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Analytic fit of the He-H_2 energy surface in the repulsive region

Arnold Russek
Physics Department, The University of Connecticut, Storrs, Connecticut 06268

Ramiro Garcia G.*
Instituto de Fisica, Universidad Naçional Autonoma de Mexico, Mexico 20, Distrito Federal
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Single-configuration Hartree-Fock calculations are reported on the HeH_2 triatomic-molecular system in the range of small He-H_2 separation, R, to complement earlier studies, so that the entire energy surface of interest to He on H_2 collisions in the low-keV collision-energy regime has now been determined. It is found that strong *repulsive* three-body polarization forces exist which dominate the physics of this collision-energy regime. Because a Legendre-polynomial expansion in the angular variable is found to be useless in this region of the energy surface, a new parametrization is introduced which includes both binary and three-body terms. The three-body terms are needed because the electron distribution in H_2 is different from the sum of the distributions of two individual H atoms.

I. INTRODUCTION

Recent scattering experiments between rare-gas atoms and H_2 in the low-keV range of collision energies[1–3] have suggested the existence of strong, nonadditive valence forces deep in the repulsive region of the energy surface,[3] a surprising result since this region was thought to be dominated by screened Coulomb core-core type interactions, which give rise to additive forces. Indeed, the unmistakable conclusion from the experimental data was stated both tentatively and weakly in Ref. 3 for this very reason. Accordingly, it seemed worthwhile to investigate the repulsive part of the He-H_2 energy surface, the simplest of rare-gas H_2 systems and a prototype for the others, all of which behave in the same way in low-keV energy collisions.

A number of *ab initio* calculations on the He-H_2 triatomic-molecular system can be found in the literature[4–11] starting from 1963. There also exist two energy surface fittings to experimental data.[12,13] The existing literature is well summarized by Meyer *et al,*[11] and none cover the full region required by keV energy collisions. In fact, the more recent and more accurate works have concentrated on the van der Waals minimum, which is located at He-H_2 separation $R=6.5a_0$. This is approximately four times the separation r between the two protons in the H_2, so that the van der Waals minimum is located in a region where the energy surface is nearly isotropic in the angle γ between $\vec{R}$ and $\vec{r}$. As a consequence, these works were able to parametrize the energy surface by expanding the angular dependence in Legendre polynomials

$$V(R,r,\gamma)=\sum_n V_n(R,r)P_n(\cos\gamma) \tag{1}$$

and retaining only the first two terms.

On the other hand, scattering experiments in the low-keV collision-energy range probe the energy surface deep in the repulsive region, where it is far more anisotropic and does not admit of a useful Legendre-polynomial expansion. Parenthetically, it may be remarked that the van der Waals minimum for He-H_2 has a well depth of only 1.0 meV. Such a shallow well is inconsequential for scattering experiments in the keV energy range, although experiments in this collision energy range are capable of "seeing" and exploring a more substantial well.

In this work *ab initio* calculations are presented for the deep repulsive region to complete the energy surface, and a new parametrization is developed to extend the Tang and Toennies theoretical model for the energy surface[14] to cover the entire energy surface. The Tang and Toennies model was originally introduced to describe the energy surface at intermediate and large distances ($R\geq 4a_0$), which includes the region of the van der Waals minimum. For $R\geq 4a_0$, the first two terms of the Legendre-polynomial expansion are found to suffice; moreover, the coefficients of P_0 and P_2 can be taken as

functions of R only. Tang and Toennies further decomposed V_0 and V_2 into a self-consistent-field (SCF) contribution, a dispersion contribution, and a coupling correction:

$$V_n(R,r)=V_{n,\mathrm{SCF}}(R)+V_{n,\mathrm{disp}}(R)+V_{n,\mathrm{corr}}(R)\ . \tag{2}$$

