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Molecular treatment of $He^+ + H$ collisions

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Total cross sections for the reactions ${}^4He^+(1s) + H(1s) \rightarrow {}^4He^+(1s) + H(2p)$, ${}^4He^+(1s) + H(1s) \rightarrow {}^4He(1s2p\ {}^{1,3}P) + H^+$ are calculated in an impact-parameter formalism, for collision energies 0.5–30 keV, using a molecular approach. The molecular energies are calculated at large internuclear distances by a configuration-interaction method, and at short distances by a block-diagonalization method. The radial couplings between the molecular wave functions are evaluated exactly, and turn out to depend strongly on the choice of origin of electronic coordinates; as a consequence, the cross sections also depend on this choice. The effect of the anomalous rotational couplings which decrease like R^{-1} is shown to be negligible, and a method to integrate them is proposed in the Appendix. Choosing the center of mass as origin of electronic coordinates, we obtain good agreement with experimental data, but we find no *a priori* reason to favor this choice. As an important conclusion, the main effect of the so-called momentum-transfer problem, which is the origin dependence of the cross sections, is due to the form of the molecular wave functions at short internuclear distances.

I. INTRODUCTION

In the application of the molecular model to atomic collisions, two-electron systems provide an intermediate situation between (one-electron) systems for which the molecular states can be exactly calculated, and which have been extensively studied, and (many-electron) systems whose molecular wave functions are known with much less accuracy. In the present work, we have studied the simplest heteronuclear two-electron system HeH^+; more specifically, we have treated the reactions

$$ {}^4He^+(1s) + H(1s) \rightarrow {}^4He^+(1s) + H(2p), \quad (1)$$

$$ {}^4He^+(1s) + H(1s) \rightarrow {}^4He(1s2p\ {}^{1,3}P) + H^+. \quad (2)$$

Our main reasons for choosing this particular collision are as follows:

(i) There is a great amount of recent experimental data[1-4] on the total cross sections of reactions (1) and (2), for collision energies ranging from 0.5 to 30 keV; previous theoretical work[5] has only studied the range 0.5–5 keV. Exploration of the higher-energy range will contribute to clarify the domain of validity of the molecular model.

(ii) The basic mechanism which is responsible for processes (1) and (2) has been proposed by Fayeton *et al.*,[5] and is basically correct. However, these authors employed molecular energies calculated from a very crude model, which were further empirically corrected, and couplings extracted from a model potential calculation.[6] The HeH^+ system is sufficiently simple so that accurate wave functions can be constructed, and their dynamical couplings can be calculated exactly[7,8] without excessive difficulty.

(iii) A very important feature of the molecular states involved in processes (1) and (2) is the fact that some of their dynamical couplings depend strongly on the choice of origin of electronic coordinates. At high nuclear velocities, the branching ratio between the cross sections of (1) and (2) has, therefore, a considerable origin dependence. We show that, contrary to what is often assumed in the study of momentum-transfer problems, this dependence is due to the behavior of the couplings at short internuclear distances. We also study in the Appendix the numerical integration of the slowly (R^{-1}) decreasing rotational couplings.

For the range of nuclear velocities considered in this work, we have used a semiclassical approach with rectilinear trajectories along the z direction. The program PAMPA of Gaussorgues *et al.*[9] was slightly modified to integrate the anomalous rotational couplings, as explained in the Appendix. This work was performed simultaneously with similar calculations of Harel and Salin,[10] who used a different molecular expansion. Atomic units will be used unless otherwise stated.

II. ENERGIES AND COUPLINGS

We present in Fig. 1 the correlation diagram corresponding to the molecular states involved in processes (1) and (2). The basic mechanism which is responsible for these processes is very simple. The system is initially represented by a statistical mixture of singlet $|2\,{}^1\Sigma\rangle$ and triplet $|1\,{}^3\Sigma\rangle$ molecular states. These states evolve independently; their energies cross diabatically those of the $|3\,{}^1\Sigma\rangle$ and $|2\,{}^3\Sigma\rangle$ states, respectively, at short distances, and they are coupled rotationally to the states $|1, 2\,{}^1\Pi\rangle$ and $|1, 2\,{}^3\Pi\rangle$ (primary

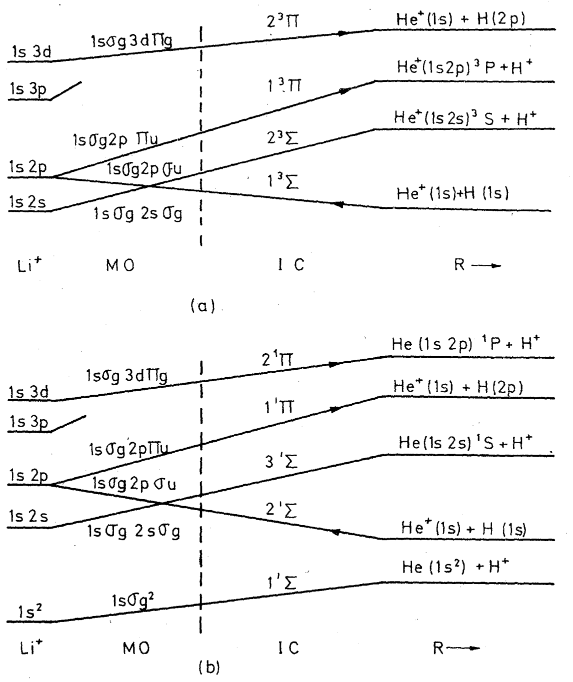

FIG. 1. Qualitative correlation diagrams for the singlet (a) and triplet (b) subsystems, for reactions (1) and (2) of text. The molecular orbital labels indicate the approximate symmetry of the wave functions for small internuclear distances.

mechansim). The radial couplings $\langle 1\,^{1,3}\Pi|d/dR|2\,^{1,3}\Pi\rangle$ provide the secondary mechanism that further governs the branching ratio between reactions (1) and (2).

