Generation of Diatomic Diabatic States by a General Multi-State Rotation

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We present a general multi-state orthogonal transformation program that generates a set of diatomic electronic diabatic states from a set of vibronically interacting adiabatic states of the same symmetry.

Introduction

We are concerned with the problem of constructing a general program that generates a group of diatomic diabatic states by rotating a group of vibronically coupled adiabatic states of the same symmetry using explicitely their coupling strengths. For diatomic molecules, a strictly diabatic representation is formally defined as the one that diagonalizes the radial part of the generalized nuclear momentum matrix, or as the one for which the nuclear momentum coupling matrix is the null matrix [1, 2]. Diabatic states are non-stationary and are very important whenever the Born-Oppenheimer approximation brakes down.

In practice only approximate diabatic states having a small but non-zero interaction can usually be generated, and the problem is the accurate calculation of the rotation matrix. Numerous such calculations have been reported in the literature for two-state problems where the rotation matrix is well known.

Multi-state rotations, however, are also important for certain kinds of problems where more than two interacting states are involved. A general method for multi-state rotations has been proposed [3] which requires the numerical solution of a matrix differential equation with non-constant coefficients. The numerical solution of this equation can be achieved by a propagation technique. To date, however, this technique has been applied only to model potentials or to special cases [4–7]. The purpose of this work is to present a program implementing the propagation technique in such a way that any number of diatomic adiabatic states can be rotated.

Theoretical Framework

Let $\boldsymbol{\phi}(\boldsymbol{r};R)$ be the column vector of the adiabatic electronic eigenfunctions of the diatom, and let $\boldsymbol{\chi}(R)$ be the column vector of the corresponding radial eigenfunctions. $\boldsymbol{r}$ is the vector of the electronic coordinates and R is the internuclear distance. For simplicity we have neglected the angular motion since we are concerned only with radial couplings. Then the total wavefunction is

$$\Psi(\boldsymbol{r},R)=\boldsymbol{\phi}^{\dagger}(\boldsymbol{r},R)\cdot\boldsymbol{\chi}(R), \tag{1}$$

The Schroedinger equation for the radial wavefunctions of the diatom in the adiabatic representation is given by the well known relation

$$\left(-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}R^2}\mathbb{I}-\mathbb{V}(R)+E\,\mathbb{I}\right. \tag{2a}$$
$$\left.+\frac{\hbar^2}{2\mu}\left[2\,\mathbb{A}(R)\frac{\mathrm{d}}{\mathrm{d}R}+\mathbb{Q}(R)\right]\right)\boldsymbol{\chi}(R)=\mathbb{0},$$

where $\mathbb{I}$ is the unit matrix, $\mathbb{V}$ the diagonal potential matrix corresponding to $\boldsymbol{\phi}$, E the total energy, and $\mathbb{A}$ and $\mathbb{Q}$ are the matrices of the vibronic (radial) coupling strengths. That is

$$A(R)_{ij}=\langle\phi_i|\,\mathrm{d}/\mathrm{d}R\,|\phi_j\rangle$$

and

$$Q(R)_{ij}=\langle\phi_i|\,\mathrm{d}^2/\mathrm{d}R^2\,|\phi_j\rangle.$$

It is well known that $\mathbb{A}$ is antisymmetric and that the following relation holds for a complete basis (although it is assumed correct for a finite basis as well):

$$\mathbb{Q}=\mathbb{A}\cdot\mathbb{A}+\mathrm{d}\mathbb{A}/\mathrm{d}R\,.$$

If the generalized momentum matrix

$$\mathbb{P}=\mathbb{A}+\mathbb{I}\,\mathrm{d}/\mathrm{d}R$$

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is introduced [1], (2a) may be written more concisely as

$$\{\mathbb{P}(R)\cdot\mathbb{P}(R)+\mathbb{U}(R)\}\,\boldsymbol{\chi}(R)=\mathbb{0}, \tag{2b}$$

where $\mathbb{U}(R)=2\,\mu\,[E\,\mathbb{I}-\mathbb{V}(R)]/\hbar^2$.

