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The Forces Between Hydrogen Molecules

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A quantitative calculation is made of the entire interaction called into play when two hydrogen *molecules* approach. The forces consist of three parts: exchange, quadrupole, and dispersion (van der Waals) forces. By compounding these, it is possible to account in a fundamental way for the size and the shape of the molecules. Also, the interaction curves (Fig. 2) are in reasonable agreement with empirical curves derived from second virial coefficients. Because of the complexity of the exchange force calculation, a simple state function of the Wang type (but with undetermined screening constant) was used in this work to represent the charge distribution within the molecule. Quadrupole moments are computed (Table V), and comments are made on the relation between the molecular problem treated in this paper, and the corresponding atomic problem (interaction between helium atoms).

IN the field of intermolecular forces, interest has chiefly centered about the long range attractive effects which can be calculated with relative ease. Except in the simplest cases of atomic interaction,[1] rather crude devices are in use for estimating the short range forces of repulsion, devices which depend in most instances on empirical knowledge of the gas kinetic sizes of the atoms. For molecules, no attempts have apparently been made to derive the quantitative aspects of the repulsive forces, despite the fact that knowledge of them is indispensable for an adequate understanding of such fundamental properties as molecular size, shape, rigidity. Nor is it possible to determine the position of the van der Waals minimum of the interaction curve without a fairly accurate picture of the repulsive exchange forces.

To obtain these forces without the tedium of an *a priori* calculation, numerous workers[2] have undertaken the useful task of deriving them from observed data, such as second virial coefficients, energies of crystal lattices, Joule-Thomson coefficients, and the like. The relative success of this procedure has created an attitude of satisfaction and apparently a waning of interest in the fundamental problem involved. Endeavor has been shifted toward correlation of diverse gas kinetic phenomena by means of a single set of interaction curves, without much regard to the basic credentials of these curves. The present paper is a step in the opposite direction inasmuch as it derives interaction curves from the elements of quantum mechanics. This may entail a sacrifice in numerical accuracy of the results, but it should fill the gap between semi-empirical reasoning and theoretical understanding.

In the case of molecular hydrogen, the total interaction consists of three main types: First, the exchange forces just mentioned which owe their origin to the interpenetration of the electronic clouds; they are responsible for the rigidity of the molecule. In the calculations they appear as first-order effects, arising when state functions of the proper symmetry are used. They depend very strongly on the relative orientation of the interacting molecules. The major part of this paper is devoted to their study.

Secondly, there are the forces resulting from the presence of a permanent quadrupole moment in the H_2 molecule. Their dependence on orientation is also strong, but they vanish in the mean over all orientations. In comparison with the other types, the quadrupole forces are small except at distances of separation much greater than those of interest in connection with gas-kinetic phenomena. In the calculation, they appear in the same formalism as do the exchange forces, being first-order effects and associated with the symmetry of the molecule. Their

[1] For He, cf. J. C. Slater, Phys. Rev. **32**, 349 (1928); G. Gentile, Zeits. f. Physik **63**, 795 (1930); H. Margenau, Phys. Rev. **56**, 1000 (1939).

[2] Among them are: J. E. Lennard-Jones, Proc. Roy. Soc. **A106**, 463 (1924). For a full review of this work see R. H. Fowler, *Statistical Mechanics*. M. Born and J. E. Mayer, Zeits. f. Physik **75**, 1 (1932). J. O. Hirschfelder, R. B. Ewell, and J. R. Roebuck, J. Chem. Phys. **6**, 205 (1938).

magnitude is a sensitive function of the concentration of electronic charge about the nuclei.

In the third place, the attractive van der Waals forces are to be included.[3] As is well known, they represent the instantaneous attractions between the electronic multipoles as they rotate, within one molecule, in partial phase agreement with the multipoles in the other. These may be calculated by a second-order approximation method and with the use of state functions lacking the correct symmetry. In the H_2 problem, it is necessary to include in the treatment both dipoles and quadrupoles,[3] and it is safe to neglect the interaction of higher multipoles.

I. EXCHANGE FORCES; NOTATION AND METHOD OF CALCULATION

The method used in the calculation of the exchange forces is based on the work of Slater;[4] some of its features, as they relate to the four-electron problem, are discussed by Glasstone, Laidler, and Eyring.[5] In order to achieve simplicity, these authors neglect all multiple exchange effects, thereby reducing the number of exchange integrals from 24 to 7. Unfortunately this curtailment invalidates all quantitative conclusions one might wish to draw, for the exchange integrals do not arrange themselves in descending order of magnitude as the number of transpositions characterizing the exchange increases. They are, in fact, nearly all of comparable magnitude; even if the non-orthogonality between orbitals is small, exchange integrals may well be large. Furthermore, in the case of the hydrogen molecule, the non-orthogonality integral has the value 0.72 and cannot be neglected.

In order to carry through the work, it appears necessary to use the simplest possible type of state function for the H_2 molecule. A function similar to that employed by Wang[6] was therefore chosen. It will be seen, however, that the value of the nuclear charge Z, which gives the lowest energy for a single molecule, leads to erroneous consequences in the present problem. The meaning of this will be discussed in due course; we note at present that this fact enforces the preliminary use of an undetermined Z.

Let the four protons in the two interacting molecules be labeled a, b, c, d. They are first taken to be located at arbitrary, fixed points. The symbols a to d will also be used to represent the hydrogenic wave functions of an electron about the nuclei a to d. Thus, for example,

$$b=(Z^3/\pi a_0^3)^{\frac{1}{2}} \exp(-Zr_b/a_0), \tag{1}$$

r_b denoting the distance of the electron from nucleus b. We note that this function satisfies the Schrödinger equation

$$\left(\frac{\hbar^2}{2m}\nabla^2+\frac{Ze^2}{r_b}\right)b=\tfrac{1}{2}Z^2\frac{e^2}{a_0}\cdot b. \tag{2}$$

The electron coordinates will be numbered from 1 to 4, so that, for instance, $b(3)$ represents electron 3 centered about nucleus b. If the spin functions α, β are introduced in the usual way, a product function like

$$\varphi_1=a(1)\alpha(1)\cdot b(2)\beta(2)\cdot c(3)\alpha(3)\cdot d(4)\beta(4) \tag{3a}$$

signifies a unique assignment of electrons to nuclei. From this product function, an antisymmetric Pauli determinant may be constructed; this, when normalized, will be written in the form:

$$|a\alpha \quad b\beta \quad c\alpha \quad d\beta|. \tag{3}$$

The state of the four atoms under consideration is a singlet state, being composed of two molecules in singlet states. The only functions of type (3) which can cooperate in forming that state are those having a total spin $\Sigma_z=0$, and they are 6 in number:

$$\begin{aligned}
\Psi_1&=|a\alpha \quad b\beta \quad c\alpha \quad d\beta|,\\
\Psi_2&=|a\alpha \quad b\alpha \quad c\beta \quad d\beta|,\\
\Psi_3&=|a\alpha \quad b\beta \quad c\beta \quad d\alpha|,\\
\Psi_4&=|a\beta \quad b\alpha \quad c\alpha \quad d\beta|,\\
\Psi_5&=|a\beta \quad b\alpha \quad c\beta \quad d\alpha|,\\
\Psi_6&=|a\beta \quad b\beta \quad c\alpha \quad d\alpha|.
\end{aligned} \tag{4}$$

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[3] For a review of the theory of these forces see H. Margenau, Rev. Mod. Phys. **11**, 1 (1939). Further calculations dealing specifically with H_2 were made by H. S. W. Massey and R. Buckingham, Proc. Ir. Acad. **45**, 31 (1938). See Sec. V of the present paper.

[4] J. C. Slater, Phys. Rev. **38**, 1109 (1931).

[5] S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill, 1941).

[6] S. C. Wang, Phys. Rev. **31**, 579 (1928).

TABLE I. List of symbols used for (1) $\int (P_k\varphi_1)H\varphi_1 d\tau$ and (2) $\int (P_k\varphi_1)\varphi_1 d\tau$. Symbol for integral is given opposite the permutation P_k (which is written in the form of cycles). Unprimed symbols refer to (1), primed symbols to (2).

$(a)(b)(c)(d)$	ϵ, ϵ'	(ab)	u_1, u_1'	(abc)	v_1, v_1'	$(ab)(cd)$	w_1, w_1'	$(abcd)$	z_1, z_1'
		(ac)	u_2, u_2'	(bac)	v_1, v_1'	$(ac)(bd)$	w_2, w_2'	$(dcba)$	z_1, z_1'
		(ad)	u_3, u_3'	(abd)	v_2, v_2'	$(ad)(bc)$	w_3, w_3'	$(bacd)$	z_2, z_2'
		(bc)	u_4, u_4'	(bad)	v_2, v_2'			$(abdc)$	z_2, z_2'
		(bd)	u_5, u_5'	(acd)	v_3, v_3'			$(acbd)$	z_3, z_3'
		(cd)	u_6, u_6'	(cad)	v_3, v_3'			$(dbca)$	z_3, z_3'
				(bcd)	v_4, v_4'				
				(cbd)	v_4, v_4'				

Of these, two singlet functions can be constructed by known rules:[7]

$$\Psi_A=\tfrac{1}{2}(\Psi_1-\Psi_3-\Psi_4+\Psi_5),$$
$$\Psi_B=\tfrac{1}{2}(\Psi_2-\Psi_3-\Psi_4+\Psi_6). \tag{5}$$

Between Ψ_A and Ψ_B the Hamiltonian is to be diagonalized, and this process leads to the secular equation

$$\begin{vmatrix} H_{AA}-E\Delta_{AA} & H_{AB}-E\Delta_{AB} \\ H_{AB}-E\Delta_{AB} & H_{BB}-E\Delta_{BB} \end{vmatrix}=0. \tag{6}$$

When the matrix elements appearing in this equation are expanded with the use of (5), each of them becomes a linear combination of elements H_{ij} and Δ_{ij}, respectively, where the subscripts i, j refer to the set of functions (4). The evaluation of H_{ij} and Δ_{ij} proceeds as follows.

