Wavepacket Propagation in the Determination of Microscopic Eigenenergies: I: The Spectral Method

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Abstract: Examining the relationship between chemical structure and dynamics should be fundamental to the undergraduate study of microscopic systems. With this in mind wavepacket propagation, which is traditionally used in application to dynamical problems, is used here as the foundation for determining eigenenergies. The system is propagated in space and time from an initial wavepacket as in a traditional dynamical study. We then proceed to determine eigenenergies from the appearance of resonances in a spectrum of energies that is generated from the spatial projection of the wavepacket onto the initial wavepacket. Application of the spectral method is made to a classic electronic structure problem; resonances are observed at energies which match the known energy structure of the problem. Finally, the relevance of wavepacket propagation to the elucidation of structure and dynamics at the undergraduate level is discussed.

Introduction

A student should take away from the core undergraduate courses in physical chemistry some appreciation of the relationship between chemical structure and dynamics. It is therefore surprising to us that there has been no significant effort to present structure and dynamics from a common methodology. Of course, the wish for such integration must be tempered by what is possible; one observes for example that structural and dynamical problems display disparate characters. Nevertheless, the potential rewards from the presentation of a methodology that can be applied to both varieties of problem are, in the opinion of the authors, so high that the effort is justified. This is the focus of work that we have initiated with this paper.

An important approach to dynamical problems depends upon first choosing an initial (non-stationary) wavepacket and then propagating the wavepacket in space and time[1]. Such an approach to dynamical problems is essential when the Hamiltonian is time-dependent, but is also useful in dealing with problems where the Hamiltonian is time-independent. We here present a technique for determining eigenenergies of a microscopic system, that like the aforementioned dynamical analysis, uses wavepacket propagation. The "spectral method" depends upon a time-to-energy Fourier transform of the spatial-projection of a propagated wavepacket onto the initial wavepacket. The eigenenergies then appear as resonances in the transform where the intensity of a given resonance is determined by the contribution of the corresponding eigenstate to the wavepacket[2].

The paper is organized as follows: (1) in section II, the basic problem is described; (2) in section III, we present a scheme for propagating wavepackets in a microscopic system; (3) in section IV, the spectral method for determining the corresponding system eigenenergies is described; (4) in section V, application of the method to the determination of electronic energy structure in the H atom is presented; (5) in section VI, a brief discussion of the work is given, including its relevance for presentations to undergraduates on chemical structure and dynamics; (6) in an Appendix to the paper, we outline how the Fourier transforms, which are integral to both the propagation scheme and the spectral method, are discretized and how the resulting discrete transforms are efficiently computed.

The Basic Problem

We are concerned with an *N*-particle system as represented by the operators:

$$\hat{\mathbf{T}} = \sum_{i=1}^{N} -\frac{\hbar^2}{2m_i}\left(\frac{\partial^2}{\partial x_i^2}+\frac{\partial^2}{\partial y_i^2}+\frac{\partial^2}{\partial z_i^2}\right) \tag{1a}$$

$$\hat{\mathbf{V}} = \mathbf{V}\left(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N\right) \tag{1b}$$

where $\hat{\mathbf{T}}$ and $\hat{\mathbf{V}}$ are the system kinetic and potential energy operators, respectively. The mass of the *i*th particle is denoted by m_i in eq. 1a; x_i, y_i, z_i are the spatial (Cartesian) coordinates of the *i*th particle; x_i, y_i, z_i are collected in the vector $\mathbf{r}_i$.

Now consider the following time-dependent (non-relativistic) Schrödinger wave equation for the motion of wavepacket $\Psi(\mathbf{r},t)$ in the *N*-particle system:

$$i\hbar\frac{\partial}{\partial t}\Psi\left(\mathbf{r},t\right) = \hat{\mathbf{H}}\Psi\left(\mathbf{r},t\right) \tag{2a}$$

$$\hat{\mathbf{H}} = \hat{\mathbf{T}} + \hat{\mathbf{V}} \tag{2b}$$

The space of vectors $\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N$, is abbreviated as $\mathbf{r}$ in eq. 2a; $\hat{\mathbf{H}}$ is the time-independent system Hamiltonian operator. It is advantageous as we set up the problem for propagating in section III to rewrite the wave equation in a form which emphasizes the time-development of the system.

