Optimization of approximate solutions to the time-dependent Schrödinger equation

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Approximate solutions to the time-dependent Schrödinger equation can be sought in terms of time-dependent parameters. In this work, a reasonable definition of the "best" values for these parameters is given by requiring that the time integral of the deviation of the approximate solution from the exact solution be minimized. A procedure for specifically evaluating the parameters to optimize the approximate solution is given in terms of equations analogous to Hamilton's equations of classical mechanics, which produce a minimum-deviation integral in analogy to Hamilton's principle. A comparison of this technique with previous approaches is made, both in terms of general principles, and in terms of a simple hypothetical example of a system subjected to a time-dependent perturbation.

I. INTRODUCTION

The exact solution ψ of the time-dependent Schrödinger equation

$$G\psi=\left(H-i\frac{\partial}{\partial t}\right)\psi=0 \tag{1}$$

also satisfies the equivalent stationary integral equation[1]

$$\delta\int\langle\psi|G\psi\rangle dt=0\,. \tag{2}$$

In most applications one seeks an approximation to ψ in terms of a trial solution ψ_{tr}, which depends on time-dependent parameters $\alpha_1,\alpha_2,\ldots$. The problem is to select a procedure for evaluating the parameters so that ψ_{tr} will approximate ψ as closely as possible within the limited subspace spanned by ψ_{tr}.

One approach is to assume that the trial function either satisfies a principle analogous to the exact equation, or a property satisfied by the exact solution. For example, several authors[2] have assumed that by forcing the integral analogous to Eq. (2) to be stationary,

$$\delta I=\delta\int\langle\psi_{tr}|G\psi_{tr}\rangle\,dt=0\,, \tag{3}$$

"optimized" values of the parameters will be obtained. The success of this method critically depends on the extent to which the space spanned by the trial solution includes the exact solution. In actual cases, the difficulty is that one never knows the adequacy of the space spanned by ψ_{tr}. Equation (3) does not guarantee the "best" choice of parameters in ψ_{tr} in any consistent sense.

In previous work,[3] a deviation integral was defined:

$$J(\psi_{tr})\equiv\int_{-\infty}^{+\infty}D\,dt\equiv\int_{-\infty}^{+\infty}\langle G\psi_{tr}|G\psi_{tr}\rangle\,dt\,, \tag{4}$$

where

$$D=\langle G\psi_{tr}|G\psi_{tr}\rangle \tag{5}$$

and methods may be sought to minimize $J(\psi_{tr})$. J is a measure of the degree of adequacy of ψ_{tr} in approximating ψ. The parameters in ψ_{tr} required for J to be minimized are then properly described as "optimized" in this strict mathematical sense.

In previous work,[3] several methods were suggested for analytically adjusting parameters in ψ_{tr} to minimize J. Storm and Rapp[4,5] carried out calculations involving repetitive arbitrary variation of parameters in ψ_{tr} in a charge-exchange problem to seek a minimum J by trial and error. They showed that the result of using Eq. (3) does not lead to a minimum J.

Chang and Rapp[3] suggested two methods for seeking a minimum in J. In a simple approximate method, one quite arbitrarily sets

$$\frac{\partial D}{\partial\alpha}=0 \tag{6}$$

for every real or complex parameter. This leads[3] to the equation

$$\mathrm{Im}\left(\left\langle\frac{\partial\psi_{tr}}{\partial\alpha}\middle|G\psi_{tr}\right\rangle\right)=0 \tag{7}$$

for a real parameter α, and $\langle\partial\psi_{tr}/\partial\alpha|G\psi_{tr}\rangle=0$ for a complex α. Chang and Rapp[3] also described a more proper method, in which the Euler-Lagrange procedure was applied to $J(\psi_{tr})$. The result for a real parameter was

$$\mathrm{Re}\left(\left\langle\frac{\partial\psi_{tr}}{\partial\alpha}\middle|G^2\psi_{tr}\right\rangle\right)=0\,. \tag{8}$$

Equation (8) gives the exact analytic function $\alpha(t)$ which minimizes J.

In the present work, there are two main contributions. First is the development of a new method based on Hamilton's equations which serves as an

alternative to Eq. (8) for calculating parameters to exactly minimize $J(\psi_{tr})$.

This method (i) conveys new insights into the relation between ψ and ψ_{tr}, (ii) relates the methods of Eq. (3) and of minimizing $J(\psi_{tr})$, and (iii) leads to equations which are more easily integrated than Eq. (8) and its complex counterpart in actual applications. A second contribution of this paper is the application of several methods [Eq. (3), Eq. (7), and the method based on Hamilton's equations] to a specific simple example, namely, a hypothetical perturbed hydrogen atom with a nuclear charge that varies with time. A similar problem was originally treated by Chang.[6] The comparison of the various methods when applied to this problem leads to interesting insights into the useful regions of applicability of the methods.

