

## Sign-consistent *ab initio* molecular wave functions

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*Abstract:* We present a method to ensure the sign consistency of molecular wave functions and the dynamical couplings that are obtained from them. The method also allows to systematically “diabatize” avoided crossings between two potential energy surfaces, including conical intersections.

*Keywords:* molecular wave functions, sign-consistency, non-adiabatic couplings, diabatization.

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### 1 Introduction

The theoretical treatment of atom (ion)-atom (molecule) collisions, at low energies, is usually carried out by employing a molecular expansion (see e.g. [1]) of the collisional wave function in terms of the electronic wave functions of the (quasi)molecule formed by the colliding systems. This method involves a first step where one solves the clamped-nuclei electronic equation in the Born-Oppenheimer approximation to obtain the adiabatic molecular functions (MFs) and potential energy surfaces (PES). Excitation and charge transfer processes then take place through non-adiabatic transitions between the Born-Oppenheimer states, induced by the dynamical or non-adiabatic coupling terms. Also, non-adiabatic transitions are relevant in some reactive processes.

PES and couplings are the required input of the dynamical calculation. The calculation of MFs may require large configuration interaction (CI) expansions and the evaluation of non-adiabatic couplings is an important practical aspect for which numerical and analytical techniques have been proposed (see [5] and references therein) and implemented [2, 3].

An important practical drawback of the method is the erratic sign of the calculated dynamical couplings. These show, in general, unphysical teeth-saw shapes because the overall sign of the MFs is arbitrary; indeed, it depends on the numerical diagonalization procedure of the Hamiltonian matrix.

In [4], we have proposed a method based on the calculation of the delayed overlap matrix (DOM) to solve this problem. Here we summarize this method and show an application with a calculation of a radial non-adiabatic coupling for the  $H^+ + N_2$  collisional system, of relevance in modeling proton precipitation in the Earth’s upper atmosphere.

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## 2 Basic equations

In a molecular treatment of ion-atom and ion-molecule collisions, the collisional wave function is expanded in terms of MFs,  $\Phi_l$ , which are (approximate) solutions of the equation:

$$H_{\text{elec}}\Phi_l(\mathbf{q}; \mathbf{Q}) = E_l(\mathbf{Q})\Phi_l(\mathbf{q}; \mathbf{Q}) \quad (1)$$

where  $H_{\text{elec}}$  is the clamped-nuclei electronic Hamiltonian,  $\mathbf{q}$  and  $\mathbf{Q}$  denote electronic and nuclear coordinates, respectively, and  $E_l(\mathbf{Q})$  are the PES.

To solve this equation, one often employs the configuration interaction method (CI), in which the system wave function is expanded as a linear combination of configurations,  $\psi_j$ :

$$\Phi_l(\mathbf{q}; \mathbf{Q}) = \sum_j c_{jl}\psi_j(\mathbf{q}; \mathbf{Q}) \quad (2)$$

Here, the coefficients  $c_{jl}$  are obtained variationally from the secular equation and the electronic configurations  $\psi_j$  are spin- and symmetry- adapted, antisymmetrized products of molecular spin-orbitals.

The collisional wave function is then written as a linear combination of the MFs:

$$\Psi(\mathbf{Q}, \mathbf{q}) = \sum_l F_l(\mathbf{Q})\Phi_l(\mathbf{q}; \mathbf{Q}) \quad (3)$$

where  $F_l(\mathbf{Q})$  are calculated by substituting the expansion (3) in the corresponding full (dynamical) Schrödinger equation, yielding a set of differential equations that are solved numerically. Transitions between molecular states are induced by non-adiabatic couplings, which are the matrix elements of the nuclear gradient operator  $\nabla_{\mathbf{Q}}$ :

$$M_{lm} = \langle \Phi_l(\mathbf{q}; \mathbf{Q}) | \hat{\mathbf{X}} \cdot \nabla_{\mathbf{Q}} | \Phi_m(\mathbf{q}; \mathbf{Q}) \rangle \quad (4)$$

where  $\hat{\mathbf{X}}$  is a unit vector in any direction of  $\mathbf{Q}$ -space.

