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Reprojection method for inelastic processes in atomic collisions within Born–Oppenheimer approach

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Abstract. The paper provides a detailed description of the reprojection method for the exact solution of the nonadiabatic nuclear dynamics within the Born–Oppenheimer formalism. In particular, it discusses the asymptotic behaviour of a state-to-state transition probability when a nonadiabatic radial coupling for this transition has a nonzero asymptotic value—a fundamental feature of the Born–Oppenheimer approach. It is known that the conventional Born–Oppenheimer approach leads to divergency of inelastic cross sections and inelastic rate coefficients, while the reprojection method provides convergences. The article describes physical background of the reprojection method.

Keywords: scattering theory, inelastic collision processes, nonadiabatic transitions, atomic data

Introduction

Inelastic atomic collisions govern the behaviour of gaseous and plasma media in many important domains, e. g., stellar and planetary atmospheres, interstellar media, laser media, etc. Consequently, there is a constant demand for inelastic collisional processes data, especially for low energies. In the great majority of cases, the required atomic data are not available. In general, information about inelastic collisions can be obtained from both experimental measurements and theoretical calculations. Experiments in this field are often very difficult, and numerical calculations remain the main source for inelastic collisional process data. It is therefore highly desirable to use reliable methods for numerical calculations of state-to-state transition probabilities, corresponding inelastic cross sections and rate constants.

The quantum studies of atomic collisions have been accomplished practically since the beginning of the quantum mechanics foundations (Born, Oppenheimer 1997), and now the atomic collision theory seems to be a well-developed part of quantum mechanics. The approaches to study atomic collisions include the conventional Born–Oppenheimer (BO) approach (Born, Oppenheimer 1997; Macías, Riera 1982; Mott, Massey 1949; Nikitin, Umansky 1984), the approach based on the Faddeev equations (Faddeev 1961; Faddeev, Merkuriev 1993), the hyperspherical adiabatic approach (Lin 1995: Macek et al. 1987), to mention a few. However, a vast majority of the theoretical studies in inelastic heavy-particle collision processes is performed within the Born–Oppenheimer approach, which is based on the idea of (Born, Oppenheimer 1997) about the separation of electronic and nuclear motion. The appropriate BO procedure was first formulated by (Mott, Massey 1949). The solution of the problem falls into two steps. First, the electronic fixed-nuclei Hamiltonian is treated and the electronic molecular states are determined, and then the nuclear dynamics is studied using an expansion of the total wave functions in terms of electronic molecular-state wave functions. The first step ("quantum chemical" treatment) yields the potential energy curves of the collisional quasimolecule and a number of coupling matrix elements. These data enter into a set of coupled channel equations solved in the second step. Thus, the BO approach treats a heavy-particle (atomic, ionic, molecular, etc.) collision in terms of molecular states. In general, one should distinguish between the Born-Oppenheimer approach and the Born–Oppenheimer approximation: the BO approximation treats a single molecular state, while the BO approach takes into account an infinite number of molecular states.

Although the BO approach looks straightforward, it is difficult to put it into practice. The problem was first recognized by (Bates, McCarroll 1958). The most severe problem is that the coupling matrix elements can remain nonzero as the internuclear distance *R* goes to infinity, providing inelastic transitions between molecular states under the influence of a collision partner at an arbitrarily large distance. So, the problem can be called the molecular-state problem. The nonzero asymptotic couplings are a fundamental feature of the BO approach. It was found (Belyaev 2009; 2010; 2015; Belyaev et al. 2001; Grosser et al. 1999) that the asymptotic couplings are required to obtain exact asymptotic wave functions within the molecular state representation. Using this idea, the so-called reprojection method (Belyaev 2009; 2010; 2015; Belyaev et al. 2001; Grosser et al. 1999) was developed within a full quantum BO approach to solve the molecular-state problem, including the nonvanishing asymptotic couplings.

The efforts to solve the molecular-state problem have continued, and resulted, in particular, in the development of the quantum reprojection method (Belyaev 2009; 2010; 2015; Belyaev et al. 2001; Grosser et al. 1999). Initially, the method was proposed for a single-electron case. Later, it was scaled out for a multi-electron case (Belyaev 2010). Conceptually, the method is rather simple. It uses BO molecular potential energies and nonadiabatic couplings as they come from quantum-chemical calculations, including nonvanishing couplings. The method has been applied to a number of heavy-particle inelastic collisions, including charge-exchange. The rigorous reprojection method is discussed below.

It is worth emphasizing the importance of taking nonvanishing asymptotic nonadiabatic radial couplings into account correctly. Ref. (Belyaev 2010) shows that if a nonvanishing asymptotic coupling is taken into account the common way within the conventional BO approach, then a corresponding state-to-state transition probability remains nonzero up to infinity, and inelastic cross section and rate coefficient diverge. Finally, such results have no meaning at all. On the contrary, if the reprojection method is used, convergences are reached and the calculated state-to-state transition probabilities, inelastic cross sections and rate coefficients are reliable. Moreover, calculations performed by the reprojection method are the most accurate among those computed within the BO formalism.