II. COMMENT ON THE METHOD OF EQ.(3)

In this section we examine the use of Eq. (3) for real and complex parameters. Consider arbitrary complex variations which either (a) conserve normalization (i.e., $N=\langle\psi_{tr}|\psi_{tr}\rangle$, $\delta N=0$) or (b) vanish at the end points in time. For such arbitrary complex variations, one can imply that for any allowed variation $\delta\psi_{tr}$, $i\delta\psi_{tr}$ is also an allowable variation and consequently Eq. (3) can be written

$$\mathrm{Re}\int\langle\delta\psi_{tr}|G\psi_{tr}\rangle\,dt=0\,. \tag{9}$$

Substituting $i\delta\psi_{tr}$ for the variation in Eq. (9) and adding and subtracting this from Eq. (9):

$$\int\langle\delta\psi_{tr}|G\psi_{tr}\rangle\,dt=0 \tag{10}$$

and

$$\int\langle G\psi_{tr}|\delta\psi_{tr}\rangle\,dt=0\,. \tag{11}$$

That Eqs. (10) and (11) can be derived from Eq. (9) demonstrates that even though the variations $\delta\psi_{tr}$ and $\delta\psi_{tr}^{*}$ are not independent,[1] they can be treated as though they were.

When arguments analogous to those leading to Eqs. (10) and (11) are used for the exact solution ψ and $\delta\psi$, Eq. (2) can be shown to be equivalent to Eq. (1).[1]

For a variation of ψ_{tr} due to a complex parameter α,

$$\delta\psi_{tr}=\frac{\partial\psi_{tr}}{\partial\alpha}\delta\alpha\,.$$

For any arbitrarily chosen ψ_{tr}, $\partial\psi_{tr}/\partial\alpha$ is a specific complex function. However, since $\delta\alpha$ is arbitrary and complex, $\delta\psi_{tr}$ is an arbitrary complex variation. Then a new variation $i\delta\psi_{tr}$ can be considered which is generated by $i\delta\alpha$. Therefore, for variations in ψ_{tr} produced by variations in a complex parameter, both $\delta\psi_{tr}$ and $i\delta\psi_{tr}$ may be taken as variations. For variations in ψ_{tr} due to variations in a real parameter,

$$\delta\psi_{tr}=\frac{\partial\psi_{tr}}{\partial z}\delta z\,,$$

where for an arbitrarily chosen ψ_{tr}, $\partial\psi_{tr}/\partial z$ is a specific complex function. Now, however, δz is an arbitrary real variation and consequently $\delta\psi_{tr}$ is not a general complex variation. $\delta\psi_{tr}$, in this case, is a general real multiple of $\partial\psi_{tr}/\partial z$. Therefore, if the variation δz produces a variation $\delta\psi_{tr}$, this does not imply that $i\delta\psi_{tr}$ is also a variation. Arbitrary complex variations of ψ_{tr} cannot be generated by variations in a real parameter. The use of the analogue of Eq. (2) for a ψ_{tr} depending on a real parameter necessitates the imposition of a property of the exact solution on the trial solution (since $G\psi$ vanishing implies $\mathrm{Re}\int\langle\delta\psi|G\psi\rangle\,dt$ vanishes). Therefore, for a real parameter satisfying condition (b), Eq. (9) is appropriate whereas Eqs. (10) and (11) are not. For the case of a real parameter z, Eq. (9) takes the form

$$\mathrm{Re}\left\langle\frac{\partial\psi_{tr}}{\partial z}\middle|\left[H-i\left(\frac{\partial}{\partial t}\right)_{r,z}-i\dot{z}\frac{\partial}{\partial z}\right]\psi_{tr}\right\rangle=0\,. \tag{12}$$

Since $\dot{z}$ and $\langle\partial\psi_{tr}/\partial z\,|\,\partial\psi_{tr}/\partial z\rangle$ are real, Eq. (12) becomes

$$\mathrm{Re}\left\langle\frac{\partial\psi_{tr}}{\partial z}\middle|H-i\left(\frac{\partial}{\partial t}\right)_{r,z}\middle|\psi_{tr}\right\rangle=0\,. \tag{13}$$

This is an algebraic equation for $z(t)$.

A shortcoming of using Eq. (3) for variations due to a real parameter is that the result Eq. (9) is the analogue of a necessary but not sufficient condition that ψ be an exact solution of Eq. (1). It always results in an algebraic equation rather than a differential equation, which one might expect from the analogue of the variational principle which is equivalent to the Schrödinger partial differential equation. To approximate a differential equation by an algebraic one is a much more serious alteration than replacing it with a simpler differential equation (as occurs for complex parameters).

III. THE METHOD OF HAMILTON'S EQUATIONS

There are two mathematically equivalent methods which will make $J(\psi_{tr})$ stationary with respect to variations in the parameters. One is the method in which the Euler-Lagrange equation

$$\frac{d}{dt}\left(\frac{\partial D}{\partial\dot{\alpha}_i}\right)-\frac{\partial D}{\partial\alpha_i}=0 \tag{14}$$

is applied to independent variations of α_i. A problem with Eq. (14) is the presence of the G^2 operator, which leads to a nonlinear $\dot{\alpha}^2$ term in the differential equation.

