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Approach to electron translation in low-energy atomic collisions

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We consider two conceptional problems that arise in the quantum-mechanical calculation of inelastic atomic collisions. The definition of the coupling matrix elements, which govern the inelastic transitions, seems to be ambiguous and the matrix elements can remain nonzero as the internuclear distance goes to infinity. We show that there is no ambiguity in the coupled equations, which describe inelastic collisions, and we demonstrate that the asymptotic couplings are required for a correct description of the asymptotic part of the scattering wave function. We develop on this basis a straightforward and simple procedure to deal with the asymptotic couplings in the framework of a full quantum approach and we apply it to a simple example of H+Na collisions. [S1050-2947(99)07402-8]

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I. INTRODUCTION

Inelastic collisions between low energy atoms (or atoms and ions) govern the behavior of gaseous media in many cases of practical importance, e.g., laser media or nonlocal thermodynamic equilibrium stellar atmospheres. It is therefore highly desirable to possess a reliable method for the numerical calculation of the corresponding cross sections. The appropriate procedure was formulated by Mott and Massey [1]. The problem is attacked in two steps: The first one deals with the motion of the electrons assuming space fixed nuclei and the second one with the motion of the nuclei and the transitions between electronic states. The first step (''quantum chemical'' treatment) yields the potential curves of the collisional quasimolecule and a number of coupling matrix elements. These data enter into a set of coupled-channel equations, which have to be solved in the second step. This seems to be a straightforward procedure, but one encounters several problems in the practical application. First, the coupling matrix elements, which cause the electronic transitions, seem to be defined in an ambiguous manner. This has been discussed repeatedly [2,3] and is often interpreted as a conceptional shortcoming of the entire method (see, for example, Ref. [2], p. 112). We will show in Sec. II that there is actually no ambiguity at all. The arguments that we use for this point are not new (see Refs. [4,5]), but we work out this point in some detail because it is widely unknown. A much more severe problem is that the coupling matrix elements can happen to remain nonzero as the internuclear distance goes to infinity, suggesting inelastic transitions under the influence of a collision partner at an arbitrarily large distance. It is well known [6,7] that the asymptotic couplings are required to correct for a neglect that is usually made implicitly: The nucleus of an atom and its center of mass are assumed to coincide. Using this idea, we develop a method to deal with the asymptotic couplings in a full quantum approach (Sec. III) and we apply it to a realistic example of H+Na collisions (Sec. IV).

High-energy inelastic collisions are usually treated assuming a classical trajectory for the motion of the nuclei [classical trajectory (CT) methods [2]]. These methods encounter similar problems. In the framework of the CT approach, there exists a well established remedy, the inclusion of ''electron translation factors'' (ETF's) [2,5,7,8] into the expansion of the wave function. CT methods are limited to high (typically keV) collision energies however. They are no longer valid in the eV region, that is, for the applications discussed above. Low-energy inelastic collisions require a full quantum-mechanical treatment, which includes the degrees of freedom of the heavy particle motion. We will continue to denote the undesired properties of the coupling matrix elements as ''electron translation problems,'' as is familiar from the CT approach. Unfortunately, in a quantum-mechanical description, ETF's do not provide a practical way to deal with the electron translation problem [5]. Delos and Thorson [6,7] showed that the use of state-specific coordinates in the expansion of the wave function provides a possibility to deal with the electron translation problem in a full quantum formulation; a summary can be found in Ref. [2]. More recent approaches rely on the use of special coordinates. Solov'ev and Vinitsky [9] and Macek *et al.* [10] proposed the use of hyperspherical coordinates, which are indeed frequently used in neighboring fields of research; see, for instance, Refs. [11,12]. Robert and Baudon [13] drew attention to the suitability of Eckart coordinates. The full quantum approaches were reviewed by McCarroll and Crothers [5], who discuss their interrelation and their limitations. All methods are conceptionally rather complicated, at least when compared to Masseys original concept, and they have not found wide application to atom-atom or ion-atom scattering problems so far (for examples, see Refs. [14,15]). The present approach follows Masseys original formulation. We use the simplest adequate coordinates and the original form of the coupled equations. We use state-specific coordinates only to find the correct interpretation of the asymptotic wave function. It turns out that, in contrast to previous assertions [5], it is possible to extract a meaningful *S* matrix from the solution of the coupled equations, even when there are

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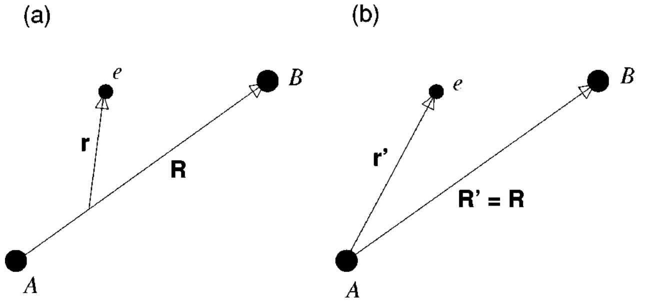

FIG. 1. (a) Jacobi coordinates for the three-particle system used in the present work. *A* and *B* are the nuclei and *e* denotes the active electron. **r** is measured from the center of mass of *A* and *B*. (b) An alternative coordinate system. This choice of coordinates leads to exactly the same set of coupled equations as that of (a).

nonvanishing asymptotic couplings.

The goal of the present paper is to introduce the approach in its simplest form. We consider therefore a special situation: a heteronuclear system with only one active electron; we consider only radial couplings and we neglect a number of small terms. Not all of these assumptions are necessary, but we postpone the corresponding discussion until some practical experience with the procedure will have been gained.