The atomic basis sets used in the calculation of the molecular energies are presented in Table I, and the corresponding molecular potentials in Table II. For distances $R \leqslant 0.6$ a.u., the diabatic states corresponding to the energies that cross in the correlation diagrams of Fig. 1 were constructed by block diagonalization,[11] using one-center Gaussian orbital expansions for the wave functions. More explicitly, consideration of the Berat-Lichten diagram indicates that the diabatic states have the molecular orbital configuration, and the approximate gerade or ungerade character, shown in Fig. 1; all configurations involving only 1s Gaussian-type orbitals (GTO's) $\{\sigma_g\sigma_g'\}$ were constructed from the basis set, and the Hamiltonian matrix was set up in this representation and diagonalized, yielding the wave functions that correlate in the Configuration Interaction (CI) region to the $|1,3\,^1\Sigma\rangle$ and $|2\,^3\Sigma\rangle$ states. A similar calculation involving all configurations made up of 1s and $2p_z$ (GTO's) $\{\sigma_g\sigma_u\}$ yielded the diabatic states that correlate to the $|2\,^1\Sigma\rangle$ and $|1\,^3\Sigma\rangle$ states. The interaction between these functions at the crossing point was seen to be negligible.

When a full $\{\sigma_g\sigma_g', \sigma_g\sigma_u\}$ CI treatment is carried out, the asymmetry due to the different nuclear charges causes the crossings to be substituted by avoided crossings, and strong radial couplings appear between the corresponding adiabatic states. In the range of short internuclear distances, the diabatic Π states were constructed using the same technique. For $R > 0.6$ a.u., we used a full CI approach, with approximately optimized basis sets, centered on each nucleus (Table I).

The most accurate calculations on HeH^+ found in the literature are those of Green *et al.*[12,13]; they differ from our results at most by 0.017 a.u. for the Π states (for $|2\,^1\Pi\rangle$ at $R = 1$ a.u.) and by 0.038 a.u. for the Σ states ($|2\,^1\Sigma\rangle$ at $R = 1$ a.u.). We did not employ the accurate data of Green *et al.*[12,13] because it is insufficient to tackle the collision problem; for instance, we need rotational couplings and the dependence with the origin of all dynamical couplings. Moreover, the accur-

TABLE I. Exponents of the Gaussian orbitals used in the molecular calculation.

One-center expansion [a]	Two-center expansions							
Σ and Π states	Π states [b]			Σ states [c]			Σ states [d]	
	He		H	He		H	He	H
$\alpha_{1s,2p_z,2p_x}$	α_{1s}	α_{2p_x}	α_{2p_x}	α_{1s}	α_{2p_z}	α_{1s}	α_{1s}	α_{1s}
0.01	0.02	0.01	0.005	0.01	0.08	0.05	0.1	0.005
0.04	0.08	0.03	0.015	0.5	0.5	0.2	0.3	0.18
0.16	0.32	0.1	0.045	2.5	3.0	0.75	1.1	0.6
0.64	1.2	0.3	0.13	12.0		2.8	3.6	0.2
2.56	4.8	1.0	0.4			10.5	12.0	0.7
10.24	19.0		1.2					2.5
40.96	76.0							8.6

[a] Origin: center of charges. $R \leqslant 0.6$ a.u.
[b] $R > 0.6$ a.u.
[c] $0.6 < R < 3$ a.u.
[d] $R \geqslant 3$ a.u.

TABLE II. Molecular energies obtained using the basis sets of Table I, for singlet (a) and triplet (b) states. We use the method of block-diagonalization (see text) for $R \leq 0.6$ a.u., and full configuration interaction for $R > 0.6$ a.u.

(a)

R	$2^1\Sigma$	$1^1\Pi$	$2^1\Pi$
0.0	−4.9686	−4.9686	−4.6979
0.1	−4.8890	−4.8878	−4.4900
0.2	−4.7031	−4.6983	−4.3300
0.3	−4.4865	−4.4759	−4.2200
0.35	−4.3786	−4.3642	−4.1100
0.4	−4.2736	−4.2550	−4.0200
0.5	−4.0900	−4.0793	−3.8166
0.6	−3.9413	−3.8961	−3.6343
0.7	−3.8629	−3.7500	−3.5000
0.8	−3.7505	−3.6200	−3.4000
0.9	−3.6544	−3.5000	−3.3000
1.0	−3.5644	−3.4096	−3.1683
2.0	−3.2311	−2.9150	−2.7207
3.0	−3.0949	−2.7000	−2.6000
4.0	−2.9739	−2.5893	−2.4759
6.0	−2.9178	−2.4600	−2.3900
8.0	−2.7348	−2.3740	−2.3397
10.0	−2.6647	−2.3238	−2.3053
12.0	−2.6514	−2.2894	−2.2796
14.0	−2.6276	−2.2649	−2.2595
16.0	−2.6200	−2.2468	−2.2433
18.0	−2.6111	−2.2330	−2.2302
20.0	−2.6000	−2.2221	−2.2195
24.0	−2.5840	−2.2025	−2.2032
∞	−2.5720	−2.1940	−2.1915

(b)

