Title
CLASSICAL MODEL FOR ELECTRONIC DEGREES OF FREEDOM IN NON-ADIABATIC COLLISION PROCESSES: PSEUDO-POTENTIAL ANALYSIS AND CALCULATIONS FOR F(2p) + H^,Xe-^F(2p) + H+,Xe

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Publication Date
1978-11-01

Submitted to the Journal of Chemical Physics

LBL-8425
Preprint

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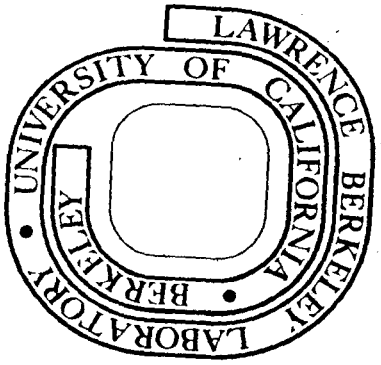
November 1978

Prepared for the U. S. Department of Energy
under Contract W-7405-ENG-48



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Classical Model for Electronic Degrees of Freedom in Non-Adiabatic Collision Processes: Pseudo-Potential Analysis and Calculations for $F(^2P_{1/2}) + H^+,Xe \rightarrow F(^2P_{3/2}) + H^+,Xe$

By

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Abstract

It is shown how the classical version of a pseudo-potential analysis can be used to obtain classical models for the electronic degrees of freedom in a molecular collision system. This allows one to construct a completely classical model for electronically non-adiabatic collision processes, which has the virtue that electronic and heavy particle degrees of freedom are described dynamically consistently (i.e., by classical trajectories). Application of this approach to fine-structure changing collisions of F by collision with H^+ and Xe gives encouraging agreement with quantum mechanical coupled-channel calculations, suggesting that this model may in general be of useful accuracy for describing electronically non-adiabatic processes.

I. Introduction.

Semiclassical theories of electronically non-adiabatic collision processes[1] usually describe the electronic (and perhaps rotation and vibrational) degrees of freedom quantum mechanically, i.e., as quantum mechanical states, and treat the heavy particle degrees of freedom (perhaps only translation) by classical mechanics, i.e., with coordinates and momenta that follow trajectories. The many variants and extensions of the Landau-Zener model are in this general category. A particularly useful approach of this type is the "surface hopping" model introduced by Tully and Preston;[2] it treats all the heavy particle degrees of freedom (translation, rotation and vibration) classically, as classical trajectories moving on a potential energy surface (i.e., in a specific Born-Oppenheimer electronic state), allowing localized "hops" between potential energy surfaces.

It has been recently pointed out,[3] however, that such approaches can sometimes miss important dynamical features in non-adiabatic collision processes because the electronic and the heavy particle degrees of freedom are treated on different dynamical footings, i.e., by quantum and by classical mechanics, respectively. To avoid these shortcomings it has been argued[4] that one needs to treat all degrees of freedom on the same dynamical footing, and this means that one either treats them all quantum mechanically--which is usually not feasible--or treats them all by classical mechanics, including the electronic degrees of freedom. To pursue this latter idea it is necessary to construct a classical model for the relevant electronic states. One thus replaces the several potential energy surfaces by one potential energy surface but for a system which has an additional coordinate and momentum, the electronic degree of freedom, and then all the coordinates and momenta are assumed to

follow trajectories determined by the classical equations of motion. A previous paper,[4] to be referred to hereafter as paper I, has shown in several specific cases how such classical models can be constructed.

The purpose of this paper is twofold. First, Section II shows another way, somewhat more general and well-founded than that of paper I, of deriving classical models for the electronic degrees of freedom, namely the classical version of a pseudo-potential approach. For the specific examples discussed in paper I this pseudo-potential analysis actually leads to the same results as before,[4] but it has the capability of being extended to more general systems.

Second, Section III describes the first application of this approach which treats both electronic and heavy particle degrees of freedom by classical trajectories, the process being quenching of the excited fine structure state of fluorine atom by collision with H^+ and with Xe,

$$F(^2P_{1/2}) + B \rightarrow F(^2P_{3/2}) + B \quad , \tag{1.1}$$

with B = H^+ or Xe. The results of these calculations are extremely encouraging, being of the same level of accuracy that quasiclassical trajectory calculations give for rotationally and vibrationally inelastic collisions.[5]

In concluding this introduction it should be emphasized that the goal of this classical treatment of electronic degrees of freedom is not to find alternative ways of computing Born-Oppenheimer electronic energies; it is the desire to treat electronic degrees of freedom on the same dynamical footing as the heavy particle degrees of freedom that necessitates the use of classical mechanics for both. It should be noted, too, that even though this classical model for non-adiabatic processes treats curve crossing (or

more correctly, localized avoided crossing) situations correctly, Landau-Zener and other "surface hopping" models also do a good job in these cases and are simpler. The most useful aspect of classical models of the type discussed in this paper is thus expected to be the ability to treat more general non-adiabatic processes that do not necessarily take place via isolated curve crossings.

II. Classical Pseudo Potential Formalism.

In this section we show how the idea of a classical pseudo-potential can be used to construct classical models for the relevant electronic states in several specific examples.

a. A(nj) + B

The first and simplest case is the collision of a "one electron" atom A, with the electron in an (nj) orbital (e.g., n = 2, j = 1 for a 2p orbital), with a closed shell ^1S atom B. Atom A is not literally a one electron atom, i.e., hydrogen, but has one "active electron" outside a closed shell, and we will model only the electronic states involving this one electron. The situation is also the same for atoms with one "hole", e.g., the halogen atoms; this includes the example

$$F(^2P_{1/2}) + Xe,H^+ \rightarrow F(^2P_{3/2}) + Xe,H^+ \tag{2.1}$$

for which calculations are reported in Section III and for which the spin-orbit interaction has also been included. For the discussions in this section, however, spin-orbit interactions will not be included; they can be introduced afterward when necessary.

The case of a pseudo one-electron atom colliding with a closed shell atom is a three particle system, the same as an atom-diatom collision system, for example, for which the classical Hamiltonian has been derived previously:[6]

$$H_J(P,R,p_e,r_e,j,q_j,m,q_m) = \frac{P^2}{2\mu} + \frac{\ell^2}{2\mu R^2} + \frac{p_e^2}{2m_e} + \frac{j^2}{2m_e r_e^2}$$

$$+ v(r_e) + V(R,r_e,\gamma) \quad ; \tag{2.2}$$

Figure 1 depicts the coordinates for the system. r_e is the distance between the electron and nucleus A (the "vibrational" coordinate of "diatom" A-e), R the distance between atoms A and B, and γ the angle between $\vec{r}_e$ and $\vec{R}$; $v(r_e)$ is the effective one-electron potential (the "vibrational" potential for the "diatom" A-e), and $V(R,r_e,\gamma)$ is the interaction potential; j is the angular momentum of the electron (the "rotational" angular momentum of the "diatom" A-e), and m is its projection onto $\vec{R}$; p_e and P are the momenta conjugate to r_e and R, respectively, and q_j and q_m the angle variables conjugate to j and m. ℓ is the orbital angular momentum of A relative to B and is given in terms of the other variables by[6]

$$\ell^2 \equiv |\vec{J}-\vec{j}|^2$$

$$= J^2-m^2 + j^2-m^2 - 2\sqrt{J^2-m^2}\sqrt{j^2-m^2}\cos q_m \quad , \tag{2.3}$$

where J is the total angular momentum (which is conserved). The angle γ is given in terms of the canonical variables by[6]

$$\cos\gamma = \sqrt{1-m^2/j^2}\cos q_j \quad . \tag{2.4}$$

The Hamiltonian of Eq. (2.2) is in the "helicity representation" (m is the helicity) which is most convenient for present purposes.

To proceed further we replace the variables (r_e,p_e) by the action-angle variables (n,q_n), as is done for the atom-diatom case;[6] in Eq. (2.2) one thus has the replacements

$$\frac{p_e^2}{2m_e} + \frac{j^2}{2m_e r_e^2} + v(r_e) \to \varepsilon(n,j) \tag{2.5a}$$

$$r_e \to r_e(n,q_n) \quad , \tag{2.5b}$$

where $\varepsilon(n,j)$ is the WKB eigenvalue for the potential $v(r_e)$ expressed in terms of the "vibrational" and "rotational" quantum numbers n and j. For the present, moreover, we are seeking the Hamiltonian which describes the interaction between atom A(nj) and atom B, where the electron has definite, fixed values for n and j; e.g., the interaction between $C^+(2p)$ and He, for which n = 2 and j = 1. We thus seek a Hamiltonian for which n and j are constants of the motion, i.e., a Hamiltonian that is <u>independent of q_n and q_j</u>, and the most straight-forward way of obtaining this is to average the above Hamiltonian over q_n and q_j. This corresponds physically to the vibrational and rotational motion being so fast that n(t) and j(t) are constant in time. The desired reduced Hamiltonian is thus given by

$$\begin{aligned} H_J(P,R,m,q_m) &\equiv (2\pi)^{-2} \int_0^{2\pi} dq_n \int_0^{2\pi} dq_j \; H_J(P,R,n,q_n,j,q_j,m,q_m) \\ &= \frac{P^2}{2\mu} + [J^2-m^2+j^2-m^2-2\sqrt{J^2-m^2}\sqrt{j^2-m^2}\cos q_m]/(2\mu R^2) \\ &\quad + V(R,m) \quad , \end{aligned} \tag{2.6}$$

where $r_e \equiv \langle r_e \rangle$ is a constant (the time average of r_e) in $V(R,r_e,\gamma)$ and has thus been omitted, and where the constant term $\varepsilon(n,j)$ has been dropped from the Hamiltonian; the interaction potential V(R,m) is defined by

$$\begin{aligned} V(R,m) &\equiv (2\pi)^{-1} \int_0^{2\pi} dq_j \; V(R,\cos\gamma) \\ &= (2\pi)^{-1} \int_0^{2\pi} dq_j \; V(R,\sqrt{1-m^2/j^2}\cos q_j) \quad . \end{aligned} \tag{2.7}$$