There are two practical ways of dealing with (2b). In the usual adiabatic representation $\mathbb{U}$ is diagonal while $\mathbb{P}$ is not. If the off-diagonal elements of $\mathbb{P}$ are small or irrelevant for the problem at hand, they may be neglected and the equations in (2b) can be decoupled in the usual way. However, if the off-diagonal elements are important, a rotation matrix may be introduced which makes $\mathbb{P}$ diagonal (or approximately diagonal) but generates a non-diagonal $\mathbb{U}$.

Let $\mathbb{C}(R)$ be such a rotation matrix. What one needs is as complete a separation between the electronic and nuclear functions as possible. Thus one may write

$$\boldsymbol{\phi}(\boldsymbol{r};R)=\mathbb{C}(R)\,\boldsymbol{\eta}(\boldsymbol{r};R_0), \tag{3a}$$

$$\boldsymbol{\chi}(R)\quad=\mathbb{C}(R)\,\boldsymbol{\zeta}(R), \tag{3b}$$

where $\boldsymbol{\eta}(\boldsymbol{r};R_0)$ is a new diabatic basis evaluated at a given internuclear distance R_0, and $\boldsymbol{\zeta}(R)$ is the new nuclear function containing all the R dependence of $\Psi(\boldsymbol{r};R)$. One must have the same total wavefunction in either representation; that is

$$\Psi(\boldsymbol{r};R)=\boldsymbol{\eta}^\dagger(\boldsymbol{r};R_0)\cdot\boldsymbol{\zeta}(R).$$

This means that one should expect that $\mathbb{C}^\dagger\cdot\mathbb{C}=\mathbb{I}$ (see below). By replacing (3) into 2b) one obtains

$$\{\mathbb{P}^\mathrm{d}(R)\cdot\mathbb{P}^\mathrm{d}(R)+\mathbb{W}(R)\}\,\boldsymbol{\zeta}(R)=\mathbb{0}, \tag{2c}$$

where

$$\mathbb{W}(R)=\mathbb{C}^\dagger(R)\cdot\mathbb{U}(R)\cdot\mathbb{C}(R) \tag{4}$$

and

$$\mathbb{P}^\mathrm{d}(R)=\mathbb{C}^\dagger(R)\cdot\mathbb{P}(R)\cdot\mathbb{C}(R)=\mathbb{A}^\mathrm{d}(R)+\mathbb{I}\,\mathrm{d}/\mathrm{d}R$$

with

$$\mathbb{A}^\mathrm{d}(R)=\mathbb{C}^\dagger(R)\cdot\mathbb{A}(R)\cdot\mathbb{C}(R)+\mathbb{C}^\dagger(R)\cdot[\mathrm{d}\mathbb{C}(R)/\mathrm{d}R].$$

One must now determine $\mathbb{C}$ by the requirement that $\mathbb{P}^\mathrm{d}$ be diagonal, or that $\mathbb{A}^\mathrm{d}$ be the null matrix. Thus, one must solve the matrix differential equation

$$\frac{\mathrm{d}}{\mathrm{d}R}\mathbb{C}(R)+\mathbb{A}(R)\cdot\mathbb{C}(R)=\mathbb{0}. \tag{5}$$

Once this is done, one may neglect the $\mathbb{A}^\mathrm{d}$ term in the expression for $\mathbb{P}^\mathrm{d}$ above, so that (2c) finally becomes

$$\mathbb{I}\frac{\mathrm{d}^2}{\mathrm{d}R^2}\boldsymbol{\zeta}(R)+\mathbb{W}(R)\,\boldsymbol{\zeta}(R)=\mathbb{0}. \tag{6}$$

We now turn to the solution of (5). Note that (5) assures the orthogonality of $\mathbb{C}$ (see Appendix 2 of [8]). Let $\boldsymbol{c}(R)$ represent a column vector of order n. Then the n linearly independent solutions of the equation

$$\mathrm{d}\boldsymbol{c}(R)/\mathrm{d}R=-\mathbb{A}(R)\cdot\boldsymbol{c}(R) \tag{7}$$

are the columns of the solution matrix $\mathbb{C}(R)$ of (5). If $\mathbb{A}$ were a constant matrix, the equations (7) could be decoupled by diagonalizing $\mathbb{A}$, the eigenvalues of which are either zero or pure imaginary on account of its antisymmetry (see Appendix A of [5]). Then a solution of (7) would be given by