II. COUPLED EQUATIONS

We consider the case of two nuclei A and B with masses M_A and M_B and one electron (mass m_e). It is of course expected that a case with one active electron and a number of inactive electrons, which accompany one or the other of the nuclei, is represented in a reasonable way by this approach as well. H+Na collisions, which are considered below as an example, can be treated in this way: The inner Na electrons up to the $2p$ shell are considered as inactive and the ensemble of the Na nucleus and the ten inactive electrons is treated as a single particle, and similarly for the H atom. We describe the system in Jacobi coordinates [7]. Let $\mathbf{R}$ be the vector connecting the nuclei and $\mathbf{r}$ the coordinate of the active electron, measured from the center of mass of the nuclei [Fig. 1(a)]. The Hamiltonian for the entire system is

$$H=-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial\mathbf{R}^2}-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial\mathbf{r}^2}+H_{int}(\mathbf{r},\mathbf{R}). \tag{1}$$

The kinetic-energy term for the center of mass of the entire system can be separated off and has therefore been omitted. M is the reduced mass of the nuclei and m that of the electron, formed with the sum of the nuclear masses. The definitions of the reduced masses are collected in Table I. H_{int} contains all interactions; for simplicity, we consider at present only electrostatic interactions. We call

$$H_{el}=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial\mathbf{r}^2}+H_{int} \tag{2}$$

the electronic Hamiltonian; it depends on $\mathbf{R}$ as a parameter. The wave function for the total system is expanded as

$$\Psi(\mathbf{r},\mathbf{R})=\sum_j G_j(\mathbf{R})\phi_j(\mathbf{r},\mathbf{R}). \tag{3}$$

The ϕ_j form a set of suitable electronic basis functions; they are allowed to vary with $\mathbf{R}$. After multiplying the stationary Schrödinger equation $(H-E)\Psi=0$ by ϕ_k^* and integrating over the electron coordinate, one obtains a set of coupled-channel equations for the functions G_j,

$$\left[-\frac{\hbar^2}{2M}\frac{d^2}{d\mathbf{R}^2}+V_j(\mathbf{R})-E\right]G_j$$
$$=-\sum_{k\neq j}\left\langle\phi_j\left|H_{el}-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial\mathbf{R}^2}\right|\phi_k\right\rangle G_k$$
$$+\frac{\hbar^2}{M}\sum_k\left\langle\phi_j\left|\frac{\partial}{\partial\mathbf{R}}\right|\phi_k\right\rangle\frac{dG_k}{d\mathbf{R}}. \tag{4}$$

The matrix elements denote integrals over the electron coordinate. They are functions of $\mathbf{R}$, in general. E is the total energy and V_j are the potentials,

$$V_j(\mathbf{R})=\left\langle\phi_j\left|H_{el}-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial\mathbf{R}^2}\right|\phi_j\right\rangle. \tag{5}$$

It has often been argued that the matrix elements $\langle\phi_j|\partial/\partial\mathbf{R}|\phi_k\rangle$ and in particular the radial components $\langle\phi_j|\partial/\partial R|\phi_k\rangle$ depend on the choice of the origin for the electron coordinates and therefore the coupled equations are ambiguous. The first part of this statement is indeed true; the second part is wrong.

We consider the coordinates $\mathbf{r}'$ and $\mathbf{R}'$ shown in Fig. 1(b) as an alternative. It is easily shown that

TABLE I. Definitions of the reduced masses and the scaling factors γ_j. The channel specific masses m_j and M_j are required only 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*	$\frac{m_e(M_A+M_B)}{m_e+M_A+M_B}$	$\frac{M_AM_B}{M_A+M_B}$	$\frac{m_eM_A}{m_e+M_A}$	$\frac{(M_A+m_e)M_B}{m_e+M_A+M_B}$	$-\frac{M_B}{M_A+M_B}$
Electron travels with nucleus *B*			$\frac{m_eM_B}{m_e+M_B}$	$\frac{(M_B+m_e)M_A}{m_e+M_A+M_B}$	$\frac{M_A}{M_A+M_B}$

$$\left\langle \phi_j \left| \frac{\partial}{\partial \mathbf{R}} \right| \phi_k \right\rangle = \left\langle \phi_j \left| \frac{\partial}{\partial \mathbf{R}'} \right| \phi_k \right\rangle + \frac{M_B}{M_A+M_B} \left\langle \phi_j \left| \frac{\partial}{\partial \mathbf{r}'} \right| \phi_k \right\rangle . \tag{6}$$

This is embarrassing because $\mathbf{R}=\mathbf{R}'$, but the behavior is normal for partial derivatives. The matrix elements of $\partial/\partial\mathbf{R}$ indeed change their values when another choice is made for the origin of the electron coordinates (for numerical examples see, e.g., Ref. [3]).

However, in the present context, the choice for the origin of the electron coordinates was made before writing down Eq. (1). The differentiations in Eq. (1) as well as in the matrix elements in question are partial derivatives, which change their meaning when another set of coordinates is used. Therefore, as long as Eq. (4) is derived from Eq. (1), the use of coordinates other than **r** and **R** for the calculation of the matrix elements is prohibited. We consider, therefore, the Hamiltonian in the new coordinates. One finds

$$H = -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial \mathbf{R}'^2} - \left(\frac{\hbar^2}{2m} + \frac{\hbar^2 M_B}{2(M_A+M_B)M_A} \right) \frac{\partial^2}{\partial \mathbf{r}'^2} - \frac{\hbar^2}{M_A}\frac{\partial^2}{\partial \mathbf{R}'\partial \mathbf{r}'} + H_{int} . \tag{7}$$

