PHYSICAL REVIEW A VOLUME 30, NUMBER 5 NOVEMBER 1984

Practical criterion for the determination of translation factors

A. Riera
Departamento de Química Física y Química Cuántica, Universidad Autónoma de Madrid, Canto Blanco, Madrid 34, Spain

(Received 15 November 1983)

Following an idea of Rankin and Thorson, a method is proposed to determine translation factors in the molecular model of atomic collisions, and for low and intermediate nuclear velocities. The method is based on the minimization of a measure of all (electrostatic and dynamical) couplings between the states included in, and those left out from, the molecular expansion. The properties of this measure are discussed. In particular, its evaluation involves the calculation of a few new matrix elements, and this can be performed analytically when Gaussian-type orbitals are used to construct the wave functions. The method also provides a comparison between all approaches that employ translation factors, and a test of the conditions that are usually enforced on these factors.

I. INTRODUCTION

As is well known, the main difficulties of the molecular treatment of atomic collisions—pointed out by Bates *et al.*[1] and currently known as the "momentum-transfer problem"—are the origin dependence of calculated cross sections and the existence of residual couplings at infinite internuclear separation. The practical effects of these difficulties have recently become conspicuous (see, e.g., Refs. 2 and 3) and many authors consider incomplete a collision treatment that ignores the momentum-transfer problem.

To tackle that problem, two formalisms have been proposed:[2] the use of translation factors[1,4] (TF) and the use of reaction coordinates[5] (RC). Although by now the literature on both methods is quite abundant, it is by no means clear[2] which form of TF or RC one should use for finite internuclear distances. Not only is there a lack of agreement among authors, but comparison between different approaches is rendered more difficult by the fact that approximations are often introduced [such as neglect of terms $O(v^2)$] that are unrelated to the form of the TF and are not justifiable in general. And yet a criterion other than intuition is needed to determine TF (or RC), since their form is known to considerably influence the results of calculations.[6,7]

In this respect, several methods that have been proposed in order to provide guidelines to determine TF at finite distances are particularly appealing, though often difficult to apply. They are usually based[8-10] on a Euler-Lagrange approach[11] which, although not strictly variational[12] for finite basis sets (in the sense that the functional be stationary within the trial space), possesses the property that transitions amplitudes obtained are accurate to second order.[13] However, this method leads, for a general form of TF, to a complicated set of nonlinear differential equations that are difficult to solve, and it does not provide an extremum principle, like the Rayleigh-Ritz method for bound-state problems. The latter criticism does not apply to the procedure of Chang and Rapp,[14] but this method is even more arduous to apply than those of Refs. 11 and 8.

A different type of approach to determine TF has been proposed by Rankin and Thorson.[15] Given a trial space, their method consists of minimizing the dynamical couplings between each discrete state and a set of electronic continuum states of the system; this stresses the fact that incompleteness of the (truncated) molecular expansion is at the root of the momentum-transfer problem. By minimizing couplings between the states included in, and those left out from, the expansion, one optimizes in some way the molecular representation of the collision process. A disadvantage is that one has to calculate the discrete-continuum couplings; this calculation and the overall minimization of these couplings are nontrivial problems in the general case (e.g., the method is only feasible for the exactly soluble one-electron systems[16]). Also, one should explicitly minimize electrostatic and discrete-discrete[16] couplings, too.

In this work we develop the basic idea of Ref. 15 so as to avoid its disadvantages; in our approach only matrix elements involving discrete states are required, and minimization is restricted to a single functional, just as for the usual variational methods. As in Ref. 15 the determination of IF's is decoupled from that of the expansion coefficients; this results in a considerable simplification of the computational work. Unlike Ref. 15, however, a state-by-state determination of TF is not proposed, but more generally that they be optimized for a given manifold of molecular wave functions; the dimension of this manifold, can, of course, be taken to be equal to one if so desired. In Sec. II the optimization criterion is proposed and its characteristics are discussed. Then we consider the practical calculation of the functional to be minimized. For simplicity, we shall only study the optimization of TF in the impact-parameter formalism; the treatment can be generalized to the quantum-mechanical formalism and RC. On the other hand, the form of the TF (that is, of the trial space) will be left quite general; for example, they can be different, or not, for each molecular state. In this way, we aim at obtaining a practical criterion, not only to determine TF within a trial space, but also to compare different approaches. Atomic units are used throughout.