R	$1^3\Sigma$	$1^3\Pi$	$2^3\Pi$
0.0	−5.0052	−5.0052	−4.7200
0.1	−4.9275	−4.9255	−4.6284
0.2	−4.7470	−4.7392	−4.4412
0.3	−4.5383	−4.5205	−4.2218
0.4	−4.3700	−4.3045	−4.0045
0.5	−4.2200	−4.0991	−3.8003
0.6	−4.0886	−3.9104	−3.6123
0.7	−3.9754	−3.7700	−3.4700
0.8	−3.8809	−3.6526	−3.3606
0.9	−3.8018	−3.5500	−3.2600
1.0	−3.7351	−3.4598	−3.1750
1.2	−3.6100	−3.3092	−3.0350
2.0	−3.3554	−2.9463	−2.7262
3.0	−3.1275	−2.7266	−2.5657
4.0	−2.9814	−2.6015	−2.4847
5.0	−2.8800	−2.5187	−2.4339
6.0	−2.8182	−2.4592	−2.3977
7.0	−2.7700	−2.4145	−2.3695
8.0	−2.7347	−2.3797	−2.3466
9.0	−2.7000	−2.3519	−2.3274
10.0	−2.6847	−2.3293	−2.3100
11.0	−2.6650	−2.3108	−2.2966
12.0	−2.6514	−2.2954	−2.2840
13.0	−2.6400	−2.2824	−2.2729
14.0	−2.6276	−2.2715	−2.2630
16.0	−2.6097	−2.2530	−2.2463
18.0	−2.5910	−2.2402	−2.2329
20.0	−2.5800	−2.2294	−2.2221
24.0	−2.5600	−2.2130	−2.2060
∞	−2.5570	−2.2016	−2.1940

acy of our results is adequate enough for the present work.

The radial couplings between our approximate wave functions were calculated exactly, using the method proposed by Macías and Riera.[7,8] They can be written

$$\left\langle \chi_2 \left| \left(\frac{d}{dR}\right)_{\vec{r}} \right| \chi_1 \right\rangle = \underline{c}_2^\dagger \underline{S} \frac{d}{dR} \underline{c}_1 + \underline{c}_2^\dagger \underline{B}\, \underline{c}_1 = R^{\mathrm{I}} + R^{\mathrm{II}}, \tag{3}$$

where $\chi_1 \chi_2$ are the molecular wave functions, $\vec{r}$ denotes the set of electronic coordinates, $\underline{B}$ the matrix of d/dR, and $\underline{S}$ the overlap matrix, corresponding to the basic configurations used to expand χ_1 and χ_2; $\underline{c}_1$ and $\underline{c}_2$ are the expansion coefficients. When the origin of electronic coordinates is changed from a position $\vec{\mathcal{O}}$ to $\vec{\mathcal{O}} + \vec{R}\delta$, the term R^{II} in Eq. (3) varies:

$$R^{\mathrm{II}\prime} = R^{\mathrm{II}} + \delta \underline{c}_2^\dagger \underline{\Gamma}\, \underline{c}_1 . \tag{4}$$

The corresponding change in the L_y matrix element is

$$\langle \chi_2 | iL_y)_{\vec{r}\,'} | \chi_1 \rangle = \langle \chi_2 | iL_y)_{\vec{r}} | \chi_1 \rangle + \delta \underline{c}_2^\dagger \underline{\Omega}\, \underline{c}_1 R . \tag{5}$$

In expressions (4) and (5), $-i\underline{\Gamma}$ and $-i\underline{\Omega}$ are the matrices of the electronic linear momentum along the z and x axis, respectively.

We have drawn in Fig. 2 the dynamical couplings which are involved in our three-state calculations for the singlet and triplet subsystems, choosing the proton and the center of mass as two possible origins of electronic coordinates.

Let us first consider the radial couplings $\langle 1^{1,3}\Pi | d/dR | 2^{1,3}\Pi \rangle$. For internuclear distances $R < 10$ a.u., the dominant term is R^{II}. This term is due to the variation of the basis set required to describe the change in the wave functions that take place in going from $R \simeq 0$ to the molecular region. This change is the same for singlet and triplet states, and, accordingly, the values of R^{II} are very similar. It will be noticed that $R^{\mathrm{II}} \not\to 0$ at the united atom limit; in fact, the exact limit can be easily estimated, and seen to agree with our result.

For internuclear distances $R > 10$ a.u., R^{I} dominates the radial couplings; it presents a maximum at $R \simeq 15$ a.u. due to a delocalization (or Demkov) process. Taking into account the correlation limits (see Fig. 1)

$$\begin{aligned} |1\,^1\Pi\rangle &\xrightarrow[R\to\infty]{} \mathrm{He}^+(1s) + \mathrm{H}(2p), \\ |2\,^1\Pi\rangle &\xrightarrow[R\to\infty]{} \mathrm{He}(1s2p\,^1P) + \mathrm{H}^+, \\ |1\,^3\Pi\rangle &\xrightarrow[R\to\infty]{} \mathrm{He}(1s2p\,^3P) + \mathrm{H}^+, \\ |2\,^3\Pi\rangle &\xrightarrow[R\to\infty]{} \mathrm{He}^+(1s) + \mathrm{H}(2p), \end{aligned} \tag{6}$$

we can explain the behavior of the radial couplings by using the well known two-state model as follows:

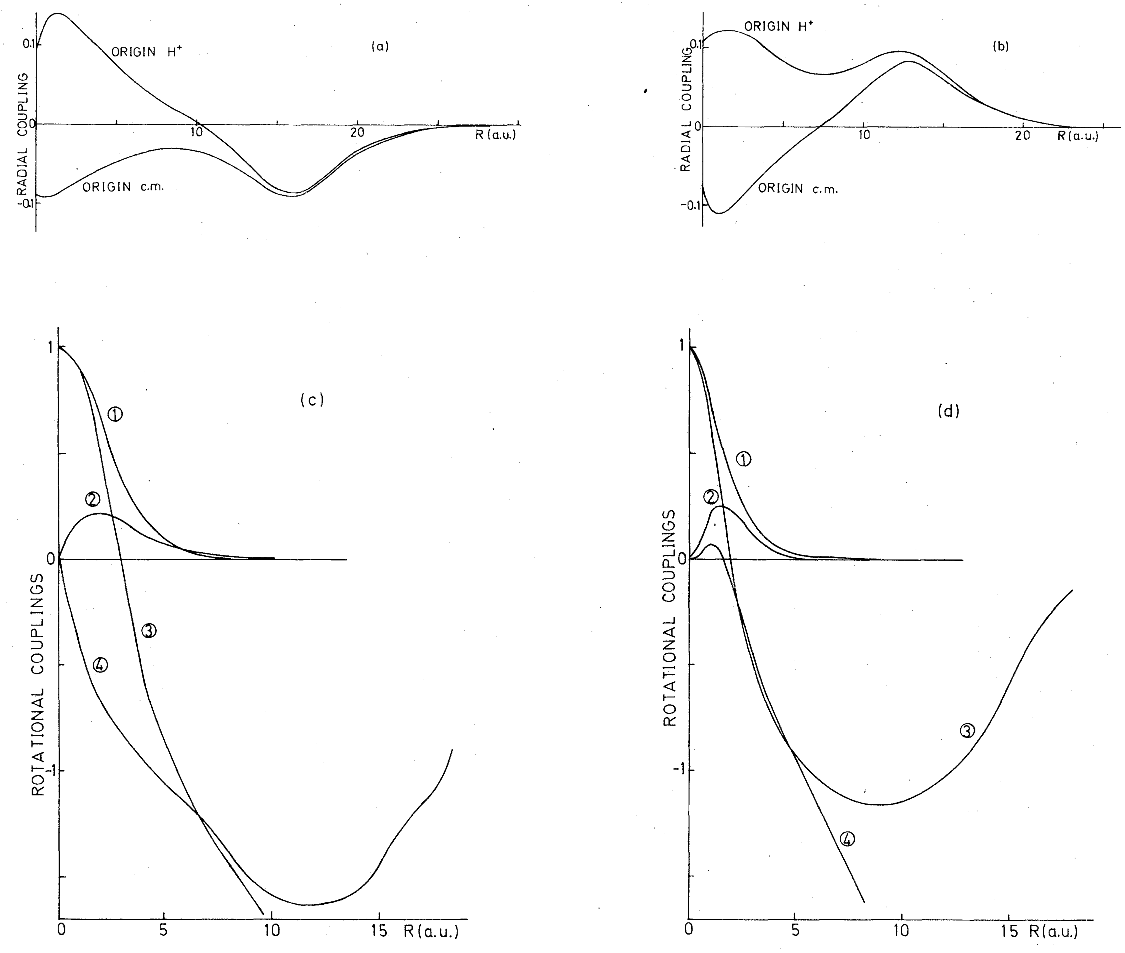

FIG. 2. Radial couplings for the singlet (a) and triplet (b) subsystems. Rotational couplings for the singlet (c): (1) $2\,^1\Sigma$-$1\,^1\Pi$ coupling, origin on the proton; (2) $2\,^1\Sigma$-$2\,^1\Pi$ coupling, origin on the proton; (3) $2\,^1\Sigma$-$1\,^1\Pi$ coupling, origin on the center of mass; (4) $2\,^1\Sigma$-$2\,^1\Pi$ coupling, origin on the center of mass. Rotational couplings for the triplet (d) subsystems: (1) $1\,^3\Sigma$-$1\,^3\Pi$ coupling, origin on the proton; (2) $1\,^3\Sigma$-$2\,^3\Pi$ coupling, origin on the proton; (3) $1\,^3\Sigma$-$1\,^3\Pi$ coupling, origin on the center of mass; (4) $1\,^3\Sigma$-$2\,^3\Pi$ coupling, origin on the center of mass.

$$\begin{aligned} &\chi_1 \simeq \cos\theta\phi_1 - \sin\theta\phi_2, \quad \chi_1' \simeq \sin\theta'\phi_1' + \cos\theta'\phi_2', \\ &\chi_2 \simeq \sin\theta\phi_1 + \cos\theta\phi_2, \quad \chi_2' \simeq -\cos\theta'\phi_1' + \sin\theta'\phi_2', \end{aligned} \tag{7}$$

for the singlet $\{\chi_1, \chi_2\}$ and triplet $\{\chi_1', \chi_2'\}$ Π states. The functions $\phi_{1,2}$, $\phi_{1,2}'$ represent diabatic states which at long distances are quasiatomic in character:

$$\begin{aligned} &\phi_1 \xrightarrow[R\to\infty]{} \phi_H, \quad \phi_1' \xrightarrow[R\to\infty]{} \phi_H', \\ &\phi_2 \xrightarrow[R\to\infty]{} \phi_{He}, \quad \phi_2' \xrightarrow[R\to\infty]{} \phi_{He}'. \end{aligned} \tag{8}$$

Since $\chi_{1,2} \xrightarrow[R\to\infty]{} \phi_{1,2}$ and $\chi_{1,2}' \xrightarrow[R\to\infty]{} \phi_{2,1}'$, Eq. (7) yields $\theta(\infty) = \theta'(\infty) = 0$.

According to Smith's definition, the transformation angles θ, θ' are given by integration of the radial couplings $R^{\rm I} + R^{\rm II}$, but the origin dependence of $R^{\rm II}$ precludes a univocal definition of θ, θ', hence of the diabatic states $\phi_{1,2}$, $\phi_{1,2}'$ at short distances.

