Variational formulation of the coupled-state impact-parameter method*

Robin Shakeshaft and Larry Spruch
Department of Physics, New York University, New York, New York 10003
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In the coupled-state impact-parameter method, the exact impact-parameter wave function is approximated by a trial impact-parameter wave function which is a finite linear combination of N basis vectors with time-dependent coefficients. In the standard approach the coefficients are determined by solving the equations obtained by projecting the impact-parameter Schrödinger equation with the exact wave function replaced by the trial wave function onto the N basis vectors which define the trial wave function. It is well known that this method gives variational estimates of the transition amplitudes if the basis vectors represent physical states. However, if in proton–hydrogen-atom scattering Sturmian basis vectors, which are for the most part nonphysical basis vectors, are used, the method is not variational. In this paper it is shown that if Sturmian basis vectors are used the method can be made variational by projecting the Schrödinger equation with the exact wave function replaced by the trial wave function onto the *physical* basis vectors of interest rather than onto the Sturmian basis vectors; the resultant equations are no more difficult to solve than the standard equations. It is also shown that useful *variational* bounds on the error of the estimate of a transition amplitude exist only if the trial wave function is expanded in terms of a physical basis set.

I. INTRODUCTION

In the impact-parameter approximation to proton–hydrogen-atom collisions, the two protons are treated as classical particles which move with constant velocity. Thus the protons become moving centers of force which subject the electron to a time-dependent potential, and the electron may undergo transitions to various states. In order to calculate the various transition amplitudes, the time-dependent impact-parameter Schrödinger equation for the electron is solved approximately; a commonly used approximation is the coupled-state (or close-coupling) method. In this method the exact impact-parameter state vector $|\Psi_i(t)\rangle$ (where i denotes the initial state of the system) is approximated by a trial impact-parameter state vector $|\Psi_{i,\mathrm{tr}}(t)\rangle$ which satisfies the same initial boundary condition as $|\Psi_i(t)\rangle$ but is written as a linear combination of a *finite* number N of specified basis vectors $|\phi_{in}(t)\rangle$, $n=1,\ldots N$, with time-dependent coefficients. In the standard approach, the coefficients are determined by solving the set of N coupled differential equations that are obtained by first replacing $|\Psi_i(t)\rangle$ by $|\Psi_{i,\mathrm{tr}}(t)\rangle$ in the impact-parameter Schrödinger equation, and then projecting this modified equation onto the N basis vectors $|\phi_{in}(t)\rangle$. The approximate transition amplitude to a given final state f is then given by $\langle\Phi_f(T)|\Psi_{i,\mathrm{tr}}(T)\rangle$, where $|\Phi_f(t)\rangle$ is the vector which represents the unperturbed state f and where T is very large and positive.

The question naturally arises as to the accuracy of the above approximation. It is well known[1] that if the basis states are physical states—states which tend to the true states of the proton–hydrogen-atom system when the protons are far apart—the standard approach is variational. This means that the error in the calculated transition amplitude is of the order of the *square* of some weighted average of $\Psi_i - \Psi_{i,\mathrm{tr}}$. However, Gallaher and Wilets[2] have adopted the standard approach and used a Sturmian basis set. The virtue of a Sturmian basis set is that the Sturmian functions form a *discrete* set which is complete. However, for any given angular momentum, all but one Sturmian function is nonphysical, and although the results of Gallaher and Wilets appear to be quite good, the standard approach is not variational when a Sturmian basis set is used. One purpose of the present paper is to develop a method which *is* variational for a Sturmian basis set. The difficulty in using Sturmian states arises because, although the initial state can usually be represented by a finite linear combination of Sturmian basis vectors, the final state often cannot be so represented. We overcome this difficulty by introducing a second trial state vector $|\Psi_{f,\mathrm{tr}}(t)\rangle$ which, for large positive times, represents the final state f of interest. We also introduce a second set of N basis vectors $|\phi_{fn}(t)\rangle$, $n=1,\ldots N$, and $|\Psi_{f,\mathrm{tr}}(t)\rangle$ is written as a linear combination of the $|\phi_{fn}(t)\rangle$. One can consider transitions to those physical states which are represented by linear combinations of the $|\phi_{fn}(t)\rangle$. As will be seen below, in order to calculate a variational estimate of the transition amplitude, it is only necessary to know $|\Psi_{i,\mathrm{tr}}(t)\rangle$, and it is unnecessary to know $|\Psi_{f,\mathrm{tr}}(t)\rangle$. However, the coefficients in the expansion of $|\Psi_{i,\mathrm{tr}}(t)\rangle$ are determined not from the

standard equations but from the N coupled equations which are obtained by replacing $|\Psi_i(t)\rangle$ by $|\Psi_{i,\mathrm{tr}}(t)\rangle$ in the Schrödinger equation, and by projecting the modified equation onto the $|\phi_{fn}(t)\rangle$, rather than onto the $|\phi_{in}(t)\rangle$. As will be shown later, these new equations will always have a solution if every vector in the subspace spanned by the $|\phi_{fn}(t)\rangle$ has a nonzero projection onto the subspace spanned by the $|\phi_{in}(t)\rangle$. The new equations are no more difficult to solve than the standard equations and they have the advantage of leading to variational and well-defined estimates of the transition amplitudes.

The derivation of our variational result is straightforward. We first obtain an identity of the form

$$A_{fi}=A_{fi}^{(0)}+A_{fi}^{(1)}+R_{fi}^{(2)}, \tag{1.1}$$

where A_{fi} is the exact impact-parameter transition amplitude. The precise form of the terms on the right-hand side is given in Sec. II. For present purposes, we need merely note that $A_{fi}^{(0)}$ is a zeroth-order estimate which can be determined immediately from the asymptotic form of the trial state vector $|\Psi_{i,\mathrm{tr}}(t)\rangle$, while $A_{fi}^{(1)}$ is a first-order correction which is obtained by integrating over all time a matrix element involving both trial wave functions. The last term $R_{fi}^{(2)}$ is formally a second-order error term. However, $R_{fi}^{(2)}$ involves a double integral over time with infinite ranges of integration and, even though the value of the integrand is everywhere of second order, one must make certain that $R_{fi}^{(2)}$ does in fact exist. Assuming that $R_{fi}^{(2)}$ exists, and is therefore truly of second order, its omission gives the variational estimate

$$A_{fi}^{(v)}\equiv A_{fi}^{(0)}+A_{fi}^{(1)}. \tag{1.2}$$

Since A_{fi} exists, it follows from Eqs. (1.1) and (1.2) that $R_{fi}^{(2)}$ exists if, and only if, $A_{fi}^{(v)}$ exists. [It is important to realize that Eq. (1.2) does not give a variational estimate unless $R_{fi}^{(2)}$ exists. An example of where $R_{fi}^{(2)}$ is neglected even though it oscillates without a limit is in the Brinkman-Kramers approximation for charge transfer; hence this approximation is not variational, in contrast to the Born approximation.] Given *any* two trial wave functions which are such that $R_{fi}^{(2)}$ exists, Eq. (1.2) generates a variational estimate, although, in general, one has to perform a complicated integral to evaluate $A_{fi}^{(1)}$. However, it turns out that if one determines the expansion coefficients of the trial state vectors so that the variation $\delta A_{fi}^{(v)}$ vanishes, $A_{fi}^{(1)}$ also vanishes, and one then has the very simple variational estimate $A_{fi}^{(v)}=A_{fi}^{(0)}$. The equations obtained from the requirement $\delta A_{fi}^{(v)}=0$ are just the equations mentioned above.

