Quantum dynamics of the collision in an adiabatic representation

For the sake of simplicity, let us consider two ionic cores A^{q+} and B^{+} of masses m_a and m_b and an electron with mass m_e(=1 in atomic units). The many particle kinetic energy operator takes its simplest form in Jacobi coordinates (see figure 2.)

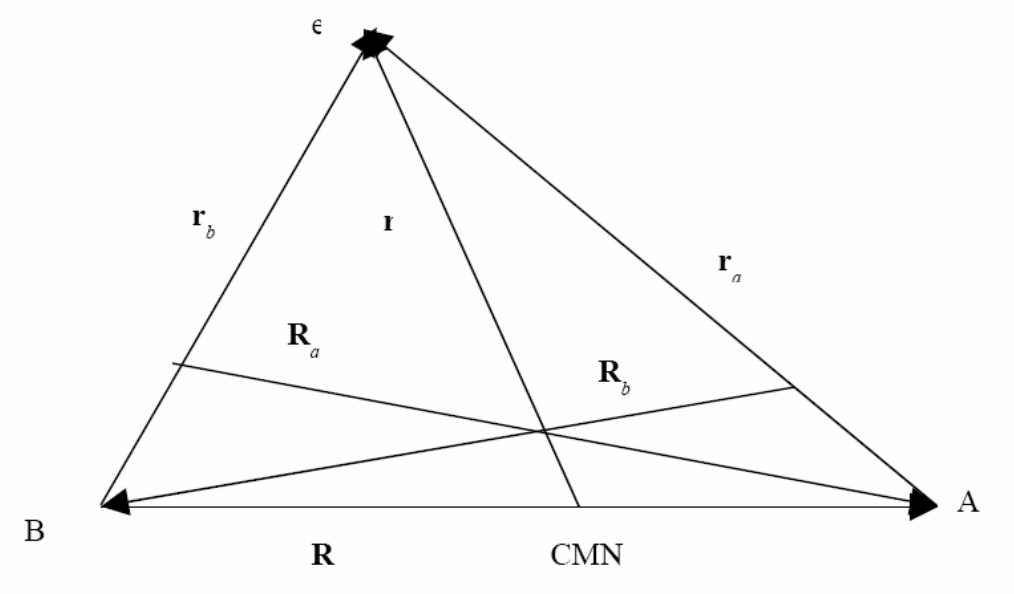

Figure 2. Schematic diagram of the Jacobi coordinates of a three particle system.

For three particles, there exist three equivalent sets of Jacobi coordinates where are respectively the position vectors of the electron relative to A, B and CMN (the centre of mass of nuclear cores A and B) while are respectively the position vectors of A relative to the centre of mass of (B+e) and of B relative to the centre of mass of (A+e). Since the adiabatic states are defined by a clamped nuclei approximation, the most natural choice of Jacobi coordinates would appear to be ($\mathbf{r}, \mathbf{R}$).

After separation of the kinetic operator of the centre of mass of the total system, the Hamiltonian for the entire system may be written as

$$H = -\frac{1}{2m_{ab}}\Delta_{\mathbf{R}} - \frac{1}{2m_e}\Delta_{\mathbf{r}} + V_{\text{int}}(\mathbf{r}, \mathbf{R})$$

where the operator $V(\mathbf{r},\mathbf{R})$ contains all interactions between the particles and $m_{ab} = m_a m_b /(m_a + m_b)$ is the reduced nuclear mass.

In the clamped nuclei limit, the motion of the electrons is governed by the electronic Hamiltonian

$$\sum_{i=1}^{n} X_i Y_i$$

The eigenfunctions and eigenvalues of H_e are defined by

$$H_e \chi_j(\mathbf{r};\mathbf{R}) = E_j(R)\chi_j(\mathbf{r};\mathbf{R})$$

Since the interaction potential is invariant with respect to the orientation of **R** in space, the eigenvalues E_n(R) depend only on the distance *R*. On the other hand, the eigen functions depend not only on the distance *R* but also on the direction of **R**. It is therefore convenient to define the adiabatic eigenfunctions in a reference frame fixed with respect to the internuclear axis AB. In this *body-fixed* frame of reference, the axis is taken, by convention, to lie along the line from B to A: that is to say in the direction of the vector **R**.

In the body-fixed frame, the position vector of the electron is denoted by $\bar{\mathbf{r}}$. Geometrically, the vectors $\bar{\mathbf{r}}$ and **r** are identical, but $\bar{\mathbf{r}}$ is expressed in terms of body fixed coordinates ($\bar{x}, \bar{y}, \bar{z}$) whereas **r** is expressed in terms of space-fixed coordinates (x, y, z). In the body-fixed frame, the adiabatic eigenfunctions , $\chi_j(\bar{\mathbf{r}};R)$ depend only on $\bar{\mathbf{r}}$ and on the distance *R*. In addition, they can also be chosen as eigenfunctions of the component $L_{\bar{z}}$ of the electronic angular momentum along the $O\bar{z}$ axis

$$L_{\bar{z}}\chi_j(\bar{\mathbf{r}},R) = \pm\Lambda_j\chi_j(\bar{\mathbf{r}},R)$$

where $\Lambda_j = 0,\ 1,\ 2,...$ correspond to Σ, Π, Δ,.. states.

The eigenfunctions of H_e constitiute a basis set for a description of the collision complex. So we expand the wave function in the form.

But we should observe that while we may use any coordinates in which to express the clamped nuclei eigen functions, the choice of adiabatic corodinate is not rigourously defined.

The standard adiabatic expansion, used in the Born-Oppenheimer separation of the electornic from the ro-vibrational nuclear motion, takes **R** as the adiabatic coordinate. Unfortunately, this does not allow for a perfect description of the asymptotic conditions.

