Boundary-Free Propagation with the Time-Dependent Schrödinger Equation

E. Y. Sidky and B. D. Esry
Department of Physics, Cardwell Hall, Kansas State University, Manhattan, Kansas 66506

(Received 26 June 2000)

We present two methods that allow for the efficient numerical propagation of continuum wave packets to large times. Time-dependent solutions of the Schrödinger equation that include continuum components are numerically challenging to solve because the wave packet travels, spreads, and acquires a spatial phase gradient. The methods we propose account for these kinematic effects analytically in general and numerically tractable schemes.

PACS numbers: 34.10.+x, 32.80.Rm, 34.50.Fa

In recent years direct solution of the time-dependent Schrödinger equation (TDSE) has been a rapidly growing theoretical technique for studying atomic and molecular collision processes. This method has been applied to such diverse systems as laser-atom interactions [1–3], electron impact ionization [4], photoionization [5], and heavy particle impact ionization [6,7]. In part, the impetus for a direct solution of the TDSE reflects the exponential growth of computing capability, but there is also an important physical motivation. Namely, almost all systems studied by direct integration involve continuum processes.

Time-dependent methods are particularly well suited for continuum problems since they require no knowledge of the asymptotic boundary conditions. This freedom from boundary conditions is in clear contrast to standard time-independent scattering formulations for which the asymptotic solution is needed for matching. For systems such as doubly ionized helium, the boundary conditions for the two continuum electrons are approximate at best. In the time-dependent approach, the ionized electronic wave packet occupies a finite—albeit increasingly large—volume of space. It is thus sufficient to set the wave function to zero at the boundary of this volume. Moreover, time-dependent methods provide very intuitive physical pictures of the dynamics.

Direct integration of the TDSE is ideal for systems involving short duration perturbing interactions, i.e., collision times comparable to the time scale of oscillations in the unperturbed system. When the interaction time is long, however, wave packet propagation becomes prohibitively expensive computationally because the continuum component of the wave function travels and expands and because an increasingly large spatial phase gradient develops in the wave function with time. The first point requires that the extent of the spatial grid be large, while the second dictates that the grid density should also be high.

To illustrate the difficulty of direct wave packet propagation applied to long-interacting systems involving the continuum, we offer the simple example of a free, expanding Gaussian wave packet. The time evolution of such a packet is analytic (atomic units will be used throughout):

$$\psi(x,t) = \mathcal{N} e^{ivx} e^{-(i/2)v^2 t} \times \exp\left[-\frac{1}{2}\frac{w - it}{w^2 + t^2}(x - vt)^2\right]. \quad (1)$$

Here $\mathcal{N}$ is a time-dependent normalization factor, and $\sqrt{w}$ is proportional to the width of the Gaussian. The wave packet travels with a constant mean velocity v and exhibits the usual expansion proportional to time. A numerical representation of Eq. (1) will eventually face difficulties when the numerical boundary is reached. One sees that there will also be difficulties since the phase increases *quadratically* with distance from the center of the wave packet. Physically, this phase dependence reflects the fact that the outer edge of the wave packet is moving faster than the inner part. Indeed, ionization has been likened to the Hubble expansion of the universe, where the velocity between two points in space is proportional to the distance between them [8]. From a numerical point of view, this phase can be as problematic as boundary effects since one must have a dense set of grid points to account for the spatial oscillations.

One way to deal with the wave packet expansion is to introduce boundary conditions that reduce or eliminate artificial reflections from the numerical boundary. Several such schemes have been proposed and used in the literature, including imaginary potentials and masking functions [9,10], Siegert state expansions [11], complex rotations [12], and temporally nonlocal boundary conditions [13–15]. To some extent, the problem with the increasing phase gradient is also solved with these schemes since the phase at the packet edge will increase only until it encounters the numerical boundary. But if the interaction volume is large, the inability to represent the fine oscillations at the edge of the packet will distort the propagation long before the grid boundary is reached. Even in momentum space, the phase gradient causes problems. It is true that the range of momenta required is fixed, but the phase gradient still demands a dense grid in momentum space [16,17].

Two other approaches that seek to remove the boundary reflections are worth noting. The first involves a coordinate transformation that maps the entire space onto a

0031-9007/00/85(24)/5086(4)$15.00

finite domain [2,18], and the second propagates the wave function in the interaction representation [19,20]. The coordinate transformation eliminates reflections effectively, but it does not address the phase gradient issues pointed out here. On the other hand, the interaction representation seems ideal since it removes all of the effects of kinetic energy, but it is difficult to implement efficiently.

