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Electron translation and asymptotic couplings in low-energy atomic collisions

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The calculation of cross sections for inelastic and charge-exchange atomic collisions encounters a principal difficulty. The coordinates used to describe the collision event are usually not appropriate for the description of the collision partners long before and after the collision. As a consequence, the coupling matrix elements that govern inelastic transitions can remain nonzero for large internuclear distance. We present a simple procedure to deal with this situation in the framework of a full quantum-mechanical treatment. It applies to radial as well as rotational coupling mechanisms. We demonstrate the practical applicability by numerical examples.

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I. INTRODUCTION

Inelastic and charge-exchange collisions between atoms or ions at low energy govern the behavior of gaseous media in many cases. This concerns a wide range of questions of practical importance from astrophysics and the fusion plasma edge to laser media and industrial applications of plasma physics. The numerical calculation of cross sections appears as a straightforward way to provide the data that are required for a quantitative understanding of these media. The computation of cross sections usually proceeds in two steps, the quantum chemical treatment of the collisional quasimolecule, and the subsequent treatment of the heavy particle dynamics. The second step encounters a severe difficulty, however. The matrix elements coupling different electronic states may remain nonzero at large internuclear distance [1–3]. As this seems to imply inelastic transitions under the influence of an arbitrarily distant collision partner, the corresponding formulation of the theory is often regarded as defective. In fact, the nonvanishing asymptotic couplings reflect a less obvious but more fundamental shortcoming. The coordinates used to describe the collision complex are usually not suited for the description of the free atoms [4], and the corresponding representation of the asymptotic wave function is therefore not suited for a straightforward interpretation.

For high-energy collisions, where the motion of the nuclei may be treated classically, a solution is well known, namely, the inclusion of ‘‘electron translation factors’’ (ETF’s) [1,2] in the expansion of the electronic wave function. For low-energy collisions, the use of classical approximations is not adequate, rather, a full quantum treatment of both the electronic and the nuclear motion is required. Full quantum approaches are usually based on an expansion of the scattering wave function in terms of a set of electronic basis functions, leading to a system of coupled channel equations. A straightforward generalization of the ETF method to the coupled channels approach does not exist. Several alternative approaches [5–10] have been discussed, practical applications of these proposals have remained limited, however. Rather, empirical methods are widely applied, in which for instance, artificial modifications of the coupling matrix elements are constructed. The question has been discussed for more than 40 years. Being known as a difficult problem for so long time, the problem was more and more considered to be unsolvable. The statement that it is ‘‘not possible to extract a meaningful *S* matrix’’ [11] from the solution of the coupled equations correctly reflected the state of the art at the time when the statement was made. Unfortunately, it was frequently understood as an absolute truth. We have shown in a previous paper [12], however, how to construct a meaningful *S* matrix. The present paper extends this approach by considering rotational in addition to radial coupling mechanisms.

Whereas previous approaches concentrated on a search for better-suited coordinates or for a formulation without asymptotic couplings, we formulate the coupled equations using standard coordinates. The asymptotic couplings are not removed in our formulation. Rather, we concentrate on the question how the solutions of the coupled equations must be interpreted in the asymptotic region. It turns out that a correct interpretation can be achieved by a straightforward and simple reprojection procedure.

Besides the problem discussed so far, there exists a second problem, an apparent ambiguity in the definition of certain coupling matrix elements. The question is often discussed in connection with the present one, but may be solved independently. As observed by numerous authors, e.g. [3,13], one obtains different values for certain matrix elements when one chooses different origins for the electron coordinates. This seems to make the calculation of cross sections ambiguous. However, as shown by Bottrell [14], the changes are compensated by additional terms in the coupled equations, which were usually ignored. The ambiguity in the coupling matrix elements does not lead to a corresponding ambiguity in the coupled equations, therefore. In practice, Bottrell’s result leads to the following simple rule: When the standard form of the coupled equations [Eq. (5) below] is used, the matrix elements have to be calculated using Jacobi coordinates, that is, with the origin of the electron coordinates at the center of mass of the nuclei. An arbitrary choice of the coordinate origin is not justified. The details were worked out in our previous paper [12]. We use Bottrell’s result, therefore, without further discussion.

II. THE COUPLED EQUATIONS

We consider at present only systems with one active electron, and we treat them as one electron systems, considering every nucleus with its nonactive electrons as a single particle *A* or *B*. We use Jacobi coordinates **r** and **R** for the three-body problem; **R** connects the two heavy particles, **r** measures the position of the electron with respect to the center of mass of the heavy particles. Omitting the kinetic-energy operator of the center of mass of the total system, the Hamiltonian reads

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

with the reduced masses $m=m_e(M_A+M_B)/(m_e+M_A+M_B)$ and $M=M_AM_B/\ (M_A+M_B)$ and m_e, M_A, and M_B the masses of the three particles. H_{int} contains the interactions; we consider only electrostatic interactions, for simplicity. The electronic Hamiltonian,

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

depends on **R** only as parameter. We introduce a set of electronic basis functions $\psi_{j\Lambda\sigma}(\mathbf{r},\mathbf{R})$. They are allowed to vary with the internuclear distance, but are supposed to be body fixed. For the precise definition of this notion, we introduce spherical coordinates $R,\ \vartheta,\ \varphi$ for **R** and a body fixed coordinate system $\xi,\ \eta,\ \zeta$ for **r**, see Fig. 1. When expressed in these coordinates, body fixed functions depend on $\xi,\ \eta,\ \zeta$, and *R*, but not on ϑ and φ. The functions are distinguished by a running index *j* and by the usual angular projection quantum number $\Lambda=0,1,\ldots,$ $(\Sigma,\ \Pi,\ldots,$ states). The quantum number $\sigma=\pm1$ indicates the reflection symmetry at the body fixed $\xi\zeta$ plane. States with $\Lambda>0$ occur in pairs with $\sigma=\pm1$, the two components transform into each other by a rotation around the ζ axis. The scattering wave function can be written as a sum of terms $\Psi(\mathbf{r},\mathbf{R})=\Psi^J_{M_Jst}(\mathbf{r},\mathbf{R})$, each of which is characterized by the following good quantum numbers: (1) The total angular momentum quantum numbers *J* and M_J with $M_J\geqslant0$, (2) the reflection symmetry quantum number $s=\pm1$, such that Ψ multiplies by *s* under the reflection of both coordinates **r** and **R** at the space-fixed *xz* plane, and (3) the type quantum number $t=\pm1$. The type quantum number is closely related to the parity, but is more convenient in the present context. Every single term may be expanded in the form

$$\Psi(\mathbf{r},\mathbf{R})=\sum_{j\Lambda} I_{j\Lambda}F_{j\Lambda}(R)/R \tag{3}$$

with

$$\begin{aligned}I_{j\Lambda}=&\cos(M_J\varphi)\Theta^J_{M_J\Lambda q}(\vartheta)\psi_{j\Lambda s}\\&+i\sin(M_J\varphi)\Theta^J_{M_J\Lambda-q}(\vartheta)\psi_{j\Lambda-s}.\end{aligned} \tag{4}$$