As useful as variational principles may be, their use does not provide a knowledge of the sign of the error, nor any real estimate of the magnitude of the error. Variational bounds, on the other hand, can provide such knowledge. Variational bounds, though they may, in fact, be infinite, and therefore useless, can be obtained within the impact-parameter approximation by using the Schwarz inequality to eliminate the unknown quantity (namely the time-translation operator) from $R_{fi}^{(2)}$.[3] A second purpose of this paper is to investigate the conditions under which the variational bounds are finite.[4] It turns out (somewhat unfortunately) that the variational bounds are finite only if $|\Psi_{i,\mathrm{tr}}(t)\rangle$ and $|\Psi_{f,\mathrm{tr}}(t)\rangle$ are both expanded in terms of a physical basis set. Numerical values of the variational bounds have been obtained[5] in the two-state approximation, and the additional effort involved in calculating numerical bounds is only a small fraction of the effort involved in solving the coupled-state equations. In Appendix A we give a rapid numerical technique for evaluating certain integrals which appear in the calculation of variational bounds in proton–hydrogen-atom scattering.

The entire analysis of this paper will be restricted to the proton–hydrogen-atom system. (However, this analysis can be generalized immediately to other systems for which the initial state and the relevant final states of the isolated systems are known.) In Sec. II we derive a variational approximation to the amplitude for the electron to undergo a particular transition in a finite duration. In Sec. III we let the length of this duration become infinite, and we show that the appropriate limits exist.

II. COUPLED-STATE EQUATIONS

A. Variational principle

Let $\vec{r}$ be the coordinate of the electron relative to the target proton A, which we assume is always at rest, and let $\vec{R}(t)$ be the coordinate of the incident proton B relative to A. The protons are treated classically and B is assumed to move with constant velocity, and we have

$$\vec{R}(t)=\vec{b}+\vec{v}t,$$

where $\vec{b}$ is the impact parameter and $\vec{v}$ is the velocity of B relative to A. The Hamiltonian is (we use atomic units hereafter)

$$H(t)\equiv -\tfrac{1}{2}\nabla_{\vec{r}}^2-\frac{1}{r}-\frac{1}{|\vec{r}-\vec{R}(t)|}+\frac{1}{R(t)}. \tag{2.1}$$

If the term $1/R(t)$ is omitted from $H(t)$, the exact

transition amplitude has an infinite phase factor. We retain the term $1/R(t)$; the transition amplitude then exists,[6] the infinite phase factor having been eliminated, and Eqs. (2.4) below are satisfied.

Initially, before some large negative time T_i, the electron is bound to proton A in the state i. For times $t<T_i$, the electron is effectively unperturbed and its normalized state vector is $|\Phi_i(t)\rangle$ where, in coordinate space,

$$\left(-\tfrac{1}{2}\nabla_{\vec{r}}^2-\frac{1}{r}-i\frac{\partial}{\partial t}\right)\Phi_i(\vec{r},t)=0. \tag{2.2}$$

With the definitions

$$h(t)\equiv H(t)-i\frac{\partial}{\partial t},\qquad \|\,|\phi\rangle\,\|=\langle\phi|\phi\rangle^{1/2}, \tag{2.3}$$

it follows from Eqs. (2.1) and (2.2) that for large $|t|$,

$$\begin{aligned}\|h(t)|\Phi_i(t)\rangle\|^2&=\int d\vec{r}\left|\left(\frac{1}{R(t)}-\frac{1}{|\vec{r}-\vec{R}(t)|}\right)\Phi_i(\vec{r},t)\right|^2\\ &\sim\frac{1}{[R(t)]^4}\int d\vec{r}\,|\vec{r}\cdot\hat{R}(t)\Phi_i(\vec{r},t)|^2\\ &\sim\frac{1}{v^4t^4}\int d\vec{r}\,|\vec{r}\cdot\hat{v}\Phi_i(\vec{r},t)|^2=O\left(\frac{1}{t^4}\right),\end{aligned}$$

where the caret denotes a unit vector and where, in the second step, we used the fact that the presence of $\Phi_i(\vec{r},t)$ restricts the range of r in the integrand. We note that $\Phi_i(\vec{r},t)$ need not be a stationary state, so that the integrand $|\vec{r}\cdot\hat{v}\Phi_i(\vec{r},t)|^2$ may contain bounded oscillating terms in t as well as constant terms. It follows from the above that

$$\lim_{t\to\pm\infty} t\,\|h(t)|\Phi_i(t)\rangle\|=0. \tag{2.4a}$$

If at some large positive time T_f the electron is bound to either A or B in the state f, then it will remain in that state for times $t>T_f$, being effectively unperturbed. Let $|\Phi_f(t)\rangle$ be the normalized state vector of the state f. Then $\Phi_f(\vec{r},t)$ will satisfy the same equation (2.2) as $\Phi_i(\vec{r},t)$ does if, in the state f, the electron is bound to A; if, however, the electron is bound to B in the state f, then $\Phi_f(\vec{r},t)$ satisfies the equation

$$\left(-\tfrac{1}{2}\nabla_{\vec{r}}^2-\frac{1}{|\vec{r}-\vec{R}(t)|}-i\frac{\partial}{\partial t}\right)\Phi_f(\vec{r},t)=0.$$

In either case it can be shown, as above, that

$$\lim_{t\to\pm\infty} t\,\|h(t)|\Phi_f(t)\rangle\|=0. \tag{2.4b}$$

[Note that if the electron is bound to B in state f, then $\Phi_f(\vec{r},t)$ restricts the range of $|\vec{r}-\vec{R}(t)|$.] Equations (2.4) will be used later. These equations are sufficient conditions for $|\Phi_i(t)\rangle$ and $|\Phi_f(t)\rangle$ to be possible incoming or outgoing state vectors of the electron, and these state vectors represent so-called physical states.[6]

With the initial boundary condition that the electron is in the state i at time T_i, the state vector of the electron at times $t>T_i$ is

$$|\Psi_i(t)\rangle=U(t,T_i)|\Phi_i(T_i)\rangle, \tag{2.5}$$

where the time-translation operator $U(t,t_0)$ is defined by

$$h(t)U(t,t_0)=0;\quad U(t_0,t_0)=1. \tag{2.6}$$

We shall make use of the following properties of U, which are easily derived:

$$U(t,t)=1, \tag{2.7a}$$

$$U(t,\tau)^\dagger=U(\tau,t), \tag{2.7b}$$

$$U(t,\tau)^\dagger U(t,\tau)=1, \tag{2.7c}$$

$$U(t,\tau)U(\tau,t')=U(t,t'), \tag{2.7d}$$

for all finite times t, τ, and t'.

The transition amplitude for finding the electron in the state f at the large positive time T_f is

$$A_{fi}(T_f,T_i)=\langle\Phi_f(T_f)|U(T_f,T_i)|\Phi_i(T_i)\rangle. \tag{2.8}$$

By using properties (2.7b) and (2.7d), we can rewrite Eq. (2.8) in the form

$$\begin{aligned}A_{fi}(T_f,T_i)&=\langle\Phi_f(T_f)|U(t,T_f)^\dagger U(t,T_i)|\Phi_i(T_i)\rangle\\ &=\langle\Psi_f(t)|\Psi_i(t)\rangle\end{aligned} \tag{2.9}$$

for any time t, where $|\Psi_i(t)\rangle$ is defined by Eq. (2.5), and where

$$|\Psi_f(t)\rangle=U(t,T_f)|\Phi_f(T_f)\rangle. \tag{2.10}$$

Clearly, $|\Psi_j(t)\rangle$ is the state vector of the system at time t if the system is in the state j at time T_j, where $j=i$ or f, and $|\Psi_j(t)\rangle$ is determined by the Schrödinger equation and the boundary condition $|\Psi_j(T_j)\rangle=|\Phi_j(T_j)\rangle$. Later, we take the limits $T_f\to\infty$, $T_i\to-\infty$. To avoid repetition, hereafter a subscript j is always to be understood to mean i or f.