$$\boldsymbol{c}(R)=\mathbb{T}\cdot\exp[-\mathbb{D}R]\cdot\mathbb{T}^\dagger\cdot\boldsymbol{c}(R_\mathrm{i})=\exp[-\mathbb{T}\cdot\mathbb{D}\cdot\mathbb{T}^\dagger R]\cdot\boldsymbol{c}(R_\mathrm{i})$$

or finally

$$\boldsymbol{c}(R)=\exp[-\mathbb{A}\cdot R]\cdot\boldsymbol{c}(R_\mathrm{i}),$$

where $\mathbb{T}$ would be the matrix diagonalizing $\mathbb{A}$, $\mathbb{D}$ would be the diagonal eigenvalue matrix, and $\boldsymbol{c}(R_\mathrm{i})$ would be the initial condition vector. By analogy, it may be assumed that, since $\mathbb{A}$ is R dependent, the solution of (7) is

$$\boldsymbol{c}(R)=\exp\left[-\int_{R_\mathrm{i}}^{R}\mathbb{A}(R')\,\mathrm{d}R'\right]\cdot\boldsymbol{c}(R_\mathrm{i}). \tag{8}$$

$\boldsymbol{c}(R_\mathrm{i})$ is again the initial condition vector, and R_i is an asymptotic point where all the elements of $\mathbb{A}$ are zero, i.e. where there is no interaction between the adiabatic states. However, by differentiating (8) it can immediately be seen that (8) is the solution of the equation $\mathrm{d}\boldsymbol{c}/\mathrm{d}t=-\boldsymbol{c}(R)\cdot\mathbb{A}(R)$ and not of (7). Unless the matrices $\mathbb{A}$ and $\int_{R_\mathrm{i}}^{R}\mathbb{A}(R')\,\mathrm{d}R'$ commute, which is not the case in general, (8) cannot be used as it is. An approximation is clearly needed.

A propagation type approximate solution based on (8) has been advanced [4], [7]. If the active range of R, where the coupling is non-zero, is divided into sectors, (8) may be used as the approximate solution of (7) within a single such sector, and the solutions can be propagated from one sector to the next under the boundary condition

$$\lim_{R\to\infty}\mathbb{C}(R)=\mathbb{I}. \tag{9}$$

Let us consider the sector from $R=R_{n-1}$ to $R=R_n$ with a width $\Delta R_n=R_{n-1}-R_n$. Within this sector the integral over $\mathbb{A}$ can be approximated by

$$\mathbb{A}_n=(1/\Delta R_n)\int_{R_{n-1}}^{R_n}\mathbb{A}(R)\,\mathrm{d}R,$$

and the transformation matrix may be written in analogy to (8) as

$$\mathbb{B}_n = \exp[-\Delta R_n \mathbb{A}_n].$$

$\mathbb{B}_n$ may be calculated by diagonalizing $\mathbb{A}_n$ as follows:

$$\mathbb{B}_n = \exp[-\Delta R_n(\mathbb{S}_n \cdot \mathbb{E}_n \cdot \mathbb{S}_n^\dagger)]$$

or

$$\mathbb{B}_n = \mathbb{S}_n \cdot \exp[-\Delta R_n \mathbb{E}_n] \cdot \mathbb{S}_n^\dagger, \tag{10}$$

where $\mathbb{S}_n$ is the eigenvector matrix diagonalizing $\mathbb{A}_n$, and $\mathbb{E}_n$ is the corresponding diagonal eigenvalue matrix. Then the rotation matrix at R_n is given by

$$\mathbb{C}(R_n) = \mathbb{B}_n \cdot \mathbb{B}_{n-1} \cdot \mathbb{B}_{n-2} \cdot \ldots \cdot \mathbb{B}_1 \cdot \mathbb{C}(R_\mathrm{i}),$$

where R_i is to be taken large enough so as to satisfy (9) to a good approximation. Then for all practical purposes $\mathbb{C}(R_\mathrm{i}) = \mathbb{I}$, so that finally

$$\mathbb{C}(R_n) = \mathbb{B}_n \cdot \mathbb{B}_{n-1} \cdot \mathbb{B}_{n-2} \cdot \ldots \cdot \mathbb{B}_1 \cdot \mathbb{I}. \tag{11}$$

The above results are of course well known (see [1] and [4]) but have been collected here for the convenience of the reader. In the present paper we are only concerned with a different numerical approach.

