A unified treatment of Penning ionization and excitation transfer

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It is shown how Penning ionization \((A^+ + B^- \rightarrow A + B^- + e^-)\) and excitation transfer \((A^+ + B^- \rightarrow A + B^{**}, B^{**} = \text{Rydberg state})\) can be described by essentially the same theoretical model. The physical basis of this is that in both cases the final state of species \(B\) consists of an ion core \(B^+\) with a highly excited electron, and whether the electron is slightly bound \((B^{**})\) or slightly unbound \((B^+ + e^-)\) matters little to the collision dynamics. The system \(\text{He}^*(2\Sigma^+)^+\) is analyzed as an example of this theory.

i. INTRODUCTION

The two reactions

\[
\begin{align*}
A^+ + B^- &\rightarrow A + B^- + e^- , \\
A^+ + B^- &\rightarrow A + B^{**} ,
\end{align*}
\]

are usually considered to be quite different in nature. This point of view is enhanced by the fact that the experimental techniques for detection of the products of (1, 1a) and (1, 1b) are entirely different. Process (1, 1a), known as Penning ionization, has been investigated by measurement of the ions\(^1\) and electrons\(^2\) whereas the excited states \(B^{**}\) from process (1, 1b) are usually detected by optical spectroscopy.\(^3\)

For some purposes, however, it may be useful to look at these processes by stressing their common features rather than their differences. This is done in this paper, and it is hoped that from this treatment a better understanding of both reactions arises.

In both cases one has the following physical picture of the collision process: The atom \(A^+\) is de-excited to its ground state while one electron is promoted to an excited orbital in the Coulomb field of the ion \(B^+\). The electronic transition matrix element may be formally written as

\[
V_{r-i} = \langle f | V | i \rangle , \tag{2}
\]

where \(|i\rangle\) describes the initial state \(A^+ + B^-\) which has the character of a bound state in both cases, so that only a limited range of configuration space contributes to the matrix element. From this it is evident that the final state \(|f\rangle\) \((A + B^- + e^-\), or \(A + B^{**}\), respectively) is of importance only in a finite region around nucleus \(B\). The state \(|f\rangle\) contains the orbital of the excited electron, which is a free Coulomb wave for (1, 1a) or a Rydberg state for (1, 1b), and in a finite range both of these orbitals are essentially the same except for normalization. From this consideration we draw the conclusion that it should be possible to describe Processes (1, 1a) and (1, 1b) by the same theoretical model.

A further motivation for this uniform treatment can be taken from experimental results. Cross sections have been measured\(^3\) as a function of collision energy for the following reactions:

\[
\begin{align*}
\text{He}(2\Sigma^+) + \text{Hg}^- &\rightarrow \text{He} + \text{Hg}^- + e^- \tag{1, 3a} \\
\text{Ne}^* + \text{Hg}^- &\rightarrow \text{Ne} + \text{Hg}^* + e^- \tag{1, 3b} \\
\text{Ar}^* + \text{Hg}^- &\rightarrow \text{Ar} + \text{Hg}^* + e^- \tag{1, 3c} \\
\text{Kr}^* + \text{Hg}^- &\rightarrow \text{Kr} + \text{Hg}^* + (P_1) \tag{1, 3d}
\end{align*}
\]

As shown in Fig. 1, the cross sections for all systems are remarkably similar in the thermal energy range. Figure 2 shows schematically the relevant potential curves. For (1, 3a, b, c) the potential curve \(V[X^+ - \text{Hg}^-]\) of the initial state is embedded in the continuum of \(X^+ + \text{Hg}^* + e^-\). Once ionization has occurred, the nuclei continue their path in the potential \(V[X + \text{Hg}^-]\). The picture for \(\text{Kr}^* - \text{Hg}^-\) is different since the excitation energy of \(\text{Kr}^*\) is below the ionization potential of \(\text{Hg}^-\). The potential \(V[\text{Kr}^* - \text{Hg}^-]\) is, however, embedded in a family of Rydberg state potentials \(V[\text{Kr} + \text{Hg}^{**}(n)]\). Thus, compared to reactions (1, 3a, b, c), the continuum \(X^+ + \text{Hg}^* + e^-\) is simply replaced by the quasicontinuum \(\text{Kr} + \text{Hg}^{**}(n)\), where \(n\) denotes the principal quantum number of the Rydberg states and \(\epsilon\) the energy of the emitted electron. After separation of \(\text{Kr}^*\) and \(\text{Hg}^*\) many of the Rydberg states thus formed then cascade down to \(\text{Hg}^*(P_1)\) which in turn is detected by the 254 nm line that it emits. In this picture the state \(\text{Hg}^*(P_1)\) serves as monitor for the

![Relative Cross Section](image)

**FIG. 1.** Reactive cross sections as a function of collision energy for the reactions given by Eq. (1.3). Cases 1, 2, 3 are from Ref. 2, and case 4 is from Ref. 3.
formation of all (energetically accessible) Rydberg states during the collision.