II. THEORY

The impact-parameter equation is

$$\left[i\frac{\partial}{\partial t}\bigg|_{\vec{r}} - H_{\rm el} \right]\psi(\vec{r},t)=0 , \tag{1}$$

where $\vec{r}$ denotes the set of electronic coordinates, defined with respect to a common origin $\vec{O}$; $H_{\rm el}$ stands for the electronic Born-Oppenheimer Hamiltonian; and the nuclei, separated by a distance R, are assumed to follow a straight-line trajectory $\vec{R}=\vec{b}+\vec{v}t$, with impact parameter b and velocity $\vec{v}$. Equation (1) must be solved subject to the limit condition proper to the process under study (see, e.g., Ref. 2 for details). In the modified molecular method, one chooses for ψ the ansatz

$$\psi_{\rm app}=\sum_{n=1}^{\mathcal{N}} a_n(t)\phi_n(\vec{r},t)\exp\left[i\left[U_n(\vec{r},t)-\int_0^t E_n\,dt \right]\right] , \tag{2}$$

where ψ_n, E_n are the molecular wave functions and energies, and U_n the (velocity and origin-dependent) translation factors. When $\phi_n \sim \mathcal{A}\varphi_n^A\chi_n^B$ as $R\rightarrow\infty$, representing at infinite internuclear separation an atom A with n_A electrons and an atom B with n_B electrons, U_n must fulfill[2]

$$\phi_n(\vec{r},t)e^{iU_n(\vec{r},t)} \sim \mathcal{A}\left[\varphi_n^A\chi_n^B\exp\left\{-i\left[\vec{v}\cdot\left[p\sum_{j=1}^{n_A}\vec{r}_j-q\sum_{j=n_A+1}^{n_A+n_B}\vec{r}_j\right]+\tfrac{1}{2}(n_A^2p^2+n_B^2q^2)v^2t\right]\right\}\right] \text{ as } R\rightarrow\infty , \tag{3}$$

where $\mathcal{A}$ is the antisymmetrizer and the origin $\vec{O}$ of electronic coordinates is situated at a distance pR of the nucleus of A and qR of that of B. Each term of the sum (2) then fulfills Eq. (1) when $R\rightarrow\infty$, which is equivalent to saying that the set of modified molecular wave functions $\{\phi_n e^{iU_n}\}$ presents no residual couplings at infinity. On the other hand, the standard (unmodified) molecular approach sets $U_n=0$, which does not fulfill (3), in general, and accordingly residual couplings are present between molecular states such that

$$\lim_{R\rightarrow\infty} \langle\phi_n \,|\, i\partial/\partial t - H_{\rm el} \,|\, \phi_m\rangle \neq 0 .$$

Each specific choice taken for the functions $\{U_n\}$ in Eq. (2) gives rise to a set of (new) dynamical couplings and modifies the molecular energies and electrostatic couplings.[2] Unless $v \ll 1$ a.u., these corrections to the energies and to the couplings which are responsible for transitions can be quite important, and strongly depend on the specific form of the TF.[15–17] Since this form is arbitrary at finite R—except for the obvious requirement that it be symmetric with respect to electron exchange—and an "unreasonable" form can cause unphysical transitions and render the ansatz quite useless, it is proper to question the physical appropriateness of those corrections. In practice, while some cross sections turn out to be fairly independent of the explicit form of the TF[17] (within certain limits), some other cross sections vary strongly when this form is changed.[5–7] The question is what are "reasonable" forms for TF. In this context, let us briefly discuss two aspects of the determination of TF.

First, suppose that for each term of (2) we optimize the TF using a Euler-Lagrange variational method, and suppose further that the wave function ϕ_n has strong radial or rotational couplings with other molecular functions. One can then expect[9,10] that the resulting TF will make the magnitude of $\partial/\partial t(\phi_n e^{iU_n})$ smaller than that of $\partial/\partial t\phi_n$. On the other hand, the effect of a strong coupling $\langle\phi_m \,|\, \partial/\partial t) \,|\, \phi_n\rangle$ can be very simply taken into account by the expansion coefficients a_n, a_m through transitions between the states n and m. Hence, in a state-by-state optimization of TF it is difficult[18] to separate purely "kinematical" and "dynamical" effects in the evolution of each molecular state.

Second, the simplest physical meaning to be attributed to U_n is that $\vec{\nabla}U_n$ represents a velocity field of the electron cloud due to the nuclear motion[9,19] (the corresponding current density being $\vec{j}_n=-\phi_n^2\vec{\nabla}U_n$). However, $\vec{\nabla}U_n$, being irrotational, cannot reproduce the electronic flux due to the rotation of the nuclei at short distances; on the other hand, this flux is correctly described through transitions between Σ-Π, Σ-Π-Δ, etc. molecular states. More precisely, it has been shown[9] that, in an electronic reference frame where the nuclear center of charge is at rest, the motion of the nuclei produces a null density flux in the limit $R=0$. Then, one should have $\vec{\nabla}U_n=\vec{0}$ in this limit; otherwise, one finds[7] that the unphysical character of a velocity field $\vec{\nabla}U_n$ at small R causes the expansion (2) to exhibit very poor convergence in this range of internuclear distances. The condition $\vec{\nabla}U_n=\vec{0}$ is often enforced[18] in the form of a cutoff for U_n. However, when choosing the explicit form for the cutoff factor, the obvious question is how large should be the region where $U_n\simeq 0$. As pointed out in Ref. 20, taking $U_n\simeq 0$ is equivalent to employing the unmodified (without TF) molecular expansion, with the unfortunate consequence that the origin dependence of the results of the standard molecular method can reappear, when TF are introduced, as a functional dependence on the parameters that are explicitly or implicitly introduced in those TF. When rotational and strongly origin-dependent radial couplings are both effective at small and intermediate R, there is no indication of the form U_n should have in this range of internuclear distances;[7] an optimization procedure is needed, in which rotational, radial, and electrostatic couplings are simultaneously taken into account.