When the coupled equations are rederived, using the new form of the Hamiltonian together with the old basis functions, one obtains a result that differs from Eq. (4) in two ways: (i) The coupling matrix elements must be calculated with the primed coordinates and (ii) there appear a number of new terms, due to the new terms in the Hamiltonian. The detailed calculation is straightforward; it turns out that the corrections cancel each other completely, such that the coupled equations obtained with unprimed and primed coordinates are completely identical. For instance, the matrix elements of $\partial/\partial\mathbf{R}$ are different with primed and unprimed coordinates, as expressed by Eq. (6). This difference is compensated for, however, by an additional term, which arises from the mixed differentiation term in Eq. (7). The same sort of compensation occurs for the double differentiation matrix element in the coupled equations. The argument is easily generalized: Any origin of the electron coordinates on the internuclear axis leads to the same coupled equations [4]. We conclude that there is no ambiguity for the coupling terms to be used in the coupled equations. When one uses the form of Eq. (4), all derivative matrix elements have to be calculated with the electron coordinates measured from the center of mass of the nuclei. It should be emphasized that this conclusion is in contrast to the common usage [16]. One often tries to avoid nonzero asymptotic couplings. This favors in many cases a coordinate origin at one of the nuclei as in Fig. 1(b). The use of coupling matrix elements in Eq. (4), which are calculated with such coordinates, is wrong however.

We use the coordinates **r** and **R** in what follows and we introduce polar coordinates R,Θ, and Φ for **R**. We assume that only electronic Σ states ϕ_j need to be considered. The wave function then takes the form [17]

$$\Psi(\mathbf{r},\mathbf{R}) = Y_{LM_L}(\Theta,\Phi) \sum_j \frac{F_j(R)}{R} \phi_j(\mathbf{r},\mathbf{R}). \tag{8}$$

Y_{LM_L} are the spherical harmonics and L and M_L are the quantum numbers for the angular momentum. The radial functions F_j have to obey a set of equations, which can be derived from Eq. (4),

$$\left[-\frac{\hbar^2}{2M}\frac{d^2}{dR^2} + V_j(R) + \frac{\hbar^2}{2M}\frac{L(L+1)}{R^2} - E \right] F_j = -\sum_{k\neq j} \left\langle \phi_j \left| H_{el} - \frac{\hbar^2}{2M}\frac{\partial^2}{\partial \mathbf{R}^2} \right| \phi_k \right\rangle F_k + \frac{\hbar^2}{M}\sum_k \left\langle \phi_j \left| \frac{\partial}{\partial R} \right| \phi_k \right\rangle R \frac{d}{dR}\frac{F_k}{R}. \tag{9}$$

The angular components of the matrix elements $\langle \phi_j | \partial/\partial\mathbf{R} | \phi_k \rangle$ do not appear anymore because they do not couple Σ states with each other. The matrix elements in Eq. (9) depend on R, but not on the angular coordinates. $V_j(R)$ is the same quantity $V_j(\mathbf{R})$ as before; it depends on the distance R alone now and is written correspondingly. Equations (8) and (9) are the basis of the following section.

III. ASYMPTOTIC COUPLINGS, ASYMPTOTIC WAVE FUNCTION, AND THE *S* MATRIX

Equations (8) and (9) seem to have a straightforward interpretation. When one uses, for $R\to\infty$, atomic eigenstates for the electronic basis states ϕ_j, the single terms in Eq. (8) are expected to represent, at large R, the free motion of the atoms in one or the other of their eigenstates. Only one of the terms should contain an incoming wave. Outgoing waves in the other terms occur because the right-hand side in Eq. (9) is nonzero. They represent inelastic transitions. This interpretation is not correct however.

Consider a basis function ϕ_j, which becomes an atomic eigenfunction at large internuclear distance. It travels with one of the nuclei without changing its appearance; it therefore has the form

$$\phi_j = f_j(x,y,z-\gamma_j R) \quad \text{as} \quad R\to\infty. \tag{10}$$

γ_j is a channel-specific scaling factor; see Table I. x, y, and z are the body-fixed components of the electron coordinate **r** such that the z and **R** directions coincide. It is easily shown that under these conditions

$$\left\langle \phi_j \left| \frac{\partial}{\partial R} \right| \phi_k \right\rangle \to -\gamma_k \left\langle \phi_j \left| \frac{\partial}{\partial z} \right| \phi_k \right\rangle \quad \text{as} \quad R\to\infty. \tag{11}$$

The terms on the right-hand side are not zero in general. Therefore, the coupling matrix elements $\langle \phi_j | \partial/\partial R | \phi_k \rangle$ can remain nonzero as $R\to\infty$; see Fig. 3 for examples. Together with the tentative interpretation given above, this would lead to the conclusion that electronic transitions occur at arbitrarily large distance R. As this cannot be true, the tentative interpretation must be wrong.

Equation (11) shows that the derivative coupling matrix elements in Eq. (9) do not go to zero at large R in general. It is therefore necessary to discuss the asymptotic behavior of the wave functions more accurately. We request that the basis states ϕ_j become atomic eigenstates at large R,

$$H_{el}^{at}\phi_j=V_j\phi_j \quad \text{for} \quad R\to\infty. \tag{12}$$

The atomic Hamiltonian H_{el}^{at} is similar to H_{el} in Eq. (2), but it has the atomic reduced mass m_j in the kinetic-energy term in place of m. m_j is different for atomic states traveling with nucleus A or B; for the definition of m_j see Table I. The atomic eigenfunctions have the form of Eq. (10). This can be used to show that

$$H_{el}^{at}\phi_j=\left[H_{el}-\gamma_j^2\frac{\hbar^2}{2M}\frac{\partial^2}{\partial\mathbf{r}^2}\right]\phi_j \quad \text{for} \quad R\to\infty \tag{13}$$

and

$$\langle\phi_k|H_{el}^{at}|\phi_j\rangle=\left\langle\phi_k\left|H_{el}-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial\mathbf{R}^2}\right|\phi_j\right\rangle \quad \text{for} \quad R\to\infty. \tag{14}$$

The energies V_j defined in Eq. (12) therefore coincide exactly with $V_j(\infty)$ from Eq. (5). Similarly, the first sum on the right-hand side of Eq. (9) is identical to zero at large R. It will turn out, however, that the distinction between H_{el} and H_{el}^{at} is without much importance.

