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Molecular Theory of Atomic Collisions: Fine-Structure Transitions

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The theory of fine-structure transitions in atom-atom collisions is formulated in terms of the molecular states of the diatomic collision complex. The Born–Oppenheimer (BO) electronic wave functions are implicit functions of the interatomic coordinate R, and the molecular theory is analogous to the "perturbed-stationary-state" method. Expansion in *molecular* channel states incorporates the effects of polarization, exchange, and valence forces on the electronic portion of the scattering wave function and embodies the "adiabatic" contribution of the entire set of closed-channel excited states that are generated in the more usual asymptotic-atomic-state expansion. The channel states are expressed explicitly in terms of the body-fixed molecular wave functions, and the resultant interaction matrix elements in the close-coupling scattering formalism are related to the molecular potentials. The theory is developed specifically for proton collisions with the fluorine atom in its ground $^2P_{j,\,m_j}$ state, with explicit account being taken of the spin-orbit splitting between the $j=3/2$ and $j=1/2$ multiplet states. Use is made of the accurate HF$^+$($^2\Pi$) and HF$^+$($^2\Sigma$) wave functions calculated by Wahl, Julienne, and Krauss. These molecular states asymptotically approach H$^+$ + F(^{2}P), and accurate quadrupole and induced-dipole interaction parameters which describe the asymptotic interaction potentials are obtained from the calculations. Estimates are made of the BO coupling terms and they are found to be negligible compared to the spin-orbit couplings. In the following paper close-coupling calculations are made of the cross sections for the fine-structure transitions $(j, m_j \to j', m_j)$.

I. INTRODUCTION

The wave functions that describe the scattering between two atoms A and B are equivalent to the continuum wave functions of the diatomic molecule AB, and it is well recognized[1] that the adiabatic electronic states of the molecule form a useful basis with which to formulate the low-energy scattering problem. This is known as the perturbed-stationary-state (pss) method and is expected to be superior (i.e., more rapidly convergent) to the usual expansion in asymptotic atomic states since the molecular Born–Oppenheimer (BO) states are implicit functions of the interatomic distance R and incorporate the effects of polarization, electron exchange, and valence forces. The theory has been applied extensively[1-3] but has suffered from lack of accurate molecular potentials, and/or use of approximate techniques in treating the coupling between the adiabatic states. It is only recently that some of these limitations have been removed[4-6] and the increasing availability of accurate molecular wave functions suggests the need to approach the molecular theory of atomic collisions with increased rigor. To this end it is advantageous to treat the collisions between a proton H$^+$ and a ground-state fluorine atom F(^2P). This is one case which goes beyond simple elastic scattering that can be treated with great rigor, primarily because the electrons are asymptotically situated on one center.

In the case of low-energy collisions between two ground-state ${}^1S_0$ atoms, only elastic scattering occurs, the system is usually well described by a single adiabatic state, and there is a one-to-one correspondence between the ${}^1\Sigma$ state potential calculated by the quantum chemist and the scattering potential extracted from the elastic cross sections.[7] In actual fact the pss theory is the only justification for using the concept of a local, energy-independent scattering "potential" to describe the elastic scattering between two composite systems. However, this simple relationship breaks down if the asymptotic atomic states are, say, n-fold degenerate, since there are now n molecular states which adiabatically dissociate into the atomic products, and the question arises, what is the relationship between the adiabatic potential curves that are calculated in the BO approximation and the required input to the scattering theory? The process is no longer elastic since the collision can change the magnetic sublevels within a given multiplet state, or produce transitions between the various multiplet levels which become nondegenerate owing to spin-orbit interactions. In the molecular theory the inelastic behavior is caused by the nonadiabatic couplings between the molecular states arising from the kinetic-energy operator of the relative motion, and the relativistic terms such as the spin-orbit operator which are generally ignored in the BO approximation.[8-10] These matrix elements lead to coupled differential equations in the scattering formalism and must be carefully evaluated.

In this paper the theory for collisions between a proton H^+ and a fluorine atom in the sixfold degenerate ground state $F({}^2P_j)$ is formulated in terms of the diatomic $HF^+({}^2\Pi)$ and $HF^+({}^2\Sigma)$ molecular states that characterize the collision complex and asymptotically dissociate to $H^+ + F({}^2P)$. The effect of spin-orbit interaction, which splits the ${}^2P_{3/2}$ and ${}^2P_{1/2}$ multiplet states by 404 cm^{-1}, is incorporated into the theory. Expressions are derived for the cross sections between the multiplet states $(\frac{3}{2}\rightarrow\frac{1}{2})$ and for transitions amongst the degenerate magnetic sublevels $(j,\ m_j \rightarrow j,\ m_j')$ which give rise to spatial reorientations or depolarization. It will be seen that the off-diagonal interaction matrix elements depend on the splitting between the ${}^2\Pi$ and ${}^2\Sigma$ interaction potential, while the diagonal terms are weighted averages of these two potentials. The theory is utilized in the following paper to obtain the cross sections in a quantum-mechanical close-coupling calculation.

The FH^+ system is particularly favorable to study for many reasons:

(i) For incident kinetic energies less than 3.825 eV the only accessible channels are the ${}^2P_{3/2}$ and ${}^2P_{1/2}$ states of F, which lead to six coupled-differential equations in the scattering theory. For thermal kinetic energies coupling to the higher *closed* channels probably can and will be ignored. Above 3.825 eV the channel $F^+ + H(1s)$ becomes open, and greatly complicates the scattering theory since this essentially introduces a rearrangement process that is not well understood.

(ii) For scattering by a proton the difficulty of antisymmetrizing the total scattering wave function is avoided since all the electrons are left in the target atom state which is properly symmetrized. In principle antisymmetrizing the wave function for scattering by two atoms can be handled, but great case must be taken not to introduce spurious asymptotic terms owing to the so-called mass polarization which can greatly complicate the scattering boundary conditions.

(iii) Very accurate Hartree–Fock self-consistent-field (HF-SCF) calculations of the ${}^2\Pi$ and ${}^2\Sigma$ states of FH^+ have been carried out by Wahl, Julienne, and Krauss[11] and the determination of the angular BO coupling terms using only slightly less accurate functions for these states have been made by Julienne, Krauss, and Neumann.[12] In addition, one has the added feature that the HF-SCF wave function goes accurately to the proper asymptotic atomic state $F({}^2P)$ and that correlation effects in the intermolecular potential should be negligible.

(iv) The atomic spin-orbit coupling constant for $F({}^2P)$ can be used in determining the spin-orbit constant for the molecular states due to the negligible contribution of the proton compared to F in the spin-orbit term, and the small perturbation of the electron distribution.

(v) Finally, HF^+ has a simple form for the asymptotic interaction potential which is due only to charge-quadrupole and charge-induced-dipole interaction, and is not complicated by dispersion forces.

The remainder of the paper is organized as follows. In Sec. II the atomic states of fluorine are considered, while in Sec. III the interaction of the proton with F is considered and related to the molecular states of HF^+. The molecular spin-orbit interaction is discussed in Sec. IV. The total angular momentum channel states are constructed in Sec. V in terms of the molecular electronic states, and the relation of the scattering amplitudes and the cross sections to the molecular channel states is considered in Sec. VI. The coupled-differential equations are developed in Sec. VII, and the coupling terms are derived. Section VIII considers the asymptotic structure of the interaction potentials and estimates of the BO coupling terms. Section IX summarizes the conclusions thus far. The actual calculation of the cross sections is presented in the following paper.

II. ATOMIC HAMILTONIAN AND ATOMIC WAVE FUNCTIONS

The Hamiltonian for the fluorine atom in space-fixed electron $\vec{r}_i'$ and nuclear $\vec{R}_F'$ coordinates is, in atomic units (e^2/a_0)

$$-\frac{1}{2m_F}\nabla_{\vec{R}_F'}{}^2-\frac{1}{2}\sum_{i=1}^{9}\nabla_{\vec{r}_i}{}^2+V_F(|\vec{r}_i'-\vec{r}_j'|,\ |\vec{r}_i'-\vec{R}_F'|)+V_{LS}(|\vec{r}_i'-\vec{R}_F'|),$$

where V_F represents the Coulombic potential terms, and V_{LS} is the relativistic spin-orbit operator. It is convenient to refer all coordinates to the center-of-mass (c.m.) of the atom, i.e., letting

$$\vec{R}_F=\left(m_F\vec{R}_F'+\sum_{i=1,9}\vec{r}_i'\right)M_F^{-1}, \tag{2.1}$$

where $M_F=m_F+9$, and letting $\vec{r}_i=\vec{r}_i'-\vec{R}_F$, one obtains

$$-\frac{1}{2M_F}\nabla_{\vec{R}_F}{}^2+H_F(\vec{r})+V_{LS}(\vec{r}). \tag{2.2}$$

The electron Hamiltonian $H_F(\vec{r})$ is independent of both $\vec{R}_F$ and the electron spin $\vec{S}_i$,

$$H_F(\vec{r})=-\frac{1}{2}\sum_{i=1}^{9}\nabla_{\vec{r}_i}{}^2-\frac{\vec{P}\cdot\vec{P}}{2m_F}+V_F(\vec{r}). \tag{2.3}$$

The electron linear-momentum operator $\vec{P}=-i\sum_i\nabla_{\vec{r}_i}$ occurs in the mass polarization, or isotopic, term in H_F, and V_F takes the form,

$$V_F=\frac{1}{2}\sum_{i,j}{}'|\vec{r}_i-\vec{r}_j|^{-1}-9\sum_i\left|\vec{r}_i+\sum_j\vec{r}_jm_F^{-1}\right|^{-1}$$
$$\approx\frac{1}{2}\sum_{i,j}{}'|\vec{r}_i-\vec{r}_j|^{-1}-9\sum_i r_i^{-1}. \tag{2.4}$$

The spin-orbit operator is also independent of $\vec{R}_F$, and is approximated as follows:

$$V_{LS}=\sum_i f_i\left(\left|\vec{r}_i+\sum_j\vec{r}_jm_F^{-1}\right|\right)\vec{L}_i\cdot\vec{S}_i$$
$$\approx\sum_i f_i(r_i)\vec{L}_i\cdot\vec{S}_i. \tag{2.5}$$

The electron Hamiltonian H_F commutes with the electron orbital angular momentum, $\vec{L}^2$ and $L_{Z'}$, and the electron-spin angular momentum, $\vec{S}^2$ and $S_{Z'}$; and the atomic wave functions $|(n,L,S)m_L,m_S\rangle$ are eigenfunctions of these five operators, with eigenvalues $\mathcal{E}^{n,L,S}$, $L(L+1)$, m_L, $S(S+1)$, and m_S, respectively.[13] The ground state of fluorine, $n\equiv0$, is a ^2P state with $S=\frac{1}{2}$ and $L=1$, and the total energy will be defined such that $\mathcal{E}^{0,1,1/2}\equiv0$. This state is sixfold degenerate, and will be designated simply in terms of the magnetic quantum numbers $m_L=0$, ±1, and $m_S=\pm\frac{1}{2}$:

$$H_F|(n,L,S)m_L,m_S\rangle=\mathcal{E}^{n,L,S}|(n,L,S)m_L,m_S\rangle \tag{2.6}$$

and, in particular,

$$H_F|(0,L,S)m_L,m_S\rangle\equiv H_F|m_L,m_S\rangle=0. \tag{2.7}$$

Since $L_{Z'}$ and $S_{Z'}$ do not commute with the spin-orbit operator, it is necessary to construct atomic states which are diagonal in the total electron angular momentum $\vec{j}^2$ and $j_{Z'}$, where $\vec{j}=\vec{L}+\vec{S}$, and which do commute with $\vec{L}\cdot\vec{S}$:

$$|(n,L,S)j,m_j\rangle=\sum_{m_L,m_S}(L,S,j|m_L,m_S,m_j)\times|(n,L,S)m_L,m_S\rangle. \tag{2.8}$$

$(L,S,j|m_L,m_S,m_j)$ is the Clebsch–Gordan coefficient and is defined such that

$$\begin{aligned}\vec{j}^2|j,m_j\rangle&=j(j+1)|j,m_j\rangle,\\ j_{Z'}|j,m_j\rangle&=m_j|j,m_j\rangle,\end{aligned} \tag{2.9}$$

and the stepping operator $j_\pm$ yields

$$j_\pm|j,m_j\rangle=[(j\mp m_j)(j\pm m_j+1)]^{1/2}|j,m_j\pm1\rangle.$$

For the ground state ^2P one has the six states, $j=\frac{3}{2}$, with $m_j=\pm\frac{1}{2}$, $\pm\frac{3}{2}$ and $j=\frac{1}{2}$, with $m_j=\pm\frac{1}{2}$.