From the properties of the antisymmetric functions and the symmetry of H it is clear that

$$H_{ij}=4!\sum_\mu (-1)^{p_\mu}\int \varphi_i H P_\mu \varphi_j d\tau, \tag{7}$$

where P_μ is some permutation among the four electrons whose coordinates are contained in φ_j, and p_μ is 1 for odd, 2 for even permutations. Also, φ_i is written for the simple product function of type (3a) corresponding to the ψ_i of type (3), and the integral includes summation over the spins. But an integral like $\int \varphi_i H P_\mu \varphi_j d\tau$ can always be reduced to the form

$$\int P_k\varphi_1 H\varphi_1 d\tau$$

with φ_1 given by (3a). We see, therefore, that every H_{ij} is a simple sum of several exchange integrals of this form. These fall, of course, into 5 classes, in accordance with the properties of the symmetric group on four particles. It is well to enumerate and label them by reference to the permutation P_k characterizing the particular integral in question.

In doing so, however, the spin functions may be omitted from φ_1, for they either disappear in the summation or cause the particular integral to vanish. Thus, for example, we shall mean henceforth by

$$\int P_k\varphi_1 H\varphi_1 d\tau$$

simply:

$$\int P_k[a(1)b(2)c(3)d(4)] \times Ha(1)b(2)c(3)d(4)d\tau_1 d\tau_2 d\tau_3 d\tau_4,$$

so that when P_k is (abc), for example,

$$\int P_k\varphi_1 H\varphi_1 d\tau=\int bcadHabcd\cdot d\tau.$$

In Table I we list the names which will be given to the integrals $\int P_k\varphi_1 H\varphi_1 d\tau$ opposite the P_k themselves; the latter are written in the form of cycles.

The equality among some of the integrals is due to the Hermitian character of the Hamiltonian; this causes integrals belonging to a permutation and to its reciprocal to be equal. No further equalities exist unless the position of the nuclei possesses some symmetry, but this cannot be assumed as yet.

The decomposition of H_{ij} into exchange integrals is effected by the use of formula (7); many

[7] See, for example, reference 5.

TABLE II. Matrix elements H_{ij} in terms of exchange integrals.

1	$\epsilon-u_2-u_5+w_2$	$-u_4+v_1+v_4-z_2$	$-u_6+v_4+v_3-z_3$	$-u_1+v_1+v_2-z_3$	$w_1-2z_1+w_3$	$-u_3+v_2+v_3-z_2$
2		$\epsilon-u_1-u_6+w_1$	$-u_5+v_2+v_4-z_1$	$-u_2+v_1+v_3-z_1$	$-u_3+v_3+v_2-z_2$	$w_2-2z_3+w_3$
3			$\epsilon-u_3-u_4+w_3$	$w_1+w_2-2z_2$	$-u_1+v_2+v_1-z_3$	$-u_2+v_1+v_3-z_1$
4				$\epsilon-u_3-u_4+w_3$	$-u_6+v_4+v_3-z_3$	$-u_5+v_2+v_4-z_1$
5					$\epsilon-u_2-u_5+w_2$	$-u_4+v_1+v_4-z_2$
6						$\epsilon-u_1-u_6+w_1$

permutations are absent from the sum because of the orthogonality of the spin functions. In Table II all elements $H_{ij}(=H_{ji})$ are collected.

When the matrix elements H_{AA}, H_{AB}, H_{BB}, which enter into the secular equation, are evaluated by means of Table II, the subsequent expressions result.

$$\begin{aligned}
H_{AA}&=\epsilon+u_1+u_6-\tfrac{1}{2}(u_2+u_3+u_4+u_5)\\
&\quad-(v_1+v_2+v_3+v_4)+w_1+w_2\\
&\qquad+w_3-(z_1+z_2-2z_3),\\
H_{BB}&=\epsilon+u_2+u_5-\tfrac{1}{2}(u_1+u_3+u_4+u_6)\\
&\quad-(v_1+v_2+v_3+v_4)+w_1+w_2\\
&\qquad+w_3-(z_2+z_3-2z_1),\\
2H_{AB}&=\epsilon+u_1+u_2+u_5+u_6-2u_3-2u_4\\
&\quad-(v_1+v_2+v_3+v_4)+w_1+w_2\\
&\qquad+w_3+2(z_1+z_3-2z_2).
\end{aligned}\tag{8}$$

Attention must also be given to Δ_{AA}, Δ_{AB}, and Δ_{BB}. But these are simply related to the corresponding H elements. If we define quantities ϵ', u_i', v_i', w_i', z_i' to be identical with the unprimed quantities given in Table I except that the operator H in the exchange integral is omitted, then the Δ elements result from the H elements on priming all quantities on the right of Eqs. (8).

To proceed further, it is expedient to adopt some conventions regarding the detailed treatment of the Hamiltonian operator in the four-electron problem.

In writing the Hamiltonian we use the following notation: Let r_{ai} be the scalar distance between the ith electron and nucleus a, and put

$$e^2/r_{ai}=\alpha_i,\quad e^2/r_{bi}=\beta_i \text{ etc.};\quad e^2/r_{ij}=\rho_{ij}.\tag{9}$$

Then

$$H=-\frac{\hbar^2}{2m}\sum_1^4\nabla_i^2-\sum_1^4(\alpha_i+\beta_i+\gamma_i+\delta_i)+\sum_{i>j}\rho_{ij}+E_N,$$

provided E_N stands for the repulsive Coulomb energy between the four nuclei. With the use of Eqs. (1) and (2) we now obtain

$$\begin{aligned}
Ha(1)b(2)c(3)d(4)=\Big\{&-2\frac{Z^2e^2}{a_0}\\
&-(1-Z)(\alpha_1+\beta_2+\gamma_3+\delta_4)-(\alpha_2+\alpha_3+\alpha_4\\
&+\beta_1+\beta_3+\beta_4+\gamma_1+\gamma_2+\gamma_4+\delta_1+\delta_2+\delta_3)\\
&+\sum_{i>j}\rho_{ij}+E_N\Big\}a(1)b(2)c(3)d(4).
\end{aligned}\tag{10}$$

II. EXCHANGE INTEGRALS

The exchange integrals ϵ, $u_1\cdots z_3$ listed in Table I may be decomposed into *elementary* exchange integrals, which will now be considered. While in the former the integrand is the entire Hamiltonian (10), the latter contain only one of its terms. To label them both succinctly and naturally, it is expedient to use the abbreviations (9). Thus we shall define

$$(a\gamma d)\equiv\int a(1)\frac{e^2}{r_{c1}}d(1)d\tau_1,$$

$$(ab\rho cd)\equiv\int a(1)b(2)\frac{e^2}{r_{12}}c(1)d(2)d\tau_1d\tau_2,$$

$$\Delta_{ab}\equiv(a\,|\,b)=\int a(1)b(1)d\tau_1,$$

and others in a similar manner. As to symmetry, it will be noted that

$$(a\gamma d)=(d\gamma a),$$
$$(a\alpha b)=(a\beta b),$$
$$(ab\rho cd)=(cb\rho ad)=(ad\rho cb)=(cd\rho ab)=(ba\rho dc).$$

That is to say, the order of the Roman letters on one side of the Greek letter may not be changed if that on the other remains unaltered, but a Roman letter may be shifted freely from one side of the Greek letter to the other, provided its order is unchanged.

The elementary exchange integrals fall into four categories, in accordance with the number of nuclei whose positions affect their value. All *one*-center integrals, like $(a\alpha a)$, $(b\beta b)$ etc., are of course equal and independent of the position of the nuclei. Among the *two*-center integrals one may distinguish four different types, exemplified by the following specimens:

$$(a\beta a),\quad (a\beta b),\quad (ab\rho ab),\quad (ab\rho ba).$$

These all occur in the problem of the hydrogen molecule and are well known.

Three-center integrals fall into three classes, characterized by

$$(a\beta c),\quad (ac\rho bc),\quad (ac\rho cb).$$

For special positions of the nuclei, they have been calculated by Gordadse,[8] Hirschfelder, Eyring, and Rosen,[9] and by Coulson.[10] Since they are of rather complicated structure and, in their exact forms, quite unsuggestive, it is important to have a quick way of estimating their magnitude. Consider, for example, $(a\beta c)$. The product function $a(1)c(1)$ is largest in the region halfway between the nuclei a and c; therefore, if b is far from a and c,

$$(a\beta c)\approx\Delta_{ac}e^2/R_{b,\,ac},$$

where $R_{b,\,ac}$ is the distance from b to the midpoint between a and c. In a similar way,

$$\begin{aligned}(ac\rho bc)&\approx(a\gamma b)\approx\Delta_{ab}e^2/R_{c,\,ab},\\(ac\rho cb)&\approx\Delta_{ac}\Delta_{bc}e^2/R_{ac,\,bc}.\end{aligned}\tag{11}$$

These approximations are quite accurate when the distances R involved in the formulas are several times as large as the arguments of the Δ functions. The integrals do not, however, become infinite as $R\rightarrow0$; they take simple limiting forms which are either two-center integrals or else very manageable expressions easily obtainable from references 8 and 9.

