The quantities on the right side of equation 21, determined from the slopes of plots of log A and $\Delta E^*/2.303RT$ as functions of the dielectric constant (Fig. 3) are 0.14 and 0.12, respectively. The difference between these values agrees well with the value of 0.023 for d log k/dD as determined from the slope in Fig. 2.

It can thus be seen that to the extent that the arguments presented by Hughes and Ingold apply to activation energies, the reaction here discussed fits the theory. The activation energy increases with increasing dielectric constant as predicted for ion–molecule reactions in general. The effect on the rate, however, is offset by the even greater effect of the change in log A.

The results discussed above agree neither quantitatively nor qualitatively with the Amis theory which would require a decrease in activation energy with increasing ionizing power of the solvent for an anion–molecule reaction. In addition, the Amis equations as well as the Laidler–Eyring equation predict a linear relationship between the logarithm of the rate constant and the *reciprocal* of the dielectric constant of the medium. Figure 2 shows that while a good linear relationship existed, it was with the *first power* of the dielectric constant, and from Fig. 3 it can be seen that a similar relationship (albeit over a short range) existed between the latter function, the isodielectric activation energy and the Arrhenius frequency factor.

That this linear dependence of log k, log A and ΔE^* on the dielectric constant is not unusual for ion–molecule reactions in general will be the subject of a forthcoming publication.

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Electronic Correlation in Molecules. I. Hydrogen in the Triplet State[1]

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For H_2 in the triplet state the London energy corresponding to dipole–dipole interaction is the dominant term at distances near or greater than the potential minimum. Other terms arising from hybridization are shown to be small at these distances but become important as the atoms come closer together. Since the interaction between closed electron shells is similar in essential features to that in triplet H_2, we conclude that the London energy term should be considered in binding energy calculations of complex systems.

The correlation of electronic motions has been recognized as very important in bond energy calculations and as extremely difficult to treat adequately. We are developing a scheme to estimate the contribution of correlation to the bond energy of molecules which is based on the treatment of London for intermolecular interactions. It has been recognized that the attractive force between polarizable electron clouds, first elucidated by London,[2] arises from the correlation of electron motion in the combined electron system. Born and Mayer[3] considered these forces in their treatment of ionic crystals and Davydov[4] and Simpson[5] have considered these effects in conjugated π electron systems. Also one of us[6] has published preliminary results on the halogen series. However, we are not aware of any previous general treatment of this type.

Our present paper includes an examination of the triplet state of hydrogen for the relative magnitude of various terms. Paper II contains a critical review of several formulas for the London energy together with the development of an improved formula for further calculations; while Paper III gives calculations for the paraffin hydrocarbons through the pentanes.

While several treatments[7,8] have been published for the H–H interaction in the triplet state and for the closely related problem of the interaction of two helium atoms, there remain unanswered important questions about the effect of certain terms in the wave function. These types of terms are of interest in discussions of closed shell interactions between heavier atoms.

Recently there have been suggestions[6,9,10] that interactions between closed electron subshells may contribute appreciably to chemical bonding. For example in Cl_2 the 3pπ subshell in each chlorine atom is filled with four electrons yet it is suggested that interactions with the vacant 3dπ orbitals may be such that these electrons contribute substantially to the Cl–Cl bond energy. Two different proposals have been made.

Mulliken[9] suggested that the 3pπ atomic orbitals should be hybridized by linear combination with

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[1] This research was assisted by the American Petroleum Institute through Research Project 50.

[2] F. London, *Z. physik. Chem.*, **B11**, 222 (1930); *Z. Physik*, **63**, 245 (1930).

[3] M. Born and J. E. Mayer, *ibid.*, **75**, 1 (1932).

[4] A. S. Davydov, *Zhur. Eksptl. Teoret. Fiz.*, **18**, 201 (1948).

[5] W. T. Simpson, THIS JOURNAL, **73**, 5363 (1951).

[6] K. S. Pitzer, *J. Chem. Phys.*, **23**, 1735 (1955).

[7] J. O. Hirschfelder and J. W. Linnett, *ibid.*, **18**, 130 (1951).

[8] James, Coolidge and Present, *ibid.*, **4**, 187, 193 (1936).

[9] R. S. Mulliken, THIS JOURNAL, **77**, 884 (1955).

[10] K. S. Pitzer, *ibid.*, **70**, 2140 (1948).