For large distances $R^{\rm II} \simeq 0$, and one can just eliminate $R^{\rm I}$. In this case, as we have

$$\begin{aligned} &\chi_1 \xrightarrow[R\to 0]{} \phi_1 + \phi_2, \quad \chi_1' \xrightarrow[R\to 0]{} \phi_1' + \phi_2', \\ &\chi_2 \xrightarrow[R\to 0]{} -\phi_1 + \phi_2, \quad \chi_2' \xrightarrow[R\to 0]{} -\phi_1' + \phi_2'. \end{aligned} \tag{9}$$

According to Eq. (7), $\theta'(0) \simeq -\theta(0) \simeq \pi/4$, and it is clear that $-\theta \simeq \theta'$ varies from $\pi/4$ to 0 as R goes from 0 to ∞. Hence, we have from Eq. (7)

$$R'^{\rm I} \simeq -R^{\rm I} \simeq \frac{d\theta}{dR}\,. \tag{10}$$

The transformation angles obtained by eliminating $R^{\rm I}$ are presented in Fig. 3; the corresponding diabatic states have energies which are parallel for $R > 10$ a.u., and are coupled exponentially in the most orthodox manner.[14]

For smaller distances, the situation is very different as R^{II} dominates, and we have explained that

$$\left\langle \chi_1' \left| \frac{d}{dR} \right| \chi_2' \right\rangle \simeq \left\langle \chi_1 \left| \frac{d}{dR} \right| \chi_2 \right\rangle . \tag{11}$$

Accordingly, if the transformation angles are calculated by integration of $R^{\text{I}} + R^{\text{II}}$, we have the values presented in Fig. 3 for two extreme choices of origin: the proton and the He nucleus. For the former, $\int_{-\infty}^{R} R^{\text{II}}$ (singlet) has opposite sign to $\int_{-\infty}^{R} R^{\text{I}}$ (singlet), while $\int_{-\infty}^{R} R^{\text{II}}$ (triplet) has the same sign as $\int_{-\infty}^{R} R^{\text{I}}$ (triplet), with the result that $\theta \xrightarrow[R\to 0]{} 0$, $\theta' \xrightarrow[R\to 0]{} \pi/2$. For the latter choice the contribution from R^{I} and R^{II} have the same sign in the singlet case and opposite signs in the triplet case, and $-\theta \xrightarrow[R\to 0]{} \pi/2$, $\theta' \xrightarrow[R\to 0]{} 0$. Obviously, for other choices of origin, the situation is intermediate.

We have explained in detail these features of the radial couplings because they will be useful in the interpretation of the secondary mechanism of the collision process.

Let us now consider the rotational couplings [see Fig. 2(b)]. Besides their dramatic origin dependence, an important property is that two matrix elements

$$\langle 2^1\Sigma \,|\, iL_y \,|\, 1^1\Pi\rangle \text{ and } \langle 1^3\Sigma \,|\, iL_y \,|\, 2^3\Pi\rangle$$

increase linearly with R at large distances (with the consequence that the corresponding rotational couplings decrease like R^{-1}) unless one chooses the proton as origin of electronic coordinates. This is so because the x component of the transition dipole moments

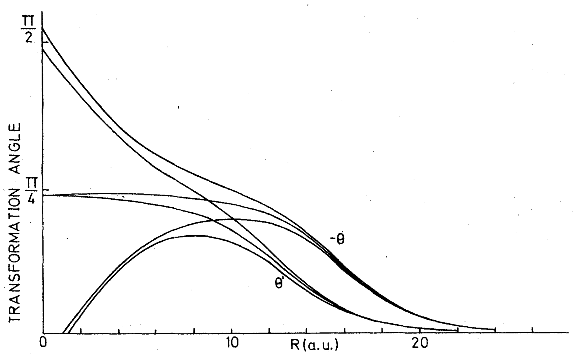

FIG. 3. Transformation angles obtained by eliminating the radial coupling between $1^1\Pi$-$2^1\Pi(\theta)$ and $1^3\Pi$-$2^3\Pi(\theta')$ (see Eq. 5). Elimination of R^{I} (Eq. 3) yields the values $-\theta(0) \simeq \theta'(0) \simeq \pi/4$. Elimination of $R^{\text{I}} + R^{\text{II}}$ (Eq. 3) yields the values $\theta(0) \simeq 0$ and $\theta'(0) \simeq \pi/2$ with the origin of electronic coordinates on the proton, and $\theta(0) \simeq -\pi/2$ and $\theta'(0) \simeq 0$ with the origin on the He nucleus.

$$\langle 2^1\Sigma \,|\, \mu_x \,|\, 1^1\Pi\rangle, \text{ and } \langle 1^3\Sigma \,|\, \mu_x \,|\, 2^3\Pi\rangle$$

do not vanish as $R \to \infty$.

This poses a problem in the integration of the coupled equations, as there is no obvious reason to prefer the proton as the origin of electronic coordinates (a preferred origin may be argued for in the simpler case of excitation[15,16]). We have thus performed calculations with the proton and the center of mass as origins of electronic coordinates. As will be shown in the Appendix, the integration of the slowly decreasing rotational couplings is full of pitfalls, but may be performed safely if one is careful.

III. RESULTS AND DISCUSSION

Total cross sections for reactions (1) and (2) have been calculated in an impact parameter formalism, using the molecular energies and couplings presented in the previous Section.