The wave equation of eq. 2a has been formally integrated in time in writing for $\Psi\left(\mathbf{r},t\right)$ that

S1430-4171(00) 04395-4, 10.1007/s00897000395a, 540175le.pdf

$$\Psi(\mathbf{r},t) = e^{-i(\hat{\mathbf{T}}+\hat{\mathbf{V}})t/\hbar}\Psi(\mathbf{r},0) \qquad (3)$$

The term $\Psi(\mathbf{r},0)$ in eq. 3 is the initial t=0 wavepacket as can be seen by setting t=0 in eq. 3. Moreover, by differentiating with respect to t on the l.h.s. and r.h.s. of eq. 3 and recalling that $\hat{\mathbf{T}}+\hat{\mathbf{V}}$ is independent of t, the original wave equation is recovered. The result in eq. 3 describes the time-development of the system from an initial wavepacket due to the action of $e^{-i(\hat{\mathbf{T}}+\hat{\mathbf{V}})t/\hbar}$.

A minor generalization of the result in eq. 3 may be given by replacing $\Psi(\mathbf{r},0)$ on the r.h.s. of eq. 3 by $\Psi(\mathbf{r},t)$, and introducing a time-step Δt, i.e.,

$$\Psi(\mathbf{r},t+\Delta t) = e^{-i(\hat{\mathbf{T}}+\hat{\mathbf{V}})\Delta t/\hbar}\Psi(\mathbf{r},t) \qquad (4)$$

While the result in eq. 4 is important, certainly as we will see below in directing the development of the propagation scheme—it should be evident that since $\hat{\mathbf{T}}$ and $\hat{\mathbf{V}}$ do not in general commute, one is going to encounter difficulties in accounting for the action of an operator of the form $e^{-i(\hat{\mathbf{T}}+\hat{\mathbf{V}})\Delta t/\hbar}$. We now describe a practical scheme for wavepacket propagation which is driven by the result in eq. (4); later we will consider how to determine system eigenenergies from the propagated wavepacket.

The Propagation Scheme

In order to propagate the wavepacket we replace the exact propagator of eq. 4 by an approximate one in which kinetic and potential energy operators are "split". We then write for the action of the split-operator propagator on a time-step Δt that [3]

$$\Psi(\mathbf{r},t+\Delta t) = e^{-i\hat{\mathbf{V}}\Delta t/2\hbar}e^{-i\hat{\mathbf{T}}\Delta t/\hbar}e^{-i\hat{\mathbf{V}}\Delta t/2\hbar}\Psi(\mathbf{r},t) \qquad (5)$$

It can be established by expanding the exponentials in eq. 5 and doing the same with the exponential in eq. 4 that the propagator of eq. 5 matches the exact propagator up to and including second order terms in Δt. It can also be established that the propagator retains certain attractive properties of the exact propagator: it preserves the norm of the wavepacket; in addition, it is time-reversible; if one changes the sign of Δt in the propagator of eq. 5 and allows it to operate on $\Psi(\mathbf{r},t+\Delta t)$ then $\Psi(\mathbf{r},t)$ is regenerated.

We now consider how the action of the propagator in eq. 5 is effected and in particular how we deal with $e^{-i\hat{\mathbf{T}}\Delta t/\hbar}$. The "trick" is to first expand $e^{-i\hat{\mathbf{V}}\Delta t/2\hbar}\Psi(\mathbf{r},t)$ in eigenstates of $\hat{\mathbf{T}}$, i.e.,

$$e^{-i\hat{\mathbf{V}}\Delta t/2\hbar}\Psi(\mathbf{r},t) = \int C(\mathbf{k},t)e^{i\mathbf{k}.\mathbf{r}}d\mathbf{k} \qquad (6a)$$

$$e^{i\mathbf{k}.\mathbf{r}} = e^{i\mathbf{k}_1.\mathbf{r}_1}e^{i\mathbf{k}_2.\mathbf{r}_2}\ldots e^{i\mathbf{k}_N.\mathbf{r}_N} \qquad (6b)$$

where the space of vectors $\mathbf{k}_1$, $\mathbf{k}_2$,… $\mathbf{k}_N$, is abbreviated as $\mathbf{k}$ and where in eq. 6a it is understood that we are integrating over the complete $\mathbf{k}$ space. One should now recognize that the coefficients $C(\mathbf{k}, t)$ of the expansion in eq. 6a are obtained as the Fourier transform of $e^{-i\hat{\mathbf{V}}\Delta t/2\hbar}\Psi(\mathbf{r},t)$ from $\mathbf{r}$ space to $\mathbf{k}$ space. We then have that

$$C(\mathbf{k},t) = \frac{1}{2\pi}\int e^{-i\hat{\mathbf{V}}\Delta t/2\hbar}\Psi(\mathbf{r},t)e^{-i\mathbf{k}\mathbf{r}}d\mathbf{r} \qquad (7)$$

where again it is understood that we are integrating over the complete space (in this case $\mathbf{r}$ space).