Next we consider the free motion of the atoms in atomic eigenstates. This can be written for large R as incoming or outgoing spherical waves of the form

$$\Psi_j^{\pm}=Y_{LM_L}(\Theta_j,\Phi_j)\frac{\exp(\pm iK_jR_j)}{R_j}\phi_j \quad \text{for} \quad R\to\infty. \tag{15}$$

R_j, Θ_j, and Φ_j are polar coordinates for the vector

$$\mathbf{R}_j=\mathbf{R}+\gamma_j\frac{m_j}{M}\,(\mathbf{r}-\gamma_j\mathbf{R}), \tag{16}$$

which connects the center of mass of the atom with the free nucleus. $\mathbf{R}_j$ is a channel-specific coordinate, which is different when the electron travels with A or B, respectively. The wave numbers K_j are given by

$$K_j=\sqrt{(2M_j/\hbar^2)[E-V_j(\infty)]}. \tag{17}$$

The channel-specific reduced masses m_j and M_j are listed in Table I.

The $\Psi_j^{\pm}$ in Eq. (15) are very similar to a single term in Eq. (8). We need some order of magnitude considerations in order to make this statement more precise. We consider in particular large distances, where the basis functions have the form of Eq. (10); the operation $\partial/\partial R$ then multiplies the basis function typically by a factor $1/a$, where a is the typical dimension of the atom.[1] The diagonal and off-diagonal matrix elements of H_{el} have the order of magnitude $\hbar^2k^2/2m \approx\hbar^2/2ma^2$, with k the typical electron wave number. The atomic kinetic energy can be estimated as $\hbar^2K^2/2M$, with K the typical atomic wave number. We consider here collision energies, which have the same order of magnitude as the electron energy. K/k is therefore of the order of $\sqrt{M/m}$. The terms on the left-hand side of Eq. (9) all have the same order of magnitude $(\hbar^2/2ma^2)F_j$. The coupling terms with H_{el} on the right-hand side are of the order of $(\hbar^2/2ma^2)F_k$. The terms with the $\partial/\partial R$ matrix elements are smaller by a factor of the order of $\sqrt{m/M}$. The terms with the matrix elements of $\partial^2/\partial\mathbf{R}^2$ and the double derivative terms in the definition of the potentials [Eq. (5)] are smaller by a factor of the order of m/M than the leading terms. The difference between $\mathbf{R}$ and $\mathbf{R}_j$ is of the order of $(m/M)a$; see Eq. (16). Upon multiplication with K_j, this contributes a correction of the order of $\sqrt{m/M}$ in the exponent in Eq. (15). We consider Eq. (15) for $R\to\infty$ in an approximation, in which only terms of the first order in $\sqrt{m/M}$ are retained. It turns out that out of the differences between Eq. (15) and the single terms in Eq. (8), only the appearance of R_j in place of R in the exponential in Eq. (15) contributes in this order. Expanding the exponential correspondingly, one obtains

$$\Psi_j^{\pm}=Y_{LM_L}(\Theta,\Phi)\frac{\exp(\pm iK_jR)}{R}\times\left[1\pm iK_j\gamma_j\frac{m}{M}(z-\gamma_jR)\right]\phi_j \quad \text{for} \quad R\to\infty. \tag{18}$$

After expanding the product $(z-\gamma_jR)\phi_j$ in terms of the ϕ_k, we arrive at

$$\Psi_j^{\pm}=Y_{LM_L}(\Theta,\Phi)\sum_k\frac{\exp(\pm iK_jR)}{R}t_{kj}^{\pm}\phi_k \quad \text{for} \quad R\to\infty \tag{19}$$

with R-independent matrices

$$t_{kj}^{\pm}=\delta_{kj}\pm iK_j\gamma_j\frac{m}{M}\langle\phi_k|z-\gamma_jR|\phi_j\rangle|_{R\to\infty}. \tag{20}$$

The ϕ_j for $R\to\infty$ are eigenstates of the atomic parity operator in general. The diagonal matrix elements of $z-\gamma_jR$ are therefore zero. Using the commutation relation $[H_{el},z] =-(\hbar^2/m)(\partial/\partial z)$, it can further be shown that the off diagonal elements of $t_{kj}^{\pm}$ are related, to the first order in $\sqrt{m/M}$, to the asymptotic values of the coupling matrix elements [Eq. (11)]

$$\langle\phi_k|\partial/\partial z|\phi_j\rangle=(m/\hbar^2)(V_j-V_k)\langle\phi_k|z-\gamma_jR|\phi_j\rangle \quad \text{for} \quad R\to\infty. \tag{21}$$

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[1] The present order of magnitude discussion applies to all distances R provided this estimate is valid. It may be necessary to replace an adiabatic basis by another (e.g., diabatic) one, when this is desired.

The $\Psi_j^{\pm}$ in Eq. (19) continue to represent the free motion of the atoms in the jth atomic eigenstate. They are now written in the form of the original expansion (8) and they have therefore an unexpected appearance: The sum not only consists of a leading term with the state ϕ_j, but it contains additional terms with other electronic states, which are smaller typically by a factor $Ka(m/M) \approx \sqrt{m/M}$. The additional terms are obviously required to correct for the use of the inadequate coordinates.