3dπ orbitals. Presumably the sign of the modifying 3d term will be such as to increase overlap in the bonding molecular orbital and to decrease overlap in the antibonding orbital. He employed estimates of overlap integrals to indicate the possible magnitude of the effects. However, one may question whether the quantitative relationship between bond energy and overlap integral found for ordinary bonds can be transferred to this problem.

The possibility that the principal effect arises from the correlation of electronic motions between the two groups of electrons has been mentioned.[6] In the case of chlorine the presence of vacant 3d orbitals would increase this effect by making the atoms more polarizable than would otherwise have been expected.

We shall see that an expansion of the wave function for the triplet state of H_2 yields several terms which can be related to the explanations in the case of chlorine. While hydrogen atoms do not have closed shells, if the two electron spins have parallel orientation, the interaction is essentially like that between closed shells.

Orbitals for Triplet State of H_2.—Let us begin by writing the symmetric and antisymmetric molecular orbitals with the inclusion of 2pσ orbitals as well as 1s orbitals. We take the positive lobes of the p orbitals toward one another along the z-axis.

$$\psi_S = 2^{-1/2}[(1 - \alpha^2)^{1/2}(1s_A + 1s_B) + \alpha(2p_A + 2p_B)] \quad (1)$$
$$\psi_A = 2^{-1/2}[(1 - \beta^2)^{1/2}(1s_A - 1s_B) - \beta(2p_A - 2p_B)] \quad (2)$$

A and B refer to the two atoms, and the signs have been selected to make α and β positive for minimum energy. The determinantal wave function for triplet H_2 may be expanded as follows (omitting the spin factors):

$$\begin{aligned}\psi = {} & (1 - \alpha^2)^{1/2}(1 - \beta^2)^{1/2}[1s_A, 1s_B] + \\ & {}^1/_2(\alpha\sqrt{1 - \beta^2} + \beta\sqrt{1 - \alpha^2}) \\ & \{[1s_A, 2p_A] + [2p_B, 1s_B]\} + {}^1/_2(\alpha\sqrt{1 - \beta^2} - \beta\sqrt{1 - \alpha^2}) \\ & \{[1s_A, 2p_B] + [2p_A, 1s_B]\} - \alpha\beta[2p_A, 2p_B] \quad (3)\end{aligned}$$

where the Slater determinants are symbolized by

$$[1s_A, 1s_B] = 2^{-1/2}\begin{vmatrix}1s_A(1) & 1s_B(1)\\ 1s_A(2) & 1s_B(2)\end{vmatrix}$$

and (1) and (2) refer to the two electrons.

In equation 3 we find four types of terms. First is the Heitler–London term; second is a sort of ionic-polarizing term with two determinants; third a covalent-polarizing term; and fourth is the σ London force term (*i.e.*, the σ dipole–dipole correlation term). While the coefficients of these four terms are given in terms of two variables, α and β, in equation 3, there is no reason why all four terms should not be introduced as independent functions in the variation method. Thus we will also study the more general wave function

$$\begin{aligned}\psi = {} & c_0[1s_A, 1s_B] + c_1\{[1s_A, 2p_A] + [2p_B, 1s_B]\} \\ & + c_2\{[1s_A, 2p_B] + [2p_A, 1s_B]\} + c_3[2p_A, 2p_B] \quad (4)\end{aligned}$$

The effective atomic number was taken as 2 for the 2p orbitals[11] and 1 for the 1s orbitals.

We now designate the determinants and sums of determinants in equation 4 by χ_i

$$\psi = c_0\chi_0 + c_1\chi_1 + c_2\chi_2 + c_3\chi_3 \quad (5)$$

and let each χ_i be normalized. Let us define

$$\left.\begin{aligned} S_{ij} &= \int \chi_i\chi_j\, d\tau \\ E_{ij} &= \int \chi_i H\chi_j\, d\tau - 2E_H S_{ij} \\ E_H &= \text{energy of hydrogen atom} \\ S &= \int \psi^*\psi\, d\tau \\ E &= S^{-1}\int \psi^* H\psi\, d\tau - 2E_H \end{aligned}\right\} \quad (6)$$

Then

$$S = \sum_{ij} c_i S_{ij} c_j \quad (7)$$
$$ES = \sum_{ij} c_i E_{ij} c_j$$

Since the effects of the perturbing terms are all very small, at the distances under consideration, the second-order cross terms were omitted. Also neglected was the effect S may have on the minimum position. The evaluation of the necessary integrals is given in the Appendix.