The operator $e^{-i\hat{\mathbf{V}}\Delta t/\hbar}$ now acts on the expansion in eq. 6a such that we have

$$e^{-i\hat{\mathbf{T}}\Delta t/\hbar}e^{-i\hat{\mathbf{V}}\Delta t/2\hbar}\Psi(\mathbf{r},t) = \int C(\mathbf{k},t)e^{-iT_k\Delta t/\hbar}e^{i\mathbf{k}\mathbf{r}}d\mathbf{k} \qquad (8a)$$

$$T_k = \sum_{i=1}^{N}\frac{\hbar^2 k_i^2}{2m_i} \qquad (8b)$$

where we see that the result is given as the (reverse) Fourier transform of $C(\mathbf{k},t)e^{-iT_k\Delta t/\hbar}$ from $\mathbf{k}$ space to $\mathbf{r}$ space. The product of $e^{-i\hat{V}\Delta t/2\hbar}$ and the result in eq. 8a completes the propagation on the time-step Δt.

We note from the discussion in the preceding paragraph that at each time-step one must perform two Fourier transforms. Such transforms are effected by discretizing the $\mathbf{r}$ and $\mathbf{k}$ spaces; a procedure for doing this is described in an appendix to the paper. We also give in the appendix an indication of how the resulting discrete transforms can be efficiently computed. One then anticipates iterating on the propagation scheme by substituting in as $\Psi(\mathbf{r},t)$ on the r.h.s. of eq. 5 the wavepacket resulting from the step just completed and continuing with this process until the total propagation time has been reached.

The Spectral Method

We now describe the spectral method as it functions to extract eigenenergies from the propagation of a system wavepacket. We begin by recognizing that the wavepacket may be written as a linear combination of contributing energy eigenstates of the system Hamiltonian, that is,

$$\Psi(\mathbf{r},t) = \sum_i a_i\psi_i(\mathbf{r})e^{-iE_it/\hbar} \qquad (9)$$

where the coefficient a_i determines the contribution of the ith eigenstate $\psi_i(\mathbf{r})$ to $\Psi(\mathbf{r},t)$. The coefficients a_i are in turn determined by what we choose for the initial wavepacket, $\Psi(\mathbf{r},0)$.

Now consider the following overlap function between wavepackets

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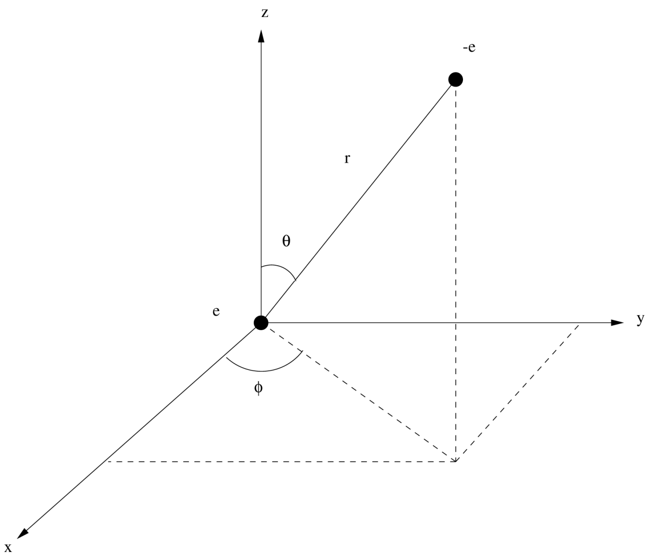

Figure 1. Coordinate picture for the one-electron problem. We show the relationship between Cartesian coordinates, *x*, *y*, *z* and spherical coordinates: *r*, *θ*, ϕ of the electron *–e*, centered on the nucleus *e*.

