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Revised Born-Oppenheimer approach and a reprojection method for inelastic collisions

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The quantum reprojection method within the standard adiabatic Born-Oppenheimer approach is derived for multielectron collision systems. 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 standard adiabatic Born-Oppenheimer approach fails and leads to paradoxes such as infinite inelastic cross sections.

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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 [1,2]. 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 wave functions in terms of electronic molecular-state wave functions. 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.

Although the BO approach looks straightforward, it encounters severe difficulties. The problem was first recognized in Ref. [3] and became known as the "electron translation (ET) problem." The proposed remedies are essentially based on (i) the inclusion of ET factors [3,4] or common translation factors [5,6] into the expansion of wave functions, or (ii) the use of state-specific reaction coordinates [7–9], (specific) hyperspherical coordinates [10], Eckart coordinates [11], and so on. The methods were reviewed in Refs. [1,2,12,13]. The remedies lead to modifications of basis functions, potentials, couplings, and dynamical equations. It has been stated that it is "not possible to extract a meaningful scattering matrix" [12], and finally the problems have been interpreted as conceptional limitations of the entire BO approach [2]. This fundamental problem still presents unresolved features, for example, infinite scattering lengths in ultralow-energy collisions [14]. Efforts to solve the ET problem have been continued, and in particular, the *one-electron* quantum reprojection method has been derived [15–17], which is conceptually rather simple and uses BO molecular potentials and couplings. This method is generalized in the present paper for a multielectron case.

In most applications, however, the ET problem is simply neglected, that is, (i) all asymptotic nonadiabatic couplings are cut off at a finite internuclear distance, and (ii) the asymptotic boundary conditions are taken in the BO (see the following) or similar form [18]. Let us refer to this application of the standard adiabatic BO approach as the "conventional BO method," because most of the cross-section calculations are carried out with this procedure, in contrast to the previously mentioned methods which take the ET problem into account. When applying the conventional BO method, it is assumed that the approximations described give negligible errors, at least for low collision energies (see, for example, [18,19]).

Taking as an example Li + Na collisions, the present Rapid Communication shows that in some cases no proper cutoff can be found to obtain reliable results and that the previously mentioned approximations can lead to errors that are several orders of magnitude larger than correct values, even at low collision energies. Moreover, it is shown that in the case of nonzero asymptotic couplings, which are the rule rather than the exception of the BO approach, the conventional BO method leads to infinitely large inelastic cross sections. Therefore, the coupling-cutoff procedure can give *any value* for an inelastic cross section.

For the sake of simplicity, let us treat atomic collisions in Σ molecular states. Within the BO approach the total wave function $\Psi_{JM_J}(\mathbf{r},\mathbf{R})$ is expanded as

$$\Psi_{JM_J}(\mathbf{r},\mathbf{R}) = Y_{JM_J}(\Theta,\Phi)\sum_k \frac{F_k(R)}{R}\phi_k(\mathbf{r},\mathbf{R}), \qquad (1)$$

with $\phi_k(\mathbf{r},\mathbf{R})$ being the electronic molecular-state wave functions, $\mathbf{r}$ and $\mathbf{R}$ being the sets of electronic and nuclear coordinates, and J, M_J being the total angular momentum quantum numbers. This results in a system of coupled channel equations (CCEs) for radial nuclear wave functions $F_k(R)$ (see Ref. [1]). Nonadiabatic transition probabilities are then calculated in the asymptotic ($R \to \infty$) region, where the conventional BO method assumes that an incoming or outgoing current in a *single atomic state* proceeds completely into a *single molecular state* and vice versa. The asymptotic boundary conditions for the total wave function read

$$\Psi_{JM_J}(\mathbf{r},\mathbf{R}) = \sum_j K_j^{-1/2}(a_j^+\Psi_j^+ + a_j^-\Psi_j^-), \qquad (2)$$

with the wave numbers K_j and the incoming or outgoing amplitudes $a_j^\pm$ in the atomic-state channel j. The conventional BO method assumes the following incoming and outgoing asymptotic ($R \to \infty$) BO wave functions:

$$^{\mathrm{BO}}\Psi_j^\pm = \frac{\exp(\pm i K_j R)}{R} Y_{JM_J}(\Theta,\Phi)\,\phi_j(\mathbf{r},\mathbf{R}). \qquad (3)$$

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The CCEs are solved numerically from zero to an upper integration limit R_0 that is large enough to calculate transition probabilities based on the asymptotic wave functions (3) [1].

