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Interaction Energy between a Helium Atom and a Hydrogen Molecule*†

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The interaction energy between a helium atom and a hydrogen molecule has been calculated from first principles using a simple wave function made up of 1*S* orbitals centered on the three nuclei. All molecular integrals encountered were accurately calculated using an IBM 709 digital computer. If r represents the distance measured along a line drawn from the helium nucleus to the midpoint of the hydrogen molecule bond, and if γ is the angle between this line and the axis of the hydrogen molecule, then the interaction energy was computed at 15° increments of γ from $r=3.8$ to 5.2 a.u. With the H_2 bond length held constant at 1.406 a.u. it was found possible to represent the computed interaction energy quite accurately by the function $Ce^{-\kappa r}[1+\delta P_2(\cos\gamma)]$, where $P_2(x)$ is a Legendre polynomial, $C=17.283$ double Ry, $\kappa=2.027$ (a.u.)$^{-1}$, and $\delta=0.375$. The spherical average of the computed interaction energy agrees quite closely with an interaction energy obtained from gas diffusion measurements. It is shown that it is impossible to represent the calculated interaction energy by means of a dumbbell-type function, i.e., a function of the form $f(\rho_{ac})+f(\rho_{bc})$, where $f(x)$ is some suitable chosen function and ρ_{ac} and ρ_{bc} represent the distance from the helium nucleus to the two hydrogen nuclei, respectively. Results are also presented for a slightly elongated H_2 bond length of 1.486 a.u.

I. INTRODUCTION

THE interaction energy between two species X and Y is defined as the energy of the composite system $X-Y$ minus the energy of the two when they are infinitely separated from one another. Such interaction energies are invaluable in interpreting kinetic theory and atomic and molecular scattering experiments as well as in formulating theories of inelastic processes and chemical reaction rates. The interaction energy between H and H_2, and H_2 and H_2 has been investigated previously.[1,2] In these calculations however, it was found necessary to approximate the three- and four-center molecular integrals encountered in the formalism. The purpose of this research is to obtain the interaction energy between a helium atom and a hydrogen molecule using no molecular integral approximations. The interaction energy is computed at a sufficient number of points so that the form of its angular dependence is apparent. To accomplish this we use a simple wave function made up of 1*S* orbitals centered on the hydrogen and helium nuclei. This represents a direct extension of the method used by Heitler and London[3] in their well-known work on the energy of the hydrogen molecule. We also investigate the question, can the hydrogen molecule be treated as a dumbbell in its interaction with a helium atom or any other atom, i.e., can the interaction energy be expressed as an interaction between the helium atom and the two ends of the hydrogen molecule. After the true interaction energy has been calculated one may see whether or not such a relationship is satisfied.

II. ENERGY OF THE HE-H_2 SYSTEM

The geometry of the helium and hydrogen nuclei is shown in Fig. 1. We treat the problem in the Born-Oppenheimer approximation, calculating the energy of the system for various fixed positions of the three nuclei. The four electrons are numbered 1 to 4 and the distance of the ith electron from the three nuclei is denoted by r_{ia}, r_{ib}, and r_{ic}, respectively. The distance between the ith and jth electron is called r_{ij}. With this notation, the Hamiltonian in double Rydbergs for the He-H_2 system can be written as

$$H=\sum_{i=1}^{4}\left\{-\tfrac{1}{2}\nabla_i^2-\frac{1}{r_{ia}}-\frac{1}{r_{ib}}-\frac{2}{r_{ic}}\right\}+\sum_{\text{pairs}\,ij}\frac{1}{r_{ij}}+\frac{1}{\rho_{ab}}+\frac{2}{\rho_{ac}}+\frac{2}{\rho_{bc}}. \tag{2.1}$$

All distances are in a.u. (Bohr radii). If we define one- and two-electron operators

$$f_i=-\tfrac{1}{2}\nabla_i^2-1/r_{ia}-1/r_{ib}-2/r_{ic}, \tag{2.2}$$

$$g_{ij}=1/r_{ij}, \tag{2.3}$$

then the Hamiltonian can be rewritten as

$$H=\sum_{i=1}^{4}f_i+\sum_{\text{pairs }ij}g_{ij}+\frac{1}{\rho_{ab}}+\frac{2}{\rho_{ac}}+\frac{2}{\rho_{bc}}. \tag{2.4}$$

The notation may be made even more compact by defining total one- and total two-electron operators

$$F=\sum_{i=1}^{4}f_i, \tag{2.2a}$$

$$G=\sum_{\text{pairs }ij}g_{ij}, \tag{2.3a}$$

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[1] A. A. Evett and H. Margenau, Phys. Rev. **90**, 1021 (1953). H. Margenau, Phys. Rev. **66**, 303 (1944).

