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July 21, 1958

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ABSTRACT

For the calculation of polarizabilities and dispersion forces it is in general not valid to use the Hasse method; one must calculate promotional energies for polarized wave functions. There occurs an important effect in the promotional energies for multielectronic atoms from the collective behavior of the electronic cloud and greatly increases the promotional energy. This is responsible for the disagreement of the London formula by a factor of two with experimental data for the noble gases.

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INTRODUCTION

In this paper I shall attempt to elucidate further the nature of the London interaction between heavy atoms in which a number of electrons are involved. We are, of course, particularly interested in its relation to the polarizability. This subject has been discussed in the past and still demands further clarification.<sup>1-6</sup> The various formulae derived for this interaction, such as the London formula,<sup>1, 2</sup> the Kirkwood-Slater formula,<sup>3</sup> and the Kirkwood-Müller formula<sup>4</sup> do not predict with a good degree of accuracy the coefficients derived from experimental data.<sup>7-10</sup>

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\*This research was performed under the auspices of the U. S. Atomic Energy Commission.

<sup>1</sup>F. London, Z. physik, Chem. B11, 222 (1930).

<sup>2</sup>F. London, Z. Physik 63, 245 (1930).

<sup>3</sup>J. C. Slater and Y. G. Kirkwood, Phys. Rev. 37, 686 (1937).

<sup>4</sup>A. Müller, Proc. Roy. Soc. (London) A154, 624 (1936).

<sup>5</sup>R. A. Buckingham, Proc. Roy. Soc. 160, 113 (1937).

<sup>6</sup>H. Margenau, Revs. Modern Phys. 11, 1 (1939).

<sup>7</sup>K. S. Pitzer, Quantum Chemistry, (Prentice-Hall, New York 1953) p. 339.

<sup>8</sup>K. S. Pitzer, J. Am. Chem. Soc. 78, 4565 (1956).

<sup>9</sup>Hirschfelder, Curtiss, and Bird, Molecular Theory of Gases and Liquids (Wiley, New York, 1954) p. 966.

<sup>10</sup>DeMarcus, Hopper, and Allens A Method for the Determination of Surface Area, K-1222, June 1955.

Pitzer<sup>7</sup> observed that the London formula,

$$E_L = - \frac{3\alpha^2}{4} I R^{-6}, \quad (1)$$

(where  $\alpha$  = polarizability,  $I$  = ionization potential,  $R$  = interatomic separation) could be brought into line with most experimental data by multiplying it by a correction factor of 2. Noteworthy exceptions are He and H<sub>2</sub>, which are in fair agreement with the uncorrected formula. Pitzer<sup>8</sup> also suggested that the Kirkwood-Slater formula, which contains explicitly the number of electrons taking part in the London interaction, could be made to agree for the noble gases by assuming an effective number of electrons, which ranges from 8 in neon to 22 in xenon. However, in calculations for the polarizability Pauling,<sup>11</sup> Buckingham,<sup>12</sup> and Sternheimer<sup>13</sup> found little contribution to the polarizability from inner-shell orbitals. Hirschfelder et al.<sup>10</sup> included in their discussion  $R^{-8}$  and  $R^{-10}$  terms with the London formula and found the same factor of 2; they said that there was no explanation for such a factor and suggested the possibility that the potential function did not have a wide enough bowl. In this work I shall develop what I believe to be the best explanation for this effect. It arises from the fact that there is a large interaction energy between polarized orbitals, which means that if there are many electrons participating in the London interaction, the promotional energy is significantly larger than the ionization potential, which is used in the London formula.

DeMarcus et al.<sup>10</sup> compared the Kirkwood-Müller formula with experimental data; there is excellent agreement for He, Na, and Ar. The experimental data fall lower for Kr and Xe than predicted. This is probably a consequence of correlation effects.

The quantitative disagreement of the Kirkwood-Slater formula must be in part related to the Hassè method,<sup>14</sup> which is used to estimate the

<sup>11</sup>L. Pauling, Proc. Roy. Soc. (London) A114, 181 (1927).

<sup>12</sup>R. A. Buckingham, Proc. Roy. Soc. 160, 94 (1937).