The most interesting part of Eq. (2.6) is the interaction potential V(R,m) of Eq. (2.7), and to develop it further we invoke the usual Legendre expansion,

$$V(R,\cos\gamma) = \sum_{n=0}^{\infty} V_n(R)\, P_n(\cos\gamma) \quad ; \tag{2.8}$$

this then gives (using Eq. (2.4))

$$V(R,m) = \sum_{n=0}^{\infty} V_n(R)(2\pi)^{-1} \int_0^{2\pi} dq_j\, P_n(\sqrt{1-m^2/j^2}\cos q_j) \quad . \tag{2.9}$$

The integral over q_j is evaluated in the Appendix, and one obtains

$$V(R,m) = \sum_{\lambda=0,2,4}^{\infty} V_\lambda(R)\, \frac{(-1)^{\lambda/2}\,\lambda!}{2^\lambda\,(\frac{\lambda}{2}!)^2}\, P_\lambda(\tfrac{m}{j}) \quad . \tag{2.10}$$

The logic of our approach is now to use the quantum mechanical Born-Oppenheimer potential curves of the A-B system to determine the various functions $V_\lambda(R)$ in Eq. (2.10). For j = 1, for example--i.e., a p electron--there will be two Born Oppenheimer potential curves arising from the A-B potential, a Σ and a Π potential. It is thus possible to determine the first two terms in Eq. (2.10) (the others being set to zero),

$$V(R,m) = V_0(R) + \frac{1}{4}(1-3m^2)V_2(R) \quad . \tag{2.11}$$

Since m = 0 corresponds to the Σ-potential and m = $\pm$1 the Π-potential, one equates

$$V(R,m=0) = V_{\Sigma}(R) \tag{2.12a}$$

$$V(R,m=\pm 1) = V_{\Pi}(R) \quad , \tag{2.12b}$$

and this determines $V_0(R)$ and $V_2(R)$ in terms of the Σ and Π potentials:

$$V_0(R) = \frac{1}{3}[2V_{\Sigma}(R) + V_{\Pi}(R)] \tag{2.13a}$$

$$V_2(R) = \frac{4}{3}[V_{\Sigma}(R) - V_{\Pi}(R)] \quad . \tag{2.13b}$$

Eq. (2.11) can be rewritten in terms of the Σ and Π potentials themselves to give the interaction potential for a p-electron finally as

$$V(R,m) = (1-m^2)\ V_{\Sigma}(R) + m^2 V_{\Pi}(R) \quad . \tag{2.14}$$

This is the same result obtained for this case in paper I, where the specific case discussed was $F(^2P) + Xe$.

For a d-electron, $j = 2$, there arise Σ, Π and Δ potential curves, so that 3 terms can be determined in Eq. (2.10). The interaction potential, expressed in terms of the Σ, Π, and Δ potential curves, is given in this case by

$$\begin{aligned} V(R,m) = {} & \frac{1}{4}(m^2-1)(m^2-4)\ V_{\Sigma}(R) \\ & + \frac{1}{3}\, m^2(4-m^2)\ V_{\Pi}(R) \\ & + \frac{1}{12}\, m^2(m^2-1)\ V_{\Delta}(R) \quad . \end{aligned} \tag{2.15}$$

For the general case, i.e., for an arbitrary value of j, the interaction

potential V(R,m) is the (unique) polynomial in m^2 of order j that equals the (j+1) quantum mechanical potential curves for m = 0,1,2, ..., j. The m-dependent coefficients of the quantum potential curves, e.g., in Eq. (2.15), are thus simply the Lagrange interpolation coefficients.

With the interaction potential V(R,m) determined in this manner, the specification of the Hamiltonian by Eq. (2.6) is complete. For the applications described in Section III, $F(^2P) + H^+$,Xe spin-orbit coupling in F is also introduced, as in paper I.

b. A(nj) + BC

The next example we consider is the collision of a pseudo one-electron atom A(nj), as in the previous section, with a closed shell $^1\Sigma$ diatomic molecule BC, where again we wish to consider only those electronic states which correspond to the one electron retaining fixed values for the electronic quantum numbers n and j. The specific example we have in mind is $F(^2P) + H_2$ in order to study the process

$$F(^2P_{1/2}) + H_2 \rightarrow F(^2P_{3/2}) + H_2 \quad , \tag{2.16}$$

but there are other interesting examples, such as $Na(3p) + N_2$. In the latter case one would want to construct a Hamiltonian that does allow n and j to change so that one could describe the quenching process

$$Na^*(3p) + N_2 \rightarrow Na(3s) + N_2 \quad . \tag{2.17}$$

From the discussion in the previous section it is clear that the pseudopotential approach models the present collision system as the interaction of two diatomic molecules, A-e^- and B-C, so that the classical Hamiltonian

is given in the helicity representation as

$$H_J(P,R,p_e,r_e,p,r,j,q_j,m_j,q_{m_j},N,q_N,m_N,q_{m_N})$$

$$= \frac{P^2}{2\mu} + \frac{\ell^2}{2\mu R^2} + \frac{p_e^2}{2m_e} + \frac{j^2}{2m_e r_e^2} + \frac{p^2}{2m} + \frac{N^2}{2mr^2}$$

$$+ v_e(r_e) + v_{BC}(r) + V(R,r_e,r,\gamma,\theta_e,\phi,\phi_e) \quad , \tag{2.18}$$

where the coordinates are depicted in Figure 2. (p_e,r_e), (j,q_j), and (m_j,q_{m_j}) are the variables of the "diatom" A-e^- for the "vibrational", "rotational" angular momentum, and projection of rotational angular momentum onto quantization axis $\vec{R}$; (p,r), (N,q_N), and (m_N,q_{m_N}) are the analogous variables for the diatom BC. (θ_e,ϕ_e) are the spherical angles of $\vec{r}_e$ with respect to the axis $\vec{R}$, and (γ,ϕ) are the analogous angles for $\vec{r}$. $v_e(r_e)$ and $v(r)$ are the potentials for the two diatomic molecules, V is the interaction potential, and the orbital angular momentum of relative translation ℓ is given in terms of the canonical variables by[4]

$$\ell^2 \equiv |\vec{J}-\vec{j}-\vec{N}|^2$$

$$= J^2+N^2+j^2-2m_N^2-2m_j^2-2m_Nm_j$$

$$- 2\sqrt{J^2-(m_N+m_j)^2}\,\sqrt{N^2-m_N^2}\,\cos q_{m_N}$$

$$- 2\sqrt{J^2-(m_N+m_j)^2}\,\sqrt{j^2-m_j^2}\,\cos q_{m_j}$$

$$+ 2\sqrt{N^2-m_N^2}\,\sqrt{j^2-m_j^2}\,\cos(q_{m_N}-q_{m_j}) \quad . \tag{2.19}$$

The spherical angles (θ_e,ϕ_e) and (γ,ϕ) are given in terms of the canonical variables by[7]

$$\hat{r}_e = \begin{pmatrix} \sin\theta_e \cos\phi_e \\ \sin\theta_e \sin\phi_e \\ \cos\theta_e \end{pmatrix} = \begin{pmatrix} \sin q_j \cos q_{m_j} + \frac{m_j}{j} \cos q_j \sin q_{m_j} \\ -\sin q_j \sin q_{m_j} + \frac{m_j}{j} \cos q_j \cos q_{m_j} \\ \sqrt{1-m_j^2/j^2}\cos q_j \end{pmatrix} \qquad (2.20a)$$

$$\hat{r} = \begin{pmatrix} \sin\gamma \cos\phi \\ \sin\gamma \sin\phi \\ \cos\gamma \end{pmatrix} = \begin{pmatrix} \sin q_N \cos q_{m_N} + \frac{m_N}{N} \cos q_N \sin q_{m_N} \\ -\sin q_N \sin q_{m_N} + \frac{m_N}{N} \cos q_N \cos q_{m_N} \\ \sqrt{1-m_N^2/N^2}\cos q_N \end{pmatrix} . \qquad (2.20b)$$