But to highlight the problem, we shall first derive the dynamical equations in the standard way.

$$\psi(\mathbf{r},\mathbf{R}) = \sum_{j}^{N} F_j(\mathbf{R})\chi_j(\bar{\mathbf{r}},R)$$

We shall then see that it is necessary to introduce a system of reaction coordinates which allow for a correct break-up of the collision complex.

Substituting in the Schrödinger equation

$$\left[-\frac{1}{2m_{a,b}}\nabla^2_{\mathbf{R}} - \frac{1}{2}\nabla^2_{\mathbf{r}} + V_{\text{int}}(\mathbf{r},\mathbf{R})\right]\psi(\mathbf{r},\mathbf{R}) = E_T\psi(\mathbf{r},\mathbf{R})$$

we obtain a system of coupled partial differential equations, which in matrix form can be written as

$$\left[\nabla^2_{\mathbf{R}} + 2m_{a,b}\left\{E_T\mathbf{I} - \mathbf{E}(R)\right\}\right]\mathbf{F}(\mathbf{R}) = \left[\mathbf{Q}(\mathbf{R}) + \mathbf{P}(\mathbf{R}).\nabla_{\mathbf{R}}\right]\mathbf{F}(\mathbf{R})$$

where **E** is a diagonal matrix, whose elements are the adiabatic energies

$$E_{ij}(R) = E_j(R)\delta_{ij}$$

The matrix elements of **Q** and **P** involve the non adiabatic coupling terms

$$Q_{ij}(R) = -\int \chi_i^*(\bar{\mathbf{r}},R)\nabla^2_{\mathbf{R}}\chi_j(\bar{\mathbf{r}},R)d\bar{\mathbf{r}} \qquad P_{ij}(R) = -2\int \chi_i^*(\bar{\mathbf{r}},R)\nabla_{\mathbf{R}}\chi_j(\bar{\mathbf{r}},R)d\bar{\mathbf{r}}$$

The differential operators in these equations, are defined with respect to the space fixed reference frame whereas the adiabatic basis functions are expressed in terms of coordinates in the body-fixed system. In calculating the matrix elements of **P** and **Q**, we may choose to express the adiabatic basis function either in terms of **r** and **R** or to transform the operators with respect to **r** fixed to operators with respect to $\bar{\mathbf{r}}$ fixed. The second alternative is simpler. So we first transform the partial differential operators $\partial/\partial R$, $\partial/\partial\Theta$, $\partial/\partial\,\Phi$ taken with respect to (x, y, z) fixed to the partial differential operators $\partial'/\partial R$, $\partial'/\partial\,\Theta$, $\partial'/\partial\,\Phi$ taken with respect to $(\bar{x}, \bar{y}, \bar{z})$ fixed, where (Θ, Φ) designate the polar angles of **R** in the space-fixed frame.

The transformation from the space fixed axis to the body fixed axis is specified by a series of two rotations of the reference frame: firstly a rotation by Φ about Oz, to yield a new set of axes ($x', \bar{y}, z$), followed by a second rotation by Θ about O to yield ($\bar{x}, \bar{y}, \bar{z}$). The axis $O\bar{z}$ is now in the direction of **R** and $O\bar{y}$ is in the space-fixed O*xy* plane. The components of the position vector in the body fixed frame are related to those in the space-fixed frame by the matrix relation

$$\begin{pmatrix} \bar{x} \\ \bar{y} \\ \bar{z} \end{pmatrix} = \begin{pmatrix} \cos\Theta & 0 & -\sin\Theta \\ 0 & 1 & 0 \\ \sin\Theta & 0 & \cos\Theta \end{pmatrix} \begin{pmatrix} \cos\Phi & -\sin\Phi & 0 \\ \sin\Phi & \cos\Phi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

More explicitly

$$\bar{x} = x\cos\Theta\cos\Phi + y\cos\Theta\sin\Phi - z\sin\Theta$$
$$\bar{y} = -x\sin\Phi + y\sin\Phi$$
$$\bar{z} = x\sin\Theta\cos\Phi + \sin\Theta\sin\Phi + z\cos\Theta$$

Using these transformations one can easily verify that

$$\frac{\partial\bar{x}}{\partial\Theta} = -\bar{z} \qquad \frac{\partial\bar{y}}{\partial\Theta} = 0 \qquad \frac{\partial\bar{z}}{\partial\Theta} = \bar{y}$$

$$\frac{\partial\bar{x}}{\partial\Phi} = \bar{y}\cos\Theta \qquad \frac{\partial\bar{y}}{\partial\Phi} = -\bar{x}\cos\Theta - \bar{z}\sin\Theta \qquad \frac{\partial\bar{z}}{\partial\Phi} = \bar{y}\sin\theta$$

from which we may deduce

$$\frac{\partial}{\partial R} = \frac{\partial'}{\partial R} \qquad \frac{\partial}{\partial\Theta} = \frac{\partial'}{\partial\Theta} + \frac{\partial x}{\partial\Theta}\frac{\partial}{\partial\bar{x}} + \frac{\partial y}{\partial\Theta}\frac{\partial}{\partial\bar{y}} + \frac{\partial z}{\partial\Theta}\frac{\partial}{\partial\bar{z}} = \frac{\partial'}{\partial\Theta} - \frac{i}{\hbar}L_{\bar{y}}$$

$$\frac{\partial}{\partial\Phi} = \frac{\partial'}{\partial\Phi} + \frac{\partial x}{\partial\Phi}\frac{\partial}{\partial\bar{x}} + \frac{\partial y}{\partial\Phi}\frac{\partial}{\partial\bar{y}} + \frac{\partial z}{\partial\Phi}\frac{\partial}{\partial\bar{z}} = \frac{\partial'}{\partial\Phi} - \cos\theta\frac{i}{\hbar}L_{\bar{z}} + \sin\Theta\frac{i}{\hbar}L_{\bar{x}}$$

where $L_{\bar{x}}, L_{\bar{y}}, L_{\bar{z}}$ are the components of the electronic angular momentum in the body fixed system.