For more accurate work, approximation (11) is not adequate. On the other hand, the general forms of $(ac\rho bc)$ and $(ac\rho cb)$ which are needed in this work are not known. Their exact calculation would seem to entail rather formidable labor. Fortunately, however, it is possible to avoid most of it by a simple reduction process now to be described.

If the function c^2 is contracted more and more about its nucleus, until finally it becomes a δ function located at the nucleus, the integral $(ac\rho bc)$ turns into $(a\gamma b)$. Alternately, if the function ab is approximated by a δ function located midway between nuclei a and b, the same integral reduces to the two-center integral[11] $(c\overline{\alpha\beta}c)\cdot\Delta_{ab}$. When one distance is larger than the others—as is true in the interaction of two molecules—these reductions can always be made and lead to nearly equal numerical results. This we regard as a test of the validity of the reductions, and we take

$$(ac\rho bc)\cong\tfrac{1}{2}[(a\gamma b)+\Delta_{ab}(c\overline{\alpha\beta}c)].$$

Similar reasoning shows that

$$(ac\rho cb)\cong\tfrac{1}{2}[\Delta_{ac}(c\overline{\alpha\gamma}b)+\Delta_{cb}(a\overline{\gamma\beta}c)].$$

[8] G. S. Gordadse, Zeits. f. Physik **96**, 542 (1935).
[9] J. Hirschfelder, H. Eyring, and N. Rosen, J. Chem. Phys. **4**, 121 (1936).
[10] C. A. Coulson, Proc. Camb. Phil. Soc. **33**, 104 (1937).
[11] $\overline{\alpha\beta}$ here stands for the reciprocal of the electron distance from the midpoint between a and b.

The remaining integrals are known.[9] To give an example of the extent to which this procedure is reliable we consider the case in which the nuclei a, b, c are collinear, c is between a and b and the distance c–b is three times the distance c–b, the latter being the internuclear distance in H_2. The two terms in the above expansion of $(ac\rho cb)$ then have the values 0.1448 and 0.1417 atomic unit, respectively. For larger distances c–b, the reduction works still better.

All *four*-center exchange integrals are of the form $(ab\rho cd)$. Their exact calculation would be extremely tedious if it can be carried out at all. But here again the scheme just described will be used. The reduction can be effected in two ways, and if the results do not differ beyond the tolerated limit of error, their mean is taken as the value of the four-center integral. Thus

$$(ab\rho cd)\approx\tfrac{1}{2}[\Delta_{ac}(b\overline{\alpha\gamma}d)+\Delta_{bd}(a\overline{\beta\delta}c)].$$

When a and c belong to the same molecule, the two terms on the right become very nearly equal, and each approaches $\Delta_R{}^2(e^2/R)$ in the limit in which R, the distance between molecular centers, is large.

We do not wish to lengthen the present paper by an inclusion of the detailed formulas for the residual integrals, which may, if they are found useful in other molecular problems, form the substance of a later communication. As far as our present purposes are concerned, the reader will be relieved to know that an even simpler scheme than the alternate reductions here studied, a scheme which will be described in a later section, leads to significant results for the interaction energy of molecular hydrogen.

When the exchange integrals ϵ, $u_1\cdots z_3$ are expressed in terms of their elements, certain combinations often occur. These will first be singled out. We define

$$\begin{aligned}
A&=(a\alpha a)=Ze^2/a_0,\\
D&=-\tfrac{1}{2}Z^2e^2/a_0,\\
B_{ab}&=e^2/R_{ab}-(a\beta a),\\
C_{ab}&=e^2/R_{ab}+(ab\rho ab)-2(a\beta a),\\
T_{ab}&=(a\beta b)/\Delta_{ab},\\
X_{ab}&=e^2/R_{ab}+(ab\rho ba)/\Delta_{ab}^2-2T_{ab}.
\end{aligned}\tag{12}$$

Here C_{ab} will be recognized as the "Coulomb energy," X_{ab} as the "exchange energy" between two hydrogenic atoms at a and b. All these expressions are functions of only R_{ab}, the distance between a and b, and most of them vanish exponentially at large distances. In addition we need the following more complicated combinations:

$$\begin{aligned}
X'_{ab}&=2[(ac\rho bc)+(ad\rho bd)-(a\gamma b)-(a\delta b)]/\Delta_{ab},\\
U_{abc}&=\frac{e^2}{R_{ab}}+\frac{e^2}{R_{ac}}+\frac{e^2}{R_{bc}}-(b\alpha c)/\Delta_{bc}-(a\beta c)/\Delta_{ac}-(a\gamma b)/\Delta_{ab}\\
&\qquad+(ab\rho bc)/\Delta_{ab}\Delta_{bc}+(ac\rho ba)/\Delta_{ab}\Delta_{ac}+(bc\rho ca)/\Delta_{bc}\Delta_{ac},\\
U'_{abc}&=\frac{(ad\rho bd)-(a\delta b)}{\Delta_{ab}}+\frac{(bd\rho cd)-(b\delta c)}{\Delta_{bc}}+\frac{(ad\rho cd)-(a\delta c)}{\Delta_{ac}},\\
V_{ab,cd}&=\frac{e^2}{R_{ac}}+\frac{e^2}{R_{ad}}+\frac{e^2}{R_{bc}}+\frac{e^2}{R_{bd}}+4\frac{(ac\rho bd)}{\Delta_{ab}\Delta_{cd}}-2[(a\gamma b)+(a\delta b)]/\Delta_{ab}-2[(c\alpha d)+(c\beta d)]/\Delta_{cd},\\
W_{abcd}&=E_N+\frac{(bc\rho ab)}{\Delta_{ab}\Delta_{bc}}+\frac{(bd\rho ac)}{\Delta_{ab}\Delta_{cd}}+\frac{(ba\rho ad)}{\Delta_{ab}\Delta_{ad}}+\frac{(bc\rho cd)}{\Delta_{bc}\Delta_{cd}}+\frac{(ca\rho bd)}{\Delta_{bc}\Delta_{ad}}+\frac{(da\rho cd)}{\Delta_{cd}\Delta_{ad}}\\
&\qquad-[(a\gamma b)+(a\delta b)]/\Delta_{ab}-[(b\alpha c)+(b\delta c)]/\Delta_{bc}-[(c\alpha d)+(c\beta d)]/\Delta_{cd}-[(a\beta d)+(a\gamma d)]/\Delta_{ad}.
\end{aligned}\tag{13}$$

By permutation of subscripts, other functions can be constructed from this list. Not all of these are different; for instance it will be seen on inspection that there are four different U functions (U_{abc}, U_{abd}, U_{acd}, U_{bcd}), three different V functions ($V_{ab,cd}$, $V_{ac,bd}$, $V_{ad,bc}$), and three different W functions (W_{abcd}, W_{bacd}, W_{acbd}). Only X' and U' have the property of vanishing when a reduction of the type (11) is performed, which may be taken as an indication that they are generally small. They disappear when the nuclei in each molecule coalesce.

The function $V_{ab,cd}$ has a rather interesting significance. When it is "reduced," it represents the electrostatic interaction between two linear quadrupoles, one consisting of protons at a and b with two electrons at the midpoint between them, the other of protons at c and d and two electrons at their midpoint. We shall show later that this is indeed its true significance, and that the value of this integral is well approximated by this quadrupole interaction.

