A comparative study of time dependent quantum mechanical wave packet evolution methods

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We present a detailed comparison of the efficiency and accuracy of the second- and third-order split operator methods, a time dependent modified Cayley method, and the Chebychev polynomial expansion method for solving the time dependent Schrodinger equation in the one-dimensional double well potential energy function. We also examine the efficiency and accuracy of the split operator and modified Cayley methods for the imaginary time propagation.

I. INTRODUCTION

One approach for calculating the dynamical properties of a quantum mechanical system is to solve the time dependent Schrodinger equation, for which several numerical methods exist.[1-59] It is also possible to calculate directly thermally averaged properties of systems; e.g., thermal rate coefficients can be calculated by using the solutions of the time dependent Schrodinger equation to compute the flux-flux correlation function at an appropriate dividing surface.[60,61] The efficiency of these methods becomes critical when one wants to calculate the thermal rate coefficients of systems in which a few quantum degrees of freedom interact with a large number of classical ones, as in proton transfer in proteins. In such cases, we must compute the expectation values of various quantum mechanical operators over all possible classical configurations.[62] Numerically, a large number of classical configurations must be used to insure small deviations in the averages. This means that for each important classical configuration, one needs to carry out a quantum calculation for the quantum degrees of freedom, and hence the efficiency of this portion of the calculation becomes critical. Three particularly promising methods for solving the time dependent Schrodinger equation are the split operator[11,31,43,44,50] (SO), time dependent modified Cayley method[51-53] (MC), and Chebychev polynomial expansion[15,22,26-30,33,39-42,45-48] (CP) method. Prior to the present study, the split operator method has been used for both real time and imaginary time evolution calculations, the Chebychev polynomial method has been used for real time, and for imaginary time determination of eigenvalues of bound systems,[15] whereas the modified Cayley method has been applied to real time propagation problems. Recently, a comparison study of different propagation schemes, in particular, the split operator, Chebychev polynomial expansion, and iterative Lanczos methods, has been reported[63] for a one dimensional Morse potential. However, one can expect the comparison results may be somewhat different for a different potential energy function.

In this study, we present a detailed comparison of the efficiency and accuracy of the split operator, modified Cayley, and Chebychev polynomial expansion methods for solving the time dependent Schrodinger equation. We also extend the modified Cayley method to propagate the wave function in imaginary time and compare it to the split operator method. The one dimensional double well potential energy function is used in this study, since it is the first step in our development of a mixed quantum and classical dynamical method for studying quantal processes in biological systems such as proton transfer in proteins.

II. METHODOLOGY

For convenience, atomic units are used in the present study. The quantal time evolution of the system described by the wave function ψ is governed by the time dependent Schrodinger equation

$$i \frac{\partial}{\partial t} \psi(r,t) = \mathbf{H}\psi(r,t),\tag{1}$$

where $\mathbf{H} = \mathbf{K} + \mathbf{V}$, with $\mathbf{K}$ and $\mathbf{V}$ the kinetic and potential operators, respectively. The formal solution to the differential equation, with $\mathbf{H}$ independent of time, is

$$\psi(r,t + \tau) = e^{-i\mathbf{H}\tau}\psi(r,t).\tag{2}$$

If $\mathbf{H}$ is time dependent, this solution is approximate, and we must take τ small enough that there is effectively no variation in $\mathbf{H}$ over the time τ. The exponential operator

$$\mathbf{U} = e^{-i\mathbf{H}\tau}\tag{3}$$

contains two noncommuting operators $\mathbf{K}$ and $\mathbf{V}$; therefore, they cannot be diagonalized simultaneously. Further, dia-

gonalization of H itself requires solution of the full time independent Schrodinger equation. Thus, evaluation of U is nontrivial. Similarly, in calculating the quantum thermal rate constant using the flux–flux correlation method, one encounters an imaginary time propagator of the form

$$U = e^{-Hd\beta/2}, \qquad (4)$$

where $d\beta$ is a step-size parameter of β which is $1/k_B T$; k_B is the Boltzmann constant and T is the temperature.

A. Split operator method

If τ is sufficiently small, the evolution operator U can be approximated by the split operator method.[11] There exist both second and third order methods. There are, in fact, two distinct forms of any approach which is based on splitting the Hamiltonian into a reference and disturbance Hamiltonian.[52] These are designated as kinetic or potential referenced. For example, for the second order split operator method, one can use either the kinetic referenced expression, which we denote as KRSO, which is expressed as[52]

$$U = e^{-iV\tau/2} e^{-iK\tau} e^{-iV\tau/2} \qquad (5)$$

or the potential referenced expression, denoted as VRSO,[52]

$$U = e^{-iK\tau/2} e^{-iV\tau} e^{-iK\tau/2}. \qquad (6)$$

Both approximations give the error of order τ^3. Bandrauk and Shen[11] recently proposed a third order method, denoted as VRSO3 in this work, which has the error of order τ^4, and has the form

$$U = e^{-i\gamma K\tau/2} e^{-i\gamma V\tau} e^{-i(1-\gamma)K\tau/2} e^{-i(1-2\gamma)V\tau}$$

$$\times e^{-i(1-\gamma)K\tau/2} e^{-i\gamma V\tau} e^{-i\gamma K\tau/2}, \qquad (7)$$

where γ is $1/(2 - 2^{1/3})$. The power of the split operator methods stems from the fact that if we use coordinate and momentum representations, we can evaluate the kinetic and potential energy operators in their respective local representation spaces, then use the fast Fourier transforms (FFT) to convert representations from coordinate space to momentum space, and vice versa. Each FFT requires $N \log_2 N$ operations, where N is the number of coordinate grid points. Thus, for each time step, we must perform 2 FFT's for the second order methods, and 6 FFT's for the third order one. (However, there are methods, other than finite difference methods, currently under study which involve performing the entire calculation in the coordinate representation.[51])

Similar procedures can be used to approximate the imaginary time operator U in Eq. (4).