We may write $\nabla_{\mathbf{R}}$ and $\nabla^2_{\mathbf{R}}$ in spherical polar coordinates

$$\nabla_{\mathbf{R}} = \mathbf{u}_R \frac{\partial}{\partial R} + \frac{1}{R}\mathbf{u}_\Theta \frac{\partial}{\partial \Theta} + \frac{1}{R\sin\Theta}\mathbf{u}_\Phi \frac{\partial}{\partial \Theta}$$

where $\mathbf{u}_R$, is the unit vector in the direction of **R**, $\mathbf{u}_\Theta$ the unit vector perpendicular to **R** in the plane containing **R** and Oz, $\mathbf{u}_\Phi = \mathbf{u}_R \times \mathbf{u}_\Theta$ the unit vector perpendicular to **R** and Oz

$$\nabla^2_{\mathbf{R}} = \frac{\partial^2}{\partial R^2} + \frac{2}{R}\frac{\partial}{\partial R} + \frac{1}{R^2}\left[\frac{\partial^2}{\partial \Theta^2}\cot\Theta\frac{\partial}{\partial\Theta}\frac{1}{\sin^2\Theta}\frac{\partial^2}{\partial\Theta^2}\right]$$

Using the fact that the adiabatic basis functions depend neither on Θ nor on Φ, we find

$$\mathbf{P}_{ij}.\nabla_{\mathbf{R}} = -\left\langle i\left|\frac{\partial}{\partial R}\right|j\right\rangle\frac{\partial}{\partial R} + \frac{2i}{R^2}\left\langle i\left|L_{\bar{y}}\right|j\right\rangle\frac{\partial}{\partial\Theta} + \frac{2i\Lambda_j}{R^2\sin\Theta}\left[\left\langle i\left|L_{\bar{x}}\right|j\right\rangle + \Lambda_j\delta_{ij}\cot\Theta\right]\frac{\partial}{\partial\Phi}$$

$$\mathbf{Q}_{ij}. = -\left\langle i\left|\frac{\partial^2}{\partial R^2} + \frac{2}{R}\frac{\partial}{\partial R}\right|j\right\rangle + \frac{1}{R^2}\left\langle i\left|L^2_{\bar{x}} + L^2_{\bar{y}}\right|j\right\rangle + \frac{2\cot\Theta}{R^2}\Lambda_j\left\langle i\left|L_{\bar{x}}\right|j\right\rangle + \frac{\Lambda_j^2\cot^2\Theta}{R^2}\delta_{ij}$$

We observe that $\left\langle i\left|L^2_{\bar{x}} + L^2_{\bar{y}}\right|j\right\rangle$ =0 if $\Lambda_i \neq \Lambda_j$

and $\left\langle i\left|L_{\bar{x}}\right|j\right\rangle = \left\langle i\left|L_{\bar{x}}\right|j\right\rangle$ =0 if $\Lambda_i \neq \Lambda_j \pm 1$

The coupled equations can now be written in the form

$$\left[\frac{\partial^2}{\partial R^2} - \frac{\mathbf{J}^2 - \Lambda^2}{R} + 2m_{a,b}\left\{E_T\mathbf{I} - \mathbf{E}(R)\right\}\right] R\mathbf{F}(\mathbf{R}) = \left\{\mathbf{V}^{(r)}(R) + \mathbf{V}^{(c)}(R)\right\} R\mathbf{F}(\mathbf{R})$$

where the matrix **V**(r) is designated as the radial coupling matrix

$$\mathbf{V}_{ij}^{(r)} = \left[\left\langle i\right| - \frac{\partial^2}{\partial R^2} + \frac{L_{\bar{x}}^2 + L_{\bar{y}}^2}{R^2}\left| j\right\rangle - 2\left\langle i\right| - \frac{\partial}{\partial R}\left| j\right\rangle \frac{\partial}{\partial R}\right] \delta(\Lambda_i, \Lambda_j)$$

and the matrix **V**(*c*) as the rotational (or Coriolis) coupling matrix

$$\mathbf{V}_{ij}^{(c)} = \frac{1}{R^2}\left[2i\left\langle i\right| L_{\bar{y}} - \frac{1}{\sin\Theta} L_{\bar{x}}\left| j\right\rangle \frac{\partial}{\partial\Theta} - 2\Lambda_j \left\langle i\right| L_{\bar{x}}\left| j\right\rangle\right] \delta(\Lambda_i, \Lambda_j \pm 1))$$

The matrices **Λ** and $\mathbf{J}^2$ are both diagonal. The elements of **Λ** are while those of $\mathbf{J}^2$ are differential operators defined as

$$\mathbf{J}^2 = \left[-\frac{\partial^2}{\partial\Theta^2} + \cot\Theta\frac{\partial}{\partial\Theta} + \frac{1}{\sin^2\Theta}\left(\frac{\partial}{\partial\Phi} - i\Lambda\cos\Theta\right)^2 - \Lambda^2\right]$$

It can be shown (see lecture notes) that **J** is the total angular momentum, the sum of **N** the nuclear and **L** the electronic angular momentum. While neither **N** nor **L** are conserved during a collision, the total angular momentum is a constant of the motion.