In order to obtain a variational approximation to A_{fi} we introduce trial state vectors $|\Psi_{j,\mathrm{tr}}(t)\rangle$ which satisfy the same boundary conditions as $|\Psi_j(t)\rangle$. These trial vectors are each chosen to be linear combinations of N normalizable, linearly independent, not necessarily orthogonal, and, in general, time-dependent, basis vectors. We have

$$|\Psi_{j,\mathrm{tr}}(t)\rangle=\sum_{n=1}^{N}a_{jn,\mathrm{tr}}(t)|\phi_{jn}(t)\rangle, \tag{2.11}$$

where the trial coefficients $a_{jn,\mathrm{tr}}$ are to be determined from a variational procedure which leads, of course, to a set of coupled differential equations. Hereafter we drop the subscript tr from the trial coefficients for otherwise the notation is rather cumbersome. The basis vectors $|\phi_{jn}(t)\rangle$ span an N-dimensional subspace $\mathcal{K}_{jN}(t)$, and $P_j(t)$ is defined to be the projection operator which projects onto this subspace.

The boundary condition on $|\Psi_{j,\mathrm{tr}}(t)\rangle$ is

$$|\Psi_{j,\mathrm{tr}}(T_j)\rangle = |\Phi_j(T_j)\rangle \tag{2.12}$$

and Eq. (2.12) can only be satisfied if $|\Phi_j(T_j)\rangle$ is contained within the subspace $\mathcal{K}_{jN}(T_j)$, that is, if

$$P_j(T_j)|\Phi_j(T_j)\rangle = |\Phi_j(T_j)\rangle. \tag{2.13}$$

We note that if the state i is the ground state of the hydrogen atom, the boundary condition on $\Psi_{i,\mathrm{tr}}$ can be satisfied with a Sturmian basis set. However if, for example, the state f is the $2s$ state of the hydrogen atom (with nucleus A or B), the boundary condition on $\Psi_{f,\mathrm{tr}}$ cannot be satisfied with a Sturmian basis set, since the $2s$ wave function of the hydrogen atom cannot be formed from a finite number of Sturmian functions.

To proceed further, we introduce operators $U_j(t, t_0)$ which govern the time development of the trial vectors. We have, for all t and t_0,

$$|\Psi_{j,\mathrm{tr}}(t)\rangle = U_j(t, t_0)|\Psi_{j,\mathrm{tr}}(t_0)\rangle. \tag{2.14}$$

We need not specify the U_j and in fact the choice is not unique. From Eq. (2.14) and the boundary condition (2.12) we have

$$|\Psi_{j,\mathrm{tr}}(t)\rangle = U_j(t, T_j)|\Phi_j(T_j)\rangle \tag{2.15}$$

and it follows that

$$U_j(T_j, T_j)|\Phi_j(T_j)\rangle = |\Phi_j(T_j)\rangle. \tag{2.16}$$

We note that it is not necessarily true that $U_j(t, t) = 1$, in contrast to Eq. (2.7a), and the only property of the trial operators that we require is that Eq. (2.16) be satisfied. Using Eq. (2.16) we can rewrite Eq. (2.8) in the form

$$A_{fi}(T_f, T_i) = \langle \Phi_f(T_f)|U_f(T_f, T_f)^\dagger \times U(T_f, T_i)U_i(T_i, T_i)|\Phi_i(T_i)\rangle. \tag{2.17}$$

We now obtain an integral equation for the operator appearing in Eq. (2.17) by considering the expression[3]

$$-i\int_{t_0}^{t} d\tau \{U(t,\tau)h(\tau)U_j(\tau, t_0) - [h(\tau)U(\tau, t)]^\dagger U_j(\tau, t_0)\}. \tag{2.18}$$

In this expression, and in all subsequent expressions, it is to be understood that $h(\tau)$ never operates beyond a bra, a ket, or a square or curly bracket. With the additional understanding that Eq. (2.18) is to be evaluated in a scalar product between *normalizable* functions, we can reduce this expression by using the Hermiticity of $H(\tau)$. With the aid of Eq. (2.7b), we see that the terms in $H(\tau)$ cancel and Eq. (2.18) reduces to

$$-\int_{t_0}^{t} d\tau \frac{\partial}{\partial\tau}[U(t,\tau)U_j(\tau, t_0)],$$

that is, to

$$U(t, t_0)U_j(t_0, t_0) - U_j(t, t_0), \tag{2.19}$$

where we have used Eq. (2.7a). Equating Eq. (2.19) to Eq. (2.18), and noting that by Eq. (2.6) the term in square brackets in Eq. (2.18) vanishes, we obtain

$$U(t, t_0)U_j(t_0, t_0) = U_j(t, t_0) - i\int_{t_0}^{t} d\tau_1 U(t, \tau_1)h(\tau_1)U_j(\tau_1, t_0), \tag{2.20}$$

where we have replaced the variable of integration τ by τ_1. Taking the adjoint of Eq. (2.20), using Eq. (2.7b), and replacing t_0 by t, t by τ_1, τ_1 by τ_2, and j by j', where $j' = i$ or f, we obtain

$$U_{j'}(t, t)^\dagger U(t, \tau_1) = U_{j'}(\tau_1, t)^\dagger - i\int_{\tau_1}^{t} d\tau_2 [h(\tau_2)U_{j'}(\tau_2, t)]^\dagger U(\tau_2, \tau_1). \tag{2.21}$$

We now premultiply both sides of Eq. (2.20) by $U_{j'}(t, t)^\dagger$ and then use Eq. (2.21) in the right-hand side of the resulting equation. We obtain

$$U_{j'}(t, t)^\dagger U(t, t_0)U_j(t_0, t_0) = U_{j'}(t, t)^\dagger U_j(t, t_0) - i\int_{t_0}^{t} d\tau_1 U_{j'}(\tau_1, t)^\dagger h(\tau_1)U_j(\tau_1, t_0) - \int_{t_0}^{t} d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 [h(\tau_2)U_{j'}(\tau_2, t)]^\dagger U(\tau_2, \tau_1)h(\tau_1)U_j(\tau_1, t_0), \tag{2.22}$$

where we have used the relation

$$\int_{\tau_1}^{t} d\tau_2 \int_{t_0}^{t} d\tau_1 = \int_{t_0}^{t} d\tau_2 \int_{t_0}^{\tau_2} d\tau_1$$

to change the limits of the double integral.