B. Time dependent modified Cayley method

The time dependent Schrodinger equation can be rewritten as

$$\left(i\frac{\partial}{\partial t} - K\right)\psi(r,t) = V\psi(r,t), \qquad (8)$$

where $V\psi(r,t)$ is treated as an unknown inhomogeneity. We note here that V can contain an explicit time dependence. Solving the first order differential equation with unknown inhomogeneity yields

$$\psi(r,t'') = -i\int_{t'}^{t''} e^{-iK(t''-t)}V\psi(r,t)dt + e^{-iK\tau}\psi(r,t'). \qquad (9)$$

Furthermore, the kinetic and potential energy operators are separated; hence, they can be evaluated in their respective local representations. However, notice that $\psi(r,t'')$ does appear in both sides of Eq. (9). By using the trapezoidal rule to approximate the integral over t, it can be factored out and yield[53]

$$\psi(r,t'') = \left(1 + \frac{i\tau}{2}V\right)^{-1} e^{-iK\tau}\left(1 - \frac{i\tau}{2}V\right)\psi(r,t'), \qquad (10)$$

where in this form, we have implicitly taken V to be time independent. Thus, the modified Cayley method also requires two FFT's per time step. The magnitude of the error which depends on τ^3 results from the use of the trapezoidal rule. The results from this method are referred to as KRMC. We also note that there is a potential referenced modified Cayley[52] (VRMC) for which we give results.

To extend the modified Cayley method to the case of imaginary time propagation, one needs to solve the corresponding imaginary time differential equation

$$\frac{\partial}{\partial\beta}\phi_\beta = -\frac{H}{2}\phi_\beta. \qquad (11)$$

Following the same derivation as for real time, we obtain

$$\phi(\beta'') = \left(1 + \frac{d\beta}{4}V\right)^{-1} e^{-Kd\beta/2}\left(1 - \frac{d\beta}{4}V\right)\phi(\beta'), \qquad (12)$$

where $d\beta$ is the magnitude of the imaginary time step size, $d\beta = \beta'' - \beta' = \beta/L$ with L the number of imaginary time steps. This equation shows how the thermal wave function propagates in imaginary time.

C. Chebychev polynomial expansion

In this method, the evolution operator U is approximated by a Chebychev series as

$$U = \sum_{m=0}^{M} a_m \Phi_m(-iH\tau), \qquad (13)$$

where M is large enough to ensure the convergence of the series, a_m are the expansion coefficients, and Φ_m are complex Chebychev polynomials. Since the range of the argument of these polynomials is from $-i$ to i, one needs to shift the Hamiltonian to

$$H_{norm} = 2\frac{H - I(\Delta E/2 + V_{min})}{\Delta E}, \qquad (14)$$

where I is the identity operator, and $\Delta E = E_{max} - E_{min}$ is the spectral range of energy of the discretized Hamiltonian H. The maximum and minimum of the total energy, E_{max} and E_{min}, respectively, are defined over the grid by

$$E_{max} = V_{max} + \frac{p_{max}^2}{2m}, \qquad (15a)$$

$$E_{min} = V_{min}, \qquad (15b)$$

where m is the mass of the particle, and the maximum momentum is expressed in terms of the grid spacing Δx as

$$p_{\max} = \frac{\pi}{\Delta x}.\qquad(16)$$

With this definition the time evolution operator can be approximated as

$$\mathbf{U} = e^{-i(\Delta E/2 + V_{\min})\tau} \sum_{m=0}^{M} a_m(\alpha)\Phi_m(-i\mathbf{H}_{\text{norm}}),\qquad(17)$$

where a_m is defined as

$$a_0 = J_0(\alpha),\qquad(18a)$$

$$a_m = 2J_m(\alpha), \quad \text{for } m = 1,M,\qquad(18b)$$

where J_m are the cylinder Bessel functions and $\alpha = \Delta E\tau/2$. This propagation requires the calculation of the effect of the operator Φ_m on ψ, and this can be evaluated by using the recursion relation

$$\Phi_{m+1} = -2i\mathbf{H}_{\text{norm}}\Phi_m + \Phi_{m-1}.\qquad(19)$$

Note that this method requires $2M$ FFT's per time step. The maximum order M can be chosen such that accuracy is dominated by the accuracy of the computer. In practice, M is often slighty larger than the theoretical limit $\Delta E\tau/2$.

III. RESULTS AND DISCUSSION

We have carried out extensive testing on these four quantum evolution methods. However, due to limited space we only present the most important features of this comparative study, and point out the advantages and disadvantages of each in the ongoing development of dynamical methods to study quantum processes in biological systems.

Since our goal is to study proton transfer in proteins, it is most informative to use a double well potential to test these time evolution methods. In this case, we use the previously reported one-dimensional double well potential, $V(x;R)$, for proton transfer in the $[\text{H}_3\text{NH}^+ \cdots \text{NH}_3]$ complex.[64] The functional form and the new and better fitted parameters for the potential $V(x;R)$, where x is the distance from the proton to the geometrical center, and R is the equilibrium distance between two heavy atom centers in this case, are given in Table I. This potential has the barrier height of 1.91 kcal/mol above the potential minimum, and located at the origin, and the two minima are symmetrically located at $x = \pm 0.44\, a_0$ ($a_0 = 0.529$ Å).

A. Real time evolution

For the real time propagation, the initial wave function is a Gaussian wave packet centered at $x = -0.44\, a_0$. The average energy at time $t = 0$ is set at 3.0 kcal/mol which yields a Gaussian packet, well localized in the left hand well.