In practice, the PES and couplings are evaluated in a set of nuclear geometries  $\{\mathbf{Q}_i, \dots, \mathbf{Q}_N\}$ , and they are then interpolated at the points needed to numerically solve the system of differential equations for the functions  $F_l(\mathbf{Q})$ . In these interpolation nodes, the couplings can be evaluated numerically to first order in  $\delta$ , by taking

$$M_{lm}(\mathbf{Q}_i) = \delta^{-1}O_{lm}(\mathbf{Q}_i) + \mathcal{O}(\delta^2) \quad (5)$$

where  $O_{lm}$  is the DOM between two nearby points:

$$O_{lm} = \langle \Phi_l(\mathbf{q}; \mathbf{Q}_i) | \Phi_m(\mathbf{q}; \mathbf{Q}_i + \delta\hat{\mathbf{X}}) \rangle \quad (6)$$

and can be evaluated as explained in [3].

To calculate the dynamical couplings of Eq. (5), we need to solve Eq. (1) at two different grid points:  $\mathbf{Q}_i$  and  $\mathbf{Q}_i + \delta\hat{\mathbf{X}}$ . If one employs a basis of real functions, both  $-\Phi_l$  and  $\Phi_l$  are solutions of this equation, which means that the sign of  $\Phi_l(\mathbf{q}; \mathbf{Q})$  is arbitrary, leading to arbitrary signs of the matrix elements  $M_{lm}(\mathbf{Q}_i)$ . A locally sign consistent coupling is obtained from the original coupling by using the sign of the diagonal elements of the DOM:

$$M_{lm}^s(\mathbf{Q}_i) = k_m M_{lm}(\mathbf{Q}_i) \quad (7)$$

where

$$k_m = \frac{|O_{mm}(\mathbf{Q}_i)|}{O_{mm}(\mathbf{Q}_i)} \quad (8)$$

### 3 Sign consistency

The procedure explained above only ensures that dynamical couplings between different electronic states are sign consistent at a given nuclear geometry,  $\mathbf{Q}_i$ . Now, we are interested in obtaining sign consistent couplings in a set of nuclear geometries defining a path or a domain of nuclear configurations. For this purpose, we construct a new set of sign-consistent molecular states  $\{\Phi_i^c\}$ , as explained below.

Let  $\{\mathbf{Q}_1, \dots, \mathbf{Q}_N\}$  be an ordered grid of points along a given path in the nuclear configuration space, where the set of adiabatic molecular states  $\{\Phi_j\}$  are known. We assume that the erratic sign of  $\Phi_j$  can only arise in the CI step.

The first step is the evaluation of the DOM:

$$O_{jj}(\mathbf{Q}_i) = \langle \Phi_j(\mathbf{Q}_{i-1}) | \Phi_j(\mathbf{Q}_i) \rangle \quad (9)$$

with  $i = 2, \dots, N$ . Next, we define  $n_i(j, j)$  from the following mapping:

$$n_i(j, j) = \begin{cases} 0 & \text{if } |O_{jj}(\mathbf{Q}_i) - 1| < \epsilon_1 \\ 1 & \text{if } |O_{jj}(\mathbf{Q}_i) + 1| < \epsilon_1 \\ 2 & \text{otherwise} \end{cases} \quad (10)$$

where  $\epsilon_1$  is a given threshold (0.2 in our calculations). In these expressions,  $n_i(j, j) = 0$  means that the state  $\Phi_j$  does not change sign when going from  $\mathbf{Q}_{i-1}$  to  $\mathbf{Q}_i$ , while  $n_i(j, j) = 1$  implies that there was a change of sign. In either case, we define a new MF  $\Phi_j^c$  by taking:

$$\Phi_j^c(\mathbf{Q}_i) = (-1)^{n_i(j, j)} \Phi_j(\mathbf{Q}_i) \quad (11)$$

On the other hand,  $n_i(j, j) = 2$  may indicate that there is an avoided crossing between the energy of  $\Phi_j$  and some other state,  $\Phi_{j'}$ , in the path from  $\mathbf{Q}_{i-1}$  to  $\mathbf{Q}_i$ . To check this possibility, we calculate the delayed overlaps with “energetically-near” states:

$$O_{jj'}(\mathbf{Q}_i) = \langle \Phi_j(\mathbf{Q}_{i-1}) | \Phi_{j'}(\mathbf{Q}_i) \rangle \quad (12)$$

which leads, for each  $j'$ , to the mapping  $n_i(j, j')$ :

$$n_i(j, j') = \begin{cases} 0 & \text{if } |O_{jj'}(\mathbf{Q}_i) - 1| < \epsilon_1 \\ 1 & \text{if } |O_{jj'}(\mathbf{Q}_i) + 1| < \epsilon_1 \\ 2 & \text{otherwise} \end{cases} \quad (13)$$

If  $n_i(j, j') \neq 2$  for any  $j'$ , we proceed to “diabatize” the crossing:

$$\phi_j^c(\mathbf{Q}_i) = (-1)^{n_i(j, j')} \phi_{j'}(\mathbf{Q}_i) \quad (14)$$

This means that the energies of MFs  $j$  and  $j'$  must be exchanged when going from  $\mathbf{Q}_{i-1}$  to  $\mathbf{Q}_i$ .