With these characteristics in mind, we consider, like Rankin and Thorson,[15] the set of TF $\{U_n\}$, besides eliminating residual couplings at infinity through condition

(3), as modifying the convergence properties of the molecular expansion:

$$\psi(\vec{r},t)=\sum_{n=1}^{\infty} a_n(t)\phi_n(\vec{r},t) \times\exp\left[i\left[U_n(\vec{r},t)-\int_0^t E_n\,dt\right]\right] , \tag{4}$$

where the summation in (4) contains an integration over continuum electronic wave functions. The ansatz (2) corresponds to the truncation of (4) after $\mathcal{N}$ terms. A good choice for $\{U_n\}$ speeds up the convergence of (4) (e.g., this is always so for $R\to\infty$) and a bad choice can slow it down so much that the approximation (2) is useless. Direct study of the convergence of transition probabilities or of cross sections as functionals of $\{U_n\}$ is exceedingly laborious, and we search for a much simpler criterion to approximately optimize the TF, within a trial space and for a given set of molecular wave functions $\{\phi_n\colon n=1,\ldots,\mathcal{N}\}$, for small nuclear velocities. Incidentally, it is basic to our reasoning that we *assume* that the right-hand side (rhs) of Eq. (4) converges to the exact solution of Eq. (1), even in the weak sense; otherwise, the molecular treatment is questionable. This is a point that we shall not dwell upon in this work; we notice, however, that formal convergence has only been proved in very special instances: the common RC approach of Thorson and Delos[21] and the common TF method of Schneiderman and Russek[19,6] (see Ref. 20).

Introducing the ansatz (2) in Eq. (1) is equivalent to solving

$$P\left[i\frac{\partial}{\partial t}\bigg|_{\vec{r}}-H_{\text{el}}\right]P\psi_{\text{app}}(\vec{r},t)=0 , \tag{5}$$

where P is the projector over the manifold spanned by the set of functions $\{\phi_n e^{iU_n}\colon n=1,\ldots,\mathcal{N}\}$, hereafter called P space and P functions, respectively. On the other hand, Eq. (1) can be written

$$\left[P\left[i\frac{\partial}{\partial t}\bigg|_{\vec{r}}-H_{\text{el}}\right]P+Q\left[i\frac{\partial}{\partial t}\bigg|_{\vec{r}}-H_{\text{el}}\right]P +P\left[i\frac{\partial}{\partial t}\bigg|_{\vec{r}}-H_{\text{el}}\right]Q+Q\left[i\frac{\partial}{\partial t}\bigg|_{\vec{r}}-H_{\text{el}}\right]Q\right]\psi=0 \tag{6}$$

with $Q=1-P$. We call Q space the complementary space and Q functions those forming the set $\{\phi_n e^{iU_n}\colon n>\mathcal{N}\}$. From Eq. (6) we notice that $P\psi$ does not fulfill (5); hence $P\psi\neq\psi_{\text{app}}$. Also, for nonorthogonal bases, the Q space is a *proper* subspace of the span of $\{\phi_n e^{iU_n}\colon n>\mathcal{N}\}$.

At small velocities, provided that the basis set of P functions has been adequately chosen, the wave function ψ_{app} of (5) approximates the exact solution of (1) [or (6)]. One has $\psi\neq\psi_{\text{app}}$, however, because

$$\left[i\frac{\partial}{\partial t}\bigg|_{\vec{r}}-H_{\text{el}}\right]\psi_{\text{app}}=Q\left[i\frac{\partial}{\partial t}\bigg|_{\vec{r}}-H_{\text{el}}\right]P\psi_{\text{app}}\neq 0 , \tag{7}$$

and the operator $Q[i(\partial/\partial t)|_{\vec{r}}-H_{\text{el}}]P$ couples P functions to those of the complementary space and takes the state vector ψ out of P space [see (6)] even if initially ($t\to-\infty$) it belonged to this space. We are thus led, as a criterion to improve the convergence properties of the expansion (2), prior to and uncoupled from the calculation of the expansion coefficients, to choose the set of TF $\{U_n\}$ that minimizes[15] the couplings between the set $\{\phi_n e^{iU_n}\colon n=1,\ldots,\mathcal{N}\}$ and those spanning the complementary space (P-Q coupling).

To apply our criterion, we require a measure of P-Q coupling, which can then be used as a functional of the set of TF $\{U_n\}$. For a general choice of these TF, however, one has to be careful because P and Q functions can have a large overlap; in this case the magnitude of the coupling matrix elements is not directly relevant, and a prior orthogonalization of the Q to the P functions is obviously excluded for practical reasons.