<sup>13</sup>R. M. Sternheimer, Phys. Rev. 96, 951 (1954); Phys. Rev. 107, 1565 (1957).

<sup>14</sup>H. R. Hassè, Proc. Cambridge Phil. Soc. 26, 542 (1930); Proc. Cambridge Phil. Soc. 27, 66 (1931).



promotional energy integrals. The calculation from wave functions for these integrals would be expected to yield somewhat different values.

### Polarizability

I shall use in this part of my paper the Hartree-Fock approximation and develop the treatment very much along the lines of Buckingham.<sup>5, 12</sup> The ground-state wave function is given by

$$\psi = (N!)^{-\frac{1}{2}} \det \{ \psi_1 \psi_2 \cdots \psi_k \cdots \psi_N \}. \quad (2)$$

For the polarizability the perturbing field is given as

$$V' = \sum_{p=1}^N F \cdot z_p, \quad (3)$$

and we write our perturbing wave function as a sum of states

$$\phi = \sum_k a_k \phi_k, \quad (4)$$

where

$$\phi_k = (N!)^{-\frac{1}{2}} \det \{ \psi_1 \psi_2 \cdots \phi_k \cdots \psi_N \}, \quad (5)$$

when  $\phi_k$  is such a function that  $\langle \psi_k / V' / \phi_k \rangle$  has a value. Our perturbing energy is now given by

$$h' = 2F \sum_k a_k \langle \psi / z / \phi_k \rangle + \sum_k \sum_l \langle \phi_k / H - E_0 / \phi_l \rangle a_k a_l \quad (6)$$

( $\langle \rangle$  denote integration over all space,  $E_0 = \langle \psi / H / \psi \rangle$ , and H is the unperturbed Hamiltonian). Equation (7) considers terms up to square powers in F. We now define

$$h_k = \langle \psi / z / \phi_k \rangle \quad (7)$$

$$Q_{kl} = \langle \phi_k / H / \phi_l \rangle - E_0 \langle \phi_k \phi_l \rangle, \quad (8)$$

and make a variational treatment with respect to  $a_k$  to find

$$\frac{\partial h'}{\partial a_k} = 0 = 2Fh_k + 2 \sum_l a_l Q_{kl}. \quad (9)$$

The solution of Eq. (9) is given by determinant theory as

$$a_k = -F \left[ \begin{array}{ccc|ccc} Q_{11} & \dots & h_1 & \dots & Q_{1N} \\ \vdots & & \vdots & & \vdots \\ Q_{k1} & \dots & h_k & \dots & Q_{kN} \\ \vdots & & \vdots & & \vdots \\ Q_{N1} & \dots & h_N & \dots & Q_{NN} \\ \hline Q_{11} & \dots & Q_{1k} & \dots & Q_{1N} \\ \vdots & & \vdots & & \vdots \\ Q_{k1} & \dots & Q_{kk} & \dots & Q_{kN} \\ \vdots & & \vdots & & \vdots \\ Q_{N1} & \dots & Q_{Nk} & \dots & Q_{NN} \end{array} \right] = -A_k F \quad (10)$$

Substituting Eqs. (8) and (10) into (7) we find

$$h' = -F^2 \left( 2 \sum_k A_k h_k - \sum_k \sum_l A_k A_l Q_{kl} \right) \quad (11)$$

From determinant theory can be proven

$$\sum_l A_l Q_{kl} = h_k \quad (12)$$

therefore

$$h' = -F^2 \sum_k A_k h_k \quad (13)$$

$$a = -\frac{2h'}{F^2} = 2 \sum_k A_k h_k \quad (14)$$

Before we now go to a development of the London-force formulae it is appropriate to consider the evaluation of the quantities  $Q_{kl}$  and  $h_k$  defined in (8). No problem is presented by  $h_k$  - it simply is given as

$$h_k = \langle \psi_k | z | \phi_k \rangle - \sum_{l \neq k} \langle \psi_l | \phi_k \rangle \langle \psi_l | z | \psi_k \rangle \quad (15)$$