General idea of the Born–Oppenheimer approach

A quantum treatment of an atomic collision represents a many-body problem (at least a three-body one) and, hence, is a complicated challenge for the quantum scattering theory. A quantum study of a many-body problem requires an appropriate approach. As mentioned in the Introduction, the most widely used approach to inelastic heavy-particle collision processes is the standard adiabatic Born–Oppenheimer approach.

The general idea of the BO approach is to separate electronic and nuclear motion (Born, Oppenheimer 1992). The problem is handled in two stages: (i) electronic structure calculations of the adiabatic BO fixed-nuclei molecular-state potentials and corresponding nonadiabatic couplings, (ii) a quantum treatment of the nonadiabatic nuclear dynamics.

A detailed derivation of the basic equations within the BO formalism can be found elsewhere, see, e. g., (Belyaev 2009; 2010; Belyaev et al. 2001; Bransden, McDowell 1992; Grosser et al. 1999, Macías, Riera 1982) and references therein. The present paper provides only final equations.

The stationary Schrödinger equation is solved in the form of expansion into partial waves for the total wave function. Each partial wave with given total angular momentum quantum numbers J and M_J also satisfies the Schrödinger equation. The information about inelastic transition probabilities contains in asymptotical parts of the radial nuclear wave functions.

Single-electron collisional system with radial couplings

Let us consider a heteronuclear atomic-collisional system of two nuclei A and B with masses M_A and M_B and one electron e (mass m_e). For the sake of simplicity, let us consider only radial couplings first and neglect a number of small terms. For this purpose, we assume that only electronic Σ molecular states should be considered.

Jacobi coordinates and Hamiltonian

After some manipulation with coordinates, Hamiltonian, and the Schrödinger equation, one has the following: in the interaction region, the system is treated in the molecular Jacobi coordinates, see Fig. 1 (m). In these coordinates the internuclear vector R connects the nuclei, and the electronic coordinate r is measured from the center of nuclear mass (CNM).

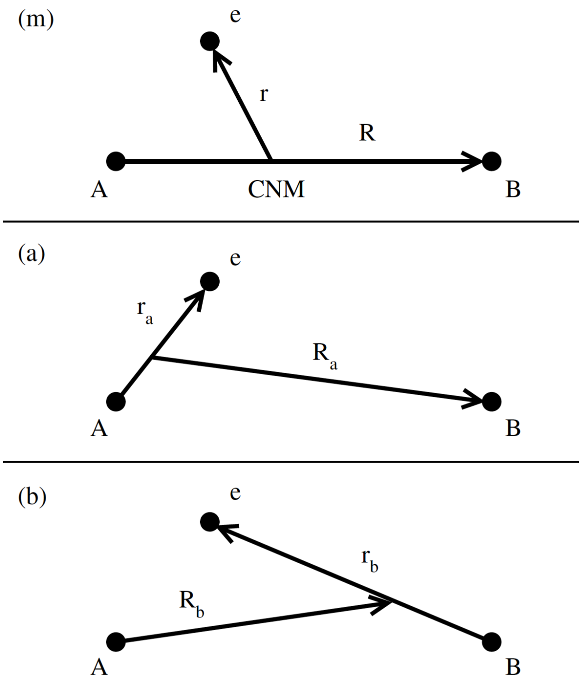

Fig. 1. The 3-body Jacobi relative coordinates. A and B are nuclei, e—an electron. (m)—the molecular coordinates r, R; the vector R connects the nuclei and the electron is measured from the center of nuclear mass. (a)—the scattering (atomic) coordinates r_a, R_a; the electron is measured from the nucleus A and the nucleus B is measured from the center of mass of A and e. (b)—the scattering (atomic) coordinates r_b, R_b; the electron is measured from the nucleus B and the vector R_b connects the nucleus A and the center of mass of B and e

It is worth pointing out the differences between the internuclear and interatomic vectors first noticed by (Bates, McCarroll 1958). Although the differences are small, they do not disappear even in the asymptotic ($R \to \infty$) region (Table 1). They result in certain physical effects discussed below.

Table 1. The definitions of the reduced masses and the scaling factors γ_j. The channel specific masses m_j and M_j are required in the region of large atomic distances. Their values are different for states traveling with nucleus A or B. The differences $m_j - m$ and $M_j - M$ are small throughout

	m	M	m_j	M_j	γ_j
Electron travels with nucleus A	$\frac{m_e(M_A + M_B)}{m_e + M_A + M_B}$	$\frac{M_A M_B}{M_A + M_B}$	$m_a = \frac{m_e M_A}{m_e + M_A}$	$M_a = \frac{(M_A + m_e) M_B}{m_e + M_A + M_{B>}}$	$\gamma_a = -\frac{M_B}{M_A + M_B}$
Electron travels with nucleus B			$m_b = \frac{m_e M_B}{m_e + M_B}$	$M_b = \frac{(M_B + m_e) M_A}{m_e + M_A + M_B}$	$\gamma_b = \frac{M_A}{M_A + M_B}$

