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COLLISIONAL QUENCHING OF METASTABLE
HYDROGEN ATOMS*

by

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ABSTRACT

Quenching of metastable hydrogen atoms by low energy collisions with atoms and molecules is considered, the actual process being $H(2s) + X \rightarrow H(2p) + X$. The Born approximation, with long-range multipole-multipole interactions, is used to describe collisions of $H(2s)$ with molecules, and simple formulas for the cross section result. Collisions with spherically symmetric species (i.e., rare gas atoms) are treated in the adiabatic approximation, and the process is seen to be formally identical to symmetric charge transfer. Numerical results for collisional quenching by helium, based on accurately computed potential curves, are presented.

I. INTRODUCTION.

Unperturbed hydrogen atoms in the 2s state have a natural lifetime of $\sim \frac{1}{7}$ second, the decay being by two-photon spontaneous emission¹. The 2p states, however, which are nearly degenerate with the 2s state (within 1 cm^{-1}), are connected to the 1s ground state by ordinary dipole selection rules and have a radiative lifetime of $\sim 10^{-9}$ seconds. Unlike other atomic and molecular metastable species, therefore, 2s hydrogen atoms are "fragile", for external perturbations induce $2s \rightarrow 2p$ transitions quite efficiently; this is not so readily possible with other metastable species because of a much larger energy separation from other (short-lived) states.

This paper investigates the destruction, or quenching, of 2s hydrogen atoms by low energy collisions with neutral atoms and molecules; collisional quenching by charged particles has been treated by Purcell² and Seaton³. Quenching by neutrals has also been considered recently by Gersten⁴ and Byron and Gersten⁵. More specifically, the process

is treated, and quenching actually takes place by subsequent spontaneous emission of the 2p states⁶. Although there is the possibility of quenching by direct transitions

or by other indirect paths

the cross sections for such non-resonant processes⁷ at thermal energy is expected to be small, no more than $\sim 1 \text{ \AA}^2$; as shall

be seen, the cross section for Eq.(1) is usually much larger than this.

Section II considers collision partners with permanent multipole moments (i.e., molecules). Because of the long-range nature of the interaction, a Born approximation treatment is possible and simple analytic formulas for the quenching cross sections result. Section III treats the case of a collision partner with no permanent multipole moments (i.e., a rare gas atom), and Section IV presents results for the $\text{He} + \text{H}(2s)$ collision based on accurately computed potential curves.

II. COLLISION PARTNERS WITH PERMANENT MULTIPOLE MOMENTS.

Consider the collision process in Eq.(1) where X is a molecule whose first non-zero multipole moment is of order L (L=1 is a dipole, L=2 is a quadrupole, etc.). For the collision only channels in which hydrogen is in 2s and 2p states are considered, and X is in its ground electronic state (but in all possible rotational states). As interaction potential we take the standard long-range expression⁸ (a sum of multipole-multipole interactions) and apply the Born approximation. In this approximation the S-matrix is related simply to matrix elements of the interaction potential

$$\begin{aligned} & \langle pM, j_2 M_2, \ell_2 m_2 | S | s, j_1 M_1, \ell_1 m_1 \rangle \\ &= -2i \frac{2m}{\hbar^2} \langle pM, j_2 M_2, \ell_2 m_2 | V | s, j_1 M_1, \ell_1 m_1 \rangle \end{aligned} \quad (3)$$

where ℓ_1, m_1 (ℓ_2, m_2) are the initial (final) orbital angular momentum of relative translation and its projection on a space-fixed axis; j_1, M_1 (j_2, M_2) are the initial (final) rotational angular momentum of X and its projection; s is the 2s state of hydrogen, and pM (M=0, ±1) are the three components of the 2p state; m is the reduced mass of H and X.

