

## Convergence of diabatic to adiabatic scattering calculations

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We investigate the convergence of diabatic scattering representations that make use of the commonly applied closure relation (which eliminates first and second derivative coupling terms from the Schrödinger equation for the scattering wave function) to the adiabatic scattering formulations from which they are derived (wherein the internal basis states depend upon the collision coordinate). Numerical examples using a simple model of electron transport in a tapered waveguide are presented. The convergence of the diabatic to the adiabatic results with respect to the number of basis states is extremely slow. We discuss the significance of these findings to atomic and molecular scattering calculations.

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Many problems in atomic and molecular physics and solid-state physics are most naturally represented in an adiabatic formulation wherein the internal basis states are parametrically dependent upon the scattering coordinate. For example, atomic and molecular scattering problems are most naturally represented in terms of an adiabatic formulation, since the structure calculations used to determine the internal molecular states solve for the eigenvalues and eigenvectors of the electronic Hamiltonian  $H_e$  in an adiabatic basis. Electronic structure calculations determine the eigenvalues  $\{E_\mu(R_1, \dots, R_N)\}$  and eigenvectors  $\{\psi_\mu(x_1, \dots, x_n; R_1, \dots, R_N)\}$  of  $H_e$  that depend parametrically upon the nuclear coordinates,

$$H_e(x_1, \dots, x_n; R_1, \dots, R_N)\psi_\mu = E_\mu(R_1, \dots, R_N)\psi_\mu, \quad (1)$$

where  $x_i$  represents the  $i$ th electronic coordinate and  $R_p$  represents the  $p$ th nuclear coordinate. A number of popular computer programs are available for this purpose [1]. Adiabatic time-independent collision dynamics can be formulated in terms of the solution to the Schrödinger equation  $\Psi_{E,\gamma}(\eta, r)$ , where  $r$  is a scattering coordinate and  $\eta$  is a set of internal coordinates that includes the electronic coordinates and may include nuclear coordinates orthogonal to  $r$  [2],

$$H\Psi_{E,\gamma} = E\Psi_{E,\gamma}. \quad (2)$$

Here  $H = T + H_e$ ,  $T$  is the nuclear kinetic-energy operator,  $\gamma$  is an initial channel index, and  $\Psi_{E,\gamma}$  can be expanded in an *adiabatic* orthonormal basis  $\{\psi_\gamma(\eta, r)\}$ ,

$$\Psi_{E,\gamma}(\eta, r) = \sum_{\gamma'} \psi_{\gamma'}(\eta, r) F_{\gamma',\gamma}(r)/r, \quad (3)$$

where  $\mathbf{F}$  is the scattering wave function. As we shall see, in addition to the eigenvalues and eigenvectors in Eq. (1), the matrix elements  $\langle \psi_\gamma | \partial/\partial r | \psi_{\gamma'} \rangle_\eta$  and  $\langle \psi_\gamma | \partial^2/\partial r^2 | \psi_{\gamma'} \rangle_\eta$  are also needed to calculate dynamics. The computer programs of Ref. [1] (or any other commercially available programs) do not calculate the nuclear derivative coupling matrix elements.

It is common to transform the dynamical equations resulting from the adiabatic formulation into diabatic ones, and to use closure to explicitly eliminate the first and second derivative coupling terms from the resulting diabatic dynamical equations of motion [3–6]. In this Rapid Communication we review the nature of this transformation and investigate the convergence of the closure approximation and its effect on the resulting diabatic scattering results.

Upon substituting Eq. (3) into Eq. (2) and taking matrix elements with the internal basis functions, the following equation for  $\mathbf{F}(r)$  is obtained [2–6]:

$$\frac{d^2}{dr^2} \mathbf{F}(r) + \left( 2\mu[E\mathbf{1} - \mathbf{U}(r)] + \mathbf{B}(r) + 2\mathbf{A}(r) \frac{d}{dr} \right) \mathbf{F}(r) = 0, \quad (4)$$

where  $\mathbf{U}(r)$  is the potential-energy matrix and  $\mathbf{1}$  is the unit matrix. The first derivative coupling matrix elements are given by

$$A_{\gamma,\gamma'}(r) = \left\langle \psi_\gamma(\eta, r) \left| \frac{\partial}{\partial r} \right| \psi_{\gamma'}(\eta, r) \right\rangle_\eta, \quad (5)$$

and the second derivative coupling matrix elements are

$$B_{\gamma,\gamma'}(r) = \left\langle \psi_\gamma(\eta, r) \left| \frac{\partial^2}{\partial r^2} \right| \psi_{\gamma'}(\eta, r) \right\rangle_\eta. \quad (6)$$