The functions $\Theta^J_{M_J\Lambda\pm1}(\vartheta)$ are generalized spherical harmonics [15–17], *q* stands for the product *st*. Note the particular case $\Theta^J_{M_J0-1}=0$. The factors $I_{j\Lambda}$ represent the electronic motion and the angular part of the heavy particle motion. The $F_{j\Lambda}$ describe the radial motion of the atoms, they have to obey a system of coupled equations

$$\begin{aligned}&\left[-\frac{\hbar^2}{2M}\frac{d^2}{dR^2}+V_{j\Lambda}(R)+\frac{\hbar^2}{2MR^2}[J(J+1)-\Lambda^2]-E\right]F_{j\Lambda}\\&=-\sum_{j'\neq j}\langle\psi_{j\Lambda t}|H_{el}|\psi_{j'\Lambda t}\rangle F_{j'\Lambda}+\frac{\hbar^2}{M}\sum_{j'\neq j}\left\langle\psi_{j\Lambda t}\left|\frac{\partial}{\partial R}\right|\psi_{j'\Lambda t}\right\rangle\frac{dF_{j'\Lambda}}{dR}\\&\quad-\frac{\hbar}{MR^2}\sum_{j'}\sqrt{(J+\Lambda+1)(J-\Lambda)}\langle\psi_{j\Lambda t}|-iL_\eta|\psi_{j'\Lambda+1t}\rangle F_{j'\Lambda+1}\\&\quad-\frac{\hbar}{MR^2}\sum_{j'}\sqrt{(J-\Lambda+1)(J+\Lambda)}\langle\psi_{j\Lambda t}|iL_\eta|\psi_{j'\Lambda-1t}\rangle F_{j'\Lambda-1}\\&\quad-\frac{1}{2M}\sum_{j'}\langle\psi_{j\Lambda t}|L_\xi^2+L_\eta^2|\psi_{j'\Lambda t}\rangle F_{j'\Lambda}+\frac{\hbar^2}{2M}\sum_{j'}\left\langle\psi_{j\Lambda t}\left|\frac{\partial^2}{\partial R^2}\right|\psi_{j'\Lambda t}\right\rangle F_{j'\Lambda}.\end{aligned} \tag{5}$$

Remember that Λ takes nonnegative values only; the term with $F_{j'\Lambda-1}$ does not occur for $\Lambda=0$. L_η and L_ξ are the η and ξ components of the electronic angular momentum operator. The matrix element notation denotes an integration over the electron coordinates, the matrix elements remain functions of *R*. The functions $\psi_{j\Lambda\sigma}$ may be chosen to be real. In this case, $\langle\psi_{j'\Lambda\sigma}|\partial/\partial R|\psi_{j\Lambda\sigma}\rangle=-\langle\psi_{j\Lambda\sigma}|\partial/\partial R|\psi_{j'\Lambda\sigma}\rangle$ and in particular $\langle\psi_{j\Lambda\sigma}|\partial/\partial R|\psi_{j\Lambda\sigma}\rangle=0$, which has already been used in Eq. (5). Similarly, $\langle\psi_{j\Lambda\sigma}|-iL_\eta|\psi_{j'\Lambda\pm1\sigma}\rangle=\langle\psi_{j'\Lambda\pm1\sigma}|iL_\eta|\psi_{j\Lambda\sigma}\rangle$ is real. The potentials are given by

$$V_{j\Lambda}(R)=\langle\psi_{j\Lambda\sigma}|H_{el}|\psi_{j\Lambda\sigma}\rangle. \tag{6}$$

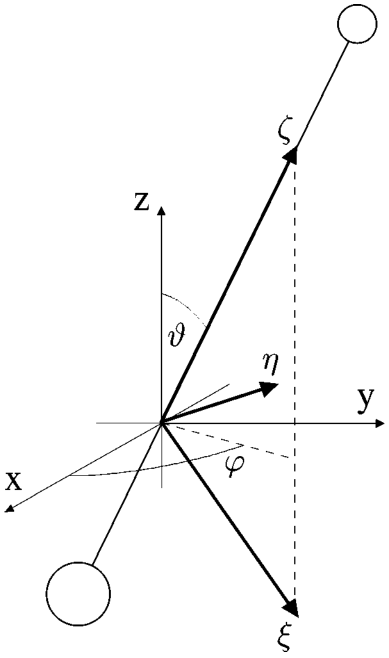

FIG. 1. Coordinates. ϑ and φ describe the direction of the vector **R** that connects the heavy particles. x, y, and z are space-fixed and ξ, η, ζ body-fixed electron coordinates. The z, ζ, and ξ axes are in a plane, the η axis is at right angles.

They are the same for both components $\sigma=\pm 1$ of the $\Lambda \neq 0$ states. Equation (5) exists in two versions, corresponding to the two possible values of the type quantum number. Note that for $t=+1$, there occur no Σ^- states in Eq. (3) and no corresponding couplings in Eq. (5), and similarly for $t=-1$, no Σ^+ states and no corresponding couplings. In practice, many collision processes start in a Σ^+ state; the scattering wave function may then entirely be constructed from terms with $s=t=+1$. For the derivation of Eqs. (3) to (5) see [15]. The theory is formulated for other coordinates in this paper, but the starting Hamiltonian has the same form as at present, and the mathematical steps leading from the Hamiltonian to the coupled equations are identical. Further, the coupling matrix elements are now expressed by functions with well-defined reflection symmetry σ, at variance with the formulation in [15].