The use of electronic molecular states leads to the following fundamental features. Both radial and rotational nonadiabatic couplings [1,15,20,21], as well as the form of CCEs [15,21], depend on the origin of the electron coordinates, although the CCEs themselves are independent of the origin choice [15,21,22]. The CCEs take their standard and simplest form in Jacobi coordinates, where the electrons are measured from the center of nuclear mass (CNM) (neglecting the mass-polarization term). The asymptotic values of the radial nonadiabatic couplings calculated with the electron origin at the CNM read [15,16]

$$\langle j|\frac{\partial}{\partial R}|k\rangle_\infty = \gamma_k \frac{m}{\hbar^2}[V_j(\infty) - V_k(\infty)]\langle j|d_z^{\mathrm{at}}|k\rangle, \tag{4}$$

with $\langle j|d_z^{\mathrm{at}}|k\rangle$ being the atomic transition dipole moment, m the electron-nuclei reduced mass, and $V_j(R)$ an adiabatic potential. The scalar factors γ_k depend on with which nucleus an active electron is bound in the asymptotic region:

$$\gamma_k = \begin{cases} \gamma_A = -\frac{M_B}{M_A+M_B}, & \text{an electron bound with } A, \\ \gamma_B = +\frac{M_A}{M_A+M_B}, & \text{an electron bound with } B. \end{cases} \tag{5}$$

The nuclei labeled A and B have masses M_A and M_B. See Ref. [16] regarding the rotational couplings. It is seen that some radial nonadiabatic couplings remain nonzero in the asymptotic region, even for the noninteracting model system n + H [17,21]. Note that choosing another electron origin (e.g., at one of the nuclei) does not help to avoid nonzero asymptotic couplings in the CCEs, because the same nonzero values appear in the equations due to new terms in the Hamiltonian [15,21]. According to the BO approach, nonzero couplings provide transitions between molecular states even at $R \to \infty$.

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. The correct asymptotic incoming or outgoing wave functions [1,3,12,15,16]

$$\Psi_j^\pm = \frac{\exp\left(\pm iK_jR_j^{\mathrm{at}}\right)}{R_j^{\mathrm{at}}} Y_{JM_J}(\Theta,\Phi)\,\phi_j \tag{6}$$

are written in another set of Jacobi coordinates and are different from the BO functions (3). The vector $\mathbf{R}_j^{\mathrm{at}}$ connects the centers of mass of the atoms, in contrast to $\mathbf{R}$ which connects the nuclei.

The reprojection method for multielectron collision systems consists of the following. The vector $\mathbf{R}_j^{\mathrm{at}}$ can be written as follows:

$$\mathbf{R}_j^{\mathrm{at}} = \mathbf{R} + \mathbf{b}_j, \tag{7}$$

where the vector $\mathbf{b}_j$ is equal to a sum over all electrons

$$\mathbf{b}_j = \sum_\alpha \gamma_j^\alpha \frac{m_j^\alpha}{M}(\mathbf{r}^\alpha - \gamma_j^\alpha \mathbf{R}), \tag{8}$$

with index α labeling the electrons, $\mathbf{r} = \{\mathbf{r}^\alpha\}$. The value of m_j^α, the electron-nucleus reduced mass in the channel j, is $m_j^\alpha = m_e M_A/(m_e + M_A)$, if the electron α is bound to nucleus A, and $m_j^\alpha = m_e M_B/(m_e + M_B)$, if it is bound to nucleus B, where m_e is the electron mass. M is the reduced mass of the nuclei. The shift $\mathbf{b}_j$ depends on the asymptotic electron rearrangement in the channel j and hence can be different for different channels. It is small, but it does not vanish at infinity and therefore should be taken into account.