We have recently developed a stable invariant imbedding algorithm for solving for the  $\mathbf{S}$  matrix contained in the asymptotic form of the wave function  $\mathbf{F}(r)$  given in Eq. (4) and demonstrated its implementation [7,8]. Other methods for calculating adiabatic dynamics also exist [9]. These algorithms eliminate the necessity for going to a diabatic representation. However, the  $\mathbf{A}(r)$  and  $\mathbf{B}(r)$  terms need to be in hand in order to calculate the dynamics.

The first derivative term  $\mathbf{A} d\mathbf{F}/dr$  in Eq. (4) can be eliminated by making an orthogonal transformation using the integrating factor [10]  $\mathbf{C}(r)$  that satisfies the equation

$$\frac{d\mathbf{C}}{dr} = \mathbf{C}\mathbf{A} \quad (7)$$

(or  $d\mathbf{C}'/dr = -\mathbf{A}\mathbf{C}'$ , since  $\mathbf{A}$  is antisymmetric). Substituting  $\mathbf{F} = \mathbf{C}'\mathbf{g}$  into Eq. (4), and making use of Eq. (7), we obtain a Schrödinger equation for  $\mathbf{g}$  that does not contain a first derivative term,

$$\frac{d^2\mathbf{g}}{dr^2} + \mathbf{C} \left\{ 2\mu(E\mathbf{1} - \mathbf{U}) + \mathbf{B} - \mathbf{A}\mathbf{A} - \frac{d}{dr}\mathbf{A} \right\} \mathbf{C}'\mathbf{g} = 0. \quad (8)$$

This transformation can be viewed as one from an *adiabatic* basis set  $\{\psi_{\gamma'}(\eta, r)\}$  to an *r*-independent *diabatic* basis set  $\{\phi_{\alpha'}(\eta)\}$ :

$$\psi_{\gamma'}(\eta, r) = \sum_{\alpha'} \phi_{\alpha'}(\eta) C_{\alpha', \gamma'}(r), \quad (9)$$

with

$$C_{\alpha', \gamma'}(r) = \langle \phi_{\alpha'}(\eta) | \psi_{\gamma'}(\eta, r) \rangle_{\eta}. \quad (10)$$

Hence,

$$\begin{aligned} \Psi_{E, \gamma}(\eta, r) &= \sum_{\gamma'} \psi_{\gamma'}(\eta, r) F_{\gamma', \gamma}(r)/r \\ &= \sum_{\alpha'} \phi_{\alpha'}(\eta) g_{\alpha', \gamma}(r)/r, \end{aligned} \quad (11)$$

with

$$\mathbf{g}(r) = \mathbf{C}(r)\mathbf{F}(r). \quad (12)$$

The transformation matrix  $C_{\alpha', \gamma'}(r)$  can be calculated from  $A_{\gamma, \gamma'}(r)$  by inserting a complete set of diabatic states into Eq. (5):

$$\begin{aligned} A_{\gamma, \gamma'}(r) &= \left\langle \psi_{\gamma}(\eta, r) \left| \sum_{\alpha'} \left| \phi_{\alpha'}(\eta) \right. \right. \right\rangle \\ &\quad \times \left\langle \phi_{\alpha'}(\eta) \left| \frac{\partial}{\partial r} \right| \psi_{\gamma'}(\eta, r) \right\rangle, \\ &= \sum_{\alpha'} C_{\alpha', \gamma}(r)^t \frac{d}{dr} C_{\alpha', \gamma'}(r), \end{aligned} \quad (13)$$

i.e., if the basis  $\{|\phi_{\alpha'}(\eta)\rangle\}$  is complete,  $d\mathbf{C}/dr = \mathbf{C}\mathbf{A}$ . Moreover, the first and second derivative coupling terms  $\mathbf{A}$  and  $\mathbf{B}$  can be eliminated from Eq. (8), provided the adiabatic basis is complete, since then  $\mathbf{B}(r) = \mathbf{A}(r)\mathbf{A}(r) + (d/dr)\mathbf{A}(r)$ , as is easily demonstrated:

$$\begin{aligned} B_{\gamma, \gamma'}(r) &= \left\langle \psi_{\gamma}(\eta, r) \left| \frac{\partial^2}{\partial r^2} \right| \psi_{\gamma'}(\eta, r) \right\rangle \\ &= \left\langle \psi_{\gamma}(\eta, r) \left| \frac{\partial}{\partial r} \sum_{\beta} \left| \psi_{\beta}(\eta, r) \right. \right. \right\rangle \\ &\quad \times \left\langle \psi_{\beta}(\eta, r) \left| \frac{\partial}{\partial r} \right| \psi_{\gamma'}(\eta, r) \right\rangle \\ &= \sum_{\beta} A_{\gamma, \beta}(r) A_{\beta, \gamma'}(r) + \frac{d}{dr} A_{\gamma, \gamma'}(r). \end{aligned} \quad (14)$$

Hence, for a complete adiabatic basis, Eq. (8) becomes

$$\frac{d^2\mathbf{g}(r)}{dr^2} + 2\mu\{E\mathbf{1} - \mathbf{C}(r)\mathbf{U}(r)\mathbf{C}'(r)\}\mathbf{g}(r) = 0. \quad (15)$$

This is the commonly used diabatic form of scattering [3,4,11].

For a finite adiabatic basis,  $\{\psi_{\gamma'}(\eta, r), \gamma' = 1, \dots, N\}$ , one can make a transformation to a finite diabatic basis,  $\{\phi_{\alpha'}(\eta), \alpha' = 1, \dots, M\}$ , with an  $[M \times N]$  transformation matrix  $C_{\alpha', \gamma'}(r) = \langle \phi_{\alpha'}(\eta) | \psi_{\gamma'}(\eta, r) \rangle_{\eta}$ . The wave function in the adiabatic representation can be expressed in terms of the  $M$ -dimensional diabatic representation,

$$\sum_{\gamma'=1}^N \psi_{\gamma'}(\eta, r) F_{\gamma', \gamma}(r)/r \approx \sum_{\alpha'=1}^M \phi_{\alpha'}(\eta) g_{\alpha', \gamma}(r)/r, \quad (16)$$

where the second equality in Eq. (11) becomes an approximation because the diabatic basis is not complete. Nevertheless, Eq. (8) for the  $[M \times N]$ -dimensional matrix  $\mathbf{g}$  is equivalent to Eq. (4) for the  $[N \times N]$ -dimensional matrix  $\mathbf{F}$ , as can be shown using the  $[M \times N]$ -dimensional integrating factor in Eq. (7) and the definition  $\mathbf{F} = \mathbf{C}'\mathbf{g}$ . However, Eq. (15) is an approximation to Eq. (8) for a finite adiabatic basis because the closure relation  $\mathbf{B}(r) = \mathbf{A}(r)\mathbf{A}(r) + (d/dr)\mathbf{A}(r)$  is not exact. To calculate the scattering using Eq. (15), one must first calculate the  $[M \times N]$ -dimensional matrix  $\mathbf{C}(r)$  using Eq. (7) and then form  $\mathbf{C}(r)\mathbf{U}(r)\mathbf{C}'(r)$ . To do so,  $\mathbf{A}(r)$  must be known, but  $\mathbf{B}(r)$  need not be. Alternatively, and *without* approximation [but with the price of having to compute  $\mathbf{C}(r)$ ], one can calculate the scattering using Eq. (8). Clearly, both  $\mathbf{A}(r), \mathbf{B}(r)$  and  $\mathbf{C}(r)$  must be in hand to use Eq. (8). Hence,  $\mathbf{C}(r)$  must be numerically determined using Eq. (7) before using either Eq. (8) or (15); this can be at least as computationally intensive as solving the original scattering equation, Eq. (4). Therefore, there is no compelling reason to use a diabatic representation [either Eq. (8) or (15)] for problems originally formulated in an adiabatic representation, since methods of solving Eq. (4) are available.

