative intensities to be J_α. Then one may easily verify that

$$f_{1\alpha} = \frac{\beta J_\alpha}{v_\alpha^3} \equiv \beta\phi_\alpha, \tag{9}$$

since $J_\alpha = \text{const.} (E_\alpha - E_1)^4 r_{1\alpha}^2$. β is another undetermined constant. To determine β and γ we have first (7), which may be written on account of (8) and (9):

$$\beta {\sum_\alpha}' \phi_\alpha + \frac{\gamma}{2} = Z_0 \tag{10}$$

and second the expression for the polarizability in a static field:

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[4] For complex structures, this sum rule is merely an approximation.

$$\alpha = \frac{1}{m}\left(\frac{eh}{2\pi}\right)^2 \sum_{\alpha}' \frac{f_{1\alpha}}{(E_\alpha - E_1)^2},$$

or, explicitly,

$$\alpha = \frac{1}{m\epsilon_1{}^2}\left(\frac{eh}{2\pi}\right)^2 \left\{ \sum_{\alpha}' \frac{f_{1\alpha}}{v_\alpha{}^2} + \int_0^\infty \frac{(df_{1E}/dE)dE}{(1+E)^2} \right\} \tag{11a}$$

whence

$$\beta \sum_{\alpha}' \frac{\phi_\alpha}{v^2{}_\alpha} + \frac{\gamma}{4} = m\epsilon_1{}^2\left(\frac{2\pi}{eh}\right)^2 \alpha. \tag{11}$$

(10) and (11) supply the required numerical values of β and γ. If line intensities are not known, we may put the first $\phi = 1$ and all others equal to 0. The evaluation of (6) is now an easy matter.

In cases where $Z_0 = 1$ (no multiple jumps) the contribution of the region beyond the series limit is usually small. It may then be advisable to write (6)

$$\Delta_1 E = -\frac{F}{2}\left\{ \sum_{\alpha\beta}'(1+P_{\alpha\beta})f_{1\alpha}f_{1\beta} + 2\sum_{\alpha}' \int_0^\infty (1+P_{\alpha E})f_{1\alpha}\frac{df_{1E}}{dE}\,dE \right.$$
$$\left. + \int_0^\infty \int_0^\infty (1+P_{E'E''})\frac{df_{1E'}}{dE'}\frac{df_{1E''}}{dE''}\,dE'dE'' \right\},$$

with the abbreviations

$$P_{\lambda\mu} = \frac{1 - v_\lambda v_\mu(v_\lambda + v_\mu)/2)}{v_\lambda v_\mu(v_\lambda + v_\mu)/2)},$$

v_E being $1+E$.

Using (7), this goes over into

$$\Delta_2 E = -\frac{F}{2}\left\{ Z_0{}^2 + \sum_{\alpha\beta}' P_{\alpha\beta}f_{1\alpha}f_{1\beta} + 2\sum_{\alpha}' P_{\alpha E}f_{1\alpha}\frac{df_{1E}}{dE}\,dE \right.$$
$$\left. + \int_0^\infty \int_0^\infty P_{E'E''}\frac{df_{1E'}}{dE'}\frac{df_{1E''}}{dE''}\,dE'dE'' \right\}. \tag{12}$$

Recalling the definition of the v's we see that in some cases where the energy of all excited states is small compared with that of the lowest state they do not differ greatly from 1, which makes the P's small. Then one may expect to attain a fair approximation to the polarization forces by retaining in the $\{\ \}$ of (12) only the term $Z_0{}^2$. For hydrogen, the last 3 terms contribute about 8 percent of the total. If we make use of (8), (9), (10), and (11) expression (12) becomes:

$$\Delta_2 E = -\frac{F}{2}\left\{ Z_0{}^2 + \beta^2 \sum_{\alpha\beta}' P_{\alpha\beta}\phi_\alpha\phi_\beta + \beta\gamma \sum_{\alpha}' R_\alpha\phi_\alpha - 10.170\gamma^2 \right\}, \tag{13}$$

where

$$R_\alpha = \frac{4}{v_\alpha{}^2}\left[\frac{1}{3} - \frac{1}{2v_\alpha} + \frac{1}{v_\alpha{}^2} - \frac{1}{v_\alpha{}^3}\log\,(1 + v_\alpha)\right] - 1.$$

For hydrogen, this expression gives $\Delta_2 E$ to within 1 percent if only 4ϕ's are used.