The *entire* set of atomic states may be used as a basis for solving the total Hamiltonian H_F+V_{LS}. However, since the excited states $n>0$ have energies orders of magnitude greater than the spin-orbit splitting, we need only include the ground ^2P states in our expansion, and the energy matrix is essentially diagonalized by the $|j,m_j\rangle$ states,

$$\begin{aligned}\langle\tfrac{3}{2},m_j|H_F+V_{LS}|\tfrac{3}{2},m_j'\rangle&=\delta_{m_j,m_j'}(-\tfrac{1}{2}a),\\ \langle\tfrac{1}{2},m_j|H_F+V_{LS}|\tfrac{1}{2},m_j'\rangle&=\delta_{m_j,m_j'}(a),\\ \langle\tfrac{1}{2},m_j|H_F+V_{LS}|\tfrac{3}{2},m_j'\rangle&=0,\end{aligned} \tag{2.10}$$

where $\frac{3}{2}a=404\ \text{cm}^{-1}$ is the spin-orbit splitting of the $F(^2P)$. The structure of the $F(^2P_{j,m_j})$ states is shown in Fig. 1. Now consider the interaction of F with a proton.

III. INTERACTION OF H^++F: MOLECULAR WAVE FUNCTIONS

If one refers the proton coordinate $\vec{R}_H'$ to the *fluorine* center of mass $\vec{R}_F$ in (2.1),

$$\vec{R}=\vec{R}_H'-\vec{R}_F=\vec{R}_H'-\vec{R}_F'-\sum_i\vec{r}_i'm_F^{-1}, \tag{3.1}$$

and eliminates the center of mass $\vec{C}$ of the entire H^++F system from the total Hamiltonian of the interacting system,

$$\vec{C}=(m_F\vec{R}_F'+m_H\vec{R}_H'+\sum_i\vec{r}_i')/(m_H+m_F+9),$$

the following Hamiltonian in space-oriented coordinates moving with the F c.m. is obtained:

$$H=-(\nabla_{\vec{R}}{}^2/2\mu)+H_F(\vec{r})+V(\vec{r},\vec{R})+V_{LS}(\vec{r},\vec{R}), \tag{3.2}$$

where $\mu=m_HM_F/(m_H+M_F)$, and V is the Coulombic interaction between the proton and the fluorine,

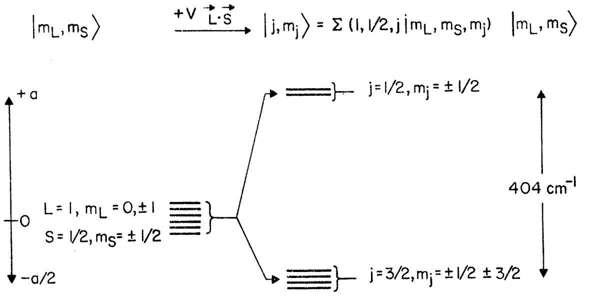

FIG. 1. Energy levels of F(^2P). On the left the eigenvalues of the nonrelativistic atomic Hamiltonian are sixfold degenerate with wave functions $|m_L, m_S\rangle$, designated by the electron spin projection $m_S = \pm\frac{1}{2}$, and electron orbital angular momentum projection $m_L = 0, \pm 1$. The spin-orbit operator V_{LS} is diagonalized by the total angular momentum states $|j, m_j\rangle$ which for F are well represented by the combination of $|m_L, m_S\rangle$ states determined by the Clebsch–Gordan coefficients $(1, \frac{1}{2}, j\,|m_L, m_S, m_j)$. The $j=\frac{1}{2}$ state is twofold degenerate and 404 cm^{-1} above the fourfold degenerate, $j=\frac{3}{2}$ ground state.

$$V = -\sum_i |\vec{r}_i - \vec{R}|^{-1} + 9\,|\vec{R} + \sum_j \vec{r}_j m_F^{-1}|^{-1}$$
$$\approx -\sum_i |\vec{r}_i - \vec{R}|^{-1} + 9/R\,. \tag{3.3}$$

The electron terms $H_F + V$ define the electronic Hamiltonian for the HF^+ molecule in the adiabatic Born (AB) approximation, and closely approximates the more usual BO Hamiltonian where the mass-polarization terms $\vec{P}\cdot\vec{P}$, and the electron c.m. terms $\sum_j \vec{r}_j m_F^{-1}$ are neglected by referring the electron coordinates to the nuclear centers rather than the atom c.m. However, in this form one gains the important advantage that asymptotically, as $R \to \infty$ and $V \to 0$, the molecular Hamiltonian approaches the exact atomic Hamiltonian $H_F(\vec{r})$, and is rigorously independent of R, and the remainder of the Hamiltonian in (3.2) does not contain any spurious cross terms $\nabla_{\vec{R}}\cdot\nabla_{\vec{r}_i}$ which complicate the asymptotic boundary conditions[14]:

$$H_{AB}(\vec{R}, \vec{r}) \equiv H_F(\vec{r}) + V(\vec{r}, \vec{R}) \underset{R\to\infty}{\sim} H_F(\vec{r})\,. \tag{3.4}$$

In practice the BO solutions will be used, but since the mass-polarization terms in H_F contribute both to the molecular and the asymptotic atomic states it would seem reasonable to ignore their effects and assume their contribution is independent of R. Also the effect of approximating the nuclear repulsion terms in (3.3) by $9/R$ should be insignificant, although the effect could be tested by perturbation theory. These approximations seem particularly valid for HF^+ since asymptotically the electrons are all located on one center. The role of the various mass-polarization terms which can arise in other systems, particularly when electron exchange can occur, remains to be considered.

The total Hamiltonian can be represented in molecule-fixed coordinates by rotating the space-fixed axis through the Eulerian angles $(\phi, \theta, 0)$, where ϕ and θ are the polar coordinates of $\vec{R}$. The new vector components are represented by the unprimed variables $X, Y, Z \equiv R$. Since H_{AB} is invariant to these rotations, the only complication occurs in rotating the $\nabla_{\vec{R}}^2$ operator. The transformed Hamiltonian (3.2) becomes

$$H(R, \theta, \phi, \vec{r}) = -\frac{1}{2\mu}\left(\frac{\partial^2}{\partial R^2} + \frac{2}{R}\frac{\partial}{\partial R}\right) + \frac{\vec{L}_R^2(\theta, \phi)}{2\mu R^2}$$
$$+ H_{AB}(R, \vec{r}) + V_{LS}(\vec{r}, \vec{R})\,, \tag{3.5}$$

where $\vec{L}_R$ is the nuclear angular momentum in body-fixed coordinates,

$$\vec{L}_R = -i\vec{R}\times\nabla_{\vec{R}} \equiv \vec{J} - \vec{j} = \vec{J} - \vec{L} - \vec{S} \tag{3.6}$$

and is a function of θ, ϕ. Since the total angular momentum $\vec{J}$ is the sum of the nuclear $\vec{L}_R$ and electronic $\vec{j}$ angular momentum, it proves convenient to express $\vec{L}_R = \vec{J} - \vec{j}$, and treat $\vec{J}$ as a formal operator (see Appendix B). Note, by definition $\vec{L}_R \cdot \vec{R} = 0$.

The molecular wave functions are solutions of $H_{AB}(R, \vec{r})$ and are implicit functions of R. Since $H_{AB} \sim H_F(\vec{r})$ as $R \to \infty$, each eigenfunction can be associated with the particular atomic state to which it dissociates adiabatically. The molecular states are represented by introducing the variable R into the atomic notation, i.e., $|R, (n, L, S)\Lambda, m_S\rangle$, where

$$H_{AB}(R, \vec{r})\,|R, (n, L, S)\Lambda, m_S\rangle$$
$$= W_{|\Lambda|}^{n,L,S}(R)\,|R, (n, L, S)\Lambda, m_S\rangle \tag{3.7}$$

such that

$$|R, (n, L, S)\Lambda, m_S\rangle \underset{R\to\infty}{\sim} |(n, L, S)\Lambda, m_S\rangle \tag{3.8}$$

and the R-dependent eigenvalue (molecular potential!) approaches $\mathcal{E}^{n,L,S}$:

$$W_{|\Lambda|}^{n,L,S}(R) \underset{R\to\infty}{\sim} \mathcal{E}^{n,L,S}\,. \tag{3.9}$$

Since H_{AB} is independent of $\vec{S}$, the quantum numbers S and m_S are valid for all R and the molecular functions are eigenfunctions of $\vec{S}^2$ and $S_{Z'}$. Similarly, since H_{AB} is invarient to a coordinate rotation about the $Z \equiv R$ axis in molecule-fixed coordinates, the Z component of the electronic orbital angular momentum will be quantized:

$$\vec{L} = -i\sum_j \vec{r}_j \times \nabla_{\vec{r}_j}\,,$$
$$(\vec{R}\cdot\vec{L}/R)\,|R, (n, L, S)\Lambda, m_S\rangle \tag{3.10}$$
$$= \Lambda\,|R, (n, L, S)\Lambda, m_S\rangle\,.$$

Λ is used to represent the molecule-fixed projec-

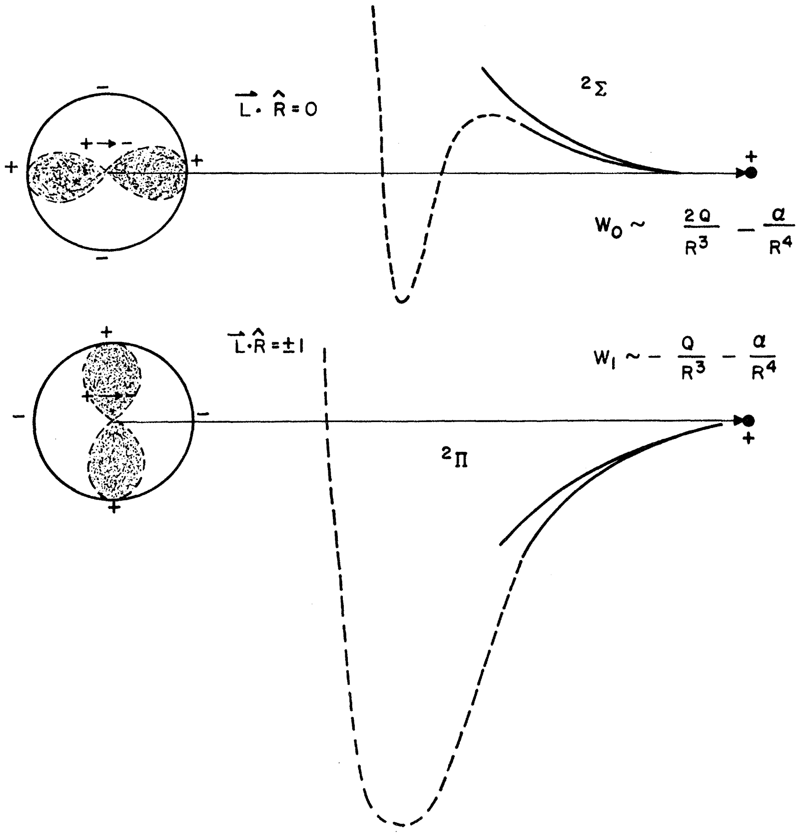

FIG. 2. Schematic picture of $H^+ + F(^2P)$ interaction energy. The proton, approaching from the right, initially interacts as R^{-3} with the permanent quadrupole moment of the P state. This interaction is repulsive in the $^2\Sigma$ state where $\vec{L}\cdot\hat{R}=0$, and attractive in the $^2\Pi$ state where $\vec{L}\cdot\hat{R}=\pm 1$. The next order of interaction is an attractive charge-induced dipole which increases as R^{-4}. The polarizability is close to isotropic, and α is approximately the same for both states. At smaller distances distinct molecular formation occurs; the important qualitative features of the short-range potential are sketched in by the dashed curves.

tion of $\vec{L}$ along the interatomic axis $\vec{R}$, while m_L designates the space-fixed projection.