As in the previous section, we now replace (p_e, r_e) by the action-angle variables (n, q_n) and then average the Hamiltonian over q_n and q_j so as to obtain the Hamiltonian for which n and j are constants of the motion; this gives

$$H_J(P,R,p,r,N,q_N,m_N,q_{m_N},m_j,q_{m_j}) = \frac{P^2}{2\mu} + \frac{\ell^2}{2\mu R^2}$$

$$+ \frac{p^2}{2m} + \frac{N^2}{2mr^2} + v_{BC}(r) + V(R,r,\gamma,\phi,m_j,q_{m_j}) \quad , \qquad (2.21)$$

where again r_e has been replaced by its average value and thus suppressed. The interaction term $V(R,r,\gamma,\phi,m_j,q_{m_j})$, which is the interesting part of the Hamiltonian, is defined by

$$V(R,r,\gamma,\phi,m_j,q_{m_j}) \equiv (2\pi)^{-1} \int_0^{2\pi} dq_j \; V(R,r,\gamma,\theta_e,\phi,\phi_e) \quad , \qquad (2.22)$$

where the q_j dependence of the integrand comes from the dependence of θ_e and ϕ_e on q_j through Eq. (2.20a). The function $V(R,r,\gamma,\theta_e,\phi,\phi_e)$ can be expanded in the generalized Legendre expansion

$$V(R,r,\gamma,\theta_e,\phi,\phi_e) = \sum_{\lambda,\lambda'=0}^{\infty} \sum_{\mu=0}^{\min(\lambda,\lambda')} V_{\lambda\lambda'}{}^{\mu}(R,r)\, P_{\lambda'}{}^{\mu}(\cos\gamma)\, P_{\lambda}{}^{\mu}(\cos\theta_e)$$

$$\times\, (-1)^{\mu} \cos[\mu(\phi-\phi_e)] \qquad (2.23)$$

but here it is simpler for present purposes to leave the γ-dependence unexpanded:

$$V(R,r,\gamma,\theta_e,\phi,\phi_e) = \sum_{\lambda=0}^{\infty} \sum_{\mu=0}^{\lambda} V_{\lambda}{}^{\mu}(R,r,\gamma)\, P_{\lambda}{}^{\mu}(\cos\theta_e)(-1)^{\mu}\cos[\mu(\phi-\phi_e)]$$

$$= \mathrm{Re} \sum_{\lambda,\mu} V_{\lambda}{}^{\mu}(R,r,\gamma)\, P_{\lambda}{}^{\mu}(\cos\theta_e)(-1)^{\mu}\, e^{-i\mu\phi}\, e^{i\mu\phi_e} \quad . \qquad (2.23b)$$

With the dependence of θ_e and ϕ_e given by Eq. (2.20a), it is shown in the Appendix that

$$(2\pi)^{-1} \int_0^{2\pi} dq_j \quad P_{\lambda}{}^{\mu}(\cos\theta_e)\, e^{i\mu\phi_e}$$

$$= \frac{(-1)^{\frac{\lambda}{2}}\, \lambda!}{2^{\lambda}\, (\frac{\lambda}{2}!)^2}\, e^{i\mu(\frac{\pi}{2} - q_{m_j})}\, P_{\lambda}{}^{\mu}(\tfrac{m_j}{j}) \quad , \qquad (2.24)$$

for λ even (the integral is zero for odd λ), so that with Eq. (2.23b) the interaction potential defined in Eq. (2.22) becomes

$$V(R,r,\gamma,\phi,m_j,q_{m_j}) = \sum_{\lambda=0,2,4}^{\infty} \sum_{\mu=0}^{\lambda} V_{\lambda}{}^{\mu}(R,r,\gamma)$$

$$\times \frac{(-1)^{\frac{\lambda}{2}}\, \lambda!}{2^{\lambda}\, (\frac{\lambda}{2}!)^2}\, P_{\lambda}{}^{\mu}(m_j/j)\, \cos[\mu(\phi+q_{m_j}+\tfrac{\pi}{2})] \quad . \qquad (2.25)$$

For the case of a p-electron, j = 1, for example, we retain only the lowest order terms (λ = 0,2) in Eq. (2.25), and the interaction potential is

$$V(R,r,\gamma,\phi,m_j,q_{m_j}) = V_0^{\,0} + \frac{1}{4}(1-3m_j^{\,2})V_2^{\,0}$$

$$+ \frac{3}{2}\, m_j\sqrt{1-m_j^{\,2}}\,\sin(\phi+q_{m_j})\; V_2^{\,1} + \frac{3}{2}(1-m_j^{\,2})\,\cos(2\phi+2q_{m_j})V_2^{\,2}\;, \quad (2.26)$$

where $V_\lambda^{\,\mu} \equiv V_\lambda^{\,\mu}(R,r,\gamma)$. We note that this expression is of essentially the same form as that obtained for the $F(^2P) + H_2$ system in paper I. (The only difference is that the earlier result[4] had the factor $m_j^{\,2}$ rather than $1-m_j^{\,2}$ in the last term of Eq. (2.26), but it was emphasized that the approach used there was somewhat ambiguous in determining the m_j-dependence of the various terms in the Hamiltonian.) Comparing with this earlier result[4] leads to the following identification of the potential functions $V_\lambda^{\,\mu}(R)$:

$$V_0^{\,0} = \frac{1}{6}(H_{xx}+H_{yy}) + \frac{2}{3}\,H_{zz} \quad (2.27a)$$

$$V_2^{\,0} = \frac{4}{3}\left(H_{zz} - \frac{H_{xx}+H_{yy}}{2}\right) \quad (2.27b)$$

$$V_2^{\,1} = -\frac{4}{3}\,H_{yz} \quad (2.27c)$$

$$V_2^{\,2} = \frac{1}{3}(H_{yy}-H_{xx}) \quad , \quad (2.27d)$$

where H_{xx}, H_{yy}, H_{zz}, and H_{yz} are the quantum mechanical diabatic potential energy surfaces (functions of R,r,γ) discussed by Lester and Rebentrost.[8]

The four functions V_0^0, V_2^0, V_2^1, and V_2^2 are thus determined by the four quantum mechanical functions H_{xx}, H_{yy}, H_{zz} and H_{yz}. Expressed in terms of the quantum mechanical diabatic potential energy surfaces, the interaction potential is given in this case by

$$V(R,r,\gamma,\phi,m_j,q_{m_j}) = (1-m_j^2)\, H_{zz}(R,r,\gamma) + m_j^2\, \tfrac{1}{2}[H_{xx}(R,r,\gamma) + H_{yy}(R,r,\gamma)]$$

$$- \sin(\phi+q_{m_j})\, 2m_j\sqrt{1-m_j^2}\, H_{yz}(R,r,\gamma)$$

$$+ (1-m_j^2)\cos(2\phi+2q_{m_j})\, \tfrac{1}{2}[H_{yy}(R,r,\gamma) - H_{xx}(R,r,\gamma)]. \qquad (2.26')$$

In general, for an electron with orbital angular momentum j, one would retain terms in Eq. (2.25) up to $\lambda = 2j$.

In summary, the classical pseudo-potential Hamiltonian for the A(nj) + BC collision system is given by Eq. (2.21) with ℓ^2, γ, and ϕ defined in terms of the canonical variables by Eqs. (2.19) and (2.20b), and with the interaction potential given by Eq. (2.25). The most difficult and least precise step is determining the potential functions $V_\lambda^\mu(R,r,\gamma)$ in Eq. (2.25). The expressions obtained above, Eq. (2.27), made use of the results of paper I. The classical electronic Hamiltonian is thus determined by a combination of inputs: the pseudo-potential approach fixes the <u>form</u> of the Hamiltonian function, and the semiclassical analysis of paper I is useful in determining the parameters (i.e., the functions V_λ^μ) in the Hamiltonian. Another useful input is the "eigenvalue test" described in paper I, i.e., to require that the semiclassically computed Born-Oppenheimer electronic eigenvalues agree with the quantum mechanical

ones. Thus with R,r,ϕ, and ϕ fixed, the Born-Oppenheimer electronic eigenvalues are determined semiclassically by the Bohr-Sommerfeld quantum condition,

$$\oint dq_{m_j}\ m_j(q_{m_j},E) = 2\pi\ X(\text{integer}) \quad , \tag{2.28a}$$

where the function $m_j(q_{m_j},E)$ is defined implicitly by

$$E = V(R,r,\gamma,\phi,m_j,q_{m_j}) \quad , \tag{2.28b}$$

with R,r,γ,ϕ fixed. The procedure in this case is to adjust the quantities $V_0^{\ 0}$, $V_2^{\ 0}$, $V_2^{\ 1}$, $V_2^{\ 2}$ in Eq. (2.26), for example, so that the semiclassical eigenvalues determined by Eq. (2.28) agree with the quantum mechanical Born-Oppenheimer eigenvalues (for all values of R,r,γ,ϕ). (The eigenvalues are actually independent of ϕ.) In general, of course, this "eigenvalue criterion" will determine a different interaction potential, e.g., the relations between $V_\lambda^{\ \mu}$ and H_{xx}, H_{yy}, etc., may be different than those in Eq. (2.27). If this is the case, then one must test the different classical models in applications to see which is more realistic.

c. $\underline{A(np^2)}$

We now consider two examples to show how the classical pseudo-potential approach can be extended to model electronic states arising from systems with <u>two</u> active electrons. Rather than treating the most general case, we specialize to a np^2 configuration and consider first the isolated atom $A(np^2)$ itself to show that the three electronic states arising from this configuration--S,P, and D--are described qualitatively correctly by the model. The simplest example is the carbon atom, $C(2p^2)$, and the case of two holes, e.g., $O(2p^4)$ is also the same.