A mathematically equivalent approach is derived using Hamilton's equations[7] in which a "momentum" is defined conjugate to each parameter. For a ψ_{tr} that depends on N complex parameters α_j and M real parameters λ_i one defines

$$P_{\alpha_j} \equiv \frac{\partial D}{\partial \dot{\alpha}_j} \text{ (complex)}, \quad j=1,\ldots,N \tag{15a}$$

$$P_{\lambda_i} \equiv \frac{\partial D}{\partial \dot{\lambda}_i} \text{ (real)}, \quad i=1,\ldots,M \tag{15b}$$

and a pseudo-Hamiltonian K,

$$K=\sum_{j=1}^{N}(\dot{\alpha}_j P_{\alpha_j}+\dot{\alpha}_j^* P_{\alpha_j}^*)+\sum_{i=1}^{M}\dot{\lambda}_i P_{\lambda_i}-D\,.$$

Hamilton's equations[7] are then

$$\dot{\alpha}_j=\frac{\partial K}{\partial P_{\alpha_j}} \quad (j=1,2,\ldots,N)\,, \tag{16a}$$

$$\dot{P}_{\alpha_j}=\frac{-\partial K}{\partial \alpha_j}=\frac{\partial D}{\partial \alpha_j} \quad (j=1,2,\ldots,N)\,, \tag{16b}$$

$$\dot{\lambda}_i=\frac{\partial K}{\partial P_{\lambda_i}} \quad (i=1,2,\ldots,M)\,, \tag{16c}$$

$$\dot{P}_{\lambda_i}=-\frac{\partial K}{\partial \lambda_i}=\frac{\partial D}{\partial \lambda_i} \quad (i=1,2,\ldots,M)\,. \tag{16d}$$

The simultaneous solution of the first-order differential equations (16) determines the ψ_{tr} that makes $J(\psi_{tr})$ stationary for parameters α_j and λ_i that have no variation at the end points.

It turns out that more is achieved than merely the replacement of a number of second-order Euler-Lagrange differential equations by twice as many first-order Hamilton differential equations. The momenta conjugate to the parameters can be interpreted as a measure of how well the subspace of the trial solution covers the space of the exact solution.

IV. HAMILTON'S EQUATIONS FOR THE EXPANSION COEFFICIENTS

Consider a system described by a Hamiltonian H_0 with known eigenfunctions $\phi_1, \phi_2, \ldots$. Let a perturbation $V(r,t)$, with the property $V \to 0$ as $t \to \pm\infty$, act on the system, where r represents the positional coordinates.

The exact solution of the equation

$$G\psi=\left(H_0+V-i\frac{\partial}{\partial t}\right)\psi \tag{17}$$

can be expanded in terms of the ϕ_i as

$$\psi=\sum_{j=1}^{\infty}a_j(t)\phi_j(r,t)\,, \tag{18}$$

where

$$\dot{a}_k=\frac{1}{i}\sum_{j=1}^{\infty}\langle k|V|j\rangle a_j\,.$$

Now suppose an approximate solution is sought in terms of a trial function that is a truncated expansion in the ϕ_j:

$$\psi_{tr}=\alpha_1\phi_1+\alpha_2\phi_2\,. \tag{19}$$

One common method for estimating $\alpha_1(t)$ and $\alpha_2(t)$ is to use truncated forms of Eq. (18):

$$\dot{\alpha}_k=-i\sum_{j=1}^{2}\langle k|V|j\rangle\alpha_j\,. \tag{20}$$

This method is based on the concept that as the space spanned by ψ_{tr} is increased by including more of the ϕ_j, the α_j will approach the a_j. However, for any finite truncation, there is no guarantee that the α_j produced by Eq. (20) are the "best" functions of time. Some authors[2] have made the point that Eq. (20) can be derived from Eq. (3), and used this to "justify" the use of Eq. (20). However, Eq. (3) does not produce "best" parameters unless the space spanned by ψ_{tr} is very close to that spanned by ψ. Therefore, Eq. (20) may give very poor values of $\alpha_j(t)$ [in the sense that $\alpha_j(t)$ is not close to $a_j(t)$].

The Hamilton's-equations method outlined in Sec. III of this paper will now be used to obtain optimized $\alpha_j(t)$ in the sense that for the choice of Eq. (19) as ψ_{tr}, $J(\psi_{tr})$ is minimized.

Let the set of expansion coefficients that minimize $J(\psi_{tr})$ be denoted by $\alpha_j(t)$. A necessary condition for a minimum $J(\psi_{tr})$ is

$$\left(\frac{dJ}{d\epsilon}\right)\Big|_{\epsilon=0}=\sum_{j=1}^{2}\int_{t_i}^{t_f}\left[\frac{d}{dt}\left(\frac{\partial D}{\partial \dot{\alpha}_j}\right)-\frac{\partial D}{\partial \alpha_j}\right]\eta_j(t)\,dt + \sum_{j=1}^{2}\eta_j(t)\frac{\partial D}{\partial \alpha_j}\Big|_{t_i}^{t_f}=0\,, \tag{21}$$

where $\delta\alpha_j$ is characterized by the arbitrary function $\eta_j(t)$ and the parameter ϵ.[7]

Assuming that $\psi \to \phi_1$ at $t=t_i$, the trial function becomes exact at this time and one can set $\eta_j(t_i)=0$ for each value of j. At time t_f, the values of $a_j(t_f)$ are not usually known, and therefore $\eta_j(t_f)$ cannot be set equal to zero. In order to apply the Euler-Lagrange or Hamilton's-equations methods to the determination of $\alpha_j(t)$, it is necessary to force

$$\left(\frac{\partial D}{\partial \dot{\alpha}_j}\right)\eta_j(t)\Big|_{t=t_f}=0 \quad (j=1,2)\,. \tag{22}$$

Equation (22) will be satisfied if the momentum conjugate to α_j is made to vanish at $t=t_f$. Bound-

ary conditions given by Eq. (22) are well known[8] in calculus of variations problems with fixed and free end points.

