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The Forces Between a Hydrogen Molecule and a Hydrogen Atom

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The paper contains the results of calculations of (1) repulsive exchange forces, (2) attractive van der Waals forces between H^2 and H atoms. The method used is that developed in an earlier communication. Results for small distances of separation differ considerably from published data on interaction energies deduced from collision cross sections. Reasons for the discrepancy are discussed. Figures 1 and 2 represent potential energy curves for the region around the van der Waals minimum; they exhibit the asymmetry of the interaction.

I. THEORY

THE forces between H_2 molecules have been calculated with the use of a simple molecular wave function in a recent publication.[1,2] The method and many of the details there developed lend themselves readily to the calculation of the interaction between an atom and a molecule, a matter regarding which there is some experimental information.[3] In the present paper we present the significant points of the theory and the results, making use throughout of the notation of reference 1. The simplifications formerly made will again be used; in particular, a Heitler-London function with adjustable screening constant is chosen to represent the molecule. The atom will in this case be described by a function having the same screening constant as the molecule, a procedure which reduces the complexity of computations greatly without, it seems, falsifying the results in an essential way. To show the effect of the somewhat arbitrary choice of screening constant, the calculations are carried out for several values of this parameter. The preceding paper[1] will hereafter be referred to as I.

Let the nuclei of the three interacting atoms be localized at the points a, b, and c. These letters will also be used to denote the electronic orbital functions centered about these points. Thus, in the notation of I, three state functions describing the three-particle system can be formed for which the Z component of the total spin is zero:

$$\begin{aligned}\Psi_1&=|a\alpha \quad b\beta \quad c\alpha|,\\ \Psi_2&=|a\beta \quad b\alpha \quad c\alpha|,\\ \Psi_3&=|a\alpha \quad b\alpha \quad c\beta|.\end{aligned} \tag{1}$$

Of these, we can construct by known rules two doublet functions:

$$\psi_A=\surd\tfrac{1}{2}(\Psi_1-\Psi_2),\quad \psi_B=\surd\tfrac{1}{2}(\Psi_3-\Psi_2).$$

In general, the correct Ψ is a combination of these two, and the energy E is given by

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

We note, however, that ψ_A represents a bond between atoms a and b, ψ_B a bond between a and c. (The criterion for existence of a bond between two atoms is symmetry with respect to an interchange of the bonded nuclei.) If, then, we suppose that a and b form our molecule, we may limit our consideration to ψ_A alone. In this case, the determinantal equation reduces to

$$E=\frac{H_{AA}}{\Delta_{AA}}. \tag{2}$$

The functions a, b, c used in Eqs. (1) are all one-electron orbitals and hence include no ionic terms. At close distances of separation ionic states certainly make a contribution to the energy and, in an exact calculation, have the effect of lowering it. Even when the functions describing the atom and the molecule at infinite

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[1] H. Margenau, Phys. Rev. **63**, 131 (1943).

[2] Meanwhile, an interesting paper by J. DeBoer, Physica **9**, 363 (1942), dealing with the same problem, has come to my attention. His final results, which do not differ greatly from ours, are obtained more simply and with much less labor by neglecting most of the exchange integrals, to the investigation of which reference 1 was chiefly devoted. As DeBoer admits and as shown in reference 1, these are quite as large as the terms retained in his calculation. It appears that because of this difference in treatment, DeBoer obtains agreement with observation for $Z=1.166$, whereas we were forced to assume a greater value.

[3] I. Amdur, J. Chem. Phys. **11**, 157 (1943).

separation are not exact, as is the case in the present instance, a similar effect is to be expected. Neglect of ionic states is one of the more serious approximations made in these calculations.

In the notation of I,

$$H_{AA}=\tfrac{1}{2}(H_{11}+H_{22}-2H_{12}),\qquad \Delta_{AA}=\tfrac{1}{2}(\Delta_{11}+\Delta_{22}-2\Delta_{12}). \tag{3}$$