A single term in the expansion (1), describing a current in the molecular state k, does not coincide with a single term in Eq. (2), describing a current in the corresponding atomic state [see Eq. (6)]. An incoming or outgoing current in a *single atomic state* is distributed among *several molecular states* and vice versa. Projecting the atomic-channel asymptotic wave functions (6) on the molecular asymptotic wave functions (3) gives

$$\Psi_j^\pm = \frac{\exp(\pm iK_jR)}{R} Y_{JM_J}(\Theta,\Phi) \sum_k t_{kj}^\pm \phi_k(\mathbf{r},\mathbf{R}), \tag{9}$$

where the elements of the matrices $\underline{\underline{t}}^\pm$ represent the reprojection coefficients

$$t_{kj}^\pm = \langle k|\exp\left(\pm iK_j b_{j_z}\right)|j\rangle_\infty. \tag{10}$$

At low collision energies these matrix elements can be approximately evaluated via corresponding atomic transition dipole moments and furthermore, taking into account Eq. (4), via asymptotic values of the derivative couplings calculated in the Jacobi molecular coordinates

$$t_{kj}^\pm = \delta_{kj} \pm \frac{iK_j\hbar^2}{M[V_k(\infty) - V_j(\infty)]}\langle k|\frac{\partial}{\partial R}|j\rangle_\infty, \tag{11}$$

where all values are taken in the asymptotic region. Thus the asymptotic couplings are responsible for the correct asymptotic wave functions in the $\mathbf{r}$, $\mathbf{R}$ coordinates.

A numerical solution of the CCEs for a molecular channel at $R \to \infty$ gives a superposition of the BO asymptotic wave functions in atomic channels. Within the reprojection method, the CCEs with nonzero asymptotic nonadiabatic couplings are integrated numerically from zero up to a large distance R_0, resulting in the R matrix ($\underline{\underline{R}}$). Finally, taking into account Eq. (9), the S matrix is expressed via the R matrix as follows:

$$\begin{aligned}\underline{\underline{S}} = {} & (-1)^J \exp(-i\underline{\underline{K}}R_0)\underline{\underline{K}}^{-1/2}(\underline{\underline{t}}^- + i\underline{\underline{R}}\,\underline{\underline{t}}^-\underline{\underline{K}}) \\ & \times (\underline{\underline{t}}^+ - i\underline{\underline{R}}\,\underline{\underline{t}}^+\underline{\underline{K}})^{-1}\underline{\underline{K}}^{1/2}\exp(-i\underline{\underline{K}}R_0). \end{aligned} \tag{12}$$

The formula (12) is valid for multielectron collisions and turns into the formula derived previously in the limiting one-electron case [15,16]. The difference between the conventional BO method and the reprojection method is in the presence of the $t^\pm$ matrices in the latter instead of the unit matrix in the former [see Eq. (12)]. Implementation of the reprojection method (also called the t-matrix method) is no more complicated than the implementation of the conventional BO method and does not require additional input data if Eq. (11) is used.

Let us consider Li + Na collisions. The adiabatic potentials for the three lowest LiNa($^1\Sigma^+$) states and the radial nonadiabatic couplings between them are plotted in Fig. 1. The *ab initio* potentials are taken from Ref. [23], while the nonadiabatic couplings have been calculated in the present

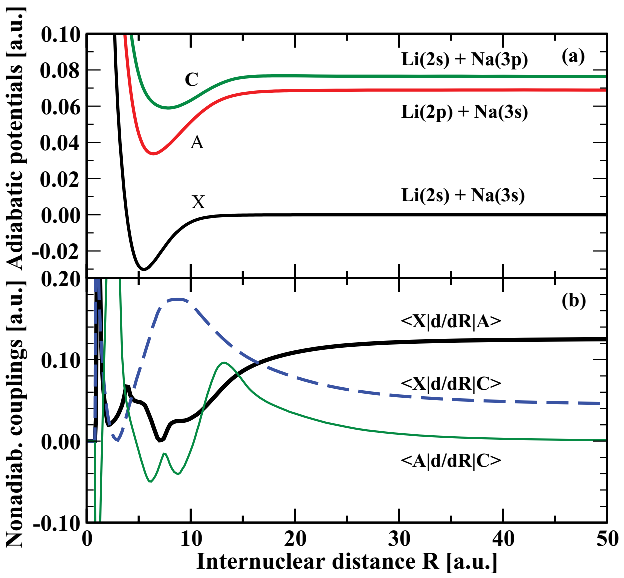

FIG. 1. (Color online) The adiabatic potentials (a) for the three lowest LiNa($^1\Sigma^+$) states (X, A, C) and the radial nonadiabatic couplings (b) between these states.