The set of coupled equations

$$\begin{aligned}
\frac{da_0}{dt} &= -\frac{bv}{R^2}\langle \chi_0 | iL_y | \chi_1\rangle \exp\left(-i\int^r (E_1 - E_0)dr\right)a_1 \\
&\quad - \frac{bv}{R^2}\langle \chi_0 | iL_y | \chi_2\rangle \exp\left(-i\int^r (E_2 - E_0)dr\right)a_2 \,, \\
\frac{da_1}{dt} &= -\frac{bv}{R^2}\langle \chi_1 | iL_y | \chi_0\rangle \exp\left(-i\int^r (E_0 - E_1)dr\right)a_0 \\
&\quad - \frac{Zv}{R}\left\langle \chi_1 \left| \frac{d}{dR} \right| \chi_2 \right\rangle \exp\left(-i\int^r (E_2 - E_1)dr\right)a_2 \,, \\
\frac{da_2}{dt} &= -\frac{bv}{R^2}\left\langle \chi_2 \left| iL_y \right| \chi_0 \right\rangle \exp\left(-i\int^r (E_0 - E_2)dr\right)a_0 \\
&\quad - \frac{Zv}{R}\left\langle \chi_2 \left| \frac{d}{dR} \right| \chi_1 \right\rangle \exp\left(-i\int^r (E_1 - E_2)dr\right)a_1
\end{aligned} \tag{12}$$

was solved numerically using the program PAMPA[9] with the semianalytical modification proposed in the Appendix to integrate correctly the slowly decreasing rotational couplings. In (12) the wave functions χ_n correlate, in the CI region, to

$$\{|2^1\Sigma\rangle, |1^3\Sigma\rangle\}, \quad |1^{1,3}\Pi\rangle, \text{and } |2^{1,3}\Pi\rangle$$

for $n = 0, 1, 2$, respectively (see Fig. 1); $\vec{b}$ is the impact parameter and Z the nuclear coordinate. We notice that the states χ_0 (singlet and triplet) cross diabatically the $1s\sigma_g$ $2s\sigma_g$ states (Fig. 1); for the range of nuclear velocities considered here, we did not include the (very small) electronic coupling between these diabatic states.

Our resulting cross sections are plotted in Figs. 4(a) and 4(b) for reactions (1) and (2), respectively, together with the experimental data.[1-4] We have not drawn lines through this data because

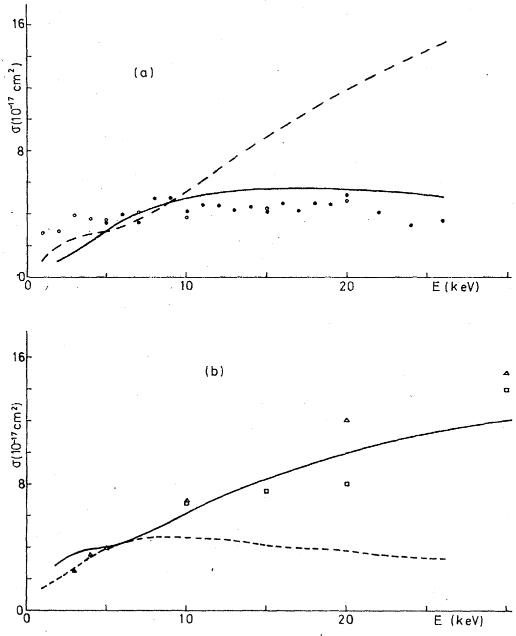

FIG. 4. Total cross section for reaction $^4He^+(1s) + H(1s) \rightarrow {}^4He^+(1s) + H(2p)$(a) and for $^4He^+(1s) + H(1s) \rightarrow {}^4He(1s2p\,{}^{1,3}P) + H^+$(b). Our results: —— origin on the center of mass, ---- origin on the proton. Experimental results: ○ Ref. 1, ● Ref. 2, □ Ref. 3, △ Ref. 4.

we think that the resulting oscillations would be misleading, unless one takes into account the uncertainties of the data (we have not included the error bars for the sake of clarity). Analogously, there are very slight oscillations in our results which we have smoothed out because they fell within the numerical errors of our calculation; as we shall show in the Appendix, any error in the integration of the slowly decreasing rotational couplings produces oscillations in the resulting cross sections.

For incident energies $E < 8$ keV (relative nuclear velocities $v < 0.3$ a.u.) the cross sections calculated with the origin placed on the proton agree better with experiment than all other reasonable choices. For $E > 8$ keV, those results depart rapidly from the experimental points, while the cross sections calculated with the origin at the center of mass agree well with the experimental data (taking the error bars into account).

Our findings may be readily explained by the mechanism invoked in the previous section. The population of the Π states occurs mainly through $2\,{}^1\Sigma - 1^1\Pi$ and $1^3\Sigma - 1^3\Pi$ rotational couplings at short distances. The rotational couplings between the entrance channels and the $2\,{}^{1,3}\Pi$ states do not have a strong influence in the process, and only modify the secondary mechanism provided by the radial couplings. An explanation is that at large distances the greatest of these couplings are those which decrease like R^{-1}, and we have shown that, if properly treated (see the Appendix), the influence of these couplings is small. The same reasoning applies to other states which are not coupled directly to the entrance channel, and which were therefore not included in the calculation. The introduction of states such as $4^1\Sigma$ and $4^3\Sigma$ which correlate to $He^+(1s) + H(2p)$ would only slightly modify our results, but considerably complicate the numerical treatment because these states present a nonvanishing coupling with the entrance channel at infinite distances. It may be pointed out, however, that these couplings will become very important in the region of nuclear velocities much higher than those considered here,[3,4] but in that region the molecular approach itself is questionable.

As mentioned in the previous section, the branching ratio between reactions (1) and (2) is governed by the radial couplings between the Π states (secondary mechanism). At high enough energies the system is well represented by the diabatic wave functions $\phi_{1,2}, \phi'_{1,2}$ of Eq. (5), because the molecular energies keep close to one another down to very small distances.