Equation (2.22) is the desired equation. Setting $j' = f$, $j = i$, $t = T_f$, and $t_0 = T_i$ in Eq. (2.22), and using this equation in Eq. (2.17), we obtain

$$A_{fi}(T_f, T_i) = A_{fi}^{(0)}(T_f, T_i) + A_{fi}^{(1)}(T_f, T_i) + R_{fi}^{(2)}(T_f, T_i), \quad (2.23)$$

where, using Eqs. (2.15) and (2.16),

$$A_{fi}^{(0)}(T_f, T_i) = \langle \Phi_f(T_f) | \Psi_{i,\mathrm{tr}}(T_f) \rangle, \quad (2.24)$$

$$A_{fi}^{(1)}(T_f, T_i) = -i \int_{T_i}^{T_f} dt \langle \Psi_{f,\mathrm{tr}}(t) | h(t) | \Psi_{i,\mathrm{tr}}(t) \rangle, \quad (2.25)$$

and

$$R_{fi}^{(2)}(T_f, T_i) = -\int_{T_i}^{T_f} dt_2 \int_{T_i}^{t_2} dt_1 \langle h(t_2) \Psi_{f,\mathrm{tr}}(t_2) | \times U(t_2, t_1) | h(t_1) \Psi_{i,\mathrm{tr}}(t_1) \rangle. \quad (2.26)$$

Equations (2.23)–(2.26) were derived previously,[3] but with the restriction that the trial operators satisfy $U_j(t, t) = 1$ for all t. The present derivation is, therefore, slightly more general than that of Ref. 3; also, here we emphasize the role of the trial wave functions, whereas in Ref. 3 the role of the trial operators was emphasized. (See also note added in proof in Ref. 3.) Note that the trial operators do not appear in the final expressions (2.23)–(2.26), their lack of uniqueness playing no role.

Now since

$$h(t) | \Psi_{j,\mathrm{tr}}(t) \rangle = h(t) | \Omega_j(t) \rangle,$$

where $\Omega_j = \Psi_{j,\mathrm{tr}} - \Psi_j$, it follows that $R_{fi}^{(2)}$ is of second order in the average error of the trial wave functions; therefore, supressing the arguments of T_f and T_i when no confusion might arise, the expression

$$A_{fi}^{(v)} = A_{fi}^{(0)} + A_{fi}^{(1)} \quad (2.27)$$

is a variational approximation to A_{fi}. The error term can, in fact, be bounded. Since U has the isometric property (2.7c), we can eliminate U from Eq. (2.26) by using the Schwarz inequality. In this way, we obtain the bound

$$|R_{fi}^{(2)}| \leq R_{fi}^{\mathrm{Bd}}, \quad (2.28a)$$

where

$$R_{fi}^{\mathrm{Bd}} = \int_{T_i}^{T_f} dt_2 \int_{T_i}^{t_2} dt_1 \| h(t_2) | \Psi_{f,\mathrm{tr}}(t_2) \rangle \| \times \| h(t_1) | \Psi_{i,\mathrm{tr}}(t_1) \rangle \|. \quad (2.28b)$$

We therefore have the variational bounds[3,4]

$$|A_{fi}^{(v)}| - R_{fi}^{\mathrm{Bd}} \leq |A_{fi}| \leq |A_{fi}^{(v)}| + R_{fi}^{\mathrm{Bd}}. \quad (2.29)$$

B. Derivation of equations

The coefficients $a_{jn}(t)$ satisfy boundary conditions at $t = T_j$. These coefficients can be determined variationally by requiring that $A_{fi}^{(v)}$ be stationary for variations $\delta a_{jn}(t)$ subject to the conditions $\delta a_{jn}(T_j) = 0$. Let us first consider variations in $a_{fn}(t)$. Since $A_{fi}^{(0)}$ is independent of a_{fn}, we have $\delta A_{fi}^{(0)} = 0$, and therefore

$$\delta A_{fi}^{(v)} = \delta A_{fi}^{(1)} = -i \sum_{n=1}^{N} \int_{T_i}^{T_f} dt\, \delta a_{fn}^*(t) \times \langle \phi_{fn}(t) | h(t) | \Psi_{i,\mathrm{tr}}(t) \rangle. \quad (2.30)$$

We require that $\delta A_{fi}^{(v)}$ be zero for arbitrary variations $\delta a_{fn}^*(t)$, and this is only possible if

$$\langle \phi_{fn}(t) | h(t) | \Psi_{i,\mathrm{tr}}(t) \rangle = 0, \quad n = 1, \ldots, N \quad (2.31)$$

which implies that $A_{fi}^{(v)} = A_{fi}^{(0)}$. Thus if we know $\Psi_{i,\mathrm{tr}}(t)$, we obtain, very simply, a variational expression for the transition amplitude. Using the expansion (2.11) for $\Psi_{i,\mathrm{tr}}(t)$, Eqs. (2.31) lead to a set of N first-order coupled differential equations for the coefficients $a_{in}(t)$. We can combine the equations of (2.31) formally into the single equation

$$P_f(t) h(t) | \Psi_{i,\mathrm{tr}}(t) \rangle = 0. \quad (2.32)$$

Note that Eq. (2.32) is not necessarily equivalent to the standard coupled-state equations, since P_f need not be equal to P_i. The standard coupled-state equations can be written formally as the single equation

$$P_i(t) h(t) | \Psi_{i,\mathrm{tr}}^{\mathrm{stan}}(t) \rangle = 0. \quad (2.33)$$

If $P_f \neq P_i$, then $|\Psi_{i,\mathrm{tr}}(t)\rangle$ and $|\Psi_{i,\mathrm{tr}}^{\mathrm{stan}}(t)\rangle$ satisfy different equations (but the same boundary conditions), and the difference between these two vectors is generally not orthogonal to P_f, so that different values for the transition amplitude are obtained.

We now consider variations in $a_{in}(t)$. From Eq. (2.24) we have

$$\delta A_{fi}^{(0)} = \sum_{n=1}^{N} \delta a_{in}(T_f) \langle \Phi_f(T_f) | \phi_{in}(T_f) \rangle. \quad (2.34)$$

From Eq. (2.25) we have, with a dot representing a time derivative,

$$\delta A_{fi}^{(1)} = -i \sum_{n=1}^{N} \int_{T_i}^{T_f} dt\, \delta a_{in}(t) \times [\langle \Psi_{f,\mathrm{tr}}(t) | h(t) | \phi_{in}(t) \rangle - i \delta \dot{a}_{in}(t) \langle \Psi_{f,\mathrm{tr}}(t) | \phi_{in}(t) \rangle]. \quad (2.35)$$

If we integrate by parts the term in $\delta \dot{a}_{in}$, noting that $\delta a_{in}(T_i) = 0$, we obtain, using the Hermiticity of $H(t)$ and Eq. (2.12), and combining terms,

$$\delta A_{fi}^{(1)} = -i \sum_{n=1}^{N} \int_{T_i}^{T_f} dt\, \delta a_{in}(t) \langle \phi_{in}(t) | h(t) | \Psi_{f,\mathrm{tr}}(t) \rangle^* - \sum_{n=1}^{N} \delta a_{in}(T_f) \langle \Phi_f(T_f) | \phi_{in}(T_f) \rangle. \quad (2.36)$$

It follows from Eqs. (2.27), (2.34), and (2.36) that

$$\delta A_{fi}^{(v)} = -i \sum_{n=1}^{N} \int_{T_i}^{T_f} dt\, \delta a_{in}(t) \langle \phi_{in}(t) | h(t) | \Psi_{f,\mathrm{tr}}(t) \rangle^* . \tag{2.37}$$

We require that $\delta A_{fi}^{(v)}$ be zero for arbitrary variations $\delta a_{in}(t)$, and this is only possible if

$$\langle \phi_{in}(t) | h(t) | \Psi_{f,\mathrm{tr}}(t) \rangle = 0 , \quad n = 1, \ldots, N . \tag{2.38}$$

