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# On time-step bounds in unitary quantum evolution using the Lanczos method

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**Abstract**

To solve the non-relativistic time dependent Schrödinger equation using the Lanczos method, Park and Light have provided an approximate expression for the time step for a given accuracy. We provide an exact expression for the time step in terms of the eigenvalues and eigenvectors of the resulting tridiagonal matrix. For two test problems, the values of the time step provided by Park and Light differ significantly from the exact values provided by the present method. We also indicate upper and lower bounds for the time step in terms of the maximum and minimum eigenvalues. These bounds indicate the possibility of using a new time step given by the geometric mean of the eigenvalues of the tridiagonal matrix.


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## 1. Introduction

Quantum time evolution is required for a variety of problems in chemistry and physics including reaction dynamics [1,2] and photochemistry [3–5]. Time evolution in "imaginary time" provides a computational route to quantum statistical mechanics [6]. Key to the success of these calculations are reliable estimates of maximum time steps for stable time evolution. In this article, we derive exact expressions for such time-step bounds based on the Lanczos method reported in 1986 by Park and Light [7]. This method builds the solution to the time-dependent Schrödinger equation (tdse) in a Krylov space through iterative Gram–Schmidt orthogonalization. Our new time-step bounds are rigorously tied to allowed error tolerances, require only data already obtained during time evolution, and guarantee stable wavepacket evolution.

The remainder of this article is organized as follows: in Section 2 we review Park and Light's Lanczos time evolution approach; in Section 3 we derive the exact time-step bound; in Section 4 we derive a simplified time-step bound using Gershgorin's theorem; in Section 5 we test our bound on numerical wavepacket evolution in a harmonic potential; in Section 6 we further test the bound on wavepacket scattering from an Eckart barrier; and in Section 7 we conclude.

## 2. Solution of tdse by the Lanczos method

Consider the time dependent Schrödinger equation (tdse) with a time independent Hamiltonian $H_0$, in one dimension

$$H_0 = \frac{-\hbar^2}{2\mu}\frac{d^2}{dx^2} + V(x), \tag{1}$$

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$$i\hbar\frac{\partial}{\partial t}\psi(x,t) = H_0\psi(x,t). \tag{2}$$

In the following, $\|\cdot\|$ denotes the standard $L_2$ norm and column vectors are denoted by bold letters. To solve the above equation, we write the wave function $\psi(x,t)$ in terms of an appropriate set of orthonormal basis functions $\{\phi_i(x)\}$ as

$$\psi(x,t) = \sum_{i=1}^{N} a_i(t)\phi_i(x); \quad \langle\phi_i|\phi_j\rangle = \delta_{ij}. \tag{3}$$

We need to solve for the expansion coefficients $\{a_i(t)\}$ denoted by the vector $\mathbf{a}(t)$. Let $H$ denote the $n$ by $n$ Hamiltonian matrix with elements $H_{ij}$ given by

$$H_{ij} = \langle\phi_i|H_0\phi_j\rangle = \int \phi_i^*(x)H_0\phi_j(x)\,\mathrm{d}x. \tag{4}$$

The Schrödinger equation gets recast as

$$i\hbar\frac{\partial\mathbf{a}}{\partial t} = H\mathbf{a}(t) \tag{5}$$

with the initial condition

$$\mathbf{a}(0) = \mathbf{b}(0), \tag{6}$$

$$b_i(0) = \big\langle\phi_i\big|\psi(x,0)\big\rangle. \tag{7}$$

The formal solution and a $p$ term approximation to the formal solution are given by

$$\mathbf{a}(t) = e^{-(it/\hbar)H}\mathbf{a}(0) = \sum_{k=0}^{\infty}\frac{(-it/\hbar)^k}{k!}H^k\mathbf{a}(0) \simeq \sum_{k=0}^{p-1}\frac{(-it/\hbar)^k}{k!}H^k\mathbf{a}(0). \tag{8}$$

In the above approximation, the $p$-dimensional subspace is spanned by the vectors $\{\mathbf{a}(0), H\mathbf{a}(0), H^2\mathbf{a}(0), \ldots, H^{p-1}\mathbf{a}(0)\}$. In the Lanczos method, the $p$-dimensional subspace is spanned by an alternate set of linearly independent vectors $\{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3, \ldots, \mathbf{a}_p\}$ generated by a recursive process defined below.