For the discussion of the efficiency and accuracy of the various methods, we have considered several methods of error analysis for the norm and the phase of the coordinate space wave function and the total energy of the particle (hydrogen atom in this case). The relative average energy error (AEE) is defined by

$$\text{AEE} = \left|\frac{E(t=0) - \langle E \rangle}{E(t=0)}\right|,\qquad(20)$$

where $E(t = 0)$ is the average total energy at $t = 0$, and

TABLE I. Potential energy function and parameters for the proton bound ammonia dimer $[\text{H}_3\text{NH}^+ \cdots \text{NH}_3]$ (kcal/mol, Å). The fitted potential is valid for $V < 10$ kcal/mol.

$V(x;R) = C(R) + B(R)x^2 + A(R)x^4,$

where
$C(R) = p_1 + p_2 R + p_3 R^2 + p_4 R^3,$
$B(R) = p_5 + p_6 R + p_7 R^2 + p_8 R^3,$
$A(R) = p_9 + p_{10}R + p_{11}R^2 + p_{12}R^3.$

p_1	2 090.232 50
p_2	− 2 094.022 88
p_3	685.471 15
p_4	− 72.752 64
p_5	8 084.935 86
p_6	− 7 147.818 64
p_7	2 061.221 36
p_8	− 196.930 14
p_9	20 700.629 80
p_{10}	− 16 210.357 90
p_{12}	− 380.810 30
R	2.72

$$\langle E \rangle = \frac{1}{N_t} \sum_i E_i,\qquad(21)$$

with E_i the total energy at the time step i. Here N_t is the number of steps at which the detailed analysis is carried out. In the present study, the analysis is carried out every ten time steps, or at time intervals of 10τ. We also examine the rms deviation of the relative total energy (rms E) which is expressed as

$$\text{rms } E = \frac{1}{\langle E \rangle}\left\{\frac{1}{N_t}\sum_{i=0}^{N_t}(\langle E \rangle - E_i)^2\right\}^{1/2}\qquad(22)$$

and the rms deviation of the norm (rms N) given by

$$\text{rms } N = \left\{\frac{1}{N_t}\sum_{i=0}^{N_t}(1 - n_i)^2\right\}^{1/2}\qquad(23)$$

where n_i is the norm at the step i. To investigate the error in the phase of the wave function, we monitor the survival probability which is defined as the square of the overlap between the final wave function of a run and the final wave function of the reference calculation. The survival probability error is then expressed as

$$\text{survival prob. error} = 1 - |\langle \psi(t_f)|\psi_{\text{ref}}(t_f)\rangle|^2.\qquad(24)$$

The reference wave function is calculated using a very small time step of 0.05 fs.

For the short time propagators, the split operators are unitary, therefore the norm is conserved. We found that the rms N for the split operator methods are quite small for the time step τ up to 1.5 fs. The modified Cayley method on the other hand is not automatically unitary, and as a result the rms N is much larger. In Fig. 1, we plot the largest of the three error measures in the norm and the energy as defined in Eqs. (21)–(23) vs the time step for the split operator and modified Cayley methods, after propagation for the total time of 1 ps. In this case, the grid spacing, Δx, is equal to 0.04 and the total number of points, N, is 256. It is interesting to notice that the second order potential referenced split operator (VRSO) method is somewhat more stable than the sec-
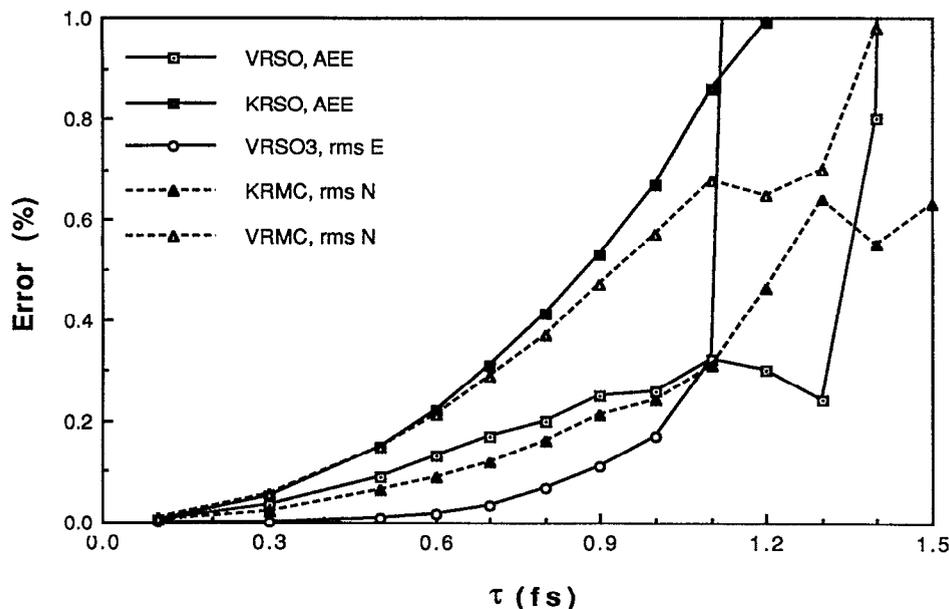
FIG. 1. The largest error (%) among the relative average energy error, rms deviation of the relative total energy, and rms of the norm, after the packet is propagated a total of 1 ps, plotted vs the time step (fs) for the second and third order potential referenced split operator (VRSO and VRSO3, respectively), kinetic referenced split operator (KRSO), and kinetic and potential referenced modified Cayley (KRMC and VRMC, respectively) methods. The grid spacing, Δx, is 0.04, and N, the number of x-grid points is 256.