The second set of terms was already given by Buckingham<sup>11</sup> and arises because the  $h\phi_e$  are not orthogonal to all the ground-state orbitals. The  $Q_{kk}$  presents trickier problems. It was estimated to be  $\frac{1}{2}$  (for  $\phi_k = z\psi_k$ ) by Kirkwood and Slater<sup>3</sup> and Buckingham.<sup>12</sup> In the simple Hartree method this approximation can be shown to be exact. Complications arise in the

Hartree-Fock method from the exchange integrals. However, past treatments of the polarizability generally neglected the off-diagonal elements, which are given as

$$Q_{kl} = \left\langle \phi_k^{2*} \psi_k^2 \left| \frac{1}{r_{12}} \right| \psi_l^* \phi_l^1 \right\rangle - \left\langle \phi_k^{2*} \phi_l^2 \left| \frac{1}{r_{12}} \right| \psi_l^1 \psi_k^1 \right\rangle, \quad (16)$$

given the assumption that  $\phi_l$  and  $\phi_k$  are orthogonal to all  $\psi_k$ . That these  $Q_{kl}$  terms are important will now be demonstrated.

If we consider Eq. (10) for  $A_k$  we can see that, if the orbitals are equivalent,  $A_k$  is given by

$$A_k = h_k / \sum_l Q_{kl}. \quad (17)$$

In the noble gas atoms the outermost subshell is most important and effective for polarization, and these can be arranged in an equivalent fashion. If for Ne we calculate  $\frac{1}{6} \sum_{k \neq l} \sum_l Q_{kl}$ , where  $k, l$  refer to all 2p orbitals, we get an estimate for the effect. We did this, using Slater orbitals with  $Z_{\text{eff}} = 6.31$  and  $4.77$  - values derived by Lowdin<sup>15</sup> for neon. The values we obtain are 0.325 and 0.430 when our polarized orbitals are  $^2p_m \cdot z$ . This is of the order of  $\frac{1}{2}$  and we can see that these terms are indeed important. We also calculated for Ne the average of the terms  $Q_{lk}$  between orbitals alike except for spin. These are 0.140 and 0.184, or about 40% of the total effect, which shows that the effect depends importantly on the number of electrons in the shell being polarized.

#### London Forces

Our perturbing Hamiltonian of induced-dipole-induced dipole interaction is given by

$$H' = \frac{2 \sum_i z_{Ai} \sum_j z_{Bj} - \sum_i x_{Ai} \sum_j x_{Bj} - \sum_i y_{Ai} \sum_j y_{Bj}}{R_{AB}^6} \quad (18)$$

( $x_{Ai}$  is the X coordinate of the  $i$  electron on system A, B refers to system B).<sup>1</sup> This treatment neglects overlap and higher-order interactions as well

<sup>15</sup>P. O. Lowdin, Phys. Rev. 94, 1600 (1954).

as exchange. For A and B each having spherical symmetry we can write

$$H' = \sqrt{6} \frac{\sum_i z_{Ai} \sum_j z_{Bj}}{R_{AB}^6} \quad (19)$$

We write our wave function in the Hartree-Fock approximation as

$$\psi' = \psi_A \psi_B + \sum_k \sum_p b_{kp} \phi_k \phi_p, \quad (20)$$

where  $\phi_k$  and  $\psi$  are defined as in Eqs. (5) and (6). In our treatment we more or less assume that the  $\phi_k$  terms are approximately the same as for the polarizability. This is not exactly true and we may use simple H-atom interaction to demonstrate the order of approximation.

We write

$$\begin{aligned} \psi_A &= \frac{2e^{-rA1}}{\sqrt{4\pi}} & \psi_B &= \frac{2e^{-rB2}}{\sqrt{4\pi}}, \\ \phi_A &= \frac{2}{\sqrt{4\pi}} e^{-\xi rA1} z_{A1} & \phi_B &= \frac{2e^{-\xi rB2}}{\sqrt{4\pi}} z_{B2}. \end{aligned} \quad (21)$$

For  $\xi = 1$ , we have  $\alpha = 4$ ,  $E_L = -6.00 R^{-6}$ . When maximizing for best  $\alpha$  we find

$$\begin{aligned} \xi &= 0.796, \\ \alpha &= 4.438 \\ E_L &= -6.19 R^{-6}. \end{aligned}$$