With the use of these abbreviations, the exchange integrals take on symmetrical—even if somewhat complicated—forms, *viz.*:

$$
\begin{aligned}
\epsilon &= 4D+4(Z-1)A+C_{ab}+C_{ac}+C_{ad}+C_{bc}+C_{bd}+C_{cd},\\[6pt]
u_1 &= \Delta_{ab}^2[4D+2(Z-1)(A+T_{ab})+X_{ab}+B_{ac}+B_{ad}+B_{bc}+B_{bd}+C_{cd}+X'_{ab}],\\
u_2 &= \Delta_{ac}^2[4D+2(Z-1)(A+T_{ac})+X_{ac}+B_{ab}+B_{ad}+B_{bc}+B_{cd}+C_{bd}+X'_{ac}],\\
u_3 &= \Delta_{ad}^2[4D+2(Z-1)(A+T_{ad})+X_{ad}+B_{ab}+B_{ac}+B_{bd}+B_{cd}+C_{bc}+X'_{ad}],\\
u_4 &= \Delta_{bc}^2[4D+2(Z-1)(A+T_{bc})+X_{bc}+B_{ab}+B_{ac}+B_{bd}+B_{cd}+C_{ad}+X'_{bc}],\\
u_5 &= \Delta_{bd}^2[4D+2(Z-1)(A+T_{bd})+X_{bd}+B_{ab}+B_{ad}+B_{bc}+B_{cd}+C_{ac}+X'_{bd}],\\
u_6 &= \Delta_{cd}^2[4D+2(Z-1)(A+T_{cd})+X_{cd}+B_{ac}+B_{ad}+B_{bc}+B_{bd}+C_{ab}+X'_{cd}],\\[6pt]
v_1 &= \Delta_{ab}\Delta_{ac}\Delta_{bc}[4D+B_{ad}+B_{bd}+B_{cd}-(2-Z)(T_{ab}+T_{ac}+T_{bc})+(Z-1)A+U_{abc}+U'_{abc}],\\
v_2 &= \Delta_{ab}\Delta_{bd}\Delta_{ad}[4D+B_{ac}+B_{bc}+B_{cd}-(2-Z)(T_{ab}+T_{bd}+T_{ad})+(Z-1)A+U_{abd}+U'_{abd}],\\
v_3 &= \Delta_{ac}\Delta_{cd}\Delta_{ad}[4D+B_{ab}+B_{bc}+B_{bd}-(2-Z)(T_{ac}+T_{cd}+T_{ad})+(Z-1)A+U_{acd}+U'_{acd}],\\
v_4 &= \Delta_{bc}\Delta_{cd}\Delta_{bd}[4D+B_{ab}+B_{ac}+B_{ad}-(2-Z)(T_{bc}+T_{cd}+T_{bd})+(Z-1)A+U_{bcd}+U'_{bcd}],\\[6pt]
w_1 &= \Delta_{ab}^2\Delta_{cd}^2[4D+X_{ab}+X_{cd}+2(Z-1)(T_{ab}+T_{cd})+V_{ab,cd}],\\
w_2 &= \Delta_{ac}^2\Delta_{bd}^2[4D+X_{ac}+X_{bd}+2(Z-1)(T_{ac}+T_{bd})+V_{ac,bd}],\\
w_3 &= \Delta_{ad}^2\Delta_{bc}^2[4D+X_{ad}+X_{bc}+2(Z-1)(T_{ad}+T_{bc})+V_{ad,bc}],\\[6pt]
z_1 &= \Delta_{ab}\Delta_{bc}\Delta_{cd}\Delta_{ad}[4D-(2-Z)(T_{ab}+T_{bc}+T_{cd}+T_{ad})+W_{abcd}],\\
z_2 &= \Delta_{ac}\Delta_{ab}\Delta_{cd}\Delta_{bd}[4D-(2-Z)(T_{ac}+T_{ab}+T_{cd}+T_{bd})+W_{bacd}],\\
z_3 &= \Delta_{ac}\Delta_{bd}\Delta_{bc}\Delta_{ad}[4D-(2-Z)(T_{ac}+T_{bd}+T_{bc}+T_{ad})+W_{acbd}].
\end{aligned}
\tag{14}
$$

Thus far our development has been quite general. We can now afford to make specific assumptions: Protons a and b belong to one molecule, protons c and d to the other; the distances a–b and c–d are equal. Functions with subscripts ab and cd may therefore be written without subscripts, the understanding being that they are to be evaluated for the internuclear distance of the H_2 molecule. It is also possible to distinguish different orders of magnitude among the various constituents of Eqs. (14). All quantities without subscripts (or with subscripts ab, cd) are large, all others small. Whether a term can be totally neglected can only be decided by inspection of the Δ functions which multiply it. This overlap integral has the well-known simple form

$$\Delta_{ab}=\Delta(s)=(1+s+\tfrac{1}{3}s^2)e^{-s},$$

s being $(Z/a_0)R_{ab}$. The ratio Δ_{ac}/Δ_{ab} is therefore always fairly small, and it is safe to neglect its fourth power, though not the second. We are thus enabled to simplify the list (14) somewhat, as follows:

$$
\begin{aligned}
&\epsilon=4D+4(Z-1)A+2C+C_{ac}+C_{ad}+C_{bc}+C_{bd},\\[6pt]
&u_1=\Delta^2[4D+X+C+2(Z-1)(A+T)+B_{ac}+B_{ad}+B_{bc}+B_{bd}],\\
&u_2=\Delta_{ac}^2[4D+2B+2(Z-1)A+X_{ac}+X'_{ac}+2(Z-1)T_{ac}],\\
&u_3=\Delta_{ad}^2[4D+2B+2(Z-1)A+X_{ad}+X'_{ad}+2(Z-1)T_{ad}],\\
&u_4=\Delta_{bc}^2[4D+2B+2(Z-1)A+X_{bc}+X'_{bc}+2(Z-1)T_{bc}],\\
&u_5=\Delta_{bd}^2[4D+2B+2(Z-1)A+X_{bd}+X'_{bd}+2(Z-1)T_{bd}],\\
&u_6=u_1,\\[6pt]
&v_1=\Delta\Delta_{ac}\Delta_{bc}[4D+B-(2-Z)T+(Z-1)A+U_{abc}+U'_{abc}-(2-Z)(T_{ac}+T_{bc})],\\
&v_2=\Delta\Delta_{bd}\Delta_{ad}[4D+B-(2-Z)T+(Z-1)A+U_{abd}+U'_{abd}-(2-Z)(T_{bd}+T_{ad})],\\
&v_3=\Delta\Delta_{ac}\Delta_{ad}[4D+B-(2-Z)T+(Z-1)A+U_{acd}+U'_{acd}-(2-Z)(T_{ac}+T_{ad})],\\
&v_4=\Delta\Delta_{bc}\Delta_{bd}[4D+B-(2-Z)T+(Z-1)A+U_{bcd}+U'_{bcd}-(2-Z)(T_{bc}+T_{bd})],\\[6pt]
&w_1=\Delta^4[4D+2X+4(Z-1)T+V_{ab,\,cd}],\\
&w_2=w_3=0,\\[6pt]
&z_1=\Delta^2\Delta_{bc}\Delta_{ad}[4D-2(2-Z)T-(2-Z)(T_{bc}+T_{ad})+W_{abcd}],\\
&z_2=\Delta^2\Delta_{ac}\Delta_{bd}[4D-2(2-Z)T-(2-Z)(T_{ac}+T_{bd})+W_{bacd}],\\
&z_3=0.
\end{aligned}
\tag{14b}
$$

In u_1 the term X' has been dropped because of its smallness, and in u_2 to u_5, the C functions are neglected. Numerical comparison with terms retained will justify this curtailment.

The primed functions, defined in Table I, are easily obtained from this list; for they are simply the product of Δ functions which appears in the equations for their unprimed mates. Thus, for example, $\epsilon'=1$, $u_1'=\Delta^2$, $v_4=\Delta\Delta_{bc}\Delta_{bd}$ etc. We are now ready to compute the two roots E of Eq. (6).

III. GENERAL EXPRESSION FOR EXCHANGE ENERGY

Of the two solutions of the determinantal Eq. (6), the one of interest is that which will represent the energy of two H_2 molecules at infinite internuclear distance. It is convenient, therefore, to solve the equation first of all "in zeroth order," i.e., with the neglect of all terms which vanish at infinite separation.

As a preliminary, let us recall the results of the Heitler-London treatment of the single molecule and translate them into the present notation. Here we have

$$\psi_1=|a\alpha\quad b\beta|,\quad \psi_2=|a\beta\quad b\alpha|,$$

and $\psi_\pm=\psi_1\pm\psi_2$. The function ψ_+ represents the triplet, ψ_- the singlet or normal state of the molecule. In view of Eqs. (2) and (12)

$$Hab=[2D+(Z-1)(\alpha_1+\beta_2)-\alpha_2-\beta_1+\rho_{12}+e^2/R_{ab}]ab$$

so that

$$\int\psi_\pm H\psi_\pm d\tau=2\{2D+C+2(Z-1)A\mp[2D+2(Z-1)T+X]\Delta^2\}$$

whereas

$$\int\psi_\pm{}^2 d\tau=2[1\mp\Delta^2].$$

For the ratio of these, which represents the energy of the molecule, we have

$$E(H_2)=2D+(1\mp\Delta^2)^{-1}\{C+2(Z-1)A\mp\Delta^2[X+2(Z-1)T]\},\tag{15}$$

where the *lower* signs refer to the stable state. The second part of this expression represents the molecular energy since $2D$ is the energy of two hydrogen atoms of nuclear charge Ze (cf. Eq. (12)). Wang has found the value of Z which minimizes (15) to be 1.166.