For the trial function in Eq. (19) with G defined in Eq. (17), one finds

$$D(t)=\sum_{k=1}^{2}|\dot{\alpha}_k|^2+\sum_{k,m=1}^{2}\dot{\alpha}_k^*\alpha_m V_{km}^2 + i\sum_{k,m=1}^{2}\dot{\alpha}_k^*\alpha_m V_{km}-i\sum_{k,m=1}^{2}\dot{\alpha}_k\alpha_m^* V_{mk}, \quad (23)$$

where

$$V_{km}^n=\langle\phi_k|V^n|\phi_m\rangle. \quad (24)$$

The momenta conjugate to α_k^* $(k=1,2)$ are

$$P_{\alpha_k^*}=\frac{\partial D}{\partial\dot{\alpha}_k^*}=\dot{\alpha}_k+i\left(\sum_{j=1}^{2}V_{kj}\alpha_j\right)=(P_{\alpha_k})^*. \quad (25)$$

The first pair of Hamilton's equations can be found by inverting Eq. (25) obtaining

$$\dot{\alpha}_k=P_{\alpha_k^*}+\frac{1}{i}\sum_{j=1}^{2}V_{kj}\alpha_j \quad (k=1,2). \quad (26)$$

The second pair of Hamilton's equations are

$$\dot{P}_{\alpha_k}=\frac{\partial D}{\partial\alpha_k}=i(P_kV_{kk}+P_mV_{mk}) + \alpha_k^*(V_{kk}^2-|V_{kk}|^2-|V_{km}|^2) + \alpha_m^*(V_{mm}^2-V_{mk}V_{kk}-V_{mm}V_{mk}) \quad (27)$$

in which $m=2$ if $k=1$, and $m=1$ if $k=2$. By inserting the operator $\sum_{n=1}^{\infty}|n\times n|$ in the V^2 terms in Eq. (27), one finds

$$\dot{P}_{\alpha_k}=i(P_kV_{kk}+P_mV_{mk})+\alpha_k^*\sum_{n=3}^{\infty}V_{kn}V_{nk} + \alpha_m^*\sum_{n=3}^{\infty}V_{mn}V_{nk}, \quad (28)$$

where again $m=2$ if $k=1$ and $m=1$ if $k=2$.

This equation shows that in some way the values of P_{α_1} and P_{α_2} partly compensate for the effect of the missing states $\phi_3,\phi_4,\ldots$, which were not included in ψ_{tr}. Comparing Eqs. (26) and (18) for $\dot{\alpha}_k$ and $\dot{a}_k$, respectively, one can make the identification of α_k as the best approximation to a_k in the sense of minimizing $J(\psi_{tr})$, and in the same sense identify the $P_{\alpha_k^*}$ with the best single-term approximation to $(1/i)\sum_{j=3}^{\infty}\langle k|V|j\rangle a_j$. Further support for this interpretation is found from using Eq. (26) to obtain

$$\frac{d}{dt}(|\alpha_1|^2+|\alpha_2|^2)=\alpha_1P_{\alpha_1}+\alpha_1^*P_{\alpha_1}^*+\alpha_2P_{\alpha_2}+\alpha_2^*P_{\alpha_2}^*, \quad (29)$$

which shows that probability is not conserved in this model due to the implicit flow of probability between states $(1,2)$ and $(3,4,5,\ldots)$. This demand for an average contribution from all the higher states results in our inability to have a normalized two-state approximation which minimizes $J(\psi_{tr})$. However it is necessary that

$$\frac{d}{dt}(|\alpha_1|^2)=\frac{d}{dt}(|\alpha_2|^2)=0$$

as $V(r,t)\to 0$. At $t=t_i$, $|\alpha_1|^2=1$ and $|\alpha_2|^2=0$. Setting $\alpha_1=e^{i\theta}$ and $\alpha_2=0$ at t_i, one can show from (26) that at $t=t_i$ it is required that:

$$\mathrm{Re}(P_{\alpha_1})=\mathrm{Im}(P_{\alpha_1})\tan\theta$$

to ensure

$$\frac{d}{dt}(|\alpha_1|^2)=\frac{d}{dt}(|\alpha_2|^2)=0$$

at t_i.

Now one can choose θ, $\mathrm{Im}(P_{\alpha_1})$, $\mathrm{Re}(P_{\alpha_2})$, and $\mathrm{Im}(P_{\alpha_2})$ at $t=t_i$, so that $\mathrm{Re}(P_{\alpha_1})$, $\mathrm{Im}(P_{\alpha_1})$, $\mathrm{Re}(P_{\alpha_2})$, and $\mathrm{Im}(P_{\alpha_2})$ all vanish at $t=t_f$. Then one can choose $\mathrm{Re}(P_{\alpha_1})$ at $t=t_i$ equal to $\mathrm{Im}(P_{\alpha_1})\tan\theta$. The arrangement of the P_{α_k} such that they vanish at $t=t_f$ will not only lead from Eq. (21) to the Euler-Lagrange or Hamilton equations minimizing $J(\psi_{tr})$ but also to

$$\frac{d}{dt}(|\alpha_1|^2)=\frac{d}{dt}(|\alpha_2|^2)=0$$

at $t=t_f$.