We deal here with kinetic energies of the heavy particles, which are of the same order of magnitude as the typical kinetic energies of the electron. The wave-numbers K for the heavy particles and k for the electron have therefore a ratio of typically $k/K \approx \sqrt{m/M}$. Normally, the basis functions vary slowly with the internuclear distance, such that approximately

$$\frac{\partial}{\partial R}\psi_{j\Lambda\sigma} \leqslant \frac{1}{a}\psi_{j\Lambda\sigma}, \tag{7}$$

with $a \approx 1/k$ the typical dimension of the atoms. Under this condition, the first term on the right-hand side of Eq. (5) is of the same order as the terms on the left, the next three terms are by a factor of $\sqrt{m/M}$ smaller, and the last ones by a factor of m/M. The theory to be developed is of the first order in $\sqrt{m/M}$. Terms, which are of the order of m/M smaller than the leading terms, will be neglected. The assumption expressed by Eq. (7) is not automatically fulfilled, but a corresponding choice of the basis (diabatic or nearly diabatic) can always be made. For the region of large distances, which is the subject of the present paper, the assumption holds for any reasonable choice of the basis, see Eq. (8) below.

Equation (5) is an adequate starting point for a numerical treatment. The potentials and the matrix elements must be known in advance, for instance from a quantum chemical treatment of the system. The off-diagonal matrix elements of H_{el} and $\partial/\partial R$ are denoted as radial (or homogeneous), those of iL_η as rotational (centrifugal, Coriolis, or heterogeneous) coupling matrix elements.

III. ASYMPTOTIC COUPLINGS

The electronic basis functions vary with the internuclear distance R, in general. Two requirements seem obvious: They should become atomic eigenfunctions at large R and they should no more depend on R at the same time. The first requirement can easily be fulfilled, the innocent second one cannot, however. Atomic eigenfunctions travel with the atom, and they have, therefore, the form

$$\psi(\mathbf{r},\mathbf{R}) = f(\xi,\eta,\zeta-\gamma_{j\Lambda}R) \tag{8}$$

with

$$\gamma_{j\Lambda} = -\frac{M_B}{M_A+M_B} \quad \text{or} \quad \gamma_{j\Lambda} = \frac{M_A}{M_A+M_B} \tag{9}$$

for functions travelling with atom A or B, respectively. We will exclusively use basis functions that have the form of Eq. (8) at large distances. They clearly depend on R and can therefore give rise to nonvanishing radial coupling matrix elements at large R. Introducing atom-centered coordinates $\xi_{at}=\xi$, $\eta_{at}=\eta$, and $\zeta_{at}=\zeta-\gamma_{j\Lambda}R$, one finds

$$\langle \psi_{j\Lambda\sigma}|\partial/\partial R|\psi_{j'\Lambda\sigma}\rangle = \langle \psi_{j\Lambda\sigma}|\partial/\partial R|\psi_{j'\Lambda\sigma}\rangle^{at} - \gamma_{j'\Lambda}\langle \psi_{j\Lambda\sigma}|\partial/\partial\zeta_{at}|\psi_{j'\Lambda\sigma}\rangle. \tag{10}$$

The matrix element on the left is that one, which enters the coupled equations. The partial differentiation is carried out with the electronic wave function expressed in the coordinates ξ, η, and ζ, and R. The first term on the right is calculated using ξ_{at}, η_{at}, ζ_{at}, and R instead; this matrix element vanishes at large R, because the wave functions have the form of Eq. (8). The second term on the right is nonzero at large R when both wave functions travel with the same atom and a dipole transition between them is allowed. It follows that, in general, the $\partial/\partial R$ coupling matrix elements in Eq. (5) go to a nonzero constant value as $R\rightarrow\infty$. Similarly,

$$\begin{aligned}\langle \psi_{j\Lambda\sigma}|iL_\eta|\psi_{j'\Lambda\pm1\sigma}\rangle &= \langle \psi_{j\Lambda\sigma}|iL_\eta^{at}|\psi_{j'\Lambda\pm1\sigma}\rangle \\ &\quad + \gamma_{j'\Lambda\pm1}\langle \psi_{j\Lambda\sigma}|\partial/\partial\xi_{at}|\psi_{j'\Lambda\pm1\sigma}\rangle \times \hbar R.\end{aligned} \tag{11}$$

The matrix element on the left, which enters the coupled equations, is calculated with the angular momentum referring to the center of mass of the nuclei. In contrast, the first matrix element on the right is obtained with the angular momentum referring to the nucleus, which carries the electron away. Here, both terms on the right can remain nonzero at large R. The first term couples the magnetic substates of an atomic level. Its physical significance is well understood; it describes the decoupling of the electronic wave function from the rotating molecular axis [15]. The second term is similar to the second term in Eq. (10) and can be nonzero under the same conditions. Both matrix elements have constant values for large R. In the coupled equations, they provide terms that vary as $1/R^2$ and $1/R$, respectively. Atomic eigenfunctions have the property [12]

$$\langle \psi_{j\Lambda\sigma} | H_{el} | \psi_{j'\Lambda\sigma} \rangle = 0 \quad \text{for} \quad j' \neq j. \tag{12}$$

Actually, the Hamiltonian of the free atom is not exactly H_{el}, because the reduced electron mass is slightly different. Equation (12) is not exact, therefore. However, the error is smaller than the leading terms in Eq. (5) by a factor of the order of m/M and can therefore be neglected. The last two terms in Eq. (5) can remain nonzero as well as R becomes large; again, these terms are of the order of m/M compared to the leading terms and will therefore be neglected. We deal with asymptotic couplings originating from the second, third, and fourth terms on the right-hand side of Eq. (5).

Using the relation $(m/\hbar^2)[\mathbf{r}_{at}, H_{el}] = \partial/\partial \mathbf{r}_{at}$, one finds

$$\begin{aligned}\langle \psi_{j\Lambda\sigma} | \partial/\partial \mathbf{r}_{at} | \psi_{j'\Lambda'\sigma} \rangle = {}& (m/\hbar^2)(V_{j'\Lambda'} - V_{j\Lambda}) \\ & \times \langle \psi_{j\Lambda\sigma} | \mathbf{r}_{at} | \psi_{j'\Lambda'\sigma} \rangle,\end{aligned} \tag{13}$$

which relates the asymptotic couplings to atomic dipole transition matrix elements. Again, Eq. (13) is not exact, but the errors are small of the order m/M and will be disregarded.