In the general case, the wave function at large R is a superposition of the $\Psi_j^{\pm}$,

$$\Psi = \sum_j K_j^{-1/2} [a_j^+ \Psi_j^+ + a_j^- \Psi_j^-]. \tag{22}$$

The factor $K_j^{-1/2}$ has been introduced because in this way the $|a_j^{\pm}|^2$ represent the incoming and outgoing currents in the different atomic states. Writing Ψ in the form of Eq. (8), the radial functions at large R are found to be

$$F_j = \sum_k K_k^{-1/2} [t_{jk}^+ a_k^+ \exp(iK_k R) + t_{jk}^- a_k^- \exp(-iK_k R)] \quad \text{for } R \to \infty. \tag{23}$$

One shows easily that these F_j satisfy the coupled channel equations (9) for large R to the first order in $\sqrt{m/M}$. As this is true for any arbitrary choice of the $a_j^{\pm}$, Eq. (23) is the general form for the asymptotic behavior of the solutions. Note that we refer here to the coupled-channel equations in the correct form, which possess nonvanishing asymptotic couplings.

To summarize so far, Eq. (23) represents the asymptotic form for the solutions of the coupled equations. The corresponding wave function can be written in the form of Eq. (22), where every single term represents the free motion of an atom in an atomic eigenstate. The factors $a_j^{\pm}$ represent the probability amplitudes to find the atoms in the corresponding states. Equation (23) therefore constitutes the relation between the solutions F_j of the coupled-channel equations and the true probability amplitudes. The remaining task is to find the $a_j^{\pm}$ once the coupled equations have been solved.

Suppose that the coupled-channel equations (9) 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 the form of Eq. (23). Of course, the solutions have to obey the usual boundary conditions $F_k \to 0$ as $R \to 0$. All solutions with this property are characterized by a matrix R_{jk} that relates the values and the derivatives of the radial functions at the upper integration limit,

$$F_j = \sum_k R_{jk} \frac{dF_k}{dR} \quad \text{at } R_0. \tag{24}$$

The R matrix forms a convenient and well established way [18–20] to express all properties of the solutions $F_j(R)$, which are needed for their continuation to the asymptotic region $R > R_0$. We describe in the Appendix how we obtain the R_{jk} from a numerical treatment of the coupled equations.

Upon a comparison of Eq. (24) with Eq. (23), one finds that the amplitudes a^+ and a^- are related by an S matrix,

$$a_j^+ = (-1)^{L+1} \sum_k S_{jk} a_k^-, \tag{25}$$

which can be expressed by the R matrix; the factor $(-1)^{L+1}$ appears here only to match the usual definition of the S matrix. For better readability, the relation is given in matrix notation. $\underline{R}$, $\underline{S}$, 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 $\exp(-iK_jR)$:

$$\begin{aligned} \underline{S} = {} & (-1)^L \exp(-i\underline{K}R_0) \underline{K}^{1/2} (\underline{t}^+ - i\underline{R}\ \underline{t}^+ \underline{K})^{-1} \\ & \times (\underline{t}^- + i\underline{R}\ \underline{t}^- \underline{K}) \underline{K}^{-1/2} \exp(-i\underline{K}R_0). \end{aligned} \tag{26}$$

Equation (26) is our central result. The $a_j^{\pm}$ are the correct incoming and outgoing amplitudes. They are related to each other by the S matrix. Equation (26) shows how the correct S matrix is obtained from the solution of the coupled equations, which are expressed by the matrix $\underline{R}$. When one replaces the t matrices by a unit matrix (this means that one disregards the difference between the atomic and nuclear coordinates), Eq. (26) reduces to the relation

$$\begin{aligned} \underline{S} = {} & (-1)^L \exp(-i\underline{K}R_0) \underline{K}^{1/2} (\underline{1} - i\underline{R}\ \underline{K})^{-1} \\ & \times (\underline{1} + i\underline{1}\ \underline{K}) \underline{K}^{-1/2} \exp(-i\underline{K}R_0), \end{aligned} \tag{27}$$

where $\underline{1}$ is the unit matrix. This expression for $\underline{S}$ is valid in the absence of asymptotic couplings, that is, it is the normal relation between the R and S matrices. A comparison of the two expressions for $\underline{S}$ shows that the present procedure is only slightly more complicated than the normal procedure to obtain the S from the R matrix.

Equation (26) is not convenient for numerical applications because in order to find $\underline{R}$ one has to integrate the coupled equations from zero to a very large distance. This is especially due to the presence of the centrifugal term in Eq. (9), which can be neglected only at very large distance. Suppose that there exists a smaller distance R_1 beyond which the electronic states and the coupling matrix elements are given with sufficient accuracy by their limiting forms as expressed by Eqs. (12) and (11). Neglecting again terms of the order of m/M, a WKB approximation to the solution of Eq. (9) at $R > R_1$ is

$$F_j = \sum_k \kappa_k^{-1/2} [\tau_{jk}^+ a_k^+ \exp\{i\Phi_k(R)\} + \tau_{jk}^- a_k^- \exp\{-i\Phi_k(R)\}], \tag{28}$$

with

$$\tau_{kj}^{\pm} = \delta_{kj} \pm i\kappa_j \gamma_j \frac{m}{M} \langle \phi_k | z - \gamma_j R | \phi_j \rangle,$$

$$\Phi_j(R) = -\int_R^{\infty} (\kappa_j - K_j) dR' + K_j R,$$

and

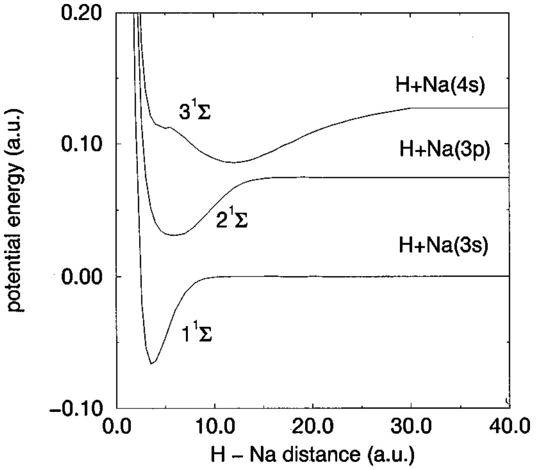

FIG. 2. Three lowest $^1\Sigma$ potential curves of the NaH system that we use for our model calculation.