There are three sets of the Jacobi coordinates for a 3-body system, as shown in Fig. 1. For applying the BO approach, there is the only set of the Jacobi coordinates, that is, the molecular coordinates depicted in Fig. 1 (m), provides a fixed-nuclei treatment in the interaction region. In the molecular coordinates, the Hamiltonian for the entire system in the center of mass frame reads

$$\begin{aligned} H &= -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + H_{int}\left(r,R\right) \\ &= -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial R^2} + H_e\ , \end{aligned} \tag{1}$$

and the electronic fixed-nuclei Hamiltonian is defined as follows

$$H_e = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + H_{int}\left(r,R\right), \tag{2}$$

H_{int} (r,R) being the interaction potential

$$H_{int}\ (r,R) = V_{eA} + V_{eB} + V_{AB} \tag{3}$$

V being 2-body potentials. The reduced masses are defined in Table 1.

In the adiabatic representation, adiabatic fixed-nuclei electronic molecular wave functions $\phi_j(r;R)$ are defined as the eigenfunctions of the electronic Hamiltonian (2)

$$H_e\,\phi_j\,(r;R) = U_j\,(R)\,\phi_j\,(r;R)\,. \tag{4}$$

The eigenvalues $U_j\,(R)$ of the electronic Hamiltonian are the adiabatic potential energies. The molecular wave functions $\phi_j\,(r;R)$ form a set of suitable electronic basis functions.

Coupled channel equations

According to the general idea of the BO approach, the total (electronic and nuclear) scattering wave function for the entire system $\varPsi_{JM_J}\left(r,R\right)$ is expanded over the electronic molecular basis functions. For practical applications it is convenient to single out wave functions $F_k\,(R)$ for the description of the radial motion of the nuclei. More specifically, for Σ molecular states treated in the present paper, the expansion of the total wave function has the form (Grosser 1986; Grosser et al. 1999; Macías, Riera 1982)

$$\varPsi_{JM_J}\left(r,R\right) = Y_{JM_J}\left(\varTheta,\varPhi\right)\sum\nolimits_k \frac{F_k\left(R\right)}{R}\,\phi_k\left(r,R\right). \tag{5}$$

Y_{JM_J} are the spherical harmonics, while R, $\varTheta$, $\varPhi$, are the spherical coordinates for R. The wave functions $F_k\,(R)$ are found to obey a system of equations, which can be derived from the Schrödinger equation by using the expansion (5). In the adiabatic representation, the set of coupled channel equations for the radial nuclear wave functions $F_j\,(R)$ reads (Grosser et al. 1999)

$$\begin{gathered} \left[-\frac{\hbar^2}{2M}\frac{d^2}{dR^2} + U_j^{eff}\left(R\right) - E_{tot}\right]F_j = \\ \frac{\hbar^2}{M}\sum\nolimits_{k\neq j}\left\langle \phi_j \left|\frac{\partial}{\partial R}\right| \phi_k\right\rangle \frac{dF_k}{dR} + \frac{\hbar^2}{2M}\sum\nolimits_{k\neq j}\left\langle \phi_j \left|\frac{\partial^2}{\partial R^2}\right| \phi_k\right\rangle F_k\,, \end{gathered} \tag{6}$$

where the effective potentials $U_j^{eff}\left(R\right)$ are defined as

$$U_j^{eff}\left(R\right) = U_j\left(R\right) + \frac{J\left(J+1\right)\hbar^2}{2MR^2} - \frac{\hbar^2}{2M}\left\langle \phi_j \left|\frac{\partial^2}{\partial R^2}\right| \phi_j\right\rangle. \tag{7}$$

The angular components of the matrix elements $\langle\phi_j|\partial/\partial R|\phi_k\rangle$ do not appear any more, because they do not couple Σ states with the others. The matrix elements in Eq. (6) depend on R, but not on the angular coordinates. $U_j(R)$ depends on the distance R alone now, and it is written correspondingly. Equations (5) and (6) are the basis of the following treatment.

Boundary conditions and R-martix

The coupled channel equations (6) should be solved with proper boundary conditions. For regular solutions, the correct boundary conditions at $R \to 0$ read

$$F_j(R) \to 0 \text{ as } R \to 0 \tag{8}$$

At large distances, the boundary condition consists in matching a numerical solution of the coupled channel equations at a large distance with an asymptotic (analytical) solution at larger distances.

At present, the numerical solution of the coupled channel equations is obtained in the form of an R-matrix. Suppose that the coupled channel equations (6) have been solved between small distances and a fixed large distance R_0. R_0 should be so large that the coupled channel equations have their asymptotic form at R_0 and hence the radial functions have an asymptotic form discussed below. The solutions have to obey the usual boundary conditions Eq. (8) as $R \to 0$. All solutions with this property are characterized by the R-matrix, elements of which, R_{jk}, relate the values of the radial functions at the upper integration limit and their derivatives

$$F_j = \sum\nolimits_k R_{jk} \frac{dF_k}{dR} \text{ at } R_0 \tag{9}$$

The R-matrix forms a convenient and well-established way to express all properties of the solutions $F_j(R)$ needed for their continuation into the asymptotic region $R > R_0$ (Burke, Noble 1995; Lane, Thomas 1958; Light 1979).