We now turn to Eq. (6), in which the H elements must be expressed in terms of the functions (12) and (13) via Eqs. (8) and (14). Before doing this it is well to note the effect of subtracting $E\Delta_{AA}$ from H_{AA}. From what has been said about the Δ elements it is apparent that this subtraction merely amounts to the replacement, in H_{AA}, of every term $4D$ by $4D-E$. The same is true regarding $H_{AB}-E\Delta_{AB}$ and $H_{BB}-E\Delta_{BB}$. We therefore define new matrix elements, K_{AA}, K_{AB}, K_{BB}, which differ from the corresponding components of H merely in the substitution of

$$-E'\equiv 4D-E$$

for $4D$. According to its definition, E' is the total molecular energy of the two interacting partners, including the binding energy of each molecule. Equation (6) now reads

$$\begin{vmatrix} K_{AA} & K_{AB} \\ K_{AB} & K_{BB} \end{vmatrix}=0.\tag{16}$$

In zeroth approximation, only those parts of (14b) need be retained which bear no subscripts. This leaves us only with parts of ϵ, u_1, u_6, and w_1. When these are used in (8), we find

$$\begin{aligned}\overset{0}{K}_{AA}&=-E'+2C+4(Z-1)A+2\Delta^2[-E'+X+C+2(Z-1)(A+T)]+\Delta^4[-E'+2X+4(Z-1)T],\\ \overset{0}{K}_{BB}&=-E'+2C+4(Z-1)A-\Delta^2[-E'+X+C+2(Z-1)(A+T)]+\Delta^4[-E'+2X+4(Z-1)T],\\ \overset{0}{K}_{AB}&=\tfrac{1}{2}\overset{0}{K}_{AA}.\end{aligned}\tag{17}$$

On insertion of these expressions into (16) there results

$$\overset{0}{K}_{AA}(\overset{0}{K}_{BB}-\tfrac{1}{4}\overset{0}{K}_{AA})=0,$$

and this allows the two roots to be determined by putting

$$\overset{0}{K}_{AA}=0 \quad\text{and}\quad \overset{0}{K}_{BB}=\tfrac{1}{4}\overset{0}{K}_{AA}.$$

When these are solved for E', the first leads to $2E(H_2)$ as given by Eq. (15) with the choice of the positive signs, the second to the same equation, but with negative signs. Our interest is therefore confined to that root of Eq. (16) which is given in zeroth approximation by the equation

$$\overset{0}{K}_{AA}=0.\tag{18}$$

We now show that the interaction energy which is being sought is similarly a solution of

$$K_{AA}=0\tag{19}$$

so that we need not calculate the elements K_{BB} and K_{AB} at all for the purposes of the present problem.

Let us put

$$K_{AA}=-LE'+L_0+lE'+l_0$$

where $-LE'+L_0$ represents $\overset{0}{K}_{AA}$ (the coefficients L and L_0 are easily identifiable from (17)), the remainder being small. We may then treat L and L_0 as "large," l and l_0 as small coefficients. Similarly

$$K_{AB}=-ME'+M_0+mE'+m_0$$

and we know from (17) that $M=\frac{1}{2}L$, $M_0=\frac{1}{2}L_0$. Finally,

$$K_{BB}=-NE'+N_0+nE'+n_0.$$

In solving (16), it is now convenient to write

$$E' = E_0' + \eta,$$

E_0' being the solution of (18), i.e. the energy of the two H_2 molecules at infinite separation. The determinant (16) then reads

$$\begin{vmatrix} -LE_0'+L_0-L\eta+lE_0'+l_0 & -ME_0'+M_0-M\eta+mE_0'+m_0 \\ -ME_0'+M_0-M\eta+mE_0'+m_0 & -NE_0'+N_0-N\eta+nE_0'+n_0 \end{vmatrix} = 0.$$

In expanding it, the squares of small terms may be omitted, and we know that only the first two summands of each element are large. Also, $E_0' = L_0/L$. Insertion of this causes all large terms in the elements of the first row to disappear because $L/L_0 = M/M_0$. Expansion then gives

$$\eta = L^{-1}(lE_0' + l_0), \tag{20}$$

and this is simply the condition (19). We turn, therefore, to the evaluation of K_{AA}. When the terms are suitably grouped, there results

$$\begin{aligned} K_{AA} = &-(1+\Delta^2)^2\eta + [\tfrac{1}{2}E_0' - B - (Z-1)A](\Delta_{ac}^2 + \Delta_{ad}^2 + \Delta_{bc}^2 + \Delta_{bd}^2) \\ &+ C_{ac} + C_{ad} + C_{bc} + C_{bd} + 2\Delta^2(B_{ac} + B_{ad} + B_{bc} + B_{bd}) - \tfrac{1}{2}\Delta_{ac}^2[X_{ac} + X'_{ac} + 2(Z-1)T_{ac}] \\ &- \tfrac{1}{2}\Delta_{ad}^2[X_{ad} + X'_{ad} + 2(Z-1)T_{ad}] - \tfrac{1}{2}\Delta_{bc}^2[X_{bc} + X'_{bc} + 2(Z-1)T_{bc}] \\ &- \tfrac{1}{2}\Delta_{bd}^2[X_{bd} + X'_{bd} + 2(Z-1)T_{bd}] + \Delta(\Delta_{ac}\Delta_{bc} + \Delta_{ad}\Delta_{bd} + \Delta_{ac}\Delta_{ad} + \Delta_{bc}\Delta_{bd}) \\ &\times [E_0' - B - (Z-1)A + (2-Z)T] - \Delta\Delta_{ac}\Delta_{bc}[U_{abc} + U'_{abc} - (2-Z)(T_{ac} + T_{bc})] \\ &- \Delta\Delta_{ad}\Delta_{bd}[U_{abd} + U'_{abd} - (2-Z)(T_{ad} + T_{bd})] - \Delta\Delta_{ac}\Delta_{ad}[U_{acd} + U'_{acd} - (2-Z)(T_{ac} + T_{ad})] \\ &- \Delta\Delta_{bc}\Delta_{bd}[U_{bcd} + U'_{bcd} - (2-Z)(T_{bc} + T_{bd})] + \Delta^2(\Delta_{bc}\Delta_{ad} + \Delta_{ac}\Delta_{bd})[E_0' + 2(2-Z)T] \\ &- \Delta^2\Delta_{bc}\Delta_{ad}[W_{abcd} - (2-Z)(T_{bc} + T_{ad})] - \Delta^2\Delta_{ac}\Delta_{bd}[W_{bacd} - (2-Z)(T_{ac} + T_{bd})] + \Delta^4 V_{ab,cd}. \end{aligned} \tag{21}$$

η is the exchange energy we are seeking; it is found by equating K_{AA} to zero.

IV. NUMERICAL RESULTS

When preliminary computations based on the use of Eq. (21) were made, a rather curious fact emerged. At first Z was taken to be 1, then 1.166 (Wang's value), and in both cases did η become *negative* at all significant distances of interaction. In this work, alternate reductions were made as described earlier, and careful attention was paid to the approximations involved; the conclusion was reached that the negative result was not occasioned by inaccuracies in the numerical evaluation of the integrals. To test the matter further, the integrals constituting η were simplified by allowing the nuclei of each molecule to coalesce. The result was then identical formally with the interaction energy of two helium atoms. In that problem, too, η is negative for $Z=1$ and 1.166. It is possible to show, moreover, that the helium interaction, calculated by means of hydrogenic functions, is repulsive only for values of Z above the critical value $Z=11/8$. Since this appears to be a somewhat interesting feature of the 4-electron interaction, we shall prove it in a later section. For He, of course, the matter is unimportant since the value of Z which minimizes the atomic energy is 27/16, well above the critical value. One would expect, then, that in our problem Z also possesses such a critical value, presumably in the neighborhood of 11/8.

In a sense, this is a rather sad commentary on the adequacy of the Wang function for the purpose at hand,[12] which might induce one to look for better wave functions. The complexity of the present calculation, however, definitely counsels against that undertaking. The situation appears even more embarrassing when it is noted that Wang's value of Z describes the polariza-

[12] A more favorable, literal interpretation of this result would entail the consequence that hydrogen molecules, while indeed attracting each other dynamically at nearly all distances, are kept apart for reasons of entropy. This, however, we do not believe to be the case.

bility of H_2 surprisingly well,[13] gives a good account of its magnetic susceptibility and a reasonable one of the dispersion forces.[14]

But on further reflection, the puzzling aspects fade away. The effective nuclear charge has no definite physical significance—except insofar as it measures roughly the concentration of the electron cloud—and may well take on different values in different physical problems. In particular, there is nothing unique about the Z which minimizes the molecular energy. It happens that in the calculations of the polarizability, the susceptibility, and the dispersion forces the *mean square* of the charge distribution is of importance, and this would account for a common Z. The present problem, however, has altogether different features.

The change in Z from 1 to 1.166 which occurs as we pass from the free hydrogen atom to the molecule is a measure of the increased electron concentration about each proton occurring as a result of the repulsion by the other electron. The term "screening," though quite adequate in atomic problems, loses its significance here. Now, when two molecules interact, there is not only *one* electron which tends to drive a given electron back to its nucleus, but *three*. This crude picture may be made to give a qualitative indication of the value of Z to be chosen in the present problem: If one electron causes an increase in Z from 1 to 1.166, three might increase it from 1 to about 1.5. A similar result could be argued in this way: as the two nuclei of the H_2 molecule coalesce, Z changes from 1 to 2; as the four nuclei here under consideration are made to coalesce, Z changes from 1 to 4 (except for screening, which is neglected in both instances). Wang's value of Z represents a stage in the process of coalescence 1/6 on its way toward completion; the corresponding stage in the four-electron problem is given by $Z=1.5$. This result is likely to be too large, of course, because the distance between nuclei in the different molecules is greater than in H_2.

[13] J. O. Hirschfelder, J. Chem. Phys. **3**, 555 (1935). We have computed the polarizability of H_2 as a function of Z and have found that $Z=1.167$ gives about the best fit with observation.

[14] H. S. W. Massey and R. Buckingham, Proc. Ir. Acad. **45**, 31 (1938).