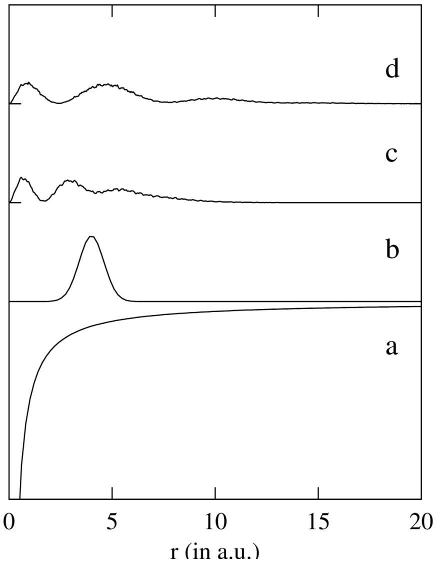

Figure 2. (a) Potential curve (in a.u.) for $\ell = 0$ and as a function of radial coordinate *r* (in a.u.). (b)–(d) Absolute value squared of the corresponding wavepacket, $\chi_{\ell=0}(r,t)$, for: (b) $t = 0$; (c) $t = (2^7–1)\,\Delta t$; (d) $t = (2^8-1)\,\Delta t$; $\Delta t = 0.05$ a.u.

$$\int \Psi(\mathbf{r},0)^* \Psi(\mathbf{r},t)d\mathbf{r} = \int \sum_{i'} \left[a_i \psi_i(\mathbf{r})\right]^* \sum_i a_{i'} \psi_{i'}(\mathbf{r}) e^{-iE_{i'}t/\hbar} d\mathbf{r} \tag{10}$$

where the integration again is over the complete **r** space. Because the eigenstates, $\psi_i(\mathbf{r})$, in eq. 10, are understood to be orthonormal we can then write for eq. 10 that

$$\int \Psi(\mathbf{r},0)^* \Psi(\mathbf{r},t)d\mathbf{r} = \sum_i |a_i|^2 e^{-iE_i t/\hbar} \tag{11}$$

It follows from eq. 11 that by a time-to-energy Fourier transform of the overlap function one may then identify E_i values as resonances in the transform.

Application

Application is made here to the electronic structure of the H-atom. We begin by briefly outlining the problem and then move on to explore how a wavepacket propagates in the system. Finally we consider use of the spectral method in determining eigenenergies.

We are examining then the following electronic Hamiltonian:

$$\hat{\mathbf{H}} = -\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}\right) - \frac{e^2}{r} \tag{12}$$

which describes the motion of an electron in a Coulombic potential $–e^2/r$. The variables *x*, *y*, *z*, are Cartesian electron coordinates centered on the system nucleus (see Figure 1); *r* is the separation between the nucleus and the electron (again see Figure 1). We have assigned a charge *-e* to the electron and correspondingly a charge of *e* to the proton; m_e is the system reduced mass (which, because the proton is understood to be far more massive than the electron, is essentially equal to the electron mass).

We address this problem by first expanding wavepacket $\Psi(\mathbf{r},t)$ in terms of radial wavepackets $\chi_\ell(r,t)$, i.e.,

$$\Psi(\mathbf{r},t) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} a_{\ell m} \frac{\chi_\ell(r,t)}{r} Y_{\ell m}(\theta,\phi) \tag{13}$$

where $Y_{\ell m}(\theta,\phi)$ are (orthonormal) spherical harmonics in electron angular coordinates *θ*, *ϕ* (again see Figure 1). The quantities ℓ and *m* are the corresponding orbital angular momentum and magnetic quantum numbers respectively.

When the expansion in eq. 13 is substituted into the time-dependent Schrödinger equation corresponding to the Hamiltonian of eq. 12, one finds that the problem separates into the solution of radial equations:

$$i\hbar\frac{\partial}{\partial t}\chi_\ell(\mathbf{r},t) = \mathbf{H}^\ell \chi_\ell(\mathbf{r},t) \tag{14a}$$

$$\hat{\mathbf{H}}^\ell = -\frac{\hbar^2}{2m_e}\left[\frac{\partial^2}{\partial r^2} - \frac{\ell(\ell+1)}{r^2}\right] - \frac{e^2}{r} \tag{14b}$$

One must then propagate radial wavepacket $\chi_\ell(r,t)$ in a potential that, in general, includes both Coulombic and centrifugal interactions [4].