The SCF contribution (a single-configuration Hartree-Fock calculation) yields a purely repulsive energy and is sufficient to describe the repulsive region of the energy surface at smaller values of R. In the limited range of R, which Tang and Toennies consider, they find that $V_{0,\mathrm{SCF}}$ and $V_{2,\mathrm{SCF}}$ can be accurately described by Born-Mayer potentials: $A_n\exp(-b_nR)$. The dispersion contribution, on the other hand, can only arise from a configuration interaction (CI) calculation; its existence altogether depends on electron-electron correlation. It is expressed as a series in inverse powers of R^2:

$$\sum_{i\geq 3} C_{n,i}/R^{2i}\ .$$

Finally, their correction term takes into account the effect of the repulsion on the dispersion.

In this work, the decomposition of the potential into V_{SCF}, V_{disp}, and V_{corr} is retained, with V_{disp} and V_{corr} as given by Tang and Toennies.[14] Only V_{SCF} has to be modified to encompass the extended range of R here considered. *Ab initio* SCF calculations are here reported for values of R from 0 to $3a_0$, thus completing the range of R for which the energy surface has been calculated. In this small R region, neither the dispersion nor the coupling terms of the Tang and Toennies model make any appreciable contribution, so that only V_{SCF} need here be considered. It is found that a Legendre-polynomial expansion of V_{SCF} is inadequate in this small R region and that the dependence on the H-H separation, r, is quite important. Indeed, without the r dependence of the energy surface, the experimentally observed vibrational excitation could not take place. Calculations were therefore carried out for $r=1.2$, 1.4, and $1.6a_0$. Moreover, a finer mesh of 30° increment was used for the angular dependence. A new parametrization for V_{SCF} is described in Sec. III, which adequately fits the calculated energy surface over a range of energy variation which spans more than four orders of magnitude. At the same time, this parametrization has the correct limiting forms at the singular points $R_A=0$ and $R_B=0$, and the nonsingular, ordinary point $R=0$. Finally, the individual terms in the new parametrization have physical significance and provide a better intuitive understanding of the energy surface.

II. CALCULATIONS

SCF-LCAO-MO calculations (where LCAO and MO represent linear combination of atomic orbitals and molecular orbitals, respectively) have been made on the ground-state energy surface of the He-H_2 triatomic-molecular system using the IBMOL program and the SCF mode of the *GVB* program. The Gaussian basis set, taken from Brown and Hayes,[15] contained: (a) five s-type Gaussian functions contracted to four s-type atomic orbitals along with two p-type Gaussians centered on each H and (b) six s-type Gaussians contracted to four atomic orbitals along with two p-type Gaussians centered on the He. This basis set adequately describes polarization contributions to the energy surface.

As a single-configuration calculation, it can give only the V_{SCF} contribution of the Tang and Toennies model. Consequently, there was no point to extending the calculations beyond $R=3$, which is well into the asymptotic region of V_{SCF} and provides sufficient overlap for comparison with the accurate results of Meyer *et al.*[11] It can be seen from Table I that at $R=2$ and 3, their SCF energies differ from the present results by approximately 0.002 hartree (1 hartree $=27.2$ eV). Moreover, at the two comparison values of R, the best multiconfiguration results of Meyer *et al.* are lower than the SCF results by an amount less than 0.007 hartree, thereby validating the use of SCF calculations for representing the repulsive region of the energy surface. The accuracy of the present calculations, including correlation corrections from a CI calculation, are, therefore, or the order of 0.01 hartree. For this reason,

TABLE I. Comparison with the results of Meyer *et al.*

			E_{int}			
γ	R	r	Present	Meyer *et al.*[a] SCF	Meyer *et al.*[a] CI
0°	2	1.2	0.195	0.195	0.188
		1.4	0.215	0.211	0.205
		1.6	0.232	0.230	0.226
	3	1.2	0.030	0.031	0.029
		1.4	0.036	0.036	0.033
		1.6	0.042	0.041	0.038
90°	2	1.2	0.152	0.153	0.145
		1.4	0.154	0.154	0.146
		1.6	0.155	0.154	0.145
	3	1.2	0.024	0.025	0.022
		1.4	0.026	0.026	0.023
		1.6	0.029	0.028	0.024

[a]Reference 11.