While we do not wish to ascribe much quantitative significance to the present argument, we are forced, in the absence of more conclusive evidence, to use it. The exchange forces do not depend as sensitively on Z as, for example, the second-order forces. Our results will not be changed decisively by a change in Z from 1.4 to 1.5. In the following we select one approximately "right" value, $Z=1.428$, and one "wrong" value, $Z=1.785$ for comparison. Their exact choice was dictated by numerical convenience; the first makes the parameter Zd/a_0, wherein d is the internuclear distance of H_2, equal to 2, the second to 2.5.

The preliminary calculations further indicate that a certain simplification is permitted. Among the functions occurring in η, there are many which vary slowly as the nuclei of each molecule are made to coalesce. In these we may proceed to the limit in which $R_{ab}=R_{cd}=0$. Then, if we denote the distance between molecular centers by R,

$$\begin{aligned}
\text{all}\quad & X'\to 0,\\
& U'\to 0,\\
& U_{abc}\to X(R)+B(R)+M(R)\\
&\qquad -\frac{2e^2}{R}+\frac{e^2}{R_{ac}}+\frac{e^2}{R_{bc}}+\frac{e^2}{d},\\
& W_{abcd}\to X(R)+2B(R)\\
&\qquad +C(R)+2M(R)-2T(R)\\
&\qquad +\frac{2e^2}{d}+\frac{e^2}{R_{ac}}+\frac{e^2}{R_{ad}}+\frac{e^2}{R_{bc}}+\frac{e^2}{R_{bd}}-\frac{4e^2}{R},\\
& W_{bacd}=W_{abcd}.
\end{aligned}$$

The other three U functions are formed by fairly obvious permutations of subscripts. The new quantity M which appears here is given by

$$M_{ac}=2(aa\rho ac)/\Delta_{ac}.$$

$M(R)$ may be approximated by either $2T(R)$ or, better, by $T(R)+(2e^2/R)-B(R/2)$. We finally introduce the abbreviations $E(abc)$ for the electrostatic repulsive energy between protons a, b, and c (and similarly $E(abcd)$ for the former E_N),

$$\kappa\equiv Z-1$$

TABLE III. Values of numerical constants used. All energies are stated in units Ze^2/a_0.

Z	1.428	1.785
Zd/a_0	2.0	2.5
Δ	0.5865	0.4583
A	1	1
B	0.0275	0.0094
C	− .0191	− .0128
X	− .349	− .348
T	0.692	0.626
E_0'	1.370	2.794

and obtain from (21)

$$\begin{aligned}\eta=&(1+\Delta^2)^{-2}\{2\Delta^2(B_{ac}+B_{ad}+B_{bc}+B_{bd})\\&+C_{ac}+C_{ad}+C_{bc}+C_{bd}\\&+(\Delta_{ac}^2+\Delta_{ad}^2+\Delta_{bc}^2+\Delta_{bd}^2)(\tfrac{1}{2}E_0'-B-\kappa A)\\&-\tfrac{1}{2}\Delta_{ac}^2(X_{ac}+2\kappa T_{ac})-\tfrac{1}{2}\Delta_{ad}^2(X_{ad}+2\kappa T_{ad})\\&-\tfrac{1}{2}\Delta_{bc}^2(X_{bc}+2\kappa T_{bc})-\tfrac{1}{2}\Delta_{bd}^2(X_{bd}+2\kappa T_{bd})\\&+\Delta(\Delta_{ac}\Delta_{bc}+\Delta_{ad}\Delta_{bd}+\Delta_{ac}\Delta_{ad}+\Delta_{bc}\Delta_{bd})\\&\times[E_0'-B+(1-\kappa)T-\kappa A-X(R)\\&-B(R)-2\kappa T(R)+(2e^2/R)]\\&-\Delta[\Delta_{ac}\Delta_{bc}E(abc)+\Delta_{ad}\Delta_{bd}E(abd)\\&+\Delta_{ac}\Delta_{ad}E(acd)+\Delta_{bc}\Delta_{bd}E(bcd)]\\&+\Delta^2(\Delta_{bc}\Delta_{ad}+\Delta_{ac}\Delta_{bd})\\&\times\left[E_0'+2(1-\kappa)T-X(R)-2B(R)-C(R)\right.\\&\left.-2\kappa T(R)+\frac{4e^2}{R}-E(abcd)\right]+\Delta^4V_{ab,\,cd}.\end{aligned}\tag{22}$$

For reference, we recall:

$$E_0'=2\frac{C+\Delta^2X+2\kappa(A+\Delta^2T)}{1+\Delta^2}.$$

The numerical results now to be reported were based on this approximation. Equation (22) is slightly less sensitive to orientation of the molecules than (21), but the economy of labor which it effects recommends its use despite this fault. The values of constants are collected in Table III. From the last entry the *binding energy* of the molecule for the assumed value of Z may be obtained, since, as may easily be verified, it is given by $E_0'Z/2-(Z^2-1)$. This is -1.65 ev for the smaller, $+8.33$ ev for the larger Z. In the latter case, therefore, the hydrogen molecule would not be stable at all.

Three relative orientations of the molecules have been treated. In

Case (a): both molecular axes are parallel to R, the line joining the centers;
Case (b): one axis is parallel, the other is perpendicular to R;
Case (c): both axes are perpendicular to R.

The results for η, exclusive of the term $\Delta^4 V_{ab,\,cd}$, are given in Table IV. It is perhaps worth mentioning that in the region here of interest η can be approximated fairly well by an expression of the form

$$\eta=Ae^{-bS}$$

in which b differs but little in all 6 cases, having the value 1.55 ± 0.10, while A varies markedly from instance to instance. The quantity S represents the distance R measured in units a_0/Z.

V. QUADRUPOLE FORCES

We have already interpreted the last term of Eq. (22), $[\Delta^2/(1+\Delta^2)]^2V_{ab,\,cd}$, as the quadrupole energy on the evidence that V "reduces" to the electrostatic interaction between the two structures of Fig. 1 when the approximation (11) is made. In this approximation, then, V is given by the formula[15] appropriate for *linear* quadrupoles,

$$V=\frac{3Q^2}{4R^5}f(\theta_1,\,\theta_2,\,\varphi),\tag{23}$$

in which Q, the quadrupole moment, is $2e^2(d/2)^2$, and f is the function characteristic of this type of interaction. Explicitly, if θ_1 and θ_2 are the angles which the molecular axes make with R, the line between centers, and φ is the difference between azimuths in a plane at right angles to R, then

$$\begin{aligned}f=&1-5\cos^2\theta_1-5\cos^2\theta_2-15\cos^2\theta_1\cos^2\theta_2\\&+2(4\cos\theta_1\cos\theta_2+\sin\theta_1\sin\theta_2\cos\varphi)^2.\end{aligned}\tag{24}$$

Our calculation shows that this interaction between *point* charges must be multiplied by the "diffuseness factor" $[\Delta^2/(1+\Delta^2)]^2$ in order to represent the true interaction between the charge clouds.

The present approximation is in fact suffi-

[15] See review article, reference 3.

ciently good for our purposes, but it is interesting to point out that an accurate calculation merely causes the term Q in (23) to be multiplied by 4/5. A calculation of this kind has already been made by Massey and Buckingham,[14] whose work was limited to one special value of Z. Since their result is written in a rather cumbersome form which veils its simplicity, and our derivation is short, we shall give it here.

Equation (23) is valid in general, provided we replace Q by its quantum mechanical equivalent:

$$Q'=\tfrac{1}{2}\sum_i e_i\langle r_i^2-3z_i^2\rangle_{\text{Av}}.$$

Here r_i and z_i refer to the positions of the various charges e_i, and the average is a quantum one. The sum extends over the 4 particles composing the molecule. We take the Z axis along the molecule. The protons will then contribute to this sum the amount $-4e(d/2)^2$. For the electrons, $\langle r_i^2\rangle_{\text{Av}}=\langle 2x_i^2\rangle_{\text{Av}}+\langle z_i^2\rangle_{\text{Av}}$; hence their contribution to the sum is $-4e(\langle x^2\rangle_{\text{Av}}-\langle z^2\rangle_{\text{Av}})$. The subscript may here be dropped because the electrons are indistinguishable. In view of these simple facts,

$$Q'=-2e\left(\frac{d^2}{4}-\langle z^2\rangle_{\text{Av}}+\langle x^2\rangle_{\text{Av}}\right).$$

The mean values appearing here are not difficult to calculate when hydrogenic wave functions are used—they also occur in the theory of polarizabilities.[13] In general,

$$\langle z^2\rangle_{\text{Av}}=(1+\Delta^2)^{-1}\left[\langle z_0^2\rangle_{\text{Av}}+\frac{d^2}{4}+\Delta\int\zeta^2 ab d\tau\right],$$

TABLE IV. Exchange energy (η) as function of intermolecular separation (R).