At finite R the proton interaction causes a splitting of the asymptotically degenerate Λ states. In the BO approximation the molecular interaction is a function of $|\Lambda|$ only, and the R-dependent eigenvalues are expressed as $W^{n,L,S}_{|\Lambda|}(R)$. Since the ground state of $F(^2P)$ has $L=1$, Λ can take the values 0, ±1, and $F(^2P)$ correlates with the lowest $\Sigma(\Lambda=0)$ and doubly-degenerate $\Pi(\Lambda=\pm 1)$ state of HF^+. As with the atomic states [Eq. (2.7)] the ground-state notation is simplified by retaining only the magnetic quantum numbers $\Lambda=0$, ± 1, and $m_s = \pm\frac{1}{2}$, i.e.,

$$H_{AB}(R, \vec{r})|R, \Lambda, m_s\rangle = W_{|\Lambda|}(R)|R, \Lambda, m_s\rangle , \tag{3.11}$$

$$|R, \Lambda, m_s\rangle \underset{R\to\infty}{\sim} |\Lambda, m_s\rangle , \tag{3.12}$$

and

$$W_{|\Lambda|}(R) \underset{R\to\infty}{\sim} 0 . \tag{3.13}$$

The behavior of the $^2\Pi$ and $^2\Sigma$ states are shown in Fig. 2. The initial splitting of the Λ states as R becomes finite is due to the charge-quadrupole interaction (R^{-3}) between the proton and the fluorine. This interaction is repulsive for $\Lambda=0$, and attractive for $\Lambda=\pm 1$. This interaction, together with the attractive charge induced-dipole (R^{-4}) interaction that contributes equally to both states is discussed fully in Sec. VI. The accurate interaction potentials calculated by Wahl, Julienne, and Krauss are shown in Figs. 3 and 4.

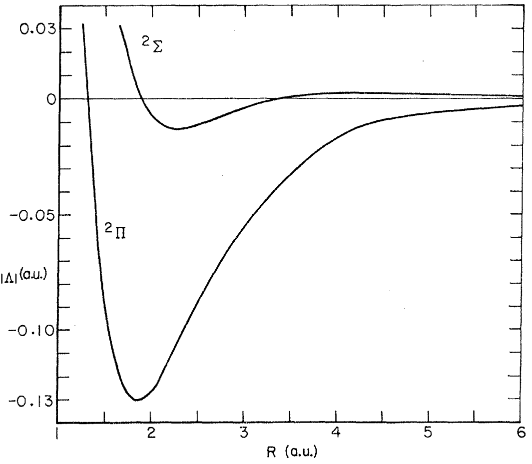

FIG. 3. Calculated interaction potentials of $HF^+(^2\Sigma)$ and $HF^+(^2\Pi)$ states. These potentials are accurate HF-SCF curves calculated by Wahl, Julienne, and Krauss.

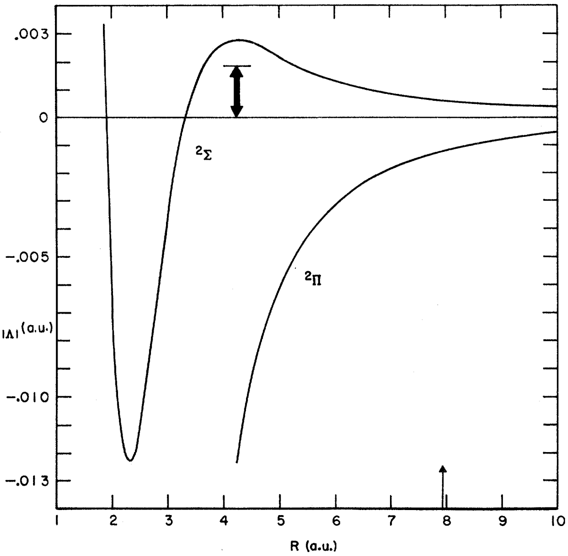

FIG. 4. Interaction potentials in the region of the $HF^+(^2\Sigma)$ barrier. Note that the barrier height is about $\frac{3}{2}$ times larger than the spin-orbit splitting as shown by the broad arrow. The splitting between the $^2\Sigma$ and $^2\Pi$ curves approximately equals the spin-orbit splitting at $R = 8$ a.u. The molecular wave functions at large distance were used to obtain accurate values for the quadrupole and polarization potential parameters.

IV. MOLECULAR SPIN-ORBIT INTERACTION

The cylindrical symmetry of the $H^+ + F$ interaction destroys the spherical symmetry of the isolated F atom, and thus the total electron orbital angular momentum $\vec{L}^2$ does not commute with $H_{AB}(R, \vec{r})$, except as $R \sim \infty$. As indicated in the molecular notation (3.7) each molecular state can be characterized by the orbital angular momentum of the asymptotic atomic state, but only in the limit does L become an eigenvalue,

$$\vec{L}^2 |R, (n, L, S)\Lambda, m_S\rangle \underset{R\to\infty}{\sim} L(L+1)|(n, L, S)\Lambda, m_S\rangle . \tag{4.1}$$

Both the $^2\Pi$ and $^2\Sigma$ ground states of course approach $L = 1$.

It is convenient to define linear combinations of molecular states which become diagonal in $\vec{j}^2$ and j_z, as $R \to \infty$, i.e.,

$$|R, j, \Omega\rangle = \sum_{\Lambda, m_S} (L, S, j|\Lambda, m_S, \Omega)|R, \Lambda, m_S\rangle . \tag{4.2}$$

Thus, these "states" approach atomic states which diagonalize the spin-orbit operator, i.e.,

$$|R, j, \Omega\rangle \underset{R\to\infty}{\sim} |j, \Omega\rangle , \tag{4.3}$$

where Ω is the projection of $\vec{j} = \vec{L} + \vec{S}$ along the interatomic coordinate $\vec{R}$ (m_j will be reserved to denote the space-fixed projection of j). The molecular states (4.2) are eigenfunctions of j_z for all R,

$$j_z|R, j, \Omega\rangle = \Omega|R, j, \Omega\rangle , \tag{4.4}$$

but only become eigenfunctions of $\vec{j}^2$ in the limit,

$$\vec{j}^2|R, j, \Omega\rangle \underset{R\to\infty}{\sim} j(j+1)|j, \Omega\rangle . \tag{4.5}$$

The spin-orbit operator $V_{LS}(\vec{r}, R)$ in the total Hamiltonian H will consist of two terms: (i) a contribution from the electron interactions with the fluorine nucleus identical to Eq. (2.5), and (ii) a similar contribution from the interaction with the incident proton;

$$V_{LS}(\vec{r}, \vec{R}) = V_{LS}(\vec{r}) + V^{H}_{LS}(\vec{r} - \vec{R}) . \tag{4.6}$$

Since $V_{LS} \propto (Z_{\text{nuc}})^4$ the contribution from the proton interaction will be negligible, i.e., $\approx 10^{-4} V_{LS}(\vec{r}_i)$. This is substantiated by the calculations of Walker and Richards.[15,16] The proton can also influence the fluorine term, $V_{LS}(\vec{r})$, indirectly since the perturbation of the fluorine atom's electron distribution owing to polarization, and chemical bonding will influence the expectation value of V_{LS}. However, these valence forces should not seriously affect this matrix element which is dominated by the electron wave function in the vicinity of the F nucleus, and one may assume that

$$\langle R, j, \Omega| V_{LS}(\vec{r}, \vec{R})|R, j', \Omega\rangle \cong \langle j, \Omega| V_{LS}(\vec{r})|j', \Omega\rangle , \tag{4.7}$$

which is given by (2.10). At $R = R_{\text{eq}}$ the calculations of Walker and Richards[15] predict $a = 306\ \text{cm}^{-1}$ as compared to $269\ \text{cm}^{-1}$ as given by Eq. (2.10). However it is difficult to assess the accuracy of the calculation, and one would tend to place more reliability on the use of the atomic value in *this* case. However, in general, the molecular spin-orbit operator should be examined, and the explicit R dependence of the matrix (4.7) should be assessed if possible.

The matrix elements of the molecular states in the j, Ω representation over the molecular Hamiltonian H_{AB} are diagonal in Ω, but not in j and the total matrix over $H_{AB} + V_{LS}$ is found from (3.11), (4.2), and (4.7) to be,

$$\langle R, j, \Omega|H_{AB} + V_{LS}|R, j', \Omega'\rangle = \delta_{\Omega,\Omega'}[(W_1 + \mathcal{E}_j)\delta_{j,j'} + (W_0 - W_1)(1, \tfrac{1}{2}, j|0, \Omega, \Omega) \times (1, \tfrac{1}{2}, j'|0, \Omega, \Omega)], \tag{4.8a}$$

or explicitly,

$$\langle R, \tfrac{3}{2}, \pm\tfrac{3}{2}|H_{AB} + V_{LS}|R, \tfrac{3}{2}, \pm\tfrac{3}{2}\rangle = W_1 - \tfrac{1}{2}a ,$$

$$\langle R, \tfrac{3}{2}, \pm\tfrac{1}{2}|H_{AB} + V_{LS}|R, \tfrac{3}{2}, \pm\tfrac{1}{2}\rangle = \tfrac{1}{3}(2W_0 + W_1) - \tfrac{1}{2}a ,$$

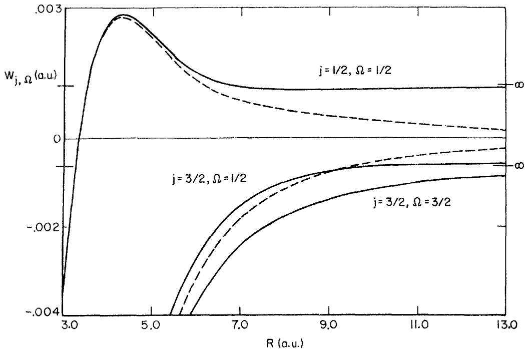

FIG. 5. Calculated interaction potentials $W_{j,|\Omega|}(R)$ for HF^+. Both the electronic Hamiltonian H_{AB} and the spin-orbit interaction V_{LS} have been diagonalized. The dashed curves are the $W_{|\Lambda|}(R)$ interaction potentials for the $^2\Pi$ and the $^2\Sigma$ states which diagonalize H_{AB}. At distances shorter than ~5.0 a.u., $W_{1/2,1/2}=W_0$, $W_{3/2,1/2}=W_1+\frac{1}{2}a$, and $W_{3/2,3/2}=W_1-\frac{1}{2}a$.

$$\langle R,\ \tfrac{1}{2},\ \pm\tfrac{1}{2}|H_{AB}+V_{LS}|R,\ \tfrac{1}{2},\ \pm\tfrac{1}{2}\rangle=\tfrac{1}{3}(W_0+2W_1)+a\ ,$$

$$\langle R,\ \tfrac{1}{2},\ \pm\tfrac{1}{2}|H_{AB}+V_{LS}|R,\ \tfrac{3}{2},\ \pm\tfrac{1}{2}\rangle=\pm\tfrac{1}{3}\sqrt{2}(W_1-W_0)\ , \qquad (4.8b)$$

and, of course, reduces to the atomic values (2.10) as $R\to\infty$ and W_0, $W_1\to 0$. By *arbitrarily* choosing the linear combination of molecular states in Eq. (4.2), one ensures that the $|R,\ j,\ \Omega\rangle$ states asymptotically yield accurate atomic wave functions which are eigenvalues of the exact fluorine atom Hamiltonian (H_F+V_{LS}), but as evidenced by the off-diagonal element in (4.8) these states no longer diagonalize H_{AB} at finite R. It is this off-diagonal term which is mainly responsible for the $j=\frac{1}{2}\to j=\frac{3}{2}$ coupling in the scattering theory, while the differences in the diagonal matrix elements for $j=\frac{3}{2}$ in the various Ω states eventually lead to the transitions among the magnetic substates.

