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DERIVATIVE COUPLING ELEMENTS IN ELECTRONICALLY ADIABATIC REPRESENTATIONS AND THEIR USE IN SCATTERING CALCULATIONS

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INTRODUCTION

The Born-Oppenheimer electronically adiabatic basis provides the most convenient representation for obtaining molecular-structure and potential-energy-surface information for systems of chemical interest. In this representation the electronic Hamiltonian is diagonal, and the adiabatic energies may be defined and calculated accurately by the variational principle. For systems in which the adiabatic states are well separated in energy, the nuclear motion at chemical energies can be treated adequately using a single adiabatic potential energy surface. For systems in which the coupling of electronic states is important, the coupling can be included consistently in this

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representation through matrix elements of the nuclear-motion derivative operators.

A diabatic representation is any representation in which the electronic Hamiltonian is not diagonal. As compared to adiabatic representations, suitably chosen diabatic basis sets may have the advantage of providing representations that are more uncoupled for high-energy collisions and narrowly avoided adiabatic curve crossings. These representations can also be used to define potential energy surfaces which are more smoothly varying functions of internuclear coordinates than the adiabatic surfaces are. A further advantage of diabatic representations is that they may be chosen so that the coupling of electronic states is dominated by potential coupling terms rather than nuclear-motion derivative terms.

Diabatic bases often provide the most convenient representation for performing scattering calculations in which the electronic states are coupled; however, as already mentioned, adiabatic bases are the most convenient for obtaining accurate potential energy surfaces. A review and discussion of selected aspects of the coupling of electronically adiabatic and diabatic states has been presented elsewhere.¹ In this article we examine one of the fundamental problems of obtaining accurate derivative coupling terms in adiabatic representations—the fact that the derivative coupling terms depend upon the location of the origin of the electronic coordinates.² A further complication is that for an arbitrary origin of the electronic coordinates the derivative coupling terms do not in general vanish at large internuclear separations. Some methods for dealing with this long-range coupling are discussed in this article.

To illustrate these considerations we consider atom-atom collisions; however, the fundamental problems are general ones, and similar considerations are required for atom-molecule scattering. The particular examples chosen for the present study are collisions of ³⁹K with protium (¹H) and with a fictitious heavy isotope of hydrogen (³⁹H). For these examples the derivative coupling terms are examined, and scattering calculations for several different choices of electronic origin are compared.

COUPLED-CHANNEL EQUATIONS

General Theory

A fundamental problem in defining the derivative coupling terms is their dependence upon the choice of origin for the electronic coordinates.² For collisions at energies of chemical interest of systems with narrowly avoided adiabatic curve crossings, the origin

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dependence of the coupling terms is expected to have only a small effect on the calculated cross sections. However, for systems with weak coupling or nonlocalized interactions or for high collision energies, the origin dependence of the derivative coupling terms is more important. Although the choice of origin has been discussed in the context of high-energy ion-atom collisions,³ the effects of the origin dependence of the derivative coupling terms have not been tested for collisions at chemical energies. In this section we write the quantum mechanical coupled-channel equations for a general choice of origin for the electronic degrees of freedom, and we discuss some methods of correctly imposing asymptotic boundary conditions on the solutions of these equations. Further discussion of these topics is presented elsewhere.¹

We consider a system of two nuclei A and B of masses m_A and m_B respectively and N electrons of mass m_e , with the center of mass at rest. Spin is neglected, the charges of A and B are assumed different, and ionization processes are excluded. We define the relative internuclear coordinate R' in a space-fixed system as the vector from nucleus A to nucleus B. (We denote coordinates in space-fixed systems with primes, and we will denote the magnitude of a vector $\mathbf{x}'$ by x' .) The vector from nucleus A to electron i is denoted $\mathbf{x}_{Ai}'$. The origin for electron i can be redefined to any point along the internuclear axis by the definition

$$\mathbf{x}_{ni}' = \mathbf{x}_{Ai}' - n_i \mathbf{R}' \quad (1)$$

where n_i is an arbitrary number. For $n_i = 0$ the origin of electron i is at nucleus A, whereas for $n_i = 1$ the origin is at nucleus B. For the set of coordinates $R', \{r_{ni}'\}_{i=1}^N$, which we will denote by the shorthand $(R', \mathbf{x}_{ni}')$, the total Hamiltonian for the electronic and nuclear degrees of freedom is

$$H = H_e - \frac{\hbar^2}{2\mu_{AB}} \nabla_{R'}^2 - \sum_{i=1}^N \left(\frac{\hbar^2}{2m_A} - \frac{n_i}{m_B} \right) \nabla_{\mathbf{x}_{ni}'}^2 + \sum_{i,j=1}^N \frac{\hbar^2}{2} \left(\frac{1-2n_i+n_j}{m_A} + \frac{n_i n_j}{m_B} \right) \nabla_{\mathbf{x}_{ni}'} \cdot \nabla_{\mathbf{x}_{nj}'} \quad (2)$$

where the electronic Hamiltonian is defined as

$$H_e = -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_{\mathbf{x}_{ni}'}^2 + V(\mathbf{x}_{ni}', R') \quad (3)$$

and

$$\mu_{AB} = \frac{m_A m_B}{m_A + m_B} \quad (4)$$

R' is the same as R , however $\nabla_{\mathbf{x}_{ni}'}$ denotes that $\{\mathbf{x}_{ni}'\}_{i=1}^N$ are fixed during the variation of R' .