As an illustration, let us compute the polarization energy of two Na-atoms by the method here outlined. α can here be calculated since the f-values happen to be known.[5] They will also afford a check on our β and γ. α turns out to be 24.2×10^{-24}. (We omit the details of the calculation, which is made with the aid of Eq. (11).) We shall use only ϕ_2, corresponding to the resonance transition, and put it equal to 1. v_2 is then 0.409; $\epsilon_1 = 8.145\times10^{-12}$ ergs. Eqs. (10) and (11) give

$$\beta + \frac{\gamma}{2} = 1; \quad \frac{\beta}{0.409^2} + \frac{\gamma}{4} = 5.88,$$

so that $\beta = 0.888$ and $\gamma = 0.224$. From (13) one then obtains

$$\Delta_2 E = \frac{12.5}{R^6} \times 10^{-58} \text{ ergs} = \frac{790}{r^6} \text{ volts},$$

if r is measured in $\mathring{A}$. The correct value, which may be calculated from Sugiura's work, is

$$\Delta_2 E = \frac{14.5}{R^6} \times 10^{-58} \text{ ergs}.$$

It may be approximated as closely as desired, of course, by taking a greater number of ϕ's into account. We note in passing that these results suggest the existence of very strong polarization forces and the formation of polarization molecules, such as were observed in K_2 by Kuhn.[6]

Another more interesting application is to He, where our calculations can be no longer controlled by a sufficiently accurate knowledge of the f-values. There exist intensity measurements on the emission lines of the "principal" series[7] from which the ϕ_α's may be obtained by (9). We have considered 10 of them, but it turns out that very few of them would have been sufficient, because the main contribution to the f's seems to come from the region beyond the series limit. Taking α as 0.206×10^{-24}, Eqs. (10) and (11) become

$$\beta \sum_\alpha{}' \phi_\alpha + \tfrac{1}{2}\gamma = 2$$

$$\beta \sum_\alpha{}' \frac{\phi_\alpha}{v_\alpha{}^2} + \frac{1}{4}\gamma = 1.122.$$

If now we use the relative intensity data in Hopfield's arbitrary units $\Sigma_\alpha{}'\phi_\alpha =$

[5] Y. Sugiura, Phil. Mag. **4**, 495 (1927).

[6] Kuhn, Naturwissenschaften **18**, 332 (1930). See also Oldenberg, Zeits. f. Physik **47**, 184 (1928) and **55**, 1 (1929).

[7] Hopfield, Astrophys. J. **72**, 133 (1930).

293.7, and $\Sigma_\alpha' \phi_\alpha/v_\alpha{}^2 = 351.1$, whence $\beta = 5.97 \times 10^{-4}$ and $\gamma = 3.64$. The surprising magnitude of γ shows clearly, and probably over-emphasizes, the important rôle of the transitions to states beyond the ionization limit of one electron. That these states need not belong to the continuous spectrum, and that our integration (instead of summation) is dictated by convenience and lack of data to handle them more properly has already been pointed out. Substituting β and γ in (6), or more conveniently in (13) (where now, of course, on account of the size of γ only the second term in $\{\}$ may be neglected) we find

$$\Delta_2 E = \frac{9.68}{R^6} \times 10^{-61}(1.49) \text{ ergs} = \frac{14.4}{R^6} \times 10^{-61} \text{ ergs} = \frac{0.91}{r^6} \text{ volts, if } r \text{ is in } \overset{\circ}{A}. \quad (14)$$

(The somewhat smaller value reported previously[8] was obtained by considering only transitions of one electron, putting $Z_0 = 1$, which is not legitimate.) (14) agrees very well indeed with the result of Slater and Kirkwood, calculated with a variational method, namely

$$\Delta_2 E = \frac{14.9}{R^6} \times 10^{-61} \text{ ergs}.$$

The latter authors suggest that the large difference between their result and the one obtained by applying London's simple approximation, which yields an upper limit $\Delta_2 E_{\max} = 12.4 \times 10^{-61}$ ergs, is occasioned by the neglect of double jumps in London's expression. The calculations presented here make this evident.

[8] See ref. 1.