TABLE II. He-H_2 interaction energy. Interaction energy as a function of R, r, and γ. Columns labeled E_{int} give the *ab initio* calculations. Columns labeled V_{par} give the results of the parameteric fit, Eq. (7), with $Z_H Z_{He}=2$, $\lambda_c=3.20$, $A_2=1.2$, $\lambda_p=1.742$, $A_3=2.76$, $B=2.18$, and $b=2.20$.

		$\gamma=0°$		$\gamma=30°$		$\gamma=60°$		$\gamma=90°$	
R	r	E_{int}	V_{par}	E_{int}	V_{par}	E_{int}	V_{par}	E_{int}	V_{par}
0	1.2	2.41	2.40	2.41	2.40	2.41	2.40	2.41	2.40
	1.4	1.88	1.89	1.88	1.89	1.88	1.89	1.88	1.89
	1.6	1.53	1.56	1.53	1.56	1.53	1.56	1.53	1.56
0.5	1.2	16.70	16.19	4.00	3.93	1.81	1.81	1.58	1.46
	1.4	6.87	6.73	2.90	2.96	1.44	1.53	1.36	1.26
	1.6	3.76	3.84	2.06	2.23	1.24	1.30	1.18	1.10
1.0	1.2	2.35	2.31	1.36	1.36	0.84	0.77	0.78	0.64
	1.4	3.64	3.57	1.47	1.50	0.78	0.73	0.73	0.59
	1.6	6.59	6.42	1.51	1.59	0.70	0.69	0.68	0.55
1.5	1.2	0.52	0.53	0.45	0.43	0.37	0.32	0.36	0.28
	1.4	0.60	0.64	0.47	0.47	0.37	0.32	0.35	0.27
	1.6	0.74	0.80	0.49	0.52	0.35	0.31	0.34	0.26
2.0	1.2	0.20	0.19	0.18	0.17	0.16	0.14	0.15	0.12
	1.4	0.22	0.22	0.19	0.18	0.16	0.14	0.15	0.12
	1.6	0.23	0.25	0.20	0.20	0.17	0.14	0.16	0.12
3.0	1.2	0.030	0.033	0.029	0.030	0.025	0.026	0.024	0.024
	1.4	0.036	0.036	0.033	0.032	0.028	0.026	0.026	0.023
	1.6	0.042	0.040	0.038	0.034	0.032	0.026	0.029	0.023

the results presented in Table II are given only to two decimal places, except at $R=3$, where they are given to two significant figures.

With the geometry shown in Fig. 1, the energy surface is given for 63 coordinate sets, R, r, γ, in the columns labeled E_{int} of Table II, where

$$E_{\text{int}}=V_{\text{SCF}}-E_{\text{He}}-E_{H_2}(r)\ . \tag{3}$$

Hence, for any value of r, E_{int} is the interaction energy between a He atom and an H_2 molecule with proton-proton separation r. Physically, it represents the scattering potential for a slow (low-keV) He atom impinging on a ground-state H_2 molecule with fixed separation r during the interaction time. For all practical purposes, such is the case for small angle scattering in the low-kV energy regime. On the one hand, the collision is slow enough so that the adiabatic electronic energy acts as an effective potential for the nuclear motion. On the other hand, the collision time, of the order of 10^{-16} sec, is short compared with vibrational periods ($\sim 10^{-14}$ sec) and rotational periods ($\sim 10^{-12}$ sec), so that $\vec{r}$ effectively remains constant in both magnitude and direction during the collision. For convenience in converting from E_{int} to V_{SCF} at the three values of r here considered:

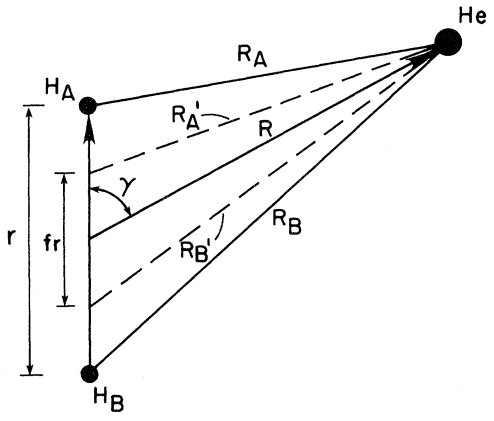

FIG. 1. Molecular geometry. Independent coordinates are R, r, and γ. Distances between the He nucleus and the two H nuclei are denoted by R_A and R_B. Distances R_A' and R_B' are defined in Eqs. (9).

$$E_{\text{int}} = V_{\text{SCF}} + \begin{cases} 3.984 \ \textit{hartree} \text{ at } r = 1.2a_0, \\ 3.994 \ \textit{hartree} \text{ at } r = 1.4a_0, \\ 3.988 \ \textit{hartree} \text{ at } r = 1.6a_0. \end{cases} \quad (4)$$

III. ENERGY SURFACE

A. Atom-atom potential

For heuristic purposes, the two-body atom-atom energy will be considered first, because an understanding of this interaction is essential to the understanding of the atom-molecule energy. At small internuclear separations, where the Coulomb repulsion between the nuclei dominates, the interaction energy should be a screened Coloumb type, essentially a Bohr potential. This arises from point nuclei, each partially screened by a rigidly fixed electron cloud held so firmly in place by the respective parent nucleus that it is negligibly distorted by the other atom. At longer ranges, the interaction energy goes over to a Born-Mayer type, which somehow takes into account the Pauli contribution to the energy as the two electron clouds overlap, thus making it a polarization contribution to the energy. At still larger internuclear separations, the van der Waals attraction, which is also a polarization contribution, dominates. That term will, however, be omitted from the present discussion, so that the atom-atom potential is of the form

$$V_{\text{atom-atom}} = \frac{Z_1 Z_2}{R_{12}} e^{-\lambda_c R_{12}} + A e^{-\lambda_p R_{12}} . \quad (5)$$

where R_{12} is the internuclear separation. From the above discussion, it is reasonable to expect that λ_c should be larger than λ_p so that the screened Coulomb core interaction is shorter range than the Born-Mayer polarization interaction. The potential form given by Eq. (5) is indeed found to describe the He-H interaction, with the relative sizes of the respective ranges conforming to expectation.

B. Atom-molecule potential

Purely additive two-body forces would yield for the He-H_2 atom-molecule interaction:

$$V_{\text{two-body}} = Z_{\text{H}} Z_{\text{He}} \left[\frac{e^{-\lambda_c R_A}}{R_A} + \frac{e^{-\lambda_c R_B}}{R_B} \right] + A(e^{-\lambda_p R_A} + e^{-\lambda_p R_B}) ,$$

where R_A and R_B are the distances from the He nucleus to the respective protons. This cannot, however, be the full interaction. The second term on the right-hand side of Eq. (5) has been characterized as a polarization term, due to the overlap of electron wave functions and the Pauli exclusion principle. Being a polarization term, it should therefore alter when two hydrogen atoms combine to form a molecule, since the H_2 molecule has an excess electron distribution between the two protons drawn at the expense of the electron distributions centered on each proton. Consequently, one would expect the strength, A, of the two-body polarization term for the He-H_2 system to be reduced from that which was found for the He-H atom-atom system. This reduction should be compensated by the appearance of an additional term of the form $A'\exp(-\lambda_p R)$ to take into account the electron distribution of the H_2 which is centered midway between the two protons, i.e., at $R = 0$. One additional correction must be made. The point $R = 0$ has no potential singularity; it is a perfectly ordinary point in the eigenvalue equation for the electronic wave function. Therefore, it cannot have a discontinuous slope at $R = 0$, so that the R-dependent polarization should be of the form