With two active electrons, the system is that of a 3-particle system (with one particle infinitely heavy), for which the classical Hamiltonian is given in the "orbital angular momentum representation" by [6]

$$H_J(p_1,r_1,p_2,r_2,j_1,q_{j_1},j_2,q_{j_2}) = \frac{p_1^2}{2m_e} + \frac{j_1^2}{2m_e r_1^2} + \frac{p_2^2}{2m_e} + \frac{j_2^2}{2m_e r_2^2}$$

$$+ v(r_1) + v(r_2) + V(r_1,r_2,\gamma) \quad , \tag{2.29}$$

where the coordinates are depicted in Figure 3; j_1 and j_2 are the angular momenta of the two electrons, and the angle γ is given in terms of the canonical variables by[6]

$$\cos\gamma = \cos q_{j_1} \cos q_{j_2} + \frac{j_1^2+j_2^2-J^2}{2\, j_1 j_2} \sin q_{j_1} \sin q_{j_2} \quad . \tag{2.30}$$

$v(r)$ is the one electron pseudo-potential, and V is the interaction potential. As before, we replace (p_1,r_1) and (p_2,r_2) by the action-angle variables (n_1,q_{n_1}) and (n_2,q_{n_2}) which are defined with respect to the one-electron potential v, and to obtain a Hamiltonian that conserves n_1,n_2,j_1, and j_2 (e.g., with $n_1=n_2=2$, $j_1=j_2=1$) we average the Hamiltonian in Eq. (2.29) over q_{n_1}, q_{n_2}, q_{j_1} and q_{j_2}, giving

$$H_J = \text{constant} + (2\pi)^{-2} \int_0^{2\pi} dq_{j_1} \int_0^{2\pi} dq_{j_2}\, V(\gamma) \quad , \tag{2.31}$$

with γ given by Eq. (2.30). r_1 and r_2 take on their average values and are not denoted. Also as before, the interaction potential V is expanded in a

Legendre expansion, keeping only terms thru P_2:

$$V(\gamma) = V_0 + V_1 P_1(\cos\gamma) + V_2 P_2(\cos\gamma) \quad , \tag{2.32}$$

and it is easy to show that Eqs. (2.30) and (2.32) then give

$$H_J = \text{constant} + V_0 + \frac{1}{8} V_2 \left[3\left(\frac{j_1^2 + j_2^2 - J^2}{2 j_1 j_2}\right)^2 - 1\right] \quad , \tag{2.33}$$

or

$$H_J \equiv E_J = a - bJ^2 + cJ^4 \quad , \tag{2.34}$$

where a,b, and c are positive constants. Eq. (2.34) shows that the classical model gives the correct qualitative dependence of the atomic energy levels on J, i.e., an upward parabola as a function of J^2; cf. the ordering of levels in a $2p^2$ atom, i.e., P(J=1) < D(J=2) < S(J=0). It is actually possible to obtain the <u>exact</u> (i.e., experimental) spacing between the three energy levels by adding a small fraction to the integer values of $j_1 = j_2 = 1$, J = 0,1, or 2, in Eq. (2.33).

d. <u>$A(np^2) + B$</u>

As the final example we consider the collision of a $2p^2$ atom with a closed shell ^1S atom; e.g., $C(2p^2)$ + He. The system is pictured in Figure 4, and the classical Hamiltonian is

$$H_J(P,R,p_1,r_1,p_2,r_2,j_1,q_{j_1},m_1,q_{m_1},j_2,q_{j_2},m_2,q_{m_2})$$
$$= \frac{P^2}{2\mu} + \frac{\ell^2}{2\mu R^2} + \frac{p_1^2}{2m_e} + \frac{j_1^2}{2m_e r_1^2} + \frac{p_2^2}{2m_e} + \frac{j_2^2}{2m_e r_2^2} + v(r_1) + v(r_2) + V(R,r_1,r_2,\theta_1,\theta_2,\phi_1,\phi_2)$$

(2.35)

where the variables have the same meaning as before. ℓ^2 is given in terms of the canonical variables by

$$\ell^2 \equiv |\vec{J}-\vec{j}_1-\vec{j}_2|^2$$

$$= J^2 + j_1^2 + j_2^2 - 2m_1^2 - 2m_2^2 - 2m_1m_2$$

$$- 2\sqrt{J^2-(m_1+m_2)^2}\sqrt{j_1^2-m_1^2}\,\cos q_{m_1}$$

$$- 2\sqrt{J^2-(m_1+m_2)^2}\sqrt{j_2^2-m_2^2}\,\cos q_{m_2}$$

$$+ 2\sqrt{j_1^2-m_1^2}\sqrt{j_2^2-m_2^2}\,\cos(q_{m_2}-q_{m_1}) \qquad (2.36)$$

and the spherical angles (θ_1,ϕ_1) of $\hat{r}_1$ and (θ_2,ϕ_2) of $\hat{r}_2$ are given in terms of the canonical variables by

$$\hat{r}_1 = \begin{pmatrix} \sin\theta_1\cos\phi_1 \\ \sin\theta_1\sin\phi_1 \\ \cos\theta_1 \end{pmatrix} = \begin{pmatrix} \sin q_{j_1}\cos q_{m_1} + \frac{m_1}{j_1}\cos q_{j_1}\sin q_{m_1} \\ -\sin q_{j_1}\sin q_{m_1} + \frac{m_1}{j_1}\cos q_{j_1}\cos q_{m_1} \\ \sqrt{1-m_1^2/j_1^2}\,\cos q_{j_1} \end{pmatrix} \qquad (2.37a)$$

$$\hat{r}_2 = \begin{pmatrix} \sin\theta_2\cos\phi_2 \\ \sin\theta_2\sin\phi_2 \\ \cos\theta_2 \end{pmatrix} = \begin{pmatrix} \sin q_{j_2}\cos q_{m_2} + \frac{m_2}{j_2}\cos q_{j_2}\sin q_{m_2} \\ -\sin q_{j_2}\sin q_{m_2} + \frac{m_2}{j_2}\cos q_{j_2}\cos q_{m_2} \\ \sqrt{1-m_2^2/j_2^2}\,\cos q_{j_2} \end{pmatrix} . \qquad (2.37b)$$

The variables (p_1,r_1) and (p_2,r_2) are replaced by the action-angle variables (n_1,q_{n_1}) and (n_2,q_{n_2}), and averaging over q_{n_1}, q_{n_2}, q_{j_1}, and q_{j_2} gives the Hamiltonian for the $A(2p^2) + B$ system as

$$H_J(P,R,m_1,q_{m_1},m_2,q_{m_2}) = \frac{P^2}{2\mu} + \frac{\ell^2}{2\mu R^2}$$

$$+ V(R,m_1,m_2,q_{m_1},q_{m_2}) \quad , \tag{2.38}$$

where r_1 and r_2 take on the average values and have not been denoted, and where the interaction potential is given by

$$V(R,m_1,m_2,q_{m_1},q_{m_2}) = (2\pi)^{-2} \int_0^{2\pi} dq_{j_1} \int_0^{2\pi} dq_{j_2}\, V(R,\theta_1,\theta_2,\phi_1,\phi_2) \quad . \tag{2.39}$$

The potential V is expanded in the Legendre expansion

$$V(R,\theta_1,\theta_2,\phi_1,\phi_2) = \sum_{\lambda=0}^{\infty} \sum_{\lambda'=0}^{\infty} \sum_{\mu=0}^{\min(\lambda,\lambda')} V_{\lambda\lambda'}^{\mu}(R)\, P_\lambda^\mu(\cos\theta_1)\, P_{\lambda'}^\mu(\cos\theta_2)(-1)^\mu$$

$$\cos[\mu(\phi_2-\phi_1)]$$

$$= \mathrm{Re} \sum_{\lambda,\lambda',\mu} V_{\lambda\lambda'}^{\mu}(R)\, P_\lambda^\mu(\cos\theta_1) e^{i\mu\phi_1} (-1)^\mu P_{\lambda'}^\mu(\cos\theta_2) e^{-\mu\phi_2} \quad , \tag{2.40}$$

and the averages over q_{j_1} and q_{j_2} involve integrals of the type evaluated in the Appendix. Carrying them out one obtains

$$V(R,m_1,m_2,q_{m_1},q_{m_2}) = \sum_{\lambda=0,2,4} \sum_{\lambda'=0,2,4} \sum_{\mu=0}^{\min(\lambda,\lambda')} V_{\lambda\lambda'}^{\mu}(R)$$

$$\times \frac{(-1)^{\frac{\lambda+\lambda'}{2}} \lambda!\lambda'!}{2^{\lambda+\lambda'}(\frac{\lambda}{2}!\ \frac{\lambda'}{2}!)^2} P_\lambda^{\mu}(\tfrac{m_1}{j_1})\ P_{\lambda'}^{\mu}(\tfrac{m_2}{j_2})\ (-1)^{\mu} \cos[\mu(q_{m_2}-q_{m_1})] \quad , \quad (2.41)$$

and if we specialize to $j_1 = j_2 = 1$ and retain only the lowest terms $\lambda,\lambda' = 0,2$, this becomes

$$V(R,m_1,m_2,q_{m_1},q_{m_2}) = V_{00}^0(R) - \tfrac{1}{2} P_2(m_1)\ V_{20}^0(R) - \tfrac{1}{2} P_2(m_2)\ V_{02}^0(R)$$

$$+ \tfrac{1}{4} P_2(m_1)\ P_2(m_2)\ V_{22}^0(R) - \tfrac{1}{4} P_2^1(m_1)\ P_2^1(m_2) \cos(q_{m_2}-q_{m_1})\ V_{22}^1(R)$$

$$+ \tfrac{1}{4} P_2^2(m_1)\ P_2^2(m_2) \cos(2q_{m_2}-2q_{m_1})\ V_{22}^2(R)$$

$$= V_{00}^0(R) + \tfrac{1}{4}(1-3m_1^2)\ V_{20}^0(R) + \tfrac{1}{4}(1-3m_2^2)\ V_{02}^0(R)$$

$$+ \tfrac{1}{16}(1-3m_1^2)(1-3m_2^2)\ V_{22}^0(R) - \tfrac{9}{4} m_1 m_2 \sqrt{1-m_1^2}\sqrt{1-m_2^2} \cos(q_{m_2}-q_{m_1})\ V_{22}^1(R)$$

$$+ \tfrac{9}{4}(1-m_1^2)(1-m_2^2) \cos(2q_{m_2}-2q_{m_1})\ V_{22}^2(R) \quad . \quad (2.42)$$

For the symmetrical case, e.g., $2p^2$, we note that symmetry requires $V_{20}^0(R) = V_{02}^0(R)$.