Eq.(3) takes on a relatively simple form because the product of the 2s and 2p hydrogenic states has dipole symmetry-- thus the integral over the electronic degrees of freedom of hydrogen selects only the dipole term on the hydrogen center. The (diagonal) matrix element over the electronic degrees of freedom of X selects, of course, the Lth moment on that center. Thus the matrix element of the potential in Eq.(3) looks just

like the classical interaction between a permanent dipole on the hydrogen center with the L-pole on the X center; this gives

$$\begin{aligned} \langle pM, j_2 M_2, \ell_2 m_2 | S | s, j_1 M_1, \ell_1 m_1 \rangle &= -2i \left(\frac{2m}{h} \right) \mu_H q_L (4\pi)^{\frac{3}{2}} \\ &\left[\frac{L+1}{3(2L+3)} \right]^{\frac{1}{2}} \langle \ell_2 | R^{-L-2} | \ell_1 \rangle \sum_{m_1', m_2'} C(1, L, L+1; m_1' m_2') \\ &\langle 1M | 1m_1' | 00 \rangle \langle j_2 M_2 | L m_2' | j_1 M_1 \rangle \langle \ell_1 m_1 | L+1, m_1' + m_2' | \ell_2 m_2 \rangle, \quad (4) \end{aligned}$$

where the radial integral is

$$\langle \ell_2 | R^{-S} | \ell_1 \rangle = k \int_0^\infty dR R^2 j_{\ell_2}(kR) R^{-S} j_{\ell_1}(kR), \quad (5)$$

q_L is the L-pole moment⁹ of X, and μ_H is the transition dipole of $2s \rightarrow 2p$

$$\mu_H = \langle 2s | \mu_z | 2p_z \rangle = 3 e a_0; \quad (6)$$

the matrix elements in the summation of Eq.(4) are integrals over three spherical harmonics and are thus given in terms of Clebsch -Gordan coefficients¹⁰. [Note that the initial and final translational energy have been taken as equal, the change in rotational energy of X being neglected.]

From the above S-matrix the net probability for the $2s \rightarrow 2p$ transition is constructed by summing the square modulus of S over M, j_2, M_2, ℓ_2 , and m_2 , and averaging over M_1 . Carrying out this procedure is tedious but straight-forward; the calculation is parallel to that of Cross and Gordon¹¹ for the dipole-dipole interaction, and the result one obtains is independent of m_1 and j_1 :

$$P(b) = \left(\frac{m \mu_H q_L}{\hbar^2} \right)^2 \frac{16}{3} (L+1) \sum_{\ell_2} C(\ell_1, L+1, \ell_2; 0,0)^2 \langle \ell_2 | R^{-L-2} | \ell_1 \rangle^2, \quad (7)$$

where $b = (\ell_1 + \frac{1}{2})/k$ is the incident impact parameter. Under the usual semiclassical conditions ($\ell_1, \ell_2 \gg 1$, $|\ell_1 - \ell_2| \ll \ell_1$) one has

$$\langle \ell_2 | R^{-s} | \ell_1 \rangle = \frac{\pi}{2^s} \frac{1}{k b^{s-1}} \left(\frac{s-2}{s+\ell_2-\ell_1} - 1 \right) \quad (8)$$

$$C(\ell_1, \ell_2; 0,0)^2 = 4^{-\lambda} \left(\frac{\lambda-\ell_2+\ell_1}{2} \right) \left(\frac{\lambda+\ell_2-\ell_1}{2} \right), \quad (9)$$

so that Eq.(7) becomes

$$P(b) = A_L \left(\frac{\mu_H q_L}{\hbar v} \right)^2 b^{-2L-2}, \quad (10)$$

where v is the incident velocity, and the constant A_L is

$$A_L = \frac{\pi^2 (L+1)}{3 \cdot 4^{2L+1}} \sum_n \left(\frac{L}{2} \right)^2 \left(\frac{L+1-n}{2} \right) \left(\frac{L+1+n}{2} \right), \quad (11)$$

and the sum is over values $n = L+1, L-1, L-3, \dots, -L-1$; e.g.,

$$A_0 = \frac{4}{3} \quad (12a)$$

$$A_1 = \frac{8}{9} \quad (12b)$$

$$A_2 = \frac{32}{45} \quad (12c)$$

$$A_3 = \frac{64}{105} \quad (12d)$$

From the transition probability in Eq.(10) one constructs the cross section in the usual way

$$\sigma(v) = 2\pi \int_0^\infty db \, b \, P(b); \quad (13)$$

since $P(b)$ exceeds 1 for small b , one cuts off the integration in this region in the spirit of the Massey-Mohr approximation¹². [Because of the use of the long-range potential and the Born approximation, Eq.(10) is actually only valid for large b .] The transition probability in Eq.(10) is the sum of the transition probability from the 2s state of hydrogen to all three 2p states; since only four states of hydrogen are considered and since the $2s \rightarrow 2s$ transition is zero via the dipole-L-pole interaction, it is clear that the value of b at which the integration should be cut off is that value for which $P = 1$; for all $b < B$, one takes $P(b) \equiv 1$. Thus