For our calculations here we have fixed $\ell = 0$ and in Figure 2a we have plotted the resulting potential as a function of *r*. The corresponding initial (normalized) radial wavepacket is chosen as:

$$\chi_{\ell=0}(r,t=0) = \left(2\pi\delta^2\right)^{-1/4} e^{-(r-r_0)^2/4\delta^2} \tag{15}$$

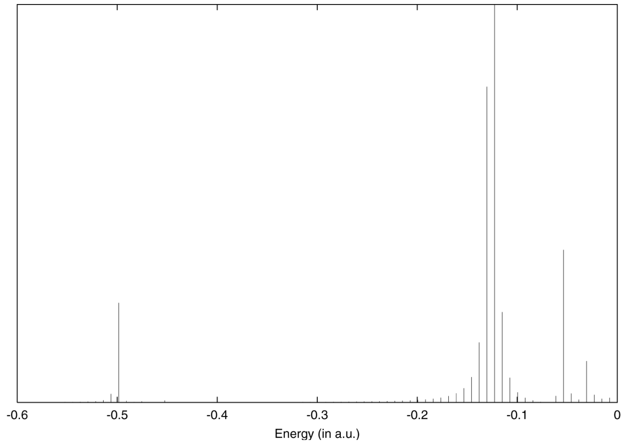

Figure 3. Energy spectrum from the time-to-energy Fourier transform of the correlation function, $\int_0^\infty \chi_{\ell=0}(r,0)^* \chi_{\ell=0}(r,t)\,dr$. The wavepacket $\chi_{\ell=0}(r,t)$ was propagated for a time $t = (2^{14} - 1)\,\Delta t$ where $\Delta t = 0.05$ a.u.

which describes a Gaussian wavepacket of width δ centered about $r=r_0$. The width parameter δ is set equal to 0.6 a.u. and the centering parameter r_0 is set equal to 4.0 a.u. The absolute value square of $\chi_{\ell=0}(r,t=0)$ is displayed as a function of *r* in Figure 2b.

A time-step $\Delta t = 0.05$ a.u. is used in propagating the wavepacket and in Figures 2c and 2d we show the resulting absolute value square of the wavepacket as a function of *r* after 2^n-1 steps in Δt for *n*=7 and *n*=8 respectively [5]. As the wavepacket is propagated we see that it spreads in *r* as compared to the *t*=0 wavepacket of Figure 2b. In Figure 2c, we see the wavepacket spreading both to the left and right in *r* of its center in Figure 2b. We also see that the wavepacket has developed several peaks in *r* space in contrast to the single peak of Figure 2b. In Figure 2d we see that the wavepacket has further spread to the right of the initial wavepacket; like the wavepacket in Figure 2c it peaks in several regions of the *r* space.

We now turn to propagating wavepackets on a much longer time scale in order to be able to pin down the system eigenenergies. We then propagated for a time $t = (2^{14} - 1)\Delta t$ where Δt is again set equal to 0.05 a.u. [5]. The resulting energy spectrum is plotted in Figure 3 where we observe a strong resonance at an energy of around –0.125 a.u., and three satellites, one at a lower energy than the –0.125 a.u., and two at higher energies. Each of these peaks may be associated with one of the exact system eigenenergies as given by $E_n = -1/2n^2$ (in a.u.). The strong resonance in Figure 3 may then be associated with the *n*=2 state while the satellites may be associated with energies of –0.5, –0.055 and –0.03125 a.u., corresponding to states, *n* = 1, 3 and 4, respectively.

Discussion

We have considered here the determination of eigenenergies from wavepacket propagation and the spectral method. The system of interest is propagated in space and time from an initial wavepacket and an energy spectrum is generated from a time-to-energy Fourier transform of the spatial projection of the propagated wavepacket onto the initial wavepacket. Eigenenergies appear as resonances in this spectrum where the intensity of a given resonance is determined by the contribution of the corresponding eigenstate to the wavepacket.

As asserted in the introduction to this paper, the presentation of topics in chemical structure and dynamics to undergraduates who are taking the core physical chemistry courses can be significantly enhanced by making use of a methodology that integrates the analysis of structural and dynamical problems. It should be a given that a student's appreciation of microscopic chemical structure is going to be deepened as the student gets to see wavepacket motion in whatever system may be of interest. In this paper we have drawn attention to the spectral method that connects such motion to the system's underlying energy structure. A variety of structural problems, including ones with relevance to electronic, vibrational, and/or rotational degrees of freedom, can be used to illustrate the connection. The student is at this point primed to view microscopic chemical dynamics in terms of the development of wavepackets. For example, a discussion of the dynamics of chemical reaction may be framed by a wavepacket dividing itself between reactants and products.