S	R (in A)	η (in volts) Pos. a	Pos. b	Pos. c
$Z=1.428$				
6	2.22	0.358	0.249	0.150
7	2.59	0.102	0.0602	0.0344
8	2.96	0.0231	0.0135	0.00744
9	3.33	0.00504	0.00287	0.00153
10	3.70	0.00104	0.000582	0.000302
11	4.07	0.000200	0.000114	0.0000579
$Z=1.785$				
6	1.78	1.390	0.754	0.325
7	2.07	0.426	0.192	0.0764
8	2.37	0.100	0.0449	0.0173
9	2.66	0.0247	0.00986	0.00354
10	2.96	0.00545	0.00205	0.000711
11	3.25	0.00113	0.000451	0.000137

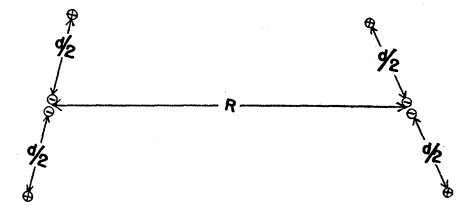

FIG. 1. Molecular structure and arrangement for calculation of electrostatic energy.

$$\langle x^2\rangle_{\text{Av}}=(1+\Delta^2)^{-1}\left[\langle x_0^2\rangle_{\text{Av}}+\Delta\int\xi^2 ab d\tau\right].$$

Here $\langle z_0^2\rangle_{\text{Av}}=\langle x_0^2\rangle_{\text{Av}}$ are averages taken over the electron in the H atom, ξ and ζ are, respectively, the x and z coordinates measured from the *center* of the molecule. For the functions here used,

$$\int\zeta^2 ab d\tau=\frac{a_0^2}{Z^2}e^{-s}\left(1+s+\frac{9}{20}s^2+\frac{7}{60}s^3+\frac{1}{60}s^4\right),$$

$$\int\xi^2 ab d\tau=\frac{a_0^2}{Z^2}e^{-s}\left(1+s+\frac{2}{5}s^2+\frac{1}{15}s^3\right),\quad s=\frac{dZ}{a_0}.$$

Remembering the form of Δ (cf. appendix), we find

$$\langle x^2\rangle_{\text{Av}}-\langle z^2\rangle_{\text{Av}}=-\frac{d^2}{4}(1+\Delta^2/5)\Big/(1+\Delta^2)$$

and finally

$$Q'=-2e\cdot\frac{4}{5}\frac{\Delta^2}{1+\Delta^2}\frac{d^2}{4}. \tag{25}$$

The quadrupole moment depends on Z only through the overlap integral Δ, and in this simple way; the factor $\Delta^2/(1+\Delta^2)$ appears automatically in the calculation, justifying our former remarks. Collecting the results of the present section, we write for the quadrupole energy

$$E_Q=\frac{3}{25}\left(\frac{\Delta^2}{1+\Delta^2}\right)^2\frac{e^2d^4}{R^5}\cdot f(\theta_1,\theta_2,\varphi). \tag{26}$$

The function f (cf. Eq. (24)) causes E_Q to vanish when a mean value is formed over all orientations.

The quadrupole moment is listed as a function of Z in Table V, where $-Q'$ is stated in units ea_0^2. The values of E_Q, given in Table VI for cases (a), (b), and (c), are seen to be small in comparison with the exchange energy in Table IV.

VI. LONG RANGE VAN DER WAALS FORCES

The dipole-dipole part of the long range forces has been calculated for the present problem by Massey and Buckingham using $Z=1.166$. As to the dependence of these forces on orientation, their result indicates a variation of about 50 percent as we pass from case (c) to case (a). The corresponding variation in η is measured by a factor 3. When compounding the various components of the total interaction, we shall therefore permit ourselves to neglect the dependence on orientation of the long range forces.[16] The numerical result for the mean over all orientations given by the aforementioned authors is

$$\bar{E}_{\text{v.d.w}} = -16.0\frac{e^2}{a_0}\left(\frac{a_0}{R}\right)^6; \tag{27}$$

they also point out that it agrees reasonably well with empirical facts as far as they are available.

In using this result in the present calculation we should be guilty of employing different values of Z in different parts of the problem. As has been noted, there is nothing basically contradictory in such a procedure because a variation in the best choice of Z may well be expected to occur as we pass from one calculation to another. Nevertheless we do not wish to leave this point without further investigation, which will also throw some light on the accuracy of Eq. (27).

In the first place, it is easy to obtain $\bar{E}_{\text{v.d.w}}$ for other values of Z by use of the variation method of reference 14. Taking $Z=1.428$, we find

$$\bar{E}_{\text{v.d.w}} = -5.4\frac{e^2}{a_0}\left(\frac{a_0}{R}\right)^6,$$

which is almost certainly too low. Roughly, the dipole-dipole energy is proportional to Z^{-5}.

Perhaps the most accurate semi-empirical method[3] of computing the term here in question is to employ dispersion f values which, for H_2, are known with considerable accuracy. For this purpose, London's formula may be used:

$$\bar{E}_{\text{v.d.w}} = -\frac{3}{2}\frac{e^4}{m^2}\frac{\hbar^4}{R^6}\sum_{ij}\frac{f_if_j}{\Delta E_i\Delta E_j(\Delta E_i+\Delta E_j)},$$

where the f's are oscillator strengths and the ΔE's the corresponding excitation frequencies. For H_2, Wolf and Herzfeld[17] find that the dispersion curve can be represented with remarkable accuracy by a two-term formula in which

$$f_1=0.69,\quad E_1=2.71\times10^{-11}\ \text{erg}=0.630e^2/a_0,$$
$$f_2=0.84,\quad E_2=2.12\times10^{-11}\ \text{erg}=0.492e^2/a_0.$$

These data yield

$$\bar{E}_{\text{v.d.w}} = -10.9\frac{e^2}{a_0}\left(\frac{a_0}{R}\right)^6 \tag{28}$$

in place of (27). This, incidentally, confirms the author's former conjecture that the variational Hassé method, employed by Massey and Buckingham, usually gives too large an answer for the van der Waals force. (It does not, of course, contradict the variation principle!)

But the difference between (28) and the empirically better substantiated result (27) is to be accounted for by the inclusion of the dipole-quadrupole interaction. A method for estimating the latter has been given.[18] It involves the use of a *one*-term dispersion formula. To adapt it to

TABLE V. Quadrupole moment of H_2 (in units ea_0^2) as a function of Z.

Z	1	1.166	1.428	1.785
$-Q'$	0.284	0.252	0.200	0.137

TABLE VI. Quadrupole energy (E_Q) as function of intermolecular separation (R).

S	R (in A)	E_Q (in volts) Pos. a	Pos. b	Pos. c
$Z=1.428$				
6	2.22	0.000962	−.000481	0.000361
7	2.59	0.000445	−.000223	0.000167
8	2.96	0.000228	−.000114	0.0000857
9	3.33	0.000127	−.0000634	0.0000475
10	3.70	0.0000748	−.0000374	0.0000281
11	4.07	0.0000465	−.0000232	0.0000174
$Z=1.785$				
6	1.78	0.00134	−.000672	0.000504
7	2.07	0.000632	−.000316	0.000236
8	2.37	0.000321	−.000160	0.000120
9	2.66	0.000180	−.0000901	0.0000676
10	2.96	0.000106	−.0000528	0.0000396
11	3.25	0.0000662	−.0000331	0.0000248

[16] This, in a sense, counteracts the simplification made in the exchange integrals leading to Eq. (22).

[17] K. L. Wolf and K. F. Herzfeld, *Handbuch der Physik* (1928), Vol. 20.

[18] H. Margenau, J. Chem. Phys. **6**, 896 (1938).

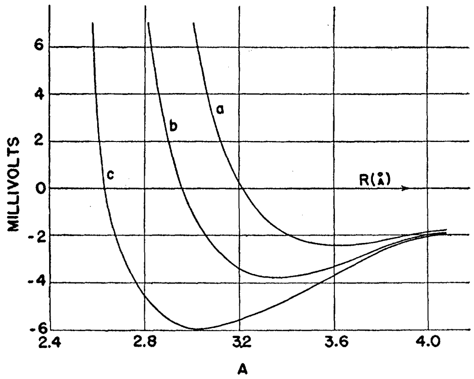

FIG. 2. Interaction energies when the approximately "right" value of Z ($Z=1.428$) is used.

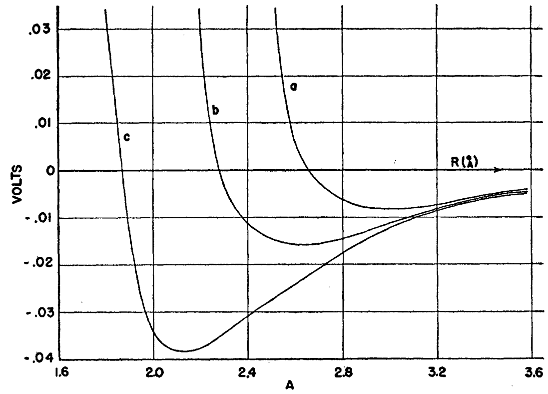

FIG. 3. Curves similar to those in Fig. 2 but with the "wrong" value of Z ($Z=1.785$).

the problem at hand, we shall take mean values of the f's and ΔE's in Herzfeld and Wolf's expression obtaining the contribution

$$-31\times 10^{-76}/R^8 \text{ erg}.$$

When this is added to (28), and both terms are expressed in ev, we have

$$\bar{E}_{\text{v.d.w}} = -\left(\frac{6.38}{R^6}+\frac{19.4}{R^8}\right) \text{ volts}, \tag{29}$$

provided R is measured in A. At $R=3\text{A}$, the d.-q. term contributes about $\frac{1}{3}$, at $R=2.5\text{A}$ about $\frac{1}{2}$ as much as the d.-d. term. If, therefore, we wished to approximate (29) by means of a single term proportional to R^{-6} as is often done, we should in this range of R (where the van der Waals minimum occurs) increase the d.-d. contribution by about 40 percent, thus obtaining

$$\bar{E}_{\text{v.d.w}} = -\frac{9.0}{R^6} \text{ volts} = -\frac{15.4}{R^6}\frac{e^2}{a_0}\left(\frac{a_0}{R}\right)^6. \tag{29a}$$

This is not far from the result (27) which was obtained by Massey and Buckingham for the d.-d. interaction alone.