$$\sigma(v) = \pi B^2 + 2\pi \int_B^{\infty} db \, b \, P(b) , \quad (14)$$

where B is determined by

$$P(B) = 1, \quad (15)$$

and with Eq.(10) this becomes

$$\sigma(v) = \pi B^2 (1+1/L)$$

or

$$\sigma(v) = C_L \left(\frac{\mu_H q_L}{\hbar v} \right)^{2/L+1}, \quad (16)$$

where

$$C_L = \pi (1+1/L) A_L^{1/L+1}, \quad (17)$$

with A_L as in Eq.(11); e.g.,

$$C_1 = \frac{4\pi}{3} \sqrt{2} = 5.924 \quad (18a)$$

$$C_2 = \frac{3\pi}{2} \left(\frac{32}{45} \right)^{\frac{1}{3}} = 4.206 \quad (18b)$$

$$C_3 = \frac{4\pi}{3} \left(\frac{64}{105} \right)^{\frac{1}{4}} = 3.701 . \quad (18c)$$

Eqs. (16)-(18) are the final result. A similar expression has been derived by Gersten⁴ using a time-dependent approach, but constants different from C_L above were obtained; in particular, the coefficients for $L = 1$ and 2 are factors of $3^{\frac{1}{2}}$ and $3^{\frac{1}{3}}$ greater than those in Eq. (18). This is somewhat surprising, since Cross and Gordan¹¹ found that the Born approximation and the time-dependent, straight-line trajectory approach gave identical results. One can readily verify that the $L = 1, 2$ coefficients from Eqs. (17), (18) are the ones obtained for ordinary dipole-dipole¹³ and dipole-quadrupole¹⁴ scattering.

Table I shows the cross sections from Eq. (16) for quenching by several molecules, compared to the results of Fite *et al.*¹⁵; the agreement is quite good. A subsequent Erratum¹⁶, however, indicated that the experimental values should be increased by 50%. Still later work¹⁷ has shown that the assumptions on which the Erratum was based are incorrect; revised values for the quenching cross sections, however, were not given.

Finally, it is interesting to note that quenching by charged particles^{2,3} ($L=0$) can also be treated in the Born approximation, but that here the non-degeneracy of the $2s$ and $2p$ states must be considered--otherwise the second term in Eq. (14) is infinite. The radial matrix element in Eq. (8) is modified to permit $k_1 \neq k_2$; Cross¹⁸ has worked out the necessary expressions, and if $\Delta k/k \ll 1$, one has

$$\langle \ell_2 | R^{-s} | \ell_1 \rangle = \frac{\pi}{2^s} \frac{1}{kb^{s-1}} \frac{z^{s-1} e^{-z/2}}{\Gamma\left(\frac{s+\ell_2-\ell_1}{2}\right)} U\left(\frac{s-\ell_2+\ell_1}{2}, s, z\right), \quad (19)$$

where U is the confluent hypergeometric function¹⁹, and

$$z = 2b\Delta k \approx 2b(\Delta E/\hbar\nu); \quad (20)$$

as $z \rightarrow 0$, one recovers Eq.(8). For large b , therefore, one finds that

$$P(b) \sim e^{-2b\Delta k/b};$$

application of Eqs.(14) and (15), with the more rigorous $P(b)$, gives essentially the same results as Purcell² and Seaton³.

III. QUENCHING BY SPHERICALLY SYMMETRIC COLLISION PARTNERS.

If the collision partner in Eq.(1) has no permanent multipole moments, then the matrix element of the long-range potential vanishes; i.e., the interaction is of shorter range and thus more difficult to deal with in a simple manner. At low collision energies, however, one may take advantage of the 2s-2p degeneracy and the Born-Oppenheimer approximation to simplify the treatment.