Section II summarizes more completely the essential physical ideas of our theoretical approach. It is shown in Sec. III that the autoionization width $\Gamma$ is indeed continuous at $\epsilon = 0$, the transition between processes (1.1a) and (1.1b), and a simple model for evaluating $\Gamma$ approximately is described in Sec. IV. Sections V–VII then apply the approach to the He$^+ + F$ system.

II. BASIC IDEAS

We approach the unified treatment of Reactions (1.1a, b) by considering a system $A^* + B$ which can react in both ways:

$$A^* + B \rightarrow A^* + B^* + e^-(\epsilon)$$

$$\rightarrow A + B^{**}(n)$$ (2.1)

This is possible if the entrance potential curve $V_e = V[A^* + B]$ is asymptotically in the continuum of $A^* + B^* + e^-(\epsilon)$ but has a strongly attractive well which falls below the ionization limit (see Fig. 3). The crossing point between $V_+ = V[A^* + B]$ is denoted as $R_c$. For distances $R > R_c$ Penning ionization occurs, whereas in the range $R < R_c$, transitions into the states $A^* + B^{**}$ take place since $V_+$ crosses through a quasicontinuum of potential curves which dissociate to $A$ and Rydberg states $B^{**}$. The crossing points of $V_+$ with Rydberg state potentials are $R_n$ (thus $R_n = R_c$) and the potentials are denoted as $V_n = V[A^* + B^{**}(n)]$.

We consider first the expression for the probability that system $A^* + B$ is elastically scattered, i.e., without undergoing ionization or transition into a Rydberg state. The probability for reaching the turning point $R_0$ is

$$P(\omega, R_0) = P(\omega, R_c) \cdot P(R_c, R_0)$$ (2.2)

where $P(\omega, R_c)$, the probability that the system does not autoionize for $R$ in the interval $R < R_c$ is familiar from Penning ionization

$$P(\omega, R_c) = \exp \left( -\int_{R_c}^{\omega} \frac{\Gamma(R)}{\hbar \nu_b(R)} \right)$$ (2.3)

where $\Gamma(R)$ is the autoionization width (units of energy) and $\nu_b(R)$ is the radial velocity for impact parameter $b$. $P(R_c, R_0)$, the probability that the system does not undergo transition into any of the Rydberg states for $R$ in the interval $R_0 < R < R_c$, is given by a product of Landau-Zener probabilities:

$$P(R_n, R_0) = \prod_n P_n$$ (2.4)

with

$$P_n = \exp \left( -\frac{2\pi |V_{x,xn}|^2}{\hbar \nu_b(R_n) |d/dR(V_n - V_{x,xn})|} \right)$$ (2.5)

i.e., the probability of not transferring into any Rydberg state is the product of the probabilities of surviving each crossing elastically. Combining Eqs. (2.4) and (2.5) gives

$$P(R_n, R_0) = \exp \left( -\sum_n \frac{2\pi |V_{x,xn}|^2}{\hbar \nu_b(R_n) |d/dR(V_n - V_{x,xn})|} \right)$$ (2.6)

In Eqs. (2.5) and (2.6) $V_{x,xn}$ is the coupling between the initial state, $A^* - B$, and the $n$th Rydberg state, $A - B^{**} (n)$, evaluated at the crossing point $R_n$. We now wish to rewrite Eq. (2.6) so that it looks as much as possible like Eq. (2.3), i.e., so that the probabilities of not autoionizing and of not undergoing transition into the Rydberg states are treated in a unified manner. To do this one considers the Rydberg states as a continuum and $n$ as a continuous variable. In Eq. (2.6)

$$\sum_n \int dn = \int_{R_0}^{R_n} dR \left( \frac{dn}{dR} \right)$$ (2.7)

where $n(R)$ is the inverse function of $R(n)$ ($R(n)$ is the

\[\text{FIG. 2. Schematic potential energy curves for the reactions in Eq. (1.3b). Upper curve is appropriate to reactions (1.3a), (1.3b), and (1.3c) and the lower one to reach (1.3d).}\]

\[\text{FIG. 3. Sketch of the potential curve for A* - B}. \text{ For R > R_c it is embedded in a continuum of curves of the type A - B* + e^- and for R < R_c it crosses the infinite family of curves of the type A - B** with B** being a Rydberg state of B.}\]
crossing point $R_0$ for continuous $n$). Eq. (2.6) then takes the same form of Eq. (2,3),

$$P(R_0, R_0) = \exp \left( - \int_{R_0}^R \frac{\Gamma(R)}{\hbar v_{\text{th}}(R)} \, dr \right).$$  

(2.8)