ond order kinetic referenced one (KRSO), though they both have the same order of error, theoretically. The third order potential referenced split operator (VRSO3) method is found to have larger stable range up to $t = 1$ fs. However, recall that VRSO3 requires 6 FFT per time step whereas the second order ones require only 2 FFT per step. We also found that the kinetic referenced modified Cayley (KRMC) method is somewhat more stable compared to the VRSO method, though it also requires only 2 FFT per time step. In particular, for a given level of accuracy, e.g., less than 0.1% error in the norm and energy, the time step must be less than or equal to 0.4 fs for KRSO, 0.5 fs for VRSO, 0.9 fs for VRSO3, 0.4 fs for VRMC, and 0.6 fs for KRMC method. Furthermore, we found that these error measures did not change significantly for calculations with the total time of 5 ps. For the error in the phase, we plotted the survival probability errors as functions of time step for calculations with the total time of 1 and 5 ps in Figs. 2(a)–2(b), respectively. The survival probability errors accumulate over time as seen by comparing results from Figs. 2(a) and 2(b). Notice that at larger time steps in the 5 ps run, the split operator methods, and the potential referenced modified Cayley show some oscillatory behavior in the survival probability error that is probably due to the periodicity of the phase, and the inteference between the phase error accumulated over time and the phase. However, we found that the KRMC gives more stable results in the phase for a wider range of time step. Consequently, among the short time propagators, the KRMC method is preferred. And since it has no restriction on the form of the Hamiltonian, thus, for the case of time dependent potential, the KRMC method would be the method of choice among those we consider here for the real time evolution.

It is an interesting and important question to ask why the potential referenced split operator is better than the kinetic referenced one whereas the kinetic referenced modified
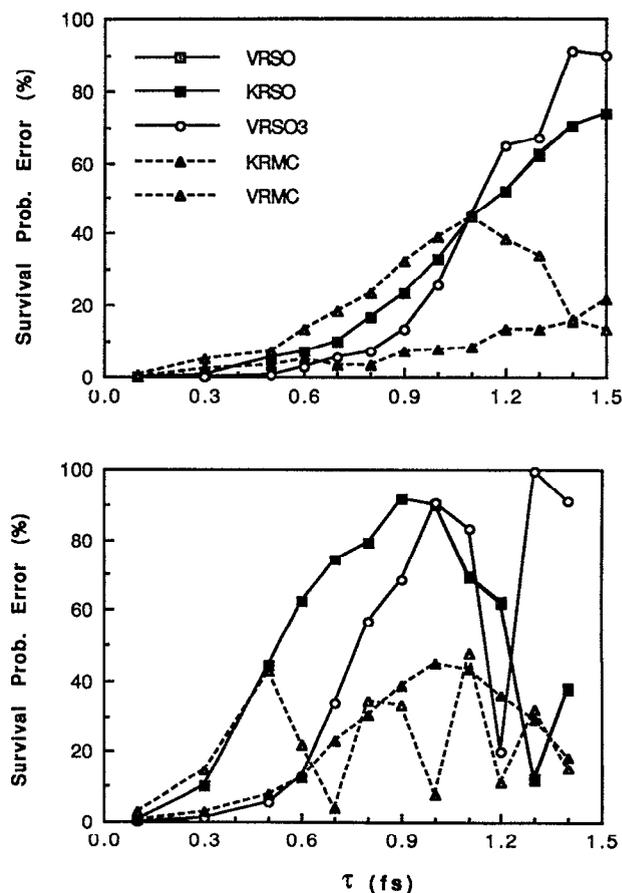
FIG. 2. The survival probability error (%) plotted vs the time step (fs) for the second and third order potential referenced split operator (VRSO and VRSO3, respectively), kinetic referenced split operator (KRSO), and kinetic and potential referenced modified Cayley (KRMC and VRMC, respectively) methods. (a) is for the total time of 1 ps and (b) is for the total time of 5 ps. The grid spacing, Δx, is 0.04, and N, the number of x-grid points is 256. The results for VRSO and KRSO are nearly identical.