One could, of course, use the entire set of molecular states [in either the $(\Lambda,\ m_S)$ or $(j,\ \Omega)$ representation] to generate spin-orbit molecular wave functions $|R,\ j,\ \Omega,\ \vec{L}\cdot\vec{S}\rangle$ which diagonalize the $(H_{AB}+V_{LS})$ Hamiltonian. If, as in the atomic case, only the ground molecular states $|R,\ \Lambda,\ m_S\rangle$ are included, one would obtain an expansion similar to (4.2), but with R-dependent coefficients,

$$|R,\ j,\ \Omega,\ \vec{L}\cdot\vec{S}\rangle=\sum_{\Lambda,m_S}A_{\Lambda,m_S;j,\Omega}(R)|R,\ \Lambda,\ m_S\rangle\ ,$$

where $A(R)$ are the eigenvectors of (4.8),

$$\langle R,\ j,\ \Omega,\ \vec{L}\cdot\vec{S}|H_{AB}+V_{LS}|R,\ j',\ \Omega',\ \vec{L}\cdot\vec{S}\rangle$$

$$=\delta_{j,j'}\delta_{\Omega,\Omega'}W_{j,|\Omega|}(R)\ .$$

Asymptotically, the coefficients approach the Clebsch-Gordan coefficients in (4.2),

$$A_{\Lambda,m_S;j,\Omega}(R)\underset{R\to\infty}{\sim}(L,\ S,\ j|\Lambda,\ m_S,\ \Omega)\ .$$

The spin-orbit interaction potentials $W_{j,|\Omega|}(R)$ obtained from diagonalizing (4.8) are plotted in Fig. 5. At small R, where $|W_1-W_0|\gg a$, the $j=\frac{1}{2}$ eigenvalue approaches the "pure" $W_0(R)$ state, and the $j=\frac{3}{2}$ eigenvalues approach $W_1(R)\pm\frac{1}{2}a$ as expected for a $^2\Pi$ state [Hund's case (a)].

It might appear that using such an expansion in place of (4.2) would eliminate the $j=\frac{1}{2}\to j=\frac{3}{2}$ spin-orbit coupling; however, upon using these diagonalized states in the total Hamiltonian (3.5) complicated $\nabla_{\vec{R}}$ coupling terms are introduced owing to the action of $\nabla_{\vec{R}}^2$ on the expansion coefficients $A(R)$, and it can be shown that both approaches lead to *identical* results. This is not surprising since no new "physics" is introduced unless additional excited molecular states are included in the expansion. This is very similar to the relationship between the adiabatic and diabatic representations discussed by Smith[9]; both representations are connected by a unitary transformation, and as long as *all* the *off*-diagonal terms are properly included, *and* the resultant coupled equations are solved *exactly* the results will be identical. We shall use (4.2) and leave (4.8) in the nondiagonal form. Since it is very cumbersome, and often expensive, to extract $\nabla_{\vec{R}}^2$ matrix elements from numerically derived electronic wave functions there would seldom appear to be any advantage in including the V_{LS} operator directly in the calculation of molecular states.

The molecular states $|R,\ j,\ \Omega\rangle$ are defined in molecule-fixed coordinates, and if all the excited molecular states are included, they form a complete set which spans the entire domain of the electron coordinate space. The scattering events occur, and are measured, in space-fixed coordinates and are defined by the transitions between the space-fixed atomic states $|j,\ m_j\rangle$. The entire set of molecular states may be used to define the entire set of atomic states.

One may construct space-fixed molecular states by the following coordinate rotation:

$$|R,\ j,\ m_j\rangle=\sum_{\Omega}D^{j*}_{m_j,\Omega}(\phi,\ \theta,\ 0)|R,\ j,\ \Omega\rangle\ , \qquad (4.9)$$

where D^{j*} is the Wigner rotation matrix,[17] and ϕ,θ are the polar coordinates of the interatomic axis $\vec{R}$. In the limit, as $R\to\infty$:

$$|\vec{R},\ j,\ m_j\rangle\underset{R\to\infty}{\sim}|j,\ m_j\rangle\ . \qquad (4.10)$$

These space-fixed molecular states are eigenfunctions of the *total* angular momentum $\vec{J}=\vec{L}_R+\vec{j}$, i.e.,

$$\vec{J}^2|\vec{R},\ j,\ m_j\rangle=j(j+1)|\vec{R},\ j,\ m_j\rangle\ ,$$

$$J_{z'}|\vec{R},\ j,\ m_j\rangle=m_j|\vec{R},\ j,\ m_j\rangle\ .$$

In the limit, $R=\infty$, both $\vec{j}$ and $\vec{L}_R$ commute with the total Hamiltonian (3.5), and the $|R,\ j,\ m_j\rangle$ states become diagonalized eigenstates of $\vec{j}$, with $\vec{L}_R = 0$.

In the terminology of scattering theory the molecular states $|R, j, \Omega\rangle$ or $|\vec{R}, j, m_j\rangle$ are perturbed stationary states, and may be used as a basis set to expand the total wave function.

In Sec. V the molecular channel states are constructed, i.e., total angular momentum states, which are required in the subsequent scattering theory.

V. ATOMIC AND MOLECULAR CHANNEL STATES

The scattering "event" is measured at $R \sim \infty$, and is described by the asymptotic behavior of the total wave function $\Psi(E)$ which is a *particular* solution of total Hamiltonian at total energy E, i.e., $(H - E)\Psi(E) = 0$, where

$$H(\vec{R}, \vec{r}_i) = -\frac{1}{2\mu}\left(\frac{\partial^2}{\partial R^2} + \frac{2}{R}\frac{\partial}{\partial R}\right) + \frac{\vec{L}_R^2}{2\mu R^2} + [H_\mathrm{F} + V_{LS} + V(\vec{R}, \vec{r})] \; . \qquad (5.1)$$

The asymptotic wave function may be expanded in the complete set of eigenfunctions of $H(R = \infty)$ in the limit where the interaction $V(\vec{R}, \vec{r}) = 0$. In this, limit the three terms in (5.1) become separable, and the set of asymptotic solutions is infinitely degenerate and can be represented by products of the individual eigenfunctions of these terms, or combinations of these terms, such that their eigenvalues sum to E. It is usual to refer to the eigenstates of the latter two terms in (5.1) (the nuclear angular momentum and the target atom Hamiltonian) as the channel states. The channel states $|\alpha\rangle$ form a complete set which spans the nuclear angular coordinates (θ, ϕ) and the electron coordinates $\vec{r}_i$ and will be characterized by a set of quantum numbers α and eigenvalues $\mathcal{E}_\alpha$.[18] The asymptotic wave function can be expanded in this set,

$$\Psi(E) \underset{R\to\infty}{\sim} \sum_\alpha F_\alpha(R)|\alpha\rangle , \qquad (5.2)$$

where the "radial" functions $F_\alpha(R)$ can be expressed as a linear combination of, say, the regular $j_\alpha(k_\alpha R)$ and irregular $n_\alpha(k_\alpha R)$ independent solutions of the radial terms in (5.1),

$$F_\alpha(R) \sim A_\alpha j_\alpha(k_\alpha R) + B_\alpha n_\alpha(k_\alpha R) , \qquad (5.3)$$

where

$$\left[-\frac{1}{2\mu}\left(\frac{\partial^2}{\partial R^2} + \frac{2}{R}\frac{\partial}{\partial R}\right) + \mathcal{E}_\alpha - E\right] F_\alpha(R) \underset{R\to\infty}{\sim} 0 \qquad (5.4)$$

and

$$k_\alpha^2 = 2\mu(E - \mathcal{E}_\alpha)\big|_{R=\infty} . \qquad (5.5)$$

The channels are referred to as closed, or open, depending on whether k_α^2 is negative or positive. The scattering is completely determined by the as-yet-undetermined coefficients A_α and B_α which yield the scattering matrix $S_{\alpha,\alpha'}$ in the α representation (see Sec. VI).

The choice of representation is arbitrary since the operators $\vec{L}_R^2$ and $(H_\mathrm{F} + V_{LS} + V)$, which define the channel states, may be expanded in various complete sets, and their products collected in a variety of ways such that they form eigenfunctions of other operators which commute with $H(R = \infty)$. Obviously, one wants the channel states to be, or asymptotically approach, eigenfunctions of the target atom $(H_\mathrm{F} + V_{LS})$ and the total angular momentum of the electrons $\vec{j}^2$, since these are the "observables" in the scattering experiment. {The entire set of atomic quantum numbers $[(n, S, L)j, m_j]$ will be abbreviated by $[j, m_j]$ with eigenvalue $\mathcal{E}_j$, since ultimately we will only be considering the ground state $|j, m_j\rangle$.} For example to this end one can use either the atomic functions $|j, m_j\rangle$ or the molecular functions $|R, j, \Omega\rangle$ which approach $|j, \Omega\rangle$. Beyond this requirement the choice of channel states is arbitrary and dictated by mathematical convenience.

Since H commutes with the total angular momentum of the $\mathrm{H}^+ + \mathrm{F}$ system, $\vec{J} = \vec{L}_R + \vec{j}$, it is most expedient to construct channel states that are eigenfunctions of $\vec{J}^2$ and $J_{z'}$, with eigenvalues $J(J+1)$ and space-fixed projection M: such channel states will diagonalize H for *all* R. As seen in Eq. (5.1), the asymptotic H commutes with the nuclear angular momentum $\vec{L}_R$, and it is advantageous to have channel states which are eigenfunctions of $\vec{L}_R^2$ with eigenvalues $l(l+1)$.[19] This is known as the partial-wave expansion, and the channel states are designated as $|\alpha\rangle \equiv |J, M, j, l\rangle$. The choice of basis functions is still arbitrary.

The simplest choice of basis functions are the spherical harmonics $Y_{l,m_l}(\theta, \phi)$, which are eigenfunctions of $\vec{L}_R^2$, and the atomic states $|j, m_j\rangle$. These may be combined in the following way to form what may be called the "atomic" channel states:

$$|J, M, j, l\rangle = \sum_{m_l, m_j} (l, j, J|m_l, m_j, M) \times Y_{l,m_l}(\theta, \phi)|j, m_j\rangle . \qquad (5.6)$$

$(l, j, J|m_l, m_j, M)$ is the Clebsch–Gordan coefficient which constructs the total angular momentum state J, M. These states are orthonormal, and have the eigenvalue $\mathcal{E}_\alpha = \mathcal{E}_j + l(l+1)/2\mu R^2$. The required solutions of the radial Eq. (5.4) are thus the spherical Bessel functions $j_l(k_j R)$ and $n_l(k_j R)$ (Rose, Ref. 17, p. 132) or $j_l(k_j R)$ and $h_l(k_j R)$.