If for $R < R_0$, one defines $\Gamma(R)$ as

$$\Gamma(R) = \frac{2\pi |V_{nm}|^2}{(d/dR)(V_{n} - V_{m})} \frac{dn}{dR},$$

(2.9)

To see that Eq. (2.9) is the same definition of $\Gamma$ as for Penning ionization, we assume (as usual) that the Rydberg potential curve $V_{n}(R)$ is the same shape as $V_{*}(R)$, simply shifted by the energy of the Rydberg electron:

$$V_{n}(R) = V_{*}(R) + \epsilon_n,$$  

(2.10)

The crossing point $R(n)$ is defined by

$$V_{*}(R) = V_{n}(R) = V_{*}(R) + \epsilon_n,$$

(2.11)

or

$$\epsilon_n = V_{*}(R) - V_{n}(R).$$

(2.12)

Defining $\epsilon(R)$ by

$$\epsilon(R) = V_{*}(R) - V_{R},$$

(2.13)

which is the same definition as in Penning ionization, one has

$$\left| \frac{d}{dR} \left( V_{*} - V_{n} \right) \right| = \left| \epsilon'(R) \right|,$$

(2.14)

so that

$$\left| \frac{dn}{dR} \right| = \left| \frac{dn}{dR} \right| \left( V_{*} - V_{n} \right) = \frac{dn}{d\epsilon} = \rho(\epsilon).$$

(2.15)

Equation (2.9) thus takes the following form for $R < R_0$,

$$\Gamma(R) = 2\pi |V_{nm}|^2 \rho(\epsilon),$$

(2.16)

where $\rho(\epsilon)$ is the density of states per unit energy. This definition of $\Gamma(R)$ for $R < R_0$, Eq. (2,16), is also recognized as the familiar "golden rule" expression for $\Gamma(R)$ that is found in treating Penning ionization$^d$ for $R > R_0$. It will be shown in the next section that the definition of the density of states in Eq. (2,16) is the same as that for $R > R_0$, so that $\Gamma(R)$ is indeed continuous at $R = R_0$.

We have thus shown that the probability of transitions into the true continuum (Penning ionization) and into the quasicontinuum of Rydberg states is given by the same theoretical expression, and this is the basis of the unified treatment of all inelastic processes which occur during the A$^*$-B collision. All of the formulae previously derived for Penning ionization$^d$ can thus be applied directly to the entire problem:

$$A^* + B \rightarrow A + B^* + e^*, \quad \epsilon > 0$$

(2.17a)

$$- A + B^{**}, \quad \epsilon < 0$$

(2.17b)

If, for example, the total inelastic probability is small, then the energy distribution of the electron is

$$\sigma(\epsilon) = \int_0^\infty db \left| 2\pi \frac{\Gamma(R)}{\hbar v_{\text{th}}(R)} \right| \frac{1}{\epsilon^2(\epsilon)} \, R = R(\epsilon),$$

(2.18)

where $R(\epsilon)$ being the inverse function of $\epsilon(R)$. The integral

$$\int_0^\infty db \left| 2\pi \frac{\Gamma(R)}{\hbar v_{\text{th}}(R)} \right| \frac{1}{\epsilon^2} \, R = R(\epsilon),$$

(2.19)

with $v = \sqrt{2E/\mu}$. The interpretation of $\sigma(\epsilon)$ for $\epsilon > 0$ is that $\sigma(\epsilon')d\epsilon'$ is the cross section for the ionized electron to have an energy in the increment $(\epsilon, \epsilon + d\epsilon)$. For $\epsilon < 0$ the quantity $\sigma(\epsilon')d\epsilon'$ is the cross section for formation of the Rydberg state $B^{**}$ whose energy lies in the interval $(\epsilon, \epsilon + d\epsilon)$.

III. BEHAVIOR OF $\Gamma(R(\epsilon))$ NEAR $\epsilon = 0$

From the previous section it is seen that the width function $\Gamma(R)$ is given by

$$\Gamma(R) = 2\pi \rho(\epsilon) \left| V_{nm} \right|^2,$$

(3.1)

with $\epsilon = \epsilon(R)$, and where

$$V_{nm} = b_{n} \Phi_{n-1} |V| \Phi_{n}.$$  

(3.2)

$\Phi_{n}$ is the (Born-Oppenheimer) electronic wavefunction of $A^* - B$, $b_{n-1}$ the wavefunction of $A - B^*$, $\chi_{n}$ is the one-electron orbital for the Nth electron in the final state, and $V$ is the operator (actually the total electronic Hamiltonian) which couples the states.

In this section we show that $\Gamma(R)$ is a smooth, continuous function at $R = R_0$, i.e., at $\epsilon = 0$. This is intuitively clear, since for purposes of evaluating the matrix element in Eq. (3,2) there seems little difference between an electron that is "just bound," or "just unbound," in the attractive Coulomb potential.