Usually, a set of the coupled channel equations is truncated. A truncated system of N coupled channel equations possesses $2N$ linearly independent solutions. Normally, there exist N independent regular solutions $F_j^{(n)}(R)\ \left(j,n=1,\ldots,N\right)$, which obey the correct boundary condition (8) at small R, j, being the channel number, n the number of the solution. Assume that these solutions are known at a distance R_0 and denote

$$P_{jn} = F_j^{(n)}(R_0) \tag{10}$$

and

$$Q_{jn} = \left.\frac{dF_j^{(n)}}{dR}\right|_{R=R_0} . \tag{11}$$

Provided $\underline{Q}^{-1}$ exists, it easily shown that Eq. (9) holds for every regular solution of the coupled equations (that is, every linear combination of the $F_j^{(n)}$) at R_0, with

$$\underline{R} = \underline{P}\ \underline{Q}^{-1} . \tag{12}$$

Under the present conditions, N regular solutions are easily obtained by numerical computation. Equation (12) is used to compute the R-matrix from the numerical solutions. The R-matrix is a convenient way to match the numerical solution at the boundary R_0 to the analytic solution at $R > R_0$.

Asymptotic couplings

The most important information about an inelastic process, in particular inelastic transition probabilities, is contained in regular solutions of the coupled channel equations in the asymptotic ($R \to \infty$) region. Both initial and final states of an inelastic collisional process are determined by the free motion of colliding partners in some or other eigenstates, that is, by scattering channels when colliding partners before and after a collision (in the asymptotic region) are in well-defined electronic atomic states.

It has been shown, see, e. g., (Belyaev 2010; Belyaev et al. 2001; 2002; Grosser et al. 1999), that the asymptotic values of the radial nonadiabatic couplings calculated with the electron origin at the Center of Nuclear Mass (CNM) read

$$\left\langle \phi_j \left| \frac{\partial}{\partial R} \right| \phi_k \right\rangle_{\infty} = \gamma_k \frac{m}{\hbar^2} \left[U_j(\infty) - U_k(\infty) \right] \left\langle \phi_j \left| z^{at} \right| \phi_k \right\rangle , \tag{13}$$

$\langle \phi_j | z^{at} | \phi_k \rangle$ being the atomic transition dipole moment for an atom with which an active electron travels in the asymptotic region. Therefore, the coupling matrix elements $\langle \phi_j | \partial / \partial R | \phi_k \rangle$ can remain nonzero as $R \rightarrow \infty$.

Asymptotic wave functions

Inelastic transition (state-to-state) probabilities of a collisional process are determined by asymptotic wave functions in scattering (atomic-state) channels with well defined electronic states of colliding atoms or/and ions. In the asymptotic region, electronic molecular-state wave functions are converted into atomic eigenfunctions, so it looks natural to assume that incoming and outgoing wave functions in a scattering channel and in a molecular channel coincide. Equations (5) and (6) seem to have a straightforward interpretation. When one uses, for $R \rightarrow \infty$, atomic eigenstates for the electronic basis states ϕ_j, the single terms in Eq. (5) are expected to represent, at large R, the free motion of the atoms in one or the other of their eigenstates. It seems natural that only one of the terms should contain an incoming wave, and outgoing waves in the other terms occur because the right hand sides in Eq. (6) are nonzero; they represent inelastic transitions. This tentative interpretation is not correct, however.

In the general case, the total (electronic and nuclear) wave function $\Psi_{JM_J}(r, R)$ in the asymptotic ($R \rightarrow \infty$) region is a superposition of the incoming Ψ_j^- and outgoing Ψ_j^+ wave functions describing the free motion of the atomic particle in atomic eigenstates

$$\Psi_{JM_J}(r, R) = \sum_j K_j^{-1/2} \left(a_j^+ \Psi_j^+ + a_j^- \Psi_j^- \right) , \tag{14}$$

with

$$K_j = \sqrt{2M_j \left(E_{tot} - U_j^{eff}(\infty) \right)} / \hbar \tag{15}$$

being the wave number in the scattering channel j. $a_j^{\pm}$ are the outgoing and incoming amplitudes in the scattering (atomic-state) channel j, they are constants. The channel-specific reduced masses M_j are listed in Table 1; they are equal to M_a or M_b depending on the nucleus binding the electron in the asymptotic region. The factor $K_j^{-1/2}$ in Eq. (14) has been introduced because in this way the $| a_j^{\pm} |^2$ represent the outgoing and incoming probability currents in the scattering channel j.