Cayley method is better than the potential referenced one. We have propagated the initial wave function through one time step of size 1 fs, and found that the AEE error is 0.13% for the KRSO and 0.02% for the VRSO method. This indicates that there is a fundamental difference in the computational accuracy by splitting the kinetic operator in VRSO and the potential operator in KRSO. In Figs. 3 and 4, we show the real components of the unsplit and split (resulting in the square root) forms of the exponential kinetic and potential operators, respectively, in the SO method. The imaginary components are found to have similar features. Note that there is little difference in the split and unsplit exponential potential operator (see Fig. 4) whereas the split exponential kinetic operator has noticeably fewer oscillations compared to the unsplit one (see Fig. 3). Now in the KRSO method, the split exponential potential operator occurs as a factor *twice*, leading to an extremely oscillatory behavior. In the VRSO method, the unsplit exponential potential operator occurs as a factor once, and it is essentially no more oscillatory than a single split exponential potential operator. We thus expect that it will involve a substantial reduction in the oscillations, leading to a more easily and accurately computed evolution operator. In the case of VRMC, the unsplit exponential potential operator occurs as a single factor, multiplied by smooth functions $(1 \mp i\mathbf{K}t/2)^{\pm 1}$ in k space. By contrast, the KRMC involves the much less oscillatory un-
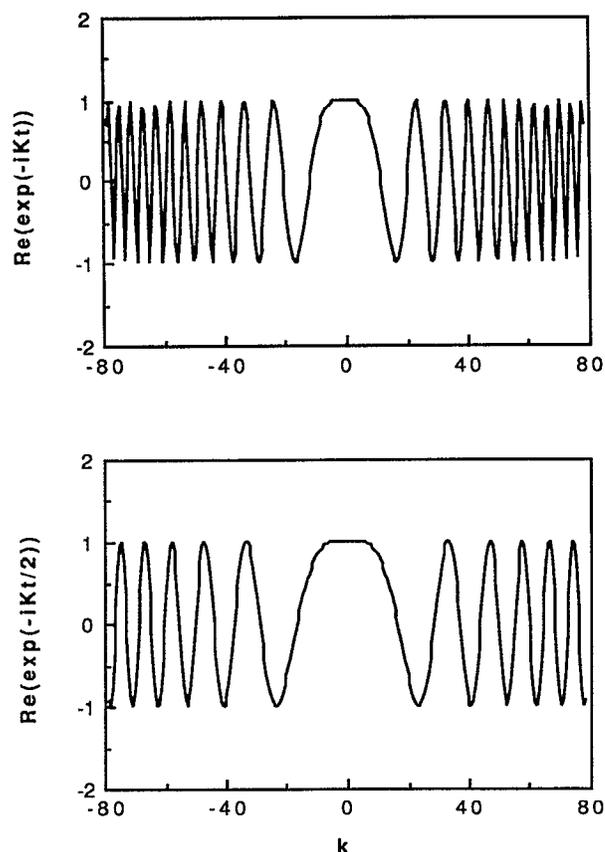
FIG. 4. The real components of the exponential unsplit and split potential operators, Re $[\exp(-iVt)]$ and Re $[\exp(-iVt/2)]$, respectively, are plotted vs the coordinate x in atomic units. The time t is 1 fs.

split exponential kinetic operator, multiplied by smooth functions $(1 \mp iVt/2)^{\pm 1}$ in x space. As a result, we expect the KRMC will involve the least oscillatory quantity, and thus lead to the most efficient computational algorithm, as was found.

The Chebychev polynomial expansion method, which is a global propagator, has an additional parameter in determining the stability of the method, that being the order of the polynomial, M. We therefore discuss this method separately. In the present study, the time step used is smaller than 4 fs, and the order of the Chebychev polynomial M did not exceed 80. In all test runs we found that the Chebychev method gave stable results for grid spacing, Δx, between 0.08 to 0.1 a_0, which is about factor of 2 larger than for the short time propagators. Consequently, the number of grid points is smaller for a given reaction range. Furthermore, it is not monotonically dependent on the grid spacing. To illustrate this point, in Fig. 5 we plotted the average energy error vs the grid spacing for the case of $M = 30$ and 40, $N = 64$ points, and the total time of 1 ps. Note that for smaller grid spacing, to obtain accuracy a higher order of polynomial is needed to cover the larger spectral range of the Hamiltonian [see Eqs. (15) and (16)]. Thus, in this respect, the Chebychev method is complementary to the split operator and modified Cayley methods in which accuracy can only be obtained using their smaller grid spacing. Furthermore, for a given level of

FIG. 3. The real components of the exponential unsplit and split kinetic operators, Re $[\exp(-iKt)]$ and Re $[\exp(-iKt/2)]$, respectively, are plotted vs the momentum k in atomic units. The time t is 1 fs.
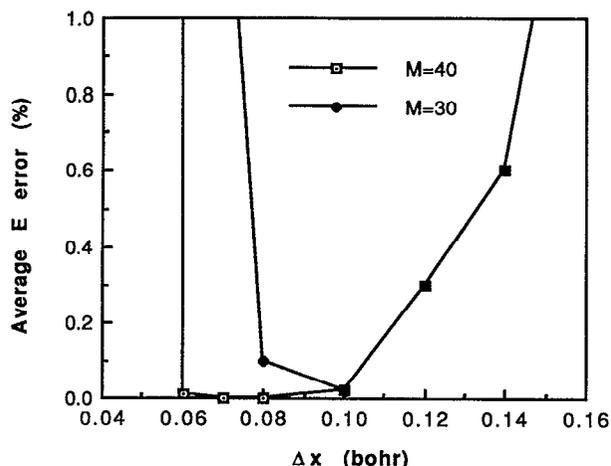
FIG. 5. The average energy error ($\%$) plotted vs the grid spacing Δx for the Chebychev polynomial expansion method for the order of $M = 30$ and 40. The time step is 1 fs for the total time of 1 ps, and N is 64 in this case.

accuracy, the Chebychev method can accomodate a larger time step providing one uses a higher order polynomial. Furthermore, we found that the error measures in the norm and the phase of the wave function, and the energy are about the same order of magnitude. In particular, Fig. 6 shows the minimum order of the Chebychev polynomial must be used for a given time step that ensures the average energy error is less than 0.1%. Note that the time step for the Chebychev method can be as large as 3.5 fs which is more than a factor of 3 larger than can be used by the modified Cayley method. If the FFT is the time consuming step, then the Chebychev method is much more expensive than the modified Cayley method. For instance, if τ is 0.5 fs the modified Cayley requires 2 FFT whereas the Chebychev requires at least 38 FFT (minimum M equals 19) to give the error of less than 0.1% (see Figs. 1 and 5). However, if the potential is the time consuming step, then the Chebychev method might be preferable because its grid spacing and time step can be much larger, making the potential subroutine calls much less frequent.
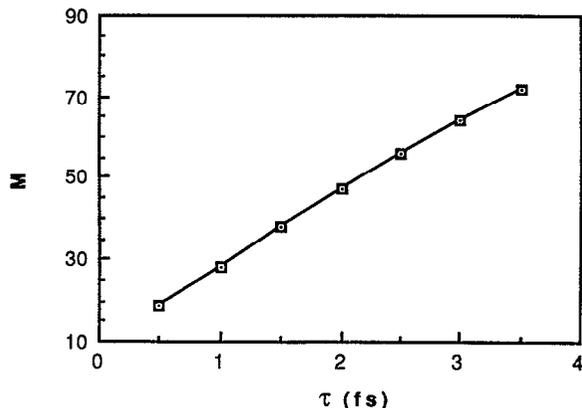
FIG. 6. The minimum order of the Chebychev polynomial expansion which gives the error of less than 0.1% in error measures in the norm and the energy plotted vs the time step (fs).