To facilitate the analysis we define

$$\psi_{n} = \sqrt{\epsilon} \chi_{n},$$

(3.3)

and

$$\overline{V}_{nm} = \langle \psi_{nm} | V | \psi_{n} \rangle,$$

(3.4)

in terms of which $\Gamma$ is given by

$$\Gamma(R) = 2\pi \left| \overline{V}_{nm} \right|^2$$

(3.5)

The $\epsilon$ dependence is now all contained in the function $\psi_{n}$, and it is thus necessary only to consider it in the vicinity of $\epsilon = 0$. Furthermore, since $\psi_{n}$ is a bound state function, one is only interested in $\psi_{n}(r)$ for $r$ in a finite region about the origin, for this is the only region which contributes to the matrix element.

We thus consider the WKB approximation for $\psi_{n}(r)$. First, for $\epsilon > 0$, one has

$$\chi_{n}(r) = \sin \left[ \frac{2\pi}{\hbar} \int_{r}^{r'} dv' k(v') \right] \sin \left( \frac{1}{2} k^2 \right),$$

(3.6)

where

$$k(r) = \sqrt{\frac{2 \epsilon - \frac{\hbar^2 (l + 1)}{2 \mu}}{\mu^2}},$$

(3.7)

and where atomic units are being used. $l$ is the orbital angular momentum of the electron, and $r_{i}$ is the inner turning point,

$$r_{i} = - \frac{1 + \sqrt{1 + 2\epsilon (l + 1)}}{2\epsilon}.$$
For $\chi_n$ normalized this way one has $\rho(\epsilon) = 2/\pi$, so that
\[ \psi_n(r) = \sqrt{\frac{2}{\pi}} \sin \left[ \frac{1}{2} \pi + \int_{r_c}^r dr' k(r') \right] \sqrt{k(r)} . \] (3.8)

For $\epsilon < 0$ the WKB approximation for the normalized orbital $\chi_n(r)$ is
\[ \chi_n(r) = C \sin \left[ \frac{1}{2} \pi + \int_{r_c}^r dr' k(r') \right] \sqrt{k(r)} . \] (3.9)

The normalization constant $C$ is determined in the usual fashion:
\[ 1 = C^2 \int_{r_c}^\infty dr \sin^2 \left[ \frac{1}{2} \pi + \int_{r_c}^r dr' k(r') \right] \frac{1}{k(r)} ; \] (3.10)

Differentiation of the WKB eigenvalue relation
\[ \left( \frac{\hbar^2}{2} \frac{d^2}{dr^2} - \frac{\hbar^2}{2} \frac{d}{dr} \right) \psi_n(r) = \sqrt{\epsilon} \phi_n(r) \] (3.11)
gives
\[ \frac{dn}{d\epsilon} \pi = \int_{r_c}^\infty dr \frac{1}{k(r)} , \] (3.12)
and together with Eq. (3.10) this gives $C$ as
\[ C = \frac{1}{\sqrt{\frac{\hbar^2}{2} \pi}} . \] (3.13)

According to Eq. (2.15), $\rho(\epsilon) = dn/d\epsilon$ for $\epsilon < 0$, and with these Eqs. (3.9) and (3.13) give
\[ \psi_n(r) = \sqrt{\frac{2}{\pi}} \sin \left[ \frac{1}{2} \pi + \int_{r_c}^r dr' k(r') \right] \sqrt{k(r)} \]
\[ = \frac{dn}{d\epsilon} \sqrt{\frac{2}{\pi}} \frac{d}{dr} \sin \left[ \frac{1}{2} \pi + \int_{r_c}^r dr' k(r') \right] \sqrt{k(r)} \]
\[ = \frac{2}{\pi} \sin \left[ \frac{1}{2} \pi + \int_{r_c}^r dr' k(r') \right] \sqrt{k(r)} , \] (3.14)

which is identical to Eq. (3.8) for $\epsilon > 0$ and establishes our principal assertion.

The above analysis has employed WKB radial functions for the Coulomb orbital, but this is not an essential limitation of the result. The WKB wavefunctions could, for example, be replaced by uniform approximations valid also in the vicinity of the inner turning point $r_c$. The cases $\epsilon > 0$ and $\epsilon < 0$ differ only then in that there is no outer turning point for $\epsilon > 0$, while there is for $\epsilon < 0$. Since this region of $r$ contributes negligibly to the matrix element, this difference has negligible effect.