[2] E. A. Mason and J. O. Hirschfelder, J. Chem. Phys. **26**, 756 (1957).

[3] W. Heitler and F. London, Z. Physik **44**, 455 (1927).

whence,

$$H=F+G+1/\rho_{ab}+2/\rho_{ac}+2/\rho_{bc}. \qquad (2.4a)$$

We define 1S orbitals a and b centered on the hydrogen nuclei as follows:

$$a(i)=(\alpha^3/\pi)^{1/2}e^{-\alpha r_{ia}}, \quad b(i)=(\alpha^3/\pi)^{1/2}e^{-\alpha r_{ib}}. \qquad (2.5)$$

A 1S orbital centered on the helium nucleus is called c and is defined by

$$c(i)=(\beta^3/\pi)^{1/2}e^{-\beta r_{ic}}. \qquad (2.6)$$

We denote the two possible electron spin assignments in these orbitals by the superscripts + and −, respectively. Thus, from the three spacial orbitals a, b, and c, six spin orbitals a^+, a^-, b^+, b^-, c^+, and c^- may be formed. From these spin orbitals we form two four-electron determinantal functions as follows

$$A=(4!)^{-1/2}\begin{vmatrix} a^+(1) & a^+(2) & a^+(3) & a^+(4) \\ b^-(1) & b^-(2) & b^-(3) & b^-(4) \\ c^+(1) & c^+(2) & c^+(3) & c^+(4) \\ c^-(1) & c^-(2) & c^-(3) & c^-(4) \end{vmatrix}, \qquad (2.7)$$

$$B=(4!)^{-1/2}\begin{vmatrix} a^-(1) & a^-(2) & a^-(3) & a^-(4) \\ b^+(1) & b^+(2) & b^+(3) & b^+(4) \\ c^+(1) & c^+(2) & c^+(3) & c^+(4) \\ c^-(1) & c^-(2) & c^-(3) & c^-(4) \end{vmatrix}. \qquad (2.8)$$

In an extension of the Heitler-London method, we take the wave function for the He-H$_2$ system to be

$$\Psi=(2)^{-1/2}(A-B). \qquad (2.9)$$

The wave function of Eq. (2.9) is not normalized. To normalize it, we let

$$\begin{aligned} S^2&=\int d\tau\, \Psi^*\Psi \\ &=\frac{1}{2}\int d\tau(A^*A+B^*B-A^*B-B^*A), \qquad (2.10) \end{aligned}$$

where $d\tau$ denotes integration over the spacial coordinates and summation over the spin coordinates of all four electrons. It is easy to show that a normalized wave function is obtained by dividing the right side of Eq. (2.9) by S. It is easily shown that

$$\begin{aligned} S^2&=\int d\tau A^*A-\int d\tau A^*B, \\ &=S_{AA}-S_{AB}. \qquad (2.10a) \end{aligned}$$

The energy of the He-H$_2$ system is obtained by evaluating the expression

$$E=S^{-2}\int d\tau\, \Psi^*H\Psi, \qquad (2.11)$$

$$\begin{aligned} E=(S_{AA}-S_{AB})^{-1}\Big[\int d\tau A^*FA+\int d\tau A^*GA \\ -\int d\tau A^*FB-\int d\tau A^*GB\Big] \\ +1/\rho_{ab}+2/\rho_{ac}+2/\rho_{bc}. \qquad (2.12) \end{aligned}$$

Equation (2.12) represents a complete formal solution for the energy of the He-H$_2$ system given the wave function of Eq. (2.9). However, in order to use this expression for actual calculations it is most convenient to express the integrals in Eq. (2.12) in terms of integrals over the orbitals a, b, and c. To do this we make use of the formalism developed by Löwdin for evaluating matrix components of operators between determinantal wave functions made up of nonorthogonal orbitals.[4,5] The procedures are straightforward but tedious and exacting. To express the final results we define the following basic integrals. Here $u_i(1)$, $u_j(1)$, etc., stand for any one-electron orbitals, i.e., $a(1)$, $b(1)$, etc.

Overlap integrals:

$$s_{ij}=\int dv_1\, u_i(1)u_j(1), \qquad (2.13)$$

where dv_1 denotes integration over the spacial coordinates of electron 1.