The Born-Oppenheimer electronically adiabatic space-fixed basis functions are the solutions of

$$H_e \phi_{\eta\alpha}^{Sa}(\mathbf{x}_{ni}', R') = \epsilon_{\alpha}^a(R) \phi_{\eta\alpha}^{Sa}(\mathbf{x}_{ni}', R') \quad (5)$$

where η denotes the collection of n_i values, α is a collective index for the electronic quantum numbers, and $\epsilon_{\alpha}^a(R)$ is the adiabatic energy which depends only upon the magnitude of R ($\equiv R'$) of R' .

The coupled-channel scattering equations can be obtained by expanding the total wavefunction ψ_{α_0} in the Born-Oppenheimer basis functions

$$\psi_{\alpha_0} = (1/R') \sum_{\alpha} \phi_{\eta\alpha}^{Sa}(\mathbf{x}_{ni}', R') g_{\eta\alpha\alpha_0}^a(R') \quad (6)$$

and substituting this expansion into the Schrodinger equation where the Hamiltonian is given by equation (2). The index α_0 indicates the initial quantum state of the system. The coupled equations are then given by

$$\begin{aligned} & \left[-\frac{\hbar^2}{2\mu_{AB}} \nabla_{R'}^2 + \epsilon_{\alpha}^a(R) - E \right] g_{\eta\alpha\alpha_0}^a(R') = \sum_{\beta} \left[\frac{\hbar^2}{2\mu_{AB}} \langle \phi_{\eta\alpha}^{Sa} | \nabla_{R'}^2 | \phi_{\eta\beta}^{Sa} \rangle_{\mathbf{x}_{ni}'} \right. \\ & + 2 \langle \phi_{\eta\alpha}^{Sa} | \nabla_{\mathbf{x}_{ni}'} \cdot \nabla_{\mathbf{x}_{n\beta}'} | \phi_{\eta\beta}^{Sa} \rangle_{\mathbf{x}_{ni}'} + \hbar^2 \sum_{i=1}^N \left(\frac{1-n_i}{m_A} - \frac{n_i}{m_B} \right) \\ & \times \langle \phi_{\eta\alpha}^{Sa} | \nabla_{\mathbf{x}_{ni}'} \cdot \nabla_{\mathbf{x}_{n\beta}'} | \phi_{\eta\beta}^{Sa} \rangle_{\mathbf{x}_{ni}'} + \langle \phi_{\eta\alpha}^{Sa} | \nabla_{\mathbf{x}_{ni}'} \cdot \nabla_{\mathbf{x}_{n\beta}'} | \phi_{\eta\beta}^{Sa} \rangle_{\mathbf{x}_{ni}'} \\ & + \frac{\hbar^2}{2} \sum_{i,j=1}^N \left(\frac{1-2n_i-n_j}{m_A} + \frac{n_i n_j}{m_B} \right) \langle \phi_{\eta\alpha}^{Sa} | \nabla_{\mathbf{x}_{ni}'} \cdot \nabla_{\mathbf{x}_{nj}'} | \phi_{\eta\beta}^{Sa} \rangle_{\mathbf{x}_{ni}'} \\ & \left. \times g_{\eta\beta\alpha_0}^a(R') \right] \quad (7) \end{aligned}$$

where the subscript on a matrix element denotes the variables integrated over. Equation (7) is general for any choice of origins for the electronic degrees of freedom. The terms on the right hand side of equation (7) are the nonadiabatic coupling terms; and we are free to use any choices of origin for these terms. A convenient choice is that which eliminates the cross terms between the nuclear and electronic kinetic energy. This choice is the center of mass of the nuclei (CMN) and is specified by setting all n_i to the value

$$C = \frac{m_B}{m_A + m_B} \quad (8)$$

The first-derivative coupling term for any arbitrary choice of origin is related to the coupling term for the origin at the CMN by

$$\begin{aligned} \langle \phi_{Ca}^a | \nabla_{R_i} | \phi_{Cb}^a \rangle_{\chi_{ni}} &= \langle \phi_{na}^a | \nabla_{R_i} | \phi_{nb}^a \rangle_{\chi_{ni}} + \sum_{i=1}^N (C - n_i) \\ &\times \langle \phi_{na}^a | \nabla_{R_i} | \phi_{nb}^a \rangle_{\chi_{ni}} \end{aligned} \quad (9)$$

We emphasize that the origin used in defining the first-derivative coupling matrices should be consistent with the origin used for the other terms in the coupled equations.