When calculating  $E_L$  directly and maximizing with respect to  $\xi$  we find

$$\begin{aligned} \xi &= 0.866, \\ E_L &= -6.45 R^{-6}. \end{aligned}$$

(Pauling and Wilson<sup>16</sup> give values for  $\alpha$  and  $E_L$  of 4.5 and  $-6.50 R^{-6}$  respectively.) The effect of using polarizability-type wave functions for London-force calculations is of the order of 4% here. It is therefore unlikely that this effect is responsible for order-of-2 factors, as was observed in the heavier rare gases.

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<sup>16</sup>L. S. Pauling and E. B. Wilson, Introduction to Quantum Mechanics (McGraw-Hill, New York) p. 195-198, 387-388.

We then proceed to write out our London energy in the same notation as in the preceding part:

$$E_L = + \frac{\sqrt{6}}{R^3} \sum_k \sum_p h_k^A h_p^B b_{kp} + \sum_{klpq} b_{kp} b_{lg} R_{kplg}, \quad (22)$$

$$R_{kplg} = Q_{kl}^A g_{pq}^B + Q_{pq}^B g_{kl}^A, \quad (23)$$

$$g_{kl} = \langle \phi_k \phi_l \rangle.$$

We design all pairs  $kplq, m, v, \dots$  as  $\lambda, \mu, \nu, \dots$ , and  $E_L$  now is

$$E_L = \frac{\sqrt{6}}{R^3} 2 \sum_{\lambda} b_{\lambda} (h^A h^B)_{\lambda} + \sum_{\lambda} \sum_{\mu} b_{\lambda} b_{\mu} R_{\lambda\mu} \quad (24)$$

and using variational treatment, we find

$$b_{\nu} = - \frac{\sqrt{6}}{R^3} \frac{\det | R_{\lambda\mu} + ((h^A h^B)_{\lambda} - R_{\lambda\mu}) S_{\mu\nu} |}{\det | R_{\lambda\mu} |} \quad (25)$$

$$= - \sqrt{6}/R^3 B_{\nu}$$

Again, as in previous treatments,

$$E_L = - \frac{6}{R^6} \sum_{\lambda} B_{\lambda} (h^A h^B)_{\lambda} = - \frac{6}{R^6} \sum_{k,p} B_{kp} h_k^A h_p^B \quad (26)$$

In the case where only equivalent orbitals are important

$$B_{kp} = \frac{h_k^A h_p^B}{\sum_l \sum_q R_{klpq}} \quad (27)$$

$$= \frac{h_k^A h_p^B}{\sum_l Q_{kl}^A \sum_q g_{pq}^B + \sum_l g_{kl}^A \sum_q Q_{pq}^B}$$

$$E_L = - \frac{6}{R^6} \sum_k [(h_k^A)^2 / \sum_l Q_{kl}^A] \sum_p [(h_p^B)^2 / \sum_q Q_{pq}^B]$$

$$\left. \begin{aligned} & \frac{\sum_l Q_{kl}^A}{\sum_l g_{kl}^B} \quad , \quad \frac{\sum_q Q_{pq}^A}{\sum_q g_{pq}^B} \\ & \times \frac{\sum_l Q_{kl}^A}{\sum_l g_{kl}^A} + \frac{\sum_q Q_{pq}^B}{\sum_q g_{pq}^B} \end{aligned} \right\} \quad (28)$$