One-electron integrals:

$$[i|j]=\int dv_1\, u_i(1)f_1u_j(1), \qquad (2.14)$$

Two-electron integrals:

$$[ij|kl]=\int\int dv_1dv_2\, u_i(1)u_j(1)\frac{1}{r_{12}}u_k(2)u_l(2). \qquad (2.15)$$

Using the above integrals, we find that

$$S_{AA}=(1-s_{ac}^2)(1-s_{bc}^2), \qquad (2.16)$$

$$S_{AB}=-(s_{ab}-s_{ac}s_{bc})^2, \qquad (2.17)$$

$$\begin{aligned} \int d\tau A^*FA=[a|a](1-s_{bc}^2)+[b|b](1-s_{ac}^2)+[c|c](2-s_{bc}^2-s_{ac}^2) \\ -2s_{ac}[a|c](1-s_{bc}^2)-2s_{bc}[b|c](1-s_{ac}^2), \qquad (2.18) \end{aligned}$$

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[4] P. O. Löwdin, Phys. Rev. **97**, 1474, 1490 (1955).

[5] J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill Book Company, Inc., New York, 1963), Vol. I, Appendix 9, p. 285.

$$\int d\tau A^*FB=2(s_{ab}-s_{ac}s_{bc})\{s_{ac}[b|c]+s_{bc}[a|c]-s_{ab}[c|c]-[a|b]\}, \tag{2.19}$$

$$\int d\tau A^*GA=[aa|bb]+[aa|cc](2-s_{bc}^2)+[bb|cc](2-s_{ac}^2)+[cc|cc]-2s_{bc}[aa|bc]-2s_{ac}[bb|ac] \\ +4s_{ac}s_{bc}[ca|cb]-2s_{ac}[cc|ca]+[ac|ac](s_{bc}^2-1)+[bc|bc](s_{ac}^2-1)-2s_{bc}[cc|cb], \tag{2.20}$$

$$\int d\tau A^*GB=-[ab|ab]+2s_{bc}[ab|ac]+2s_{ac}[ba|bc]+2(s_{ab}-2s_{ac}s_{bc})[ca|cb]+2(s_{ac}s_{bc}-2s_{ab})[cc|ab] \\ -s_{bc}^2[ac|ac]-s_{ac}^2[bc|bc]+2s_{ab}s_{bc}[cc|ca]+2s_{ab}s_{ac}[cc|cb]-s_{ab}^2[cc|cc], \tag{2.21}$$

The energy E of the He-H_2 system may now be expressed in terms of the basic integrals by substituting Eqs. (2.16) through (2.21) into Eq. (2.12).

III. INTERACTION ENERGY

The expression (2.12) allows us to compute the energy of the He-H_2 system once the values of ρ_{ab}, ρ_{ac}, ρ_{bc}, α, and β are given. The quantities ρ_{ab}, ρ_{ac}, and ρ_{bc} determine the geometry of the three nuclei (Fig. 1) while α and β are the screening constants of the $1S$ orbitals defined in Eqs. (2.5) and (2.6). We can see how to pick the values for α and β as well as how to obtain the interaction energy from the energy of the composite system by examining the expression (2.12) in the limit of infinite separation between the helium atom and the hydrogen molecule. In this limit, the overlaps s_{ac} and s_{bc} are zero as are all two-electron integrals containing the orbital c and either a or b. In the limit $r\rightarrow\infty$, the energy of the system becomes

$$E_{r\rightarrow\infty}=E_1+E_2, \tag{3.1}$$

where

$$E_1=\frac{[a|a]+[b|b]+2s_{ab}[a|b]+[aa|bb]+[ab|ab]}{(1+s_{ab}^2)}+\frac{1}{\rho_{ab}}, \tag{3.1a}$$