The values obtained are

$$c_i = -\frac{c_0E_{0i}}{E_{ii}} \quad (8)$$
$$E_i = -\frac{c_0^2(E_{0i})^2}{SE_{ii}} \quad (9)$$
$$E = E_0 + E_1 + E_2 + E_3 \quad (10)$$

In Table I the values of E_i are tabulated, where E_0 corresponds to the Heitler–London, E_1 to the "ionic-polarized" term, E_2 to the "covalent-polarized" term, and E_3 is the σ-London term. The values of c_i are shown in Table II, where c_3 is compared to the Hirschfelder–Linnett c_3. The discrepancy at the lower R values probably arises from the fact that Hirschfelder and Linnett varied the effective nuclear charge while we held it at unity. Also in Table I the total interaction energy, E, is tabulated for the molecular orbital wave function of equation 3 as well as the more general equation 4.

TABLE I

ENERGY TERMS FOR TRIPLET H_2

(E is in cal./mole; R is in Bohr radii, 0.529 Å.)

R	6	7	8	10	12
E_0 (eq. 10)	245.0	47.22	8.66	0.263	0.0077
E_1 (eq. 10)	−15.05	− 2.90	− .52	− .015	− .0004
E_2 (eq. 10)	− 0.27	− 0.01	...	...	...
E_3 (eq. 10)	−46.0	−19.92	−9.30	−2.500	−0.8399
E (eq. 4)	184	24.4	−1.16	−2.252	−0.8326
E (eq. 3)	230	44.3	8.14	0.248	0.0073

From Table I it can be seen that the London term is here the more important one, while the "covalent-polarized" term is negligible and the "ionic-polarized" term becomes significant only at the shorter distances.[12] At the longer distances the London term alone gives a good approximation since it even

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[11] This selection of $Z = 2$ for the effective atomic number in the 2p orbital, which makes the exponent in the 2p function the same as that in the 1s function, is usually near the optimum for calculations of this type and greatly simplifies the work. For the wave function with only c_0 and c_3 non-zero, the optimum value was determined to be $Z = 1.732$ and the energy decrease arising from the c_3 term was then 7% greater. This improvement is so small that the complex calculations required for other Z values in the c_1 and c_2 terms did not seem to be justified.

[12] A large second-order exchange energy (23 cal. at $R = 7$) for H_2 in the triplet state was obtained by Margenau [*Phys. Rev.*, **56**, 1000 (1939)] in calculations based upon integrals reported by Eisenschitz and London [*Z. Physik*, **60**, 491 (1930)]. Since one of the important integrals is only evaluated to a first approximation, it seems likely that the difference between Margenau's result and ours is to be ascribed to this approximation.

TABLE II

ENERGY TERMS (IN ATOMIC UNITS) AND COEFFICIENTS FOR H_2 IN TRIPLET STATE

R	6	7	8	10	12
E_{01} (eq. 6)	−0.004033	−0.001814	−0.000779	−0.000133	−0.0000211
E_{11} (eq. 6)	.6748	.7104	.7330	.7616	.7795
E_{02} (eq. 6)	.000453	.000096	.0000186	.00000055	.000000016
E_{22} (eq. 6)	.505	.505	.501	.50	.50
E_{03} (eq. 6)	.0086702	.0056769	.0038671	.0019998	.0011573
E_{33} (eq. 6)	1.0222	1.0142	1.0016	1.0012	1.0001
S_{01} (eq. 6)	0.1992	0.1097	0.05757	0.01421	0.0032
S_{02} (eq. 6)	− .0096	− .0025	− .00056	....	....
S_{03} (eq. 6)	− .0206	− .0061	− .00017	−0.0001	0.0000
c_0 (eq. 5)	.9993	.9998	1.0000	1.0000	1.0000
c_1 (eq. 5)	.005973	.002553	0.001063	0.000175	0.0000271
c_2 (eq. 5)	− .000897	− .000190	− .000037	− .0000011	− .00000003
c_3 (eq. 5)	− .008482	− .005597	− .003861	− .001997	− .001157
c_3 (H + L)	− .01048	− .006111	− .003963	− .002001	− .001157
$\beta = \alpha$ (eq. 3)	+ .004175	+ .001796	+ .000749	.000123	.0000192