IV. A PRIMITIVE APPROXIMATION TO THE FUNCTION $\Gamma(\mathcal{A})$

The process
\[ A^* + B \to A + B^* + e^* (\epsilon) \quad (\text{all } \epsilon) \], (4.1)
can basically be understood as the rearrangement of two electrons (cf. Fig. 4). One electron from B falls into the empty orbital of $A^*$ while the second electron is excited to energy $\epsilon$ which might be positive or negative with respect to the ionization limit of B. In the initial state $A^* + B$ the two orbitals involved are denoted as $\phi_A$ and $\phi$, where $\phi_A$ represents the excited orbital. In the final state $A + B^* + e^*(\epsilon)$ the two orbitals are $\chi_n$ and $\xi$,

\[ \langle \chi_n(1) \xi(2) | V | \phi_A(1) \phi(2) \rangle , \] (4.2)

where $\chi_n$ describes the continuum or Rydberg state. From the fact that the two electrons are indistinguishable it follows that the matrix element $V_{\chi\xi}$ in Eq. (3.2) consists of two terms,

\[ V_{\chi\xi} = \langle \chi_n(2) \xi(1) | V | \phi_A(1) \phi(2) \rangle \]
\[ - \langle \chi_n(1) \xi(2) | V | \phi_A(1) \phi(2) \rangle , \] (4.3)

where 1 and 2 denote the electrons. As long as the two atoms are sufficiently far apart that the molecular orbitals may be described by atomic orbitals, $\xi$ belongs to A and $\phi$ to B. From this point of view the second term has been called the exchange matrix element, $\xi$. In the case of weak interaction between $A^*$ and B the orbital $\phi_A$ is mainly located near nucleus A. Therefore the first term in Eq. (4.2) describes a process which can be thought of as the de-excitation $A^* - A$ and the emission of a virtual photon which then excites B to $B^*$ or $B^* + e^*$. From this aspect the first term is called the non-exchange, or radiative matrix element. In the case of strong interaction between $A^* + B$ it might well be that for small distances the configuration looks more like $A^* + e^*$ than like $A^* + B$. Obviously the orbital $\phi_A$ is then located near the nucleus B and the first term also involves an electron exchange between A and B. Hopf and Niehaus have given some experimental evidence that only the exchange matrix element is of importance if $A^*$ is a metastable, i.e.,

\[ V_{\chi\xi} = - \langle \chi_n(1) \xi(2) | V | \phi_A(1) \phi(2) \rangle . \] (4.3)

Figure 4 illustrates this matrix element for weak ($A^* + B$) and strong ($A^* + B^*$) interaction.

Our primitive approximation of $V_{\chi\xi}$ is constructed as follows: Guided by physical intuition rather than by a rigorous derivation we assume that the exchange matrix element can be approximated as

\[ V_{\chi\xi} \approx - \langle \chi_n(1) \xi(2) | V | \phi_A(1) \phi(2) \rangle . \] (4.3)
Since $\chi_s$ and $\phi_0$ are thought of as atomic orbitals, the $R$ dependence of $V_{ss}(R)$ in Eq. (4.4) is contained entirely in the second factor, whereas the overlap $\langle \chi_s | \phi_0 \rangle$ describes the $\epsilon$ dependence of $V_{ss}(R)$. To check these assumptions we have compared the known $\Gamma(R)$ of the Penning ionizing systems He$(2^3S)$–He, He$(2^3S)$–Ar and He$(2^3S)$–Ar$^+$ with the quantity $|H_{AB}(R)|^2$. We found the slope to be in almost perfect agreement. This does not hold for the systems He$(2^1S)$–He and He$(2^1S)$–Ar. It is interesting to note that these latter cases are possible candidates for systems where the radiative matrix element of Eq. (4.2) might play an important role via mixing to the He$(2^1P)$ state.

Thus, as long as we deal only with the exchange matrix element, we believe the factor $|H_{ss}(R)|^2$ describes the $R$ dependence of $\Gamma(R)$ reasonably well. The factor $2\langle \phi_0 | \chi_s \rangle^2$ then serves as a scaling factor. The application to the systems He$(2^3S)$–He, Ar shows that this scaling factor is the right order of magnitude. Our heuristic formula for $\Gamma(R)$ is then

$$\Gamma(R) = 2\langle \phi_0 | \chi_s \rangle^2 |H_{AB}(R)|^2$$

which we believe to be reliable to within a factor of 5 or so. Even though not of great accuracy this expression is useful in a case where one wishes to predict whether an unknown total cross section is in a measurable range for today's experimental techniques. All relative differential cross sections which are calculated with the aid of Eq. (4.7) are believed to be even more reliable since the slope of $\Gamma(R)$ is described quite well.

### V. 1$^2$S: POTENTIAL CURVES FOR SYSTEM HELIUM–FLUORINE

The remainder of the paper describes application of the above theoretical model to the He$^+$–F system. The potential curves for the system of He$^+$ F $(1^2S$ states only) are shown in Fig. 5, and one sees that a potential curve $V_{ss}$ exists which crosses both ranges, the continuum states He$^+$ F$(1^2P)$ and the Rydberg states He$^+$ F$^*$. Diabatically, $V_{ss}$ dissociates to He$^+$ F, adiabatically to He$^*(2^3S)$–F.