VII. SUMMARY OF RESULTS

In Figs. 2 and 3 we have compounded the partial interaction energies represented by Eqs. (22), (26), and (29) or (29a), obtaining a graph which expresses the total repulsive-attractive behavior of the molecules. Figure 2, drawn for what we have determined to be the approximately "right" value of Z, should be about correct. Figure 3, on the other hand, based on the "wrong" value of Z, is presented to show the effect of this choice. In view of the uncertainty in this parameter, it is difficult to estimate the accuracy of our exchange force calculation, but we believe it to be not greatly inferior to the accuracy with which the long range van der Waals forces can be obtained.

The shape of the molecule is reflected in the relative positions of the three minima, the one implying end-on collisions being much farther out than that for broadside collisions. Interesting also is the fact that the minima are of entirely different depths. In actual impact problems, an average of the three behaviors here depicted will have to be considered.

Comparison with experimental facts can at present only be made in an indirect way. Lennard-Jones and his collaborators[19] have analyzed available measurements of the second virial coefficient of H_2. The procedure is based on the assumption that the interaction energy can be represented sufficiently well by a *single* function of spherical symmetry and of the form $(\nu/R^n)-(\mu/R^6)$. It is found that the data can be accommodated by several values of the exponent n. The curves obtained have minima in the region from 3.3 to 3.5A, and depths at minimum ranging from 2.7 to 2 millivolts. If curve b of Fig. 2 is taken to be illustrative of the "mean" behavior, the agreement with the results of Lennard-Jones is rather satisfactory.

[19] See R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, 1939).

VIII. REMARKS ON THE EXCHANGE INTERACTION OF TWO HELIUM ATOMS

The exchange forces between helium atoms have been the subject of several investigations;[1] in fact the Wang function used in this work has been applied to the helium problem by Gentile. We are here interested in only one feature of this problem which appears to have received no attention, namely the dependence of the forces on the assumed value of Z.

Instead of using published results[20] (which seem to be somewhat disfigured by typographical errors) it will be found simpler for our purposes to start anew and use our compact notation. The ground state of a single helium atom is represented by

$$\psi_0 = |a\alpha \quad a\beta|.$$

This leads, by simple steps, to the energy

$$E_0 = H_{00} = 2D - 2(2-Z)A + (aa\rho aa). \qquad (30)$$

If now we note that

$$D = -\tfrac{1}{2}Z^2, \quad A = Z, \quad (aa\rho aa) = \tfrac{5}{8}Z, \qquad (31)$$

all in units e^2a_0, then (30) will become a minimum for $Z = 27/16$, a fact which is well known.

In the interaction problem, the ground state of the two atoms is described by

$$\psi = |a\alpha \quad a\beta \quad c\alpha \quad c\beta|.$$

Here the total energy becomes

$$E = \bar{H}/\epsilon$$

with

$$\bar{H} = (aacc|H|aacc) - 2(caac|H|aacc) + (ccaa|H|aacc)$$

$$\epsilon = (1-\Delta^2)^2,$$

$$\Delta = \int acd\tau.$$

Thus we find

$$\begin{aligned}(1-\Delta^2)^2E = {} & 2(1-\Delta^2)^2E_0 + 4C \\ & -2\Delta^2[B + C + X + 2(2-Z)A - 2(aa\rho aa) \\ & -2(3-Z)T + 4(aa\rho ac)/\Delta] \\ & +\Delta^4[4(2-Z)A - 2(aa\rho aa) + 4X \\ & \qquad -4(2-Z)T + 2(ac\rho ca)/\Delta^2] \qquad (32)\end{aligned}$$

[20] G. Gentile, Zeits. f. Physik **63**, 795 (1930).

where all functions without subscripts now refer to the interatomic distance R, and E_0 is given by (30).

With the neglect of terms in Δ^4, this expression could also have been obtained—though with more labor—by letting the distance s in Eq. (21) go to zero. Now it is permissible to neglect Δ^4 and hence the last row of (32). Since the function C is always much smaller and decreases faster than Δ^2, the contribution to the exchange energy comes almost entirely from the second row of (32). The only terms inside the bracket multiplying Δ^2 which do not vanish as R becomes large are

$$2(2-Z)A - 2(aa\rho aa).$$

If, therefore, we wish $E - 2E_0$ to be positive, we must require

$$(aa\rho aa) > (2-Z)A.$$

In view of Eqs. (31) this implies $Z > 11/8$. The mathematical situation encountered in the H_2 problem when Z was chosen to be 1.166 is thus explained. Whether this phenomenon has any physical interest, as for example in the interaction between two negative ions of atomic hydrogen where Z is certainly smaller than the limiting value, is perhaps difficult to say.

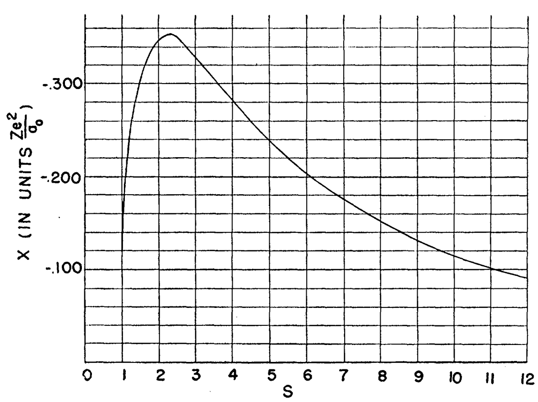

FIG. 4. Graph for the determination of X in terms of S.

The author wishes to acknowledge gratefully the computational help given him by two undergraduate students, C. E. Hummel and R. A. Peck.

APPENDIX

A list of the more important functions encountered in this paper is here appended.

$$S = ZR/a_0,$$
$$\Delta = e^{-S}(1+S+S^2/3),$$
$$B = (Ze^2/a_0)(1+S^{-1})e^{-2S},$$
$$C = \frac{Ze^2}{a_0}\left(S^{-1}+\frac{5}{8}-\frac{3}{4}S-\frac{S^2}{6}\right)e^{-2S},$$
$$T = \frac{Ze^2}{a_0}(1+S)\bigg/\left(1+S+\frac{S^2}{3}\right).$$

X is a more complicated function involving Sugiura's integral. In terms of the functions used and defined in Pauling and Wilson,[21]

$$X = \frac{Ze^2}{a_0}\left(\frac{1}{S}+\frac{2K(S)}{\Delta(S)}+\frac{K'(S)}{\Delta^2(S)}\right).$$

For calculations, the graph of X given in Fig. 4 will be found more convenient.

[21] L. Pauling and E. B. Wilson, fr., *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, New York). See p. 342 et seq.

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The Energies of the γ-Rays from Radioactive Scandium, Gallium, Tungsten, and Lanthanum

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The energies of some γ-rays have been determined by the method of semicircular focusing of Compton recoils in a magnetic spectrograph. The results thus obtained are as follows:

Radioelement	Sc^{48}	Ga^{72}	W^{187}	La^{140}
Quantum energies (Mev)	1.35 ± 0.03	1.17 ± 0.02, 2.65 ± 0.06	0.94 ± 0.02	2.04 ± 0.04

The two quanta emitted in the disintegration of Ga^{72} are present with equal intensity, which suggests that they may be in cascade. The γ-ray activity of Ga^{72} was followed for 100 hours and was found to decay with a half-period of 14.25 ± 0.20 hr.

INTRODUCTION

THE energies of the γ-rays emitted in the disintegration of several radio-elements have been measured by means of a magnetic spectrograph which has been previously described.[1] Compton recoil electrons are focused by a magnetic field, and coincidences are then observed as a function of $H\rho$. The radius of curvature of the path of the recoils is 5.50 cm.

Because of the fact that slow electrons are heavily absorbed and scattered from the focused beam by the walls of the counters and by the argon-alcohol counter mixture which is present throughout the magnet box, it has been found advisable to employ double coincidence counting, using the counters T_1 and T_2 (Fig. 1, reference 1), when making observations on quanta of an energy less than 1 Mev. Triple coincidence counting, with the counters T_1, T_2, and T_3, is especially suitable for obtaining end points of distributions in regions of higher energy (greater than 1 Mev), since the gamma-ray background is then very small. The absorption of the slow electrons also leads to a lower limit of satisfactory measurement. The recoils arising from γ-rays of energy less than about 0.5 Mev are not observable.

The treatment of the background count and the corrections which are applied to data obtained with this spectrograph have been previously outlined[1] and are obviously the same,

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[1] C. E. Mandeville, Phys. Rev. **62**, 309 (1942); Phys. Rev. **63**, 387 (1943).