The result  $n_i(j, j') = 2 \forall j'$  indicates that  $\mathbf{Q}_i$  is too far from  $\mathbf{Q}_{i-1}$  to obtain a DOM close to 1 for any  $j'$ . In this case, we add an intermediate point to the grid and repeat the process.

In the new  $\{\Phi_j^c\}$  basis, the corrected couplings  $M_{lm}^c(\mathbf{Q}_i)$ , sign-consistent with those at  $\mathbf{Q}_{i-1}$ , are:

$$M_{lm}^c(\mathbf{Q}_i) = (-1)^{n_i(l, l') + n_i(m, m')} M_{l'm'}^s(\mathbf{Q}_i) \quad (15)$$

where  $l'$  and  $m'$  are those for which  $n_i$  is either 0 or 1.

In this work, we have applied this method to the calculation of a radial coupling in  $\text{H}^+ + \text{N}_2$  collisions. Here we take  $\text{H}^+$  at the origin,  $\mathbf{R}$ , the position vector of the center of mass of  $\text{N}_2$ ,  $\boldsymbol{\rho}$ , the vector between the two N nuclei and  $\alpha$  the angle between  $\mathbf{R}$  and  $\boldsymbol{\rho}$ . The radial non-adiabatic

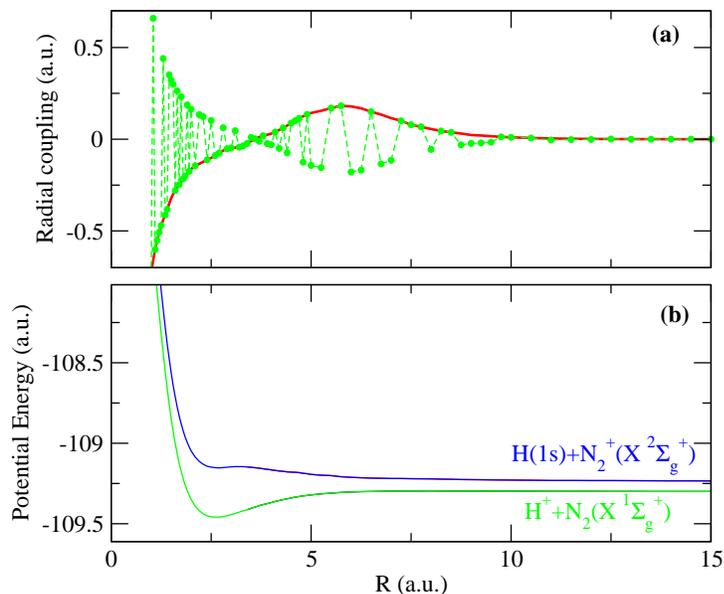


Figure 1: (a): radial coupling between the states of panel (b), in the  $\{\Phi\}$  ( $\bullet$ ) and  $\{\Phi^c\}$  (solid line) representations. (b) Energies of the first two  $^1A'$  MFs of  $H^++N_2$  as functions of  $R$  for  $\rho = 2.08 a_0$  and  $\alpha = 45^\circ$ .

coupling between two electronic states is, then,  $\langle \Phi_l | \partial \Phi_m / \partial R |_{\rho, \alpha} \rangle$ . In panel (a) of Fig. 1 we show the raw  $M_{12}^s$  coupling of eq. (15) with symbols and the sign-corrected one,  $M_{12}^c$ , with solid line. We can see that the original couplings (symbols) jump erratically, while those in the  $\{\Phi^c\}$  basis (11) (solid line) are perfectly smooth. The potential energy curves of the two electronic states involved (the first two  $^1A'$  MFs of  $H^++N_2$  with  $\rho = 2.08 a_0$  and  $\alpha = 45^\circ$ , for  $1 \leq R \leq 15$ ) are shown in Fig. 1(b).

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