The coupled equations (7) are useful for displaying how the choice of electronic origin affects the various coupling terms; however, this form of the equations is impractical for computations. Computationally convenient scattering equations can be obtained using a body-fixed coordinate system (R, χ) in which the z-axis lies along the internuclear axis. (Body-fixed coordinates are denoted without primes.) The total scattering wavefunction is expanded in coefficients of the irreducible representations of the rotation group and the Born-Oppenheimer basis functions.⁴ The coefficients of this expansion are the radial wavefunctions for relative motion of the nuclei. The details of this procedure as well as the dependence of the body-fixed coupled-channel radial equations upon electronic origin are given elsewhere.¹ We will present here approximate equations in which the mass polarization term [i.e., the cross terms in the electronic kinetic energy, the last term of equation (7)] and the angular coupling terms are neglected. The effect of neglecting the angular coupling terms for collisions at thermal energies requires further study; in the present article we are not interested in obtaining totally converged cross sections for a specific problem but instead are interested in examining the importance of the origin dependence of the derivative coupling elements in physically realistic model systems. By neglecting angular coupling we neglect coupling ℓ states

to ℓ states in atom-atom collisions; then the body-fixed radial equations for ℓ states, with the electronic origin at the CMN, are given by

$$\begin{aligned} \left[-\frac{\hbar^2}{2\mu_{AB}} \frac{d^2}{dR^2} + \frac{\hbar^2 \ell(\ell+1)}{2\mu_{AB} R^2} - E \right] \chi_{Ca\alpha_0}^a(R) + \sum_{\beta} [H_{\alpha\beta}^a(R) + 2F_{Ca\beta}^a(R)] \frac{d}{dR} \\ + C_{Ca\beta}^a(R) \chi_{Cb\alpha_0}^a(R) = 0 \end{aligned} \quad (10)$$

where

$$H_{\alpha\beta}^a(R) = \langle \phi_{Ca}^a | H_e | \phi_{Cb}^a \rangle_{\chi} = \epsilon_{\alpha}^a(R) \delta_{\alpha\beta} \quad (11)$$

$$F_{Ca\beta}^a(R) = -\frac{\hbar^2}{2\mu_{AB}} \langle \phi_{Ca}^a | \left(\frac{\partial}{\partial R} \right)_{\chi} | \phi_{Cb}^a \rangle_{\chi} \quad (12)$$

$$C_{Ca\beta}^a(R) = -\frac{\hbar^2}{2\mu_{AB}} \langle \phi_{Ca}^a | \left(\frac{\partial^2}{\partial R^2} \right)_{\chi} | \phi_{Cb}^a \rangle_{\chi} \quad (13)$$

and χ is χ_{Ca}^a . We have denoted the body-fixed electronic wavefunctions as $\phi_{Ca}^a(\chi, R)$, a special case of $\phi_{na}^a(\chi_{ni}, R)$.

The simple form of equation (10) is a result of taking the origin of the electronic degrees of freedom to be the center of mass of the nuclei; this removes the nuclear-electronic derivative cross terms. The analog of equations (10) for a different choice of electronic origin can be obtained by re-introducing the inconvenient nuclear-electronic derivative cross terms and transforming the nuclear first- and second-derivative coupling terms to the new origin. For example, for a new electronic origin somewhere else on the internuclear line, the required relation for the nuclear first-derivative term is

$$\begin{aligned} \langle \phi_{Ca}^a | \left(\frac{\partial}{\partial R} \right)_{\chi} | \phi_{Cb}^a \rangle_{\chi} &= \langle \phi_{na}^a | \left(\frac{\partial}{\partial R} \right)_{\chi_{ni}} | \phi_{nb}^a \rangle_{\chi_{ni}} \\ &+ \sum_i (C - n_i) \langle \phi_{na}^a | \left(\frac{\partial}{\partial z_{ni}} \right) | \phi_{nb}^a \rangle_{\chi_{ni}} \end{aligned} \quad (14)$$

where z_{ni} is the internuclear-axis-component of χ_{ni} .

In this article, rather than actually calculating the matrix elements $C_{\alpha\beta}^a(R)$ from the electronic wavefunctions, we assume they

are given by the relation

$$G_{\eta}^a(R) = \frac{dF_{\eta}^a}{dR} - \frac{2\mu_{AB}}{\hbar^2} [F_{\eta}^a(R)]^2 \quad (15)$$

This equation holds rigorously for an infinite basis set, but we apply it even though our matrices are only of order 3. Tests of this assumption have been made for the KH system;⁵ they show that it makes a negligible difference in the transition probabilities in low-energy collisions.