When the Hamiltonian function for the three-particle system is written down and use is made of the Schrödinger equations satisfied by a, b, and c, there results

$$\begin{aligned}H\{a(1)b(2)c(3)\}=\{&3D-(1-Z)(\alpha_1+\beta_2+\gamma_3)\\&-(\alpha_2+\alpha_3+\beta_1+\beta_2+\gamma_1+\gamma_2)\\&+\rho_{12}+\rho_{13}+\rho_{23}+E_N\}a(1)b(2)c(3)\end{aligned}$$

where again $D=-\frac{1}{2}Z^2e^2/a_0$, and E_N is the electrostatic energy of the three nuclei. If, in analogy with I, we define

$$\epsilon=(abc|H|abc),\quad u_1=(bac|H|abc),$$
$$u_2=(cba|H|abc),\quad u_4=(acb|H|abc),$$
$$v_1=(bca|H|abc)$$

and denote the corresponding matrix elements of unity by primed symbols, we find

$$H_{11}=\epsilon-u_2,\quad H_{12}=-u_1+v_1,\quad H_{22}=\epsilon-u_4,$$

and hence by (3)

$$\begin{aligned}H_{AA}&=\epsilon+u_1-\tfrac{1}{2}(u_2+u_4)-v_1,\\ \Delta_{AA}&=\epsilon'+u_1'-\tfrac{1}{2}(u_2'+u_4')-v_1'.\end{aligned} \tag{4}$$

The exchange integrals now have the following form:

$$\epsilon=3D+3\kappa A+C_{ab}+C_{ac}+C_{bc},$$
$$u_1=\Delta^2{}_{ab}\{3D+X_{ab}+B_{ac}+B_{bc}+\kappa(A+2T_{ab})+X'_{ab}\},$$

where X'_{ab} now has the simpler form

$$2\frac{(ac\rho bc)-(a\gamma b)}{\Delta_{ab}}, \tag{5}$$

$u_2=u_1$ with interchange of b and c

$u_4=u_1$ with interchange of a and c

$$v_1=\Delta_{ab}\Delta_{ac}\Delta_{bc}\{3D+(\kappa-1)(T_{ab}+T_{ac}+T_{bc})+U_{abc}\},$$
$$\kappa\equiv Z-1.$$

Henceforth quantities bearing subscripts ab, i.e., pertaining to the *molecule*, will be written without indices. When atom and molecule are very far apart, the exchange integrals above reduce to

$$\epsilon=3D+C+3\kappa A,\qquad \epsilon'=1,$$
$$u_1=\Delta^2\{3D+X+\kappa(A+2T),\qquad u_1'=\Delta^2,$$
$$u_2=u_4=v_1=0,\qquad u_2'=u_4'=v_1'=0.$$

On using these in (4) and (2) there results

$$E^0=3D+\kappa A+\frac{C+2\kappa A+\Delta^2(X+2\kappa T)}{1+\Delta^2}. \tag{6}$$

This, however, is the energy of a single molecule [cf. I, Eq. (15)] plus $D+\kappa A$, an increment which represents the energy of one hydrogen atom computed with the function a, that is, $D+\kappa A=\int a\mathrm{H}_{\mathrm{atom}}a d\tau$. Hence, in order to find the exchange energy between the molecule and the atom, it is necessary to subtract E^0 given by (6) from E computed in accordance with Eq. (2).

In proceeding further, prohibitive labor is encountered unless use is made of the reduction described in I. The approximations called for are different when the distance of approach is small and when it is large. We consider the case of very small separations first.

TABLE I. Exchange energies for small distances of separation. Atoms a and b form a molecule. R_{ac} and R_{bc} are the distance of atom c from a and b, respectively. R is the distance of c from center of molecule.

	Z	R_{ac}(A)	R_{bc}(A)	R(A)	$E-E^0$ (ev)
a	1.071	0.57	0.17	0.20	104
b	1.071	0.42	0.42	0.20	72
c	1.071	0.84	0.10	0.47	117
d	1.071	0.60	0.60	0.47	26
e	1.20	0.83	0.09	0.46	142
f	1.20	0.58	0.58	0.45	29
g	1.30	0.82	0.08	0.45	150
h	1.30	0.45	0.45	0.26	56

II. SMALL DISTANCES OF SEPARATION

Let atoms b and c come very close together. It is then necessary to retain all terms in the exchange integrals, but the slowly varying functions bearing indices b and c may be replaced by their limiting forms in which the distance between atoms b and c is put equal to zero. In