Using the explicit forms of the components of the angular momentum operators **N** and **L,** it is straightforward to verify that

$$J_x + iJ_y = \left(N_x + iN_y\right) + \left(L_x + iL_y\right) = e^{i\Phi}\left[\left(\frac{\partial'}{\partial\Theta} + i\cot\Theta\frac{\partial'}{\partial\Phi}\right) + \frac{L_{\bar{z}}}{\sin\Theta}\right]$$

$$J_x - iJ_y = \left(N_x - iN_y\right) + \left(L_x - iL_y\right) = e^{-i\Phi}\left[\left(-\frac{\partial'}{\partial\Theta} + i\cot\Theta\frac{\partial'}{\partial\Phi}\right) + \frac{L_{\bar{z}}}{\sin\Theta}\right]$$

$$J_z = -i\frac{\partial'}{\partial\Phi}$$

Using the fact that the adiabatic basis functions $\chi_j(\bar{\mathbf{r}}, R)$ depend neither on Θ nor on Φ, it can be shown without difficulty that

$$\mathbf{J}^2\chi(\bar{\mathbf{r}}, R)F_j(\mathbf{R}) = -\chi(\bar{\mathbf{r}}, R)\left[\frac{\partial'^2}{\partial\Theta^2} + \cot\Theta\frac{\partial'}{\partial\Theta} + \frac{1}{\sin^2\Theta}\left(\frac{\partial'}{\partial\Phi} - i\Lambda_j\cos\Theta\right)^2 - \Lambda_j^2\right]F_j(\mathbf{R})$$

Recalling that when operating on a function only of **R,** there is no distinction between the primed and unprimed partial differentials: in other words in , $\partial'/\partial\Theta = \partial/\partial\Theta$ $\partial'/\partial\Phi = \partial/\partial\Phi$ This justifies the interpretation of $\mathbf{J}^2$ as the square of the total angular momentum.

Section 6. Partial wave expansion

In order to reduce the system of coupled partial differential equations to a system of coupled ordinary differential equations which can be solved numerically, it is necessary to make a partial wave expansion of the functions F_n. The most natural choice is to use as expansion basis the simultaneous eigen functions of $\mathbf{J}^2$ and J_z , These are designated by $U^J_{M\Lambda}(\Theta,\Phi)$

$$\mathbf{J}^2 U^J_{M\Lambda} = J(J+1)U^J_{M\Lambda} \qquad J_z U^J_{M\Lambda} = M U^J_{M\Lambda}$$

The explicit form of the functions $U^J_{M\Lambda}(\Theta,\Phi)$ can be expressed as

$$U^J_{M\Lambda}(\Theta,\Phi) = (-)^{\Lambda+M}\, d^J_{M\Lambda}(\Theta) \exp iM\Phi$$

where $d^J_{M\Lambda}(\Theta)$ is the reduced rotation matrix

$$d^J_{M\Lambda}(\Theta) = N^J_{M\Lambda} \frac{\sqrt{1-\mu}^{(\Lambda-M)}}{\sqrt{1+\mu}^{(\Lambda+M)}} \left[\left(\frac{\partial}{\partial\mu} \right)^{J-M} (1-\mu)^{J-\Lambda} (1+\mu)^{J+\Lambda} \right]$$

with $\mu \equiv \cos\Theta$ and $N^J_{M\Lambda}$ is a normalization constant, chosen such that

$$\int_{-1}^{1} d\mu \int_{0}^{2\pi} d\Phi U^{J}_{M\Lambda}{}^{*}(\Theta,\Phi) U^{J'}_{M'\Lambda}(\Theta,\Phi) = \frac{4\pi}{2J+1} \delta(J,J')\delta(M,M')$$

We may observe that in the case M=0,

$$U^{J}_{0\Lambda}(\Theta,\Phi) = (-)^{\Lambda}\sqrt{\frac{4\pi}{2J+1}}Y_{J,\Lambda}(\Theta,\Phi=0)$$

Expanding each channel function in the form

$$F_j(\mathbf{R}) = \frac{1}{R}\sum_{J=0}^{\infty} f_j^J(R)U^J_{M\Lambda_j}(\Theta,\Phi)$$

and making use of the orthogonality property (6.4) and the following relation (see[16])

$$\left[\mp\frac{\partial}{\partial\Theta} + \frac{i}{\sin\Theta}\frac{\partial}{\partial\Phi} + \Lambda\cot\Theta\right]U^J_{M\Lambda}(\Theta,\Phi) = \sqrt{(J\pm\Lambda+1)(J-\Lambda)}U^J_{M\Lambda\pm1}(\Theta,\Phi)$$

it is be easily demonstrated that the radial functions are solutions of the

$$\left[\frac{d^2}{dR^2} + \frac{\Lambda_j^2 - J(J+1)}{R^2} + 2m_{a,b}\left\{E_T - E_j(R)\right\}\right]f_j^J(R) = \sum_j\left(V_{ij}^{(r)} + V_{ijJ}^{(c)}\right)f_j^J(R)$$

or in matrix form

$$\left[\frac{d^2}{dR^2} + \frac{\Lambda^2 - J(J+1)}{R^2} + 2m_{a,b}\left\{E_T\mathbf{I} - \mathbf{E}(R)\right\}\right]\mathbf{f}^J(R) = \left[\mathbf{V}^{(r)}(R) + \mathbf{V}_J{}^{(c)}(R)\right]\mathbf{f}^J(R)$$

The radial coupling matrix $\mathbf{V}^{(r)}$ (independent of J) is given as previously and the Coriolis coupling $\mathbf{V}_J^{(c)}$ (which depends on J) can be reduced to the form

$$V_{ijJ}^{(c)}(R) = \frac{2}{R^2}\langle i | iL_{\bar{y}} | j \rangle \left[\delta(\Lambda_i, \Lambda_j - 1)\sqrt{(J + \Lambda_i)(J - \Lambda_j + 1)} - \delta(\Lambda_i, \Lambda_j + 1)\sqrt{(J - \Lambda_i)(J + \Lambda_j + 1)} \right]$$