B. Imaginary time evolution

For the imaginary time propagation, the initial wave function is the eigenfunction of the coordinate operator at $x = 0.0$, $|x = 0\rangle$, which is a delta function centered at the origin. However, the first step in both the split operator and kinetic referenced modified Cayley methods can be solved analytically and yields a Gaussian function which then be used numerically to propagate in the subsequent steps. In particular, let η be the resulting wave function after the first two operations of the first step. For the second order kinetic referenced split operator, we have

$$\eta = e^{-\mathbf{K}d\beta/2}e^{-\mathbf{V}d\beta/4}\delta(x) = \left(\frac{m}{\pi\,d\beta}\right)^{1/2}e^{-mx^2/d\beta}e^{-V(0)d\beta/4} \tag{25}$$

and for the second order potential referenced split operator, we have

$$\eta = e^{-\mathbf{V}d\beta/2}e^{-\mathbf{K}d\beta/4}\delta(x)$$
$$= \left(\frac{2m}{\pi\,d\beta}\right)^{1/2}e^{-V(x)d\beta/2}e^{-2mx^2/d\beta}. \tag{26}$$

The initial wave function η for the kinetic referenced modified Cayley method is expressed as

$$\eta = e^{-\mathbf{K}d\beta/2}\left(1 - \frac{d\beta}{4}\,\mathbf{V}\right)\delta(x)$$
$$= \left(\frac{2m}{\pi d\beta}\right)^{1/2}\left(1 - \frac{d\beta}{4}\,V(0)\right)e^{-mx^2/d\beta}. \tag{27}$$

Note that the width of η is dependent on the magnitude of the imaginary time step size $d\beta$. For accuracy in the integration, $d\beta$ is required to be small, but this results in a small spread of the delta function, and thus it requires a very fine grid spacing to represent the initial wave function adequately. In other words, there is no absolute convergence of the final wave function as $d\beta$ decreases, however a relative convergence analysis is valid as seen below. Thus, care must be taken in choosing the grid spacing and step size. For this reason, since the width of η for the potential referenced split operator method in Eq. (26) is smaller than that for the kinetic referenced split operator method in Eq. (25), the kinetic referenced split operator is more efficient than the potential referenced one. Consequently, the kinetic referenced split operator method is chosen to compare with the kinetic referenced modified Cayley method, which also has the same width, for the imaginary time evolution. The first step of the Chebychev polynomial expansion method and the potential referenced modified Cayley method in the imaginary time evolution does not yield a Gaussian wave packet, and thus it is not used in this test.

For this study, the grid spacing, Δx, is set to 0.01 a_0 with a total of 512 grid points. As mentioned earlier, there is no absolute convergence of the final wave function as the time step $d\beta$ decreases, thus to analyze the accuracy of the integration methods, we examine the relative convergence of the correlation error of the norm of the final wave function which is defined as

$$(\text{correl. error of norm})_k = \frac{N_k - N_{k-s}}{N_{k-s}}, \tag{28}$$

where N_x is the norm of the final wave function using the total of x steps. The correlation error of the norm as a function of the total number of steps is shown in Fig. 7 for the temperature of 100 and 300 K. Notice that at low temperature the KRSO converges much faster than the KRMC method. However, as temperature increases the difference between two methods becomes smaller. It is important to point out that for the imaginary time evolution, the first factor in the right hand side of Eq. (12) can vanish, and thus, the modified Cayley method has the possibility of being unstable. In conclusion, for the imaginary time evolution, the kinetic referenced split operator method is more stable and has faster convergence than the kinetic referenced modified Cayley method.

IV. CONCLUSION

We have carried out a detailed study of the accuracy and stability of quantum mechanical wave packet evolution methods, namely, the second and third order split operator methods, a time dependent modified Cayley method, and the Chebychev polynomial expansion method for both real time and, for the SO and MC methods, imaginary time integrations. We found that for real time integration, if the fast Fourier transform is the time consuming step, the kinetic referenced modified Cayley method is preferred. However, if the potential is the time consuming step then the Chebychev polynomial expansion method might be more advantageous since it can use larger grid spacing and time step. For imaginary time integration, we found that the kinetic referenced split operator method is preferable.

Finally, we point out that of the methods considered, only the modified Cayley approach holds in general, regardless of whether the potential is time independent or dependent. The trapezoidal rule is exact for a linear time dependence over the interval τ, and approximate for other dependences. The other methods are valid only if τ is made short enough that the potential is effectively constant. Thus,
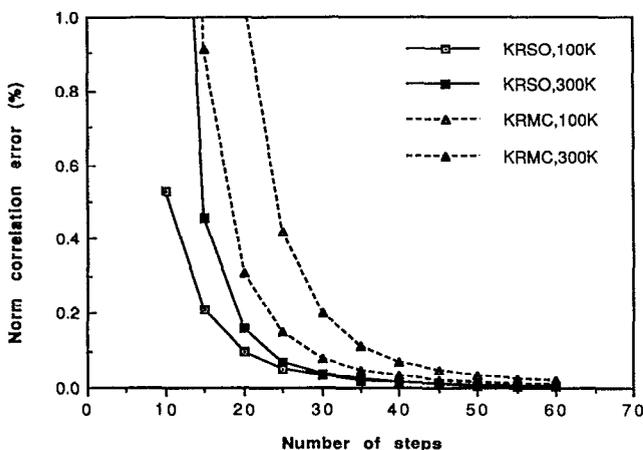
we anticipate that the kinetic referenced modified Cayley method should be capable of handling larger time steps for such problems. Further, the Chebychev method will no longer be able to accomodate such large τ's since it too is valid only for short enough τ that the potential is constant with time. We are currently engaged in the initial computations for the main problem of interest, namely, quantal processes in biological molecules.