One can proceed further by noting that since the interaction potential in Eq. (2.42) depends on q_{m_1} and q_{m_2} only as their difference $q_{m_1}-q_{m_2}$, the quantity $m_1 + m_2$ is conserved by this term in the Hamiltonian. (There are, of course, other terms in the Hamiltonian, e.g., coriolis coupling, that

involve q_{m_1} and q_{m_2} individually and thus prevent $m_1 + m_2$ from being conserved by the total Hamiltonian.) This fact can be exploited by making a canonical transformation to replace the action-angle variables (m_1,q_{m_1}) and (m_2,q_{m_2}) by the new action angle variables (M,q_M) and (L,q_L), where M and L are defined in terms of the old variables by

$$M = m_1 + m_2$$

$$L^2 = |\vec{j}_1 + \vec{j}_2|^2 = j_1^2 - m_1^2 + j_2^2 - m_2^2 + 2\sqrt{j_1^2 - m_1^2}\sqrt{j_2^2 - m_2^2}\cos(q_{m_2} - q_{m_1}) \quad , \tag{2.43a}$$

or since $j_1 = j_2 = 1$,

$$L^2 = (1 - m_1^2) + (1 - m_2^2) + 2\sqrt{1 - m_1^2}\sqrt{1 - m_2^2}\cos(q_{m_2} - q_{m_1}) \quad . \tag{2.43b}$$

This transformation is the classical analog of the Clebsch-Gordon transformation of quantum mechanics, i.e., the transformation from the uncoupled variables j_1,j_2,m_1,m_2 to the coupled variables j_1,j_2,L,M, and it has been discussed in detail previously.[9] As noted, the new momentum M is conserved by the electronic interaction V, so that it is independent of the angle variable q_M. It is not hard to show that the old variables are expressed in terms of the new variables by

$$m_1 = \frac{M}{2} + \frac{\sqrt{4 - L^2}\sqrt{L^2 - M^2}}{2L}\cos q_L \tag{2.44a}$$

$$m_2 = \frac{M}{2} - \frac{\sqrt{4 - L^2}\sqrt{L^2 - M^2}}{2L}\cos q_L \tag{2.44b}$$

$$\sqrt{1 - m_1^2}\sqrt{1 - m_2^2}\cos(q_{m_2} - q_{m_1}) = \frac{L^2}{2} - 1 - \frac{M^2}{4} + \frac{(L^2 - M^2)(4 - L^2)}{4L^2}\cos^2 q_L \quad . \tag{2.44c}$$

Using Eqs. (2.44) we can express the electronic interaction of Eq. (2.42) in terms of M, L, q_L:

$$V(R, m_1, m_2, q_{m_1}, q_{m_2}) \rightarrow V(R, M, L, q_L) \quad . \tag{2.45}$$

M is the Λ-quantum number of diatomic molecule spectroscopy, the projection of the total electronic orbital angular momentum onto the atom-atom axis; M = 0,1,2 corresponds to Σ, Π, and Δ electronic states, respectively.

The six functions $V^{\mu}_{\lambda,\lambda'}(R)$ in Eq. (2.43) can be determined by requiring that the semiclassical electronic eigenvalues be the same as the quantum mechanical ones. For the $A(2p^2)$-B system there are three Σ potential curves, two Π potentials, and one Δ potential. With R and M (= 0,1, or 2) fixed in Eq. (2.45), the semiclassical eigenvalues are determined by

$$\oint dq_L \; L(q_L, E) = 2\pi \; X(\text{integer}) \quad , \tag{2.46a}$$

where $L(q_L, E)$ is the function defined (for fixed R and M) by

$$V(R, M, L, q_L) = E \quad . \tag{2.46b}$$

If $E_L(R,M)$ are these semiclassical eigenvalues (with $L \geq |M|$, then one equates the semiclassical and quantum mechanical eigenvalues:

$$E_2(R,2) = V_{\Delta}(R) \tag{2.47a}$$

$$E_1(R,1) = V_{\pi_1}(R) \tag{2.47b}$$

$$E_2(R,1) = V_{\pi_2}(R) \tag{2.47c}$$

$$E_0(R,0) = V_{\Sigma_0}(R) \tag{2.47d}$$

$$E_1(R,0) = V_{\Sigma_1}(R) \tag{2.47e}$$

$$E_2(R,0) = V_{\Sigma_2}(R) \quad , \tag{2.47f}$$

where $V_\Delta(R)$, $V_{\Pi_1}(R)$, etc., are the quantum mechanical potential curves. Since $E_L(R,M)$ is a function of the functions $V_{\lambda\lambda'}^{\mu}(R)$, as determined by the semiclassical eigenvalue relation, Eq. (2.47) determines a relation between the six quantum mechanical potential curves and the six functions $V_{\lambda\lambda'}^{\mu}(R)$. Eq. (2.47a) is particularly simple, for example, and is

$$V_\Delta(R) = V_{00}^0(R) - \frac{1}{2}\,[V_{20}^0(R) + V_{02}^0(R)] + \frac{1}{4}\,V_{22}^0(R) \quad . \tag{2.48}$$

The other equations for M = 0,1 are more complicated than this but can, at least in principle, be used to determine the functions $V_{\lambda\lambda'}^{\mu}(R)$ in terms of the quantum mechanical potential curves.

III. Application to Fine Structure Transition in Fluorine

a. The Specific Model

As a first application of the classical models developed above and in paper I, we have considered collisional quenching of the excited fine-structure state of the fluorine atom by H^+ and by Xe,

$$F(^2P_{1/2}) + H^+ \text{ or Xe} \rightarrow F(^2P_{3/2}) + H^+ \text{ or Xe} \quad . \tag{3.1}$$

These are interesting test cases since quantum mechanical coupled channel calculations[10,11] have been carried out for these systems and thus provide the standards for comparison.

The ground state F atom has electronic configuration $2p^5$, so the classical electronic Hamiltonian is that of Section IIa, with the addition of spin-orbit coupling in the F atom. The complete Hamiltonian is derived in paper I and is

$$H_J(P,R,j,q_j,m_j,q_{m_j}) = \frac{P^2}{2\mu} + \frac{\ell^2}{2\mu R^2} + Bj^2 + (1-m_L^2)\, V_\Sigma(R) + m_L^2\, V_\pi(R) \quad , \tag{3.2}$$

where here $L = 1$ and $S = \frac{1}{2}$ are the magnitudes of the orbital and spin angular momentum of the 2p electron hole, and j is the total electronic angular momentum. ℓ is the orbital angular momentum of relative motion of the two atoms, m_L is the projection of $\vec{L}$ onto the atom-atom axis, and they are given in terms of the canonical variables by[4]

$$\ell^2 = J^2 - m_j^2 + j^2 - m_j^2 - 2\sqrt{J^2 - m_j^2}\sqrt{j^2 - m_j^2}\cos q_{m_j} \qquad (3.3a)$$

$$m_L = \frac{\alpha\sqrt{j^2 - m_j^2}\cos q_j + m_j(j^2 + L^2 - S^2)}{2j^2} \quad , \qquad (3.3b)$$

where

$$\alpha = \sqrt{(L+S)^2 - j^2}\sqrt{j^2 - (L-S)^2} \quad ; \qquad (3.3c)$$

J is the (conserved) total angular momentum. $V_\Sigma(R)$ and $V_\pi(R)$ in Eq. (3.2) are the Σ and Π potential curves for the $F(^2P) + H^+$ or Xe system (computed ignoring spin-orbit coupling). The constant B in Eq. (3.2)--the "rotation constant" of the fluorine atom--is chosen so that this term in the Hamiltonian reproduces the 404 cm^{-1} fine-structure splitting of the isolated F atom; i.e., with the Langer modification $j \to j + \frac{1}{2}$, B is chosen so that

$$B(\tfrac{1}{2} + \tfrac{1}{2})^2 - B(\tfrac{3}{2} + \tfrac{1}{2})^2 = 404 \text{ cm}^{-1} \quad ,$$

or

$$B = -134.7 \text{ cm}^{-1} \quad .$$

The classical Hamiltonian in Eq. (3.2) is the precise classical analog of the Hamiltonian operator used by Mies[10] for his $F + H^+$ coupled-channel calculations (and which was also used for the similar F + Xe calculations[11]), and in order to assess the merit of the classical model we have used the same Σ and Π potentials as in these quantum scattering calculations.