The following method has been used to estimate the potential $V_{ss}$, He$(2^3S)$ and Li are quite similar chemically because in both species the outer $2s$ electron sees an +1 nuclear charge and is excluded from the inner shell by the Pauli principle. The adiabatic potential $V[He(2^3S)$–F] is therefore assumed to have a similar equilibrium distance $r_0$, well depth $D_0$, and curvature $V''(r_0)$ as $V[Li–F]$. A slight adjustment has been made to take into account the difference between the ionization potentials of He$(2^3S)$ and Li (see Table 1). The long range part of the He$(2^3S)$–F potential is assumed to be well described by $F[He^+ + F]$.

#### TABLE 1. Comparison of potential parameters for Li–F and He(2$^3S$)–F.

<table>
<thead>
<tr>
<th>System</th>
<th>IP(A) (eV)</th>
<th>Reduced mass</th>
<th>$V''(r_0) (eV/\AA^2)$</th>
<th>$D_0 (eV)$</th>
<th>$\omega_c (eV)$</th>
<th>$r_0 (\AA)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li–F</td>
<td>5.392</td>
<td>4.560</td>
<td>0.1995$^a$</td>
<td>4.40</td>
<td>5.889 ± 0.087$^a$</td>
<td>3.956$^a$</td>
</tr>
<tr>
<td>He(2$^3S$)–F</td>
<td>4.768</td>
<td>3.304</td>
<td>4.40$^b$</td>
<td>6.5$^b$</td>
<td>3.0$^b$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Reference 17.

$^b$Estimated values.

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The crossing between the diabatic potentials \( V[\text{He}(2\,^5S) - F] \) and \( V[\text{He}^+ - F^+] \) is at \( R_c = 20.6 \ a_0 \). From Eq. (4.5), one computes that this crossing is only weakly avoided; the separation of the adiabatic potentials is \( \sim 4 \times 10^{-5} \) hartree. For comparison, the crossing point for Li–F is at \( R_c = 13.99 \ a_0 \) and the adiabatic potentials are separated by \( \sim 9 \times 10^{-4} \) hartree. From this fact a striking difference between the systems \( \text{He}(2\,^5S) - F \) and Li–F arises: In a thermal collision the system Li–F follows the adiabatic potential curve whereas the system \( \text{He}(2\,^5S) - F \) remains in its original configuration with a probability of \( 99.9\% \) even at a collision energy as low as 10 meV. Therefore, in order to reach the attractive part of the potential curve \( V_\alpha \), which crosses \( V[\text{He}^+ - F^+] \), it is necessary to start experimentally with the system \( \text{He}^+ - F^+ \).

It is for this reason that we will treat the collision of \( \text{He}^+ - F^+ \) instead of \( \text{He}(2\,^5S) - F \):

\[
\text{He}^+ + \text{F}^- \rightarrow \text{He}^+ + \text{F}^+ + \epsilon(\epsilon),
\]

with \( \epsilon > 0 \) or \( < 0 \).

The potential \( V[\text{He}^+ - F^+] \), which will be denoted as \( V_\alpha \) from now on, has the symmetry \( \Sigma_\alpha \). Since total spin is conserved and the collision energies we consider are too low to allow for rotational coupling, the final states \( \text{He}^+ + \epsilon(\epsilon) \) must have the same symmetry. Therefore we take into account only \( \Sigma_\alpha \) potentials. After separation of the particles \( \text{F}^{**} \) must thus be in a doublet state, and its electronic angular momentum must be perpendicular to the internuclear axis.

Further, since the crossing \( R_c \) occurs in a region where neither potential curve shows strong chemical interaction, we assume that the atomic orbitals of both reaction partners are only slightly perturbed so that a description of the process in atomic orbitals is quite good. Regarding our approximate formula for \( \Gamma(R) \) in Eq. (4.7) we thus take \( \phi_2 \) to be the 2s orbital of \( \text{F}^+ \); \( \chi_4 \) must then also be a \( \rho \) orbital centered on nucleus B.