$$A_3 e^{-\lambda_p R} - B e^{-bR} \quad (6a)$$

with

$$A_3 \lambda_p = Bb \quad (6b)$$

in order to ensure continuous derivative at $R = 0$. Thus, the parametric form suggested here for the SCF contribution to the interaction energy is

$$V_{\text{SCF}} = Z_{\text{H}} Z_{\text{He}} \left[\frac{e^{-\lambda_c R_A}}{R_A} + \frac{e^{-\lambda_c R_B}}{R_B} \right] + A_2(e^{-\lambda_p R_A} + e^{-\lambda_p R_B}) + A_3 e^{-\lambda_p R} - B e^{-bR} , \quad (7)$$

where A_2 describes the strength of the additive two-body contribution to the polarization interaction, while A_3 describes the three-body correction term, with B and b characterizing the saturation of that term in the vicinity of $R = 0$. Table II and Fig. 2 show the best fit of the parametric form (7) for V_{SCF} with the *ab initio* calculations, obtained with $Z_{\text{H}} Z_{\text{He}} = 2$, $\lambda_c = 3.20$, $A_2 = 1.2$, $\lambda_p = 1.742$, $A_3 = 2.76$, $B = 2.18$, and $b = 2.2$, all quantities being given in atomic units.

It can be seen from Fig. 2 that the parametric

form (7) describes the energy surface for small values of R quite well. That is to be expected since the small-R region is dominated by the core-core repulsions and is insensitive to minor details of the electron distribution. On the other hand, the fit at larger values of R, although adequate to describe most collisions in the keV energy range, is not up to the standards demanded by chemists, who must deal with very low-energy collisions. They require better accuracy in the large-R region ($R \geq 2$ a.u.), where the parametric form (7) consistently overstates the angular dependence of the energy surface. The fault lies not with the general concept of the model here proposed, but rather with the specific form suggested in Eq. (7). There, the excess electron distribution between the two protons has, for simplicity, been taken into account by a spherically symmetric distribution centered at $R=0$. As Fig. 2 shows, even this rough approximation goes a long way toward describing the energy surface. However, an even better approximation of the distorted electron distribution in H_2 can be obtained by centering the electron distribution for each H not on the nucleus itself, but at some point between the two protons in addition to the distribution centered at $R=0$. With the centers of the displaced distributions at $\pm fr/2$, the improved parametric form is given by

$$V_{\mathrm{SCF}}=Z_{\mathrm{H}}Z_{\mathrm{He}}\left[\frac{e^{-\lambda_c R_A}}{R_A}+\frac{e^{-\lambda_c R_B}}{R_B}\right] +A(e^{-\lambda_p R'_A}+e^{-\lambda_p R'_B}) +A_3 e^{-\lambda_p R}-Be^{-bR}\,, \tag{8}$$

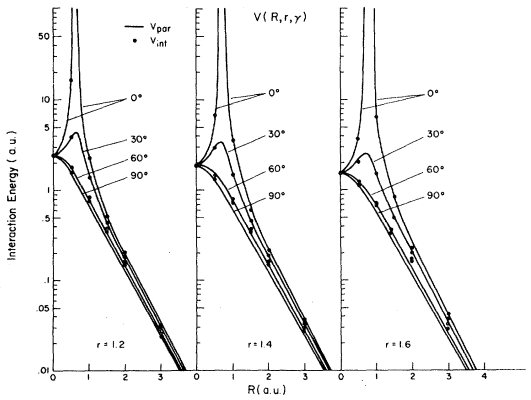

FIG. 2. He-H_2 interaction energy. Results of the *ab initio* calculations are taken from the columns labeled E_{int} of Table II, and are shown as the solid black circles. Curves show the fit obtained with the parametric form Eq. (7) with the parameters listed in Table II.