Hence, we start by considering the particular case of an orthonormal set $\{\phi_n e^{iU_n}\}$—for example, when a common TF U is employed in (2). In this case, *any* norm of the P-Q—coupling generalized matrix is a good measure of these couplings. The simplest one is the Euclidean norm, i.e., the sum of the squares of the absolute values of all P-Q couplings, including integration over continuum Q functions; the convergence of this sum will be proved in Sec. III. By writing this Euclidean norm in operational form we obtain an expression which is directly applicable to the nonorthonormal case:

$$N^2[U_n]=\sum_{m=1}^{\mathcal{N}}\left\|Q\left[i\frac{\partial}{\partial t}\bigg|_{\vec{r}}-H_{\text{el}}\right]P\phi_m \times\exp\left[i\left[U_m-\int_0^t E_m\,dt\right]\right]\right\|^2 , \tag{8}$$

where overlap effects are taken into account through the projection operators P and Q.

We thus propose to minimize $N[U_n]$ for each nuclear trajectory,[22] within a trial space for $\{U_n\}$ and for a given manifold $\{\phi_n\colon n=1,\ldots,\mathcal{N}\}$. The translation factors $\{U_n\}$ are thus viewed as providing the smallest set of couplings [in the sense provided by the norm (8)] from P to Q space. Because of the positive definite character of the functional, this minimization may be carried out either point by point or for $\int_{-\infty}^{+\infty}N\,dt$; notice that in general the former procedure entails a more flexible form of the TF than the latter, since all parameters in these TF must then be functions of time. Clearly, $N[U_n]\geq 0$, and

$$N[U_n]=0 \text{ for all } t ,$$

together with

$$\lim_{t\to-\infty}(\psi-P\psi)=0 ,$$

imply

$$\psi_{\rm app}(\vec{r},t)\equiv\psi(\vec{r},t)\ . \tag{9}$$

The proof of (9) is very simple. $N[U_n]=0$ implies that $Q[i(\partial/\partial t)\,|_{\vec{r}}-H_{\rm el}]P$ is the null operator. Then $P\psi_{\rm app}$ [the solution of Eq. (5)] is also a solution of Eq. (6). From $\lim(\psi-P\psi)=0$ and Eq. (3), it also fulfills the initial condition. Therefore, solving Eq. (5) yields, when $N[U_n]=0$, the exact solution to the collision problem. This property of the functional N is of obvious importance and links our approach to the Euler-Lagrange variational method of Ref. 11. In contrast with this latter method, however, N is *bound* below and is symmetric with respect to all P functions; in particular, it does not contain any information on the initial state of the collision system. This last property might be a slight inconvenience when some molecular states (e.g., the entrance channel) are much more strongly populated than others during the whole collision process. It is then trivial to generalize (8) to

$$N^2[U_n]=\sum_{m=1}^{\mathcal{N}} w_m \left|\left| Q\left[i\frac{\partial}{\partial t}\Big|_{\vec{r}} - H_{\rm el}\right] P\phi_m \times \exp\left[i\left[U_m-\int_0^t E_m\,dt\right]\right]\right|\right|^2 , \tag{10}$$

where w_m are appropriate weights.

The intuitive generalization (10) of $N[U_n]$ is connected to the definition in Ref. 14 of the measure of the deviation $\delta\psi=\psi-\psi_{\rm app}$ of the approximate wave function $\psi_{\rm app}$ from the exact solution ψ of Eq. (1):

$$D=\left|\left|\left[i\frac{\partial}{\partial t}\Big|_{\vec{r}} - H_{\rm el}\right]\delta\psi\right|\right|^2 . \tag{11}$$

The connection can be seen from Eqs. (2), (7), and (11) and $QP=0$:

$$\begin{aligned} D&=\left|\left| Q\left[i\frac{\partial}{\partial t}\Big|_{\vec{r}} - H_{\rm el}\right] P\psi_{\rm app}\right|\right|^2 \\ &=\left|\left| \sum_{m=1}^{\mathcal{N}} a_m(t) Q\left[i\frac{\partial}{\partial t}\Big|_{\vec{r}} - H_{\rm el}\right] P\phi_m \exp\left[i\left[U_m-\int_0^t E_m\,dt\right]\right]\right|\right|^2 \\ &\le \sum_{m=1}^{\mathcal{N}} |a_m|^2 \left|\left| Q\left[i\frac{\partial}{\partial t}\Big|_{\vec{r}} - H_{\rm el}\right] P\phi_m \exp\left[i\left[U_m-\int_0^t E_m\,dt\right]\right]\right|\right|^2 , \end{aligned} \tag{12}$$

and the rhs of (12) becomes (10) for $w_n=|a_n|^2$, in agreement with our intuitive choice. To obtain a rigorous bound of D by N^2, we require an upper bound on $|a_n|^2$. For example, in the special case of a common TF, $\sum_{n=1}^{\mathcal{N}}|a_n|^2=1$, and one has

$$0\le D\le \gamma N^2 , \tag{13}$$

where $\gamma=1$ when N is given by (8), and $\gamma=w_\nu^{-1}$ for Eq. (10), where ν is such that either

$$|a_\nu|=\max_n(|a_n|) \tag{14}$$

or

$$\left|\left| Q\left[i\frac{\partial}{\partial t}\Big|_{\vec{r}} - H_{\rm el}\right] P\phi_\nu e^{iU_\nu}\right|\right| =\max_n\left\{ \left|\left| Q\left[i\frac{\partial}{\partial t}\Big|_{\vec{r}} - H_{\rm el}\right] \times P\phi_n \exp\left[i\left[U_n-\int_0^t E_n dt\right]\right]\right|\right|\right\} , \tag{15}$$

Eq. (13) implies that when $N<\epsilon$, $0<\gamma\epsilon^2$ and a small value of ϵ means that $\delta\psi\simeq 0$, i.e., $\psi\simeq\psi_{\rm app}$.