It is our hope that the work that we have initiated with this paper will engage the chemical education community in a dialogue on how best to convey to an undergraduate audience an appreciation for the relationship between chemical structure and dynamics.

Appendix

We are concerned with the following pair of transforms of functions *f*(*r*) and *F*(*k*) on spaces *r* and *k*:

$$f(r) = \int_{-\infty}^{\infty} F(k) e^{ikr} dk \tag{A.1a}$$

$$F(k) = \frac{1}{2\pi}\int_{-\infty}^{\infty} f(r) e^{-ikr} dr \tag{A.1b}$$

We examine how the *r* and *k* spaces in the above are discretized and then how the resulting discrete transforms are efficiently computed.

Suppose that we first discretize the *r* space, sampling the function *f*(*r*) at *N* points on the range from *r* = –*X*/2 to *r* = *X*/2 (without loss of generality the range has been centered at *r* = 0). We write then the transform in eq. A.1a as correspondingly drawing on *N* (now assumed to be an even integer) independent values of *F*(*k*), i.e.,

$$f(r_p) = \sum_{n=-N/2}^{N/2} F(k_n) e^{ik_n r_p} \Delta k_n \tag{A.2}$$

A cursory examination reveals that there are *N* + 1 values of *F*(*k*) in eq. A.2; $F(-k_{N/2})$ and $F(k_{N/2})$ are however constrained to be equal to each other such that only *N* of the *N* + 1 values of *F*(*k*) are in fact independent.

The values of k_n in eq. A.2 are identified as a subset of discrete values in *k* appearing in the Fourier expansion of a continuous function (in r) on the range from $r = -X/2$ to $r = X/2$, that is,

$$k_n = \frac{2\pi n}{X} \tag{A.3}$$

where the subset is given by $n = -N/2, \ldots, N/2$, and the complete set by $n = -\infty, ..., \infty$. It follows, based on the subset of k values and recognizing that we are attempting to capture the transform in eq. A.1b that Δk_n in eq. A.2 is appropriately set equal to π/X at the end points $k_{\pm N/2}$ (of the subset) and equal to $2\pi/X$ otherwise.

Now let's consider how the N independent $F(k_n)$ values are determined. We discretize the transform in eq. A.1b as drawing upon N independent values of $f(r_p)$, that is,

$$F\left(k_n\right) = \frac{1}{2\pi}\sum_{p=-N/2}^{N/2} f\left(r_p\right) e^{-ik_n r_p} \Delta r_p \tag{A.4}$$

where it is understood that $f\left(r_{-N/2}\right) = f\left(r_{N/2}\right)$ such that only N of the $N + 1$ values of $f(r)$ in eq. A.4 are independent.

The values of r_p in eq. A.4 are identified as a subset of discrete values in r appearing in the Fourier expansion of a continuous function (in k) on the range from $k = -\pi N / X$ to $k = \pi N / X$ (a range identical to that identified earlier in discretizing the k space), that is,

$$r_p = \frac{pX}{N} \tag{A.5}$$

where the subset is given by $p = -N/2, \ldots, N/2$, and the complete set by $p = -\infty, ..., \infty$. It follows that the subset of r values in eq. A.4 lie on the range from $r = -X/2$ to $r = X/2$ as we had assumed at the outset of the discretization process in r. It also follows based on the subset of r values and recognizing that we are attempting to capture the transform in eq. A.1a that Δr_p in eq. A.4 is appropriately set equal to $X/2N$ at the end-points $r_{\pm N/2}$ (of the subset) and equal to X/N otherwise.

We now write the results in eqs. A.2 and A.4 so as to elucidate the argument of the exponential in each case. We write then that

$$f\left(r_p\right) = \sum_{n=-N/2}^{N/2} F\left(k_n\right) e^{2\pi inp/N} \Delta k_n \tag{A.6a}$$

$$F\left(k_n\right) = \frac{1}{2\pi}\sum_{p=-N/2}^{N/2} f\left(r_p\right) e^{-2\pi inp/N} \Delta r_p \tag{A.6b}$$

where eq. A.6a is obtained by making use of the result for r_p in eq. A.5 and eq. A.6b is obtained from the result for k_n in eq. A.3.