b. Computational Aspects

The calculations were carried out within the framework of the standard

quasiclassical trajectory model.[12] The Langer modification[13] was also made, i.e., "$\frac{1}{2}$" was added to the magnitudes of all angular momenta (but not to the projection m_j); i.e., wherever L,S,j, and J appear in Eqs. (3.2) and (3.3) one makes the replacements

$$L \to L + \frac{1}{2}$$

$$S \to S + \frac{1}{2}$$

$$j \to j + \frac{1}{2}$$

$$J \to J + \frac{1}{2} \quad .$$

The cross section for the $j_1 \to j_2$ transition, summed over m_{j_2} and averaged over m_{j_1}, is given by

$$\sigma_{j_2 \leftarrow j_1} = \frac{\pi}{k_1^2} \sum_{J=0}^{\infty} (2J+1)\, \bar{P}_{j_2 \leftarrow j_1}(J) \quad , \tag{3.4}$$

where we actually evaluated the sum over J as an integral,

$$\sum_{J=0}^{\infty} \to \int_{-1/2}^{\infty} dJ \quad ,$$

which has no effect on the accuracy of the result. The quasiclassical, or classical histogram approximation to the average transition probability is[14]

$$\bar{P}_{j_2 \leftarrow j_1}(J) = (2j_1+1)^{-1} \sum_{m_1=-j_1}^{j_1} (2\pi)^{-2} \int_0^{2\pi} dq_{j_1} \int_0^{2\pi} dq_{m_{j_1}} \chi[j_2(j_1, m_{j_1}, q_{j_1}, q_{m_{j_1}}) - j_2] \tag{3.5}$$

where $\chi(x)$ is the "histogram function"

$$\chi(x) = 1, \text{ if } |x| < \frac{1}{2}$$

$$0, \text{ if } |x| > \frac{1}{2} \quad .$$

The function $j_2(j_1, m_{j_1}, q_{j_1}, q_{m_{j_1}})$ in Eq. (3.5) is the final value of the variable j that results from a classical trajectory computed from the Hamiltonian of Eq. (3.2) (using Hamilton's equations of motion) with initial conditions

$$R(t_1) = R_{max} \text{ (an arbitrarily large value)} \tag{3.6a}$$

$$P(t_1) = -\sqrt{2\mu E_1} \tag{3.6b}$$

$$j(t_1) = j_1 \text{ (initial quantum number)} \tag{3.6c}$$

$$m_j(t_1) = m_{j_1} \text{ (initial quantum number)} \tag{3.6d}$$

$$q_j(t_1) = q_{j_1} \tag{3.6e}$$

$$q_{m_j}(t_1) = q_{m_{j_1}} \quad , \tag{3.6f}$$

where E_1 is the initial translational energy,

$$E_1 = \frac{\hbar^2 k_1^2}{2\mu} \quad .$$

The function χ in the integrand of Eq. (3.5) is 1 if the final quantum number $j_2(j_1, m_{j_1}, q_{j_1}, q_{m_{j_1}})$ is within a "box" of unit width centered about the value j_2, and is zero otherwise. The two integrals in Eq. (3.5) are

usually evaluated, along with that over J, by Monte Carlo methods, although this is of course not necessary.

Since we have computed cross sections for the case $j_1 = \frac{1}{2}$, $j_2 = \frac{3}{2}$, the sum over m_{j_1} in Eq. (3.5) contains only the two terms $m_{j_1} = +\frac{1}{2}$ and $m_{j_1} = -\frac{1}{2}$. However since the average probability involves a sum over m_{j_2} (which is manifested classically as the integral over $q_{m_{j_1}}$), the summand of Eq. (3.5) depends only on $|m_{j_1}|$ and is thus the same for $m_{j_1} = \frac{1}{2}$ and $m_{j_1} = -\frac{1}{2}$. One thus needs to calculate it only for $m_{j_1} = \frac{1}{2}$, say, so that in this particular case Eq. (3.5) becomes (noting also that $2j_1 + 1 = 2$

$$\bar{P}_{\frac{3}{2}\leftarrow\frac{1}{2}}(J) = (2\pi)^{-2} \int_0^{2\pi} dq_{j_1} \int_0^{2\pi} dq_{m_{j_1}} \chi[j_2(\tfrac{1}{2},\tfrac{1}{2},q_{j_1},q_{m_{j_1}}) - \tfrac{3}{2}] \quad . \tag{3.7}$$

c. $\underline{F + H^+}$

As noted above, the Σ and Π potential curves used in the classical Hamiltonian of Eq. (3.2) were the same ones employed by Mies[10] in his quantum mechanical coupled-channel calculation. Figure 5 shows the results of the present quasi-classical calculations (based on Eqs. (3.2)-(3.7)) for

$$F(^2P_{1/2}) + H^+ \rightarrow F(^2P_{3/2}) + H^+ \quad . \tag{3.8}$$

Mies' results are also shown in Figure 5 , and one sees that the classical model is in remarkably good agreement with the quantum mechanical results, much better than one might expect for a process involving such small quantum numbers (i.e., $j = \frac{1}{2}, \frac{3}{2}$), not to mention the fact that the model involves a

classical description of certain aspects of the electronic degrees of freedom. There are, however, other examples[5] of inelastic collisions involving small quantum numbers, e.g.,

$$A + H_2(j=0) \rightarrow A + H_2(j=2) \quad ,$$

with A = He and Li^+, for which the quasiclassical model has been found to be reasonably accurate, and since the present process is a "classically allowed" one, it should perhaps not be too surprising that the quasiclassical model works well.

A few variations of the computational methodology described in Section IIIb were investigated to test the sensitivity of the classical results to the particular details of the quasiclassical procedure. First, the sum over integer values of m_{j_1} in Eq. (3.5) was replaced by an integral,

$$\sum_{m_{j_1}=-j_1}^{j_1} \rightarrow \int_{-(j_1+\frac{1}{2})}^{j_1+\frac{1}{2}} dm_{j_1} \quad ,$$

and this had an insignificant effect on the results. Not making the Langer modification, however, leads to quite poor results, an order of magnitude too small. Also, the "energy transfer" model--i.e., in which $P_{\frac{3}{2}\leftarrow\frac{1}{2}}$ of Eq. (3.7) is approximated by

$$\bar{P}_{\frac{3}{2}\leftarrow\frac{1}{2}} \rightarrow \frac{\langle j_2^2\rangle - (\frac{1}{2})^2}{(\frac{3}{2})^2 - (\frac{1}{2})^2} \quad ,$$

where

$$\langle j_2^2 \rangle \equiv (2\pi)^{-2} \int_0^{2\pi} dq_{j_1} \int_0^{2\pi} dq_{m_{j_1}} \; j_2(\tfrac{1}{2}, \tfrac{1}{2}, q_{j_1}, q_{m_{j_1}})^2$$

--was tried, but it gave results more than a factor of 2 too large. (This was without the Langer modification; with it, the results are worse.) Finally, the quenching cross section was obtained by first computing the quasiclassical cross section in the endoergic direction, $\frac{3}{2} \rightarrow \frac{1}{2}$, and then obtaining the exoergic quenching cross section by microreversibility,

$$\sigma_{\frac{3}{2}\leftarrow\frac{1}{2}} = 2(E_{3/2}/E_{1/2})\sigma_{\frac{1}{2}\leftarrow\frac{3}{2}} \quad , \tag{3.9}$$

where E_j is the translational energy for channel $j = \frac{1}{2}$ and $\frac{3}{2}$; this gave a result over a factor of 2 too large. All of these results reinforce the conventional wisdom that if interference effects are unimportant, then the most generally reliable way to utilize purely classical trajectories (i.e., with no semiclassical considerations) is via the standard quasiclassical model (used in the exoergic direction).

d. F + Xe

Similar calculations have been carried out for quenching of $F(^2P_{1/2})$ by Xe,

$$F(^2P_{1/2}) + Xe \rightarrow F(^2P_{3/2}) + Xe \quad .$$

Since neutral Xe interacts with F much more weakly than does H^+, the cross section for quenching by Xe is much smaller and thus provides a more severe test of the quasiclassical model.

Figure 6 shows the quasiclassical cross section as a function of initial translational energy, compared with the quantum mechanical coupled-channel calculations of Becker.[11] Because of the weaker interaction, the cross section does not become appreciable until higher collision energies than

with H^+; i.e., there is a substantial classically forbidden, or tunneling region at low energies.

One sees again that the classical model for the electronic degrees of freedom, along with the standard quasiclassical procedure, does a reasonably good job of describing this electronically non-adiabatic collision process, although agreement with the quantum results is not as quantitative as for the $F + H^+$ example. For this example, however, microreversibility is more closely satisfied than for $F + H^+$; thus the $\frac{3}{2} \leftarrow \frac{1}{2}$ quenching cross section obtained by first computing the quasiclassical cross section for $\frac{1}{2} \leftarrow \frac{3}{2}$, and then using Eq. (3.9), is within $\sim$ 13% of the quasiclassical cross section computed for $\frac{1}{2} \leftarrow \frac{3}{2}$. To the extent that quasiclassical cross sections are observed to obey microreversibility ones confidence in the results is increased.

IV. Concluding Remarks.

Section III has shown how a classical pseudo-potential formalism can provide a more systematic way of deriving classical models for the electronic degrees of freedom. For the examples treated previously[4] this analysis leads to the same classical electronic Hamiltonian, but it shows how to proceed in more general situations.

The calculations reported in Section III are the first application of this approach, and while not of great practical significance in themselves--because it is easy enough to carry out fully quantum mechanical calculations for non-adiabatic processes in atom-atom collisions--the agreement with the correct quantum mechanical results is quite encouraging. The full advantages of this approach are in treating molecular collisions, e.g., A + BC, where the presence of rotational and vibrational degrees of freedom usually prohibits completely quantum mechanical calculations.