For fixed positions of the nuclei there are two Σ Born-Oppenheimer (BO) electronic states and one Π state arising from the ground state of X (a closed shell) and the n=2 states of hydrogen. The initial electronic configuration, X + H(2s), is obviously a Σ state, and for low collision energies it is in the spirit of the BO approximation to assume that the Σ -character of the electronic state is preserved throughout the collision. The validity of neglecting such

Σ - Π transitions has been discussed by a number of workers²⁰, who generally conclude that it is quite well justified. Lawley and Ross²¹ have applied the same approximation to molecular rotational angular momentum (neglect of coupling in their M-representation) and found it to be reasonably satisfactory even here; one expects it to be a much better approximation for the case of electronic angular momentum--i.e., the component of angular momentum of the electron along the relative position vector should "follow" the incoming atom more closely than the rotational angular momentum of a molecule.

Within this approximation, therefore, it is only necessary to consider the two $\sum$ potential curves arising from X and the $n=2$ states of hydrogen. The collision involving these two states can be simplified even further by the following arguments: for very large internuclear distances these BO states correspond to hydrogen being pure 2s and pure 2p. At an internuclear distance R_t ($\sim 19a_0$ for $X \equiv \text{He}$), however, the BO states change quite rapidly (within $1a_0$) to states for which hydrogen is essentially $2s + 2p$ and $2s - 2p$. (In chemical language, the BO states become s-p hybrids.) The character of the electronic states changes quite slowly for all smaller internuclear distances. Because the energy separation of the two states is so small at R_t , it is easy to show (see the Appendix) that the sudden approximation describes this transition region; i.e., hydrogen is initially in the 2s state (and thus one of the BO states), and after passing through the transition region at R_t , it is still in the 2s state. Now, however, the 2s state is not one of the BO states, but a linear combination of them:

$$2s = [(2s+2p)/\sqrt{2} + (2s-2p)/\sqrt{2}]/\sqrt{2}.$$

Since the electronic states vary slowly with internuclear distance for $R < R_t$, one invokes the adiabatic approximation in this region: no transitions occur between the two $\sum$ BO states for $R < R_t$ —i.e., the scattering for $R < R_t$ is pure elastic scattering on the two separate BO potentials.

The above discussion implies that the overall $2s \rightarrow 2p$ transition takes place in the same manner as symmetric charge

transfer²². In this case the initial electronic state has the electron definitely on one center; this electronic state is resolved into g and u components which then scatter independently (since the Hamiltonian preserves g-u symmetry); after collision, the g and u components are converted back into atomic states, and there is a probability that transfer has occurred because of the different scattering phase shift for the g and u potentials. The $2s \rightarrow 2p$ transition discussed above is exactly the same, except that (1) there is no exact symmetry (such as g-u) which prevents transitions between the two BO potentials--the BO approximation itself takes care of this, and (2) the pertinent phase shift difference is that out only to R_t , rather than ∞ . The mathematical details are so similar to symmetric charge transfer that we only give the result: the cross section is given by Eq.(13), where the transition probability is

$$P(b) = \sin^2[\eta_2(b) - \eta_1(b)], \quad (21)$$

where η_1 and η_2 are the phase shifts for the two Σ potential curves; with the WKB approximation for these phase shifts one has

$$\begin{aligned} \Delta\eta(b) &\equiv \eta_2(b) - \eta_1(b) \\ &= \int_{R_2}^{R_t} dR \{ 2\mu[E - V_2(R) - Eb^2/R^2]/\hbar^2 \}^{1/2} \\ &\quad - \int_{R_1}^{R_t} dR \{ 2\mu[E - V_1(R) - Eb^2/R^2]/\hbar^2 \}^{1/2}, \end{aligned} \quad (22)$$

where V_i and R_i are the two BO potentials and the classical turning points thereon. In Eq.(22) the upper limit is R_t ,

and not a value $R \rightarrow \infty$; this is the only difference between the above expressions and those for symmetric charge transfer. In practice, though, R_t is so large that it is effectively infinite.

Rather than evaluate the integral over b in Eq.(13) with the highly oscillatory transition probability of Eq.(21), one may make a Massey-Mohr¹²-like approximation. Thus B is the largest value of impact parameter for which

$$\sin^2[\Delta\eta(b)] = \frac{1}{2}, \quad (23)$$

and then

$$\sigma(v) = \pi B^2 \left(\frac{1}{2}\right) + 2\pi \int_B^\infty db \, b \sin^2[\Delta\eta(b)]. \quad (24)$$

Furthermore, since B will typically be large, one may employ the large b limit of the WKB phase shift, so that Eq.(22) becomes

$$\Delta\eta(b) = -\frac{1}{\hbar v} \int_b^{R_t} dR \, \Delta V(R) (1-b^2/R^2)^{-\frac{1}{2}}, \quad (25)$$

where $\Delta V = V_2 - V_1$ and v is the collision velocity. Most of the results in the next section were computed using Eqs.(23)-(25); some calculations were made using Eqs.(13),(21),(22) and there was less than 10% difference in results of the two procedures.