Infinite-Range Coupling

An important aspect of the coupled equations (10) is that the coupling does not necessarily go to zero for large internuclear separations. For example, consider the collision of two atoms in which all electronic excitations and deexcitations occur on one nucleus A. For the electronic origin located at A the first-derivative coupling term is

$$F_{\alpha\beta}^a(R) = -\frac{\hbar^2}{2\mu_{AB}} \lim_{\delta \rightarrow 0} \frac{1}{\delta} \langle \phi_{\alpha}^a(x_0, R) | \phi_{\beta}^a(x_0, R + \delta) \rangle_{x_0} - \delta_{\alpha\beta} \quad (16)$$

and this vanishes at large R by the orthonormality of the atomic orbitals on A. For the electronic origin at the CMN, however, we get

$$F_{\alpha\beta}^a(R) = -\frac{\hbar^2}{2\mu_{AB}} \lim_{\delta \rightarrow 0} \frac{1}{\delta} \langle \phi_{\alpha}^a(x, R) | \phi_{\beta}^a(x, R + \delta) \rangle_{x_0} - \delta_{\alpha\beta} \quad (17)$$

In (16) the nuclear displacement is carried out by moving B with A fixed, but in (17) the displacement must be carried out with the CMN fixed. Thus, at large R, the matrix element on the right side of (16) tends to an overlap of displaced atomic orbitals, and $F_{\alpha\beta}^a$ does not tend to $\delta_{\alpha\beta}$.

The infinite-range coupling of electronic states presents a problem in applying asymptotic boundary conditions to the scattering wavefunction. Bates and McCarroll⁶ have observed that imposing the usual scattering boundary conditions in the (R, x) coordinates using the usual adiabatic basis functions $\phi_{\alpha}^a(x, R)$ neglects the asymptotic motion of the electrons with respect to the CMN. Therefore they proposed including electron translation factors in the adiabatic basis to account for this asymptotic behavior. For some transitions, the infinite-range coupling can be eliminated by applying the asymptotic

boundary conditions in a coordinate system in which electronic origins are at a nucleus and the internuclear distance is replaced by the distance between the centers of mass of the two separated atoms.^{1,7,8} Unfortunately a coordinate system involving the atomic centers of mass makes the electronic part of the problem so much more difficult that it is apparently out of the question as a general computational technique. A more practical, but still rigorously correct way of treating the infinite-range coupling problem is by a diagonalization method.⁹ In this method the second order coupled equations are transformed into a set of equivalent first-order equations that can be diagonalized.

In this article we examine less rigorous, but easier ways to eliminate the infinite-range coupling. In the first method, suggested by Chen et al.,¹⁰ we use equations (10) but we replace $F_{\alpha\beta}^a(R)$ by $F_{\alpha\beta}^a(R) - F_{\alpha\beta}^a(\infty)$. Although Chen et al.¹⁰ tried to justify this by a semiclassical analysis, the method has been criticized by Thorson and coworkers.¹¹ Notice that since we always assume (15) for $G_{\eta}^a(R)$, it will vanish asymptotically if $F_{\eta}^a(R)$ vanishes.

In the second method, we retain the convenient form of equation (10), with no nuclear-electronic derivative cross terms, but we replace $F_{\alpha\beta}^a(R)$ by $F_{\alpha\beta}^a(R)$ and $G_{\eta}^a(R)$ by values calculated using $F_{\eta}^a(R)$ and (15). $F_{\eta}^a(R)$ is computed with the electronic origin on K. In this article we only consider excitations and de-excitations of K by ground-state H; thus an electronic origin on K makes the nuclear derivative coupling terms vanish at infinity. Notice the nature of the inconsistency involved in this method, namely it corresponds to using the CMN as electronic origin for the electronic-nuclear derivative cross terms but using the K as origin for the nuclear derivative coupling elements. This procedure is essentially the same as the one adopted by some workers for the semiclassical coupled equations for high-energy, ion-atom scattering problems,³ but for the quantal case it can only be justified on an ad hoc basis.