Expanding $\Psi_{f,\mathrm{tr}}(t)$, Eq. (2.38) leads to a set of N first-order coupled differential equations for the coefficients $a_{fn}(t)$. We note that we do not need these coefficients to evaluate $A_{fi}^{(v)}$. However, we do need these coefficients to evaluate the bound R_{fi}^{Bd} on the error term. The equations of (2.38) can be combined formally into the single equation

$$P_i(t)\, h(t) | \Psi_{f,\mathrm{tr}}(t) \rangle = 0 . \tag{2.39}$$

We have, up to this point, chosen the variational parameters of the trial wave functions to be linear coefficients $a_{jn}(t)$ of completely specified basis vectors. We could also build nonlinear variational parameters, such as variable effective charges, into the basis vectors themselves. Although we do *not* consider this possibility here, we mention that these "nonlinear" parameters could be determined from Euler-Lagrange equations which are obtained by requiring that $A_{fi}^{(v)}$ be stationary. Alternatively, as a slightly more practical numerical procedure, one could evaluate $A_{fi}^{(v)}$ (or R_{fi}^{Bd}) for a number of sets of values of the nonlinear parameters and then choose the nonlinear parameters to be those for which $A_{fi}^{(v)}$ (or R_{fi}^{Bd}) is estimated by interpolation to be stationary (or a minimum); even this approach is often not practical.[5]

C. Matrix form of equations

Equations (2.31) and (2.38) are not in the form most suitable for numerical integration. For this purpose it is more convenient to write these equations in matrix form. Noting that both Eqs. (2.31) and (2.38) are encompassed by

$$\left\langle \phi_{j'm}(t) \middle| h(t) \middle| \sum_{n=1}^{N} a_{jn}(t) \phi_{jn}(t) \right\rangle = 0$$

for the appropriate choices of j and j', we have

$$i \underline{\mathrm{N}}_{j'j}(t)\, \dot{\underline{\mathrm{A}}}_j(t) = \underline{\mathrm{M}}_{j'j}(t)\, \underline{\mathrm{A}}_j(t), \tag{2.40}$$

where $\underline{\mathrm{A}}_j(t)$ is the column matrix with elements $a_{jn}(t)$, and where $\underline{\mathrm{N}}_{j'j}(t)$ and $\underline{\mathrm{M}}_{j'j}(t)$ are the matrices with elements $\langle \phi_{j'm}(t) | \phi_{jn}(t) \rangle$ and $\langle \phi_{j'm}(t) | h(t) | \phi_{jn}(t) \rangle$, respectively. It is clear that Eq. (2.40) will have a solution if, and only if, $\underline{\mathrm{N}}_{j'j}(t)$ has an inverse, that is, if for all t

$$\det \underline{\mathrm{N}}_{j'j}(t) \neq 0, \tag{2.41}$$

where the symbol "det" denotes determinant. Equation (2.41) is equivalent to the condition that every vector in the subspace $\mathcal{H}_{j'N}(t)$ has a nonzero projection onto the subspace $\mathcal{H}_{jN}(t)$. We will assume the validity of Eq. (2.41).

It follows from the definition of $\underline{\mathrm{N}}_{j'j}(t)$ that

$$\underline{\mathrm{N}}_{j'j}(t)^{\dagger} = \underline{\mathrm{N}}_{jj'}(t). \tag{2.42}$$

By considering the definitions of $\underline{\mathrm{M}}_{j'j}(t)$ and $\underline{\mathrm{M}}_{jj'}(t)^{\dagger}$ and using the fact that $H(t)$ is Hermitian, it is not difficult to see that

$$i \dot{\underline{\mathrm{N}}}_{j'j}(t) = \underline{\mathrm{M}}_{jj'}(t)^{\dagger} - \underline{\mathrm{M}}_{j'j}(t). \tag{2.43}$$

It follows from Eqs. (2.43) and (2.40) that

$$\frac{d}{dt} \left[\underline{\mathrm{A}}_{j'}(t)^{\dagger} \underline{\mathrm{N}}_{j'j}(t)\, \underline{\mathrm{A}}_j(t) \right] = 0, \tag{2.44}$$

where $\underline{\mathrm{A}}_j(t)$ is any solution of Eq. (2.40), and where $\underline{\mathrm{A}}_{j'}(t)$ is any solution of the equation obtained by interchanging j and j' in Eq. (2.40). Equations (2.43) and (2.44) are generalizations of the well-known relations derived by Green[7]; these relations can be used as checks on the calculations.[2]

D. Time-reversal invariance

We now consider some useful consequences of time-reversal invariance.[7-9] We define the antiunitary operator $\mathcal{S}$ as the product of the time-reversal operator and the operator which reflects the coordinates of the electron in the plane which passes through the origin of coordinates, and is perpendicular to the velocity $\vec{v}$ of the relative motion of A and B. In order to fully exploit the rotation, reflection, and time-reversal symmetries of the system, the basis sets should be chosen so that $\mathcal{H}_{jN}(t)$ is transformed into $\mathcal{H}_{jN}(-t)$ under $\mathcal{S}$. More precisely, the basis vectors should be chosen so that

$$\mathcal{S} | \phi_{jn}(t) \rangle = d_{nn}^{j} | \phi_{jn}(-t) \rangle , \tag{2.45}$$

where the constants d_{nn}^{j} depend on the basis vectors and form the diagonal elements of a unitary diagonal matrix $\underline{\mathrm{D}}_j$. If Eq. (2.45) is satisfied for all times, it is not difficult to show that (cf. Ref. 9)

$$\underline{\mathrm{M}}_{j'j}(t) = \underline{\mathrm{D}}_{j'}\, \underline{\mathrm{M}}_{j'j}(-t)^{*}\, \underline{\mathrm{D}}_j^{*} \tag{2.46a}$$

$$\underline{\mathrm{N}}_{j'j}(t) = \underline{\mathrm{D}}_{j'}\, \underline{\mathrm{N}}_{j'j}(-t)^{*}\, \underline{\mathrm{D}}_j^{*} . \tag{2.46b}$$

The time symmetry expressed by Eqs. (2.46) enables one to cut the computing time in half. Also, we obtain a further check on the calculations by noting that [according to Eqs. (2.46)] if $\underline{\mathrm{A}}_{j'}(t)$ satisfies Eq. (2.40) (with j and j' interchanged), then so does $\underline{\mathrm{D}}_{j'}\, \underline{\mathrm{A}}_{j'}(-t)^{*}$, and therefore from Eq.

(2.44) we have

$$\frac{d}{dt}[\underline{\tilde{A}}_{j'}(-t)\underline{D}^{*}_{j'}\underline{N}_{j}(t)\underline{A}_{j}(t)]=0, \tag{2.47}$$

where the tilde over $\underline{A}_{j'}$ denotes the transpose of $\underline{A}_{j'}$.