One may attempt an estimate of $\Delta V(R)$ for large R in order to obtain a simple analytic expression for the cross section, analogous to that of Section II. Although the collision partner has no permanent multipoles, it is polarizable. The simplest approximation for ΔV thus is²³

$$\Delta V(R) \sim 12 \alpha \mu_H q_H R^{-7}, \quad (26)$$

where α is the polarizability of X , and $\mu_H = 3 e a_o$, $q_H = 6 e a_o^2$

are the dipole and quadrupole of a (2s+2p) hydrogen atom. Byron and Gersten⁵ have recently investigated this long-range interaction in detail and find that the interaction is greatly increased when proper account is taken of excited states of hydrogen, giving

$$\Delta V(R) \sim 1020 \alpha R^{-7}. \quad (27)$$

Using Eq.(27) with Eqs.(23)-(25) gives

$$\sigma(v) \approx 18 (\alpha/v)^{\frac{1}{3}}, \quad (28)$$

all quantities being in atomic units. Eq.(28), however, actually does not fit the more accurate treatment of the next section very well; Eq.(27) is just not accurate for sufficiently small R.

IV. EXAMPLE: QUENCHING BY HELIUM ATOMS.

The two $^2\Sigma$ potential curves arising from ground state He and the $n=2$ states of H have been computed by a full configuration interaction (321 configurations!) with an extended basis set: Slater orbitals $1s(1.0)$, $1s'(2.2)$, and $2p(2.0)$ on He, and Slater orbitals $2s(1.0)$, $2p(1.0)$, plus the exact hydrogenic $1s, 2s$, and $2p$ orbitals on H; the method of calculation has been described in detail elsewhere²⁴. Figure 1 shows these two $^2\Sigma$ potentials, along with the ground state He-H potential. Michels and Harris²⁵ have earlier carried out less extensive calculations for these two states, the higher one being described only roughly.

These potential curves are quite interesting, the lower one having a large attractive well of 2.50 eV at internuclear distance $1.4 a_0$. The upper curve is particularly unusual, having a well depth of 0.63 eV at $1.6 a_0$ and a maximum of 0.85 eV (above its asymptotic limit) at $3.8 a_0$.

The presence of this maximum can have interesting consequences for He-H($2s$) scattering. Consider first the angular distribution; in similarity again with symmetric charge transfer²², the differential cross section for the $2s \rightarrow 2p$ transition is

$$\sigma(\theta) = |f_2(\theta) - f_1(\theta)|^2 \quad (29)$$

where f_1 and f_2 are the elastic scattering amplitudes for the two potentials. Interference structure will be present in $\sigma(\theta)$, therefore, because of the cross term $2 \operatorname{Re}(f_1^* f_2)$ in Eq.(29). For energies below the maximum of V_2 (the upper potential),

the interference structure should be quite similar to that for symmetric charge transfer, for V_2 is effectively a purely repulsive potential and V_1 is attractive (as is typically the case for symmetric charge transfer). For energies above the maximum of V_2 , however, there is a small impact parameter orbiting singularity in V_2 . Figure 2 shows a sketch of classical deflection functions for potentials V_1 and V_2 in this energy region; the significant feature is that they must cross (this cannot happen for a collision energy below the barrier maximum). This means that the frequency of the oscillations in $\sigma(\theta)$ resulting from the interference term in Eq.(29) becomes zero as $\theta \rightarrow \theta_0$; i.e., the oscillations "stop oscillating" in the region about θ_0 . For a collision energy just above $V_2^{\max}$, $\theta_0 \approx \pi$, and as the energy increases, θ_0 decreases and can pass through zero. The orbiting singularity in θ_2 eventually becomes a finite minimum as the collision energy increases further, so that $\theta_2(b)$ has two rainbow angles.