$$\kappa_j(R)=\sqrt{(2M_j/\hbar^2)[E-V_j^{eff}(R)]}.$$

V_j^{eff} is the potential plus the centrifugal potential. Equation (28) is a good approximation as long as the conditions

$$d\kappa_j/dR \ll \kappa_j^2, \quad j=1,\ldots, \tag{29}$$

hold; these are the usual WKB conditions [21]. The WKB approximation holds under most conditions of practical interest and Eq. (28) is expected to be practically as exact for $R>R_1$ as Eq. (23) is for $R\to\infty$. As $R\to\infty$, Eq. (28) becomes identical to Eq. (23) with the same coefficients $a_j^{\pm}$. It can therefore be used to calculate the S matrix from an R matrix, which relates the F_j and the dF_k/dR as before, but at a much smaller distance R_1. One finds

$$\underline{S}=(-1)^L\exp(-i\underline{\Phi})\underline{\kappa}^{1/2}(\underline{\tau}^+-i\underline{R}\ \underline{\tau}^+\underline{\kappa})^{-1}$$
$$\times(\underline{\tau}^-+i\underline{R}\ \underline{\tau}^-\underline{\kappa})\underline{\kappa}^{-1/2}\exp(-i\underline{\Phi}). \tag{30}$$

$\exp(-i\underline{\Phi})$, $\underline{\kappa}$, and $\underline{\kappa}^{\pm 1/2}$ are diagonal matrices with elements $\exp[-i\Phi_j(R_1)]$, $\kappa_j(R_1)$, and $\kappa_j(R_1)^{\pm 1/2}$ and the matrices $\underline{\tau}^{\pm}$ have the elements $\tau_{kj}^{\pm}(R_1)$.

IV. A NUMERICAL EXAMPLE

We performed numerical calculations for the inelastic process

$$\mathrm{H}(1s)+\mathrm{Na}(3s)\to\mathrm{H}(1s)+\mathrm{Na}(3p).$$

The process is possible with collision pairs forming both a singlet and a triplet collisional quasimolecule. In the singlet system, one basic mechanism is a radial coupling associated with the pseudocrossing of two potential curves [22]. The three lowest adiabatic $^1\Sigma$ potentials and the corresponding $\partial/\partial R$ coupling matrix elements are shown in Figs. 2 and 3. The double derivative matrix elements are obtained on the basis of a reasonable model; the details [22] are without importance here. Note the nonzero asymptotes of the single derivative matrix elements, which occur because the electron coordinate was measured from the nuclear center of mass, according to the conclusions at the end of Sec. II. The three-state coupled system was solved numerically from $R=0$ to an upper integration limit R_1 varying between 17 and 40 a.u. The numerical result was expressed by the R matrix. The S matrix was then calculated from Eq. (30). Figure 4 demonstrates what happens when we vary the upper integration limit R_1. When the S matrix is calculated correctly (thick lines), the result is practically independent of R_1, as expected for a physically meaningful result, provided R_1 is large enough. The variation observed for R_1 values below 20 a.u. arise because here the $\partial/\partial R$ couplings begin to deviate from their asymptotic values. An alternative is to use Eq. (30) with $\underline{\tau}^{\pm}$ replaced by the unit matrix. This gives a relation similar to Eq. (27); the procedure corresponds to a situation in which the asymptotic couplings are included in the numerical part of the calculation from small R to R_1 but are omitted at $R>R_1$. Results computed in this way show oscil-

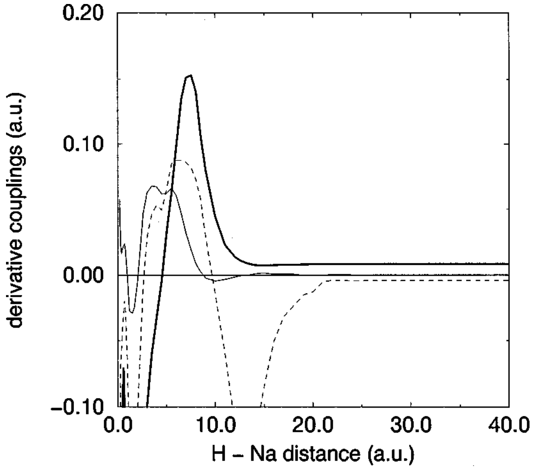

FIG. 3. Radial coupling matrix elements $\langle 1^1\Sigma|\partial/\partial R|2^1\Sigma\rangle$ (thick solid line), $\langle 1^1\Sigma|\partial/\partial R|3^1\Sigma\rangle$ (thin solid line), and $\langle 2^1\Sigma|\partial/\partial R|3^1\Sigma\rangle$ (dashed line) for the HNa system. Note that two of the coupling matrix elements have nonzero asymptotes.