Alternatively, one may construct molecular channel states with the eigenfunctions of $(H_\mathrm{F} + V_{LS} + V)$ in molecule-fixed coordinates $|R, j, \Omega\rangle$. Owing to the axial symmetry of the molecular Hamiltonian, it is advantageous to expand the angular dependence (θ, ϕ) in terms of normalized symmetric-top wave functions:

$$\Omega^J_{M,\Omega}(\theta,\ \phi)=\left(\frac{2J+1}{4\pi}\right)^{1/2} D^{J*}_{M,\Omega}(\phi,\ \theta,\ 0), \qquad (5.7)$$

rather than the spherical harmonics Y_{l,m_l}. The total angular momentum states J, M are then simply constructed as products of $\Omega^J_{M,\Omega}$ and $|R, j, \Omega\rangle$. A linear combination of these states is chosen such that *asymptotically*, as $|R,\ j,\ \Omega\rangle$ approaches $|j,\ \Omega\rangle$ and becomes an eigenfunction of $\vec{j}^2$ and j_z, the sum becomes an eigenfunction of $\vec{L}^2_R$. This yields the molecular channel states, which are, of course, implicit functions of R, i.e.,

$$|R,\ J,\ M,\ j,\ l\rangle=\sum_{\Omega} (-1)^{j+\Omega}(J,\ j,\ l|-\Omega,\ \Omega,\ 0) \times\Omega^J_{M,\Omega}|R,\ j,\ \Omega\rangle \qquad (5.8)$$

and in the limit are equivalent to the atomic channel states,

$$|R,\ J,\ M,\ j,\ l\rangle \underset{R\to\infty}{\sim} |J,\ M,\ j,\ l\rangle. \qquad (5.9)$$

This result can be derived in various ways, but is probably arrived at in the simplest manner by replacing the space-fixed atomic states in Eq. (5.6) with the space-fixed molecular states $|\vec{R},\ j,\ m_j\rangle$ defined in Eq. (4.9), and using the product rules for rotation matrices (Rose, Ref. 17). The molecular channel states are of course analogous to the rotational states in molecular spectroscopy, and the pair of terms for a given $|\Omega|$ define a rotational-electronic molecular state coupled according to Hund's case (d).[20,21] These pairs are combined in (5.8) such that as $R\to\infty$ they form an eigenstate of $\vec{L}^2_R$, [according to Hund's case (e)] and the channel-state eigenvalue approaches $l(l+1)/2\mu R^2+\mathcal{E}_j$. The asymptotic form of the radial function in (5.3) thus will be identical to that of the atomic channel states, with j_α and n_α being spherical Bessel functions.

It can be shown that the channel states in both bases form a complete orthonormal set,

$$\langle R,\ J,\ M,\ j,\ l|R,\ J',\ M',\ j',\ l'\rangle = \delta_{J,J'}\delta_{M,M'}\delta_{j,j'}\delta_{l,l'}. \qquad (5.10)$$

They have a definite parity with respect to inversion of the space-fixed coordinates, $\mathcal{I}$. In particular, for the ground-state channels of $F(^2P)$, the molecular and atomic states have the parity $\mathcal{I}|\vec{R},\ j,\ m_j\rangle=-|\vec{R}, j,\ m_j\rangle$, and therefore (see Appendix A)

$$\mathcal{I}|R,\ J,\ M,\ j,\ l\rangle=(-1)^{l+1}|R,\ J,\ M,\ j,\ l\rangle. \qquad (5.11)$$

It can be seen from the Clebsch–Gordan coefficients in (5.6) or (5.8) that in the ground atomic state only six channel states exist for a given J, M. However, since H commutes with the parity operator $\mathcal{I}$, channel states of opposite parity will be uncoupled and the channels may be grouped as in Table I.

Certainly, in view of Eq. (5.9), no advantage is derived in using the molecular channel states to describe the asymptotic scattering conditions, *given* the scattering amplitudes in Eq. (5.3). But, of course, the advantage comes in developing means of obtaining these radial functions. In the close-coupling approximation the total wave function is expanded in the channel states for all R, i.e., Eq. (5.2) is made an identity. Again if the *entire* set of states $|\alpha\rangle$ is retained and solved *exactly*, no advantage is gained, but as usual this expansion will be truncated; in the present case to include only the open channels. In this instance, the molecular channel states correspond to perturbed-stationary states, and it would appear that such a truncated expansion should be superior to the atomic channel-state expansion which does not allow for effects such as the polarization of the fluorine atom. The resultant coupled equations for $F_\alpha(R)$ are derived in Sec. VII. In Sec. VI the scattering matrix and cross sections are derived in terms of the molecular channel states.

VI. SCATTERING AMPLITUDE AND CROSS SECTIONS

There are six independent regular solutions of H for a given total energy $E<3.825$ eV, *and* total angular momentum state J, M, corresponding to the six open channels in Table I. The entire wave function can be expanded in the complete set of molecular channel states (5.8) which span the domain of the scattering angles $(\theta,\ \phi)$ and the electron coordinates $\vec{r}_i$,

$$\Psi_{j,l}(J,\ M,\ E)=\sum_{j',l'} F^{J,M;E}_{j',l';j,l}(R)|R,\ J,\ M,\ j',\ l'\rangle. \qquad (6.1)$$

Asymptotically the radial functions $F(R)$ must vanish for the subset of closed channels with $k^2_\alpha<0$. The radial functions for the six open channels with wave numbers $k^2_j>0$ which are independent of J and l, i.e.,

$$\begin{aligned} k^2_{3/2}&=2\mu(E+\tfrac{1}{2}a), & v_{3/2}&=k_{3/2}/\mu\ ; \\ k^2_{1/2}&=2\mu(E-a), & v_{1/2}&=k_{1/2}/\mu\ ; \end{aligned} \qquad (6.2)$$

asymptotically take the form of Eq. (5.3) where j_α and n_α are the regular and irregular solutions of (5.4); the coefficients then define the scattering cross sections. For convenience these degenerate solutions may be combined in a variety of prescribed ways to exhibit desirable asymptotic properties.

TABLE I. Channel states for a particular J.

Parity $(-1)^{J+1/2}$	Parity $(-1)^{J-1/2}$
$j=\frac{3}{2},\ l=J+\frac{3}{2}$	$j=\frac{3}{2},\ l=J-\frac{3}{2}$
$j=\frac{3}{2},\ l=J-\frac{1}{2}$	$j=\frac{3}{2},\ l=J+\frac{1}{2}$
$j=\frac{1}{2},\ l=J-\frac{1}{2}$	$j=\frac{1}{2},\ l=J+\frac{1}{2}$

The most useful form for numerical solution of Eq. (6.1) is a combination of solutions such that the radial functions are real functions of R. This is accomplished by employing the spherical Bessel functions $j_l(k_jR)$ and the spherical Neumann functions $n_l(k_jR)$ as the pair of independent solutions of Eq. (5.4), and requiring the radial functions to approach the following form:

$$^{\mathrm{I}}F^{J,M,E}_{j',l';j,l}(R) \underset{R\to\infty}{\sim} \left(\frac{k_j}{v_j^{1/2}}\right)^{1/2} j_l(k_jR)\delta_{j,j'}\delta_{l,l'} - K^J_{j',l';j,l}\left(\frac{k'_j}{v'^{1/2}_j}\right)^{1/2} n_{l'}(k'_jR). \quad (6.3)$$

$K^J_{j',l';j,l}$ is the 6×6 reactance matrix which is real and symmetric, and independent of the magnetic quantum number M. Asymptotically $j_l(X)\sim[\sin(X-\frac{1}{2}\pi l)]/X$ and $n_l(X)\sim-[\cos(X-\frac{1}{2}\pi l)]/X$.

The scattering amplitude is best defined in terms of an alternate set of solutions which can be formed from (6.3) and expressed in terms of the spherical Hankel functions of the first kind $h_l(k_jR)$, where

$$h_l(X)=j_l(X)+in_l(X)\sim -ie^{iX}(-i)^l/X.$$

These solutions define the transition matrix $T^J_{j',l';j,l}$,

$$^{\mathrm{II}}F^{J,M,E}_{j',l';j,l}(R) \underset{R\to\infty}{\sim} \left(\frac{k_j}{v_j^{1/2}}\right)^{1/2} j_l(k_jR)\delta_{j,j'}\delta_{l,l'} - \tfrac{1}{2}T^J_{j',l';j,l}\left(\frac{k'_j}{v'^{1/2}_j}\right)^{1/2} h_{l'}(k'_jR). \quad (6.4)$$

The T matrix is related to the scattering matrix S in the following way:

$$\underline{S}=\underline{1}-\underline{T}, \quad (6.5)$$

where $\underline{S}$ is unitary and symmetric, i.e., $\underline{S}^*\underline{S}=\underline{1}$, $\tilde{\underline{S}}=\underline{S}$; the two sets of solutions (6.3) and (6.4) are related as follows:

$$\underline{S}=(\underline{1}+i\underline{K})(\underline{1}-i\underline{K})^{-1} \quad (6.6a)$$

or

$$\underline{T}=-2i\underline{K}(\underline{1}-i\underline{K})^{-1}. \quad (6.6b)$$

The scattering cross sections are obtained from six *particular* solutions of Eq. (5.1) at total energy E which asymptotically consist of a plane wave incident on an atom in state $|j, m_j\rangle$ plus scattered radial waves off the six atomic states, i.e.,

$$\Psi_{j,m_j}(E) \underset{R\to\infty}{\sim} e^{i\vec{k}_j\cdot\vec{R}}|j, m_j\rangle + \sum_{j',m'_j} f_{j,m_j;j',m'_j}(\theta, \phi) \times\frac{e^{ik'_jR}}{R}\left(\frac{v_j}{v'_j}\right)^{1/2}|j', m'_j\rangle. \quad (6.7)$$

The differential scattering cross section for the transition $(j, m_j\to j', m'_j)$ is then given by the scattering amplitude functions f:

$$\frac{d\sigma_{j,m_j\to j',m'_j}}{d\Omega}=|f_{j,m_j;j',m'_j}|^2. \quad (6.8)$$

$\Psi_{j,m_j}(E)$ can be expressed as a linear combination of the total angular momentum solutions (6.1);

$$\Psi_{j,m_j}(E)=\sum_{J,M,l} C^{j,m_j}_{J,M,l}\Psi_{j,l}(J, M, E). \quad (6.9)$$

The coefficients C are chosen to ensure the asymptotic conditions in (6.7) Using the expression for $F(R)$ in Eq. (6.4), Eq. (6.9) is satisfied by the condition

$$C^{j,m_j}_{J,M,l}=4\pi(i)^l\left(\frac{v_j^{1/2}}{k_j}\right)Y^*_{l,M-m_j}(\hat{k}_j) \times(l, j, J|M-m_j, m_j, M),$$

where $\hat{k}_j\equiv(\theta_{k_j}, \phi_{k_j})$ denotes the polar angles of the incident wave vector $\vec{k}_j$. Using Eqs. (6.4), (6.8), (5.9), and (5.6) the scattering amplitude can be expressed as follows:

$$f_{j,m_j;j',m'_j}(\hat{k}_j, \hat{R})=\frac{i2\pi}{k_j}\sum_{l,l',M} Y^*_{l,M-m_j}(\hat{k}_j) \times Y_{l',M-m'_j}(\hat{R})(i)^{l-l'}\mathcal{G}_{l,l',M}, \quad (6.10)$$

where[22]

$$\mathcal{G}_{l,l',M}=\sum_J(l, j, J|M-m_j, m_j, M) \times(l', j', J|M-m'_j, m'_j, M)T^J_{j,l;j',l'},$$

$\hat{k}_j$ is the unit vector of the incoming plane wave incident on state j, m_j and $\hat{R}\equiv(\theta, \phi)$ is the unit vector of the waves scattered off state j', m'_j. In this form detailed balance is easily seen to exist, given $\underline{T}=\tilde{\underline{T}}$. Making use of the parity condition in (5.11), which implies that T vanishes unless $l'=l$, $l\pm 2$, the following properties for f are obtained:

$$f_{j,m_j;j',m'_j}(\hat{k}_j, \hat{R})=f_{j,m_j;j',m'_j}(-\hat{k}_j, -\hat{R}), \quad (6.11a)$$

$$k_jf_{j,m_j;j',m'_j}(\hat{k}_j, \hat{R}) =(-1)^{j+j'+m_j+m'_j}k'_jf_{j',-m'_j,j,-m_j}(\hat{R}, \hat{k}_j), \quad (6.11b)$$

$$k_jf_{j,m_j;j',m'_j}(\hat{k}_j, \hat{R})=-k'_jf^*_{j',m'_j;j,m_j}(\hat{R}, \hat{k}_j). \quad (6.11c)$$

Thus, Eq. (6.8) will yield detailed balancing for these differential cross sections, i.e.,

$$k_j^2\frac{d\sigma_{j,m_j\to j',m'_j}}{d\Omega}(\hat{k}_j, \hat{R})=k^2_{j'}\frac{d\sigma_{j',-m'_j\to j,-m_j}}{d\Omega}(\hat{R}, \hat{k}_j) =k^2_{j'}\frac{d\sigma_{j',m'_j\to j,m_j}}{d\Omega}. \quad (6.12)$$

If Eq. (6.8) is integrated over all final scattering angles the total cross section is obtained from (6.10):

$$\sigma_{j,m_j\to j',m'_j}(\hat{k}_j)=\sum_{l,l',l'',M}\left(\frac{4\pi^2}{k_j^2}\right)Y^*_{l,M-m_j}(\hat{k}_j)Y_{l'',M-m_j}(\hat{k}_j)$$

$$\times (i)^{l-l''}\mathcal{G}_{l,l',M}\ \ {}^{*}_{l'',l',M}\,. \tag{6.13}$$

This is the general expression for the total cross section when the initial and final states are quantized along the space-fixed axis Z', *and* the initial plane wave is incident from the direction $\hat{k}_j$. Now define two specialized total cross sections.