IV. THE ASYMPTOTIC SOLUTION

We consider in this section the region of very large distances, where all terms in the coupled equations can be replaced by their limit for $R \to \infty$. This means, in particular, that the centrifugal potential and the rotational asymptotic coupling terms are zero. The only coupling terms that remain are the asymptotic $\partial/\partial R$ couplings, there values are given by the second term on the right-hand side of Eq. (10). The coupled channel equations are easily solved by a perturbation approach under these conditions [12]. To the first order in the small quantity $\sqrt{m/M}$, the general solution is

$$\begin{aligned}F_{j\Lambda} = \sum_{j'} K_{j'\Lambda}^{-1/2} [& t^{+}_{j\Lambda,j'\Lambda} a^{+}_{j'\Lambda} \exp(iK_{j'\Lambda}R) \\ & + t^{-}_{j\Lambda,j'\Lambda} a^{-}_{j'\Lambda} \exp(-iK_{j'\Lambda}R)]\end{aligned} \tag{14}$$

with

$$t^{\pm}_{j\Lambda,j'\Lambda} = \delta_{jj'} \pm iK_{j'\Lambda} \gamma_{j'\Lambda} (m/M) \langle \psi_{j\Lambda t} | \zeta_{at} | \psi_{j'\Lambda t} \rangle. \tag{15}$$

$K_{j'\Lambda} = \sqrt{2M[E - V_{j'\Lambda}(\infty)]}/\hbar$ are the channel wave numbers, the $a^{\pm}_{j'\Lambda}$ are arbitrary. The corresponding wave-function Ψ is obtained by inserting Eq. (14) into Eq. (3). The result can be expressed as follows:

$$\Psi = \sum_{j\Lambda} K_{j\Lambda}^{-1/2} (a^{+}_{j\Lambda} \Psi^{+}_{j\Lambda} + a^{-}_{j\Lambda} \Psi^{-}_{j\Lambda}) \tag{16}$$

with

$$\Psi^{\pm}_{j\Lambda} = \exp(\pm iK_{j\Lambda}R)/R \sum_{j'} t^{\pm}_{j'\Lambda,j\Lambda} I_{j'\Lambda}(\mathbf{r},\mathbf{R}). \tag{17}$$

This can be shown to be equal to

$$\Psi^{\pm}_{j\Lambda} = \exp(\pm iK_{j\Lambda}R_{at})/R_{at} I_{j\Lambda}(\mathbf{r},\mathbf{R}_{at}) \tag{18}$$

to the first order in $\sqrt{m/M}$. $\mathbf{R}_{at}$ connects the bare heavy particle with the center of mass of the atom, in contrast to $\mathbf{R}$, which connects the bare heavy particles. The difference between the two coordinates is small, of the order of m/M times the atomic radius. However, the small difference is multiplied by the large atomic wave-number $K_{j\Lambda}$ in the exponential in Eq. (18), resulting in a non-negligible correction. The nondiagonal elements of the $t^{\pm}_{j'\Lambda,j\Lambda}$ in Eq. (17) can directly be traced to the appearance of R_{at} in place of R in the exponential in Eq. (18). The identity of Eqs. (17) and (18) is the central idea of the present approach. Equation (17) forms an expansion of Eq. (18) in terms of the set of electronic basis states; the two expressions are rigorously identical only as long as a complete set is used. The proof is worked out in more detail in [12]; for the present, more general formulation, the relations $\langle \psi_{j'\Lambda\sigma} | \zeta_{at} | \psi_{j\Lambda\sigma} \rangle = \langle \psi_{j'\Lambda-\sigma} | \zeta_{at} | \psi_{j\Lambda-\sigma} \rangle$ and $\Theta^{J}_{M_J 0-1} = 0$ are required in addition.

Equation (18) provides a correct description for the motion of two noninteracting atoms with the electron in an atomic eigenstate, that is, Eq. (18) and therefore as well Eq. (17), describe the true channels of the scattering problem. Equation (16) provides a corresponding decomposition of the wave function, the amplitudes $a^{\pm}_{j\Lambda}$ are the amplitudes of the incoming and outgoing currents in the different channels. Equation (14) finally shows how the amplitudes $a^{\pm}_{j\Lambda}$ are related to the solutions $F_{j\Lambda}$ of the coupled equations.

One is used to think that for large R, a single term in an expansion as Eq. (3) represents a channel of the scattering problem. This is not true for the present case. A single term in Eq. (3) would correspond to Eq. (18), but with $\mathbf{R}_{at}$ replaced by $\mathbf{R}$, or as well to Eq. (17), but with $t^{\pm}_{j'\Lambda,j\Lambda}$ replaced by $\delta_{j'j}$. Due to the presence of the asymptotic radial couplings, this would not even solve the coupled equations in the asymptotic region. The asymptotic radial couplings are obviously required to guarantee for the correct asymptotic form of the wave function.

V. THE SOLUTION AT INTERMEDIATE DISTANCE

For the calculation of cross sections, it is necessary to solve the coupled channel equations for the entire range of accessible distances from R near zero to large R. The result of the preceding section provides the correct asymptotic form and allows us to extract the correct channel amplitudes $a^{\pm}_{j\Lambda}$ from the solution of the coupled equations. This is of limited practical use, however, because it requires the knowledge of a solution, which covers the range from $R=0$ to extremely large distances. We will now derive an analytic form for the general solution, which is valid for intermediate distances, and that can be used to connect a numerical solution from intermediate distances to infinity.

We solve Eq. (5) in the intermediate region by a perturbative WKB approach. The perturbation treatment is complicated by the fact that some of the potentials $V_{j\Lambda}(R)$ converge to the same limit as $R\rightarrow\infty$. A small coupling is sufficient to cause a large perturbation in this situation. Asymptotic degeneracy occurs for instance between the substates $\Lambda=0,\dots,L_j$ of an atomic level with electronic angular momentum L_j. We deal in the following with a region of R values, in which the potential differences between asymptotically degenerate levels are already negligible,

$$V_{j\Lambda}(R)-V_{j'\Lambda'}(R)=0 \quad \text{whenever} \quad V_{j\Lambda}(\infty)-V_{j'\Lambda'}(\infty)=0, \tag{19}$$

and in which all coupling matrix elements can be replaced by the corresponding asymptotic expressions. The nonvanishing coupling matrix elements are therefore

$$\begin{aligned}
&\langle\psi_{j\Lambda t}|\partial/\partial R|\psi_{j'\Lambda t}\rangle\\
&\quad=-\gamma_{j'\Lambda}(m/\hbar^2)(V_{j'\Lambda}-V_{j\Lambda})\langle\psi_{j\Lambda t}|\zeta_{at}|\psi_{j'\Lambda t}\rangle_\infty,\\
&\langle\psi_{j\Lambda t}|iL_\eta|\psi_{j'\Lambda\pm1t}\rangle\\
&\quad=\gamma_{j'\Lambda\pm1}(m/\hbar)R\,(V_{j'\Lambda\pm1}-V_{j\Lambda})\langle\psi_{j\Lambda t}|\xi_{at}|\psi_{j'\Lambda\pm1t}\rangle_\infty\\
&\qquad+\langle\psi_{j\Lambda t}|iL^{at}_\eta|\psi_{j'\Lambda\pm1t}\rangle_\infty.
\end{aligned}\tag{20}$$