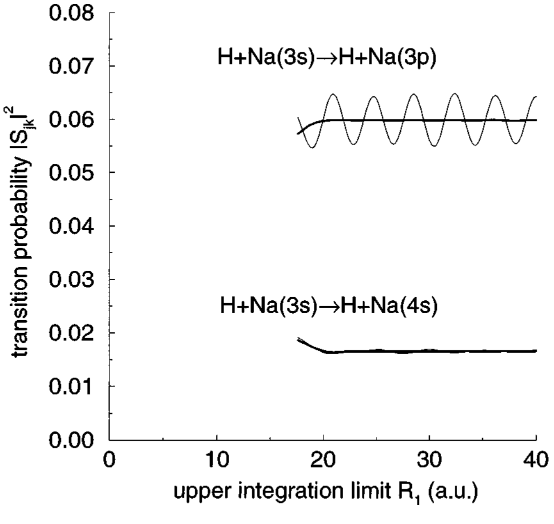

FIG. 4. Squares of the S-matrix elements $S_{3s,3p}$ and $S_{3s,4s}$, calculated with a variable upper integration limit R_1 ($E=50$ eV, $L=160$). The $|S|^2$ correspond to the outgoing currents in the excited channels H+Na($3p$) or H+Na($4s$), populated from the initial state H+Na($3s$). Thick lines, results obtained with the correct formula (30), thin lines, results obtained with $\underline{\tau}^{\pm}=\underline{1}$, that is, without an electron translation correction.

lations as a function of R_1. They represent electronic transitions between ground and excited states at large internuclear distance. However, this is obviously only due to the inadequate way in which $\underset{\sim}{S}$ is obtained from $\underset{\sim}{R}$. Transitions at large distances do not appear with the correct formula (30). The results in Fig. 4 were obtained for a collision energy of 50 eV and $L=160$. Other energies between 5 and 500 eV and other angular momenta were used as well; the general behavior remains the same.

V. DISCUSSION

The present work has two main results.

(i) We emphasize that there is an unambiguous definition for the coupling matrix elements that appear in the coupled-channel equations. The definition is different from what has been used in many cases in the past. However, when we use for HNa coupling matrix elements in Eq. (9), which are calculated with the electron coordinates measured from the Na atom, the numerical results differ only slightly from those of the correct treatment. We feel that in many cases the rigorous treatment will not lead to considerable changes.

(ii) The correct coupling matrix elements remain nonzero for large internuclear distance in general. We show how to deal with the asymptotic couplings in the frame of a full quantum-mechanical treatment. The present approach makes use of a number of approximations or simplifications.

(a) The method is of practical use only for a finite system of basis states ϕ_j. Correspondingly, the effects of the electron translation are treated here in terms of a truncated basis. In the numerical example, only one additional state Na($3p$) is used for the corresponding correction of the Na($3s$) state. The present approach is certainly correct in the limit of a complete basis. In order to estimate how many expansion terms are required for a good approximation, we consider once more Eq. (18). The coordinate correction occurs by the expansion of the product $(z-\gamma_j R)\phi_j$ in terms of the functions ϕ_k. The expansion coefficients are the dipole matrix elements $\langle\phi_k|(z-\gamma_j R)|\phi_j\rangle$, which are well known for many cases. For instance, the dipole matrix element between the $3s$ and $4p$ states in Na is by about an order of magnitude smaller than that between $3s$ and $3p$, indicating that the approach of Sec. IV might already be sufficient to achieve a reasonable description of electron translation in the $3s$ state. One might argue that electron translation effects are covered only in the asymptotic region by the present approach. This is not true because a sufficiently large basis will include all effects of this type and like for the asymptotic region, one can argue that a small number of basis states might be sufficient.

(b) There are situations in which the use of a finite basis is not adequate. In particular, ionization processes cannot be treated rigorously in such a way and they are therefore outside the range of applicability of the present approach. Collisions that involve a negative ion in the entrance or the exit channel provide another example. Negative ions possess usually only one bound state. The present approach provides a way to calculate a meaningful S matrix in these cases, but when one wishes to discuss effects explicitly, which are due to the translation of the bound electron, it would be necessary to include continuum states in the expansion (19).

(c) The results are correct only to the first order in $\sqrt{m/M}$; it is remarkable to what accuracy we obtain constant values for $|S_{jk}|^2$ in Fig. 4 already on the basis of this approximation. There remain indeed slight variations, which are too small, however, to be visible in the figure. For instance, the upper thick line in Fig. 4 shows residual oscillations with amplitude 5×10^{-5}, superimposed on the average value of about 0.06. It appears that the neglect of terms of order m/M is very well justified.

(d) We disregard rotational coupling. This is legitimate for a model calculation. It is well known, however, that in the framework of CT approaches, electron translation effects concern not only radial but also rotational couplings [23]. There are long-range contributions in the rotational coupling terms, which have the same origin as the asymptotic radial couplings; in contrast to the leading radial terms, they decrease as R^{-1} for $R\to\infty$. The terms occur also in the framework of the present full quantum treatment. We are working on a corresponding extension of the general theory.

(e) We have been considering the case of a heteronuclear system with only one active electron.