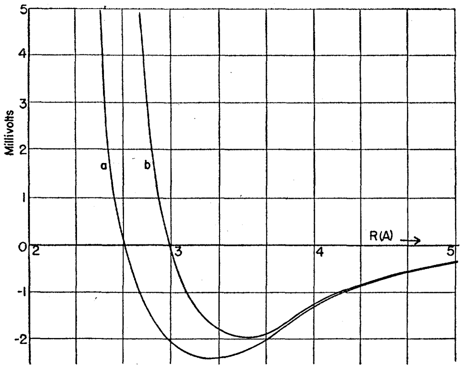

FIG. 1. Interaction between H_2 and H, calculated for $Z=1.071$. Curve a represents approach of H along bisector of molecular axis, curve b along axis.

that case

$$X'_{ab}\to X'_{ac}\to M_{ab}-2T_{ab},$$

$$X'_{bc}\to 2(ab\rho ab)-2(a\beta a),$$

$$U_{abc}\to X_{ab}+S_{ac}^{-1}+S_{bc}^{-1}-(a\beta a)+M_{ab}.$$

The only function appearing here which was not explicitly given in I is

$$M=2T-\frac{3}{4}\frac{1+2S+(4/9)S^2}{1+S+(1/3)S^2}e^{-S}\left(\frac{Ze^2}{a_0}\right).$$

As before, S is the distance indicated by the subscripts, measured in units a_0/Z.

Computations of E were made for 3 different values of Z and for certain positions of atom c relative to the molecule which were selected for numerical convenience. The results are collected in Table I. It will be noted that cases a, c, e, and g represent positions of atom c on the axis of the molecule, the others on the bisector of the axis. In the former group, the atom is close to one of the molecular nuclei; hence the interaction energy is very large. For these small separations, the distance R between atom and center of the molecule is not a significant parameter. As will appear later, the best value of Z for the present problem is probably near the first of those here chosen. The results indicate, however, that the choice of Z is not very important at these small distances of separation.

Comparison with the results of Amdur[3] yields very poor agreement indeed. If we limit our consideration to cases where the atom is situated on the bisector of the molecular axis—this being the more probable condition of impact—instances d and f should be comparable with the data given by Amdur, who finds approximately 8 and 8.5 ev instead of our 26 and 29 ev. This discrepancy by a factor greater than 3 can hardly be accounted for in its entirety by inaccuracies in the present calculations, or by our omission of ionic terms in the state function. It seems indeed that the assumption of spherical symmetry of the interaction, made in the deduction of the experimental curve from scattering data, must be at fault. The discrepancy is materially reduced if the collision radius in reference 3 is regarded as the distance of closest approach, not to the center of the molecule, but to the nucleus of one of the molecular atoms.

III. LARGE DISTANCES OF SEPARATION

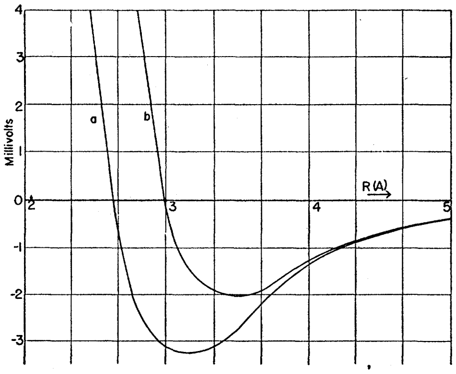

FIG. 2. Interaction between H_2 and H, calculated for $Z=1.20$. Curve a represents approach of H along bisector of molecular axis, curve b along axis.

For large distances of separation, a different set of approximations must be made in evaluating E. Numerical computation shows that the quantity X'_{ab} appearing in (5) may be neglected. Furthermore, we split H_{AA} and Δ_{AA} into their large and small constituents:

$$H_{AA}=H_{AA}^{(0)}+H_{AA}^{(2)},\quad \Delta_{AA}=\Delta_{AA}^{(0)}+\Delta_{AA}^{(2)},$$

where the large parts $H^{(0)}$ and $\Delta^{(0)}$ are those which were retained in arriving at Eq. (6). Then

$$E=\frac{H_{AA}}{\Delta_{AA}}=\frac{H_{AA}^{(0)}}{\Delta_{AA}^{(0)}}+\frac{H_{AA}^{(2)}}{\Delta_{AA}^{(0)}}-\frac{H_{AA}^{(0)}\Delta_{AA}^{(2)}}{(\Delta_{AA}^{(0)})^2},$$

if squares of the small terms are neglected. The

TABLE II. Exchange energy $E=E^0$ in units Ze^2/a_0. S is the distance between the atom and the center of the molecule in units a_0/Z. In position a, the atom lies on the bisector of the molecular axis; in position b, on the axis.