TABLE III

INTEGRALS

	R = 6	7	8	10	12
$[1s_A1s_A \mid 1s_B2p\sigma_A]$	0.03402579	0.01676708	0.007955850	0.001651491	0.000317692
$[1s_A2p\sigma_A \mid 1s_A1s_B]$	.0034876	.0014819	.00061441	.00010098	.00001572
$[1s_A1s_A \mid 1s_B2p\sigma_B]$	.02750598	.02035665	.015615536	.0099997024	.006944436
$[1s_A1s_B \mid 2p\sigma_A2p\sigma_B]$	.004764509	.001399423	.000370317	.000020862	.00000095712
$[1s_A1s_A \mid 2p\sigma_B2p\sigma_B]$	.179269	.151331	.130811	.102998	.0850694

dominates E_0, the Heitler–London exchange term. However, the use of the molecular orbitals which result in equation 3 forces much too large a ratio (c_1/c_3) and yields a poor energy. This is the Roothaan[13] scheme as applied to the present problem.[14] On the other hand the E_1 term is increasing in importance relative to E_3 as the distance R is decreased. Consequently the Roothaan scheme may well be a good approximation at ordinary bond distances.

We wish to emphasize at this point our omission of all $2p\pi$ orbital terms. For this reason our total energy values are not to be interpreted as accurate for the actual H–H interaction. Hirschfelder and Linnett's values are the best available approximation at the longer distances and Coolidge, James and Present's values at shorter distances.

Discussion.—The relative importance of the electron correlation or London energy for the interaction of atoms at large distances has been generally recognized. It is our purpose to draw attention to the importance of this effect at intermediate distances where exchange repulsion is also significant but where the overlap of the atomic orbitals is still small. Thus at a separation of six Bohr radii in triplet H_2 the correlation term reduces the Heitler–London repulsive energy by 20% (or 30% if the transverse terms are included) while other orbital polarization terms amount to only 6%. In more complex molecules the calculation of the other energy terms is very difficult, but it is relatively easy to obtain an approximate value for these electron correlation energy terms. Consequently it seems to us desirable to examine the correlation energy for electronic systems at these intermediate distances. Particular attention will be given to series of substances showing otherwise unexplained energy anomalies, such as was the case for the halogens.[6]

TABLE IV

$\Phi^{o l}_{n \bar{n}}(R, R)$ FUNCTIONS

	n	$\bar{n}$	R = 8	10	12
0	0	1	$0.0^{8}266394$	$0.0^{10}329711$	$0.0^{12}438164$
	0	3	. 334516	. 395371	. 509603
	0	5	. 442615	. 490402	. 606818
	1	1	. 294344	. 357642	. 469317
	1	2	. 328304	. 390418	. 505004
	1	3	. 370250	. 429326	. 546234
	1	4	. 423042	. 476112	. 594319
	1	5	. 490916	. 533296	. 650989
	1	6	. 580328	. 604252	. 718563
	2	3	. 413755	. 469223	. 588235
	2	5	. 549879	. 583578	. 701687
	3	3	. 467617	. 516646	. 636801
	3	4	. 535540	. 573751	. 693494
2	0	0	$.0^{9}6056^{2}$	$.0^{11}8180^{0}$	. 11624^{1}
	0	1	. 6566^{9}	. 8744^{4}	. 12303^{9}
	0	2	. 7166^{7}	. 9388^{7}	. 13066^{1}
	0	3	. 7879^{2}	$.0^{10}10136^{1}$	. 13925^{7}
	0	4	. 8737^{5}	. 10099^{5}	. 14901^{4}

Other electronic energy effects, including the correlation of electrons within bonds, are even larger than those we shall be calculating. It will be necessary to assume that these energies show regular trends or may be treated by present empirical methods, at least until more adequate theoretical methods are available.

Appendix

Most integrals needed were available in the paper of Hirschfelder and Linnett[1]; some of the func-

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[13] C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

[14] Griffing and Wehner [*J. Chem. Phys.*, **23**, 1024 (1955)] applied the Roothaan method to the He–He interaction and obtained approximately the correct energy near the potential minimum. This result is difficult to understand in view of our failure to obtain any potential minimum with equation 3.

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

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

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

Most of the $\Phi^{\alpha l}_{n\bar{n}}(\alpha,\alpha)$ and $B^{\alpha l}_{j}(\beta)$ 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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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).