III. ASYMPTOTIC LIMITS

A. Transition amplitude

In this section we pass to the asymptotic limits $T_f\to\infty$, $T_i\to-\infty$. From Eqs. (2.24), (2.25), (2.27), and (2.31) we have, with $\Psi_{i,\mathrm{tr}}(t)$ determined from (2.31),

$$A^{(v)}_{fi}(T_f,T_i)=\langle\Phi_f(T_f)|\Psi_{i,\mathrm{tr}}(T_f)\rangle. \tag{3.1}$$

We consider the limit $T_f\to\infty$ first. Let us replace T_f by the variable t. Then, from Eqs. (2.13) and (3.1) we have

$$A^{(v)}_{fi}(t,T_i)=\langle\Phi_f(t)|\Psi_{i,\mathrm{tr}}(t)\rangle=\langle P_f(t)\Phi_f(t)|\Psi_{i,\mathrm{tr}}(t)\rangle. \tag{3.2}$$

From Eq. (2.32) we have

$$iP_f(t)\frac{\partial}{\partial t}|\Psi_{i,\mathrm{tr}}(t)\rangle=P_f(t)H(t)|\Psi_{i,\mathrm{tr}}(t)\rangle \tag{3.3}$$

and using Eqs. (3.2) and (3.3), we obtain (noting that P_f is Hermitian)

$$\begin{aligned} i\frac{\partial A^{(v)}_{fi}}{\partial t}(t,T_i)&=i\left\langle\frac{\partial}{\partial t}[P_f(t)\Phi_f(t)]\middle|\Psi_{i,\mathrm{tr}}(t)\right\rangle\\ &\quad+i\langle\Phi_f(t)|P_f(t)\frac{\partial}{\partial t}|\Psi_{i,\mathrm{tr}}(t)\rangle\\ &=i\left\langle\frac{\partial\Phi_f}{\partial t}(t)\middle|\Psi_{i,\mathrm{tr}}(t)\right\rangle\\ &\quad+\langle\Phi_f(t)|H(t)|\Psi_{i,\mathrm{tr}}(t)\rangle\\ &=\langle h(t)\Phi_f(t)|\Psi_{i,\mathrm{tr}}(t)\rangle, \end{aligned} \tag{3.4}$$

where in the last step we have used the Hermiticity of H. Using the Schwarz inequality, it follows from Eq. (3.4) that

$$\left|\frac{\partial A^{(v)}_{fi}}{\partial t}(t,T_i)\right|\le\||\Psi_{i,\mathrm{tr}}(t)\rangle\|\times\|h(t)|\Phi_f(t)\rangle\| \tag{3.5}$$

and using Eq. (2.4b) we obtain (noting that $\||\Psi_{i,\mathrm{tr}}(t)\rangle\|$ is bounded by some finite number independent of t if we assume a sensible choice of basis vectors)

$$\lim_{t\to\infty}t\left|\frac{\partial A^{(v)}_{fi}}{\partial t}(t,T_i)\right|=0. \tag{3.6}$$

It follows from Eq. (3.6) that the limit of $A^{(v)}_{fi}(T_f,T_i)$ as $T_f\to\infty$ exists, that is, $A^{(v)}_{fi}(\infty,T_i)$, is well defined. To consider the limit $T_i\to-\infty$ with T_f fixed, we write Eq. (3.1) in a different form. From Eqs. (2.31) we have

$$\int_{T_i}^{T_f}d\tau\langle\Psi_{f,\mathrm{tr}}(\tau)|h(\tau)|\Psi_{i,\mathrm{tr}}(\tau)\rangle=0, \tag{3.7}$$

and by integrating by parts the term in the τ derivative, and using the Hermiticity of $H(\tau)$, we obtain

$$\begin{aligned} &-i\langle\Phi_f(T_f)|\Psi_{i,\mathrm{tr}}(T_f)\rangle+i\langle\Psi_{f,\mathrm{tr}}(T_i)|\Phi_i(T_i)\rangle\\ &\qquad+\int_{T_i}^{T_f}d\tau\,\langle\Psi_{i,\mathrm{tr}}(\tau)|h(\tau)|\Psi_{f,\mathrm{tr}}(\tau)\rangle^{*}=0. \end{aligned} \tag{3.8}$$

By Eq. (2.38), the integral of Eq. (3.8) vanishes, and therefore

$$\langle\Phi_f(T_f)|\Psi_{i,\mathrm{tr}}(T_f)\rangle=\langle\Psi_{f,\mathrm{tr}}(T_i)|\Phi_i(T_i)\rangle. \tag{3.9}$$

From Eqs. (3.1) and (3.9), we have

$$A^{(v)}_{fi}(T_f,T_i)=\langle\Psi_{f,\mathrm{tr}}(T_i)|\Phi_i(T_i)\rangle. \tag{3.10}$$

We now consider $A^{(v)}_{fi}(\infty,t)$. In just the same way that we proved Eq. (3.5), but using Eq. (2.39) rather than Eq. (2.32), we can show that

$$\left|\frac{\partial A^{(v)}_{fi}}{\partial t}(\infty,t)\right|\le\||\Psi_{f,\mathrm{tr}}(t)\rangle\|\times\|h(t)|\Phi_i(t)\rangle\| \tag{3.11}$$

and it then follows, using Eq. (2.4a), and noting that $\||\Psi_{f,\mathrm{tr}}(t)\rangle\|$ is normally bounded, that

$$\lim_{t\to-\infty}t\left|\frac{\partial A^{(v)}_{fi}}{\partial t}(\infty,t)\right|=0. \tag{3.12}$$

Hence the limit of $A^{(v)}_{fi}(\infty,T_i)$ as $T_i\to-\infty$ exists; that is, $A^{(v)}_{fi}(\infty,-\infty)$ is well defined, and is therefore truly a variational approximation to $A_{fi}(\infty,-\infty)$. We note that, although $A^{(v)}_{fi}(\infty,-\infty)$ exists, when a Sturmian i-basis set is used the coefficients $a_{in}(t)$ will not have limits as $t\to+\infty$, and they will continue to oscillate. However, in contrast to the procedure of Gallaher and Wilets, we do not need to remove the oscillating parts of the coefficients to calculate the transition amplitudes.

B. Bounds on the error term

From Eq. (2.28b) we have

$$R^{\mathrm{Bd}}_{fi}(T_f,T_i)=\int_{T_i}^{T_f}dt_2\,F_f(t_2)\int_{T_i}^{t_2}dt_1\,F_i(t_1), \tag{3.13}$$

where

$$F_j(t)\equiv\|h(t)|\Psi_{j,\mathrm{tr}}(t)\rangle\|. \tag{3.14}$$

We now take the limits $T_f\to\infty$ and $T_i\to-\infty$ in Eq. (3.13). We obtain

$$R_{fi}^{\mathrm{Bd}}(\infty,-\infty)=\int_{-\infty}^{\infty}dt\,G(t), \tag{3.15}$$

where

$$G(t)\equiv F_f(t)\int_{-\infty}^{t}dt_1\,F_i(t_1). \tag{3.16}$$

It follows from Eq. (3.15) that $R_{fi}^{\mathrm{Bd}}(\infty,-\infty)$ is finite if, and only if,

$$\lim_{t\to\pm\infty} tG(t)=0. \tag{3.17}$$

In this section we investigate the conditions under which Eq. (3.17) is satisfied.