Contrary to what has been claimed in the literature,[9] not only will Eqs. (20) not minimize $D(t)$, but in addition they will not minimize $\int_{-\infty}^{+\infty}D\,dt=J(\psi_{tr})$. The usual coupled equations (20) can be derived from Eq. (26) if the P_{α_k} are made to vanish identically. This would imply from Eq. (15a) that D does not depend on the $\dot{\alpha}_k$. If P_{α_k} vanishes identically it implies that $\dot{P}_{\alpha_k}$ and $\partial D/\partial\alpha_k$ vanish. Therefore, the usual coupled equations could only minimize $J(\psi_{tr})$ if D did not depend on either α_k or $\dot{\alpha}_k$. Since any meaningful D must depend on either the α_k and/or the $\dot{\alpha}_k$ the usual coupled equations can never minimize $J(\psi_{tr})$. Since D is always greater than or equal to zero, the fact that Eqs. (20) cannot minimize $J(\psi_{tr})$ implies that Eqs. (20) cannot minimize $D(t)$. The trouble with all the reported proofs[9] which claim to show that $D(t)$ is minimized by Eqs. (20) is their attributing to every time t a property $\delta\psi_{tr}=0$, which is only justified for the initial time.

While the Euler-Lagrange equation for the α_k would certainly be mathematically equivalent to (26) and (27), the relationship between (20) and these second-order differential equations would not be nearly as apparent as between (20) and the combined Hamilton's equations (26) and (27).

In summary, Eqs. (26) and (27) constitute a set

of four coupled linear differential equations, which when solved subject to the aforementioned boundary conditions yield a set of parameters $\alpha_1(t)$, $\alpha_2(t)$, $P_{\alpha_1}(t)$, and $P_{\alpha_2}(t)$, which minimize $J(\psi_{tr})$. These equations (or their generalization for more than two states) would be particularly well suited for problems in which either (a) a limited set $\phi_1, \phi_2, \ldots, \phi_m$ are known, whereas the higher states are important but not well known, or (b) the important states ϕ_k are known, but are of such great number or complexity that to avoid an impractical calculational problem a truncated wave function is chosen as ψ_{tr}. In this second case, only some of the important wave functions ϕ_k are treated explicitly and an average effect of the other states is treated through the conjugate momenta. This technique necessitates the inclusion in ψ_{tr} of all the states whose $\alpha_k(t)$ are to be optimized.

V. APPLICATION OF HAMILTON'S EQUATIONS TO INTERNAL PARAMETERS OF THE EXPANSION FUNCTIONS

In some applications the form of the approximate solution is conveniently chosen as

$$\psi_{tr} = \sum_j \alpha_j(t)\chi_j(r, t, z_{j_1}, z_{j_2}, \ldots)$$

in which the $z_{j_1}, z_{j_2}, \ldots$ are parameters internal to the expansion functions, and for which $\chi_j \to \phi_j$ as $t \to t_i$ or t_f. The Hamilton's-equations technique to minimize $J(\psi_{tr})$ can be used to optimize the parameters $z_{j_1}, z_{j_2}, \ldots$ as well as the $\alpha_j(t)$. Such internal parameters are very important in the theoretical treatment of charge exchange,[2] and it is desired to demonstrate the relative effectiveness of different choices of procedures for "optimizing" them.

The method will be illustrated in terms of a simple example, consisting of a hypothetical perturbed hydrogen atom with a time-dependent nuclear charge $\beta(t)$ that varies with time, with the end points satisfying $\beta(\pm\infty) = 1$. The Hamiltonian for this problem is

$$H = -\nabla^2 - 2\beta(t)/r\,, \tag{30}$$

where $\beta(t)$ can be selected arbitrarily, provided it goes to 1 as $t \to \pm\infty$. A trial function was selected in the form of a hydrogenlike function

$$\psi_{tr} = [z^3(t)/\pi]^{1/2} e^{-z(t)r} e^{+iz^2(t)t}\,, \tag{31}$$

where $z(t)$ is a parameter representing a scale factor which is to be optimized in the sense that $J(\psi_{tr})$ is minimized for any $\beta(t)$. Since $\beta(t) \to 1$ for large positive and negative times, it follows that $z(t)$ must also go to unity and that $\psi_{tr} = \psi$ at such times. Since we are dealing with a problem of two fixed end points, the calculus of variations problem is straightforward. Although simple, this example has certain important characteristics found in the standard H^+-H charge-exchange model. One could imagine the perturbed nuclear charge $\beta(t)$ being caused by the passing proton, and the form of the trial function is the archetype of that used in H^+-H charge exchange.

It is desired to utilize each of the previously described methods of evaluating $z(t)$ and $J(\psi_{tr})$ to compare the adequacy of various approaches. For any arbitrary function $z(t)$, the deviation is determined from Eqs. (30) and (31) as

$$D(t) = 8z^2[(z-\beta)^2 + (z-\beta)\dot{z}t] + \dot{z}^2(4t^2z^2 + 3/4z^2)\,. \tag{32}$$

This is evaluated and integrated over time to obtain $J(\psi_{tr})$ for each method.

First consider the method used by Cheshire[2] and others as given in Eq. (3). A simple calculation shows that this method yields the result

$$z_1(t) = \beta(t)$$

for all time. The deviation D based on this method is then

$$D_1(t) = \dot{\beta}^2(4t^2\beta^2 + 3/4\beta^2)\,. \tag{33}$$

The integral over time of $D_1(t)$ is referred to as J_1.