It is of interest to determine how many adiabatic basis states  $\{\psi_{\gamma'}(\eta, r)\}$  are necessary to numerically obtain closure [Eq. (14)] within a given accuracy, and furthermore, to determine the differences in the scattering results using Eqs. (15) and (4) as a function of basis-set size. In order to do so, we have developed a simple model for which the derivative coupling matrices  $\mathbf{A}(r)$  and  $\mathbf{B}(r)$  are analytically evaluated [12], since, to our knowledge,  $\mathbf{A}(r)$  and  $\mathbf{B}(r)$  matrices have not been published for any chemical problem, and codes to calculate them are not readily available. Consider a two-dimensional waveguide structure shown in the inset of Fig. 1, where the potential  $U(r, \eta)$  vanishes inside the waveguide and is infinite outside. The boundary conditions dictate that the internal wave functions vanish at the edges of the device,  $\eta = -w(r)/2$ , and  $w(r)/2$ , where  $w(r)$  is the  $r$ -dependent width of the device. Hence, the internal basis set depends on  $r$ ;  $\psi_{\gamma}(\eta, r) = \sqrt{2/w(r)} \sin\{\gamma\pi[\eta + w(r)/2]/w(r)\}$ ,  $\gamma = 1, 2, \dots$ , and the matrix elements of the Hamiltonian  $H = (p_r^2 + p_{\eta}^2)/2\mu + U(r, \eta)$  take the form

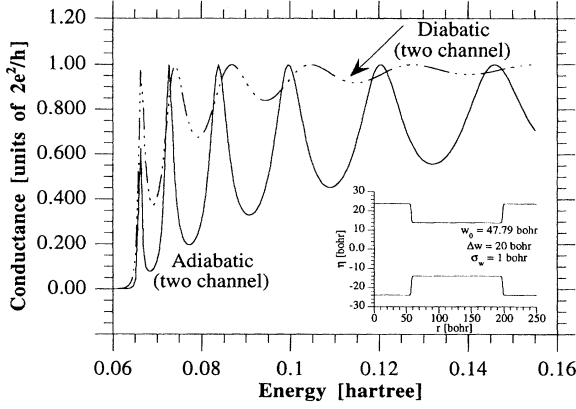


FIG. 1. Conductance  $g = (2e^2/h)\text{Tr}[\mathbf{TT}^\dagger]$  vs energy, calculated using adiabatic and diabatic two-channel representations. Inset shows the two-dimensional waveguide structure.

$$\begin{aligned} \langle \psi_\gamma(\eta, r) | H | \psi_{\gamma'}(\eta, r) \rangle_\eta = & \delta_{\gamma, \gamma'} \frac{p_r^2}{2\mu} - \frac{i}{\mu} A_{\gamma, \gamma'}(r) p_r \\ & - \frac{1}{2\mu} B_{\gamma\gamma'}(r) + U_{\gamma, \gamma'}(r), \end{aligned} \quad (17)$$

where

$$U_{\gamma, \gamma'}(r) = \frac{\gamma^2 \pi^2}{2\mu w^2} \delta_{\gamma, \gamma'}, \quad (18)$$

$$\begin{aligned} A_{\gamma, \gamma'}(r) &= \left\langle \psi_\gamma(\eta, r) \left| \frac{\partial}{\partial r} \right| \psi_{\gamma'}(\eta, r) \right\rangle_\eta \\ &= -\pi w^{-2} \frac{dw}{dr} Z_{\gamma\gamma'} - \frac{1}{2w} \frac{dw}{dr} \delta_{\gamma\gamma'}, \end{aligned} \quad (19)$$

$$\begin{aligned} B_{\gamma\gamma'}(r) &= \left\langle \psi_\gamma(\eta, r) \left| \frac{\partial^2}{\partial r^2} \right| \psi_{\gamma'}(\eta, r) \right\rangle_\eta \\ &= -\left( \gamma' \pi w^{-2} \frac{dw}{dr} \right)^2 Y_{\gamma, \gamma'}^2 \\ &\quad + \frac{1}{2w^2} \left[ 3 \left( \frac{dw}{dr} \right)^2 - w \frac{d^2w}{dr^2} \right] \delta_{\gamma\gamma'} \\ &\quad + \frac{\pi}{w^3} \left[ 3 \left( \frac{dw}{dr} \right)^2 - w \frac{d^2w}{dr^2} \right] Z_{\gamma\gamma'}. \end{aligned} \quad (20)$$