There have thus been partial solutions of the practical problems associated with continuum wave packets, but we address here the more general problem of how to best represent a time-dependent wave packet without sacrificing the bound part of the wave function. In this Letter, we propose and demonstrate two general, efficient approaches that explicitly account for the wave packet expansion while faithfully representing any bound states.

The first approach incorporates explicitly time-dependent Gaussians into a general close-coupling approach. We represent the free component of the wave packet by spreading Gaussians, as shown in Eq. (1), and the bound part by stationary Gaussians. As such the method combines the Gaussian wave packet method developed for dynamics [21] with the Gaussian basis expansion for structure in quantum chemistry [22].

We discuss here one way to implement this idea to solve the general time-dependent Schrödinger equation,

$$\begin{aligned} i\,\frac{\partial}{\partial t}\,\psi(x,t) &= [H_0 + V_I(x,t)]\psi(x,t)\,, \\ H_0 &= -\frac{1}{2}\,\frac{\partial^2}{\partial x^2} + V_0(x)\,, \end{aligned} \tag{2}$$

where the potential has been divided into a stationary term, V_0, and a time-dependent term, V_I. As is done in the standard close-coupling technique, the stationary state problem, $H_0\phi_i^B = E_i\phi_i^B$, is solved at an initial time over the set of Gaussians. This prediagonalization provides a set of bound states, $E_i < 0$, and a set of pseudostates, $E_i > 0$, upon which $\psi(x,t)$ can be expanded.

To incorporate the expanding Gaussians, we duplicate the basis functions, $\phi_i^B(x)$, and replace the stationary Gaussians by their time-dependent counterpart. Specifically, we generate another set of basis functions, $\phi_i^F(x,t)$, that satisfy

$$\begin{aligned} \phi_i^F(x,t=0) &= \phi_i^B(x)\,, \\ i\,\frac{\partial}{\partial t}\,\phi_i^F(x,t) &= -\frac{1}{2}\,\frac{\partial^2}{\partial x^2}\,\phi_i^F(x,t)\,. \end{aligned}$$

The purpose of defining the ϕ_i^F in this way is to create a freely propagating basis set that is mutually orthogonal. The only concern of linear dependence comes between the pair of functions ϕ_i^B and ϕ_i^F. The functions ϕ_i^F are added into the calculation when $|\langle\phi_i^F \mid \phi_i^B\rangle|$ becomes less than 90%. As will be demonstrated in the model problem below, the expanding part of the wave packet is effectively represented by the basis set, $\phi_i^F(x,t)$.

The second approach analytically removes the kinematic effects from the wave function by suitable transformations based upon the scaling transformation [23,24]

$$x = R(t)\xi\,. \tag{3}$$

In this expression, ξ is a dimensionless coordinate, and $R(t)$ is a scaling factor that depends only on time. The present development is for a one-dimensional Cartesian coordinate x for purposes of clarity, but the approach applies generally to any number of dimensions and to other coordinate systems. Physically, the dilation described by Eq. (3) causes the coordinates to expand with the continuum components of the wave function.

Our application of scaling is a generalization of the approach originated by Solov'ev and Vinitsky for ion-atom collisions [23]. In their work and subsequent developments [24], the scaling factor R was inextricably linked to the internuclear distance. This Letter breaks from their work by recognizing that R need not correspond to a physical quantity in the system, but can be chosen to have any convenient form.

The scaling in Eq. (3) is substituted into the time-dependent Schrödinger equation Eq. (2), and a new equation for the wave function $\phi(\xi,t)$ [23],

$$\phi(\xi,t) = \sqrt{R(t)}\,e^{-(i/2)mR\dot{R}\xi^2}\,\psi(x,t)\,,$$

is derived. The square root factor preserves the normalization in the new coordinate ξ. The exponential phase factor has been chosen to simplify the transformed Schrödinger equation. In more physical terms, it accounts for the phases of the different velocity components of the wave packet. The resulting scaled time-dependent Schrödinger equation is [23]

$$\begin{aligned} i\,\frac{\partial}{\partial t}\,\phi(\xi,t) = \Big[&-\frac{1}{2mR^2}\,\frac{\partial^2}{\partial \xi^2} + V(R\xi) + \frac{1}{2}\,mR\ddot{R}\xi^2 \Big] \\ &\times \phi(\xi,t)\,. \end{aligned} \tag{4}$$

From this equation we see that there are two primary changes due to the scaling transformation: the addition of an effective harmonic potential and the addition of a time dependence to the interaction potential. The effective potential term is analogous to more familiar terms in non-inertial frames but arises here from the "acceleration" of the dilation factor R. We note that this equation is an exact representation of the original Schrödinger equation. It can thus be solved by any convenient means and can, in principle, be incorporated into existing time evolution codes.

