Inelastic Collision Processes for Formation of Spectral Line Shapes in Stellar Atmospheres. Reprojection method.

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Abstract. Modeling of formation of spectral lines in stellar atmospheres requires accurate data on inelastic collision processes. The only source of this information is theoretical calculations mainly performed within the standard adiabatic Born-Oppenheimer approach. It is shown that the conventional application of this approach encounters severe difficulties, in particular, due to nonzero couplings in the asymptotic region. This results in the fact that the conventional applications do not provide convergences, which are necessary for calculations of inelastic cross sections, giving infinite cross sections. The proposed remedy is the quantum reprojection method within the standard adiabatic Born-Oppenheimer approach. The method takes nonvanishing asymptotic nonadiabatic couplings into account and distinguishes asymptotic currents in molecular-state channels and in atomic-state channels. The method is demonstrated for the example of low-energy inelastic Li + Na collisions for which the conventional application of the Born-Oppenheimer approach fails.

1. Introduction
Formation of spectral lines in stellar atmospheres is determined by many physical processes [1]. In addition to radiative processes directly providing spectral lines, different inelastic collision processes, mainly due to collisions of different atoms and ions with electrons as well as with hydrogen atoms and ions, play the important role, e.g., as pointed out in the talks at ICSLS 21 [2, 3]. The need for accurate data on low-energy inelastic atomic collisions involving hydrogen atoms and ions for non-LTE formation calculations is well known, see, e.g., [1, 2, 3] and references therein. In principle, this kind of data could be obtained from experimental measurements and from theoretical calculations. However, in practice, experimental data on low-energy atomic collisions are not available and calculations remain the only source of information needed. That is why it is essential to be sure that theoretical approaches used for numerical calculations are reliable and provide accurate data on inelastic collision processes.

The majority of theoretical treatments of inelastic collisions involving atoms, ions, molecules, clusters, surfaces, and so on is performed within the standard adiabatic Born-Oppenheimer (BO) approach (or simply the BO approach), which is described, for example, in [4, 5]. The approach is based on the separation of electronic and nuclear motion. 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 wavefunctions in terms of electronic molecular-state wavefunctions. The BO approach gives a clear physical picture of
the scattering process and allows one to use the well-developed quantum-chemical methods and computer programs. In addition, the BO approach has as its limitation the Born-Oppenheimer approximation which is widely used in quantum chemistry and molecular physics.

Although the BO approach looks straightforward, it encounters severe difficulties. The point is that in order to calculate inelastic cross sections within the BO approach one has to reach three kinds of convergences: (i) a convergence with respect to a number of molecular states treated (which should be infinite in general, but finite in practice); (ii) a convergence with respect to an upper integration limit for a nuclear dynamical treatment (an internuclear distance \( R \) must go to infinity); (iii) a convergence with respect of a number of partial waves calculated (should be infinite). The first kind of convergence should be studied in each particular case individually, while two others are of general features. It has recently shown [6] that conventional applications of the BO approach do not lead to convergences of the second and the third kinds in many cases providing unphysical results, and hence a special care should be taken in order to obtain reliable cross sections for collision processes.

2. The standard adiabatic Born-Oppenheimer approach

The standard adiabatic BO approach is described in details in many papers, e.g., in Ref. [4, 5], see also Ref. [6, 7, 8, 9] and references therein. In order to use the BO approach, one needs to treat fixed-nuclei molecular states, so one of the coordinates should be the internuclear distance \( R \). In order to reach the simplest and standard form of the coupled channel equations for nuclear dynamical treatment, the set of the Jacobi coordinates depicted in Fig. 1(a) should be used, that is, one of the Jacobi coordinates is the internuclear distance and the electronic coordinate should be measured from the Centre of Nuclear Mass (CNM). Using this set of the Jacobi coordinates, one calculates adiabatic potential energies \( U_j(R) \) and nonadiabatic couplings, e.g., the radial couplings \( j | \frac{\partial}{\partial R} | k \), for selected molecular (fixed-nuclear) states. Solutions of the coupled channel equations result in nonadiabatic transition probabilities \( P_{jk} \), and inelastic cross sections \( \sigma_{jk} \) are calculated via \( P_{jk} \) as follows

\[
\sigma_{jk}(E) = \frac{\pi \hbar^2 p_j^{\text{stat}}}{2M E} \sum_{J=0}^{J_{\text{max}}} P_{jk}(J, E)(2J + 1),
\]

\( M \) being the reduced nuclear mass, \( E \) being the collision energy, \( J \) being the total angular momentum quantum number, and \( p_j^{\text{stat}} \) being a statistic probability for population of the initial channel \( j \). According to the conventional interpretation of the BO approach, nonadiabatic transition probabilities \( P_{jk} \) are determined as probabilities between molecular states, and the transitions take place in regions where nonadiabatic couplings are nonzero.