In the asymptotic region, the outgoing and incoming spherical waves have the form

$$\Psi_j^{\pm} = Y_{JM_J}\left(\Theta_j , \Phi_j \right) \frac{exp\left(\pm iK_j R_j^{sc} \right)}{R_j^{sc}} \phi_j\left(r_j^{at} \right) . \tag{16}$$

R_j^{sc}, Θ_j, and Φ_j are polar coordinates for the scattering (interatomic) vector R_j^{sc} which connects the center of mass of the atom with the free nucleus, in contrast to the vector R which connects the nuclei, see Fig. 1. R_j^{sc} is a channel specific coordinate, which is different when the electron travels with a nucleus A or B, respectively. In fact,

$$R_j^{sc} = R_a \tag{17}$$

or

$$R_j^{sc} = R_b , \tag{18}$$

see Fig. 1(a) and (b).

The asymptotic radial nuclear wave functions in each scattering channel can be written in terms of the exponential functions, as in Eq. (16) or somehow else, but the important point is that the radial nuclear wave functions must be the functions of the interatomic distance R_j^{sc}, not of the internuclear distance R (Bates, McCarroll 1958; Belyaev 2010; Belyaev et al. 2001; 2002; Bransden, McDowell 1992; Grosser et al. 1999). The exponential functions (16) have the simple form and represent the incoming and outgoing asymptotic wave functions in each scattering (atomic-state) channel.

The scattering (interatomic) vector R_j^{sc} can be written as follows:

$$R_j^{sc} = R + b_j \ , \tag{19}$$

where the vector b equals

$$b_j = \gamma_j \frac{m_j}{M}\left(r - \gamma_j R\right) . \tag{20}$$

The channel specific reduced masses m_j and the scaling factors γ_j are collected in Table 1. The vector b_j depends on the asymptotic rearrangement in the channel j and hence can be different for different channels. This vector is small compared to R, but it does not vanish at infinity and therefore must be taken into account. It is worth emphasizing that the vector b_j depends on both molecular coordinates r and R.

Although the adiabatic electronic molecular-state wave functions ϕ_k convert into atomic eigenfunctions in the asymptotic region, a single term in the expansion (5), describing a wave function in the molecular state k, does not coincide with a single term in Eq. (14), describing an asymptotic wave function in the corresponding scattering (atomic-state) channel, see Eq. (16). Indeed, the basic electronic wave functions are the same, despite being written in different coordinates, but the radial nuclear wave functions are the functions of different coordinates, R and R_j^{sc}, respectively, where the latter depends not only on R, but also on r, see Eqs. (19) and (20).

Due to the dependence of the vector b_j on the electronic coordinate r, an incoming/outgoing current in a single scattering channel is distributed among several molecular states and vice versa. Projecting the asymptotic scattering-channel wave functions (16) on the molecular asymptotic wave functions (5) gives

$$\Psi_j^{\pm} = Y_{JM_J}\left(\Theta,\Phi\right) \frac{exp\left(\pm iK_j R\right)}{R} \sum\nolimits_k t_{kj}^{\pm}\ \phi_k\left(r,R\right) , \tag{21}$$

where the elements of the matrices $\underline{t}^{\pm}$ represent the reprojection coefficients (Belyaev, Dalgarno, McCarroll 2002; Belyaev 2009; Belyaev 2010)

$$t_{kj}^{\pm} = \left\langle \phi_k \left| exp\left(\pm i\, K_j b_{j_z}\right)\right| \phi_j \right\rangle_{\infty} , \tag{22}$$

b_{j_z} being a projection of the vector b_j onto the molecular axis, which coincides with the axis z:

$$b_{j_z} = \gamma_j \frac{m_j}{M}\left(z - \gamma_j R\right) . \tag{23}$$

Expanding the exponential in Eq. (22) at low collision energies, the matrix elements $t_{kj}^{\pm}$ can be evaluated via corresponding atomic transition dipole moments

$$t_{kj}^{\pm} = \delta_{kj}\left(1 - \frac{\tilde{x}_j}{2}\right) \pm i x_{kj} \ , \tag{24}$$

where

$$x_{kj} = K_j \gamma_j \frac{m_j}{M}\left\langle \phi_k \left| z - \gamma_j R \right| \phi_j \right\rangle\Bigg|_{R\to\infty} , \tag{25}$$

and

$$\tilde{x}_j = K_j^2 \gamma_j^2 \frac{m_j^2}{M^2}\left\langle \phi_j \right| (z - \gamma_j R)^2 \left| \phi_j \right\rangle\Bigg|_{R\to\infty} . \tag{26}$$

All the values are taken in the asymptotic region, $R \to \infty$. δ_{kj} is the Kronecker delta symbol. Furthermore, taking into account Eq. (13), the matrix elements $t_{kj}^{\pm}$ (24) can be written via asymptotic values of the derivative couplings calculated in the Jacobi molecular coordinates

$$x_{kj} = \frac{K_j \hbar_{\times}^2}{M\left[U_k(\infty) - U_j(\infty)\right]} \left\langle \phi_k \left| \frac{\partial}{\partial R} \right| \phi_j \right\rangle_\infty \tag{27}$$

and

$$\tilde{x}_j = \sum\nolimits_l x_{lj}^2 . \tag{28}$$

Thus, Eqs. (24), (27) and (28) allow one to calculate the matrix elements $t_{kj}^{\pm}$, which are in turn needed for the construction of the correct asymptotic wave functions (21) via asymptotic values of adiabatic potential energies $U_j(\infty)$ and asymptotic values of nonadiabatic radial couplings $\langle \phi_k | \partial/\partial R | \phi_j \rangle_\infty$.