The benefits of scaling can be illustrated with the Gaussian wave packet in Eq. (1). After applying the scaling transformation and choosing $R(t)$ to behave as γt for large t (γ is a constant with units of velocity), one finds that in this limit the wave packet becomes

$$\phi(\xi,t) \rightarrow \mathcal{N}\,\exp\!\left[-\frac{1}{2}\,w\gamma^2\Big(\xi - \frac{v}{\gamma}\Big)^2\right]. \tag{5}$$

This wave function describes a time-*independent* Gaussian centered at $\xi = v/\gamma$. Thus, the combined effects of all transformations outlined here are to remove the rapid oscillation from the wave packet, leaving just a stationary, slowly varying envelope. The constant γ determines its location and its width—both of which are fixed in time asymptotically.

For practical calculations, though, the evolution of the bound states will be as important as the continuum. For a given eigenstate $\psi_n(x)$ of the potential $V(x)$, the transformed wave function is

$$\phi_n(\xi, t) = \sqrt{R(t)}\, e^{-(i/2)R\dot{R}\xi^2} \psi_n(R\xi) e^{-iE_n t}. \tag{6}$$

The extra phase factor plays little role here since the spatial extent of the bound state ψ_n is limited. The widths of any bound states decrease in the scaled coordinate. Thus, one must simply ensure that whatever numerical method is used to solve Eq. (4) is capable of representing the bound states as they shrink during the time integration. The effort required on this account is in practice much less than that required to represent the continuum in an unscaled problem.

To illustrate how the above approaches allow for efficient solution of the TDSE without restricting the domain of the system, we consider a Hamiltonian that models an atom in a half-cycle laser pulse,

$$H = -\frac{1}{2}\frac{\partial^2}{\partial x^2} - e^{-x^2} + E(t)x\,.$$

The laser pulse $E(t)$ is given by

$$E(t) = \begin{cases} E_0 \cos^2(\frac{\pi t}{2\tau}), & -\tau < t < \tau, \\ 0, & |t|\tau, \end{cases}$$

where E_0 and τ are both 1 a.u. We chose this particular system since the resulting time-dependent wave function is simple to interpret. The short range, Gaussian potential supports only one bound state (of binding energy 0.477 390 a.u.), and the rapid, strong pulse produces a well-localized wave packet in the continuum of comparable amplitude to the bound state. Indeed, the solid lines in Fig. 1 show a sharp, stationary peak in the wave function at $x = 0$ and a spreading, leftward-traveling wave packet centered at $x < 0$ representing the bound and continuum components of the wave function, respectively.

The results shown in Fig. 1 were calculated by close coupling with freely propagating basis functions ϕ_i^F, but we have also obtained the same wave function by solving the scaled Schrödinger equation, Eq. (4), on a small set of basis splines (see Fig. 2). Comparing Figs. 1(a) and 1(b), one sees how the ejected pulse evolves with time. The continuum component of the wave function not only travels and spreads, but it also develops a large phase gradient across the wave packet as indicated by the rapidly oscillating real part of the wave function.

Using generalized close coupling, the wave function in Fig. 1 was calculated with 30 basis functions, $\phi_i^B(x)$, plus 30 more, $\phi_i^F(x,t)$. The widest pseudostate $\phi_i^B(x)$ in this basis set goes to zero by 100 a.u.; thus, using only the $\phi_i^B(x)$ set with standard close coupling, it is impossible to represent the wave function shown in Fig. 1(b), whose extent exceeds 300 a.u. Surprisingly, employing only the $\phi_i^B(x)$ pseudostates does a poor job even at $t = 10$, when the wave function is only 30 a.u. wide [see the dotted line in Fig. 1(a)]. The representation is poor because standard pseudostates have no spatial phase gradient; thus, the $\phi_i^B(x)$ basis set alone cannot track the phase evolution of $\psi(x,t)$. Adding the time-dependent functions $\phi_i^F(x,t)$, which analytically include the spreading and phase evolution of the ejected wave packet, allows accurate propagation of the wave function to arbitrarily large times.