![Figure 1. The two sets of the Jacobi coordinates for a three-body system (two nuclei A, B and an electron). The upper figure (a) shows the set used for a molecular representation, while the low figure (b) depicts the set used for a scattering representation in the asymptotic region.](image-url)
The first problem within the BO approach consists in the fact that some radial nonadiabatic couplings remain nonzero in the asymptotic region providing nonadiabatic transitions between molecular states up to an infinite internuclear distance. It has been shown analytically and confirmed numerically (see, e.g., [6, 7, 8, 9]) that the asymptotic radial couplings read

$$\langle j|\frac{\partial}{\partial R}|k\rangle_{\infty} = \gamma_k \frac{m}{h^2} [U_j(\infty) - U_k(\infty)] \langle j|z^a\rangle|k\rangle, \quad (2)$$

where \(m\) is the mass of an electron, \(\langle j|z^a\rangle|k\rangle\) is an atomic transition dipole moment, and \(\gamma_k\) is a scalar factor:

$$\gamma_k = \begin{cases} 
\gamma_A = -\frac{M_B}{M_A + M_B}, & \text{when } e^- \text{ is bound with } A \\
\gamma_B = +\frac{M_A}{M_A + M_B}, & \text{when } e^- \text{ is bound with } B 
\end{cases} \quad (3)$$

Eq. (2) shows that asymptotic couplings between optically allowed transition states do not vanish at infinity. Choosing another origin for the electronic coordinate does not remove nonzero asymptotic coupling terms in the coupled channel equations [9]. Nonvanishing coupling terms in the coupled channel equations are the fundamental feature of the BO approach.

**Figure 2.** The adiabatic potentials (a) for the three lowest \(1^\Sigma^+\) states of LiNa (X, A, C) and the radial nonadiabatic couplings (b) between these states.

Fig. 2 shows an example of adiabatic potentials and nonadiabatic radial couplings for the three lowest \(1^\Sigma^+\) states of LiNa. It is clearly seen that two asymptotic values of nonadiabatic couplings are nonzero in agreement with Eq. (2). Moreover, the nonvanishing asymptotic couplings have substantial values and cannot be neglected in the nuclear dynamics.

As the result of nonvanishing couplings, the nonadiabatic transitions between molecular states remain nonzero at an arbitrary large internuclear distance which is shown in Fig. 3 (left panels), where the nonadiabatic transition probabilities are plotted as a function of the upper integration limit \(R_0\). It is clearly seen that the conventional application of the BO approach does not provide a convergence with respect to increasing of the upper integration limit.

Since the transitions between molecular states take place at an arbitrary large distance, nonadiabatic transition probabilities remain nonzero at any angular momentum quantum numbers \(J\), see Fig. 4 (left panels). It results in the fact that the inelastic cross sections do not reach a convergence with respect to increasing of the upper summation limit \(J_{\text{max}}\) (which should go to infinity, in general), see Eq. (1). This is clearly seen in Fig. 5, where the inelastic cross sections are shown as a function of \(J_{\text{max}}\). Note that the dashed lines plot the cross sections calculated by means of the conventional application of the BO approach.
In fact, the nonvanishing asymptotic couplings are a consequence of a more fundamental shortcoming. The coordinates used to describe molecular states of the collision complex at small and intermediate distances are not suited for the description of the free atoms in the asymptotic region. Within the conventional applications of the BO approach, asymptotic wavefunctions read

$$BO\Psi_j^\pm(\vec{r}, \vec{R}) = Y_{JMj}(\Theta, \Phi) \frac{\exp(\pm i K_j R)}{R} \phi_j(\vec{r}, \vec{R}),$$

that is, the nuclear wavefunctions are written as functions of the internuclear distance $R$. The correct asymptotic incoming and outgoing wavefunctions \[5, 6, 7, 8, 10\]

$$\Psi_j^\pm(\vec{r}_j, \vec{R}_j) = Y_{JMj}(\Theta, \Phi) \frac{\exp(\pm i K_j R_j)}{R_j} \phi_j(\vec{r}_j)$$

are written in another set of Jacobi coordinates [see Fig. 1(b)] and are different from the BO functions (4). The vector $\vec{R}_j$ connects the centers of mass of the atoms, in contrast to $\vec{R}$ which connects the nuclei, see Fig. 1. The conventional BO applications do not take these differences into account.

**Figure 3.** The transition probabilities for Li($2s \rightarrow 2p$) + Na($3s$) (upper panels (a) and (b)) and Li($2s$) + Na($3s \rightarrow 3p$) (lower panels (c) and (d)) excitation calculated for $E = 5$ eV and $J = 0$ by means of the conventional BO method (transitions between molecular states; solid lines) and by means of the reprojection method (transitions between atomic states; dashed lines) as a function of the upper integration limit $R_0$.