The third method is also an analog for the quantal coupled-channels equations of a method proposed for the semiclassical equations for high-energy scattering. This method, proposed by one of the authors and Goddard (MG),^{12,13} is applicable to systems with only one active electron. In it, η becomes a function of α , β , and R , and $F_{\alpha\beta}^a(R)$ is replaced by $F_{\eta\alpha\beta}^a(R)$ [$\equiv F_{\alpha\beta}^a(R)$], again without re-introducing the electronic-nuclear derivative cross terms. $F_{\eta\alpha\beta}^a(R)$ is assumed to be given by (15) using $F_{\eta}^a(R)$. Each $\eta_{\alpha\beta}(R)$ is chosen to make $F_{\eta\alpha\beta}^a(R)$ vanish at $R=\infty$, even for systems in which electronic excitation can occur at both nuclei and for systems in which charge exchange channels are open. Rather than specify $\eta_{\alpha\beta}(R)$, it is more convenient to specify the position $z_{\alpha\beta}(R)$ of the new electronic origin by its value in the CMN coordinate system. In this coordinate system, the MG origin is

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$$z_{\alpha\beta}(R) = \frac{\langle \text{abs}[\phi_{Ca}^a(\xi, R)] | z | \text{abs}[\phi_{Cb}^a(\xi, R)] \rangle_{\xi}}{\langle \text{abs}[\phi_{Ca}^a(\xi, R)] | \text{abs}[\phi_{Cb}^a(\xi, R)] \rangle_{\xi}} \quad (18)$$

where $\text{abs}(f)$ denotes the absolute value of f . Because of the complicated dependence of this electronic origin upon the internuclear coordinate it would be difficult to derive the appropriate coupled equations consistent with this choice of origin.

CALCULATIONS

The adiabatic potential curves for the $1\Sigma^+$ states of KH were calculated by a one-electron model^{14,15} for alkali hydrides using effective core potentials to represent K^+ and H. Further details of these calculations are presented elsewhere.⁵ In review, the adiabatic energies are obtained by adding one-electron eigenvalues calculated with effective core potentials representing K^+ and H, to the KH^+ core energy. The KH^+ core energy is approximated by a calculation of KH^+ employing only a single H 1s basis function. This is called method 2H in previous work.^{5,15} The calculated adiabatic potential curves $\epsilon_{\eta}^a(R)$ are plotted in Fig. 1 for the three lowest $1\Sigma^+$ curves of KH. Also shown are the RKR curves^{16,17} for the X and A states.

The first-derivative coupling matrices $F_{\alpha\beta}^a(R)$ were calculated from the one-electron wavefunctions for two choices of electronic origin by using equations (16) and (17) with $\delta = 0.001 a_0$. For electronic origins on the internuclear line the first-derivative coupling matrix depends linearly on the choice of origin. Because of this linear relationship the first-derivative coupling matrix element $F_{\alpha\beta}^a(R)$ for any other choice of origin could be and was obtained as a linear combination of $F_{\alpha\beta}^a(R)$ and $F_{\alpha\beta}^a(R)$. For discussion purposes we define the mass-independent matrix

$$\tilde{f}_{\eta}^a(R) = -(2\mu/\hbar^2) F_{\eta}^a(R) \quad (19)$$

The derivative coupling terms $\tilde{f}_{\alpha\beta}^a(R)$ are plotted in Figs. 2-4 for four choices of origin: at the K, at the H, at the CMN for $^{39}K^1H$, and at the MG origin. Recall that the MG origin depends on α , β , and R . The CMN for $^{39}K^{39}H$ is the same as the geometrical center of the nuclei (GCN), i.e., the bond midpoint. Although the coupling matrices are not shown for the GCN origin, their shape is easily visualized since they are exactly halfway between the results shown for the origins at K and at H.

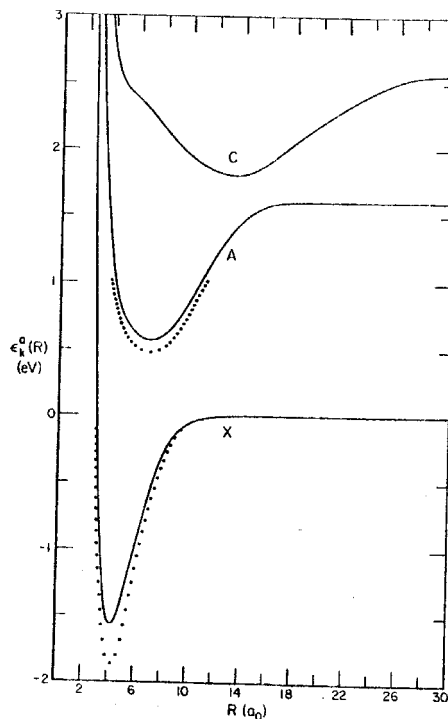


Fig. 1. Adiabatic potential energy curves as a function of internuclear distance for the three lowest $1\Sigma^+$ states of KH. The curves are the results of an ab initio pseudopotential calculation as obtained by method 2H. The points are spectroscopic RKR values for the X and A potential curves.