The approximation described by Eqs. (19) and (20) will turn out to be justified already at moderate distances. Couplings between asymptotically degenerate levels occur only by the matrix elements of L^{at}_η in this situation. The centrifugal potential and the rotational coupling terms are now no longer neglected, unlike in Sec. IV. Similarly, long range (e.g., Coulomb) potentials $V_{j\Lambda}$ are allowed. We remove in a first step the couplings between the asymptotically degenerate states. We consider the matrix

$$\begin{aligned}
W_{j\Lambda,j'\Lambda'}={}&\delta_{jj'}\delta_{\Lambda\Lambda'}[V_{j\Lambda}+\hbar^2/(2MR^2)(J(J+1)-\Lambda^2)]\\
&+\hbar/(MR^2)[\delta_{\Lambda-1\Lambda'}\sqrt{(J-\Lambda+1)(J+\Lambda)}\\
&\times\langle\psi_{j\Lambda t}|iL^{at}_\eta|\psi_{j\Lambda' t}\rangle_\infty\\
&+\delta_{\Lambda+1\Lambda'}\sqrt{(J+\Lambda+1)(J-\Lambda)}\\
&\times\langle\psi_{j\Lambda t}|-iL^{at}_\eta|\psi_{j\Lambda' t}\rangle_\infty],
\end{aligned}\tag{21}$$

which collects the effective potential and all couplings between asymptotically degenerate terms. We turn now to a matrix and vector notation in which, for instance, the radial functions $F_{j\Lambda}$ are collected in a vector F and $\underline{\mathrm{W}}$ has the matrix elements defined in Eq. (21). We define a unitary matrix $\underline{\mathrm{U}}$ by the requirement that it transforms the matrix $\underline{\mathrm{W}}$ into a diagonal matrix $\underline{\widetilde{\mathrm{W}}}$

$$\underline{\mathrm{U}}\;\underline{\mathrm{W}}\;\underline{\mathrm{U}}^\dagger=\underline{\widetilde{\mathrm{W}}}. \tag{22}$$

Because $\underline{\mathrm{W}}$ couples only asymptotically degenerate terms, $\underline{\mathrm{U}}$ connects only asymptotically degenerate states. Under the present conditions, $\underline{\mathrm{U}}$ is independent of the internuclear distance. As the coupling terms in $\underline{\mathrm{W}}$ are of the order of $\sqrt{m/M}$ compared to the typical potential energies, the diagonal terms in $\underline{\widetilde{\mathrm{W}}}$ differ from the diagonal terms in $\underline{\mathrm{W}}$ by corrections of the same order only, as well; the differences vanish as $R\rightarrow\infty$. Introducing a new set of functions

$$\widetilde{F}=\underline{\mathrm{U}}F, \tag{23}$$

one obtains a system of coupled equations for the new functions $\widetilde{F}$, which is similar to Eq. (5). The coupling matrix elements are replaced by their transforms under the matrix $\underline{\mathrm{U}}$, the effective potentials are replaced by $\underline{\widetilde{\mathrm{W}}}$, and there are no couplings between asymptotically degenerate states any more. In this form, the coupled equations are easily solved by perturbation techniques. The approximate general solution reads, after transformation back to the functions F,

$$\begin{aligned}
F(R)={}&\underline{\tau}^+\,\underline{\mathrm{U}}^\dagger\,\underline{\tilde{\kappa}}^{-1/2}\exp(\mathrm{i}\underline{\tilde{\Phi}})\,\underline{\mathrm{U}}\,a^+\\
&+\underline{\tau}^-\,\underline{\mathrm{U}}^\dagger\,\underline{\tilde{\kappa}}^{-1/2}\exp(-\mathrm{i}\underline{\tilde{\Phi}})\,\underline{\mathrm{U}}\,a^-.
\end{aligned}\tag{24}$$

$\underline{\tilde{\kappa}}$ and $\underline{\tilde{\Phi}}$ are diagonal matrices with elements

$$\tilde{\kappa}_n(R)=\sqrt{2M[E-\widetilde{W}_n(R)]}/\hbar \tag{25}$$

and

$$\tilde{\Phi}_n=\tilde{\kappa}_n(\infty)R-\int_R^\infty[\tilde{\kappa}_n(R)-\tilde{\kappa}(\infty)]dR, \tag{26}$$

and the matrices $\underline{\tau}^{\pm}$ have elements

$$\begin{aligned}
\tau^{\pm}_{j\Lambda,j'\Lambda'}={}&\delta_{jj'}\delta_{\Lambda\Lambda'}\pm i\kappa_{j'\Lambda'}\gamma_{j'\Lambda'}\frac{m}{M}\langle\psi_{j\Lambda t}|\zeta_{at}|\psi_{j'\Lambda' t}\rangle\delta_{\Lambda'\Lambda}\\
&-\sqrt{(J+\Lambda+1)(J-\Lambda)}\gamma_{j'\Lambda'}\frac{m}{M}\frac{1}{R}\\
&\times\langle\psi_{j\Lambda t}|\xi_{at}|\psi_{j'\Lambda' t}\rangle\delta_{\Lambda'\Lambda+1}\\
&+\sqrt{(J-\Lambda+1)(J+\Lambda)}\gamma_{j'\Lambda'}\frac{m}{M}\frac{1}{R}\\
&\times\langle\psi_{j\Lambda t}|\xi_{at}|\psi_{j'\Lambda' t}\rangle\delta_{\Lambda'\Lambda-1},
\end{aligned}\tag{27}$$

with $\kappa_{j\Lambda}=\sqrt{2M(E-W_{j\Lambda j\Lambda})}/\hbar$. The components of the vectors $a^{\pm}$ are arbitrary constants. As in Eq. (5), the last term in Eq. (27) does not occur for $\Lambda=0$. Equation (24) holds to the first order in $\sqrt{m/M}$, as before. In addition, the WKB approximation is applied, which means that the derivatives of the wave numbers ($\kappa_{j\Lambda}$ and $\tilde{\kappa}_n$) are neglected. This is expected to be an excellent approximation under the present conditions, certainly for the range of distances considered here. Similarly, the derivatives of the τ matrix elements are neglected. Note also that the use of the WKB formulation makes the explicit introduction of a logarithmic phase term for Coulombic potentials unnecessary; the logarithmic term arises automatically from the integral in Eq. (26).