The integrals  $Z_{\gamma\gamma'} = (2\gamma'/w) \int_{-w/2}^{w/2} d\eta \sin[\gamma\pi(\eta+w/2)/w] \eta \cos[\gamma'\pi(\eta+w/2)/w]$ ,  $Y_{\gamma, \gamma'} = \langle \psi_\gamma(\eta, r) | \eta | \psi_{\gamma'}(\eta, r) \rangle_\eta$ , and  $Y_{\gamma, \gamma'}^2 = \langle \psi_\gamma(\eta, r) | \eta^2 | \psi_{\gamma'}(\eta, r) \rangle_\eta$  can be analytically determined. Using the form  $w(r) = w_0 - \Delta w / 2 \{ \tanh[(r-r_1)/\sigma_w] - \tanh[(r-r_2)/\sigma_w] \}$ , the first and second derivatives of  $w(r)$  with respect to  $r$  can be easily evaluated. The parameters  $w_0$ ,  $\Delta w$ , and  $\sigma_w$  are specified in the inset of Fig. 1 and  $r_2 - r_1$  is taken to be 140 bohr.

Let us evaluate  $\mathbf{A}$  and  $\mathbf{B}$  for  $N=2$  to determine how well the closure relation is maintained:

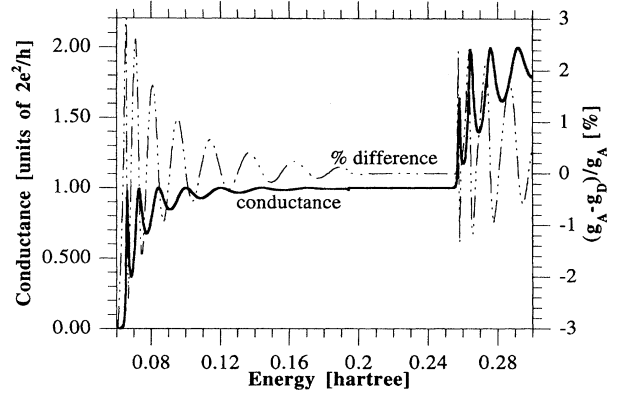


FIG. 2. Conductance vs energy calculated with  $N=15$  in the adiabatic formulation and the percent difference  $[g_A(N) - g_D(N)]/g_A(N)$  between the adiabatic and diabatic calculations for  $N=15$ .

$$\mathbf{A}(r) = -w^{-1} \frac{dw}{dr} \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix},$$

$$\mathbf{B}(r) = w^{-2} \left( \frac{dw}{dr} \right)^2 \begin{pmatrix} \frac{5\pi^2}{12} - \frac{3}{4} & 0 \\ 0 & \frac{\pi^2}{6} - \frac{3}{4} \end{pmatrix};$$

hence,  $\mathbf{B}(r) \neq \mathbf{A}(r)\mathbf{A}(r) + (d/dr)\mathbf{A}(r)$ . The closure relation is badly broken if  $w^{-1}(dw/dr)^2$  is not small. For  $N \geq 3$  this comparison becomes more tedious. Let us instead determine how the conductance changes with basis size using the adiabatic and diabatic formulations.

The conductance  $g$  as a function of energy calculated adiabatically [using Eq. (4)] and diabatically [using Eq. (15)] with two channels ( $N=2$ ) is presented in Fig. 1. The conductance is given by  $g = (2e^2/h)\text{Tr}[\mathbf{TT}^\dagger]$ , where  $\mathbf{T}$  is the transmission amplitude matrix from left to right. The threshold for the lowest internal energy channel is 0.021 61 hartrees and the second channel threshold is 0.086 43 hartrees. Below 0.0639 hartrees no channels are locally open in the constriction, whereas above this energy, one channel is locally open. Hence the conductance above this energy does not exceed unity. The differences between the approximate diabatic results using Eq. (15) and the adiabatic results are substantial, with hundreds of percent differences between them. In Fig. 2 we present the conductance vs energy calculated adiabatically with  $N=15$  and the percent difference between the adiabatic and diabatic results. For  $0.16 < E < 0.256$  hartrees the oscillations in the conductance die away with increasing  $E$ . A third asymptotic channel opens at  $E=0.1945$  hartrees, and a small blip in the conductance occurs just below this energy. At  $E=0.256$  hartrees a second channel becomes locally open in the constriction, and a series of oscillations of the conductance begins with peak conductance equal to 2. The percent difference with  $N=15$  is substantially smaller than with  $N=2$ , but the difference is still significant. The difference oscillates with energy, and the magnitude of the oscillation decreases with increasing en-