We now make explicit that we are working with only N independent values of $f(r)$ and of $F(k)$ in eqs. A.6a and A.6b. We write then that

$$f\left(r_p\right) = \sum_{n=0}^{N-1} F\left(k_n\right) e^{2\pi inp/N} \Delta k \tag{A.7a}$$

$$F\left(k_n\right) = \frac{1}{2\pi}\sum_{p=0}^{N-1} f\left(r_p\right) e^{-2\pi inp/N} \Delta r \tag{A.7b}$$

where $\Delta k = 2\pi/X$ and $\Delta r = X/N$. We have recognized in the above rewrites of eqs. A.6a and A.6b that terms $e^{2\pi inp/N}$ and $e^{-2\pi inp/N}$ are unchanged by replacements $n \to n + N$ and/or $p \to p + N$. It follows that an element, $F(k_n)$, on the range $-N/2 \le n \le 0$ in eqs. A.6a and A.6b, has been identified as $F\left(k_{n+N}\right)$ in eqs. A.7a and A.7b, and similarly that an element, $f(r_p)$, on the range $-N/2 \le p \le 0$, has been identified as $f\left(r_{p+N}\right)$.

Finally, we consider how the discretized transforms in eqs. A.7a and A.7b are efficiently computed. It appears that the effort to compute each transform necessarily grows as N^2 because in each case we are multiplying an $N \times N$ matrix by an $N \times 1$ vector. One can, however, significantly reduce the effort prior to computation by recursively factorizing the transform, a process which we'll now briefly describe. We begin by writing for the transform in, say, eq. A.7a that:

$$\begin{aligned} f\left(r_p\right) = &\sum_{n=0}^{N/2-1} F\left(k_{2n}\right) e^{2\pi i(2n)p/N} \Delta k \\ &+ \sum_{n=0}^{N/2-1} F\left(k_{2n+1}\right) e^{2\pi i(2n+1)p/N} \Delta k \end{aligned} \tag{A.8a}$$

$$\begin{aligned} = &\sum_{n=0}^{N/2-1} F\left(k_{2n}\right) e^{2\pi inp/(N/2)} \Delta k \\ &+ e^{2\pi ip/N} \sum_{n=0}^{N/2-1} F\left(k_{2n+1}\right) e^{2\pi inp/(N/2)} \Delta k \end{aligned} \tag{A.8b}$$

where in going from eq. 8a to 8b we have succeeded in writing an N-element transform in terms of two $N/2$-element transforms. By choosing N to equal 2^M and with continuing factorizations one reduces the original transform to the sum of products of 1-element transforms and coefficients of the character of the $e^{2\pi ip/N}$ introduced in eq. A.8b. The result is that the effort in computing the rearranged transform grows not as N^2 but as NM. A net search under "fast Fourier transform" will reveal many implementations of the algorithm sketched here (and also its variants) that are freely available for downloading.

References and Notes

1. See, for example, Kosloff R., *J. Phys. Chem.* **1988,** *92*, 2087; and references therein.
2. Recent applications of the spectral method are to be found in the following articles: Sadeghi R. and Skodje R. T., *J. Chem. Phys.* **1993**, *99*, 5126; Zhang D. H. and Zhang J. Z. H., *ibid.* **1994**, *101*, 3671; Dai J. and Zhang J. Z. H., *ibid.* **1995**, *103*, 1491; *ibid.* **1996**, *104*, 3664.

3. The (second-order) split-operator method was developed in Fleck Jr., J. A.; Morris, J. R.;. Feit, M. D.; *Appl. Phys.* **1976**, *10*, 129, for application to problems in optical physics.
4. Eqs. 14a and 14b must be solved subject to the boundary condition that $\chi_\ell(r,t)_{r\to 0}0$, which arises from the introduction of the factor of 1/*r* in the expansion of eq. 13. We accommodate this condition by first artificially extending the potential of eq. 14b through $r = 0$ (and hence to negative values of *r*) to form a potential that is even in *r*. The corresponding initial wavepacket, $\chi_\ell(r,t=0)$, such as we have given a few lines below in eq. 15 is then chosen to vanish as $r \to 0$ and at the same time extended to form a wavepacket that is odd in *r*. Now as one continues to propagate the extended wavepacket on the extended potential the wavepacket remains an odd function in *r* and so the boundary condition is satisfied.
5. For the results in Figures 2 and 3 the wavepacket is represented by 2^{12} equally spaced points on the range from $r = 0$ to $r = 100$ a.u.