In practice, it is not indispensable to reach the absolute minimum of (8) [or (10], which may have several relative minima. Any choice of U_n that reasonably speeds up the convergence of (2) will do; if within a region of trial space $N[U_n]$ turns out be to insensitive to the choice of $\{U_n\}$, so much the better. Comparison between different methods, and several forms of TF, is provided by the functional $N[U_n]$, for a given set of molecular wave functions $\{\phi_n:\ n=1,\ldots,\mathcal{N}\}$. In particular, if for some point along the trajectory $N[U_n]>N[0]$ in all trial space, a cutoff is needed because the TF clearly impair the description of the process by the molecular basis. The form of this cutoff can be inferred from the values of $N[U_n]$ and $N[0]$ at neighboring points of the trajectory. Analogously, one can test the appropriateness of intuitive conditions[19] enforced on TF.

The convergence property (9) of the norm (8) [or of (10)] has an interesting consequence. Suppose that the trial space of U_n contains a (proper) subspace corresponding to a common TF U; this is the case for many choices of TF proposed (see, e.g., Refs. 9, 13, 16, and 19 and lists in Ref. 2). Then one has

$$0\le N[U_n]\le N[U]\ . \tag{16}$$

Since $N[U]\to 0$ as $\mathcal{N}\to\infty$, because the set $\{\phi_n e^{iU}\}$ becomes complete in this limit and $Q\to 0$, the inequality (16) implies that $N[U_n]\to 0$ as $\mathcal{N}\to\infty$ too. We have thus shown the completeness of the set $\{\phi_n e^{iU_n}\}$ as $\mathcal{N}\to\infty$ provided that, for each value of $\mathcal{N}$, the TF $\{U_n\}$ are calculated according to our criterion.

On the other hand, the measure (8) [or (10)] should not be used as an additional (more ambitious) criterion for the convergence of (2) when $\mathcal{N}$ increases. For example, increasing the basis set always improves the description of the collision process, while it might shift strong Q-Q couplings into P-Q couplings and thereby increase $N[U_n]$. In other words, while $N[U_n]\to 0$ as $\mathcal{N}\to\infty$, this limiting procedure may not be monotonic. Formally, it is trivial to generalize (8) or (10) to obtain a monotonic function of $\mathcal{N}$, by extending the measure to include Q-P and Q-Q couplings. However, a great advantage of the present approach, shown in Sec. III, is that it does not involve the explicit calculation of P-Q couplings, whereas they should be calculated for a monotonic $N[U_n]$. For this important practical reason, we restrict our procedure to the determination of TF for a given molecular representation. In Sec. III we shall briefly consider the evaluation of the functional $N[U_n]$ of Eq. (8)—the corresponding expressions for (10) are practically identical.

III. EVALUATION OF $N[U_n]$

Using closure in Eq. (8) we obtain the expression

$$
\begin{aligned}
N^2[U_n]=&\sum_{m=1}^{\mathcal{N}}\left\langle\left[\left.i\frac{\partial}{\partial t}\right|_{\vec{r}}-H_{\rm el}\right]\phi_m\exp\left[i\left[U_m-\int_0^t E_m\,dt\right]\right]\right|1-P\left|\left[\left.i\frac{\partial}{\partial t}\right|_{\vec{r}}-H_{\rm el}\right]\phi_m\exp\left[i\left[U_m-\int_0^t E_m\,dt\right]\right]\right\rangle\\
=&\sum_{m=1}^{\mathcal{N}}\left\{\left\langle\left[\left.i\frac{\partial}{\partial t}\right|_{\vec{r}}-H_{\rm el}\right]\phi_m\exp\left[i\left[U_m-\int_0^t E_m\,dt\right]\right]\right|\left|\left[\left.i\frac{\partial}{\partial t}\right|_{\vec{r}}-H_{\rm el}\right]\phi_m\exp\left[i\left[U_m-\int_0^t E_m\,dt\right]\right]\right\rangle\right.\\
&-\sum_{k,l=1}^{\mathcal{N}}\left\langle\left[\left.i\frac{\partial}{\partial t}\right|_{\vec{r}}-H_{\rm el}\right]\phi_m\exp\left[i\left[U_m-\int_0^t E_m\,dt\right]\right]\right|\phi_m\exp\left[i\left[U_k-\int_0^t E_k\,dt\right]\right]\right\rangle\\
&\left.\times(S^{-1})_{kl}\left\langle\phi_l\exp\left[i\left[U_l-\int_0^t E_l\,dt\right]\right]\right|\left|\left[\left.i\frac{\partial}{\partial t}\right|_{\vec{r}}-H_{\rm el}\right]\phi_m\exp\left[i\left[U_m-\int_0^t E_m\,dt\right]\right]\right\rangle\right\},
\end{aligned}
\tag{17}
$$