We may observe that while the radial matrix $\mathbf{V}^{(r)}$ only connects channels *i,j* if $\Lambda_i = \Lambda_j$ while , the Coriolis part $\mathbf{V}_J^{(c)}$ connects channels *i,j* if $\Lambda_i = \Lambda_j \pm 1$

It is important to establish a phase convention for the adiabatic wave functions $\chi_j(\bar{\mathbf{r}};R)$. Introducing explicitly the coordinates of $\bar{\mathbf{r}}$ as (r,θ,ϕ) where ϕ is the azimuthal coordinate and (r,θ) the ensemble of non azimuthal coordinates, the axial symmetry of the system makes it possible to express the eigenfunction $\chi_j(\bar{\mathbf{r}};R)$ in the form

$$\chi_j(\bar{\mathbf{r}};R) = \zeta(r,\theta;R)\Phi(\phi)$$

The phase of the azimuthal part, being independent of R, is well defined for a given Λ_j and has no effect on the radial coupling matrix element. In contrast, the phase of the non-azimuthal part is not well defined for a given *R*. It is therefore customary to adopt the convention that the non azimuthal part be real. This still leaves an arbitrary overall factor of ± 1. The convention is to assume that the sign does not change with respect to small changes in R.

In practice this can be ensured by calculating numerically the overlap of the adiabatic functions at *R* and $R+\delta R$, where $\delta R << R$. If the overlap is close to +1 the phases are correct, if the overlap is close to -1, the phases are adjusted accordingly.

Non adiabatic coupling matrix elements

In order to acquire some intuition of the standard adiabatic model, it is desirable to have some quantitative idea of the nature of the radial and rotation coupling terms $V_{ij}^{(r)}$ and $V_{ij}^{(c)}$. Let us begin with the term $V_{ij}^{(r)}$.

$$\mathbf{V}_{ij}^{(r)} = \left[\left\langle i \right| - \frac{\partial^2}{\partial R^2} + \frac{L_{\bar{x}}^2 + L_{\bar{y}}^2}{R^2} \left| j \right\rangle - 2 \left\langle i \right| - \frac{\partial}{\partial R} \left| j \right\rangle \frac{\partial}{\partial R} \right] \delta(\Lambda_i, \Lambda_j)$$

This term operates on the radial function $F_j(R)$. Except for the case of extremely low energies, $F_j(R)$ is quite an oscillatory function since its associated wave number k_j>>1. For that reason, the second term dominates (roughly by a factor proportional to $\sqrt{m_{a,b}}$).

The radial coupling is therefore controlled by the matrix element

$$A_{ij} = \left\langle i \right| \frac{\partial}{\partial R} \left| j \right\rangle$$

A precise determination of A_{ij} involves a numerical differentiation of the adiabatic eigen functions with respect to the internuclear distance. But it is possible to gain some qualitative indication of its size from elementary considerations.

With the above phase convention, the diagonal elements of matrix **A** vanish. Since the eigenfunctions are normalized for all *R*

$$\frac{d}{dR}\langle i|i\rangle = \left\langle \frac{\partial}{\partial R} i \middle| i \right\rangle + \left\langle i \middle| \frac{\partial}{\partial R} i \right\rangle = 2\langle i| \frac{\partial}{\partial R} |i\rangle = 0$$

As for the off-diagonal elements, we note that $\langle i | H_e | j \rangle = 0$

$$\frac{d}{dR}\langle i|H_e|j\rangle = \left\langle \frac{\partial}{\partial R} i \middle| H_e \middle| j \right\rangle + \langle i| \frac{\partial H_e}{\partial R} |j\rangle + \langle i| H_e \left| \frac{\partial}{\partial R} j \right\rangle$$

$$= E_j(R) \left\langle \frac{\partial}{\partial R} i \middle| j \right\rangle + \langle i| \frac{\partial H_e}{\partial R} |j\rangle + E_i(R) \left\langle i \middle| \frac{\partial}{\partial R} j \right\rangle = 0$$

It therefore follows that

$$A_{ij} = \left\langle i \middle| \frac{\partial}{\partial R} j \right\rangle = \frac{-1}{\left(E_i(R) - E_j(R)\right)} \langle i| \frac{\partial H_e}{\partial R} |j\rangle \qquad \text{if } i \neq j$$

We see that the radial coupling can become large if the energy separation of the adiabatic states concerned becomes small. Of course, the energy separation between adiabatic states of the same symmetry (Wigner-von Neumann no crossing rule) can never vanish, but it become quite small. Typical examples are shown in the figures.

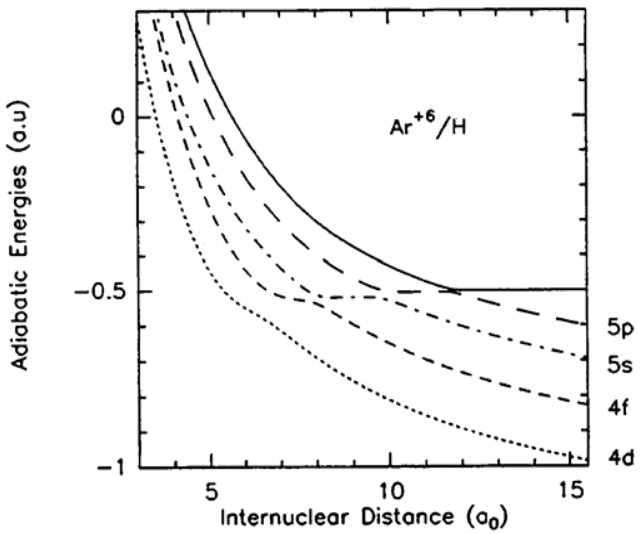

Figure 3. Adiabatic potential energies of the ArH^{6+} *molecular ion*:
-solid curve 1 [$Ar^{6+}(3s^2)$+H(1s)] ,
-long dashed curve 2 [$Ar^{5+}(3s^2 5p)+H^+$] ,
-dot dashed curve 3 [$Ar^{5+}(3s^2 5s)+H^+$],
-short dashed curve 4 [$Ar^{5+}(3s^2 4f)+H^+$],
-dotted curve 5 [$Ar^{5+}(3s^2 4d)+H^+$]