where

$$R'_A=[R^2+(fr/2)^2-frR\cos\gamma]^{1/2}\,, \tag{9a}$$

$$R'_B=[R^2+(fr/2)^2+frR\cos\gamma]^{1/2}\,. \tag{9b}$$

It should be noted that the Bohr term, which describes the contributions of the nuclei plus that part of the electronic distribution rigidly held by each nucleus, is still a function of R_A and R_B. Only the polarization terms have centers shifted to lie between the two nuclei. The subscript 2 on the strength of this potential has been dropped, since it is no longer a two-body contribution. Figure 3 and Table III show the fit obtained with the parametric form given by Eq. (8) with the parameters listed in Table III. The interaction energies which follow from Eq. (8) are presented in the columns labeled V_{par2}. For comparison, the values from Table II, which follow from Eq. (7), are listed in the columns marked V_{par1}. The *ab initio* calculations from Table II are also listed. The potential form given by Eq. (8) gives a poorer representation of the energy surface in the small-R region than does Eq. (7), and for good reason. When the He nucleus penetrates into the H_2 interior, the H_2 electron distribution will further distort, with at least some of the excess distribution between the two protons being forced out. To avoid the complexity of parameters which are R dependent in this work, the small-R region has been omitted from consideration in Fig. 3 and Table III.

Although the second term of Eq. (8) is continuous, it has unphysical discontinuities in derivative at the ordinary points $R'_A=0$ and $R'_B=0$. A realistic potential, generated by a nonsingular electron

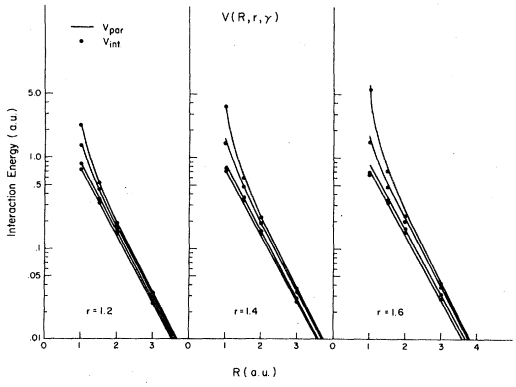

FIG. 3. He-H_2 interaction energy. Results of the *ab initio* calculations are taken from the columns labeled E_{int} of Table II. For convenience, these results are repeated in the columns labeled E_{int} in Table III. *Ab initio* calculations are shown as the solid black circles. Curves show the best fit obtained with the parameteric form Eq. (8) with the parameters listed in Table III.

TABLE III. He-H_2 interaction energy. Interaction energy as a function of R, r, and γ. Columns labeled E_{int} give the *ab initio* calculations. Columns labeled V_{par2} give the results of the parametric fit, Eq. (8), with $Z_H Z_{He}=2$, $\lambda_p=1.742$, and $b=2.20$. Remaining parameters are r dependent. For $r=1.2$, $f=0.7$, $A=1.70$, $A_3=1.73$, and $B=1.37$; for $r=1.4$, $f=0.8$, $A=1.50$, $A_3=2.51$, and $B=1.99$; for $r=1.6$, $f=0.85$, $A=1.30$, $A_3=3.74$, and $B=2.96$. Columns labeled V_{par1} are repeated from Table II for ease of comparison.