For $R \simeq 0$, the only Π channels appreciably populated are χ_1, χ'_1. Choosing the proton as the origin of electronic coordinates we find from Fig. 3 that, for $R \simeq 0$, $\chi_1 \simeq \phi_1$ and $\chi'_1 \simeq \phi'_1$. The limits (8) then indicate that reaction (1) should be favored with respect to reaction (2), and the trend of our results (Fig. 4) confirms this. Choosing the center of mass as origin we have a situation which is not so extreme as that depicted in Fig. 3 for the He nucleus, and approximately, for $R \simeq 0$, $\chi_1 \simeq -\phi_2, \chi'_1 \simeq \phi'_2$. Equation (8) then indicates that when diabatic behavior is dominant, reaction (2) is preferred, and that is what we obtain and is observed experimentally at high velocities, up to a point where radial transitions to higher excited channels begin to dominate (see above). Choosing the center of charge as origin yields results which are intermediate between those of the proton and the center of mass. The agreement between theory and experiment may be increased by an appropriate choice of origin of electronic coordinates; we have not pursued this line for obvious reasons. From the results presented in Fig. 4, one might at first sight conclude that the "correct" origin of electronic coordinates is the center of mass, or a point close to it. The question of whether there is a "proper" choice of origin has been considered by many authors, because if such a choice existed one could then avoid the use of translation factors. In particular, this point has been studied in detail by Riera and Salin,[17] who concluded that a preferred origin does not exist in general, and that the so-called momentum-transfer problem has no general solution within the standard molecular formalism. Hence, if the experimental data shown in Fig. 4 were unknown, and one was asked to predict the outcome of reactions (1) and (2), there is no specific reason to favor the center of mass as origin of electronic coordinates when solving the set of equations (12).

We summarize the conclusions of our study. As stated in the Introduction, the momentum-transfer problem has two unwelcome consequences for reactions (1) and (2): (a) some rotational couplings decrease like R^{-1} at large internuclear distances, and (b) at high velocities, the cross sections depend strongly on the choice of origin of electronic coordinates.

Contrary to what is often assumed, consequence (a) is of little importance, provided one is careful in attacking the numerical integration of the coupled equations. On the contrary, consequence (b) is a crucial problem; to solve it, translation factors are required. Work is in progress at our laboratory to include these factors in the treatment, using a basis set of traveling Gaussian orbitals,[17] and the present work may be viewed as a preliminary treatment of the problem. It is more than this, however, because even the treatment with translation factors is not straightforward, and this is an important problem which is not restricted to reactions (1) and (2). The origin dependence of our cross sections hinges on the behavior of the radial couplings for *short* internuclear distances, and the discussion as to which translation factors to choose for these distances has not reached a definite conclusion. For example, an intuitive argument often used in this respect runs as follows: The momentum-transfer problem is due to the failure of a truncated molecular expansion to fulfill the boundary conditions of the collision problem, and then it is a long distance problem [i.e., like (a) above, or the analogous case of constant radial couplings at infinity]; for these distances the Bates-McCarroll factors are appropriate, and a cutoff may be introduced in the exponent of the translation factors in order to revert to the usual molecular treatment at short distances. This would be an ideal situation, but unfortunately our example shows how this argument can be fallacious: An *ad hoc* cutoff in the translation factors would yield results practically identical to those of the present paper, and just as origin dependent.

It is precisely the difficulty in applying the more "exact" treatment with translation factors which shows the importance of testing explicitly the limitations of the molecular model, as we have done in this work, in addition to pointing out its assets: It is obviously no coincidence that, once the center of mass is chosen as origin, the cross sections of both reactions (1) and (2) can be well reproduced with a very simple mechanism, and up to high nuclear velocities.

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APPENDIX

We consider the integration of a slowly (R^{-1}) decreasing rotational coupling between two molecular wave functions,

$$\frac{bv}{R^2}\langle \chi_1 | iL_y | \chi_2 \rangle \underset{R\to\infty}{\sim} \frac{v\lambda b}{R} = \frac{v\lambda b}{(b^2+z^2)^{1/2}}\,, \tag{A1}$$

where b is the impact parameter, and λ is a constant. In the region of internuclear distances where the energy difference ΔE is approximately constant, and this coupling takes its asymptotic form, the system of coupled equations is

$$\begin{aligned} \frac{da_1}{dz} &= \lambda b (b^2+z^2)^{-1/2} a_2 \exp\left(\frac{i\Delta E z}{v}\right), \\ \frac{da_2}{dz} &= -\lambda b (b^2+z^2)^{-1/2} a_1 \exp\left(\frac{-i\Delta E z}{v}\right). \end{aligned} \tag{A2}$$

The basic difficulty in solving (A2) (hence, the exact coupled equations for all R) is that the initial condition $a_i(-\infty) = \delta_i$, must be introduced at a point $-z_M$ where the coupling is negligible. It is clear then that z_M must increase with b; for large impact parameters this becomes prohibitive because of the increase in computer time and accumulative round-off errors.

When λ is sufficiently small in (A2), a perturbative solution is appropriate:

$$a_2(\infty) \simeq -\int_{-\infty}^{\infty} \frac{\lambda b}{(b^2+z^2)^{1/2}}\, e^{-i\Delta E z/v} dz = -2b\lambda K_0\left(\frac{b\,\Delta E}{v}\right) \underset{b\to\infty}{\sim} -\left(\frac{2bv}{\Delta E}\right)^{1/2} \lambda e^{-b\Delta E/v}\,, \tag{A3}$$

where K_0 is a modified Bessel function.[18] According to Eq. (A3) the contribution of trajectories with large impact parameters to the cross section is entirely negligible. Explicit numerical tests showed that this exponential behavior is quite general, but also that λ had to be very small (<0.01 a.u.) for the specific perturbation solution (A3) to be sufficiently accurate. What happens is that, even if a_1 is very close to one in modulus, its phase changes with time, thus violating the basic assumption of perturbation theory.