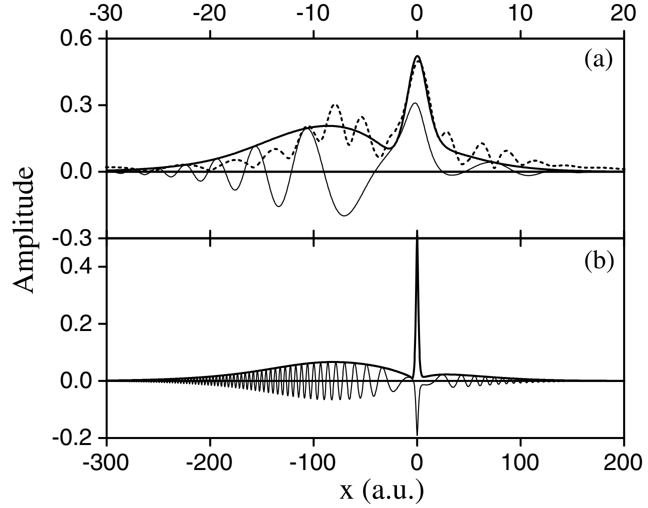

FIG. 1. The amplitude (thick line) and real part (thin line) of the wave function at (a) $t = 10$ a.u. and (b) $t = 100$ a.u. calculated by the generalized close-coupling method. The dotted line in (a) represents the amplitude of the wave function computed using only standard pseudostates.

As the continuum component of the wave function spreads, the pseudostate amplitudes go to zero like $1/t$

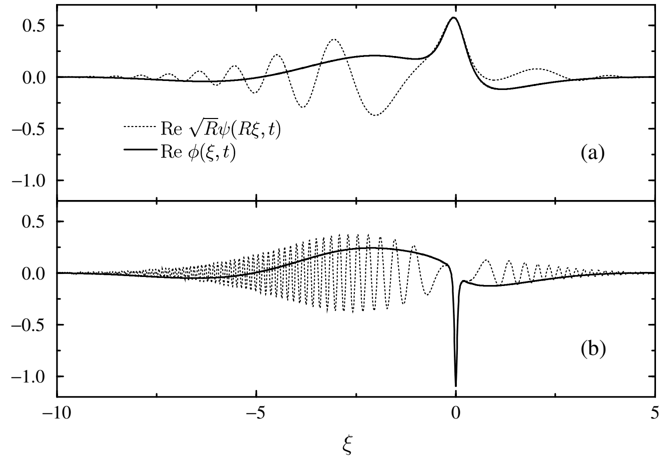

FIG. 2. The real part of the scaled and unscaled wave functions corresponding at (a) $t = 10$ a.u. [cf. Fig. 1(a)] and (b) $t = 100$ a.u. [cf. Fig. 1(b)]. Note that the unscaled wave function has been partially scaled as indicated to allow direct comparison. The scaling factor in (a) is $R = 3.48$ a.u.; and in (b) $R = 31.9$ a.u.

eventually transferring over completely to the $\phi_i^F(x,t)$ basis functions. As stated earlier, we add in each $\phi_i^F(x,t)$ when its overlap with the corresponding $\phi_i^B(x)$ goes under a threshold of 90%. Changing this threshold does not change the resulting wave function within the desired accuracy of the present calculation.

Turning now to the scaling approach, we show the real part of the scaled wave function in Figs. 2(a) and 2(b), corresponding to Figs. 1(a) and 1(b), respectively, and we compare the solution of the scaled TDSE with the usual unscaled TDSE. The ejected packet is clearly much simpler after introducing scaling; its position, height, and width all remain essentially constant with t and, in contrast to the unscaled solution, no phase gradient develops. The bound component of the wave function shrinks with time and shows the expected $\exp(-iEt)$ [see Eq. (6)] phase relative to the continuum component. For Fig. 2, we have used the scaling factor

$$R(t) = \begin{cases} 1, & t < 0, \\ (1 + 0.01t^4)^{1/4}, & t \geq 0. \end{cases}$$

This choice provides a smooth transition from $R(t) = 1$ at negative t to the desired linear function of t asymptotically.

