tions needed to calculate further integrals were also available there.

Of the five integrals listed in Table IV, four were calculated by the methods given by Roothaan[15] and Rüdenberg.[16] The notation used here is the same as that employed in these two papers.

The [$1s_A\ 1s_B | 1s_A\ 2p\sigma_A$] integral was evaluated by a modification of Rüdenberg's[16] method. This is done by recognizing that if $\bar{\Omega} = 1s_A2p\sigma_A$, it can be expressed in the form given by Rüdenberg's equation (1.13). Now let $\bar{\zeta}_a$ refer to the $1s_A$, $\bar{\zeta}_b$ to the $2p\sigma_A$ orbital (or *vice versa*). Then equation (1.13′) of Rüdenberg's paper becomes

$$\bar{\alpha} = \frac{1}{2} R(\bar{\zeta}_a + \bar{\zeta}_b) \quad \bar{\beta} = \frac{1}{2} R(\bar{\zeta}_a + \bar{\zeta}_b)$$

and (1.13″) remains as is, while the formula for $\bar{w}(\zeta, \eta)$ will have to be determined anew, which is given here for $1a_A2p\sigma_A$ in the same form as that used in Table II of Rüdenberg's paper

$$\begin{array}{c|c|c|c|c|l} 1s_A2p\sigma_A & \multicolumn{4}{c}{j \longrightarrow} & \\ n \downarrow & 0 & 1 & 2 & 3 & \\ \hline 0 & & & -1 & & cf. \\ \hline 1 & & & & 1 & {}^1/_4 \\ \hline 2 & 1 & & & & \\ \hline 3 & & -1 & & & \end{array} \qquad (19)$$

From here on this integral was calculated just like the two center exchange integrals, keeping the changes made in mind, however.

Most of the $\Phi^{01}_{n\bar{n}}(\alpha,\alpha)$ and $B^{01}_{j}(\beta)$ functions used were found in the tables of Kotani, Amemiya and Simose[17] and in Hirschfelder and Linnett.[7] Some more Φ functions were calculated by a method given in Rüdenberg's paper. Some $B^{02}_n(\beta)$ functions were calculated by the formula

$$B^{02}_n(\beta) = \sqrt{2.5}\left(\frac{3}{2} B^{00}_{n+2}(\beta) - B^{00}_n(\beta)\right) \qquad (20)$$

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(15) C. C. J. Roothaan, *J. Chem. Phys.*, **19**, 1445 (1951).

(16) Klaus Rüdenberg, *ibid.*, **19**, 1459 (1951).

(17) Kotani, Amemiya, and Simose, *Proc. Phys.-Math. Soc., Japan*, **20**, Extra No. 1 (1938); **22**, Extra No. 1 (1940).

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Electronic Correlation in Molecules. II. The Rare Gases[1]

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RECEIVED MAY 31, 1956

The coefficient of the inverse sixth power London potential term derived from second virial coefficients and viscosities for the interaction of pairs of rare gas atoms is compared with approximate theoretical calculations. The usual theoretical formulas yield too small values probably because of the neglect of inner shell electrons. Empirical values for the effective number of polarizable electrons are obtained. These values may be used in connection with the Slater–Kirkwood formula to calculate approximate interaction energies.

We wish to select a formula, necessarily approximate, which may be used to estimate that portion of the correlation energy which arises from non-overlapping parts of the electron system. Our basis will lie in the theory of the attractive force between non-polar molecules. The rare gases are of particular interest since their atoms have closed shells and thus give examples with spherical symmetry. This theory was summarized in an excellent review by Margenau[2] to which we shall make frequent reference.

Two general methods have been used: the perturbation method by Eisenschitz and London[3] and the variation method by Slater and Kirkwood.[4] In each case parallel calculations are made of the polarizability of the single atom or molecule and of the interaction energy between two such atoms or molecules. The sums of integrals which arise cannot be evaluated except in the simplest cases, but the same integrals appear in closely related sums in the two calculations. Thus one attempts to replace the sums of integrals in the interaction energy formula by the most nearly equivalent combination of the polarizability and related quantities.

In the perturbation method the resulting formulas involve f_i the oscillator strength which is the effective number of electrons participating in an optical transition, and E_i the excitation energy to the ith state. The formula for the polarizability at frequency ν is then (Margenau,[2] eq. c 8)

$$\alpha(\nu) = \frac{e^2\hbar^2}{m} \sum_i \frac{f_i}{E_i^2 - h^2\nu^2} \qquad (1)$$

The refractive indexes of many substances can be fitted to a more approximate formula involving a single f_i and E_i. Then the polarizability at low frequency becomes

$$\alpha = \frac{e^2\hbar^2 f_i}{mE_i^2} \qquad (2)$$

The more detailed formula for the interaction energy for a pair of atoms (or molecules) is

$$E_L = -\frac{3}{2}\frac{e^4\hbar^4}{m^2R^6} \sum_i \sum_j \frac{f_if_j}{E_iE_j(E_i + E_j)} \qquad (3)$$

where R is the interatomic distance and the sums

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(1) This research was assisted by the American Petroleum Institute through Research Project 50.