The potential \( V[\text{He}^+ - F^{**}](2p^4) \) in Fig. 5 is the one calculated by Liebman and Allen, and the potentials \( V[\text{He}^+ - F^{**}] \) were constructed in the following manner. From Kraus, Maldonado, and Wahlgren we took the potential curves calculated for \( \text{He} - \text{Na}^- \) and \( \text{He} - \text{Na} \ (X, A, B) \), which dissociate as

\[
\begin{align*}
\text{HeNa}^-& (X^{1S}_1) \rightarrow \text{He} + \text{Na}^-(2p^6), \\
\text{HeNa}(X^{2S}^\text{R}) & \rightarrow \text{He} + \text{Na}^-(2p^6 \ 3s\sigma), \\
\text{HeNa}(A^{2\Pi}) & \rightarrow \text{He} + \text{Na}^2p^6 \ 3p\pi, \\
\text{HeNa}(B^{2S}^\text{R}) & \rightarrow \text{He} + \text{Na}^2p^6 \ 3p\rho.
\end{align*}
\]

All four potentials were normalized to zero for \( R \rightarrow \infty \) and the following differences computed:

\[
\begin{align*}
\Delta V(3s\sigma) & = V[\text{HeNa}(X^{2S}^\text{R})] - V[\text{HeNa}^-], \quad (5.2a) \\
\Delta V(3p\pi) & = V[\text{HeNa}(A^{2\Pi})] - V[\text{HeNa}^-], \quad (5.2b) \\
\Delta V(3p\rho) & = V[\text{HeNa}(B^{2S}^\text{R})] - V[\text{HeNa}^-]. \quad (5.2c)
\end{align*}
\]

We then assumed that adding a \( 3s\sigma \), \( 3p\pi \), or \( 3p\rho \) electron to the system \( \text{He} - F^+ \) would change the potential \( V[\text{He}F^+] \) in the same way as it changes \( V[\text{HeNa}^-] \). Neglecting the symmetry of the core \( F^+(2p^4) \), we characterize the Rydberg states \( F^{**} \) with \( n = 3 \) by the outer electron only:

\[
\begin{align*}
\text{He}^+ + \text{F}^- \rightarrow \text{He}^+ + \text{F}^+ + \epsilon(\epsilon),
\end{align*}
\]

The desired \( \text{He}^{**}(n = 3) \) potential curves are then

\[
\begin{align*}
V[\text{He} - \text{F}^{**}(2p^4)(3\sigma)] & = V[\text{HeF}^+] + \Delta V(3\sigma), \\
V[\text{He} - \text{F}^{**}(2p^4)(3\pi)] & = V[\text{HeF}^+] + \Delta V(3\pi), \\
V[\text{He} - \text{F}^{**}(2p^4)(3\rho)] & = V[\text{HeF}^+] + \Delta V(3\rho).
\end{align*}
\]

with \( V[\text{HeF}^+] \) that of Ref. 12 and \( \Delta V \) defined by Eq. (5.2) with the He–Na potentials of Ref. 13.

The higher potential curves, \( \text{He}^+ - \text{F}^+(2p^4)(n \rho) \ n > 3 \), are taken to be the same shape as that of \( \text{He} - \text{F}^+ \), shifted to the asymptotic value of the atom \( F^+ \). Since the atomic energy levels of \( F(2p^4)(n \rho) \), \( n > 3 \), are not given in Moore’s tables, they were calculated in a simple manner by means of an \( n \)-dependent effective charge \( Z(n) \), in which \( Z(n) = 1 - n \rightarrow \infty \).

So far we have considered only the ground ionic state of \( F, F^+(2p^4) \) (the fine structure is neglected throughout this paper). The first excited level of \( F^+ \) is \( F^+(3\rho) \) with an excitation energy of \( 2.588 \, \text{eV} \). This ionic state gives rise to a second family of Rydberg states. Since \( V[\text{He} - \text{F}^{**}(3\rho)] \) and \( V[\text{He} - \text{F}^{**}(3\rho)] \) are very nearly parallel, this family of Rydberg potential curves can be assumed to be the same as those belonging to \( F^+(2p^4) \) except for an upward shift of \( 2.588 \, \text{eV} \).

VI. \( \Gamma(R) \) FOR SYSTEM \( \text{He}^+ \) + \( \text{F}^- \)

The width function \( \Gamma(R) \) for the collision system \( \text{He}^+ \) + \( \text{F}^- \) is determined via Eq. (4.7). Application of Eq. (4.6) yields the following expression (all quantities in atomic units)

\[
H_{ab}(R) = 0.313R \exp(-0.924R),
\]

For the energy dependent factor \( 2\rho(\epsilon) |\chi_4| \phi_2|^{\frac{1}{2}} \) we chose \( \phi_2 \) to be the Hartree–Fock \( 2p \) orbital of \( \text{F} \) and \( \chi_4 \) to be bound or free hydrogenic \( p \) orbital. The overlap was evaluated analytically for \( \chi_4 = 3p, 4p, 5p \)-hydrogen wavefunction and numerically for \( \chi_4 = \text{free Coulomb wave} \). In the first case there is of course an ambiguity in the proper choice of \( \rho(\epsilon) \); we simply used \( \rho(\epsilon) = 1/(E_{n+1} - E_n) \).

The quantity \( 2\rho(\epsilon) |\chi_4| \phi_2|^{\frac{1}{2}} \) is shown in Fig. 6. For \( \epsilon > 0 \) it is a smooth function and for the three calculated levels \( np \ (n = 3, 4, 5) \) it is shown as a histogram.