The approach to minimization of J by means of Hamilton's equations is described next. Hamilton's equations are

$$\dot{z} = (8t^2z^2 + 3/2z^2)^{-1}[P_z - 8z^2(z-\beta)t]\,, \tag{34}$$

$$\dot{P}_z = \frac{\partial D}{\partial z} = 16z[(z-\beta)^2 + (z-\beta)\dot{z}t] + 8z^2[2(z-\beta) + \dot{z}t] + \dot{z}^2(8t^2z - 3/2\dot{z}^3)\,. \tag{35}$$

The simultaneous solution of Eqs. (34) and (35) with P_z and $\dot{P}_z$ set equal to zero is $z_1(t)$, the solution derived from Eq. (3). When Eqs. (34) and (35) are simultaneously integrated, and the resulting $z_2(t)$ is used to calculate the deviation, it is designated by $D_2(t)$, and the time integral is J_2. The initial value of z is unity, but the initial value of P_z is unknown. The actual numerical integration is carried out from a large negative time as a starting point, and the initial value of P_z is adjusted until the resulting integration produces a $z(t)$ at large positive time that approaches unity.

In the method suggested by Rapp and Chang,[3] as given in Eq. (6), the basis is that $\partial D/\partial\dot{z}$ is set equal to zero at all time, and one obtains the differential equation

$$\dot{z} = \frac{-4z^2(z-\beta)t}{4t^2z^2 + 3/4z^2}\,. \tag{36}$$

TABLE I. Comparison of the deviation for various techniques in Sec. V. D_1, D_2, D_3, and D_4 are the $D(t)$ corresponding to solutions found from Eq. (3), Hamilton's equations, Eq. (36), and $z(t)=1$, respectively. ($A=0.04$, $B=0.1$, wide potential).

Time	D_1	D_2	D_3	D_4
−15.0	0.790(−6)	0.848(−3)	0.0	0.0
−12.0	0.211(−3)	0.160(−2)	0.421(−6)	0.733(−6)
−9.0	0.104(−1)	0.316(−2)	0.786(−4)	0.122(−3)
−6.0	0.784(−1)	0.439(−2)	0.363(−2)	0.449(−2)
−3.0	0.469(−1)	0.430(−2)	0.590(−1)	0.389(−1)
−1.0	0.128(−2)	0.253(−2)	0.411	0.738(−1)
0.0	0.0	0.336(−3)	0.728	0.780(−1)
1.0	0.128(−2)	0.236(−2)	0.411	0.738(−1)
3.0	0.469(−1)	0.391(−2)	0.590(−1)	0.389(−1)
6.0	0.784(−1)	0.413(−2)	0.363(−2)	0.449(−2)
9.0	0.104(−1)	0.306(−2)	0.786(−3)	0.122(−3)
12.0	0.211(−3)	0.152(−2)	0.421(−6)	0.733(−6)
15.0	0.790(−6)	0.757(−3)	0.101(−13)	0.0
Time integral (J)	0.814 [a]	0.957(−1) [a]	0.205(1)	0.501

[a] These J values were calculated with $t_i=-30.0$ and $t_f=30.0$ as in Fig. 1.

This was numerically integrated and the resulting $z_3(t)$ used to obtain $D_3(t)$ and its time integral J_3.

A very simple approximation was tried in which $z(t)$ was set equal to unity for all time. The resulting values of the deviation are denoted $D_4(t)$, and the time integral is J_4. Thus four different calculations of $D(t)$ and $J(\psi_{tr})$ were performed and compared.

The function selected for $\beta(t)$ was

$$\beta(t)=1+Be^{-At^2}.$$

Values of B equal to 0.1 and 0.2 were found to be sufficient to test the principles involved. Three values of A were chosen to represent slow, moderate, and fast variations of B with time ($A=0.04$, 1.0, and 100.0). For these values of A and B, calculations of $D(t)$ and $J(\psi_{tr})$ were made for each of the four $z(t)$ functions described above. Differential equations were integrated on a digital computer using a predictor-corrector method. It was found that there was no substantial qualitative difference between the results for $B=0.1$ and $B=0.2$. To save space, only the results for $B=0.1$ are presented here.

The resulting values of $D(t)$ at selected values of t (atomic units) are given in Table I for $A=0.04$ and $B=0.1$. The variations of $D_1(t)$, $D_2(t)$, $Z_1(t)$, and $Z_2(t)$ for $A=1.0$ and $A=100.0$ are shown in Figs. 1 and 2. The J values for the three A values and $B=0.1$ are given in Table II. In each case, as expected, the lowest value of $J(\psi_{tr})$ results from the use of Hamilton's equations to determine $z(t)$ (method 2). $z_2(t)$ is always wider in time, but not as high as $z_1(t)$. It appears that as the width of $\beta(t)$ becomes large, $z_2(t)$ will approach $\beta(t)$, whereas when $\beta(t)$ becomes exceedingly narrow, $z_2(t)$ will approach unity for all t. Thus, when the perturbation varies rapidly, the wave function does not have time to readjust to the perturbation, and when the perturbation varies slowly, the wave function can adjust almost adiabatically. Since

TABLE II. Comparison of the measure of the integrated error J for the intermediate- and narrow-potential cases in Sec. V. J_1, J_2, J_3, and J_4 correspond to the J values found with Eq. (3). Hamilton's equations, Eq. (36), and simply setting $z(t)=1$, respectively.