$$E_2=2[c|c]+[cc|cc]. \tag{3.1b}$$

A careful analysis shows that Eq. (3.1a) is identical to the expression for the energy of the hydrogen molecule as obtained by Heitler and London[3] or Wang[6] using the wave function $a(1)b(2)+a(2)b(1)$. Equation (3.1b) represents the energy of a helium atom computed with a one determinant wave function made up from the spin orbitals c^+ and c^-. Such a wave function has the simple spacial dependence $c(1)c(2)$. Thus, in the limit of infinite separation the energy of the system, provided that we pick the correct values for the screening constants α and β, approaches the lowest energy which one can obtain for an isolated helium atom and an isolated hydrogen molecule given only the $1S$ orbitals a, b, and c. The correct value of α can be obtained from the calculation of Wang[6] who did the Heitler-London calculation varying the value of α to obtain the minimum energy. He calculates this minimum energy to be -1.139 double Ry with $\alpha=1.166$ (a.u.)$^{-1}$ and the hydrogen bond length equal to 1.406 a.u. This is to be compared with an experimental energy of -1.173 at a bond length of 1.401. The problem of finding the value of β which minimizes the energy of the isolated helium atom is a trivial one[7] and the correct value of $\beta=27/16=1.6875$ (a.u.)$^{-1}$ gives an energy of -2.84766 double Ry as compared with an experimental energy of -2.90372. These were the values used for the screening constants α and β throughout the present calculation. The interaction energy of the system was taken to be the difference between the energy computed with Eq. (2.12) and the energy of the isolated species as computed with the above wave functions and screening constants, i.e., $(-1.13907)+(-2.84766)$ double Ry. The hydrogen bond length was taken to be 1.406 a.u., the value at which Wang obtained the minimum.

Using the preceding formalism and parameters, the helium-hydrogen molecule interaction energy was computed, using an IBM 709 digital computer, for many configurations of the system's geometry. Since the length of the hydrogen bond is held constant throughout

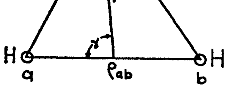

FIG. 1. Geometry of He-H_2 system.

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

[7] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vol. II, p. 36.

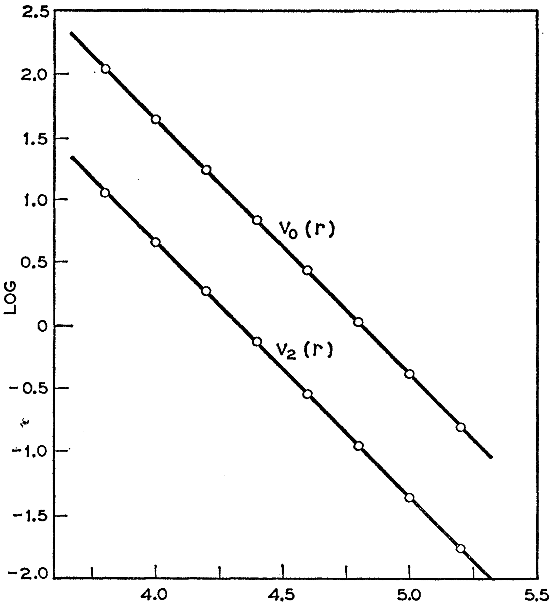

FIG. 2. Ln v_0 and ln v_2 vs r.

the calculation, it was found more convenient to denote the geometry of the system with the values of r and the angle γ rather than with the distances ρ_{ab}, ρ_{ac}, and ρ_{bc}. Here r is defined to be the distance from the helium nucleus to the middle of the H_2 bond and γ is the angle between r and the axis of the H_2 molecule (Fig. 1). All one-electron, two-electron, and overlap integrals, Eqs. (2.13), (2.14), and (2.15), were computed exactly using existing digital computer subprograms. These subprograms are based upon the zeta-function method of molecular integral evaluation developed by Barnett and Coulson.[8] All such subprograms used were checked by computing several known integrals; the subprograms should give values which are accurate to the fifth place to the right of the decimal. It required approximately six minutes on the IBM 709 computer to compute the energy of the He-H_2 system for a given geometry of the three nuclei. Most of this time was spent computing two-center exchange integrals (type $[ij|ij]$), three-center exchange integrals (type $[ij|ik]$) and three-center Coulomb integrals (type $[ii|jk]$).

TABLE I. Calculated He-H_2 interaction energy. Energy given in milli-double Ry. H_2 bond $=1.406$ a.u.

r (a.u.)	γ 0°	15°	30°	45°	60°	75°	90°
3.8	10.546	10.190	9.274	8.136	7.130	6.470	6.241
4.0	7.110	6.870	6.252	5.480	4.796	4.351	4.197
4.2	4.777	4.616	4.200	3.678	3.216	2.918	2.816
4.4	3.199	3.092	2.814	2.461	2.133	1.952	1.886
4.6	2.135	2.064	1.879	1.640	1.417	1.301	1.262
4.8	1.420	1.372	1.251	1.090	0.936	0.863	0.842
5.0	0.941	0.910	0.830	0.722	0.615	0.568	0.558
5.2	0.622	0.601	0.550	0.476	0.401	0.369	0.364

IV. NUMERICAL RESULTS

The interaction energy $V(r,\gamma)$ as computed for the He—H_2 system is tabulated in Table I. It should be noted that due to the symmetry of the hydrogen molecule, $V(r,\gamma)=V(r,\pi-\gamma)$. We, therefore, list in Table I only values of γ up to 90°. While the results in Table I are given to three decimal places, the third is probably meaningless due to errors in computing the molecular integrals.