We have not been able to solve the system (A2) in closed form in terms of well known functions. However, sufficiently accurate solutions may be used for values of b and z such that

$$\left|\frac{z}{b^2+z^2}\right| \ll 1 . \tag{A4}$$

We notice that the higher the value of b, the larger the domain of z for which (A4) is valid.

To deduce an approximate solution of (A2), one integrates this system on the formal assumption that the coupling varies little with z, much as the potential is assumed to do in the JWKB method. More specifically, we assume

$$\left|\frac{d}{dz}\ln\frac{\lambda b}{(b^2+z^2)^{1/2}}\right| \ll 1 , \tag{A5}$$

which is easily shown to be entirely equivalent to (A4). Defining

$$\omega_1 = \frac{\Delta E}{2v} + \frac{1}{2}\left(\frac{\Delta E^2}{v^2} + \frac{4\lambda^2 b^2}{b^2+z^2}\right)^{1/2} , \quad \omega_2 = \frac{\Delta E}{v} - \omega_1 \tag{A6}$$

one obtains the approximate solutions

$$\begin{aligned} a_1(z) &\simeq \omega_1\left(\omega_1^2 + \frac{\lambda^2 b^2}{b^2+z^2}\right)^{-1/2} \exp(i\omega_2 z) , \\ a_2(z) &\simeq -i\lambda b\left(\omega_1^2 + \frac{\lambda^2 b^2}{b^2+z^2}\right)^{-1/2} \exp(-i\omega_1 z) \end{aligned} \tag{A7}$$

for the initial condition $a_i(-\infty) = \delta_{i1}$. The phase $\exp(i\omega_2 z)$ oscillates slowly, while $|a_1|$ is always close to unity, as mentioned above. Explicit calculations showed the excellent degree of approximation provided by these simple expressions for a_1 and a_2, for all cases we studied. For large b, condition (A4) is fulfilled for all z; letting $z \to \infty$, we obtain $a_1(\infty) = 1$, $a_2(\infty) = 0$, showing again the steep decrease of $a_2(\infty)$ with b, and confirming that the integration of the slowly decreasing coupling can be safely neglected for b high enough that the energy difference ΔE is constant, and Eq. (A1) is fulfilled.

This does not solve the problem completely, however, as for smaller values of b we would still have to integrate over very large domains of z. The interest of the approximate solutions (A7) is that they are also valid for the exact coupled equations, for any impact parameter, provided that z is large enough that ΔE is practically constant and (A1) and (A4) are fulfilled. Therefore, we may use a semianalytical approach, as follows.

In the wings of the integration region $(-\infty, -z_M)$ and $(+z_M, +\infty)$, we use solutions of the form (A7), and in the region $(-z_M, +z_M)$ we integrate numerically. The point z_M must be chosen such that (A1) and (A4), or (A5), are fulfilled; this last condition means that the relative variation of the coupling is small, which is less restrictive than asking for the coupling itself to be small. The initial values for that numerical procedure are given by Eq. (A7); suppose its final values are $a_1(z_M) = \alpha, a_2(z_M) = \beta$. Using these as starting values, our analytical approximation yields for the transition probability amplitude, with $\hat{\omega}_{1,2} \equiv \omega_{1,2}(z_M)$,

$$\begin{aligned} a_2(\infty) \simeq &\left(\frac{i\alpha\lambda b}{(b^2+z_M^2)^{1/2}} e^{-i\hat{\omega}_1 z_M} + \hat{\omega}_1 \beta e^{i\hat{\omega}_2 z_M}\right) \\ &\times\left(\hat{\omega}_1^2 + \frac{\lambda^2 b^2}{b^2+z_M^2}\right)^{-1/2} . \end{aligned} \tag{A8}$$

This semianalytical procedure can be easily introduced in the numerical solution[9] of the system of coupled equations. Moreover, it may also be used to point out the pitfalls of ignoring the peculiarities of the rotational coupling (A1), and integrating for the range $z = -z_M$ (initial condition) to $z = +z_M$ for all values of the impact parameter, as is usually done for couplings which decrease faster than R^{-1} (Ref. 9). One then finds, instead of (A8),

$$\begin{aligned} a_2(z_M) \simeq\ & 2\hat{\omega}_1 \lambda b (z_M^2 + b^2)^{-1/2}\left(\hat{\omega}_1^2 + \frac{\lambda^2 b^2}{z_M^2 + b^2}\right)^{-1} \\ &\times \sin[(\hat{\omega}_2 - \hat{\omega}_1) z_M] . \end{aligned} \tag{A9}$$

If one integrates $\int_0^{b_{\max}} |a_2(z_M)|^2 b\,db$, the resulting cross section will present strong unphysical oscillations as a function of v; see Eqs. (A6) and (A9). Finally, if we let $b_{\max} \to \infty$ for z_M fixed, the resulting cross section diverges, as $a_2(z_M)$ of Eq. (A9) does not vanish in this limit. Clearly, it is safer to ignore trajectories with large impact parameters in this case than to attempt to integrate them partially. However, without a special treatment of the asymptotic regions, such as presented here, it is difficult to know *a priori* where one can stop the integration over the impact parameter.

Besides, one may also point out that in the calculation of inelastic cross sections, the relative precision of the integration procedure must be increased for large impact parameters, because of the factor b in the expression for the total cross section.

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