	J_1	J_2	J_3	J_4
$A=0.04$, $B=0.04$ (narrow width)	0.814	0.957(−1)	0.205(1)	0.501
$A=1.0$, $B=0.1$ (intermediate width)	0.195	0.228(−1)	0.243	0.100
$A=100.0$, $B=0.1$ (narrow width)	0.355	0.796(−2)	0.104(−1)	0.100(−1)

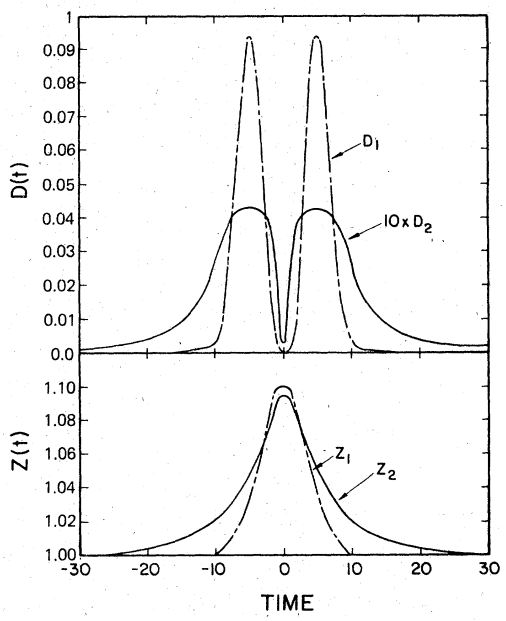

FIG. 1. Comparison of the deviations, $D_1(t)$ and $D_2(t)$, and the effective nuclear charges, $z_1(t)$ and $z_2(t)$ ($A = 1.0$, $B = 0.1$, intermediate width).

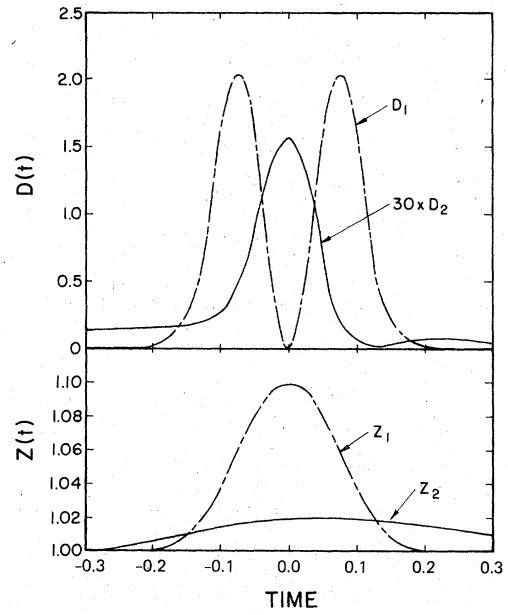

FIG. 2. Comparison of the deviations, $D_1(t)$ and $D_2(t)$, and the effective nuclear charges, $z_1(t)$ and $z_2(t)$ ($A = 100.0$, $B = 0.1$, narrow potential).

$\dot{\beta}(t) \to 0$ as $t \to 0$, $D_1(t)$ vanishes and $z_1(t)$ must be exact as $t = 0$. Nevertheless, $J_1(\psi_{tr})$ exceeds $J_2(\psi_{tr})$ even though $D_1(t) < D_2(t)$ for some periods of time. On a relative basis, the method of Hamilton's equations is the greatest improvement over the method of Eq. (3) when the perturbation varies most rapidly. Method 3, utilizing Eq. (36), gives a time-varying $z(t)$ that decreases below unity instead of rising above one. This appears to be a fundamental imperfection in this method, although it leads to better results than method 1 when the perturbation varies rapidly. Method 3 has the virtue that it leads to $z(t) \to 1$ for all t as the perturbation varies very rapidly, whereas method 1 is qualitatively incorrect in this region. On the other hand, method 3 is qualitatively incorrect for slowly varying $\beta(t)$, while method 1 is a better approximation.

The $z(t)$ and $D(t)$ produced by methods 1, 3, and 4 are symmetric about $t = 0$. However, z_2 and D_2 are not symmetric about $t = 0$, and thus P_z can be interpreted as the factor responsible for the time delay or adjustment time necessary to minimize $J(\psi_{tr})$.

To further demonstrate that $J_2(\psi_{tr})$ is a relative minimum, a calculation was performed in which the arbitrary term $0.002e^{-At^2}$ was added to or subtracted from $z_2(t)$ for all t, and $D(t)$ calculated in each case. The results are given in Table III. When small positive or negative changes are made about $z_2(t)$, $J(\psi_{tr})$ increases.

It may be concluded that: (i) The method of Hamilton's equations produces a minimum integrated deviation. (ii) The method of Eq. (3) best approximates the Hamilton's-equations method for slowly varying perturbations, where it eventually goes to the adiabatic limit at very slow rates of change. (iii) The method of Eq. (6) best approximates the Hamilton's-equations method for rapidly varying perturbations, where it eventually leads to constant parameters for very rapid rates of change. (iv) Using $z(t) = 1$ for rapidly changing perturbations is much better than the use of Eq. (3).