$$\mathbf{a}_1 = \mathbf{a}(0)/\|\mathbf{a}(0)\|; \quad \beta_0 = 0; \quad \mathbf{a}_0 = 0, \tag{9}$$

$$\text{for } j = 1 \text{ to } p, \tag{10}$$

$$\mathbf{z} = H\mathbf{a}_j, \tag{11}$$

$$\alpha_j = \langle\mathbf{a}_j|\mathbf{z}\rangle, \tag{12}$$

$$\mathbf{z}_1 = \mathbf{z} - \alpha_j\mathbf{a}_j - \beta_{j-1}\mathbf{a}_{j-1}, \tag{13}$$

$$\beta_j = \|\mathbf{z}_1\|, \tag{14}$$

$$\text{if } \beta_j = 0, \quad \text{quit}, \tag{15}$$

$$\mathbf{a}_{j+1} = \mathbf{z}_1/\beta_j, \tag{16}$$

$$\text{end for loop}. \tag{17}$$

The $p$ Lanczos vectors $\{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3, \ldots, \mathbf{a}_p\}$ define a $n$ by $p$ matrix $A_p$, given by

$$A_p = \{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3, \ldots, \mathbf{a}_p\}. \tag{18}$$

The $p$ by $p$ tridiagonal matrix $H_p$ is defined in terms of $\{\alpha_i\}$ and $\{\beta_i\}$ as follows.

$$H_p = \begin{bmatrix} \alpha_1 & \beta_1 & 0 & \ldots & 0 \\ \beta_1 & \alpha_2 & \beta_2 & \ldots & 0 \\ 0 & \beta_2 & \alpha_3 & \beta_3 & \ldots \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & \ldots & \beta_{p-2} & \alpha_{p-1} & \beta_{p-1} \\ 0 & \ldots & 0 & \beta_{p-1} & \alpha_p \end{bmatrix}. \tag{19}$$

Note that the recursive relation given by Eq. (13) can also be written as

$$H\mathbf{a}_j = \beta_j\mathbf{a}_{j+1} + \alpha_j\mathbf{a}_j + \beta_{j-1}\mathbf{a}_{j-1}. \tag{20}$$

This implies the following matrix relation

$$HA_p = A_p H_p. \tag{21}$$

By defining $\mathbf{a}(t) = A_p \mathbf{C}(t)$, one solves for $\mathbf{C}$ as follows

$$\frac{\partial \mathbf{C}}{\partial t} = (-i/\hbar) H_p \mathbf{C}, \tag{22}$$

$$\mathbf{C}(t) = e^{(-it/\hbar)H_p}\mathbf{C}(0), \tag{23}$$

$$\mathbf{C}(0) = \mathbf{C}_0 = \begin{bmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{bmatrix}. \tag{24}$$

The accuracy of this method amounts to minimizing the norm of the $p$th term $\mathbf{C}(t)_p$ of the series approximant to $\mathbf{C}(t)$ given by

$$\mathbf{C}(t) \simeq \sum_{k=0}^{(p-1)} \frac{(-it/\hbar)^k}{k!} \{H_p\}^k \mathbf{C}_0, \tag{25}$$

$$\mathbf{C}(t)_p = \frac{(-it/\hbar)^{(p-1)}}{(p-1)!} \{H_p\}^{(p-1)} \mathbf{C}_0. \tag{26}$$

By stipulating the following criterion

$$\left\| \mathbf{C}(t)_p \right\|^2 \simeq \epsilon \tag{27}$$

the error at time $t$ is kept around the permissible value of $\epsilon$. For real times the evolution indicated here is unitary, since $(\|\psi\|)^2$ is preserved with an accuracy of the order of $\epsilon$.

Essentially one needs a bound on the norm of the quantity $\{H_p\}^{(p-1)}\mathbf{C}_0$. Park and Light [7] assert one bound on this quantity given by $\prod_k^{p-1} \beta_k$. Here $\beta' s$ are the off-diagonal elements of the matrix $H_p$. With this assertion one obtains

$$\left\| \mathbf{C}(t)_p \right\|^2 \simeq \left| \frac{(-it/\hbar)^{(p-1)}}{(p-1)!} \prod_k^{(p-1)} \beta_k \right|^2. \tag{28}$$

Then the maximum permissible time step $t_{\max}$ is thus given by

$$t_{\max} \simeq \hbar \left( \epsilon \left[ \frac{(p-1)!}{\prod \beta_k} \right]^2 \right)^{\frac{1}{2(p-1)}}. \tag{29}$$

The mathematical steps leading to this bound given by

$$\left\| H_p^{(p-1)} \mathbf{C}_0 \right\| \simeq \prod_k^{(p-1)} \beta_k \tag{30}$$

are not transparent. We provide an exact expression for the time step for the real and purely imaginary times below. The time step expression involves the eigenvalues and the first component of each eigenvector of the tridiagonal matrix $H_p$. These eigenvalues and eigenvectors are needed independently for the time evolution of the initial wave packet and hence no extra computation is involved.