[1] Some recent reviews include (a) for molecule-surface scattering, R. B. Gerber, R. Kosloff, and M. Berman, Comput. Phys. Rep. **5**, 59 (1986); (b) for collinear gas phase reactive scattering, V. Mohan and N. Sathymurthy, *ibid.* **7**, 213 (1988); and (c) a general review by R. Kosloff, J. Phys. Chem. **92**, 2087 (1988).

[2] J. Mazur and R. J. Rubin, J. Chem. Phys. **31**, 1395 (1959).

[3] E. A. McCullough and R. E. Wyatt, J. Chem. Phys. **54**, 3578 and 3592 (1971).

[4] C. Zuhert, T. Kamal, and L. Zulicke, Chem. Phys. Lett. **36**, 396 (1975).

[5] E. J. Heller, J. Chem. Phys. **62**, 1544 (1975); **65**, 4979 (1976); K. C. Kulander and E. J. Heller, *ibid.* **69**, 2439 (1978); G. Drolshagen and E. J. Heller, *ibid.* **79**, 2072 (1983).

[6] A. Askar and A. S. Cakmak, J. Chem. Phys. **68**, 2794 (1978).

[7] K. C. Kulander, J. Chem. Phys. **69**, 5064 (1978); J. C. Gray, G. A. Fraser, D. G. Truhlar, and K. C. Kulander, *ibid.* **73**, 5726 (1980); A. E. Orel and K. C. Kulander, Chem. Phys. Lett. **146**, 428 (1988).

[8] C. LeForestier, G. Bergerson, and P. C. Hiberty, Chem. Phys. Lett. **84**, 385 (1981) [see also C. LeForestier, Chem. Phys. **87**, 241 (1984)].

[9] P. M. Agrawal and L. M. Raff, J. Chem. Phys. **77**, 3946 (1982).

[10] E. J. Heller, R. L. Sundberg, and D. J. Tannor, J. Phys. Chem. **86**, 1822 (1982).

[11] M. D. Feit and J. A. Fleck, J. Chem. Phys. **78**, 301 (1983); **80**, 2578 (1984); see also the symmetric split operator approach of P. De Vries, in NATO ASI series, Vol. B171, (1988) 113, and A. D. Bandrauk and H. Shen, Chem. Phys. Lett. **176**, 428 (1991).

[12] D. Kosloff and R. Kosloff, J. Comput. Phys. **52**, 35 (1983); J. Chem. Phys. **79**, 1823 (1983).

[13] C. LeForestier, Chem. Phys. **87**, 241 (1984) and, in *Theory of Chemical Reaction Dynamics*, edited by D. C. Clary (Reidel, Dordrecht, 1986), p. 235; F. le Quere and C. LeForestier, J. Chem. Phys. **92**, 247 (1990).

[14] G. Drolshagen and E. J. Heller, J. Chem. Phys. **79**, 2072 (1983).

[15] H. Tal-Ezer and R. Kosloff, J. Chem. Phys. **81**, 3967 (1984); R. Kosloff and H. Tal-Ezer, Chem. Phys. Lett. **127**, 223 (1981).

[16] R. Kosloff and C. Cerjan, J. Chem. Phys. **81**, 3722 (1984).

[17] A. T. Yinnon, R. Kosloff, and R. B. Gerber, Surf. Sci. **148**, 148 (1984); R. B. Gerber, A. T. Yinnon, and R. Kosloff, Chem. Phys. Lett. **105**, 523 (1984).

[18] D. Imre, J. Kinsey, A. Sinha, and J. Krenos, J. Phys. Chem. **88**, 3956 (1984).

[19] R. T. Skodje, Chem. Phys. Lett. **109**, 227 (1984).

[20] R. C. Mowrey and D. J. Kouri, Chem. Phys. Lett. **119**, 285 (1985).

[21] B. Jackson and H. Metiu, J. Chem. Phys. **83**, 1952 (1985); S. Sawada, R. Heather, B. Jackson, and H. Metiu, *ibid.* **83**, 3009 (1985).

[22] Z. H. Zhang and D. J. Kouri, Phys. Rev. A**34**, 2687 (1986).

[23] B. Jackson and H. Metiu, J. Chem. Phys. **84**, 3535 (1986); *ibid.* **85**, 4192 (1986); *ibid.* **86**, 1026 (1987).

[24] T. J. Park and J. C. Light, J. Chem. Phys. **85**, 5870 (1986).

[25] V. Mohan and N. Sathymurthy, Current Sci. **55**, 115 (1986).

FIG. 7. The correlation error (%) of the norm of the final thermal wave function plotted vs the total number of steps for the kinetic referenced split operator (KRSO) and kinetic referenced modified Cayley (KRMC) methods.

[26] R. C. Mowrey and D. J. Kouri, J. Chem. Phys. **84**, 6466 (1986).

[27] R. C. Mowrey and D. J. Kouri, J. Chem. Phys. **86**, 6140 (1987).

[28] D. J. Kouri and R. C. Mowrey, J. Chem. Phys. **87**, 2087 (1987).