VI. THE *S* AND *R* MATRICES

As $R \rightarrow \infty$, Eq. (24) becomes identical to Eq. (14) (Note that $\underline{\mathrm{U}}$ commutes with $\underline{\kappa}$ and $\underline{\Phi}$ as $R \rightarrow \infty$). The components of the vectors $a^{\pm}$ in Eq. (24) are therefore the amplitudes of the incoming and outgoing currents, as in Eqs. (14) and (16). We define the S matrix as usual to relate the amplitudes of the incoming and outgoing currents,

$$a^{+} = (-1)^{J+1} \underline{S}\, a^{-}. \tag{28}$$

We suppose that at a distance R_0, the R matrix is known, which relates the values $F_{j\Lambda}$ and the derivatives $dF_{j\Lambda}/dR$ of the radial functions at R_0, in matrix notation

$$F = \underline{R}\, dF/dR \quad \text{at} \quad R = R_0 . \tag{29}$$

In the examples, which we present in the next sections, $\underline{R}$ is obtained from the numerical solution of Eq. (5) between small distances and R_0. R_0 must be so large that Eqs. (19) and (20) apply for $R > R_0$. We use Eq. (29) together with Eq. (24) to find the relation between the S and R matrices. A straightforward calculation yields

$$\begin{aligned}\underline{S} = {} & (-1)^{J} \exp(-i\underline{\Phi})\underline{\kappa}^{1/2}(\underline{\tau}^{+} - i\underline{R}\ \underline{\tau}^{+}\underline{\kappa})^{-1} \\ & \times (\underline{\tau}^{-} + i\underline{R}\ \underline{\tau}^{-}\underline{\kappa})\underline{\kappa}^{-1/2}\exp(-i\underline{\Phi}),\end{aligned} \tag{30}$$

with

$$\underline{\kappa} = \underline{\mathrm{U}}^{\dagger}\,\underline{\tilde{\kappa}}\ \underline{\mathrm{U}},\ \ \underline{\kappa}^{\pm 1/2} = \underline{\mathrm{U}}^{\dagger}\,\underline{\tilde{\kappa}}^{\pm 1/2}\,\underline{\mathrm{U}},$$

and

$$\exp(-\mathrm{i}\underline{\Phi}) = \underline{\mathrm{U}}^{\dagger}\exp(-\mathrm{i}\underline{\tilde{\Phi}})\ \underline{\mathrm{U}}. \tag{31}$$

Equation (30) is our central result; it allows us to extract the correct S matrix from the numerical solution of the coupled equations.

For the interpretation, regard a form of Eq. (30), in which $\underline{\tau}^{\pm}$ and $\underline{\mathrm{U}}$ are replaced by unit matrices

$$\begin{aligned}\underline{S} = {} & (-1)^{J} \exp(-i\underline{\Phi})\underline{\kappa}^{1/2}(\underline{1} - i\underline{R}\ \ \underline{\kappa})^{-1} \\ & \times (\underline{1} + i\underline{R}\ \ \underline{\kappa})\underline{\kappa}^{-1/2}\exp(-i\underline{\Phi}),\end{aligned} \tag{32}$$

where $\underline{1}$ is the unit matrix. This is the relation between the S and R matrices, which applies in the absence of asymptotic couplings. The interpolation between intermediate and large distances occurs by WKB functions in this version, as before. The comparison demonstrates that the way in which we take the asymptotic couplings into account, is a straightforward and simple extension of standard procedures. Equation (30) differs from Eq. (32) in two ways:

(1) The asymptotic couplings between the substates of one atomic energy level are taken into account by the appearance of the matrix $\underline{\mathrm{U}}$ in the formulas. These couplings have a well-known physical significance. In the region where Eq. (24) applies, the actual electronic wave functions do not rotate with the molecular axis [15]; the transformations under $\underline{\mathrm{U}}$ are necessary to describe this behavior in terms of basis functions, which rotate with the axis at all distances.

(2) The asymptotic radial couplings and the asymptotic $1/R$ rotational coupling terms are taken into account by the appearance of the τ matrix. They correct for the use of the asymptotically inadequate coordinate $\mathbf{R}$ in place of $\mathbf{R}_{at}$. Note that this was not explicitly shown for the rotational contributions, but appears reasonable in view of the similarity with the radial terms, see Eqs. (10) and (11).

VII. NUMERICAL EXAMPLES

We studied the collision processes

$$\mathrm{H}(1s) + \mathrm{He} \rightarrow \mathrm{H}(2s,2p) + \mathrm{He},$$

$$\mathrm{H} + \mathrm{Na}(3s) \rightarrow \mathrm{H} + \mathrm{Na}(3p,4s),$$

as examples. For a numerical treatment of the coupled channel equations, the electronic basis must be reduced to a finite number of states. We used the lowest adiabatic molecular states as a basis. In order to formulate the coupled equations, the potentials and the coupling matrix elements between these states must be provided. We used a quantum chemical program working on the configuration interaction level [18,19] for this purpose. We show the adiabatic potentials and the couplings for the HHe system in Fig. 2, the HNa data can be found in Ref. [20]. The solution of the truncated coupled equations is carried out with an existing [20] numerical program, which yields the R matrix at a distance R_0. The S matrix finally has to be calculated with Eq. (30). For this step, also the τ and U matrices must be constructed. It is remarkable that this does not require any additional information. The τ matrix elements can be taken from the computed large R values of the corresponding coupling matrix elements, making use of Eq. (13). This holds similarly for the matrix $\underline{\mathrm{W}}$, which serves for the definition of the U matrix.