Note that our "best" solution is "best" in a time-averaged sense and that at any particular time the other techniques can lead to solutions having a lower $D(t)$. None of these techniques provide a minimum of $D(t)$ at every instant of time. In fact, no purely time-dependent parameter could ever lead to $D(t)$ being minimized at every instant t. If the parameter is a function of the positional coordinates and t, then this goal might be attainable. From this, one might infer for the problem of H^+-H charge exchange that as the velocity of the incident proton increases, the method of Eq. (3) will lead to progressively less accurate results. Since the Hamilton's-equations method is always the most accurate, and in particular when the potential is rapidly varying is far superior to the

TABLE III. Dependence of the deviation on small variations ($\pm 0.002\, e^{-At^2}$) about the function $z_2(t)$ found from Hamilton's equations. D_2^+ and D_2^- are the $D(t)$ corresponding to z_2^+ and z_2^-, respectively. ($A=100.0$, $B=0.1$)

Time	D_2^-	D_2	D_2^+
−0.300	0.467(−2)	0.467(−2)	0.467(−2)
−0.200	0.500(−2)	0.519(−2)	0.539(−2)
−0.100	0.718(−2)	0.849(−2)	0.101(−1)
−0.050	0.327(−1)	0.323(−1)	0.324(−1)
−0.025	0.500(−1)	0.483(−1)	0.467(−1)
0.000	0.570(−1)	0.545(−1)	0.521(−1)
0.025	0.481(−1)	0.459(−1)	0.439(−1)
0.050	0.294(−1)	0.282(−1)	0.274(−1)
0.100	0.322(−2)	0.368(−2)	0.446(−2)
0.200	0.210(−2)	0.218(−2)	0.228(−2)
0.300	0.128(−2)	0.128(−2)	0.128(−2)
Time integral (J)	0.800 19(−2) [a]	0.796 36(−2) [a]	0.800 30(−2) [a]

[a] These J values were calculated with $t_i=-0.3$ and $t_f=0.95$.

technique of Eq. (3), it is natural for application to this problem in the region of high velocities. This work is in progress.

VI. GENERALIZATION AND CONCLUDING COMMENTS

Consider a trial solution ψ_{tr} depending on any complex parameter α:

$$P_{\alpha^*} \equiv \frac{\partial D}{\partial \dot{\alpha}^*} = \frac{\partial}{\partial \dot{\alpha}^*} \langle G\psi_{tr} | G\psi_{tr} \rangle , \tag{37}$$

$$G\psi_{tr} = \left[H - i\left(\frac{\partial}{\partial t}\right)_r \right] \psi_{tr} = \left[H - i\left(\frac{\partial}{\partial t}\right)_{r,\alpha} - i\dot{\alpha}\frac{\partial}{\partial \alpha} \right] \psi_{tr} . \tag{38}$$

One then finds from (37) and (38)

$$P_{\alpha^*} = i\left\langle \frac{\partial \psi_{tr}}{\partial \alpha} \middle| G\psi_{tr} \right\rangle . \tag{39}$$

For an arbitrary complex parameter α, Eq. (10) implies that $P_{\alpha^*}=0$.

In deriving Eq. (3) [and Eq. (10)], it is assumed that ψ-ψ_{tr} is small. A comparison of Eqs. (10) and (39) shows that in order to minimize $J(\psi_{tr})$ it is necessary to have a single adjustable addition to Eq. (10), P_{α^*}, which will just compensate for the error in assuming ψ-ψ_{tr} is small. In this sense P_{α^*} incorporates the part of Hilbert space in ψ-ψ_{tr} necessary to have ψ_{tr} minimize $J(\psi_{tr})$. The time dependence of the adjustment P_{α^*}, is given by the second Hamilton equation $\dot{P}_{\alpha^*} = \partial D/\partial \alpha^*$. Unlike the earlier calculations, no assumption was made concerning the trial function's dependence on α. For a general real parameter a similar argument shows that the identical vanishing of its conjugate momentum leads to the result of Eq. (3).

Concerning the applicability of the above to problems, the following points should be emphasized:

(i) The arrangement of the P_{α_i} to satisfy the appropriate boundary conditions at t_f could be worthwhile in problems where many states play an important role. If the states are either too numerous or not known precisely, the calculation of the P_{α_i}'s in a truncated wave function could be useful and guarantee an optimized average inclusion of all the excluded states.

(ii) For an internal real parameter satisfying $\delta\theta(t=\pm\infty)=0$, the calculation of $\theta(t)$ is simple and only involves arranging the $P_\theta(t_i)$ so that θ has the appropriate asymptotic form as $t \to t_f$.

The method presented in this paper, originally thought of as a purely mathematical device equivalent to the Euler-Lagrange equations, turns out to have a special significance of its own, hidden in the original form. There are more ways than one to separate the second-order Euler-Lagrange differential equation into two first-order differential equations. For example, for a parameter β, one could substitute

$$\dot{\beta} = \mu , \tag{40}$$

and the Euler-Lagrange equation becomes a first-order differential equation for μ, the derivative of the intermediate variable to be solved simultaneously with Eq. (40). However, the particular separation of the Euler-Lagrange differential equation into two Hamilton's equations introduces a mediating parameter (the conjugate momentum) which carries its own special message.

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