work by means of the MOLPRO package (the *ab initio* Multi-Reference Configuration Interaction method). Figure 1 clearly shows that two nonadiabatic couplings remain nonzero in the asymptotic region, in agreement with Eq. (4). Their values are not negligible compared with the typical maximum value of ≈0.2 a.u.. Moreover, the X-A coupling has its maximum value in the asymptotic region (except for the range $R < 2$ a.u., which is not important for transitions). Thus no proper cutoff can be found to obtain a reliable result.

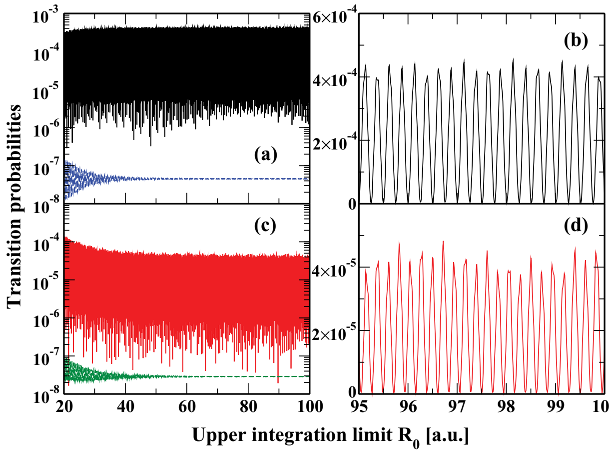

FIG. 2. (Color online) The transition probabilities for $\mathrm{Li}(2s\rightarrow 2p)+\mathrm{Na}(3s)$ (upper panels) and $\mathrm{Li}(2s)+\mathrm{Na}(3s\rightarrow 3p)$ (lower panels) excitation calculated for $E=5$ eV and $J=0$ by means of the conventional BO method (solid lines) and by means of the reprojection method (blue and green dashed lines) as a function of the upper integration limit R_0. The right panel shows the probabilities in an enlarged scale.

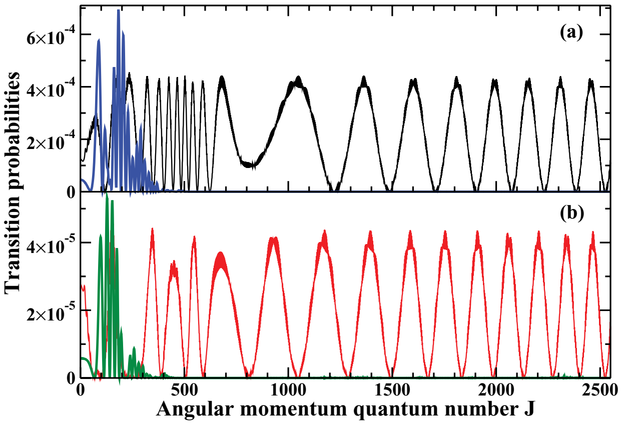

FIG. 3. (Color online) The transition probabilities for $\mathrm{Li}(2s\rightarrow 2p)+\mathrm{Na}(3s)$ (a) and $\mathrm{Li}(2s)+\mathrm{Na}(3s\rightarrow 3p)$ (b) excitation as a function of the total angular momentum quantum number J for $E=5$ eV. The black and red thin lines show the probabilities obtained by means of the conventional BO method; the blue and green thick lines depict the probabilities calculated by the reprojection method and multiplied by 1000 (a) and 200 (b).

The transition probabilities $P_{if}(J,E)$ for the $\mathrm{Li}(2s)+\mathrm{Na}(3s)\rightarrow\mathrm{Li}(2p)+\mathrm{Na}(3s)$ and $\mathrm{Li}(2s)+\mathrm{Na}(3s)\rightarrow\mathrm{Li}(2s)+\mathrm{Na}(3p)$ excitation processes are shown in Fig. 2 for collision energy $E=5$ eV and $J=0$ as a function of the upper integration limit R_0. It is seen that $P_{if}(J,E)$, calculated by means of the conventional BO method, oscillates between roughly zero and relatively large values with increasing R_0. The variations represent nonadiabatic transitions between molecular states at large R and are a consequence of the nonzero asymptotic couplings.