where

$$
S_{kl}=\left\langle\phi_k\exp\left[i\left[U_k-\int_0^t E_k\,dt\right]\right]\right|\left.\phi_l\exp\left[i\left[U_l-\int_0^t E_l\,dt\right]\right]\right\rangle .
$$

For well-behaved TF $\{U_n\}$, Eq. (17) proves the convergence of the norm (8)—and of the Euclidean norm of the P-Q—coupling generalized matrix in the particular case of an orthonormal basis $\{\phi_n e^{iU_n}\}$.

The evaluation of the second term in Eq. (17) does not present any difficulty, since it can be calculated from the knowledge of the modified electrostatic and dynamical couplings[2,23] which are needed to solve Eq. (5). The first term in (17) involves new diagonal matrix elements between P functions (i.e., no Q space discrete or continuum wave functions appear). It can be calculated exactly by extending the quantum-chemical techniques usually employed to calculate energies and couplings.[2,24] It can also be calculated to a sufficiently good approximation by assuming that the wave functions ϕ_n are exact eigenfunctions of the electronic Hamiltonian (or linear combinations of them, as in the case of diabatic states). This assumption can be exactly fulfilled for one-electron systems and can be satisfied as well as desired for many-electron systems; it drastically simplifies the evaluation of $N[U_n]$ and is a sensible approximation since one is interested in TF optimization and not in ascertaining the quality of the molecular wave functions. Then, one takes

$$
\begin{aligned}
&\left[\left.i\frac{\partial}{\partial t}\right|_{\vec{r}}-H_{\rm el}\right]\phi_m\exp\left[i\left[U_m-\int_0^t E_m\,dt\right]\right]\\
&\quad=\exp\left[i\left[U_m-\int_0^t E_m\,dt\right]\right]\left[\left.i\frac{\partial}{\partial t}\right|_{\vec{r}}+\frac{i}{2}\sum_j\nabla_j^2U_m-\frac{1}{2}\sum_j(\vec{\nabla}_jU_m)^2-\left.\frac{\partial U_m}{\partial t}\right|_{\vec{r}}+i\sum_j\vec{\nabla}_jU_m\cdot\vec{\nabla}_j\right]\phi_m\\
&\quad\equiv\exp\left[i\left[U_m-\int_0^t E_m\,dt\right]\right]\left[\left.i\frac{\partial}{\partial t}\right|_{\vec{r}}+G_m(\vec{r},t)+i\sum_j\vec{\nabla}_jU_m\cdot\vec{\nabla}_j\right]\phi_m ,
\end{aligned}
\tag{18}
$$

where the sums run over all electrons. The first term in (17) then becomes a sum of matrix elements of the form

$$
\begin{aligned}
&\left\langle\left[\left.i\frac{\partial}{\partial t}\right|_{\vec{r}}+G_m+i\sum_j\vec{\nabla}_jU_m\cdot\vec{\nabla}_j\right]\phi_m\right|\left|\left[\left.i\frac{\partial}{\partial t}\right|_{\vec{r}}+G_m+i\sum_j\vec{\nabla}_jU_m\cdot\vec{\nabla}_j\right]\phi_m\right\rangle\\
&\quad=\left\langle\left.i\frac{\partial\phi_m}{\partial t}\right|_{\vec{r}}\left|\left.i\frac{\partial\phi_m}{\partial t}\right|_{\vec{r}}\right.\right\rangle+\langle\phi_m\,|\,G_m^2\,|\,\phi_m\rangle+\sum_{j,k}\langle\vec{\nabla}_j\phi_m\cdot\vec{\nabla}_jU_m\,|\,\vec{\nabla}_k\phi_m\cdot\vec{\nabla}_kU_m\rangle+2\sum_j\left\langle\vec{\nabla}_j\phi_m\cdot\vec{\nabla}_jU_m\left|\left.\frac{\partial\phi_m}{\partial t}\right|_{\vec{r}}\right.\right\rangle\\
&\qquad+2\left\langle\phi_m\left|\mathrm{Im}(G_m)\right|\left.\frac{\partial\phi_m}{\partial t}\right|_{\vec{r}}\right\rangle+2\sum_j\langle\vec{\nabla}_j\phi_m\cdot\vec{\nabla}_jU_m\,|\,\mathrm{Im}(G_m)\,|\,\phi_m\rangle .
\end{aligned}
\tag{19}
$$