It is worth noting that the coefficients $t_{kj}^{\pm}$ are R-independent, but they depend on the collision energy E via the wave numbers K_j. In the zero collision energy limit, the matrices $\underline{t}^{\pm}$ transfer into the unit matrix. Thus, the asymptotic radial nonadiabatic couplings are responsible for the construction of the correct asymptotic wave functions in the molecular coordinates *r, R*.

At low collision energies, the $\tilde{x}_j$ are small and the diagonal matrix elements $t_{jj}^{\pm}$ are close to unit. In this case, one can keep the terms of the order of $\sqrt{m/M}$, and the expansion coefficients $t_{kj}^{\pm}$ can be approximately calculated via the nonadiabatic couplings

$$t_{kj}^{\pm} = \delta_{kj} \pm \frac{i K_j \hbar^2}{M\left[U_k(\infty) - U_j(\infty)\right]} \left\langle \phi_k \left| \frac{\partial}{\partial R} \right| \phi_j \right\rangle_\infty \tag{29}$$

or via the corresponding atomic transition dipole moments

$$t_{kj}^{\pm} = \delta_{kj} \pm i K_j \gamma_j \frac{m_j}{M} \left\langle \phi_k \left| z - \gamma_j R \right| \phi_j \right\rangle \Big|_{R \to \infty} . \tag{30}$$

Note that in the asymptotic region $z-\gamma_j R = z^{at}$, so $\langle \phi_k \mid z-\gamma_j R \mid \phi_j \rangle|_{R\to\infty}$ represents an atomic transition dipole moment $\langle \phi_k | z^{at} | \phi_j \rangle$.

Equations (22) and (23) give the most general formula for calculating the expansion coefficients $t_{kj}^{\pm}$, but they require some additional quantum chemical calculations, while Eqs. (24), (27), (28), and, in particular, Eq. (29), allow one to easily calculate the expansion coefficients via the asymptotic limits of corresponding adiabatic potentials and nonadiabatic couplings, that is, without additional quantum chemical calculations. Estimates show that Eq. (29) is typically applicable for collision energies up to at least 1 keV.

The incoming and outgoing asymptotic wave functions $\Psi_j^{\pm}$ in Eq. (21) continue to represent the free motion of the atoms in the j-th atomic eigenstate (the scattering channel j). They are now written in the form of the original expansion, Eq. (5), and, therefore, have an unexpected appearance: the sum (21) consists not only of a leading term with the molecular state ϕ_j, but it contains additional terms with other electronic molecular states, which are typically smaller by a factor of $\sqrt{m/M}$. The additional terms are obviously required as an ajustment for the use of the inadequate coordinates r and R in the asymptotic region. The point is that the molecular coordinates r and R used to describe molecular states of the collision complex at small and intermediate distances are not suitable for the description of free atoms in the asymptotic region.

Writing Ψ in the form of Eq. (5), the radial wave functions F_k in the molecular state k at large R are found to be written as follows (Belyaev 2009; Belyaev et al. 2001; Grosser et al. 1999):

$$F_k = \sum\nolimits_j K_j^{-1/2} \left[t_{kj}^{+} a_j^{+} exp\left(i K_j R\right) + t_{kj}^{-} a_j^{-} exp\left(-i K_j R\right) \right] \text{for R} \to \infty \tag{31}$$

One easily sees that the F_k satisfies the coupled channel equations Eq. (6) for large R. As this is true for any arbitrary choice of the $a_j^{\pm}$, Eq. (31) is the general form for the asymptotic behaviour of the solutions. Note that we refer here to the coupled channel equations in the correct form, which possesses nonvanishing asymptotic couplings.

To summarise so far, Eq. (31) represents the asymptotic form for the solutions of the coupled equations. The corresponding asymptotic total wave function can be written in the form of Eq. (14), where every single term represents the free motion of an atom in an atomic eigenstate (in a scattering channel). The factors $a_j^{\pm}$ represent the probability amplitudes to find the atoms in the corresponding atomic eigenstates. Therefore, equation (31) constitutes the relation between the solutions F_k of the coupled channel equations and the true probability amplitudes. The remaining task is to find the relations between a_j^{+} and a_k^{-}, once the coupled equations have been solved.