TABLE II. v_0 and v_2 vs r. Energy in milli-double Ry. H_2 bond $=1.406$ a.u.

r	Calculated				Exponential fit	
(a.u.)	v_0	v_2	$\ln v_0$	$\ln v_2$	v_0	v_2
3.8	7.676	2.870	2.038	1.054	7.806	2.929
4.0	5.168	1.942	1.642	0.664	5.204	1.953
4.2	3.470	1.308	1.244	0.268	3.470	1.302
4.4	2.324	0.876	0.843	−0.133	2.313	0.868
4.6	1.553	0.582	0.440	−0.541	1.542	0.579
4.8	1.034	0.386	0.034	−0.952	1.028	0.386
5.0	0.685	0.256	−0.378	−1.363	0.686	0.257
5.2	0.450	0.172	−0.798	−1.763	0.457	0.172

For a given value of r, the interaction energy is a function only of γ, and we may try to fit this angular dependence with some simple analytic function. If we consider the function

$$V(\gamma)=v_0+v_2P_2(\cos\gamma), \qquad (4.1)$$

where v_0 and v_2 are constants and $P_2(x)$ is a Legendre polynomial, we can pick v_0 and v_2 so that the calculated interaction energy is represented exactly at two values of γ. If we choose v_0 and v_2 so that we get an exact fit at $\gamma=0°$ and 90°, we may then evaluate the function (4.1) at intermediate values of γ and see how well it agrees with the computed values. The values thus calculated for v_0 and v_2 are listed in Table II. Using these values of

TABLE III. $v_0(r)+v_2(r)P_2(\cos\gamma)$ fit to interaction energy. Energy in milli-double Ry. H_2 bond $=1.406$ a.u.

r (a.u.)	γ 0°	15°	30°	45°	60°	75°	90°
3.8	10.546	10.258	9.470	8.394	7.318	6.530	6.241
4.0	7.110	6.915	6.382	5.654	4.926	4.392	4.197
4.2	4.777	4.646	4.287	3.797	3.306	2.948	2.816
4.4	3.199	3.111	2.871	2.543	2.214	1.974	1.886
4.6	2.135	2.077	1.917	1.699	1.480	1.320	1.262
4.8	1.420	1.382	1.276	1.131	0.986	0.880	0.842
5.0	0.941	0.916	0.845	0.749	0.653	0.583	0.558
5.2	0.622	0.604	0.557	0.493	0.429	0.381	0.364

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[8] M. P. Barnett and C. A. Coulson, Phil. Trans. Roy. Soc. **A243**, 221 (1951).

v_0 and v_2 we evaluate the function (4.1) and tabulate the results in Table III. By comparing Tables I and III, one can see that the function (4.1) represents the angular dependence of the calculated interaction energy quite well.

After computing the values of v_0 and v_2 for each value of r, we have essentially fitted the computed interaction energy with a function of the form

$$V(r,\gamma)=v_0(r)+v_2(r)P_2(\cos\gamma). \tag{4.2}$$

TABLE IV. Dumbbell model potential. Energy given in milli-double Ry. H_2 bond $=1.406$ a.u.

r (a.u.)	γ 0°	15°	30°	45°	60°	75°	90°
3.8	16.830	15.874	13.465	10.606	8.177	6.635	6.115
4.0	11.204	10.575	8.987	7.093	5.477	4.448	4.100
4.2	7.459	7.045	5.996	4.742	3.667	2.980	2.748
4.4	4.965	4.692	4.000	3.168	2.454	1.995	1.840
4.6	3.306	3.125	2.668	2.116	1.641	1.335	1.232
4.8	2.200	2.082	1.779	1.413	1.097	0.893	0.824
5.0	1.465	1.386	1.186	0.943	0.733	0.597	0.551
5.2	0.975	0.923	0.791	0.630	0.490	0.399	0.368

We may now attempt to fit the values of v_0 and v_2 listed in Table II with a simple function of r. What functional form we should try is made immediately apparent if we plot the logarithm of v_0 and v_2 versus r, as is done in Fig. 2. The result is two parallel lines, which means that we may write

$$v_0(r)=C_0e^{-\kappa r}, \tag{4.3a}$$

$$v_2(r)=C_2e^{-\kappa r}. \tag{4.3b}$$

The correct values for the constants are

$$C_0=17\,283,\quad C_2=6485 \text{ m-double Ry},$$
$$\kappa=2.027(\text{a.u.})^{-1}. \tag{4.3c}$$