The reprojection method yields transition probabilities which are independent of the upper integration limit, when it is large enough (see Fig. 2). The transition probabilities are several orders of magnitude smaller than those obtained by the conventional BO method and are not equal to averaged values of the latter. Nonadiabatic transitions between *molecular states* still remain at an arbitrary large R, but they do not produce

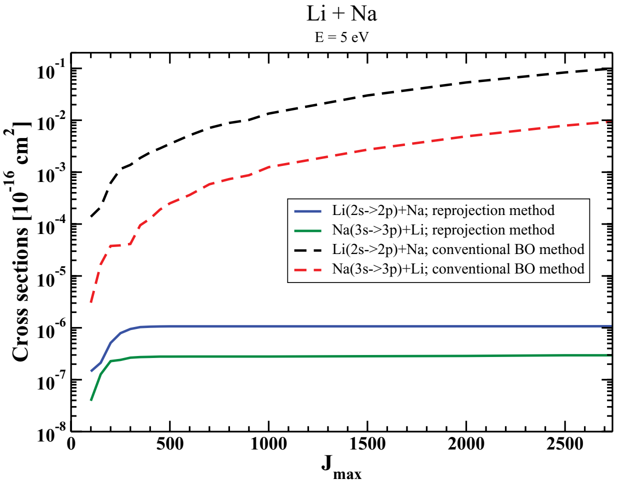

FIG. 4. (Color online) The $\mathrm{Li}(2s\rightarrow 2p)+\mathrm{Na}(3s)$ [black (top dashed) and blue (solid, third from top) lines] and $\mathrm{Li}(2s)+\mathrm{Na}(3s\rightarrow 3p)$ [red (dashed, second from top) and green (bottom solid) lines] excitation cross sections calculated by means of the conventional BO method (dashed lines) and by means of the reprojection method (solid lines) as a function of the maximum value of the angular momentum quantum number J_{max} for $E=5$ eV.

transitions between *atomic states* at large distances. The t matrices correct the S matrix (12). Thus transitions between *atomic states* in the asymptotic region are unphysical, while transitions between *molecular states* in the same region are physical.

The same probabilities $P_{if}(J,E)$ as a function of J are plotted in Fig. 3 for $E = 5$ eV, $R_0 = 500$ a.u.. The conventional BO method gives probabilities that remain oscillating with increasing J due to the nonzero asymptotic couplings: at any J a centrifugal term does not prevent reaching a nonadiabatic region. In contrast to this, 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. Note that the probabilities calculated by the reprojection method and plotted in Fig. 3 are multiplied by 1000 and 200.

The inelastic cross sections are calculated as a sum over J from 0 until infinity or a value $J_{\max}$ where convergence is reached. If the range of J with nonzero transition probabilities is unlimited, as shown in Fig. 3 for the conventional BO method results, convergence cannot be reached and cross sections infinitely increase with increasing upper summation limits $J_{\max}$, as depicted in Fig. 4. Nonzero asymptotic couplings lead to infinite inelastic cross sections obtained with the conventional BO method. A lack of convergence within the conventional BO method at high energies was noticed in Ref. [6].

Within the framework of the reprojection method, the $P_{if}(J,E)$ values are nonzero only within a limited range of J (as it must be), which leads to the convergence of the cross sections with increasing $J_{\max}$ (see Fig. 4), and finally, to the finite values of the inelastic cross sections. All remedies for the ET problem are supposed to lead to the convergence, (see, for example, [6]). Thus the conventional BO method has its limitation both in the formalism and in its applications, while the standard adiabatic BO approach with any ET remedy is free from such limitations.

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 paradoxes such as infinite inelastic cross sections even at low collision energies. The ET effects are severe for all kinds of collisions. The reprojection method takes into account nonzero asymptotic couplings and distinguishes asymptotic currents in molecular and atomic-state channels.

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