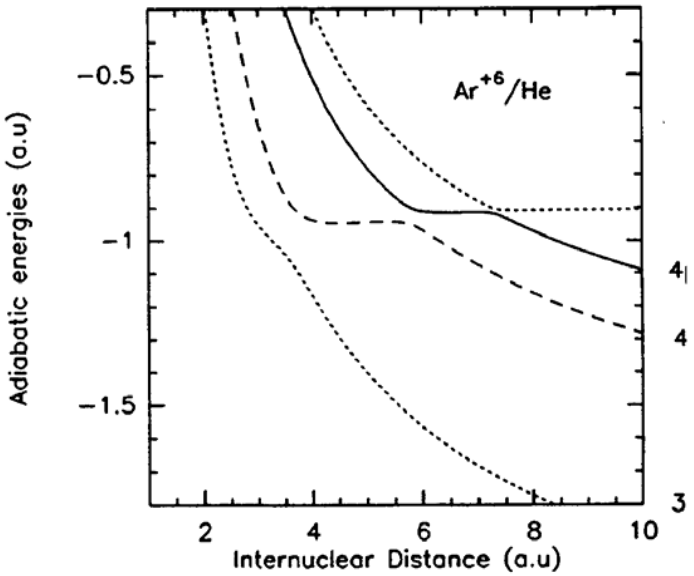

Figure 4. Adiabatic potential energies of the $ArHe^{6+}$ *molecular ion:*
-top dotted curve 1 [$Ar^{6+}(3s^2)$+He($1s^2$)],
-solid curve 2 [$Ar^{5+}(3s^2 4p)+He^+$],
-dashed curve 3 [$Ar^{5+}(3s^2 4s)+He^+$],
-bottom dotted curve 4 [$Ar^{5+}(3s^2 4f)+He^+$]

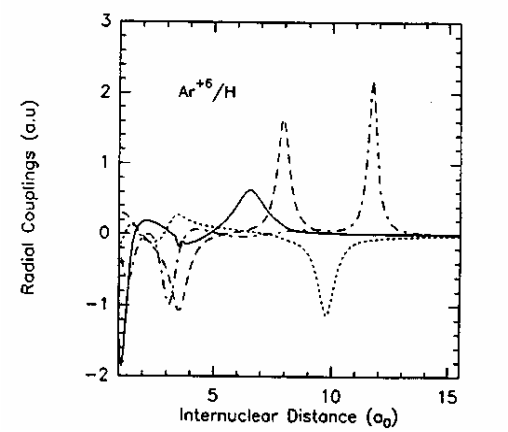

Figure 5. ArH^{6+} *radial coupling matrix elements: dot-dashed curve* A_{12}, *dotted curve* A_{23}, *dashed curve* A_{34}, *solid curve* A_{45}

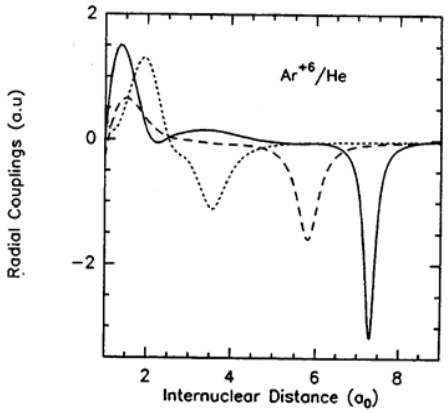

Figure 6. $ArHe^{6+}$ *radial coupling matrix elements: solid curve* A_{12}, *dashed curve* A_{23}, *dotted curve* A_{34}

It is also of interest to examine the radial coupling matrix elements in the asymptotic region as $R \to \infty$. The derivative $\partial / \partial R$ is calculated with respect to $\bar{\mathbf{r}}$ fixed. Let us assume that as $R \to \infty$, the adiabatic eigenfunction $\chi_j(\bar{\mathbf{r}}; R)$ tends to state *j* of (*A*+**e**). In that case .

$$\chi_j(\bar{\mathbf{r}}; R) \underset{R\to\infty}{\approx} \phi_j(\bar{\mathbf{r}}_a) \qquad \text{where} \qquad \bar{\mathbf{r}} = \bar{\mathbf{r}}_a + \frac{m_b}{m_a m_b}\mathbf{R}$$

It is easy to show that

$$\left.\frac{\partial}{\partial R}\right|_{\bar{\mathbf{r}}} = \left.\frac{\partial}{\partial R}\right|_{\bar{\mathbf{r}}_a} + \frac{m_b}{m_a + m_b}\left.\frac{\partial}{\partial \bar{z}}\right|_{\mathbf{R}}$$

and that, in the asymptotic limit, the radial coupling matrix is given by

$$A_{ij} = \left\langle i \left| \frac{\partial}{\partial R} \right| j \right\rangle \underset{R\leftarrow\infty}{\approx} \frac{m_b}{m_a + m_b} \left\langle i \left| \frac{\partial}{\partial \bar{z}_a} \right| j \right\rangle$$

If states *i* and *j* correlate to different centres in the asymptotic limit, the matrix element will vanish. But it does not vanish when states *i* and *j* are correlated to the same centre and when they are connected by an allowed dipole transition. The existence of such non-vanishing off-diagonal couplings makes it formally impossible to extract the S matrix from the radial equations.