The HHe system is treated with a basis of three Σ states (X, A, and C) and one Π state (B). The excited levels A, B, and C are asymptotically degenerate, converging to the $\mathrm{H}(2s,2p)$ manifold. The asymptotic radial couplings connecting the X state with both excited Σ states A and C are clearly recognized in the figure. Clearly, $\langle 1s|\zeta_{at}|2s\rangle = 0$; following Eq. (10), this seems to imply that only one of the radial couplings, XA or XC, should remain nonzero at large R. However, the A and C eigenstates are linear combinations of the $2s$ and $2p$ states at large R, allowing nonzero asymptotic couplings in both cases. The radial coupling between the A and C states is found to go to zero for large R; this is indeed expected from Eq. (13). Two types of asymptotic behavior for the rotational coupling matrix ele-

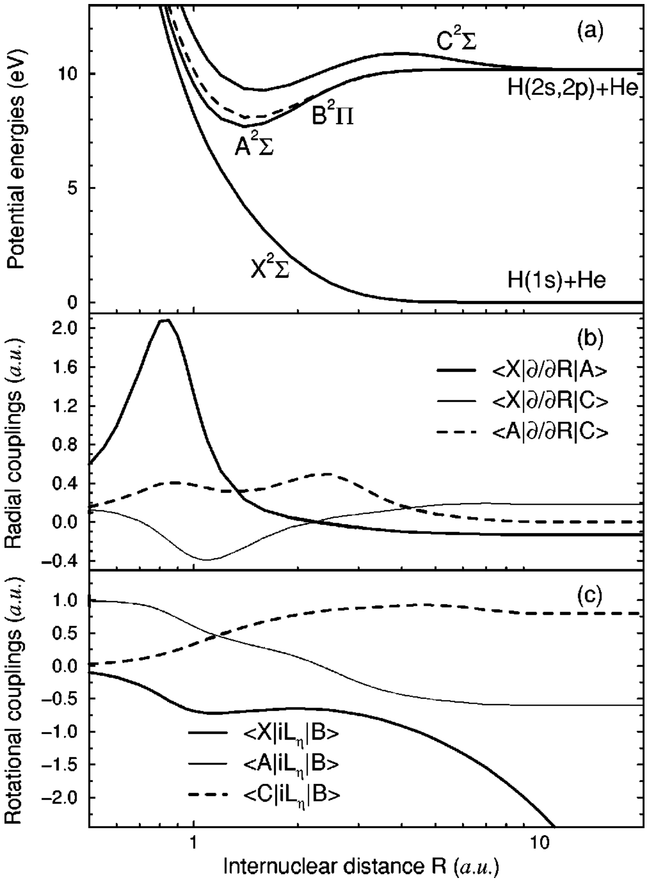

FIG. 2. The potentials (a) and the radial (b) and rotational (c) coupling matrix elements for the HHe system.

ments occur. The AB and CB matrix elements go to constant values, in agreement with Eqs. (11) and (13). The XB matrix element increases linearly with R as R becomes large, again as expected. Only the beginning of the linear increase is shown in the figure. The construction of the τ-, W, and U matrices is straightforward. τ connects all states X, A, B, and C, $\underline{U}$ mixes the asymptotically degenerate states A, B, and C states with each other. Note that the HHe system is more complex than many other cases: the asymptotically degenerate states A and C do not have a well-defined parity as $R \rightarrow \infty$. The general theory includes this situation.

Figure 3 shows numerical results for the transition probabilities, that is, the absolute squares of the S-matrix elements, calculated with variable upper limit R_0 of the numerical integration. The solid lines are calculated with the correct expression for the S matrix, Eq. (30). Except for the smallest R_0 values, they show no variation with R_0, as expected for a meaningful transition probability; the small variations at small R_0 occur, because the assumptions in Eqs. (19) and (20) do no longer apply. The dashed lines are transition probabilities obtained with the simplified formula Eq. (32). They show oscillations; the way in which these results are obtained, corresponds to a situation, in which the asymptotic terms are fully taken into account for $R < R_0$, but are switched off beyond R_0. The results seem to imply periodic inelastic transitions; this demonstrates clearly that Eq. (32) and the underlying interpretation do not apply to the present situation. The wavelength of the oscillations is governed by the energy gap between the states, which are mixed by the τ matrix, and by the particle velocity. The oscillations in the HHe system reflect the $1s$-$2s$,$2p$ energy gap in this way.

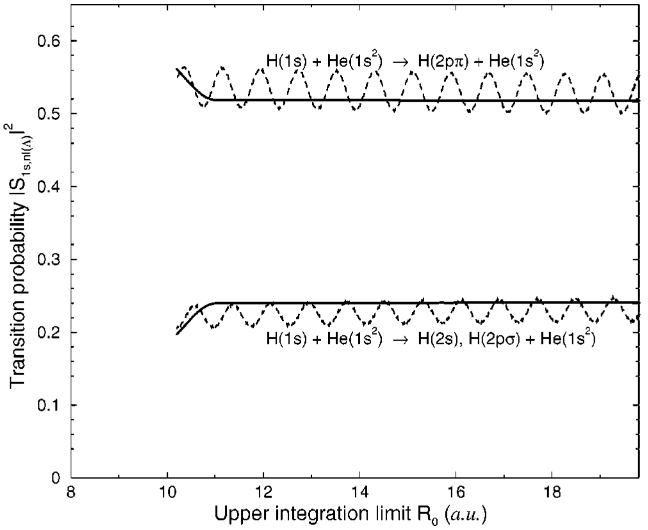

FIG. 3. Transition probabilities for the HHe system as a function of the upper integration limit. Solid lines: from Eq. (30), dashed lines: from Eq. (32). Kinetic energy 50 eV, $J=22$.