Scattering matrix

The amplitudes a_j^+ and a_k^- are related to each other by a scattering S-matrix (Grosser et al. 1999),

$$a_j^+ = (-1)^{J+1} \sum\nolimits_k S_{jk}\, a_k^- \quad . \tag{32}$$

The S-matrix can be expressed by the R-matrix. $\underline{R}$, $\underline{S}$ and $\underline{t}^{\pm}$ represent the corresponding matrices, and $\underline{K}$, $\underline{K}^{\pm 1/2}$, and $\exp(-i\underline{K}R)$ stand for diagonal matrices with elements K_j, $K_j^{\pm 1/2}$, and $\exp(-iK_jR)$ (Belyaev 2010; Belyaev et al. 2001; Grosser et al. 1999):

$$\begin{aligned} \underline{S} &= (-1)^J exp\left(-i\underline{K}R_0\right) \quad \underline{K}^{-1/2}\left(\underline{t}^- + i\underline{R}\ \underline{t}^- \underline{K}\right) \\ &\times \left(\underline{t}^+ - i\underline{R}\ \underline{t}^+ \underline{K}\right)^{-1} \underline{K}^{1/2} exp\left(-i\underline{K}R_0\right) . \end{aligned} \tag{33}$$

The $a_j^{\pm}$ are the incoming and outgoing amplitudes for the scattering channel j when the correct asymptotic wave functions are used, that is, the functions of the interatomic distances, not the internuclear ones. Equation (33) shows how the correct S-matrix is obtained from the regular solutions of the coupled channel equations expressed by the matrix $\underline{R}$ even when asymptotic nonadiabatic couplings are nonzero. This approach is called the reprojection method (Belyaev 2010).

Equation (33) can be compared to the relation between the R-and the S-matrices used in the conventional BO method. When one disregards the difference between the interatomic and internuclear coordinates and neglects asymptotic nonadiabatic couplings, the t±-matrices are replaced by the unit matrix $\underline{1}$. In this case, Eq. (33) reduces to the relation

$$\begin{aligned} \underline{S}^{conv} &= (-1)^J exp\left(-i\underline{K}R_0\right)\ \underline{K}^{-1/2}\left(\underline{1} + i\underline{R}\ \underline{K}\right) \\ &\times \left(\underline{1} - i\underline{R}\,\underline{K}\right)^{-1} \underline{K}^{1/2} exp\left(-i\underline{K}R_0\right) . \end{aligned} \tag{34}$$

This expression is the conventional relation between the R-and S-matrices. Comparison of the two expressions for $\underline{S}$ shows that the present procedure (33) is only slightly more complicated than the usual procedure to obtain the S from the R-matrix. It is worth noting that the conventional BO method assumes (i) that all asymptotic nonadiabatic couplings calculated in the molecular coordinates are equal to zero (which is not correct) and (ii) that asymptotic nuclear radial wave functions have the form of single functions of the internuclear distance (which is not correct either). As pointed out above, nonzero asymptotic couplings (13) are a fundamental feature of the BO approach and the correct asymptotic radial nuclear wave functions in molecular coordinates have the form of a superposition of functions of the internuclear distance, Eq. (31), so both assumptions of the conventional BO method are not fulfilled. The reprojection method takes into account nonvanishing asymptotic couplings in the coupled channel equations and uses the correct forms (16) for the asymptotic incoming and outgoing wave functions.

Transition probability, cross section and rate coefficient

Having the S-matrix known at a given collision energy $E = E_{tot} - U_i^{eff}(\infty)$ in the initial scattering channel i and at a given total angular momentum quantum number J, a probability $P_{if}(J,E)$ for an inelastic state-to-state transition $i \rightarrow f$ is calculated by the following formula

$$P_{if}\left(J,E\right) = \left|S_{if}\left(J,E\right)\right|^2 . \tag{35}$$

An inelastic cross section $\sigma_{if}(E)$ is calculated as a sum over the total angular momentum quantum number J

$$\sigma_{if}\left(E\right) = \frac{\pi\hbar^2 p_i^{stat}}{2ME} \sum\nolimits_{J=0}^{\infty} P_{if}\left(J,E\right)\left(2J+1\right) , \tag{36}$$

where p_i^{stat} is the statistical probability for population of the initial channel i.

An inelastic rate coefficient $K_{if}(T) = \langle \sigma_{if}\, v \rangle$ is then obtained by integrating over a collision energy E assuming that the Maxwellian distribution is valid

$$K_{if}\left(T\right)=\sqrt{\frac{8}{\pi M\left(k_B T\right)^3}}\int_0^\infty \sigma_{if}\left(E\right)\, E\,exp\left(-\frac{E}{k_B T}\right)dE \ , \tag{37}$$

T being a temperature, k_b the Boltzmann constant.

It is worth emphasizing that in order to calculate acurate nonadiabatic transition probabilities P_{if}, one has to reach a convergence for these probabilities with respect to variation of the upper integration limit for a solution of the coupled channel equations, since scattering matrix elements S_{if}, as well as the corresponding wave functions, are defined in the asymptotic ($R \rightarrow \infty$) region, see Eqs. (5), (14), (31), and (32). In order to calculate reliable cross sections, one has to reach an additional convergence for $\sigma_{if}\,(E)$ with respect to a number of partial waves taken into account, that is, to the upper summation value for the total angular momentum quantum number $J \rightarrow \infty$, see Eq. (36).