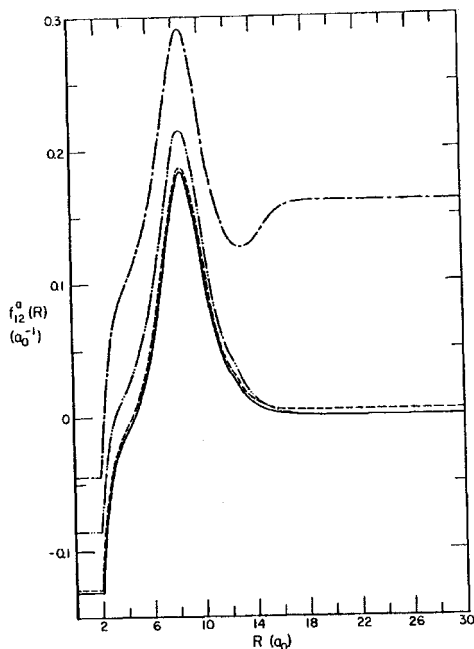


Fig. 2. First-derivative coupling term between the X and A state of KH as a function of internuclear distance. The four curves are for four different choices of the origin for the electronic coordinate. The solid curve is for the electronic origin at the K^+ core, the dashed curve is for the electronic origin at the center of mass of the K^+ core and 1H atom, the long-short dashed curve is for the electronic origin at the 1H atom, and the dash-dotted curve is for the Mulliken-Goddard prescription for the electronic origin.

Figure 2 shows the coupling $f_{12}^0(R)$ between the X and A states. Figures 3 and 4 are similar plots for the X-C coupling and A-C coupling, respectively. First note the large variation in $f_{12}^0(R)$ obtained by shifting the origin from K to H. Because the CMN for $^{39}K^1H$ is very near K the $f_{12}^0(R)$ curves for the origin at this CMN are very near to those with origin at K. At large R the coupling for the origin at either CMN does not vanish for the X-A and A-C coupling. The coupling terms with the MG electronic origins are qualitatively different from those with origins at K or at either CMN. When one or both of the interacting states has ionic character, the value of $z_{0g}(R)$ is shifted more towards the H core than the CMN for $^{39}K^1H$. This occurs for the X-A coupling between 4 and 12 a_0 and in this region $f_{12}^0(R)$ is intermediate to the results with the origin at K and those with the origin at H, but it is closer to the results for the origin at H than those for the origin at the $^{39}K^1H$ CMN. This same qualitative behavior is also seen for the A-C coupling between 8 and 10 a_0 .

Figures 2-4 illustrate an important general property of the first-derivative coupling matrices. Notice from (14) that the difference between $f_{ij}^0(R)$ for two choices of origin is proportional to the electric dipole transition matrix. Thus, in the large-R limit, the different origins lead to the same results for the X-C coupling

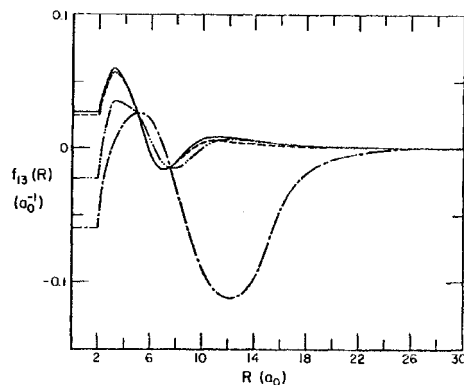


Fig. 3. Same as Fig. 2 except for coupling between the X and C states of KH as a function of internuclear distance.

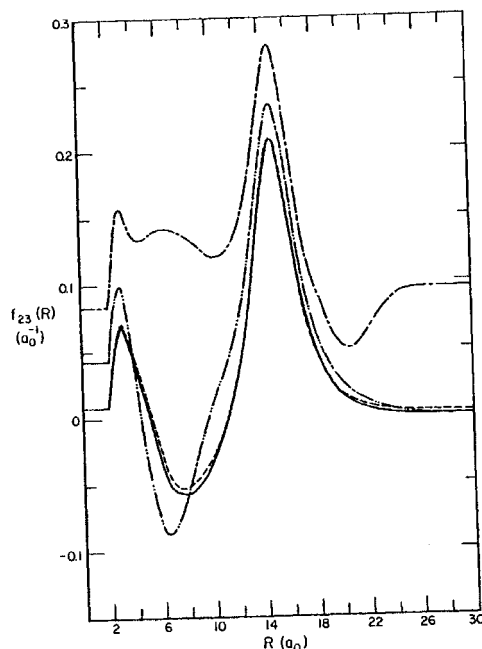


Fig. 4. Same as Fig. 2 except for coupling between A and C states of KH as a function of internuclear distance.

because the 4^2S - 5^2S transition is forbidden, but the origin choice does matter for the X-A and A-C couplings because the A state dissociates to the 4^2P state which is connected to both 4^2S and 5^2S by the electric dipole operator.