TABLE V. Calculated He-H_2 interaction energy. Energy given in milli-double Ry. H_2 bond $=1.486$ a.u.

r (a.u.)	γ 0°	15°	30°	45°	60°	75°	90°
3.8	11.452	11.021	9.919	8.568	7.391	6.626	6.364
4.0	7.737	7.446	6.700	5.782	4.981	4.464	4.289
4.2	5.210	5.013	4.511	3.887	3.346	2.998	2.880
4.4	3.496	3.364	3.026	2.605	2.240	2.008	1.933
4.6	2.338	2.249	2.024	1.739	1.492	1.339	1.294
4.8	1.558	1.499	1.349	1.157	0.989	0.888	0.862
5.0	1.033	0.995	0.896	0.767	0.651	0.582	0.568
5.2	0.683	0.658	0.595	0.506	0.424	0.375	0.367

In Table II we list the values of the functions (4.3a) and (4.3b) evaluated for the various values of r. The fit is seen to be quite good. From the preceding discussion, it is seen that the He-H_2 interaction energy may be expressed quite accurately by the function

$$V(r,\gamma)=C_0e^{-\kappa r}[1+\delta P_2(\cos\gamma)],$$
$$\delta=0.375. \tag{4.4}$$

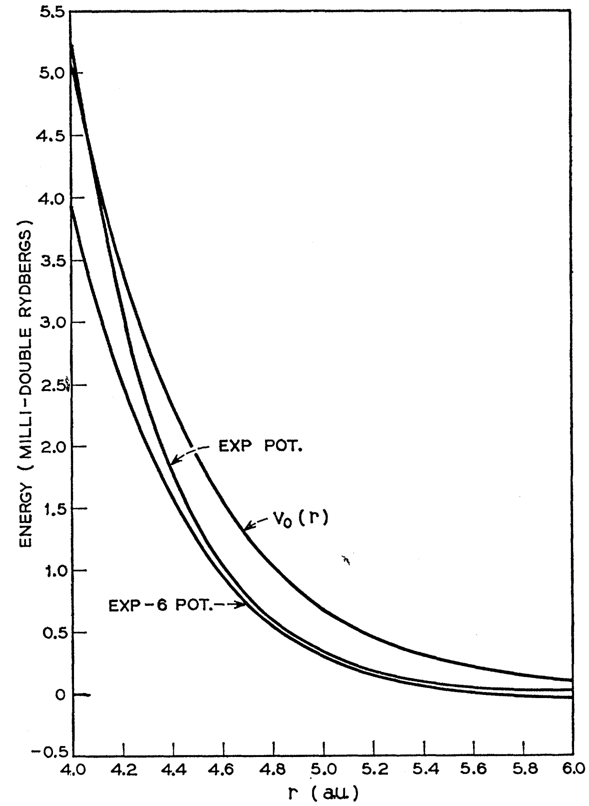

FIG. 3. Amdur-Malinauskas experimental potentials and the calculated $v_0(r)$ for the He-H_2 interaction.

In order to obtain some idea of the accuracy of our calculation, we compare our $v_0(r)$ with the spherically averaged He-H_2 interaction potential obtained by Amdur and Malinauskas[9] from gas diffusion experiments carried out below 350°K. They postulated several analytic forms for the potential and then determined the parameters in these potential functions so as to obtain the best fit to their data. In Eq. (4.5) we give the parameters for the modified Buckingham exp−6 potential determined by Amdur and Malinauskas in this way; Eq. (4.6) expresses their result in the form of a simple exponential function. They also obtained parameters for a Lennard-Jones 6–12 potential, form $\epsilon[(r_m/r)^{12}-2(r_m/r)^6]$, and for an inverse power of r function, form D/r^s, but these will not be given in the present work.

$$V_1(r)=\frac{\epsilon}{1-6/\alpha}\left[\frac{6}{\alpha}e^{\alpha(1-r/r_m)}-\left(\frac{r_m}{r}\right)^6\right],\quad r\geq r_{\max}, \tag{4.5a}$$

$$V_1(r)=\infty,\qquad r<r_{\max}, \tag{4.5b}$$

where $\alpha=13.22$, $r_m=3.375$ Å$=6.378$ a.u., $\epsilon=14.76$°K $=0.04678$ m-double Ry, $r_{\max}$=point at which Eq.

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[9] A. P. Malinauskas, thesis, Massachusetts Institute of Technology Chemistry Department, 1962 (unpublished).