For the HNa system, we consider here only singlet electronic basis states; the states converging to H $+\text{Na}(3s,3p,4s)$ were used in the calculations. Asymptotic radial couplings occur between the $3s$ and $3p\Sigma$ and the $4s$ and $3p\Sigma$ states, rotational $1/R$ coupling terms between $3s$ and $3p\Pi$ and $4s$ and $3p\Pi$, and rotational $1/R^2$ couplings between $3p\Sigma$ and $3p\Pi$. A major difference to the HHe case is that the active electron travels now with the heavy collision partner. The γ factors are considerably smaller therefore, resulting in correspondingly smaller values of the asymptotic couplings. Figure 4 shows calculated transition probabilities similar to Fig. 3. The correct formula yields once more results that are independent of the range of the

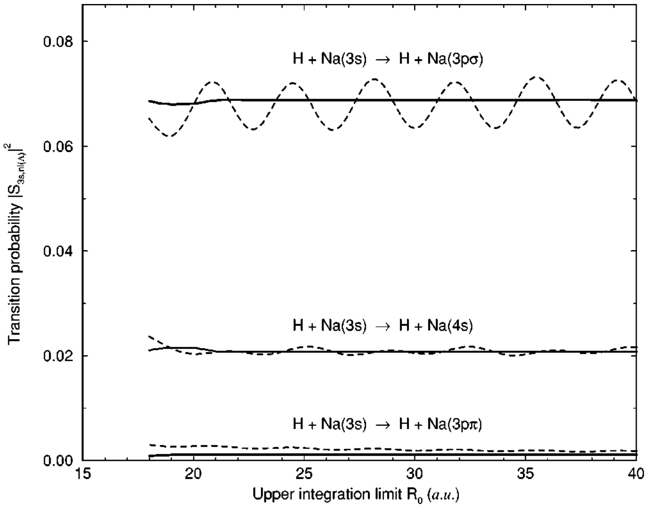

FIG. 4. Transition probabilities for the HNa system as a function of the upper integration limit. Solid lines: from Eq. (30), dashed lines: from Eq. (32). Kinetic energy 50 eV, $J=160$.

numerical integration, whereas the use of the inadequate formula results in the typical oscillations. Their frequencies reflect the $3s$-$3p$ and $4s$-$3p$ energy gaps (note in this connection the complicated oscillation pattern of the $4s$ curve). The lowest dashed line in the figure shows a slow variation superimposed on the oscillations. This is found to be caused by the replacement of the U matrix by the unit matrix. The variation reflects the fact the population of the $3p$ substates has become constant at these distances, but that the quantization axis, which is used to describe their population, continues to rotate. Accordingly, the dashed upper line in the figure shows a similar variation, however, with the opposite sign (which is less clearly visible due to the larger magnitude of the oscillations).

VIII. DISCUSSION

The examples demonstrate the practical applicability of the general procedure. The fact that the calculated transition probabilities do not vary with the upper limit of the numerical integration demonstrates that the mathematical procedures proposed to calculate S-matrix elements work satisfactorily. Actually, upon closer inspection, small residual variations can be found in the curves, which are too small to manifest themselves in the present version of the figures. They are due to the neglect of second order, i.e., m/M, terms throughout the paper. The numerical results fully justify this procedure.

The method differs considerably from previous approaches. All previous methods relied on modifications of the coupled equations. In contrast, we use the unmodified standard form of the coupled equations, including asymptotic couplings. We rather show how to interpret the solution correctly. We rely in particular on the identity of Eqs. (17) and (18) in this connection, which holds rigorously only as long as we use a complete basis of electronic basis states. In practice, the use of a complete basis is not possible, numerical computations require the use of a truncated finite basis. In the numerical examples, we use basis sets of only four states. The magnitude of the missing terms in Eq. (17) is easily estimated by looking up tabulated optical transition probabilities. These numbers usually become quickly small when going to higher states. We expect, therefore, that a small or moderate electronic basis will be sufficient in many cases. As already pointed out in Ref. [12], however, the necessity of truncation can lead to severe problems. This is particularly true when the number of bound atomic states is small, as for instance, for negative ions.

The following practical limitations should finally be mentioned:

(1) For very small energies, the couplings considered in this paper become very small: In Eq. (5), the derivatives dF/dR become smaller and smaller, and similarly, the typical values of the square roots in the rotational coupling terms. The couplings may eventually become as small as the last two terms in Eq. (5), which were neglected in the present formulation. We have then a situation with extremely small cross sections, which are governed by all coupling terms. A formulation of the theory, which includes also terms of the order m/M is desirable in order to account for this case.

(2) The theory is formulated for systems with one active electron. The extension to systems with more electrons is desirable.

(3) By Eq. (8), ungerade or gerade molecular states are not permitted as basis states. This complicates the application to homogeneous collision pairs; however, a choice of basis functions obeying Eq. (8) is certainly possible also in this case.

(4) Ionization processes cannot be dealt with by this approach.

IX. CONCLUSION

The procedure described in the present paper allows the unambiguous calculation of S-matrix elements, and hence, cross sections in a situation with nonvanishing radial and rotational asymptotic couplings. Two subsequent steps are essential. First, we show that the standard expansion of the wave function requires a reinterpretation in order to provide a meaningful description of the asymptotic motion of the collision partners. The new interpretation is given by Eqs. (16)–(18). This would be sufficient to obtain a meaningful S matrix, but it would require a (in general numerical) solution of the coupled equations from small to extremely large distances. Therefore, we present in the second step, an analytic WKB-type solution of the coupled equations. This solution can be used to continue a numerical solution from intermediate distances to infinity. We present on this basis a matrix formula Eq. (30), which permits the straightforward calculation of the S matrix when solutions for small and intermediate distances have been computed. The new formula is slightly more complicated than the corresponding relation that holds in the absence of electron translation effects. The corrections require the knowledge of the quantities, which must be provided in any case for the computation of the inelastic process, potentials and radial and rotational coupling matrix elements; the knowledge of additional quantities is not required.

We demonstrated the practical applicability of the method by two examples. Results obtained by a numerical integration of the coupled equations between small distances and an upper boundary of the order of 20 a.u. are sufficient to obtain unique results for the transition probability. In contrast, transition probabilities obtained by empirical methods, e.g., by cutting off the undesired terms, give ambiguous results, where, for instance, the calculated transition probabilities oscillate as a function of the integration range. Results obtained in this way deviate between a few percent and a factor of more than two from the results of the correct procedure.

The availabilty of this method rises a number of questions. It will be of much interest to gain experience by comparing numerical cross-section data based on the present method with experimental data, as well as with numerical results from other approaches. It would be particularly interesting to compare classical trajectory calculations (valid at high energy) to the present method, in order to see whether the two different methods are able to make similar predictions. It would be of interest as well, to study the convergence of the method using an increasing number of basis functions. The study of isotope effects (e.g., D+Na in place of H+Na) is expected to be of particular significance. Due to the different origin of the electron coordinates, the coupling matrix elements are different for the two cases; this might modify the scaling laws [21] for isotope substituted collisions.

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