Methodology

The first step in solving (5) is to fit each potential of the interacting states as well as each A_{ij} matrix element. It is very convenient to use quadratic and cubic segmented spline fits. Because of their Lorenzian shape, however, the A_{ij} matrix elements are difficult to fit with a polynomial function. Thus, if the calculated points are not dense enough around the interaction region, a few fictitious points may have to be used to force the fit, just like the manual use of a spline.

The next step is to obtain a numerical representation of each $\mathbb{A}_n$ matrix on every sector within the range of R, where $A_{ij} \neq 0$. Let us denote the initial and final values of this range by R_i and R_f, respectively. Outside these limits A_{ij} is small, and it is set exactly equal to zero; that is, the wings are neglected. R_i and R_f may be different for each A_{ij}, but it is convenient to have common initial and final R's for all A_{ij}'s. Let R_0 and R_L be these common initial and final R's, respectively, so that $A_{ij}(R_0) = A_{ij}(R_\mathrm{L}) = 0$ for all interactions. Any convenient points outside the interval delimited by the outermost R_i and R_f may be chosen for R_0 and R_L, provided the potential fit is valid there. The integration is performed inwards choosing $R_\mathrm{i} > R_\mathrm{f}$ and $R_0 > R_\mathrm{L}$ and using (9) in the form $\mathbb{C}(R_0) = \mathbb{I}$. Since the actual data and the corresponding fits of the vibronic interactions extend only between R_i and R_f, all $A_{ij}(R)$ functions between R_0 and R_i as well as between R_L and R_f are approximated by straight lines. For each A_{ij}, using the coefficients of its fit, a number of M points are generated between R_0 and R_L and are divided into sectors of uniform width, so that each sector contains N points (M being a multiple of N). The formalism accommodates sectors of variable width, but a uniform sector width is more convenient. Each A_{ij} has been integrated numerically within each consecutive sector employing a single step $h = (\mathrm{R_L} - R_0)/M$. These consecutive integrations give a numerical representation of each $\mathbb{A}_n$ at M/N equally spaced points between R_0 and R_L and are done by the trapezoidal rule rather than analytically. The program is thus independent of the form of the fitting functions except for the section generating the M points.

The third step is the generation of the $\mathbb{C}$ matrix per se, via (11). This involves the diagonalization of each of the previously computed $\mathbb{A}_n$ matrix and formation of the corresponding $\mathbb{B}_n$ matrix as shown in (10). The time expenditure for these diagonalizations is quite acceptable provided the adiabatic basis of the problem is small, which is the usual case. In practice, as soon as a matrix $\mathbb{B}_n$ is calculated, the matrix $\mathbb{C}(R_n)$ is formed by applying the relation $\mathbb{C}(R_n) = \mathbb{B}_n \cdot \mathbb{C}(R_{n-1})$ until R_L is reached ($\mathbb{C} = \mathbb{C}(R_\mathrm{L})$). The starting relation is, of course, $\mathbb{C}(R_1) = \mathbb{B}_1 \cdot \mathbb{I}$.

The final step towards the solution of (6) is the computation of $\mathbb{W}$. Once the transformation matrix $\mathbb{C}$ has been computed, a numerical representation of each of the interacting potentials has to be generated on the same mesh of R values as that of the $\mathbb{C}$ matrix. This is necessary only within the interval R_0 to R_L. Outside this interval a different step may be used as the mesh is extended up to the desired R. It is convenient, however, to use the same increment step h in this region of the potential as well. Applying (4) at each R of the mesh, the diabatic potentials are obtained as the diagonal elements of the $\mathbb{W}$ matrix. The off diagonal elements represent the interactions among the diabatic potentials thus generated. Given that the transformation begins in the asymptotic region, and since for $R > R_0$ $\mathbb{A}$ is in practice equal to the null matrix, it follows that $\mathbb{C}(R > R_0) \approx \mathbb{I}$ so that $\mathbb{W}(R > R_0) \approx \mathbb{U}(R > R_0)$. Therefore, in this region we have set $W_\mathrm{ii}(R > R_0) = U_\mathrm{ii}(R > R_0)$, and

$W_{ij}(R > R_0) = 0$, $i \neq j$. This choice saves setting R_0 equal to the largest acceptable R for a given potential fit, which would increase the CPU time since more points would be needed for a given h.