TABLE VI. v_0 and v_2 vs r. Energy in milli-double Ry. H_2 bond $=1.486$ a.u.

r	Calculated				Exponential fit	
(a.u.)	v_0	v_2	ln v_0	ln v_2	v_0	v_2
3.8	8.060	3.392	2.087	1.221	8.060	3.392
4.0	5.438	2.298	1.693	0.832	5.393	2.280
4.2	3.657	1.553	1.297	0.440	3.608	1.533
4.4	2.454	1.042	0.898	0.041	2.414	1.031
4.6	1.642	0.696	0.496	−0.363	1.616	0.693
4.8	1.094	0.464	0.090	−0.768	1.081	0.466
5.0	0.723	0.310	−0.324	−1.171	0.723	0.313
5.2	0.473	0.211	−0.749	−1.557	0.484	0.211

(4.5a) has its maximum value.

$$V_2(r)=Qe^{-\lambda r}, \qquad (4.6)$$

where $Q=1.104\times10^{8}{}^\circ\mathrm{K}=3.499\times10^5$ m-double Ry, $\lambda=5.234$ Å$^{-1}=2.770$ (a.u.)$^{-1}$. In Fig. 3 we plot our calculated $v_0(r)$ along with the Amdur-Malinauskas experimental potentials gives above. The agreement is better than one might expect from such a simple wave function as the one we used.

V. DUMBBELL MODEL FOR THE POTENTIAL

It is interesting to see whether it is possible to find a function $f(x)$ such that the calculated interaction potential may be represented by

$$V(r,\gamma)=f(\rho_{ac})+f(\rho_{bc}). \qquad (5.1)$$

If it were possible to do this, then we could say that each hydrogen atom of the hydrogen molecule interacts more or less independently with the helium atom and that the hydrogen molecule interacts as if it were a dumbbell made up from two hydrogen atoms on the end of a rod. If the relation (5.1) does hold, we can easily find out from our calculated interaction energy what the function $f(x)$ must be, for if $\gamma=\pi/2$, $\rho_{ac}=\rho_{bc}$ and

$$f(\rho_{ac})=\tfrac{1}{2}V(r,\pi/2).$$

By considering the interaction energy listed in Table I for $\gamma=90°$ as a function of ρ_{ac}, we find that $f(x)$ should be given quite closely by the simple function

$$f(x)=De^{-pr},$$
$$D=8064 \text{ m-double Ry}, \quad p=2.0345 \text{ (a.u.)}^{-1}. \qquad (5.2)$$

In Table IV we evaluate the dumbbell model expression (5.1) for various values of r and γ using Eq. (5.2) for $f(x)$. By comparing Tables I and IV, we see that the dumbbell model is not very good; it produces a potential which is much more aspherical than the true potential really is. The failure of the dumbbell model to account for the true dependence of the interaction energy upon γ causes us to look with great skepticism upon research which uses this assumption as a starting point.[10,11]

VI. RESULTS FOR LENGTHENED H_2 BOND

The interaction energy was also computed as a function of r and γ with the H_2 bond length $=1.486$ a.u., a little longer than the equilibrium distance. For this small change in bond length, the value 1.166 for α, the hydrogen $1S$ orbital screening constant, should still be quite good and this was the value used. The procedure was identical to that for the 1.406 bond length and the results are presented in Table V. These results were then fitted to the functional form of (4.1) and the values of v_0 and v_2 thus obtained listed in Table VI. The fit thus obtained to the calculated interaction energy is given in Table VII. The final analytic form obtained for the interaction energy at this expanded H_2 bond length is given by

$$V'(r,\gamma)=C_0'e^{-\kappa' r}[1+\delta' P_2(\cos\gamma)], \qquad (6.1)$$

where H_2 bond $=1.486$ a.u., $C_0'=16\,666$ m-double Ry, $\kappa'=2.009$ (a.u.)$^{-1}$, $\delta'=0.425$. The biggest change upon lengthening the bond is in the value of δ. This should have been expected since this parameter represents a measure of the asphericity of the molecule, and surely the molecule becomes less and less like a sphere as it is elongated.