There are also interesting consequences of the maximum in V_2 which appear in the total cross section. Eqs.(23)-(25) give the Massey-Mohr-like approximation to the integral over impact parameter with the transition probability of Eq.(21). Analogous to the glory contribution to total elastic cross sections¹², however, there will be an "extra" contribution to the integral over impact parameter if a point of stationary phase exists, i.e., a root of the equation

$$\Delta\eta'(b) = 0 ; \quad (30)$$

but since $\eta'(b) = \frac{1}{2}k\theta(b)$, Eq.(30) is equivalent to

$$\theta_1(b) = \theta_2(b). \quad (31)$$

As has been seen above, a root of Eq.(31) will exist if the collision energy is greater than $v_2^{\max}$. This "extra" oscillatory contribution to the total cross section is given by an expression analogous to the glory contribution for elastic scattering

$$\Delta\sigma = \pi b_o \left(\frac{\pi}{-\Delta\eta_o''} \right)^{\frac{1}{2}} \sin \left(2\Delta\eta_o - \frac{\pi}{4} \right), \quad (32)$$

where b_o is the root of Eq.(31) (the intersection of θ_1 and θ_2 in Fig. 2), $\Delta\eta_o = \Delta\eta(b_o)$, and $\Delta\eta_o'' = \Delta\eta''(b_o)$. When the oscillatory term first appears, b_o is small and $\Delta\eta_o''$ is large, so that the amplitude of the oscillations is quite small; we determined the amplitude in Eq.(32) for energies up to 3 eV and found it not to exceed $1\text{\AA}^2$. Byron and Gersten⁵ have also observed this type of oscillatory contribution to the total cross section.

Figure 3 shows the cross section for the $2s \rightarrow 2p$ transition as calculated from Eqs.(23)-(25) of the previous section. At the higher energies, of course, there is the possibility (as discussed in the Introduction) that processes other than Eq.(1) contribute to the overall quenching of $H(2s)$.

Byron and Gersten⁵ have recently reported results for this same collision system. They generated the necessary potentials by two means, a perturbation treatment and a pseudo-potential method, and performed the scattering calculation in a straight-line trajectory, time-dependent framework. The agreement between our results in Fig. 2 and their pseudo-

potential values is reasonably good, particularly so when one realizes the completely different approaches used.

The only experimental value for collisional quenching by helium at low energy is that given by Comes and Wenning²⁶, $\sigma = 8\text{\AA}^2$ at an average hydrogen velocity of $\bar{v} = 3.5 \times 10^5$ cm/sec ($\sim .064$ eV). At this energy Fig. 2 gives $\sigma \approx 85\text{\AA}^2$, a factor of 10 larger; Byron and Gersten's⁵ two methods gives $\sim 30\text{\AA}^2$ and $\sim 60\text{\AA}^2$ in this energy region. It is clear that more experimental and theoretical studies would be useful.

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Appreciation is expressed to Drs. F.W. Byron and J.I. Gersten for sending us a copy of their work (ref. 5) prior to publication.

Table I. Cross Section for Quenching of Metastable Hydrogen Atoms by Collision with Molecules

<u>Collision Partner</u>	<u>L</u> ^a	<u>q_L(ea_o^L)</u> ^b	<u>BA</u> ^c	<u>Exp</u> ^d
H ₂ O	1	0.724	981	1000
N ₂	2	1.13	111	100
H ₂	2	0.484	63	70
O ₂	2	0.29	45	60

a. Order of the multipole moment.

b. The molecular multipole moments($q_L \equiv e \langle r^L P_L \rangle$) in units of ea_o^L as given by D.E. Stogryn and A.P. Stogryn, Mol. Phys. 11, 371 (1966).

c. Cross section (in Å²) given by Eq.(16) and (18).

d. Cross section reported by Fite, et al., reference 15.

APPENDIX

The effect of the Born-Oppenheimer states changing from 2s and 2p for $R > R_t$ to $(2s \pm 2p)/\sqrt{2}$ for $R < R_t$ can be examined within the distorted wave Born approximation²⁷. The distorted wave functions are the solutions on the two adiabatic (BO) potential curves, and the non-adiabatic coupling involves derivatives of the internal functions with respect to inter-nuclear distance. If the transformation from the atomic 2s and 2p functions to the adiabatic internal functions is expressed by the unitary transformation

$$\begin{pmatrix} \cos \omega & \sin \omega \\ -\sin \omega & \cos \omega \end{pmatrix}, \quad (\text{A1})$$