The difficulty in the evaluation of the second and third terms of Eq. (19) depends completely on the analytical form chosen for U_m; usually, their calculation is trivial. For the other terms in (19), as for the usual dynamical couplings, one has to pass from laboratory-fixed axes to a molecule-fixed reference frame for the electronic coordinates, with the z axis along the internuclear vector and $\hat{X}=\hat{b}$. We do not go into the details of this well-known transformation. Finally, there appear the following new matrix elements:

$$\langle F_m \mid iL_y \mid \phi_m \rangle \,, \tag{20a}$$

$$\left\langle F_m \left| \frac{\partial}{\partial R} \right| \phi_m \right\rangle , \tag{20b}$$

$$\langle iL_y\phi_m \mid iL_y\phi_m \rangle \,, \tag{20c}$$

$$\left\langle \frac{\partial}{\partial R}\phi_m \left| \frac{\partial}{\partial R}\phi_m \right\rangle \right. , \tag{20d}$$

where F_m is a function of $\vec{r}$, and t, like $G_m\phi_m$ and L_y, is the angular momentum operator. All these matrix elements in (20) can be calculated with appropriate modifications of the usual techniques to calculate couplings in the molecular method.[2] For example, when one uses simple analytical forms for the TF[9] and a configuration-interaction (CI) treatment to construct the molecular wave functions, and the basis configurations are symmetry-adapted antisymmetrized products of Gaussian-type orbitals (GTO's) then all matrix elements (20)—like the dynamical couplings in the usual method[23,24]—can be evaluated *analytically*. This is obvious for the matrix elements [(20a), (20c)] since the application of the operator iL_y to a GTO yields a linear combination of GTO's. To calculate [(20b), (20d)] one requires the derivatives of the coefficients of the CI expansion, whose analytical evaluation is explained in detail in Refs. 2 and 24; for (20d) we need matrix elements that are also required in the quantal treatment of collision problems[25] and that can also be analytically evaluated.[2]

IV. CONCLUSION

There is a general lack of agreement as to the correct form translation factors should have at finite internuclear distances, and the need for a practical criterion to determine this form has been stressed in the introduction. Following an idea of Rankin and Thorson,[15] we propose to minimize the functional $N[U_n]$ of Eq. (8)—or its generalization (10)—as a practical solution, at low and intermediate velocities, to optimize the TF $\{U_n\}$ in a given trial space for a given set of molecular functions $\{\phi_n\colon\ n=1,\ldots,\mathcal{N}\}$. That functional N is a measure of the (electrostatic and dynamical) couplings between the states included in the molecular expansion (2) and those (discrete or continuum) states that have been left out. The properties of the functional $N[U_n]$ have been studied in Sec. II. In particular, it is always ≥ 0, and the lower bound 0 is reached for a whole trajectory when (and only when) the wave function ψ_{app} that fulfills (5) is an exact solution of (1). The procedure is closely connected to the minimization[14] of a measure of the deviation $\delta\psi=\psi-\psi_{\text{app}}$ between approximate and exact wave functions, for each point of the trajectory. Our proposal is that the collision treatment be carried out in two steps. In the first step the TF are determined by (approximate[22]) optimization of $N[U_n]$; the second step is then identical to the usual treatment—i.e., solving the system of linear differential equations[2] for the expansion coefficients a_n and calculating the transition probabilities. In this procedure the determination of TF is uncoupled from that of the expansion coefficients, and a drastic reduction of computational work is achieved with respect to a coupled determination of $\{U_n,a_n\}$; also, in routine calculations, a lower degree of accuracy may be used to evaluate (19) than is needed for the usual couplings.

The main advantage of the method proposed here to determine TF is that it is easily implemented and involves a modest amount of computational effort. It should be noticed that it does not correspond to an optimization procedure on the transition probabilities; it is in principle possible that a set of parameters in the TF that does not correspond to a minimum for N yields a more accurate value for a particular cross section than our "optimum" choice for those parameters. However, since $N\to 0$ when $\mathcal{N}\to\infty$ or $R\to\infty$, and the molecular basis is assumed to be adequately chosen (for instance, it can satisfactorily describe the collision process at lower velocities), one can reasonably expect that minimizing (8) or (10) will improve the convergence properties of the basis set. Furthermore, if one wishes to lay stress upon optimization of TF, our procedure may be viewed as providing a first approximation to the optimum choice, that may be further refined as much as desired (at the expense of more computational effort), to finally yield the coupled method of Chang and Rapp.[14] For example, intermediate approaches would involve in (10) weights w_m as close to $|a_m|^2$ as desired. In practice, to better the description of a given collision process, one can improve (i) the molecular basis, (ii) the TF functional space, and (iii) the optimization technique. Obviously, the most appropriate procedure depends upon the characteristics of the process studied and on the computational efforts involved.