The first is the conventionally defined cross section, $\sigma^0_{j,m_j\to j',m'_j}\equiv\sigma_{j,m_j\to j',m'_j}(\hat{k}_j=0)$, where the incident wave parallels the axis of quantization, i.e., $\hat{k}_j=0$. In this case, since $Y_{l,m}(0)=[(2l+1)/4\pi]^{1/2}\delta_{m,0}$ the following result is obtained from (6.13):

$$\sigma^0_{j,m_j\to j',m'_j}=\sum_{l,l',l''}\left(\frac{\pi}{k_j^2}\right)(2l+1)^{1/2}(2l''+1)^{1/2}$$
$$\times\mathcal{G}_{l,l',m_j}\mathcal{G}^*_{l'',l',m_j}\,. \tag{6.14}$$

It must be emphasized that this is a very specialized situation, and in this form the total cross section does not in fact obey detailed balance, i.e., in some instances one finds

$$k_j^2\sigma^0_{j,m_j\to j',m'_j}\neq k_{j'}^2\sigma^0_{j',m'_j\to j,m_j}\,.$$

An *averaged* total cross section $\bar{\sigma}$ may be defined which is required to describe gas-phase processes rather than a specialized beam experiment. In this situation the target atom is quantized, or oriented in space, as in Eqs. (6.13) and (6.14), but is subjected to a random isotropic distribution of incident wave vector collisions. The ensemble averaged rate will be given in terms of a cross section averaged over all initial impact orientations;

$$\bar{\sigma}_{j,m_j\to j',m'_j}\equiv\int\frac{d(\hat{k}_j)}{2\pi}\,\sigma_{j,m_j\to j',m'_j}(\hat{k}_j)$$
$$=\sum_{l,l',M}\left(\frac{\pi}{k_j^2}\right)\mathcal{G}_{l,l',M}\,\mathcal{G}^*_{l,l',M}\,. \tag{6.15}$$

In this case it is evident that $\bar{\sigma}$ does exhibit detailed balance.

Finally, the usual total cross section $\sigma_{j\to j'}$ is defined as the sum over all final magnetic quantum states $m_{j'}$, and average over all initial m_j values;

$$\sigma_{j\to j'}=\sum_{m_j,m'_j}\frac{\sigma_{j,m_j\to j',m'_j}}{(2j+1)}$$
$$=\sum_{J,l,l'}\left(\frac{\pi}{k_j^2}\right)\frac{(2J+1)}{(2j+1)}\,|T^J_{j,l;j',l'}|^2\,. \tag{6.16}$$

This result may be obtained from any of the defined total cross sections (6.13)–(6.15), and, of course, one finds the usual result,

$$(2j+1)k_j^2\sigma_{j\to j'}=(2j'+1)k_{j'}^2\sigma_{j'\to j}\,. \tag{6.17}$$

The dependence of the cross sections on the magnetic quantum numbers m_j and $m_{j'}$ is presented in its simplest form if one writes (6.10) explicitly in terms of irreducible tensors of order $\lambda=0$, 1, 2, and 3, i.e.,

$$f_{j,m_j;j',m'_j}(\hat{k}_j,\hat{R})$$
$$=\left(\frac{2\pi}{k_j}\right)\sum_\lambda\,(j,j',\lambda|m_j,-m'_j,m_j-m'_j)$$
$$\times\sum_{l,l'}\psi^{\lambda,m_j-m'_j}_{l,l'}(\hat{k}_j,\hat{R})\alpha_\lambda(j,l;j',l')\,,$$

where ψ^λ is an irreducible tensor of order λ,

$$\psi^{\lambda,m_j-m'_j}_{l,l'}=\sum_\xi Y_{l,m_j-\xi}(\hat{k}_j)Y_{l',\xi-m'_j}(\hat{R})$$
$$\times(l,l',\lambda|m_j-\xi,\xi-m'_j,m_j-m'_j)$$

and

$$\alpha_\lambda=\sum_J(2J+1)(i)^{1-2J-2\lambda}W_{J,\lambda}(j,l,j',l';J,\lambda)$$
$$\times T^J_{j,l;j',l'}\,, \tag{6.18}$$

where W is the Racah coefficient. Equation (6.15) then can be expressed as follows:

$$\bar{\sigma}_{j,m_j\to j',m'_j}=\left(\frac{\pi}{k_j^2}\right)\sum_\lambda\,(j,j',\lambda|m_j,-m'_j,m_j-m'_j)^2$$
$$\times B_\lambda(j,j') \tag{6.19}$$

with

$$B_\lambda(j,j')=\sum_{l,l'}\alpha_\lambda(j,l;j',l')\alpha^*_\lambda(j,l;j',l')\,.$$

This useful result was first derived by Grawert[23] and expresses the m_j, $m_{j'}$ dependence of the cross sections in its most irreducible form; the 36 cross sections are dependent on 8 *positive* B_λ coefficients which can greatly assist the reduction of experimental or theoretical data.

VII. COUPLED EQUATIONS

If one substitutes the expansion (6.1) into the Schrödinger equation $(H-E)\Psi_{j'',l''}=0$, and operates from the left-hand side with the molecular channel states $\langle R,J,M,j,l|$ coupled equations for the radial functions $F(R)$ are generated. Since H is diagonal in $\vec{J}^2$ and $J_{Z'}$ I shall suppress the J, M indices and the dependence on R will be left understood,

$$\sum_{j',l'}\langle j,l|H-E|j',l'\rangle F_{j',l';j'',l''}=0\,. \tag{7.1}$$

Only the six open-channel states tabulated in Table I will be included. The parity conservation (5.11) corresponds to the fact that $\langle j,l|H-E|j',l'\rangle=0$ unless $l'=l$, $l\pm2$ and Eq. (7.1) generates two sets of three coupled equations for each J, M. These elements are also independent of M, implying that the resultant $\underline{\mathrm{K}}^J$ and $\underline{\mathrm{T}}^J$ matrices in (6.3) and (6.4) are independent of M. Consider three separate terms which originate from the Hamiltonian (3.5):

$$\langle j,l|H-E|j',l'\rangle$$

$$= \delta_{j,j'}\delta_{l,l'}\left(-\frac{\partial^2}{2\mu\partial R^2} - \frac{\partial}{\mu R\partial R} + \frac{l(l+1)}{2\mu R^2} - E\right) + \langle j,\ l|H_{AB} + V_{LS}|j',\ l'\rangle \quad (7.2a)$$

$$+\langle j,\ l|\frac{\vec{L}_R^2 - l(l+1)}{2\mu R^2}|j',\ l'\rangle \quad (7.2b)$$

$$+\left[\langle j,\ l|-\frac{\partial^2}{\partial\mu\partial R^2}|j',\ l'\rangle + \langle j,\ l|-\frac{\partial}{\mu\partial R}|j',\ l'\rangle\left(\frac{1}{R} + \frac{\partial}{\partial R}\right)\right]. \quad (7.2c)$$

The first line, Eq. (7.2a), gives the elements which originate from the BO approximation, including the spin-orbit interaction. Actually some cognizance of the angular (7.2b) and radial (7.2c) BO coupling terms has been made in choosing the form of (7.2a). It will be recalled that the channel states asymptotically become eigenfunctions of $\vec{L}_R^2/2\mu R^2$ and the asymptotic eigenvalue $l(l+1)/2\mu R^2$ has been included in (7.2a) and subtracted from (7.2b) such that both (7.2b) and (7.2c) vanish identically as $R\to\infty$.

Explicit expressions are derived for the angular BO matrix (7.2b) and the radial BO matrix (7.2c) in Appendix B. However it will be shown in Sec. VIII that, for the long-range interaction, the BO terms (7.2b) and (7.2c) are quite negligible and vary as R^{-6} vs R^{-3} for the terms in (7.2a), and the matrix elements in Eq. (7.1) will be well approximated by (7.2a). It is not clear that this situation will prevail for systems other than $H^+ + F$ and as discussed in Sec. IV if the molecular states are prediagonalized with respect to $(H_{AB} + V_{LS})$ then the BO terms cannot be ignored.

The matrix $\langle j,\ l|H_{AB} + V_{LS}|j',\ l'\rangle$ can be evaluated in terms of the molecular integrals (4.8) using Eq. (5.8):

$$\langle j,\ l|H_{AB} + V_{LS}|j',\ l'\rangle = \sum_{\Omega}(-1)^{j'-j}(J,\ j,\ l|-\Omega,\ \Omega,\ 0)(J,\ j',\ l'|-\Omega,\ \Omega,\ 0)\langle R,\ j,\ \Omega|H_{AB} + V_{LS}|R,\ j',\ \Omega\rangle$$
$$= \delta_{j,j'}\delta_{l,l'}[\mathcal{E}_j + W_1(R)] + C^J_{j,l;j',l'}[W_0(R) - W_1(R)]. \quad (7.3)$$

with C^J defined as follows,

$$C^J_{j,l;j',l'} = \sum_{\Omega}(-1)^{j'-j}(J,\ j,\ l|-\Omega,\ \Omega,\ 0)(J,\ j',\ l'|-\Omega,\ \Omega,\ 0)(1,\ \tfrac{1}{2},\ j|0,\ \Omega,\ \Omega)(1,\ \tfrac{1}{2},\ j'|0,\ \Omega,\ \Omega). \quad (7.4)$$

The atomic eigenvalues are $\mathcal{E}_{1/2} = a$, and $\mathcal{E}_{3/2} = -\frac{1}{2}a$, and the coupling coefficients C^J are explicitly tabulated in Table II.

One may define an interaction matrix $\underline{U}^J(R)$,

$$U^J_{j,l;j',l'}(R) = \delta_{j,j'}\delta_{l,l'}[\mathcal{E}_j + W_1(R) + l(l+1)/2\mu R] + C^J_{j,l;j',l'}[W_0(R) - W_1(R)], \quad (7.5)$$

and the coupled equations (7.1) take the following matrix form,

$$\left[\left(-\frac{\partial^2 R}{2\mu R\partial R^2} - E\right)\underline{1} + \underline{U}^J(R)\right]\underline{F}(R) = 0, \quad (7.6)$$

where

$$\underline{F} = \{F_{j,l;j',l'}(R)\}, \quad \underline{1} = \{\delta_{j,j'}\delta_{l,l'}\}.$$

VIII. ASYMPTOTIC INTERACTIONS AND BO MATRIX ELEMENTS

One may use perturbation theory to obtain the molecular wave function $|R,\ \Lambda,\ m_S\rangle$, and its eigenvalue $W_{|\Lambda|}(R)$ in the asymptotic regions. Using the atomic functions (2.6) as a basis one obtains to first order

$$|R,\ \Lambda,\ m_S\rangle \approx |\Lambda,\ m_S\rangle - \sum_{n\neq 0,L} a^{\Lambda;m_S}_{n,L} \times |(n,\ L,\ S)\Lambda,\ m_S\rangle,$$

TABLE II. Coefficients $C^J_{j,l;j',l'}$ of electronic matrix elements for given J.