To begin, let us assume that *all* of the basis vectors represent physical states, so that, for all j and n,

$$\lim_{t\to\pm\infty} t\,\|h(t)|\phi_{jn}(t)\rangle\|=0. \tag{3.18}$$

Let us define $\underline{B}_j(t)$ to be the column matrix with elements

$$b_{jn}(t)=\langle\phi_{jn}(t)|\Psi_{j,\mathrm{tr}}(t)\rangle. \tag{3.19}$$

In just the same way that we proved that $A_{fi}^{(v)}(T_f,T_i)$ has limits as $T_f\to\infty$, $T_i\to-\infty$, we can prove that, for all j and n, $b_{jn}(t)$ has limits as $t\to\pm\infty$, so that

$$\lim_{t\to\pm\infty} t\dot{b}_{jn}(t)=0. \tag{3.20}$$

It then follows that since $\underline{A}_j(t)$ is related to $\underline{B}_j(t)$ through the nonsingular matrix with elements $\langle\phi_{jn}(t)|\phi_{jm}(t)\rangle$, we must have, for all j and n,

$$\lim_{t\to\pm\infty} t\dot{a}_{jn}(t)=0. \tag{3.21}$$

Since the norm of a sum is less than or equal to the sum of the norms, we have, by Eqs. (3.14) and (2.11),

$$\begin{aligned}F_j(t)&\le\sum_{n=1}^{N}\|[-i\dot{a}_{jn}(t)+a_{jn}(t)h(t)]\,|\phi_{jn}(t)\rangle\|\\&\le\sum_{n=1}^{N}|\dot{a}_{jn}(t)|\times\|\,|\phi_{jn}(t)\rangle\|\\&\quad+\sum_{n=1}^{N}|a_{jn}(t)|\times\|h(t)|\phi_{jn}(t)\rangle\|.\end{aligned} \tag{3.22}$$

Using Eqs. (3.18) and (3.21) in Eq. (3.22) we obtain (noting that $\|\,|\phi_{jn}(t)\rangle\|$ and $|a_{jn}(t)|$ are bounded)

$$\lim_{t\to\pm\infty} tF_j(t)=0, \tag{3.23}$$

and hence Eq. (3.17) is satisfied. Therefore, if we use physical i- and f-basis sets, we can obtain finite variational upper and lower bounds on the transition amplitude. It can be shown that these bounds fall off sufficiently rapidly with impact parameter to give finite variational bounds on the cross section.[4] We note that if the i- and f-basis sets are both physical, they must in fact be equivalent, for otherwise Eq. (2.41) would not be satisfied. With equivalent i- and f-basis sets, the new coupled-state equations reduce, of course, to the standard equations.

As we will now show, the bound $R_{fi}^{\mathrm{Bd}}(\infty,-\infty)$ does not exist if Eq. (3.18) is not satisfied for all j and n. Suppose that at least one of the i-basis vectors does not satisfy Eq. (3.18). Then it is not difficult to see that $F_i(t)$ cannot tend to zero as $t\to\infty$. [However, $F_i(t)$ will tend to zero as $t\to-\infty$ if the coefficient of the particular nonphysical i-basis vector vanishes sufficiently rapidly as $t\to-\infty$. We assume that it does; otherwise $G(t)$ does not even exist.] It follows that $G(t)$ will behave like $tF_f(t)$ for large positive t. Similarly, if at least one of the f-basis vectors does not satisfy Eq. (3.18), $F_f(t)$ cannot tend to zero as $t\to-\infty$, and then $G(t)$ behaves like $tF_i(t)$ for large negative t. In order to satisfy Eq. (3.17) in the first case, we must have

$$\lim_{t\to\infty} t^2F_f(t)=0; \tag{3.24a}$$

in order to satisfy Eq. (3.17) in the second case, we must have

$$\lim_{t\to-\infty} t^2F_i(t)=0. \tag{3.24b}$$

We now show that Eqs. (3.24) cannot be satisfied. For simplicity we assume the i- and f-basis sets are identical and we drop the subscript j from the basis vectors and from the projection operators. We introduce the projection operator $Q(t)$ which projects onto the complement of the subspace $\mathcal{H}_N(t)$, so that

$$P(t)+Q(t)=1. \tag{3.25}$$

Then we have

$$\begin{aligned}[F_j(t)]^2&=\langle h(t)\Psi_{j,\mathrm{tr}}(t)|h(t)\Psi_{j,\mathrm{tr}}(t)\rangle\\&=\langle h(t)\Psi_{j,\mathrm{tr}}(t)|P(t)+Q(t)|h(t)\Psi_{j,\mathrm{tr}}(t)\rangle\\&=\langle h(t)\Psi_{j,\mathrm{tr}}(t)|Q(t)|h(t)\Psi_{j,\mathrm{tr}}(t)\rangle\\&=\sum_{n,m=1}^{N}a_{jm}(t)^*a_{jn}(t)\\&\quad\times\langle h(t)\phi_m(t)|Q(t)|h(t)\phi_n(t)\rangle,\end{aligned} \tag{3.26}$$

where in the third step we used Eq. (2.32), and in the last step we observed that

$$Q(t)|\phi_n(t)\rangle=0,$$

so that no terms containing either $\dot{a}_{jm}$ or $\dot{a}_{jn}$ appear. Let us assume that, initially, the electron is in the state with state vector $|\phi_k(t)\rangle$, that is, $|\Phi_i(t)\rangle=|\phi_k(t)\rangle$. Then, for large negative times, only $a_{ik}(t)$ is appreciable and from Eq. (3.26) we have, as $t\sim-\infty$,

$$[F_i(t)]^2 \sim \langle h(t)\Phi_i(t)|Q(t)|h(t)\Phi_i(t)\rangle. \quad (3.27)$$

If we introduce an infinite set of orthonormal vectors $|\psi_p(t)\rangle$ which span the complement of $\mathcal{H}_N(t)$, then

$$Q(t)=\sum_{p=N+1}^{\infty}|\psi_p(t)\rangle\langle\psi_p(t)|,$$

and from Eq. (3.27) we obtain

$$[F_i(t)]^2 \sim \sum_{p=N+1}^{\infty}|\langle\psi_p(t)|h(t)|\Phi_i(t)\rangle|^2. \quad (3.28)$$

However, for large negative t we have

$$|\langle\psi_p(t)|h(t)|\Phi_i(t)\rangle| \sim (1/v^2t^2)|\langle\psi_p(t)|\vec{r}\cdot\hat{v}|\Phi_i(t)\rangle| \quad (3.29)$$

and there are an infinite number of vectors $|\psi_p(t)\rangle$ for which $\langle\psi_p(t)|\vec{r}\cdot\hat{v}|\Phi_i(t)\rangle$ is not zero. Hence from Eqs. (3.28) and (3.29), we have

$$F_i(t)\sim c/t^2,$$

where c is nonzero, and therefore Eq. (3.24b) cannot be satisfied. Similarly, Eq. (3.24a) cannot be satisfied. It can be shown, however, that a first-order bound exists, even though a variational bound does not exist.