Reprojection method and conventional BO approach

Conventional BO: A theoretical extract

Let us compare the results of applications of the reprojection method and the conventional BO approach. As mentioned above, one of the fundamental features of the BO approach is nonzero asymptotic matrix elements of the radial nonadiabatic coupling between the molecular states which asymptotically correlate to scattering channels with nonzero transition dipole moments between corresponding atomic states. Let us consider how the conventional BO approach treats this feature.

The total asymptotic wave functions written in terms of the asymptotic incoming and outgoing scattering-channel wave functions Eq. (14) can be re-written in terms of the asymptotic incoming and outgoing molecular-state wave functions and in the molecular coordinates by using the expansion (21) as follows

$$\Psi_{JM_J}\left(r,R\right)=\sum\nolimits_k K_k^{-1/2}\left(A_k^+\,\tilde{\Psi}_k^+ + A_k^-\,\tilde{\Psi}_k^-\right), \tag{38}$$

where

$$\Psi_k^{\pm}=Y_{JM_J}\left(\Theta,\Phi\right)\frac{exp\left(\pm\, iK_k R\right)}{R}\,\phi_k\left(r,R\right) \tag{39}$$

and

$$A_k^{\pm}=\sum\nolimits_j a_j^{\pm}\,T_{kj}^{\pm} \ . \tag{40}$$

The R-dependent coefficients $T_{kj}^{\pm}$> read

$$\begin{aligned} T_{kj}^{\pm} &= t_{kj}^{\pm}\frac{\sqrt{K_k}}{\sqrt{K_j}}exp\left[\pm i\left(K_k-K_j\right)R\right] \\ &=\delta_{kj}\left(1-\frac{\tilde{X}_j}{2}\right)\pm iX_{kj}^{\pm} \ , \end{aligned} \tag{41}$$

where

$$X_{kj}^{\pm}=\frac{\sqrt{K_j K_k}\,\hbar^2 exp\left[\pm i\left(K_j-K_k\right)R\right]}{M\left[U_k\left(\infty\right)-U_j\left(\infty\right)\right]}\left\langle\phi_k\left|\frac{\partial}{\partial R}\right|\phi_j\right\rangle_\infty \tag*{42)}$$

and

$$\tilde{X}_j=\tilde{x}_j \ , \tag{43}$$

see Eq. (28).

Finally, as distinct from the R-independent incoming and outgoing amplitudes $a_j^{\pm}$ in the scattering channels, the incoming and outgoing probability-current amplitudes $A_k^{\pm}$ in molecular channels, Eq. (38), depend on the internuclear distance R, see Eqs. (40)-(42). This results in R-dependence of inelastic transition probabilities between molecular states unlike the R-independent inelastic probabilities between scattering states which are expressed via the amplitudes $a_j^{\pm}$, see Eq. (14).

Na + Li collisional example

Let us consider the collisions of Na + Li as an example. For the sake of simplicity, let us take into account only three lowest molecular $^1\Sigma^+$, which asymptotically correspond to the following interactions: Na($3s$) + Li($2s$) the ground state X, Na($3s$) + Li($2p$) the excited state A, and Na($3p$) + Li($2s$) the excited state C. It is shown in Ref. (Belyaev 2010) that two of these three matrix elements have nonzero asymptotic nonadiabatic couplings.

The R dependence of the probability-current amplitudes in molecular states means no convergency with respect to the upper integration limit for the coupled channel equations. One expects the oscillatory behaviour of the transition probability up to infinity, and the numerical calculations confirm this conclusion, see Ref. (Belyaev 2010). Nonzero transition probabilities in the asymptotic region at any angular momentum quantum numbers result in no convergency with respect to the upper summation limit for the cross sections of the excitation processes in these collisions, see Eq. (36). Finally, the inelastic (excitation) cross sections increase up to infinity, although this is not physically correct at all. In contrast to the convergent BO approach, the reprojection method provides the convergency and correct results for the transition probabilities, cross sections and rate coefficients.

Conclusion

Possible sources of deviation between the experimental and numerical data can have different origin: (i) A major shortcoming of the experimental data consists in the highly indirect procedure used for determining the absolute cross section scale. The data were normalized for this purpose to the results published by other authors, which, in turn, relied on a similar normalization. The error of the experimental data was estimated to be of the order of 40% (Grosser, Krüger 1984). However, a larger error of the absolute scale seems possible. It offers a straightforward explanation for a large part of the observed discrepancy. (ii) The neglect of higher excited states in the system of coupled equations. Inclusion of the higher-lying molecular states can therefore be expected to have some effect on the numerical results, but would probably not lead to changes beyond a few tens of percent. Generally, one expects errors of this type to be less relevant for the range of energies near the threshold, compared to the 1 keV range. (iii) Errors in the calculated potentials and coupling matrix elements are expected to be smaller than for the Na + Li system referred to above and should, in general, result in correspondingly smaller deviations.

In summary, the numerical treatment of the present system offers no severe conceptual or mathematical difficulties, neither at the quantum chemical nor at the dynamical level. The degree of agreement with the experimental data makes a repetition of the experiment highly desirable.

Conflict of Interest

The author declares that there is no conflict of interest, either existing or potential.

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