The present method is applicable to collisions without and with charge exchange. The data that are required to set up the coupled equations and to calculate the S matrix are the matrix elements of the electronic Hamiltonian (in the adiabatic basis only the potentials V_j) and the coupling matrix elements $\langle\phi_k|\partial/\partial R|\phi_j\rangle$. They can be obtained from standard quantum chemical programs; see, e.g., Ref. [24]; care must be taken to calculate the single derivative coupling matrix elements with the correct origin of the electron coordinate, as discussed at the end of Sec. II. Note that the t-matrix elements, which are required for the correct computation of the S matrix, can be obtained from these data. It is not necessary to calculate any extra quantities to take account of electron translation. The definition of the potentials (5) and the asymptotic condition for the basis functions (12) are unusual. They were chosen because in this way the potentials and wave functions converge to the exact atomic limits as $R\to\infty$. However, compared to normal usage, the corrections are of the order of m/M and are therefore unimportant in the framework of the present theory. In fact, standard quantum chemical programs use an electronic Hamiltonian that has the uncorrected electron mass in the kinetic-energy term. This is different from both our H_{el} and H_{el}^{at}. Again, the difference is negligible. There is no objection against the use of adiabatic potentials and single derivative coupling matrix elements in Eq. (9), which have been calculated by standard quantum chemical programs. The error that one makes in the potentials in this way has a typical magnitude of $(m/M)V_j$, that is, 1 meV or less; this is much less than the typical uncertainty of quantum chemical data. The double derivative matrix elements in the coupled equations are usually not provided by quantum chemical programs. The corresponding terms in the coupled equations are of the order of $(m/M)V_j$ as well (this is true as long as a slowly varying basis is used; see footnote 1). They should not be neglected entirely because they are required for particle conservation [22], but a reasonable guess will be sufficient in many cases. Similarly, the expression $R(d/dR)(F_k/R)$ in the single derivative coupling term in Eq. (9) can usually be replaced by dF_k/dR, which is more familiar; again the difference is of the order of $(m/M)V_j$ only.

We consider our present results as a promising way to take care of electron translation in the frame of a full quantum approach. Additional experience and the extension to rotational coupling effects, homonuclear collision pairs, and many electron systems are required before a final judgement can be given.

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APPENDIX: THE *R* MATRIX

A truncated system of N coupled-channel equations possesses $2N$ linearly independent solutions. Normally, there exist N independent regular solutions $F_j^{(n)}(R)$ $(j,n=1,\ldots,N)$, which obey the correct boundary condition at small R,

$$F_j^{(n)}(R)\to 0 \quad \text{as} \quad R\to 0. \tag{A1}$$

j is the channel number and n is the number of the solution. Assume that these solutions are known at a distance R_0 and denote

$$P_{jn}=F_j^{(n)}(R_0), \quad Q_{jn}=\left.\frac{dF_j^{(n)}}{dR}\right|_{R=R_0}. \tag{A2}$$

Provided Q^{-1} exists, it easily shown that Eq. (24) holds for every regular solution of the coupled equations (that is, every linear combination of the $F_j^{(n)}$) at R_0, with

$$\underline{R}=\underline{P}\ \underline{Q}^{-1}. \tag{A3}$$

Under the present conditions, N regular solutions are easily obtained by numerical computation. We use Eq. (A3) to compute the R matrix from the numerical solutions.

An explicit expression for $\underline{R}$ was derived by Wigner and Eisenbud [18,25,26], which is much more complicated than the present usage. We use the R matrix as a very convenient way to match the numerical solution at the boundary R_0 to the analytic solution at $R>R_0$. The R matrix in this sense is nothing but the generalization of the inverse of the logarithmic derivative of the wave function to the many-channel case. This use of the R matrix has become familiar in numerical applications in atomic collision physics [19,20]. There are in fact different definitions of the R matrix in the literature. Except for an extra minus sign, the present usage is that of Ref. [20].

[1] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Clarendon, Oxford, 1949).

[2] B. H. Bransden and M. R. C. McDowell, *Charge Exchange and the Theory of Ion-Atom Collisions* (Clarendon, Oxford, 1992).

[3] O. Mo, A. Riera, and M. Yanez, Phys. Rev. A **31**, 3977 (1985).

[4] G. J. Bottrell, Nucl. Instrum. Methods Phys. Res. B **79**, 173 (1993).

[5] R. McCarroll and D. S. F. Crothers, Adv. At., Mol., Opt. Phys. **32**, 253 (1994).

[6] J. B. Delos and W. R. Thorson, J. Chem. Phys. **70**, 1774 (1979).

[7] J. B. Delos, Rev. Mod. Phys. **53**, 287 (1981).

[8] D. R. Bates and R. McCarroll, Proc. R. Soc. London, Ser. A **245**, 175 (1958).

[9] E. A. Solov'ev and S. I. Vinitsky, J. Phys. B **18**, L557 (1985).

[10] J. Macek, M. Cavagnero, K. Jerjian, and U. Fano, Phys. Rev. A **35**, 3940 (1987).

[11] J. Macek, J. Phys. B **1**, 831 (1968).

[12] J. Manz, Comments At. Mol. Phys. **17**, 91 (1985).

[13] J. Robert and J. Baudon, J. Phys. B **19**, 171 (1986).

[14] M. Gargaud, R. McCarroll, and P. Valiron, J. Phys. B **20**, 1555 (1987).

[15] H. Croft and A. S. Dickinson, J. Phys. B **29**, 57 (1996).

[16] J. Grosser, A. Schnecke, and H. Voigt, Z. Phys. D **17**, 251 (1990).

[17] J. Grosser, Z. Phys. D **3**, 39 (1986).

[18] A. M. Lane and R. G. Thomas, Rev. Mod. Phys. **30**, 257 (1958).

[19] V. M. Burke and C. J. Noble, Comput. Phys. Commun. **85**, 471 (1995).

[20] J. C. Light, in *Atom-Molecule Collision Theory*, edited by R. B. Bernstein (Plenum, New York, 1979), p. 239.

[21] M. S. Child, *Molecular Collision Theory* (Academic, London, 1974).

[22] A. K. Belyaev, J. Grosser, J. Hahne, and T. Menzel (unpublished).

[23] D. R. Bates and D. Sprevak, J. Phys. B **4**, L47 (1971).

[24] P. J. Bruna and S. D. Peyerimhoff, Adv. Chem. Phys. **67**, 1 (1987).

[25] E. P. Wigner and L. Eisenbud, Phys. Rev. **72**, 29 (1947).

[26] E. P. Wigner, Phys. Rev. **73**, 1002 (1948).