(2) H. Margenau, *Rev. Mod. Phys.*, **11**, 1 (1939).

(3) R. Eisenschitz and F. London, *Z. Physik*, **60**, 491 (1930); F. London, *Z. physik. Chem.*, **B11**, 222 (1930); *Z. Physik*, **63**, 245 (1930).

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

cover the excited states of the two atoms. The one term approximation yields the following equivalent formulas

$$E_L = -\frac{3}{2R^6}\frac{\alpha_A\alpha_B E_A E_B}{E_A + E_B} = -\frac{3e\hbar}{2m^{1/2}R^6}\frac{\alpha_A\alpha_B}{\left[\left(\frac{\alpha_A}{f_A}\right)^{1/2} + \left(\frac{\alpha_B}{f_B}\right)^{1/2}\right]} \tag{4}$$

where the subscripts A and B refer to the two atoms. If the atoms are identical these simplify to

$$E_L = -\frac{3\alpha_A{}^2E_A}{4R^6} = -\frac{3e\hbar\alpha_A{}^{3/2}f_A{}^{1/2}}{4m^{1/2}R^6} \tag{5}$$

We should recall, however, that the one term dispersion formula, equation 2, constitutes only a rough approximation to the pattern of excited energy levels even though it may adequately represent the refractive index as a function of frequency in the visible range. The single value of f/E^2 must be some sort of effective sum of the individual terms. In the London energy formula the sum is over terms that are effectively f^2/E^3 instead of f/E^2. Consequently, high energy of terms with large f values may contribute relatively more to the energy sum than to the polarizability sum.

The variation method[4] requires different but about equally serious approximations and yields for unlike atoms.

$$E_L = -\frac{3e\hbar}{2m^{1/2}R^6}\frac{\alpha_A\alpha_B}{\left[\left(\frac{\alpha_A}{N_A}\right)^{1/2} + \left(\frac{\alpha_B}{N_B}\right)^{1/2}\right]} \tag{6}$$

or for like atoms

$$E_L = -\frac{3e\hbar\alpha_A{}^{3/2}N_A{}^{1/2}}{4m^{1/2}R^6} \qquad 7)$$

where N_A is the number of electrons in the outer shell of the atom. The essential approximations are that inner shell electrons make a negligible contribution to the polarizability and that outer shell electrons contribute equally. The errors caused by the two approximations should be of opposite sign and tend to cancel one another.

Comparison with Experiment.—Let us now compare[5] the coefficients of R^{-6} in equations 5 and 7 with the corresponding coefficients in potential functions derived from second virial coefficients and from viscosities for the rare gases. The values are listed in Table I. The constants for the theoretical equations are those chosen by Margenau[2] and the number of outer shell electrons is taken as eight. It is apparent that the coefficients for equations 5 and 7 are too small except for the case of equation 7 for neon. In all cases equation 7 yields the larger value and one closer to those from experimental sources.

TABLE I

COEFFICIENTS OF THE R^{-6} POTENTIAL TERM FOR THE RARE GASES

(All are the negative coefficients × 10^{48} in e.v.)

	2nd Virial[a]			Theory		
Subst.	6–12	6-exp.	Visc.[b] 6–12	Eq. 5	Eq. 7	N or
Ne	5.6	5.4	5.9	2.9	5.4	8
A	65	55	68	35	46	11
Kr	143	103	145	67	86	11
Xe	355	296	350	149	178	22

[a] For A, Kr, Xe from E. Whalley and W. G. Schneider, *J. Chem. Phys.*, **23**, 1644 (1955); for Ne ref. *b*. [b] J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954.

In the last column of Table I are listed the values of N or f which yield agreement with the 6-exp. function derived from second virial coefficients. Larger N values would be required to fit the other potential functions. We see these numbers exceed eight except for neon. In the variation method, equation 7, we recall that all outer shell electrons were assumed to contribute equally to the polarizability and that inner shells were assumed to contribute negligibly. We may interpret the increase in N above 8 for atoms heavier than neon as an indication of significant contributions from inner shell polarizability.

These effective N values should be useful as empirical factors yielding approximately the correct coefficients for the inverse sixth power potential term.

Conclusion.—It seems best in further work to use the Slater and Kirkwood formula, equations 6 and 7. The number of valence shell electrons may be taken for N_A in this equation for atoms in the first octet but for heavier atoms larger values should be chosen in accordance with the results for argon, krypton, and xenon in Table I. Also we note that an uncertainty of about ±20% should be assigned to values calculated in this simple fashion.

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(5) The effect of the inverse eighth power and higher terms in the potential is not entirely negligible. However, it seems best to ignore it at this point for two reasons. We do not know the repulsive potential well enough to make the interpretation of an inverse eighth power attractive term significant. Also, others have omitted these terms in interpreting viscosity or second virial coefficient data.