		$\gamma=0°$			$\gamma=30°$			$\gamma=60°$			$\gamma=90°$		
R	r	E_{int}	V_{par1} Eq. (7)	V_{par2} Eq. (8)	E_{int}	V_{par1} Eq. (7)	V_{par2} Eq. (8)	E_{int}	V_{par1} Eq. (7)	V_{par2} Eq. (8)	E_{int}	V_{par1} Eq. (7)	V_{par2} Eq. (8)
1.0	1.2	2.35	2.31	2.31	1.36	1.36	1.42	0.84	0.77	0.87	0.78	0.64	0.75
	1.4	3.64	3.57	3.57	1.47	1.50	1.58	0.78	0.73	0.83	0.73	0.59	0.69
	1.6	6.59	6.42	6.42	1.51	1.59	1.71	0.70	0.69	0.83	0.68	0.55	0.70
1.5	1.2	0.52	0.53	0.52	0.45	0.43	0.44	0.37	0.32	0.35	0.36	0.28	0.32
	1.4	0.60	0.64	0.64	0.47	0.47	0.49	0.37	0.32	0.35	0.35	0.27	0.31
	1.6	0.74	0.80	0.81	0.49	0.52	0.56	0.35	0.31	0.37	0.34	0.26	0.32
2.0	1.2	0.20	0.19	0.19	0.18	0.17	0.17	0.16	0.14	0.15	0.15	0.12	0.14
	1.4	0.22	0.22	0.22	0.19	0.18	0.19	0.16	0.14	0.15	0.15	0.12	0.14
	1.6	0.23	0.25	0.26	0.20	0.20	0.22	0.17	0.14	0.16	0.16	0.12	0.15
3.0	1.2	0.030	0.033	0.031	0.029	0.030	0.029	0.025	0.026	0.026	0.024	0.024	0.025
	1.4	0.036	0.036	0.036	0.033	0.032	0.033	0.028	0.026	0.028	0.026	0.023	0.026
	1.6	0.042	0.040	0.042	0.038	0.034	0.038	0.032	0.026	0.031	0.029	0.023	0.028

distribution would be perfectly regular at these points. It is not difficult to modify the potential to make the derivative continuous, as was done for the R-dependent potential. However, since this potential is not being considered in the vicinity of R_A' or R_B' equal to zero, no attempt was made to do so. It should be made clear that the term "potential" has, for heuristic reasons, been used rather loosely in the above discussion. It is certainly not an electrostatic potential energy arising from a charge distribution. Rather, it is a term in the adiabatic electronic energy and includes kinetic energy of the electrons as well as electrostatic potential energy. Nevertheless, despite the fact that the adiabatic electronic energy is more complicated, any symmetry in the electronic wave functions will show up as a symmetry in the energy surface and the energy surface must be regular at any point in space where no singularity exists. That is really all that was said.

Finally, attention should be drawn to a peculiar feature of the energy surface in the vicinity of $\gamma=90°$. With the He nucleus along the perpendicular bisector to the H_2 axis, a repulsive potential, in addition to pushing the He and H_2 away from each other, would also be expected to push the two H atoms apart. Thus, E_{int} should decrease as r increases; the gradient of the energy surface with respect to r should be negative. The *ab initio* calculations for E_{int} in Table II indeed show the expected behavior at small values of R for R less than $2.0a_0$. However, at about $2.0a_0$, a crossover occurs and for larger values of R, the gradient with respect to r is positive. In this large-R region, the helium atom, while pushing the entire H_2 system away from it ($\partial E_{int}/\partial R$ is negative for all R), is actually drawing the two H atoms closer to each other. It can be seen in Table III that the improved parametrization, V_{par2}, exhibits the proper behavior at $\gamma=90°$, whereas V_{par1} does not. It is also evident that for $\gamma=0$, $\partial E_{int}/\partial r$ is always positive. Such behavior is, however, expected even from purely repulsive potentials. The He repels the closer H with a larger force than the one further away, thus pushing the two H atoms toward each other. It is therefore not surprising that both parametrizations exhibit the proper behavior at $\gamma=0°$. At intermediate angles, the situation is ambiguous, so that no qualitative conclusions can be drawn. Only at 90° is the difference in behavior clear cut. The qualitative agreement of V_{par2} with the *ab initio* calculations may not be taken as a strong verification of the parametric form given by Eq. (8), since r-dependent parameters are used in the fit. The main thrust of the argument is that the behavior of the energy surface at large R calls for r-dependent parameters. There is, moreover, good physical justification for having the parameters in the polarization terms dependent on r, since the amount and distribution

of the excess central distribution of the electrons in the H_2 molecule does, in fact, depend on r.

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