The results presented in Section III are also reassuring in another sense. While the present model has the virtue of treating electronic and nuclear degrees of freedom dynamically consistently, it is nevertheless true that a classical description of the electronic motion is cruder than the conventional "classical path" semiclassical approach that describes electrons quantum mechanically and nuclei classically. The encouraging results obtained for the quenching of excited F atoms indicate that not too much violence has been done to the electronic degrees by invoking this classical model for them.

Acknowledgments

This work has been supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy, and all calculations were carried out on a Harris Slash Four minicomputer funded by a National Science Foundation Grant CHE-7622621. WHM also acknowledges support of the Miller Institute of Sciences and HDM acknowledges the financial support from the Deutsche Forschungsgemeinschaft.

Appendix

Here we show how the integral in Eq. (2.24) is evaluated. Using Eq. (2.20a), it is not hard to show that

$$e^{i\phi_e} = \cos\phi_e + i\sin\phi_e = (\sin\theta_e\cos\phi_e + i\sin\theta_e\sin\phi_e)/\sin\theta_e$$

$$= e^{-iq_m}(\sin q + i\frac{m}{j}\cos q)/\sqrt{\sin^2 q + \frac{m^2}{j^2}\cos^2 q}$$

$$= e^{-iq_m}\exp[i\tan^{-1}(\frac{m}{j}\cot q)] \quad ,$$

or

$$\phi_e = -q_m + \tan^{-1}(\frac{m}{j}\cot q) \quad , \tag{A.1}$$

where the subscript "j" has been dropped from q_j, m_j, and q_{m_j}. The integral in Eq. (2.24) is thus

$$I \equiv (2\pi)^{-1}\int_0^{2\pi} dq\, P_\lambda^\mu(\cos\theta_e)\, e^{i\mu\phi_e}$$

$$= e^{-i\mu q_m}(2\pi)^{-1}\int_0^{2\pi} dq\; P_\lambda^\mu(\sqrt{1-m^2/j^2}\cos q)\exp[i\mu\tan^{-1}(\frac{m}{j}\cot q)] \quad . \tag{A.2}$$

Defining (θ_2,ϕ_2) by

$$\cos\theta_2 \equiv \cos\theta_e = \sqrt{1-m^2/j^2}\cos q \tag{A.3a}$$

$$\phi_2 = \tan^{-1}(\frac{m}{j}\cot q) \quad , \tag{A.3b}$$

Eq. (A.2) then reads

$$I = e^{-i\mu q_m} (2\pi)^{-1} \int_0^{2\pi} dq \; P_\lambda^{\mu}(\cos\theta_2) \; e^{i\mu\phi_2}$$

or,

$$I = e^{-i\mu q_m} \; C_{\lambda\mu}(2\pi)^{-1} \int_0^{2\pi} dq \;\; Y_{\lambda\mu}(\theta_2,\phi_2) \quad , \tag{A.4}$$

where $Y_{\lambda\mu}(\theta_2,\phi_2)$ is the usual spherical harmonic and $C_{\lambda,\mu}$ is a normalization constant relating $P_\lambda^{\mu} \; e^{i\mu\phi}$ to $Y_{\lambda\mu}$. We consider (θ_2,ϕ_2) as the spherical angles relating a unit vector $\hat{r}_2$ to a space-fixed axis, and (θ_1,ϕ_1) as the corresponding angles relating the vector $\hat{r}_1$ to the same space fixed axis. The angles (θ,ϕ) are the spherical angles which relate $\hat{r}_2$ to a new axis system which has its z-axis along $\hat{r}_1$. These various angles are related by[15]

$$\cos\theta_2 = \cos\theta_1 \cos\theta \;\; + \;\; \sin\theta_1 \sin\theta \cos q \tag{A.5a}$$

$$\sin(\phi_2-\phi_1) = \frac{\sin\theta \sin\phi}{\sin\theta_2} \quad . \tag{A.5b}$$

If we choose

$$\theta = \frac{\pi}{2} \tag{A.6a}$$

$$\phi = q \tag{A.6b}$$

$$\theta_1 = \cos^{-1}(m/j) \tag{A.6c}$$

$$\phi_1 = \frac{\pi}{2} \quad . \tag{A.6d}$$

then by using Eqs. (A.5) it is easy to show that Eqs. (A.3) are satisfied. A standard relation for angular momentum theory,[16]

$$Y_{\lambda\mu}(\theta_2,\phi_2) = \sum_{\mu'} D_{\mu\mu'}^{\lambda}(\phi_1,\theta_1,0)^* Y_{\lambda\mu'}(\theta,\phi) \quad , \tag{A.7}$$

can now be used so that with Eqs. (A.6) the integral I of Eq. (A.2) becomes

$$I = e^{-i\mu q_m} C_{\lambda\mu} \sum_{\mu'} D_{\mu\mu'}^{\lambda}(\tfrac{\pi}{2}, \cos^{-1}(\tfrac{m}{j}), 0)^* (2\pi)^{-1} \int_0^{2\pi} dq\, Y_{\lambda\mu'}(\tfrac{\pi}{2},q) \quad , \tag{A.8}$$

Since

$$(2\pi)^{-1} \int_0^{2\pi} dq\, Y_{\lambda\mu'}(\tfrac{\pi}{2}, q) = Y_{\lambda\mu'}(\tfrac{\pi}{2}, 0)\, \delta_{\mu',0} \quad ,$$

Eq. (A.8) becomes

$$\begin{aligned} I &= e^{-i\mu q_m} C_{\lambda\mu} D_{\mu,0}^{\lambda}(\tfrac{\pi}{2}, \cos^{-1}(\tfrac{m}{j}), 0)^* Y_{\lambda 0}(\tfrac{\pi}{2},0) \\ &= e^{-i\mu q_m} C_{\lambda\mu} Y_{\lambda\mu}(\cos^{-1}(\tfrac{m}{j}), \tfrac{\pi}{2})\, P_\lambda(0) \\ &= e^{i\mu(\frac{\pi}{2} - q_m)} P_\lambda^{\mu}(\tfrac{m}{j})\, P_\lambda(0) \quad , \end{aligned} \tag{A.9}$$

and using the fact that

$$P_\lambda(0) = \begin{cases} \dfrac{(-1)^{\frac{\lambda}{2}}\, \lambda!}{2^\lambda\, (\frac{\lambda}{2}!)^2} \quad , & \lambda \text{ even} \\ 0 \quad , & \lambda \text{ odd} \end{cases} \quad , \tag{A.10}$$

Eq. (2.24) follows.

References

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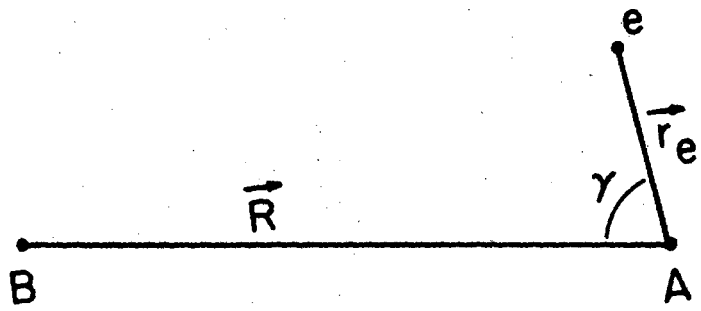
Figure Captions

1. Coordinates for the interaction of the pseudo one-electron atom A (e is the electron) and the closed shell atom B.
2. Coordinates for the interaction of the pseudo one-electron atom A with the diatomic molecule BC.
3. Coordinates for the pseudo two-electron atom A, e_1 and e_2 being the two electrons.
4. Coordinates for the interaction of the pseudo two-electron atom A and the closed shell atom B.
5. Cross section for quenching of $F(^2P_{1/2})$ to the ground state $F(^2P_{3/2})$ by collision with H^+, as a function of initial translational energy. The full curve is the quantum mechanical result of reference 10, and the points (with statistical uncertainty from the Monte Carlo integration) the present quasiclassical results.
6. Same as Figure 5, except the collision partner is Xe, and the quantum calculations are from reference 11. The lower point at E = 1 eV is obtained computing the quasiclassical cross section in the excitation direction, $\frac{3}{2} \rightarrow \frac{1}{2}$, and then using microscopic reversibility to obtain the de-excitation cross section.