To produce the scaled solution in Fig. 2, we solved the scaled TDSE Eq. (4) using sixth order basis splines and a Crank-Nicholson propagation scheme [3]. To cover the range -16 to 16 in the scaled coordinate ξ (-10 to 5 is shown in the figure), only 81 splines were required—even for the solution at $t = 100$ a.u. The splines were distributed symmetrically about $\xi = 0$ with a square root distribution to pack more splines near $\xi = 0$. In fact, 21 of the 81 splines were in the interval -1 to 1 in order to represent the shrinking bound state. Examining the real part of the unscaled wave function in Fig. 2, one can clearly see that direct solution of the TDSE would require at least an order of magnitude more basis splines to represent all of the oscillations due to the phase gradient. Since the CPU time for Crank-Nicholson propagation with basis splines scaled linearly with the number of splines, this enormous reduction in the number of splines translates directly into computational savings. Thus, the advantage of the simpler representation of the continuum far outweighs the artificial shrinking introduced in the bound states, and one does not have to resort to the schemes mentioned in the introduction for absorbing outgoing flux.

The scaled Schrödinger equation in Eq. (4) represents a natural framework in which to study time-dependent quantum phenomena, and it can easily be combined with existing techniques for solving the TDSE. We also present a straightforward extension to close coupling with Gaussian functions, employed ubiquitously in quantum chemistry and atomic physics. While the scaled TDSE is more generally applicable, its one drawback is that the bound states shrink with time. The generalized close-coupling approach avoids this shrinking by including bound and continuum components separately, but is confined to systems where a Gaussian basis is appropriate.

We have presented two complementary approaches to solving the time-dependent Schrödinger equation. Both approaches extend existing theoretical methods in a way that allows for efficient representation of the complete wave function without putting restrictions on its spatial extent. Having accounted for the basic properties of the ejected component of the wave function, the expansion and increasing phase gradient, our approaches allow for numerical propagation of the wave function to very long times.

E. Y. S. acknowledges support by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy.

[1] M. B. Gaarde *et al.,* Phys. Rev. Lett. **84**, 2822 (2000); K. J. Schafer and K. C. Kulander, Phys. Rev. Lett. **78**, 638 (1997).
[2] X.-M. Tong and S.-I. Chu, Phys. Rev. A **61**, 021802(R) (2000).
[3] E. Cormier and P. Lambropoulos, J. Phys. B **30**, 77 (1997).
[4] M. S. Pindzola, D. Mitnik, and F. Robicheaux, Phys. Rev. A **59**, 4390 (1999).
[5] M. S. Pindzola and F. Robicheaux, Phys. Rev. A **58**, 4229 (1998).
[6] D. R. Schultz, M. R. Strayer, and J. C. Wells, Phys. Rev. Lett. **82**, 3976 (1999).
[7] M. S. Pindzola, Phys. Rev. A **60**, 3764 (1999).
[8] C. Illescas and A. Riera, Phys. Rev. Lett. **80**, 3029 (1998); **81**, 1350 (1998).
[9] N. Balakrishnan, C. Kalyanaraman, and N. Sathyamurthy, Phys. Rep. **280**, 79 (1997).
[10] J. L. Krause, K. J. Schafer, and K. C. Kulander, Phys. Rev. A **45**, 4998 (1992).
[11] S. Yoshida, S. Watanabe, C. O. Reinhold, and J. Burgdörfer, Phys. Rev. A **60**, 1113 (1999).
[12] Y. K. Ho, Phys. Rep. **99**, 1 (1983).
[13] A. M. Ermolaev, I. V. Puzynin, A. V. Selin, and S. I. Vinitsky, Phys. Rev. A **60**, 4831 (1999).
[14] M. Mangin-Brinet, J. Carbonell, and C. Gignoux, Phys. Rev. A **57**, 3245 (1998).
[15] W. R. Frensley, Rev. Mod. Phys. **62**, 745 (1990).
[16] E. Y. Sidky and C. D. Lin, Phys. Rev. A **60**, 377 (1999).
[17] E. Y. Sidky, in *Applications of Accelerators in Research and Industry, Proceedings of the Fifteenth International Conference, Denton, Texas,* edited by J. L. Duggan and J. L. Morgan (University of North Texas, Denton, 1999).
[18] M. Horbatsch, Phys. Lett. A **165**, 58 (1992).
[19] G. Yao and S. I. Chu, Chem. Phys. Lett. **198**, 39 (1992).
[20] J. Z. H. Zhang, Chem. Phys. Lett. **160**, 417 (1989).
[21] E. J. Heller, J. Chem. Phys. **62**, 1544 (1975).
[22] S. F. Boys, Proc. R. Soc. London A **200**, 542 (1950).
[23] E. A. Solov'ev and S. I. Vinitsky, J. Phys. B **18**, L557 (1985).
[24] J. H. Macek, S. Y. Ovchinnikov, and E. A. Solov'ev, Phys. Rev. A **60**, 1140 (1999).