A logarithmic plot of \( \Gamma(R) \) is shown in Fig. 7. The values \( \Gamma(R_n) \), \( n = 3, 4, 5 \) are computed from the appropriate terms in Fig. 6.

For \( R > R_c \), \( \Gamma(R) \) is well described by the analytic expression \( \Gamma(R) = 2.085R \exp(-1.764 - R) \). This analytic form is extrapolated into the region \( R < R_c \), where \( \epsilon < 0 \). In this range of negative energies \( \epsilon \) there are two ways of looking at the process

\[
\begin{align*}
\text{He}^+ + \text{F}^- \rightarrow \text{He} + \text{F}^+ + \epsilon(\epsilon).
\end{align*}
\]
Either one regards the spectrum of Rydberg states $F^{**}$ as continuous and uses the smooth function $\Gamma(R)$ for $R < R_1$, as well as for $R > R_1$, or one regards the formation of a certain $F^{**}$ as the result of an isolated curve crossing. In this latter picture one requires the Landau-Zener exponent $\mu_n$,

$$\mu_n = \frac{2\pi}{R} \left| \frac{V_{\text{ext}}}{(d/dR)(V_n - V_0)} \right|^2, \quad R = R_n,$$

which is related to $\Gamma(R)$ by [cf. Eq. (2.9)]

$$\mu_n = \frac{1}{R} \int_{R_n}^{R_{n+1}} \Gamma(R) \, dR;$$

FIG. 7. The width function $\Gamma(R)$ (in hartree) as determined from Eq. (4.7).

FIG. 8. Total cross sections for the reactions $\text{He}^+ + F^- \rightarrow \text{He} + F^* (\cdots, np)$, $\text{He}^+ + F^- \rightarrow \text{He} + F^* + e^-$, as a function of collision energy.

VII. CROSS SECTIONS

This section presents cross sections for the reaction

$$\text{He}^+ + F^- \rightarrow \text{He} + F^* + e^-(\epsilon), \quad \epsilon > 0,$$

as calculated from the potential curves and the function $\Gamma$ described in the two previous sections. Figure 8 shows several total cross sections as a function of collision energy. The cross sections $\sigma_0$ for the formation of $F^{**}(n = 3, 4, 5)$ are calculated with the aid of the Landau-Zener formula. For comparison the cross section for reaching the corresponding curve crossing, i.e., $\mu^2_{\text{max}}$, is given as well. Finally the ionization cross section is shown. It is calculated using the formula given by Miller et al.,

$$\sigma_{\text{ion}} = \int_{R_n}^{\infty} dR \frac{4\pi R^2}{\hbar c} \sqrt{1 - \frac{V_0(R)}{E}} \Gamma(R).$$

For the collision energy of 1 hartree we have calculated the energy distribution of the emitted (or excited) electrons (see Fig. 9) using Eq. (2.19). The meaning of this quantity is quite clear for $\epsilon > 0$. It is experimentally accessible by means of electron spectroscopy. For $\epsilon < 0$, of course, it could be probe, however, by optical spectroscopy, i.e., by observing the light emitted from the decaying $F^{**}$.

In addition we have computed the values $\sigma_n/(E_n - E_0)$ for the $F^{**}$ states with $n = 3, 4, 5$ where the $\sigma_n$ are the Landau-Zener cross sections shown in Fig. 9. The
increasing $R$, the importance of the final states $He + F^* (1D) + e(\epsilon)$ is very small compared to the states $He + F^* (3P) + e(\epsilon)$ as long as one compares them at the same value of $\epsilon$. Thus the electron energy distribution $\sigma(\epsilon)$ is not affected much by the existence of $F^* (1D)$. If, however, one investigates the region $\epsilon < 0$ by optical spectroscopy, it might well be that the states $F^* (2\rho (1D)_n, np)_p$ do play an important role. This is because when measuring the light from the $F^* \epsilon$ states the energy of reference for both Rydberg families is the ground state of $F$ rather than the two ionizations limits $F^* (3P)$ and $F^* (1D)$. Thus, one cannot compare the relative influence of the two Rydberg series at the same $\epsilon$ (as is done in electron spectroscopy) but at $\epsilon$ for the $F^* (3P)$ core and $\epsilon + 0.095$ a.u. for the $F^* (1D)$ core.

$1^1$See, for example, E. Illenberger and A. Niehaus, J. Phys. B 20, 33 (1975).
$3^3$See, for example, W. Lee and R. M. Martin, J. Chem. Phys. 64, 678 (1976).
$15^{15}$E. Clementi, supplement to the paper IBM J. Res. Dev. 9 (1965).
$17^{17}$B. Rosen, Spectroscopic Data Relative to Diatomic Molecules (Pergamon, Oxford, 1970).