Using Eqs. (14) and (17), we obtain

$$E_L = - \frac{3}{2R^6} a_A a_B \frac{U_A U_B}{U_A + U_B} \quad , \quad (29)$$

where

$$U_A = \sum_l Q_{kl}^A / \sum_l g_{kl}^A \quad . \quad (30)$$

If for  $U_A$  only  $Q_{kk}^A$  is important, this would be of the order of the ionization energy, and we have derived the London formula. However, when there are more than two electrons active, the  $Q_{kl}$  became sizeable. It is on this basis that the experimental data for Ne, Ar, Kr, and Xe are to be interpreted — namely, that the ionization potential does not take account of the collective terms and must be corrected by a factor of about 2 to take account of these terms. It is interesting that He,  $H_2$ , and Hg with two effective electrons have U/I ratios ranging from 1.27 to 0.93, while in addition to the noble gases,  $N_2$ , CO, HCl, HI, and  $CH_4$  have U/I ratios of 2 to 2.4.  $F_2$  is quite unusual — its U/I ratio is 4.6 and difficult to explain, though, of course, we cannot expect this theory to hold for diatomic molecules. Kirkwood and Slater<sup>2</sup> postulated that two electron excitation terms made a significant contribution to the polarizability in terms of the perturbation theory. This would then cause the term which we call U to be somewhat larger than the ionization potential.

This is in a way identical to our collective effect, though by no means as clear in its physical meaning.

To derive the Kirkwood-Slater formula let us again assume equivalent orbitals.

$$\overline{Q}_A^A = \sum_l Q_{kl}^A \quad (31)$$

Also, if we use  $\phi_k = \psi_k$  we find

$$\sum_l g_{kl}^A = h_k, \quad (32)$$

$$a = \frac{2Nh_k^2}{Q} \quad (33)$$

where  $N =$  number of electrons. We find for  $E_L$

$$E_L = -\frac{3}{2R^6} a_A a_B \frac{\sqrt{2}}{\sqrt{\frac{a_A}{N_A Q_A} + \frac{a_B}{N_B Q_B}}} \quad (34)$$

If we assume  $Q \sim \frac{1}{2}$  we find

$$E_L = -\frac{3}{2R^6} a_A a_B \frac{1}{\sqrt{\frac{a_A}{N_A} + \frac{a_B}{N_B}}}, \quad (35)$$

which is the Kirkwood-Slater formula.

The assumption that for the noble gases only the outermost electrons are significantly polarizable stands on much more solid ground than  $Q \sim \frac{1}{2}$ .

We can estimate actual  $Q$ 's for the noble gases from experimental data (assuming  $N = 6$ ) to be

	$Q$
Ne	.67
Ar	.92
Kr	.92
Xe	1.8

There is another way of treating this problem. The diamagnetic polarizability  $\chi$  is given by

$$\begin{aligned}\chi &= - \frac{1}{6m_1C^2} N \langle r_{kk}^2 \rangle \\ &= - \frac{1}{2m_1C^2} N \langle z_{kk}^2 \rangle ,\end{aligned}\quad (36)$$

$\langle z_{kk}^2 \rangle$  is close to  $h_k$  as can be seen from Eq. (15). By the use of Eqs. (28) and (36), this gives us

$$E_L = 6mc^2 \alpha_A \alpha_B R^{-6} \frac{1}{\alpha_A/\chi_A + \alpha_B/\chi_B} ,\quad (37)$$

which is the Kirkwood-Müller<sup>3</sup> formula. This formula does not depend on assumptions concerning the  $Q_{lk}$ -type integrals. Its degree of correspondence with measurements depends mainly on the assumptions

$$\frac{h_k^2}{\langle z_{kk}^2 \rangle} \cong \sum_l g_{kl} .\quad (38)$$

Table I

London-force coefficients (eu cm <sup>-6</sup> )		
	Theoretical (Eq. (44))	Experimental (viscosity data)
He	0.84	0.98
Ne	4.94	5.58
Ar	69	65.2
Kr	180	118
Xe	448	292
H <sub>2</sub>	7.75	7.85

It is likely that the chief effect that enters the above formula is angular correlation lowering  $h_k$  with respect to both  $\langle z_{kk}^2 \rangle$  and  $\sum_l g_{kl}$ .



Under those circumstances it seems reasonable that the theoretical coefficients are larger than the experimental ones for the large atoms.

#### Discussion

This paper has presented a fairly thorough discussion of the effect that the "collective behavior" of electrons in polarization may have on London Forces and, I believe, it explains largely the limitations of the London formula in the case of closed-shell atom-atom interactions. The next steps should be a further development of the Hartree-Fock method for polarizability and London-force calculations, as well as the use of the configuration interaction method for these same calculations.

I wish to acknowledge my indebtedness to Professor Kenneth S. Pitzer, who suggested this problem.

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