There are three sources of error in the above procedure. First, an error is introduced by neglecting the wings of the vibronic coupling functions. Second, the shapes of $A_{ij}(R)$ may be different from the real ones. These shapes are Lorenzian, but they are usually very sharp. Unless a very dense mesh is used in the calculation of the *ab initio* points, important information as to the actual shape of the interaction may be lost. Third, the fitting of these data is difficult because of their sharp peaks, and the resulting shapes are not as smooth as desirable.

In a related method, $\mathbb{C}$ is calculated by a truncated series expansion of the exponential function [4]. The disadvantage of this last method is that the form of the resulting expression depends on the dimensionality of $\mathbb{C}$. It is this dependence that the present method avoids.

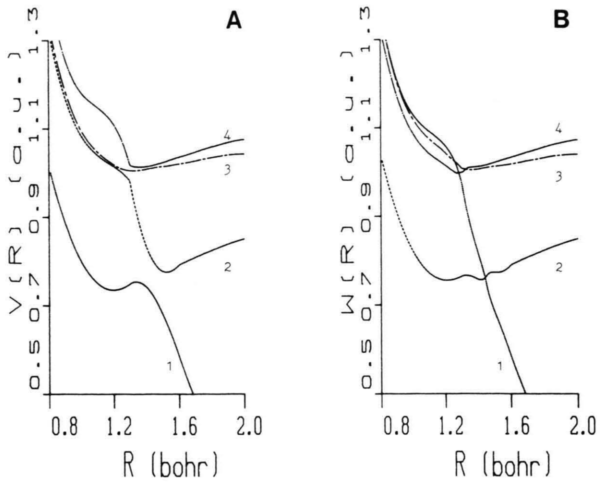

Fig. 1. A) Cubic spline fits of the potential curves of the four adiabatic states of He_2^+ involved in the transformation: 1: $1\,^2\Sigma_g^+$; 2: $2\,^2\Sigma_g^+$; 3: $3\,^2\Sigma_g^+$; 4: $4\,^2\Sigma_g^+$. B) The corresponding diabatic potential curves W_k generated by inward integration. 1: $1\sigma_g 1\sigma_u^2$, 2: $1\sigma_g^2 2\sigma_g$, 3: $1\sigma_g^2 3\sigma_g$, 4: $1\sigma_g^2 4\sigma_g$.

Test Application

We have applied the above method to the 1, 2, 3, and 4, $^2\Sigma_g^+$ adiabatic states of the He_2^+ molecular ion using data already in the literature [9]. These states interact vibronically in a region between 1.0 and 1.6 bohr. The common limits of integration for all A_{ij} are $R_0 = 1.7$ and $R_L = 0.8$ bohr for an inward integration. This interval has been divided into $M = 6000$ points, and the consecutive integrations have been done every $N = 30$ points with an increment $h = 0.00015$ bohr. This has generated a numerical representation of $M/N = 200$ points for the $\mathbb{C}$ matrix. The total CPU time is about 1.5 min on a micro VAX II machine. The code has been tested against a two-state transformation which employs directly the 2×2 sin/cos orthogonal matrix [10]. The *ab initio* potential points have been fitted to segmented cubic splines. The vibronic interactions, computed by finite differences, have been fitted to segmented quadratic splines. Figure 1 shows the *ab initio* adiabatic potentials along with the generated diabatic ones. The off diagonal matrix elements of $\mathbb{W}$ are very small, which is an indication of the strong diabaticity of the system.

A quick inspection of the diabatic curves shows that in the area of the crossings they fail to be smooth and behave somewhat erratically. This is considered to be a result of the lack of enough *ab initio* points within the range of R as well as of the fitting itself. Because of the sharp peaks of the vibronic interactions, their spline fits are not very accurate. Also, the neglect of the wings contributes to the inaccuracy, especially in the region of the linear extrapolation. With the available data it is impossible to assess the relative importance of these errors, but it is clear that a denser mesh of *ab initio* points is a must.

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