XBL 789-11121

Figure 1

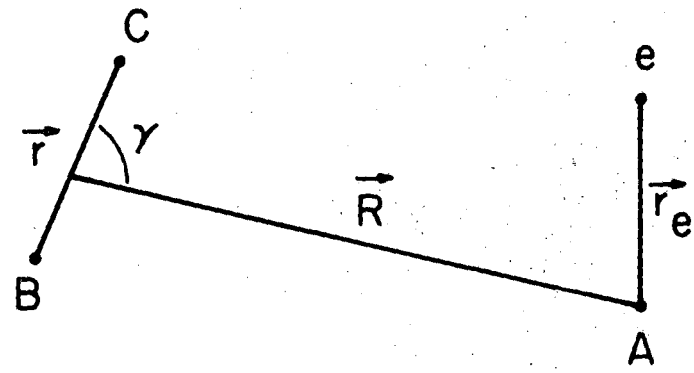


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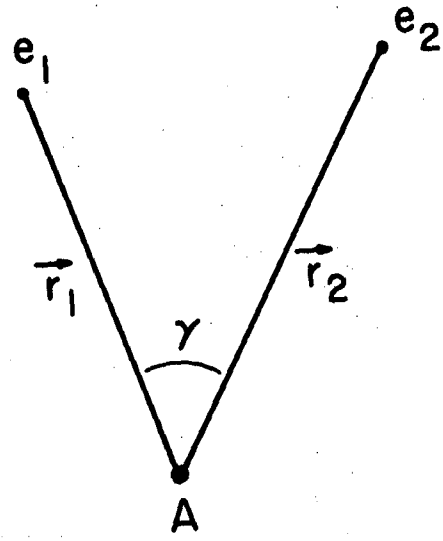
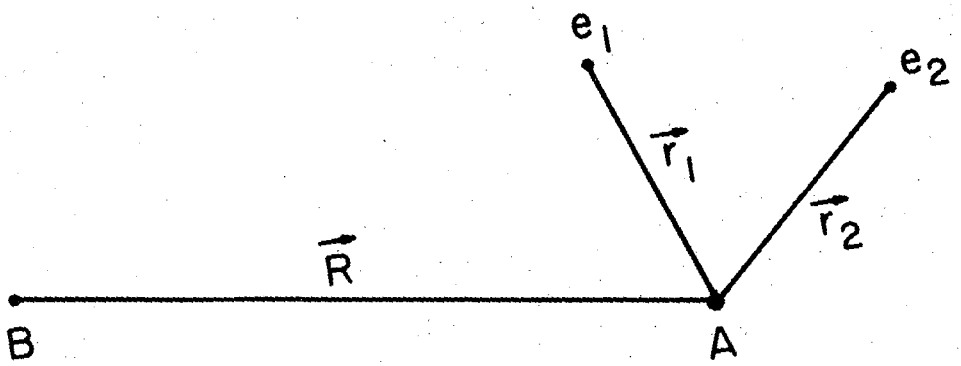
Figure 2



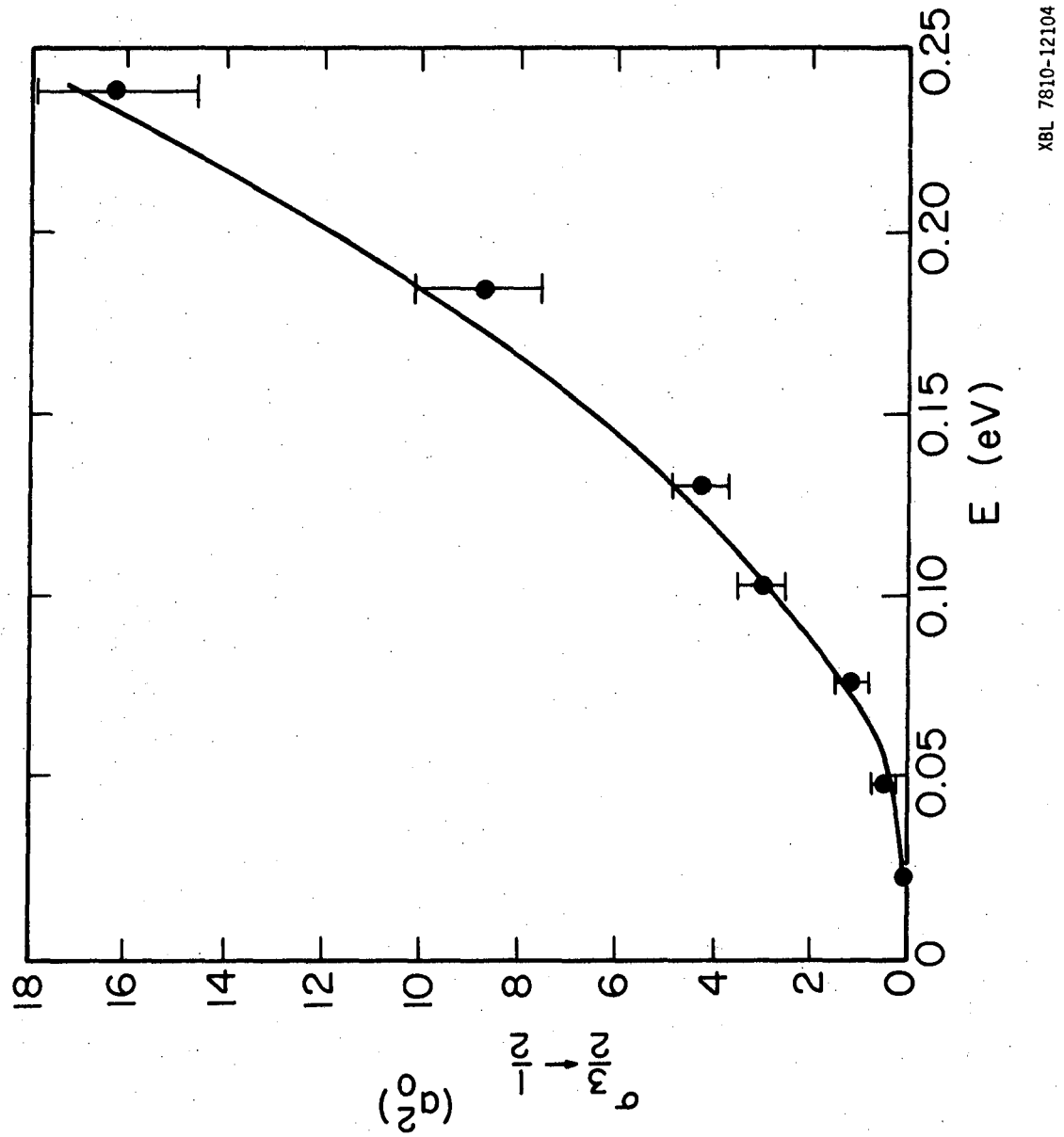
XBL 789-11118

Figure 3



XBL 789-11119

Figure 4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E (eV)
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0.10
0.15
0.20
0.25
0
2
4
6
8
10
12
14
16
18
XBL 7810-12104

Figure 5

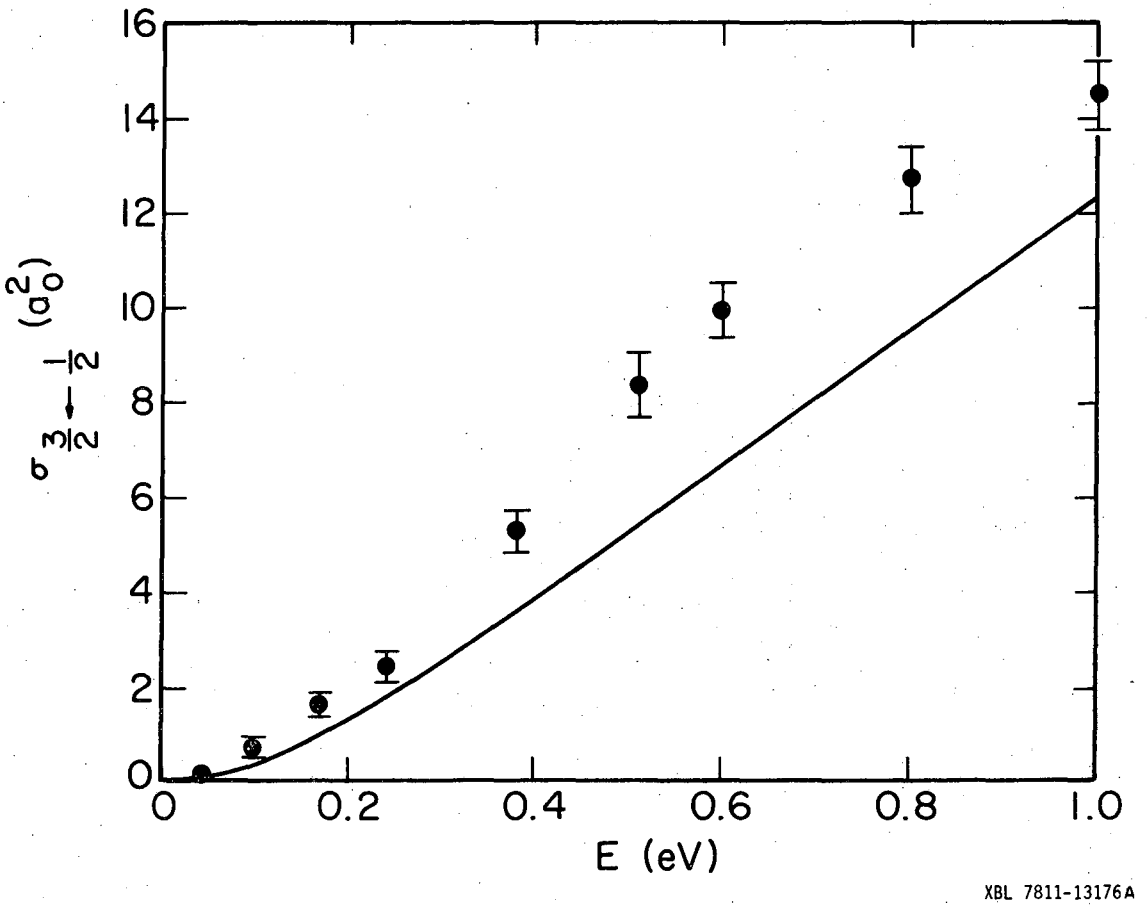
16
14
12
10
8
6
4
2
0
0
0.2
0.4
0.6
0.8
1.0
E (eV)
$\sigma_{\frac{3}{2}\rightarrow\frac{1}{2}}$ (a_0^2)
XBL 7811-13176A

Figure 6

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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