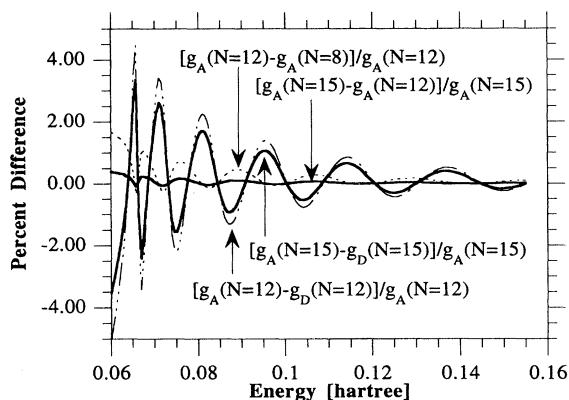


FIG. 3. Percent difference in the conductance calculated adiabatically and diabatically, as a function of energy for  $N=12$  and  $15$ , and the percent convergence of the adiabatic calculation  $[g_A(N=12)-g_A(N=8)]/g_A(N=12)$  and  $[g_A(N=15)-g_A(N=12)]/g_A(N=15)$ . The  $N=15$  results are solid curves and the  $N=12$  are dashed.

ergy until the second local channel in the constriction opens. This picture is repeated at higher energies. Figure 3 shows the percent difference in the conductance calculated adiabatically and diabatically,  $[g_A(N)-g_D(N)]/g_A(N)$ , as a function of energy for  $N=12$  and  $15$ , and the convergence of the adiabatic calculations between  $N=8$  and  $12$ ,  $[g_A(N=12)-g_A(N=8)]/g_A(N=12)$  and  $N=12$  and  $15$ ,  $[g_A(N=15)-g_A(N=12)]/g_A(N=15)$ . The percent difference between the adiabatic and diabatic results decreases extremely slowly with increasing  $N$ ; with  $N=15$  the percent difference is 3.5% at  $E=0.06$  hartrees. However, the adiabatic results have converged as a function of  $N$  to better than 0.5%.

In summary, we developed a simple model for which we tested the convergence of the diabatic dynamical results calculated making use of the closure relation, Eq. (14), to the adiabatic results, and the convergence is found to be extremely slow. To conclude, we discuss implications of the slow convergence of diabatic calculations to the results of

the adiabatic formulation from which they are derived. There is an endless variety of chemical systems for which our conclusions may have important implications; e.g., curve crossing isomerization reactions as a function of a torsional mode of a molecule; here we elaborate two examples. In the hydrogen exchange reaction and its isotopic equivalents; e.g.,  $D+H_2 \rightarrow H+HD$ , a conical intersection occurs between the two lowest potential-energy surfaces. The point of intersection is at the configuration where nuclei form an equilateral triangle. The geometric phase associated with the motion around the intersection has been shown to have dynamical consequences, even at energies below the conical intersection energy (2.7 eV about the minimum of the ground-state surface) [13,14]. To date, only adiabatic calculations on one (the lowest) potential-energy surface have been performed. However, the coupling to the upper electronic adiabatic potential-energy surface also affects the cross sections at sufficiently high energies. It is of interest to see how the coupling to the second surface (degenerate with the lowest surface at the equilateral triangle point) affects the differential cross sections for the various vibrational rotational states of the diatomic molecules. Calculation of this dynamics in the adiabatic formulation using Eq. (4), and using diabatic formulation, Eq. (15), may yield different results using two electronic basis states. The calculation should be performed using Eq. (4) without making use of the closure relation, and the diabatic calculation should be checked against the adiabatic one. As a second example, consider the scattering  $p+H(1s) \rightarrow p+H(nl)$  (or replace the proton by a rare-gas atom or even a hydrogen atom). The  $H_2^+$  potentials and the nuclear derivative coupling matrix elements between the potential-energy surfaces correlating to the same  $nl$  atomic term limits (all the molecular states correlating to the same  $n$  are asymptotically degenerate because of the hydrogen degeneracy) should be calculated. Again, Eq. (4) should be used to calculate the dynamics, and the convergence of the calculation using Eq. (15) should be studied.

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