TABLE VII. $v_0(r)+v_2(r)P_2(\cos\gamma)$ fit to interaction energy. Energy in milli-double Ry. H_2 bond $=1.486$ a.u.

r	γ						
(a.u.)	0°	15°	30°	45°	60°	75°	90°
3.8	11.452	11.111	10.180	8.908	7.636	6.704	6.364
4.0	7.737	7.506	6.875	6.013	5.151	4.520	4.289
4.2	5.210	5.054	4.627	4.045	3.462	3.036	2.880
4.4	3.496	3.391	3.105	2.714	2.324	2.038	1.933
4.6	2.338	2.268	2.077	1.816	1.555	1.364	1.294
4.8	1.558	1.511	1.384	1.210	1.036	0.908	0.862
5.0	1.033	1.002	0.917	0.801	0.685	0.600	0.568
5.2	0.683	0.662	0.604	0.525	0.446	0.388	0.367

VII. CONCLUSION

We have succeeded in calculating from first principles the interaction energy between a helium atom and a hydrogen molecule. Although a relatively simple wave function was used, no approximations had to be made for the molecular integrals encountered, and the interaction energy was obtained for many configurations of the three nuclei involved. The spherically averaged results agree quite well with an interaction energy determined by gas-diffusion measurements. It was found possible to represent the calculated interaction energy quite accurately with a function of the form $Ce^{-\kappa r}[1+\delta P_2(\cos\gamma)]$. It was shown that it is impossible to represent the calculated interaction potential by a dumbbell-type potential, i.e., $f(\rho_{ac})+f(\rho_{bc})$ where $f(x)$ is some appropriate function. In the paper following, the

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[10] R. Brout, J. Chem. Phys. 22, 934 (1954).

[11] K. F. Herzfeld and T. A. Litovitz, *Absorption and Dispersion of Ultrasonic Waves* (Academic Press Inc., New York, 1959), p. 303.

probability for rotational excitation upon collision between a helium atom and a hydrogen molecule is computed using the calculated interaction energy.

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Inelastic Scattering from a Diatomic Molecule: Rotational Excitation upon Collision between He and H_2 and H_2 and H_2†*

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The formalism developed by Arthurs and Dalgarno has been used in the distorted wave approximation to calculate the inelastic scattering cross section for rotational excitation from the $j=0$ to the $j=2$ rotational state in collisions between a helium atom and a hydrogen molecule or two hydrogen molecules. All necessary computations were done with a digital computer, thus, allowing the Arthurs-Dalgarno formalism to be applied with no added approximations. The interaction energy between He and H_2 obtained in the preceding paper was used for the He-H_2 calculation while the interaction energy given by Takayanagi was used for the H_2-H_2 problem. Values for the total inelastic cross sections are given as well as graphs for the He$-H_2$ differential scattering cross section. Incident kinetic energies up to only 0.25 eV in the center-of-mass system were considered; for these low energies, vibrational or electronic excitation is impossible so that change in rotational quantum number is the only inelastic process possible. The results obtained for the H_2-H_2 cross section do not agree with the rate of de-excitation from the $j=2$ rotational level in H_2 gas as measured by dispersion experiments with ultrasonic waves. The disagreement may be due to an incorrect H_2-H_2 interaction potential or failure to consider all important de-excitation mechanisms.

I. INTRODUCTION

WHEN a diatomic molecule collides with another particle, atom, or molecule, inelastic as well as elastic scattering may occur; the diatomic molecule may undergo changes in any of the quantum numbers describing the state of its internal coordinates. If initially the diatomic molecule is in its ground electronic, vibrational, and rotational state, and we confine ourselves to incident kinetic energies measured in the center-of-mass coordinate system that are below the energy necessary to excite the molecule to its first excited vibrational state, then the only energetically possible inelastic process is change in rotational quantum number. Under these conditions, fairly low-incident energies, and no other competing inelastic process, it is possible to compute the inelastic scattering cross section from a rigorous quantum mechanical formalism and only two approximations. The first approximation is to treat the problem in the Born-Oppenheimer or adiabatic approximation where the net effect of the electrons is to provide a potential energy function of r, the distance measured along a line from the incoming particle to the center of mass of the diatomic molecule, and γ, the angle between this line and the line joining the two nuclei of the molecule. This approximation is surely justified for low-incident velocities where the electrons have plenty of time to readjust themselves as the colliding partners move towards their rendezvous. The second necessary approximation is to use the method of distorted waves[1,2] to solve the coupled differential equations which result from the Schrödinger equation of the problem. For low-incident energies, it turns out that the distorted-wave approximation is quite good. The low-incident kinetic energies also make feasible the use of a partial wave analysis of the problem. While this is not an approximation, its use reduces the computations to solving ordinary differential equations, an easy task for a digital computer.

In the present work, the general methods described above are used to calculate the inelastic cross section for rotational excitation of a hydrogen molecule from the $j=0$ to the $j=2$ state when it collides with either

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