	Parity $(-1)^{J+1/2}$				Parity $(-1)^{J-1/2}$		
j, l	$\frac{3}{2}, J+\frac{3}{2}$	$\frac{3}{2}, J-\frac{1}{2}$	$\frac{1}{2}, J-\frac{1}{2}$	j, l	$\frac{3}{2}, J-\frac{3}{2}$	$\frac{3}{2}, J+\frac{1}{2}$	$\frac{1}{2}, J+\frac{1}{2}$
$\frac{3}{2},\ J+\frac{3}{2}$	$+\frac{J+\frac{3}{2}}{2(J+1)}$	$-\left(\frac{(J+\frac{3}{2})(J-\frac{1}{2})}{12(J+1)^2}\right)^{1/2}$	$-\left(\frac{J+\frac{3}{2}}{6(J+1)}\right)^{1/2}$	$\frac{3}{2},\ J-\frac{3}{2}$	$+\frac{J-\frac{1}{2}}{2J}$	$-\left(\frac{(J+\frac{3}{2})(J-\frac{1}{2})}{12J^2}\right)^{1/2}$	$+\left(\frac{J-\frac{1}{2}}{6J}\right)^{1/2}$
$\frac{3}{2},\ J-\frac{1}{2}$		$+\frac{J-\frac{1}{2}}{6(J+1)}$	$+\left(\frac{J-\frac{1}{2}}{18(J+1)}\right)^{1/2}$	$\frac{3}{2}, J+\frac{1}{2}$		$+\frac{J+\frac{3}{2}}{6J}$	$-\left(\frac{J+\frac{3}{2}}{18J}\right)^{1/2}$
$\frac{1}{2},\ J-\frac{1}{2}$			$+\frac{1}{3}$	$\frac{1}{2}, J+\frac{1}{2}$			$+\frac{1}{3}$

where

$$a_{n,L}^{\Lambda,m_S} = \langle (n,\ L,\ S)\Lambda,\ m_S | V | \Lambda,\ m_S \rangle / \mathcal{E}^{n,L,S} \qquad (8.1)$$

and the interaction potential V is given in Eq. (3.3). The molecular potential, to second order, is then

$$W_{|\Lambda|}(R) \approx \langle \Lambda,\ m_S | V | \Lambda,\ m_S \rangle - \sum_{n\neq 0,L} \frac{\langle (n,\ L,\ S)\Lambda,\ m_S | V | \Lambda,\ m_S \rangle^2}{\mathcal{E}^{n,L,S}}\,. \qquad (8.2)$$

The asymptotic expansion of V yields

$$V = \sum_{i=1}^{9} \left(-\frac{z_i}{R^2} - \frac{3z_i^2 - r_i^2}{2R^3} - \frac{6r_i^2 z_i + 5z_i^3}{8R^4} + \cdots \right). \qquad (8.3)$$

The leading diagonal term in the V matrix comes from the atomic quadrupole $\langle 3z^2 - r^2 \rangle$. For the Σ state, $\Lambda = 0$, one obtains

$$-\langle 0,\ m_S | \sum_i (3z_i^2 - r_i^2)/2R^3 | 0,\ m_S \rangle = \tfrac{4}{5} \langle r^2 \rangle / 2R^3\,; \qquad (8.4a)$$

$\langle r^2 \rangle$ is the expectation value of $\sum_i r_i^2$, which is positive, and the long-range $W_{|0|}(R)$ potential will thus be repulsive. For the Π states, $\Lambda = \pm 1$, an attractive matrix element is obtained:

$$-\langle \pm 1,\ m_S | \sum_i (3z_i^2 - r_i^2)/2R^3 | \pm 1,\ m_S \rangle = -\tfrac{2}{5} \langle r^2 \rangle / 2R^3\,. \qquad (8.4b)$$

The molecular data of Wahl, Julienne, and Krauss[11] yields $\langle r^2 \rangle \approx 1.545 a_0^2$.

Carrying the analysis to the next order, the leading off-diagonal term will be the dipole matrix

$$\langle (n,\ L,\ S)\Lambda,\ m_S | V | \Lambda,\ m_S \rangle \approx -\langle (n,\ L,\ S)\Lambda,\ m_S | \sum_i z_i / R^2 | \Lambda,\ m_S \rangle = -\langle z \rangle^{n,L} / R^2 \qquad (8.5)$$

and the matrix element $\langle z \rangle^{n,L}$ is independent of m_S. Again using data from Wahl *et al.* the asymptotic molecular potentials are analyzed in terms of the expansion (8.2) and one finds that for both the $^2\Pi$ and $^2\Sigma$ state the following sum has the indicated value:

$$\sum_{n\neq 0,L} \frac{\{\langle z \rangle^{n,L}\}^2}{\mathcal{E}^{n,L}} \approx 2.28 a_0^3\,. \qquad (8.6)$$

This quantity is equal to $\frac{1}{2}$ the fluorine atom polarizability and is determined from the HF$^+$ dipole moment data in a manner identical to that used in a recent study of carbon by Billingsley and Krauss.[24] The asymptotic interaction energies are to this approximation of the following form, in atomic units[25]:

$$W_0(R) \sim \frac{1.236}{2R^3} - \frac{4.55}{2R^4}\,, \qquad W_1(R) \sim -\frac{0.618}{2R^3} - \frac{4.55}{2R^4}\,. \qquad (8.7)$$

Note that the first excited state of F is about 0.47 a.u. above the ground state, and from (8.6) one can estimate that

$$\sum_{n\neq 0,L} \frac{\{\langle z \rangle^{n,L}\}^2}{(\mathcal{E}^{n,L})^2} \leqslant 4.9 a_0^4\,. \qquad (8.8)$$

This estimate is useful in determining the magnitude of the asymptotic BO terms (7.2b) and (7.2c). Substituting (8.5) into (8.1) the following expectation values for the radial BO terms are obtained ($\mu = 1745$):

$$\begin{aligned} \langle R,\ \Lambda,\ m_S | -\frac{\partial^2}{2\mu\,\partial R^2} | R,\ \Lambda,\ m_S \rangle &= -\tfrac{3}{2} \langle R,\ \Lambda,\ m_S | -\frac{\partial}{\mu R\,\partial R} | R,\ \Lambda,\ m_S \rangle \\ &\approx -\frac{3}{\mu R^6} \sum_{n\neq 0,L} \frac{\{\langle z \rangle^{n,L}\}^2}{(\mathcal{E}^{n,L})^2} \leqslant -\frac{8.3\times 10^{-3}}{R^6}\,. \qquad (8.9) \end{aligned}$$

These primitive integrals enter into Eq. (B7) of Appendix B, and it is found to first order that (8.9) only contributes to the *diagonal* elements in (B8) and the off-diagonal radial BO terms vanish identically. Since the diagonal contributions are negligible compared to (7.2a) and (7.3) the radial BO terms will be completely ignored, and even in the region of strong interaction where perturbation theory becomes invalid this approximation will be made since the spin-orbit terms undoubtedly dominate.

The angular BO term, as expressed by (B4), is proportional to $\Delta/2\mu R^2$, where Δ is obtained from Eq. (B5). The perturbation theory predicts

$$\Delta = -\sum_{n\neq 0,L} a_{n,L}^{1,m_S\,*} a_{n,L}^{0,m_S} \left(\frac{L(L+1)}{2} \right)^{1/2}.$$

Utilizing Eq. (8.8) to impose an upper bound, and a number of reasonable assumptions about the fluorine atom wave function and the matrix elements in (8.5), one obtains the following estimate for Δ:

$$\Delta \leqslant 4.9\sqrt{3}/R^4 \qquad (8.10)$$

and

$$\begin{aligned} \langle j,\ l | \frac{\vec{\mathrm{L}}_R^2 - l(l+1)}{2\mu R^2} | j',\ l' \rangle &= \frac{\Delta}{2\mu R^2} [-\sqrt{2}(-1)^{j-j'} \mathcal{A}] \\ &\leqslant \frac{4.9\sqrt{3}}{2\mu R^6} [-\sqrt{2}(-1)^{j-j'} \mathcal{A}]\,. \qquad (8.11) \end{aligned}$$

As J increases the coefficient $\mathcal{A}$ becomes proportional to J [see Eq. (B6)], and the angular BO term becomes increasingly important. Unlike the radial term, Eq. (8.11) contributes to the off-diagonal couplings, and thus, it is important to have reliable estimates of Δ at small distances where the perturbation theory is invalid. Using accurate molecular wave functions for HF$^+$ at $R = 2.2$ a.u., Julienne, Krauss, and Neumann[12] calculated $(1 - \Delta) = 0.96$ and $\Delta = 0.04$, from Eq. (B5). This is consistent with the upper bound in (8.10) which predicts $\Delta < 0.36$. Using $\Delta = 0.04$ in (8.11) the matrix element at large J is of the order $O(4\times10^{-6}J$ a.u.). This is negligible compared to the centrifugal barrier terms that contribute to the diagonal matrix elements in Eq. (7.2a) and which are of the order $O(6\times10^{-5}J^2$ a.u.). The off-diagonal terms in (7.2a) are proportional to $(W_0 - W_1)\approx 0.1$ a.u. and will dominate the BO angular term for $J < 300$. However, at these small distances only $J < O(30)$ can penetrate, and the angular BO terms are completely negligible. At larger R the perturbation result (8.11) predicts a rapid R^{-6} falloff compared to the R^{-3} falloff of $W_0 - W_1$, and the angular BO matrix elements are insignificant and can be neglected at all distances.

IX. SUMMARY AND CONCLUSIONS

The cross sections for the fine-structure transitions in $H^+ + F(^2P)$ collisions have been formulated in terms of the ground molecular states $HF^+(^2\Pi)$ and $HF^+(^2\Sigma)$. The long-ranged interactions between H^+ and F vary as R^{-3} and R^{-4} which suggest that the cross sections will be large and difficult to predict using perturbation theory. The close-coupling approximation has been developed, using a molecular "perturbed-stationary-state" representation of the six open-channel states, and the pertinent coupling matrix elements have been carefully evaluated.

One finds that the coupling is dominated by the spin-orbit matrix elements which are dependent on the splitting $W_1(R) - W_0(R)$ between the molecular $^2\Pi$ and $^2\Sigma$ interaction potentials [Eq. (7.3)]. For HF^+ the molecular spin-orbit matrix elements are well represented by their asymptotic atomic values,[15,16] but, in general, it will be necessary to make explicit evaluation of the R dependence of these terms. The BO matrix elements that are generated by the kinetic-energy operator vary asymptotically as R^{-6} and are negligible compared to the R^{-3} dependence of the spin-orbit terms. Again this conclusion is only relevant to HF^+ which has been chosen for its simplifying features, and it is important to assess this result for other systems. In particular, it is important to evaluate the *angular* BO terms [Eq. (7.2b)] since these will give rise to second-order off-diagonal terms while the *radial* BO terms (7.2c) vanish to this order. It must be emphasized that these conclusions only apply to the *non*relativistic molecular states. If the molecular states are prediagonalized with respect to the spin-orbit operator, then the BO terms are tremendously modified due to the R dependence of the expansion coefficients and the couplings are caused *entirely* by the BO terms. If the coupled equations are solved exactly this leads to identical results, and we conclude there is seldom any advantage, and generally a great deal of disadvantage, in employing relativistic molecular wave functions.

In the accompanying paper the coupled equations are solved and the cross sections are evaluated for this system.