We have already remarked that the second term of $V_{ij}^{(r)}$ is dominant because of the fact that it involves both A_{ij} and the derivative of the radial function. To within an order of magnitude

$$\frac{df_j^J}{dR} \approx k_j f_j^J \qquad \text{and} \qquad 2\langle i|-\frac{\partial}{\partial R}|j\rangle\frac{\partial}{\partial R} \approx \frac{2k_j}{a|\Delta_{ij}|}|\langle i|V|j\rangle|$$

where Δ_{ij} is the minimum value of $E_i(R)-E_j(R)$ at the avoided crossing and *a* is a length characteristic of the crossing region. Let us now examine the first term of $V_{ij}^{(r)}$ The matrix **B** designates the radial coupling matrix involving second derivative terms, defined as follows

$$B_{ij} = \langle i|\frac{\partial^2}{\partial R^2}|j\rangle$$

The matrix elements of **B** are related to those of **A** by the relation

$$\frac{d}{dR}A_{ij}(R) = \frac{d}{dR}\langle i|\frac{\partial}{\partial R}|j\rangle = \langle i|\frac{\partial^2}{\partial R^2}|j\rangle + \left\langle \frac{\partial}{\partial R}i\middle|\frac{\partial}{\partial R}j\right\rangle$$

If the adiabatic basis set were complete, the second term on the right hand side may be written as

$$\left\langle \frac{\partial}{\partial R}i\middle|\frac{\partial}{\partial R}j\right\rangle = \sum_k^\infty \langle i|\frac{\partial}{\partial R}|k\rangle\langle k|\frac{\partial}{\partial R}|j\rangle = \sum_k^\infty A_{ik}A_{kj} = (\mathbf{A}^2)_{ij}$$

Diabatic Representation

Radial matrix elements undergo a rapid variation at avoided crossings. This is why a diabatic representation is introduced. The diabatic basis functions $\chi_j^d(\bar{\mathbf{r}};R)$ are defined by means of a transformation matrix $\mathbf{C}(R)$

$$\chi_j^d(\bar{\mathbf{r}};R)=\sum_k^N \chi_k(\bar{\mathbf{r}},R)C_{kj}(R)$$

Introducing the column vector $\mathbf{g^J}(R)$, related to $\mathbf{f^J}(R)$ by the transformation

$$\mathbf{f}^J(R)=\mathbf{C}(R)\mathbf{g}^J(R)$$

We obtain

$$\left[\frac{d^2}{dR^2}+\frac{\Lambda^2-J(J+1)}{R^2}-2m_{a,b}\mathbf{U}(R)+2m_{a,b}E_T\right]\mathbf{g}^J(R)=\left[{}^d\mathbf{V}^{(r)}(R)+{}^d\,\mathbf{V}_J{}^{(c)}(R)\right]\mathbf{g}^J(R)$$

Where $\mathbf{U}^d=\mathbf{C}^{-1}\mathbf{E}(R)\mathbf{C}$ $\quad {}^d\mathbf{V}^{(r)}=\mathbf{C}^{-1}\mathbf{V}^{(r)}\mathbf{C}$ $\quad {}^d\mathbf{V}_J^{(c)}=\mathbf{C}^{-1}\mathbf{V}^{(c)}\mathbf{C}$

The matrix U may be considered as the electronic Hamiltonian on a diabatic basis. It is non-diagonal except in the asymptotic limit, where it is made diagonal by the condition $\mathbf{C}(R)$=I

The principal contribution to $\mathbf{V}^{(\prime)}$ comes from the matrix **A**. In the diabatic representation, this contribution becomes $\mathbf{A}^{d}$

$$\mathbf{A}^{d} = \mathbf{C}^{-1}\mathbf{A}\mathbf{C} + \mathbf{C}^{-1}\frac{d}{dR}\mathbf{C}$$

The usual diabatic transformation is to require that the matrix $\mathbf{A}^{d}$ vanishes. This condition is achieved by requiring the transformation matrix to be a solution of the equation

$$\mathbf{A}\mathbf{C} + \frac{d\mathbf{C}}{dR} = 0$$

It is also of interest to note that the matrix **B** transforms according to

$$\mathbf{B}^{d} = \mathbf{C}^{-1}\mathbf{B}\mathbf{C} + 2\mathbf{C}^{-1}\mathbf{A}\frac{d}{dR}\mathbf{C} + \mathbf{C}^{-1}\frac{d^{2}}{dR^{2}}\mathbf{C} = \mathbf{C}^{-1}\left(\mathbf{B} - \mathbf{A}^{2} - \frac{d\mathbf{A}}{dR}\right)\mathbf{C}$$

If the basis set is complete the diabatic matrix $\mathbf{B}^{d}$ will also vanish. In the case of a finite basis, the diabatic matrix $\mathbf{B}^{d}$ will not vanish.

In the case of a two-state approximation, it is easily verified that the transformation matrix is none other than a rotation matrix of the form

$$\mathbf{C}(R) = \begin{pmatrix} \cos\omega(R) & \sin\omega(R) \\ -\sin\omega(R) & \cos\omega(R) \end{pmatrix}$$

$$\omega(R) = \int_{R}^{\infty} A_{12}(R')dR'$$

Such a transformation matrix constitutes the basis of the Landau-Zener model of a non-adiabatic transition at an avoided crossing.