C. Useful form for $F_j(t)$

We have shown that variational bounds can be obtained when the i- and f-basis sets are identical physical basis sets. We end this paper by deriving a useful form for $F_j(t)$ when the i- and f-basis sets are identical. We have

$$[F_j(t)]^2=\langle h(t)\Psi_{j,\mathrm{tr}}(t)|h(t)\Psi_{j,\mathrm{tr}}(t)\rangle = \sum_{n=1}^{N} a_{jn}(t)\langle h(t)\Psi_{j,\mathrm{tr}}(t)|h(t)\phi_n(t)\rangle, \quad (3.30)$$

where we have used Eqs. (2.31) or Eqs. (2.38) to eliminate the terms containing $\dot{a}_{jn}(t)$. Expanding $\Psi_{j,\mathrm{tr}}(t)$ in (3.30) we obtain

$$[F_j(t)]^2 = i\sum_{m,n=1}^{N}\dot{a}_{jm}(t)^*a_{jn}(t)\langle\phi_m(t)|h(t)\phi_n(t)\rangle + \sum_{m,n=1}^{N}a_{jm}(t)^*a_{jn}(t) \times\langle h(t)\phi_m(t)|h(t)\phi_n(t)\rangle. \quad (3.31)$$

Using Eq. (2.40), the first sum in Eq. (3.31) can be written in the form

$$i\sum_{m=1}^{N}\dot{a}_{jm}(t)^*\Big(\sum_{n=1}^{N}\langle\phi_m(t)|h(t)\phi_n(t)\rangle\, a_{jn}(t)\Big) = i\underline{\dot{A}}_j(t)^\dagger\underline{M}(t)\underline{A}_j(t) = -\underline{\dot{A}}_j(t)^\dagger\underline{N}(t)\underline{\dot{A}}_j(t). \quad (3.32)$$

The second sum in Eq. (3.31) can be written in the form $\underline{A}_j(t)\underline{W}(t)\underline{A}_j(t)$, where $\underline{W}(t)$ is the matrix with elements $\langle\overline{h(t)\phi_m(t)}|h(t)\phi_n(t)\rangle$. Therefore $[F_j(t)]^2$ assumes the very simple and symmetric matrix form

$$[F_j(t)]^2=\underline{A}_j(t)^\dagger\underline{W}(t)\underline{A}_j(t)-\underline{\dot{A}}_j(t)^\dagger\underline{N}(t)\underline{\dot{A}}_j(t). \quad (3.33)$$

The quantities $\underline{A}_j(t)$, $\underline{\dot{A}}_j(t)$, and $\underline{N}(t)$ can be obtained from the (standard) coupled-state calculations. The evaluation of $\underline{W}(t)$ is discussed in Appendix A.

Note added in proof. The projection difficulties encountered in the standard approach when a Sturmian basis set is used can, in fact, be easily avoided. Suppose, for example, that we wish to calculate the transition amplitude to the $2s$ state. Using the Hylleraas-Undheim theorem an approximate $2s$ state can be defined by diagonalizing the target Hamiltonian with respect to the set of N Sturmian basis vectors. It can be shown that the approximate transition amplitude (obtained from the standard coupled-state equations) for transitions to the *approximate* $2s$ state has a well-defined value. However, this method does not appear to be variational, although this aspect is being investigated in more detail.

APPENDIX A

To compute $\underline{W}(t)$ in Eq. (3.33) it is necessary to evaluate (for the proton–hydrogen-atom system) the following two types of integrals:

$$J_1=\int d\vec{r}\, r^{N-1}e^{-ar-i\vec{v}\cdot\vec{r}}Y_{LM}(\hat{r})\rho^{N'-1}e^{-b\rho}Y^*_{L'M'}(\hat{\rho}), \quad N\geq L,\ N'\geq L' \quad (A1)$$

and

$$J_2=\int d\vec{r}\,\frac{r^N}{\rho^2}e^{-ar}Y_{LM}(\hat{r}), \quad N\geq L \quad (A2)$$

where $\vec{\rho}=\vec{r}-\vec{R}$. The integral J_1 can be evaluated by the rapid differential equation technique due to Cheshire.[10] In this appendix we describe a technique, which is similar to spirit to Cheshire's technique, for evaluating J_2.

By first expressing $1/\rho^2$ in terms of its Fourier transform, we can reduce J_2 to the form

$$J_2=2^{L+3}\pi(L+1)!\,Y_{LM}(\hat{R})\left(-\frac{\partial}{\partial a}\right)^{N-L}(aI_{KL}), \quad (A3)$$

where

$$I_{nl}=\int_0^\infty\frac{k^{l+1}j_l(kR)}{(k^2+a^2)^{n+2}}\,dk. \quad (A4)$$

The integrals I_{nl} cannot be evaluated analytically. Note that

$$\frac{\partial}{\partial a} I_{nl} = -2(n+2)\, a I_{n+1,l} \tag{A5}$$

and hence to evaluate J_2 we must evaluate the integrals I_{nL} for $n = L,\ L+1, \ldots, N$. Rather than evaluate the I_{nl} directly by numerical integration, it is more expedient to solve a certain set of coupled differential equations; we now derive this set. These equations are integrated along the projectile path.

We first differentiate I_{nl} with respect to the time t using the relation, valid for $l > 0$,

$$\frac{d}{du} j_l(u) = j_{l-1}(u) - \frac{l+1}{u}\, j_l(u). \tag{A6}$$

After some simple manipulation we obtain, for $l > 0$, the result

$$\dot{I}_{nl} = \dot{R}\{I_{n-1,l-1} - a^2 I_{n,l-1} - [(l+1)/R] I_{nl}\}, \tag{A7}$$

where the dot denotes the derivative with respect to t.

To obtain an equation for I_{n0} we differentiate I_{n0} with respect to t, using the relation

$$\frac{d}{du} j_0(u) = -j_1(u). \tag{A8}$$

We obtain

$$\dot{I}_{n0} = -\dot{R} I_{n1}; \tag{A9}$$

however from Eq. (A7) we have

$$\dot{I}_{n1} = \dot{R}[I_{n-1,0} - a^2 I_{n0} - (2/R) I_{n1}]. \tag{A10}$$

Clearly, if we can express $I_{n-1,0}$ in terms of I_{n0} and I_{n1}, then Eqs. (A9) and (A10) will constitute a closed set of coupled differential equations for I_{n0} and I_{n1}. These latter equations, coupled with Eq. (A7), will then provide a closed set of coupled differential equations for I_{nl}, $n \geq l$. To this end, we write out $I_{n-1,0}$ explicitly. From Eq. (A4) we have

$$I_{n-1,0} = \frac{1}{R} \int_0^\infty \frac{\sin kR}{(k^2+a^2)^{n+1}}\, dk \tag{A11}$$

and integrating by parts once gives

$$I_{n-1,0} = \frac{1}{R^2 a^{2n+2}} - \frac{2(n+1)}{R^2} \int_0^\infty \frac{k \cos kR}{(k^2+a^2)^{n+2}}\, dk. \tag{A12}$$

However, also from Eq. (A4), we have

$$I_{n0} - R I_{n1} = \int_0^\infty \frac{k j_0(kR) - R k^2 j_1(kR)}{(k^2+a^2)^{n+2}}\, dk = \int_0^\infty \frac{k \cos kR}{(k^2+a^2)^{n+2}}\, dk. \tag{A13}$$

Hence, from Eqs. (A12) and (A13), we have

$$I_{n-1,0} = \frac{1}{R^2 a^{2n+2}} - \frac{2(n+1)}{R^2} (I_{n0} - R I_{n1}). \tag{A14}$$

Inserting this expression for $I_{n-1,0}$ into Eq. (A10) we then obtain

$$\dot{I}_{n1} = \dot{R}\left[\frac{1}{R^2 a^{2n+2}} - \left(a^2 + \frac{2n+2}{R^2}\right) I_{n0} + \frac{2n}{R}\, I_{n1}\right]. \tag{A15}$$

Equations (A7), (A9), and (A15) provide a set of first-order coupled differential equations in time for the integrals I_{nl} with $n = l,\ l+1, \ldots, N$ and $l = 0, 1, \ldots, L$, where $N \geq L \geq 0$, but N and L are otherwise arbitrary. These equations can be integrated subject to the boundary conditions $\lim_{t\to\infty} I_{nl} = 0$ or $\lim_{t\to-\infty} I_{nl} = 0$.

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