[29] Y. Sun, R. C. Mowrey, and D. J. Kouri, J. Chem. Phys. **87**, 339 (1987).

[30] R. C. Mowrey, H. F. Bowen, and D. J. Kouri, J. Chem. Phys. **86**, 2441 (1987); R. C. Mowrey, H. F. Bowen, T. Yinnon, and R. B. Gerber, *ibid.* **89**, 3925 (1988); (in preparation).

[31] R. Heather and H. Metiu, J. Chem. Phys. **86**, 5009 (1987); **90**, 6116 (1989); **91**, 1596 (1989).

[32] D. Huber and E. J. Heller, J. Chem. Phys. **87**, 5302 (1987); **89**, 4752 (1988); D. Huber, E. J. Heller, and R. G. Littlejohn, *ibid.* **87**, 5302 (1987); D. Huber, S. Ling, D. G. Imre, and E. J. Heller, *ibid.* **90**, 7317 (1989).

[33] Y. Sun and D. J. Kouri, J. Chem. Phys. **89**, 2958 (1988).

[34] B. Jackson, J. Chem. Phys. **88**, 1383 (1988); **89**, 2473 (1988); (in press).

[35] D. Chaseman, D. J. Tannor, and D. G. Imre, J. Chem. Phys. **89**, 6667 (1988).

[36] S. O. Williams and D. G. Imre, J. Phys. Chem. **92**, 6648 (1988).

[37] D. J. Tannor and S. A. Rice, Adv. Chem. Phys. **70**, 441 (1988).

[38] R. Viswanathan, S. Shi, E. Villalonga, and H. Rabitz, J. Chem. Phys. **91**, 2333 (1989).

[39] Y. Sun, R. S. Judson, and D. J. Kouri, J. Chem. Phys. **90**, 241 (1989).

[40] D. Neuhauser and M. Baer, J. Chem. Phys. **90**, 4351 (1989); J. Phys. Chem. **93**, 2872 (1989); J. Chem. Phys. **91**, 4651 (1989).

[41] D. Neuhauser, M. Baer, R. S. Judson, and D. J. Kouri, J. Chem. Phys. **90**, 5882 (1989); **93**, 312 (1990); Comput. Phys. Commun. (in press).

[42] J. Zhang and D. G. Imre, J. Chem. Phys. **90**, 1666 (1989).

[43] X.-P. Jiang, R. Heather, and H. Metiu, J. Chem. Phys. **90**, 2555 (1989).

[44] M. Jacon, O. Atabek, and C. LeForestier, J. Chem. Phys. **91**, 1585 (1989).

[45] R. N. Dixon, Mol. Phys. **68**, 263 (1989).

[46] R. S. Judson, D. J. Kouri, D. Neuhauser, and M. Baer, Phys. Rev. A **42**, 351 (1990).

[47] M. Founargiotakis and J. C. Light, J. Chem. Phys. **93**, 633 (1990).

[48] R. N. Dixon, C. C. Marston, and G. G. Balint-Kurti, J. Chem. Phys. **93**, 6520 (1990).

[49] J. Z. H. Zhang, Chem. Phys. Lett. **160**, 417 (1989); J. Chem. Phys. **91**, 324 (1990).

[50] S. Das and D. J. Tannor, J. Chem. Phys. **92**, 3403 (1990).

[51] D. K. Hoffman, O. Sharafeddin, R. S. Judson, and D. J. Kouri, J. Chem. Phys. **92**, 4167 (1990); see also D. K. Hoffman, N. Naresh, O. A. Sharafeddin, and D. J. Kouri, J. Phys. Chem. **95**, 8299 (1991).

[52] O. A. Sharafeddin, D. J. Kouri, R. S. Judson, and D. K. Hoffman, J. Chem. Phys. **93**, 5580 (1990).

[53] R. S. Judson, D. B. McGarrah, O. A. Sharafeddin, D. J. Kouri, and D. K. Hoffman, J. Chem. Phys. **94**, 3577 (1991).

[54] D. Neuhauser and R. S. Judson, J. Chem. Phys. (in press).

[55] D. Neuhauser, R. S. Judson, R. L. Jaffe, M. Baer, and D. J. Kouri, Chem. Phys. Lett. **176**, 546 (1991).

[56] Y. Sun, D. J. Kouri, D. W. Schwenke, and D. G. Truhlar, Comput. Phys. Commun. **63**, 51 (1991).

[57] O. A. Sharafeddin, H. F. Bowen, D. J. Kouri, and D. K. Hoffman, J. Comput. Phys. (in press).

[58] D. Neuhauser, J. Chem. Phys. **95**, 4927 (1991).

[59] O. A. Sharafeddin, D. J. Kouri, S. Das, D. J. Tannor, and D. K. Hoffman, J. Chem. Phys. **95**, 4727 (1991).

[60] W. H. Miller, J. Chem. Phys. **61**, 1823 (1974); W. H. Miller, S. D. Schwartz, and J. W. Tromp, *ibid.* **79**, 4889 (1983).

[61] G. Wahnstrom and H. Metiu, Chem. Phys. Lett. **134**, 531 (1987).

[62] G. Wahnstrom, B. Carmeli, and H. Metiu, J. Chem. Phys. **88**, 2478 (1988).

[63] C. Leforestier, R. H. Bisseling, C. Cerjan, M. D. Feit, R. Friesner, A. Guldberg, A. Hammerich, G. Jolicard, W. Karrlein, H.-D. Meyer, N. Lipkin, O. Roncero, and R. Kosloff, J. Comput. Phys. **94**, 59 (1991).

[64] L. Jaroszewski, B. Lesyng, J. J. Tanner, and J. A. McCammon, Chem. Phys. Lett. **175**, 282 (1990).