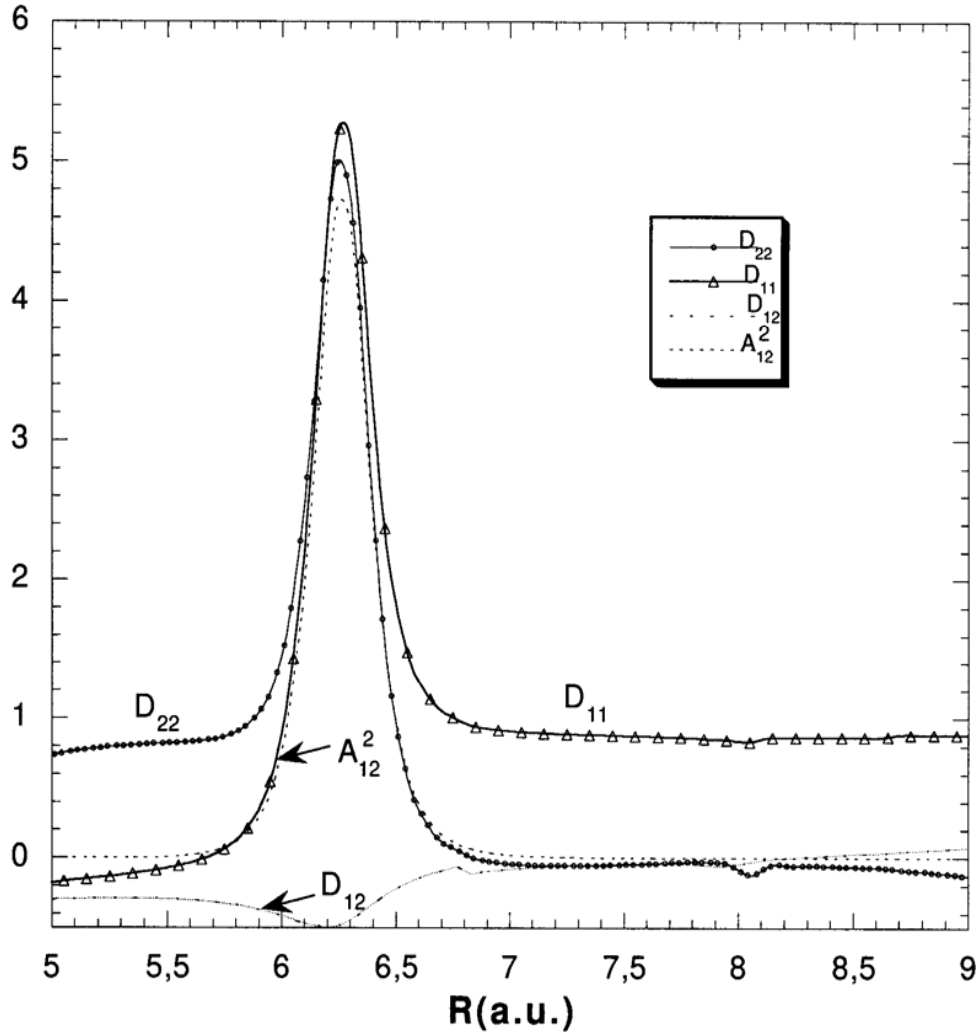

Figure 7. A comparison of the radial coupling matrix elements of **D** *and* **A** *for the two 2S states of* $SiHe^{3+}$ *responsible for electron capture by* Si^{3+} *from* He. *The radial derivatives have been calculated with the origin of electron coordinates on the Si nucleus. We may note that in this case* D_{11} *does not vanish in the asymptotic limit. Had the origin of electronic coordinates been taken on the He nucleus,* D_{11} *would vanish at the asymptotic limit but then* D_{22} *would be non zero.*

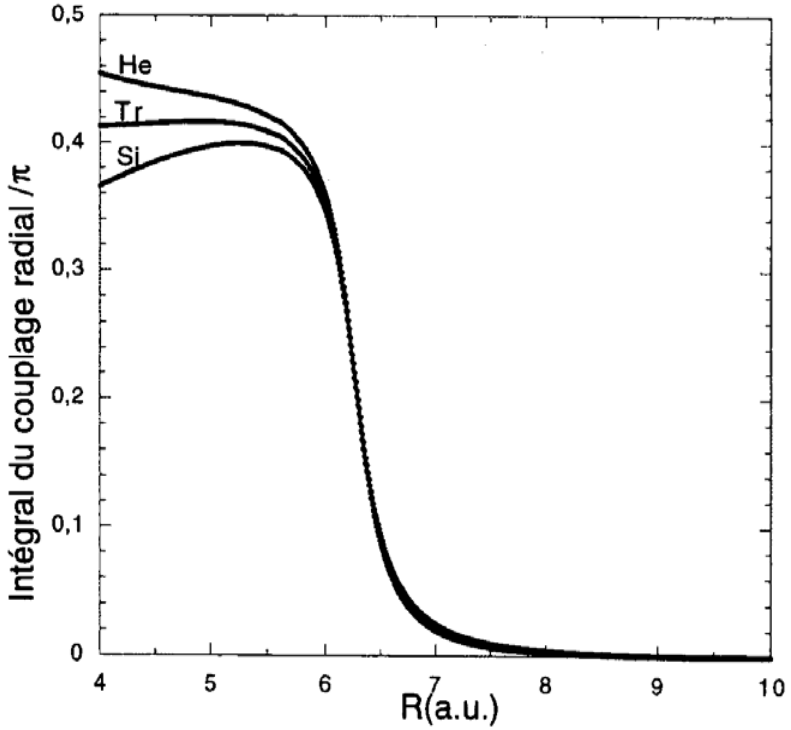

Figure 8. Diagram to illustrate how w(R) varies as a function of R for the radial coupling between the two $^2\Sigma$ states of $SiHe^{3+}$ *in the vicinity of their avoided crossing. The upper and lower curves refer to calculations where the radial derivative is taken with respect to the* He *nucleus and to the* Si *nucleus. The intermediate curve is a modified coupling to take account of translation effects (see section 6). Considerable deviation from π/2 is observed at short distances.*