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APPENDIX A: PARITY

The Hamiltonian H is invarient to inversion $\mathcal{I}$ of the space-fixed coordinates $\mathcal{I}(\vec{r}_i, \vec{R}) \rightarrow (-\vec{r}_i, -\vec{R})$. This inversion does not operate on the electron-spin "coordinates" $\mathcal{I}(\vec{\sigma}) \rightarrow (\vec{\sigma})$. In polar coordinates the nuclear $\vec{R}$ components transform as follows: $\mathcal{I}(R, \theta, \phi) \rightarrow (R, \pi - \theta, \pi + \phi)$. If the space-fixed components of the electron coordinate vector $\vec{r}_i$ are denoted with primes, the transformation yields $\mathcal{I}(\vec{r}_i) \rightarrow (-x_i', -y_i', -z_i')$. However the molecule-fixed components of $\vec{r}_i$, denoted by umprimed variables, are subjected to the following transformation: $\mathcal{I}(\vec{r}_i) \rightarrow (-x_i, y_i, z_i) \rightarrow (r_i, \theta_i, \pi - \phi_i)$. The electron spin $\vec{\sigma}$ components are *not* invarient in molecule-fixed space, and one finds the $|\pm\frac{1}{2}\rangle$ components transform as follows:

$$\mathcal{I}(|\pm\tfrac{1}{2}\rangle) \rightarrow e^{i\pi/2}|\mp\tfrac{1}{2}\rangle . \qquad \text{(A1)}$$

The phase has been chosen by adopting the following convention for the inversion of the Wigner rotation matrices for $\frac{1}{2}$ integer values of j,

$$\mathcal{I}(D^{j*}_{M,\lambda}) \rightarrow e^{-i\pi j} D^{j*}_{M,-\lambda} . \qquad \text{(A2)}$$

By this definition the spherical harmonics transform as usual,

$$\mathcal{I}(Y_{l,m}(\hat{r})) \rightarrow (-1)^l Y_{l,m}(\hat{r}) . \qquad \text{(A3)}$$

Both the atomic and molecular functions $|m_L, m_S\rangle$ and $|R, \Lambda, m_S\rangle$ are assumed to be constructed such that

$$|R, \Lambda, m_S\rangle^* = (-1)^\Lambda |R, -\Lambda, m_S\rangle$$

and

$$|(\pi - \phi_i), R, \Lambda, m_S\rangle = |(\phi_i), R, -\Lambda, m_S\rangle .$$

The parity of the space-fixed atomic states $|j, m_j\rangle$ is determined by $\mathcal{I}(Y_{L,m_L})$, where L is the total orbital angular momentum of the electrons. For the ground ^2P state, since $L = 1$, we obtain

$$\mathcal{I}(|j, m_j\rangle) \rightarrow -|j, m_j\rangle . \qquad \text{(A4)}$$

The molecular functions $|R, \Lambda, m_S\rangle$ subjected to inversion yield

$$\mathcal{I}(|R, \Lambda, m_S\rangle) \rightarrow e^{i\pi/2}|R, -\Lambda, -m_S\rangle , \qquad \text{(A5)}$$

and the Ω states defined in Eq. (4.2) transform as follows:

$$\mathcal{J}(|R,\ j,\ \Omega\rangle)\rightarrow -e^{i\pi j}|R,\ j,\ -\Omega\rangle . \tag{A6}$$

Finally, the rotated space-fixed molecular states defined in Eq. (4.9) behave as do the atomic states in (A4), i.e.,

$$\mathcal{J}(|\vec{R},\ j,\ m_j\rangle)\rightarrow -\ |\vec{R},\ j,\ m_j\rangle . \tag{A7}$$

Therefore, the parity expressed in Eq. (5.11) for the channel states (5.6) or (5.8) is obtained,

$$\mathcal{J}(|R,\ J,\ M,\ j,\ l\rangle)\rightarrow (-1)^{l+1}|R,\ J,\ M,\ j,\ l\rangle . \tag{A8}$$

APPENDIX B: BO MATRIX ELEMENTS

The nuclear angular momentum operator $\vec{\mathrm{L}}_R^2$ in Eq. (7.2b) is defined by Eq. (3.6) and must be represented in molecule-fixed coordinates. Noting that the electronic momentum $\vec{j}^2 = j_+j_- + j_Z^2 - j_Z$ and that in molecule-fixed space $j_Z \equiv J_Z$, we can express $\vec{\mathrm{L}}_R^2$ as a function of j and the total angular momentum operator $\vec{\mathrm{J}}$:

$$\vec{\mathrm{L}}_R^2 = \vec{\mathrm{J}}^2 + j_+j_- - j_+J^- - j_-J^+ - J_Z(J_Z+1) . \tag{B1}$$

The stepping operators are "normal" for $\vec{j}$, i.e., acting on the atom functions in Eq. (2.9), and the molecular functions in Eq. (4.2) one obtains,

$$j_\pm |j,\ \Omega\rangle = [(j\mp\Omega)(j\pm\Omega+1)]^{1/2}|j,\ \Omega\pm 1\rangle ,$$

$$j_\pm |R,\ j,\ \Omega\rangle = \sum_{j'}\langle R,\ j',\ \Omega\pm 1|j_\pm|R,\ j,\ \Omega\rangle \times |R,\ j',\ \Omega\pm 1\rangle . \tag{B2}$$

However, as implied by the superscript notation, for $J^\pm$ in molecule-fixed space the commutation rules are reversed, i.e., $[J_X,\ J_Y] = -iJ_Z$, $[J_Y,\ J_Z] = -iJ_X$, $[J_Z,\ J_X] = -iJ_Y$, and one finds for $J^\pm$ operating on the Wigner functions in (5.7):

$$J^\pm \Omega^J_{M,\Omega} = [(J\pm\Omega)(J\mp\Omega+1)]^{1/2}\,\Omega^J_{M,\Omega\mp 1} . \tag{B3}$$

These transformations are discussed by Van Vleck,[26] Kolos and Wolniewicz,[27] and Pack and Hirschfelder.[8]

Applying these equations to (7.2b), (5.8), and (4.2) one finds that the angular BO term is proportional to Δ:

$$\langle j,\ l|\frac{\vec{\mathrm{L}}_R^2 - l(l+1)}{2\mu R^2}|j',\ l'\rangle = -\frac{\sqrt{2}\Delta(-1)^{j-j'}}{2\mu R^2}\mathcal{A} , \tag{B4}$$

where Δ is a measure of the "distortion" of the fluorine atom charge density owing to molecular formation,

$$\langle R,\ \Lambda,\ m_S|L_\pm|R,\ \Lambda\mp 1,\ m_S\rangle = \sqrt{2}(1-\Delta) . \tag{B5}$$

As $R\rightarrow\infty$ the atomic expectation value $\sqrt{2}$ is obtained for the electron orbital angular momentum operator in (B5); hence $\Delta\rightarrow 0$ and (B4) vanishes. The coefficient $\mathcal{A}$ is J dependent, and for large J is proportional to J;

$$\mathcal{A} = \sum_{\Omega,\Lambda}(J,\ j,\ l|-\Omega,\ \Omega,\ 0)(1,\ \tfrac{1}{2},\ j|\Lambda,\ \Omega-\Lambda,\ \Omega)\,a_{\Omega,\Lambda}(J,\ j',\ l') , \tag{B6}$$

where

$$\begin{aligned} a_{\Omega,\Lambda}(J,\ j',\ l') = {} & (J,\ j',\ l'|-\Omega,\ \Omega,\ 0)[(1,\ \tfrac{1}{2},\ j'|\Lambda-1,\ \Omega-\Lambda+1,\ \Omega)+(1,\ \tfrac{1}{2},\ j'|\Lambda+1,\ \Omega-\Lambda-1,\ \Omega)] \\ & +(J,\ j',\ l'|-\Omega+1,\ \Omega-1,\ 0)[(J+\Omega)(J-\Omega+1)]^{1/2}(1,\ \tfrac{1}{2},\ j'|\Lambda-1,\ \Omega-\Lambda,\ \Omega-1) \\ & +(J,\ j',\ l'|-\Omega-1,\ \Omega+1,\ 0)[(J-\Omega)(J+\Omega+1)]^{1/2}(1,\ \tfrac{1}{2},\ j'|\Lambda+1,\ \Omega-\Lambda,\ \Omega+1) . \end{aligned}$$

Similarly for the radial matrix (7.2c) an expression is obtained which vanishes at large R, where $|R,\ \Lambda,\ m_S\rangle \sim |\Lambda,\ m_S\rangle$ and the molecular wave function becomes independent of R.

Define the molecular integral $\mathcal{R}_{|\Lambda|}(R)$:

$$\mathcal{R}_{|\Lambda|} = \langle R,\ \Lambda,\ m_S|-\frac{\partial^2}{2\mu R^2}|R,\ \Lambda,\ m_S\rangle + \langle R,\ \Lambda,\ m_S|-\frac{\partial}{\mu R\,\partial R}|R,\ \Lambda,\ m_S\rangle\left(1+R\frac{\partial}{\partial R}\right) , \tag{B7}$$

then the radial BO term can be expressed as follows:

$$\delta_{j,j'}\delta_{l,l'}\mathcal{R}_1 + (\mathcal{R}_0 - \mathcal{R}_1)\mathcal{B} , \tag{B8}$$

where the coefficient $\mathcal{B}$ is

$$\mathcal{B} = \sum_{m_S}(-1)^{j'-j}(J,\ j,\ l|-m_S,\ m_S,\ 0)(J,\ j',\ l'|-m_S,\ m_S,\ 0)(1,\ \tfrac{1}{2},\ j|0,\ m_S,\ m_S)(1,\ \tfrac{1}{2},\ j'|0,\ m_S,\ m_S) .$$

Note that the off-diagonal matrix element is proportional to and this leads to our conclusion from Eq. (8.9) that to first order the off-diagonal radial BO term vanishes.

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Molecular Theory of Atomic Collisions: Calculated Cross Sections for $H^+ + F(^2P)$

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The results of a close-coupling calculation of the fine-structure transitions ($j, m_j\to j', m_j'$) are presented for collisions between photons and $F(^2P_{j,m_j})$. The theory is formulated in the perturbed-stationary-state approximation using accurate molecular wave functions for the ground $^2\Pi$ and $^2\Sigma$ states of HF^+. Comparison is made to the predictions of the Born approximation. The magnetic selection rule ($j, m_j\to j, -m_j$) is strongly violated in the $j=3/2$ state and less strongly violated in the $j=1/2$ state. It is concluded that the important region of interaction for the $j=1/2\to j=3/2$ transition is at short-to-intermediate distances where accurate molecular potentials are required and close-coupling effects are dominant.

I. INTRODUCTION

In the preceding paper[1] the theory of fine-structure transitions in proton-fluorine collisions was developed using the ground molecular $HF^+(^2\Pi)$ and $HF^+(^2\Sigma)$ electronic states in a perturbed-stationary-state expansion of the scattering wave functions. At each total energy E, and for each total angular momentum state J, with space projection M, there exists a set of six open *molecular* channel states $|R, J, M, j, l\rangle$ arising from the six substates (j, m_j) of the $F(^2P_{j,m_j})$ ground state. The channel-state expansion (I-6.1) defines the radial functions $F^{J,M,E}_{j,l;j',l'}(R)$ which must vanish at $R=0$, and are subject to the asymptotic boundary conditions in Eq. (I-6.3) which determines the reactance matrix $K^J_{j,l;j',l'}$ and hence, the scattering cross sections. This expansion results in the coupled differential equations of Eq. (I-7.1) which may be written in the following matrix form:

$$\left[\left(-\frac{\partial^2 R}{2\mu R\,\partial R^2}-E\right)\underline{1}+\underline{U}^J(R)\right]\underline{F}^{J,M,E}(R)=0\,, \quad (1.1)$$

where

$$\underline{F}^{J,M,E}=\{F^{J,M,E}_{j,l;j',l'}\}$$

and

$$\underline{1}=\{\delta_{j,j'}\delta_{l,l'}\}\,.$$