	$Z=1.071$		$Z=1.2$		$Z=1.3$	
S	Pos. a	Pos. b	Pos. a	Pos. b	Pos. a	Pos. b
5	0.(2)1607	0.(2)192	0.(2)332	0.(2)442	0.(2)455	0.(2)644
6	0.(3)331	0.(3)412	0.(3)760	0.(2)1070	0.(2)1119	0.(2)1648
7	0.(4)638	0.(4)748	0.(3)1695	0.(3)238	0.(3)243	0.(3)383
8	0.(4)1015	0.(4)1277	0.(4)323	0.(4)495	0.(4)486	0.(4)822
9	0.(5)1970	0.(5)2141	0.(5)637	0.(5)947	0.(5)983	0.(4)1596
10	0.(6)358	0.(6)379	0.(5)1261	0.(5)183	0.(5)2001	0.(5)334

first of the three fractions on the right of this equation is E^0, hence

$$E-E^0=(\Delta_{AA}^{(0)})^{-1}(H_{AA}^{(2)}-E^0\Delta_{AA}^{(2)}).$$

When all terms on the right are inserted and the exact expression for U_{abc} is replaced by its limiting form for $R_{ab}\rightarrow 0$:

$$U_{abc}=\frac{e^2}{s}+X(S)+2T(S),$$

the result is

$$\begin{aligned}E-E^0=(1+\Delta^2)^{-1}\{&C_{ac}+C_{bc}+\Delta^2(B_{ac}+B_{bc})\\&+\tfrac{1}{2}\Delta_{ac}^2[\tfrac{1}{2}E_0'-B-X_{ac}-2\kappa T_{ac}]\\&+\tfrac{1}{2}\Delta_{bc}^2[\tfrac{1}{2}E_0'-B-X_{bc}-2\kappa T_{bc}]\\&+\Delta\Delta_{ac}\Delta_{bc}[\tfrac{1}{2}E_0'-s^{-1}-(\kappa-1)T\\&\qquad+\kappa(A-T_{ac}-T_{bc}-X(S))]\}.\end{aligned}\tag{7}$$

The notation is explained in I. If all lengths in this expression are taken in units a_0/Z, the energy is in units Ze^2/a_0.

The choice of Z calls for comment. It would seem at first sight that some mean value between that proper for the molecule and that for the atom should be used. The minimum of the molecular energy occurs for $Z=1.16$; the correct value for the atom is of course 1. In some of our calculations we have taken Z to be 1.071 (which makes $s=1.5$). In our former work (I) on the four-electron problem there appeared a peculiar difficulty: The value of Z corresponding to the minimum of molecular energy produced an attractive exchange force. On analyzing the situation we found reason to accept a larger value of Z, the chief argument involving the greater repulsive effect between the electrons. A similar difficulty does not appear in the three-electron problem; the exchange force is repulsive for all Z that were tried. Nevertheless, if the former argument is valid, a value in the neighborhood of 1.2 should be a better choice. Hence calculations were made for that case. The difference between the results for $Z=1.071$ and 1.2 is surprisingly small. To complete the picture we have also studied $Z=1.3$. But the minimum resulting from the composition of exchange and van der Waals forces is much deeper in that case and may be dismissed from consideration.

Results for $E-E^0$ are given in Table II. In position a, the atom is situated on the bisector of the molecular axis, in b on the axis.

There remains now the calculation of the long range attractive forces. The method is outlined in I. On using for the atom an oscillator strength $f=1$ and a corresponding resonance energy $0.487\ e^2/a_0$ (which gives the correct coefficient of R^{-6} in the interaction between H atoms), we obtain for the dipole-dipole energy

$$E_{2,2}=-8.40\left(\frac{a_0}{R}\right)^6\frac{e^2}{a_0}.\tag{8}$$

The dipole-quadrupole energy, calculated from a formula previously given,[4] becomes

$$E_{2,4}=-148\left(\frac{a_0}{R}\right)^8\frac{e^2}{a_0}.\tag{9}$$

When (7), (8), and (9) are finally compounded, there results the total interaction which is plotted, for 2 values of Z, in Figs. 1 and 2. There are at present no empirical data with which they may be compared. The minimum comes at about the same place as it does for the two similar positions in the bimolecular problem, but it is slightly less deep. The "shape" of the molecule again manifests itself in the differences between curves a and b.

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