It is interesting to examine how quantum scattering calculations of electronic transition probabilities are altered by changes in the electronic origin of the derivative coupling terms. If the calculations were done correctly including a complete set of electronic states and all kinds of coupling terms with a consistent choice of electronic origin, then the results would be independent of the choice of electronic origin. We wish to examine the effect of using one set of radial equations, namely equations (10)-(13), but with several different choices for the derivative coupling terms as discussed above. We neglect angular coupling and the mass polarization term; however, the model problem studied here still allows a realistic assessment of the effect of using coupling terms with arbitrary choice of electronic origin upon the calculation of transition probabilities. All the derivative coupling matrices we use vanish asymptotically; thus the boundary conditions can be applied by standard methods.

The scattering equations were solved using a R-matrix propagation method described in detail elsewhere.⁵ In all cases we use a basis of the three lowest electronically adiabatic $1F^+$ states: state 1 is the X state which dissociates to $K(4^2S)$, state 2 is the A state which dissociates to $K(4^2P)$, and state 3 is the C state which dissociates to $K(5^2S)$. The excitation energies of the 4^2P and 5^2S states are 1.61 and 2.55 eV, respectively. We neglect spin-orbit coupling.

We consider three processes:

$$K(4^2S) + H(1^2S) \rightarrow K(4^2P) + H(1^2S) \quad (1+2)$$

$$K(4^2S) + H(1^2S) \rightarrow K(5^2S) + H(1^2S) \quad (1+3)$$

and

$$K(4^2P) + H(1^2S) \rightarrow K(5^2S) + H(1^2S) \quad (2+3)$$

RESULTS

$39K^1H$

We calculated the cross sections for two total energies, 1.6327 eV and 2.7212 eV. At the lower energy, two channels are open, and at the higher energy, three. Since 2/3 of the collisions of $K(4^2P)$ with $H(1^2S)$ occur in the Π manifold, and only 1/3 in the Σ manifold, we multiplied σ_{2+3} by 1/3. With this factor the calculated

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Table 1. Cross sections (a_0^2) for excitation processes in $^{39}\text{K} + ^1\text{H}$ collisions

Electronic origin	E = 1.6327 eV		E = 2.7212 eV	
	$\sigma_{1 \rightarrow 2}$	$\sigma_{1 \rightarrow 2}$	$\sigma_{1 \rightarrow 3}$	$\sigma_{2 \rightarrow 3}$
at K	1.60(-5) ^a	9.24(-4)	1.73(-6)	4.06(-1)
at CMN	1.59(-5)	8.88(-4)	1.73(-6)	3.91(-1)
Melius-Goddard	1.22(-5)	8.71(-4)	1.70(-6)	4.04(-1)

^aNumbers in parentheses are powers of ten.

cross sections satisfy detailed balance including the threefold degeneracy of P states but neglecting spin-orbit coupling. The factors of 1/4, because only 1/4 of all collisions occur in the singlet manifold, are not included. Thus, as in reference 5, the results are cross sections for singlet collisions only. The results are given in Table 1.

As expected for $^{39}\text{K} + ^1\text{H}$, where the CMN lies so close to K, the cross sections for these two origins are very similar. The largest difference for the four cases in Table 1 is 4%. In contrast the physically motivated MG procedure leads to a much larger difference in one case; the difference is 30-31%. It is very interesting that alternative methods of coping with the formal problem of infinite-range nonadiabatic coupling terms can lead to such a difference even for the integral cross section of this reasonably simple case. We note that the difference between the results calculated with different origins is greatest for the case where the initial and final states are connected by the greatest optical oscillator strength. In general one expects¹⁹ the effects to be largest in such cases for the reasons already discussed in connection with Figs. 2-4.

Instead of comparing the cross sections we could have compared the s-wave transition probabilities. (For the probabilities we do not include the 1/3 factor for multiple potential energy curves.) This comparison is shown in Table 2. The differences are larger than those in Table 1. This could be expected since the inelastic transition probabilities are oscillatory functions of orbital angular momentum l for this example. Thus there is a certain amount of cancellation of errors in the integral cross sections. One would expect less cancellation in the differential cross sections.

Table 2. Inelastic s-wave transition probabilities for excitation processes in $^{39}\text{K} + ^1\text{H}$ collisions

Electronic origin	E = 1.6327 eV		E = 2.7212 eV	
	$P_{1 \rightarrow 2}$	$P_{1 \rightarrow 2}$	$P_{1 \rightarrow 3}$	$P_{2 \rightarrow 3}$
at K	1.56(-6)	1.84(-7)	5.70(-10)	2.15(-3)
at CMN	1.57(-6)	2.22(-7)	4.06(-10)	2.17(-3)
Melius-Goddard	1.24(-6)	6.65(-7)	2.05(-9)	2.07(-3)

$^{39}\text{K} + ^3\text{H}$

In many systems, e.g., collisions of K with a particle heavier than itself in the absence of narrowly avoided curve crossings, we would expect a larger difference between the results calculated with origin at one of the nuclei and those calculated with the origin at the CMN. To illustrate this effect of the mass of the collision partner, we calculated the s-wave transition probabilities for the same potential curves but with the masses of both particles taken as 38.964 amu. The $\sigma_{00}^s(R)$ values were also the same for the cases of origin at K or MG origin, but for the CMN origin, we must now use the results of origin at the GCN. The results we obtained for the s-wave transition probability $P_{1 \rightarrow 2}$ are shown as a function of energy in Fig. 5.