where $\omega = \omega(R)$ [note that $\omega(R) = 0$ for $R \gg R_t$ and $\frac{\pi}{4}$ for $R \ll R_t$], then the S-matrix connecting channels 1 and 2 is

$$S_{1,2} = -2i(2m/\hbar^2) e^{i(\delta_1 + \delta_2)} \int_0^\infty dR u_1(R) \left[-\frac{\hbar^2}{2m} \omega''(R) u_2(R) - 2 \left(\frac{\hbar^2}{2m} \right) \omega'(R) u_2'(R) \right], \quad (\text{A2})$$

or integrating by parts gives

$$S_{1,2} = 2i e^{i(\delta_1 + \delta_2)} \int_0^\infty dR \omega'(R) [u_1(R) u_2'(R) - u_1'(R) u_2(R)]. \quad (\text{A3})$$

With the WKB approximation for the radial functions

$$u_1(R) = k_1(R)^{-\frac{1}{2}} \sin \left[\frac{\pi}{4} + \int_{R_1}^R dR' k_1(R') \right] \quad (\text{A4})$$

and with recognition of the fact that the major contribution to the integral comes at large R for which $k_1(R) \approx k_2(R)$, this becomes

$$S_{1,2} = 2i e^{i(\delta_1 + \delta_2)} \int_0^\infty dR \omega'(R) \sin \left[\int_{R_1}^R dR' k_1(R') - \int_{R_2}^R dR' k_2(R') \right] . \quad (A5)$$

In the sudden approximation $\omega(R)$ is a step-function

$$\omega(R) = \frac{\pi}{4} h(R_t - R) , \quad (A6)$$

so that $\omega'(R)$ is a delta function

$$\omega'(R) = -\frac{\pi}{4} \delta(R_t - R) . \quad (A7)$$

In this limit, therefore, Eq.(A5) becomes

$$S_{1,2} = -i \frac{\pi}{2} e^{i(\delta_1 + \delta_2)} \sin \left[\int_{R_1}^{R_t} dR k_1(R) - \int_{R_2}^{R_t} dR k_2(R) \right] , \quad (A8)$$

and

$$|S_{1,2}|^2 = \left(\frac{\pi}{2}\right)^2 \sin^2 \left[\int_{R_1}^{R_t} dR k_1(R) - \int_{R_2}^{R_t} dR k_2(R) \right] . \quad (A9)$$

Eq.(A9) would be exactly the same as Eq.(21) of the text if $\frac{\pi}{2}$ were replaced by 1; the fact that $\frac{\pi}{2}$, rather than 1, appears in Eq.(A9) is a result of the distorted wave approximation.

To consider the more general case, suppose that $\omega'(R)$ is of the form

$$\omega'(R) = \frac{\pi}{4} \left(\frac{\alpha}{\pi}\right)^{\frac{1}{2}} e^{-\alpha(R-R_t)^2} ; \quad (A10)$$

as $\alpha \rightarrow \infty$, this reduces to the delta function of Eq.(A7). The integral in Eq.(A5) is evaluated by expanding the argument of the sine function as a quadratic about R_t ; the integral can then be evaluated analytically, and the result for $|S_{1,2}|^2$ is Eq.(A9) multiplied by the correction factor $\exp [-(\Delta k)^2/2\alpha]$. Since $\Delta k \approx \Delta E/\hbar v$ for collision energies large compared to the

energy separation of the two potentials at R_t , this correction factor is $\exp(-E_t/E)$, where

$$E_t = \frac{2m}{\hbar^2} (\Delta E)^2 / 8\alpha ;$$

from our calculation one determines $E_t \approx 3.6 \times 10^{-9} \text{ eV} \approx 4 \times 10^{-5} \text{ }^\circ\text{K}$, so that the sudden approximation is valid in the transition region for essentially all collision energies.

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Figure Captions

1. The lowest three $^2\Sigma$ states of He-H, dissociating to ground state He and 1s, 2s, 2p states of H.
2. A sketch of the classical deflection functions which correspond to the first and second excited $^2\Sigma$ states of He-H, at a collision energy greater than the relative maximum in the second excited state (see Fig. 1).
3. The cross section for $\text{He} + \text{H}(2s) \rightarrow \text{He} + \text{H}(2p)$ as a function of collision energy, as computed from the potentials in Fig. 1 and Eqs. (23)-(25) of the text.

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Fig. 1

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Fig. 2

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Fig. 3

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