**Figure 4.** The transition probabilities for Li($2s \rightarrow 2p$) + Na($3s$) (upper panels) and Li($2s$) + Na($3s \rightarrow 3p$) (lower panels) excitation as a function of the total angular momentum quantum number $J$ for $E = 5$ eV. The solid lines (left panels) show the probabilities obtained by means of the conventional BO method, while the dashed lines (right panels) depict the probabilities calculated by the reprojection method. Note different scales for different panels.
into account. The problem was first recognized in Ref. [10] and became known as the electron translation (ET) problem, although it should be called as the "molecular state (MS) problem."

3. The reprojection method
There are several remedies to deal with the MS problem. The first option is to go beyond the BO approach, for example, to use the hyperspherical coordinates or to solve the Faddeev equations. Within the BO approach, the proposed remedies are essentially based on (i) the inclusion of ET factors [10] or common translation factors [11] into the expansion of wavefunctions, or (ii) the use of state-specific reaction coordinates [12, 13], or (iii) the reprojection method [6, 7, 8, 14]. The first two remedies lead to modifications of basis functions, potentials, couplings, dynamical equations and consider all electrons explicitly, so they have been applied only to one-electron systems. The reprojection method is free from such limitations, in particular, Ref. [6] describes the multielectron reprojection method which does not require calculations of any additional quantum chemical data.

The reprojection method distinguishes molecular-state channels and atomic-state (scattering) channels, as well as probability currents in these channels. Within the reprojection method, the coupled channel equations are solved in the molecular-state representation from zero till relatively large internuclear distance $R_0$ keeping nonzero asymptotic couplings and using the correct asymptotic wavefunctions (5). Since the wavefunctions at the intermediate distances and in the asymptotic regions are written in different coordinates, they are reprojected into each other at $R_0$. In particular, the correct asymptotic wavefunctions in atomic-state (scattering) channels read

$$\Psi_j^\pm(\vec{r}, \vec{R}) = Y_{JM_j}(\Theta, \Phi) \sum_k \frac{\exp(\pm iK_j \vec{R})}{R} t_{kj}^\pm \phi_k(\vec{r}, \vec{R}),$$

where the reprojection coefficients are equal to

$$t_{kj}^\pm = \delta_{kj} \pm \frac{iK_j \hbar^2}{M (U_k(\infty) - U_j(\infty))} \left\langle \phi_k \left| \frac{\partial}{\partial \vec{R}} \right| \phi_j \right\rangle_\infty.$$  

These coefficients are used for accurate calculations of the scattering matrix from numerical solutions of the coupled channel equations, see Refs. [6, 7, 8, 14] for details and the formulae. It is seen from Eq. (7) that the nonzero asymptotic couplings are responsible for the construction of the correct asymptotic wavefunctions. It is also seen from Eq. (6) that an incoming or outgoing current in a single atomic state is distributed among several molecular states and vice versa.
Let us show how the reprojection method improves calculations of nonadiabatic transition probabilities and inelastic cross sections. The right panels of Fig. 3 show that the reprojection method leads to a convergence of the nonadiabatic transition probabilities with respect to an upper integration limit. Nonadiabatic transitions between molecular states still remain at an arbitrary large $R$, but they do not produce transitions between atomic states at large distances. The $t$-matrices correct the $S$-matrix and, finally, transition probabilities. Thus transitions between atomic states in the asymptotic region are unphysical, while transitions between molecular states in the same region are physical.

The right panels of Fig. 4 show that in contrast to the results of the conventional application of the BO approach, the transition probabilities obtained by means of the reprojection method are substantial only within a limited range of $J$, roughly up to $J \approx 500$ for $E = 5$ eV in Li + Na collisions. This leads to the convergence of the cross sections with increasing $J_{\text{max}}$ (see Fig. 5), and finally, to the finite values of the inelastic cross sections.

It has thus been demonstrated that the conventional BO method applied to collision processes with nonzero asymptotic nonadiabatic couplings, which are fundamental features of the BO approach, leads to infinite inelastic cross sections even at low collision energies. The MS problem is severe for all collisions. The reprojection method takes into account nonzero asymptotic couplings and distinguishes asymptotic currents in molecular-state and atomic-state channels.

4. Concluding remarks
Let us compare a conventional application of the BO approach and the reprojection method. (i) Within a conventional application all asymptotic nonadiabatic couplings are wanted to be zero (though some are nonzero); the reprojection method keeps nonzero asymptotic nonadiabatic couplings (as they are obtained from quantum chemical calculations). (ii) Within a conventional application asymptotic wavefunctions have the BO form as a function of the internuclear distance; the reprojection method uses the correct asymptotic wavefunctions as a function of the interatomic distance. (iii) A conventional application assumes that currents in a single atomic state proceed into a single molecular state (and vice versa); within the reprojection method, currents in a single atomic state proceed into multiple molecular states (and vice versa). Finally, conventional applications do not provide proper convergences giving unreliable results, while the reprojection method yields necessary convergences leading to reliable results.

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