We have shown in Sec. III that the evaluation of $N[U_n]$ only involves the calculation of a few matrix elements, that can be performed analytically for simple analytical forms of the TF and when atomic basis sets of GTO's are employed to build the wave functions. Work is in progress at our laboratory to set up the programs that systematically calculate these new matrix elements with the required precision to calculate $N[U]$ for the particular case of a common translation factor. The present formalism, however, is not restricted to this special case: We have left the explicit form of the TF quite general so that our criterion also permits the use of any set of TFs $\{U_n\}$, the comparison between different approaches,[26] and a test of some conditions that are usually enforced on TFs, such as the introduction of cutoff factors. One aim of our work is to provide a simple method that can be used in benchmark studies to find out which general properties are desirable for translation factors at finite internuclear distances and thus clarify the present situation. We hope that it will also encourage authors to present a more rigorous justification of new forms of TF than those solely based on physical intuition.

ACKNOWLEDGMENTS

I would like to thank Dr. L. F. Errea and Dr. V. H. Ponce for a critical reading of the manuscript.

---

[1] D. R. Bates, H. S. W. Massey, and A. L. Steward, Proc. R. Soc. London, Ser. A **216**, 437 (1953); D. R. Bates and R. McCarroll, *ibid.* **245**, 175 (1958).

[2] See, e.g., W. R. Thorson and J. B. Delos, Phys. Rev. A **18**, 117 (1978); **18**, 135 (1978); J. B. Delos, Comments At. Mol. Phys. **10**, 211 (1981); Rev. Mod. Phys. **53**, 287 (1981); A. Riera, Comments At. Mol. Phys. **12**, 95 (1982); A. Macías and A. Riera, Phys. Rep. **90**, 299 (1982).

[3] A. Salop and R. E. Olson, Phys. Rev. A **19**, 1921 (1979); A. Macíos, A. Riera, and M. Yáñez, *ibid.* **23**, 2942 (1981); **27**, 206 (1983); **27**, 213 (1983); F. Borondo, A. Macías, and A. Riera, Chem. Phys. **81**, 303 (1983).

[4] Too many calculations have been performed using TF to give detailed referencing. Many important papers are listed in the references of Ref. 2.

[5] M. H. Mittleman, Phys. Rev. **181**, 231 (1969); see also references in Ref. 2.

[6] H. Levy II and W. R. Thorson, Phys. Rev. **181**, 252 (1969).

[7] L. F. Errea, L. Méndez, and A. Riera, Phys. Rev. **28**, 3357 (1983).

[8] M. E. Riley and T. A. Green, Phys. Rev. A **4**, 619 (1971).

[9] V. H. Ponce, J. Phys. B **12**, 3731 (1979); **14**, 2823 (1981).

[10] D. S. F. Crothers and N. R. Todd, J. Phys. B **14**, 2233 (1981).

[11] N. C. Sil, Proc. Phys. Soc. London **75**, 194 (1960); I. M. Cheshire, J. Phys. B **1**, 428 (1968); R. McCarroll, R. D. Piacentini, and A. Salin, *ibid.* **3**, 137 (1970).

[12] D. Storm, Phys. Rev. A **8**, 1777 (1973); see also A. Salin, *Twelfth International Conference on the Physics of Electronic and Atomic Collisions, Invited Papers, Gatlinburg, Tenn., 1981*, edited by S. Datz (North-Holland, Amsterdam, 1982).

[13] S. Geltman, *Topics in Atomic Collision Theory* (Academic, New York, 1964); D. Storm, Phys. Rev. A **8**, 1789 (1973).

[14] C. Chang and D. R. Rapp, J. Chem. Phys. **59**, 972 (1973); A. B. Weighlein, Phys. Rev. A **17**, 1810 (1978).

[15] J. Rankin and W. R. Thorson, Phys. Rev. A **18**, 1990 (1978).

[16] W. R. Thorson, M. Kimura, J. H. Choi, and S. K. Knudson, Phys. Rev. A **24**, 1768 (1981).

[17] L. F. Errea, L. Méndez, and A. Riera, Phys. Lett. **92**, 231 (1982).

[18] G. B. Schmidt, J. Phys. B **12**, 3909 (1979); A. Salin, Comments At. Mol. Phys. **9**, 165 (1980).

[19] S. B. Schneiderman and A. Russek, Phys. Rev. **181**, 311 (1969).

[20] L. F. Errea, L. Méndez, and A. Riera, J. Phys. B **15**, 101 (1982).

[21] W. R. Thorson and J. B. Delos, Phys. Rev. A **18**, 135 (1978).

[22] In practice, detailed minimization of (8) or (10) along each trajectory is clearly unnecessary: specific trajectories (depending on whether one is interested in total or differential cross sections, on the type of processes involved, etc.) can be selected.

[23] L. F. Errea, L. Méndez, and A. Riera, J. Phys. B **12**, 69 (1979); Comput. Phys. Commun. **31**, 47 (1984).

[24] A. Macías and A. Riera, J. Phys. B **10**, 861 (1976); **11**, 1077 (1977).

[25] F. Borondo, L. R. Eguiagaray, and A. Riera, J. Phys. B **15**, 899 (1982).

[26] It is possible that a given approach is more appropriate for small internuclear distances, while the reverse situation holds for intermediate R. A direct measure of these characteristics can be obtained by drawing, for each choice of trial space, contour lines of isominimum N in the collision plane.