For all three origins, the transition probability oscillates as a function of energy. In general, the oscillations of all three cases are reasonably well in phase (the most significant exceptions being for the energy range 2.0-2.3 eV). The magnitudes of the transition probabilities at the maxima of the oscillations are in worse agreement than the phases of the oscillations. In general the results for the origin at K and those for the MG origin agree better with each other than either agrees with the GCN origin. A more detailed comparison of these results for energies near the maxima in the oscillatory curve is given in Table 3. The results for the K and MG choices agree within a factor of 2 or better for all cases in the table, but those for the K and GCN choices differ by more than a factor of 2 in half the cases. Overall the K and GCN results differ by from 6% to a factor of 3.8 in thirteen of the cases, and in one case the difference is a factor of 190. Of course the percentage deviations may be much larger if we make the comparisons near

E_{rel} (eV)

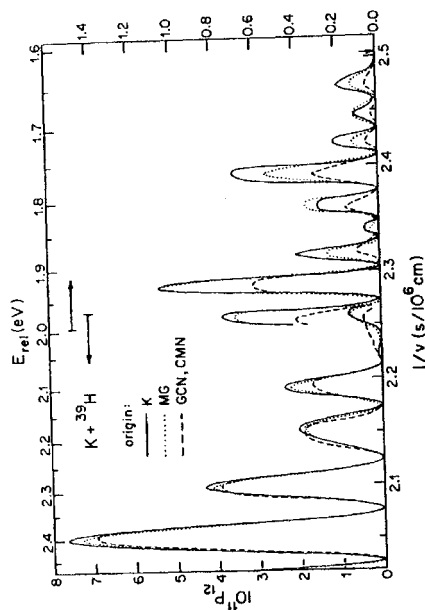


Fig. 5. S-wave transition probabilities for the $4^2S + 4^2P$ excitation in $^{39}\text{K} + ^{39}\text{H}$ collisions as a function of inverse relative velocity (bottom scale) and relative kinetic energy (top scale). The solid curve is for electronic origin at K; the dashed curve is for electronic origin at the center of mass of the nuclei, which in this case is the same as the geometrical center of the nuclei, and the dotted curve is for the Melius-Goddard prescription for the electronic origin.

Table 3. Ratios of s-wave inelastic transition probabilities for excitations from ground to first excited state in $^{39}\text{K} + ^{39}\text{H}$ collisions using different electronic origins

Energy (eV)	$P_{1+2}(\text{MG}^a)/P_{1+2}(\text{K}^b)$	$P_{1+2}(\text{GCN}^c)/P_{1+2}(\text{K}^b)$
1.6490	0.64	0.27
1.6898	1.21	0.28
1.7225	0.58	0.26
1.7633	0.73	0.42
1.8123	1.16	0.56
1.8449	0.59	0.0053
1.8776	0.66	0.31
1.9266	1.00	0.57
1.9756	0.92	0.43
2.0409	1.16	1.77
2.1062	0.95	0.73
2.1769	0.94	0.92
2.2994	0.98	0.94
2.3946	0.95	0.93

^a Melius-Goddard electronic origin.

^b Electronic origin at K nucleus.

^c Electronic origin at geometric center of the nuclei.

the minima of the oscillatory curve. Returning again to the energies near the maxima, the typical difference of the K and MG results is 25% but the typical difference of the K and GCN results is a factor of 2-3. These differences are especially noteworthy because it has been stated in the literature¹⁹ that the infinite-range coupling due to the expansion in Born-Oppenheimer functions not satisfying the correct boundary conditions does not cause significant difficulties in low-energy collisions.* More recently a contrary opinion has

*Consistent with this widely held opinion, the infinite-range coupling effect has also been neglected in low-energy atom-molecule collision studies.²⁰

been stated in the literature,²¹ but to our knowledge the present calculations are the first numerical test of this effect for low-energy collisions.

SUMMARY

We have performed numerical comparisons of three different ways of treating the first-derivative coupling terms in the quantum mechanical coupled-channel equations for atom-atom scattering in an adiabatic representation. We have shown that different ways of handling the formal problems with the derivative coupling operators can lead to errors of 25% to a factor of 2 or 3 in computed transition probabilities and inelastic cross sections. We even found a case where the predictions of two of the methods differ by a factor of 190 even for an energy near a maximum in the oscillatory curve of transition probability vs. energy.

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