## 3. Derivation of the exact time step expression

Let $U$ be the unitary matrix that diagonalizes the matrix $H_p$ to the diagonal matrix $H_{pd}$ where $U$, $U^\dagger$ and $H_{pd}$ are defined below.

$$U = \begin{bmatrix} u_{11} & u_{12} & \dots & u_{1p} \\ u_{21} & u_{22} & \dots & u_{2p} \\ \vdots & \vdots & \vdots & \vdots \\ u_{p1} & u_{p2} & \dots & u_{pp} \end{bmatrix}, \qquad U^\dagger = \begin{bmatrix} u_{11}^* & u_{21}^* & \dots & u_{p1}^* \\ u_{12}^* & u_{22}^* & \dots & u_{p2}^* \\ \vdots & \vdots & \vdots & \vdots \\ u_{1p}^* & u_{2p}^* & \dots & u_{pp}^* \end{bmatrix}, \tag{31}$$

$$U^\dagger H_p U = H_{pd} = \begin{bmatrix} \lambda_1 & 0 & \dots & 0 \\ 0 & \lambda_2 & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots \\ 0 & \dots & \dots & \lambda_p \end{bmatrix}. \tag{32}$$

We also have the following relations.

$$H_p = U H_{pd} U^\dagger, \tag{33}$$

$$(H_p)^{(p-1)} = \left(U H_{pd} U^\dagger\right)^{(p-1)} = U H_{pd}^{(p-1)} U^\dagger, \tag{34}$$

$$e^{H_p} = U e^{H_{pd}} U^\dagger, \tag{35}$$

$$U^\dagger \mathbf{C}_0 = \begin{bmatrix} u_{11}^* \\ u_{12}^* \\ \vdots \\ u_{1p}^* \end{bmatrix}, \tag{36}$$

$$H_p^{(p-1)} \mathbf{C}_0 = U H_{pd}^{(p-1)} U^\dagger \mathbf{C}_0 = \begin{bmatrix} u_{11} & u_{12} & \dots & u_{1p} \\ u_{21} & u_{22} & \dots & u_{2p} \\ \vdots & \vdots & \vdots & \vdots \\ u_{p1} & u_{p2} & \dots & u_{pp} \end{bmatrix} \begin{bmatrix} \lambda_1^{(p-1)} u_{11}^* \\ \lambda_2^{(p-1)} u_{12}^* \\ \vdots \\ \lambda_p^{(p-1)} u_{1p}^* \end{bmatrix} = U \mathbf{Y}, \tag{37}$$

where $\mathbf{Y}$ is given by

$$\mathbf{Y} = \begin{bmatrix} \lambda_1^{(p-1)} u_{11}^* \\ \lambda_2^{(p-1)} u_{12}^* \\ \vdots \\ \lambda_p^{(p-1)} u_{1p}^* \end{bmatrix}. \tag{38}$$

Since $U$ is unitary

$$\left\| H_p^{(p-1)} \mathbf{C}_0 \right\| = \|U\mathbf{Y}\| = \|\mathbf{Y}\| = \sqrt{{\lambda_1}^{2(p-1)} |u_{11}|^2 + {\lambda_2}^{2(p-1)} |u_{12}|^2 + \cdots + {\lambda_p}^{2(p-1)} |u_{1p}|^2}. \tag{39}$$

Thus the error criterion becomes

$$\epsilon = \left[ \frac{t_{\max}^{(p-1)}}{\hbar (p-1)!} \|\mathbf{Y}\| \right]^2. \tag{40}$$

Hence we get the final expression for the maximum time step as

$$t_{\max} = \hbar \left( \epsilon \left[ \frac{(p-1)!}{\|\mathbf{Y}\|} \right]^2 \right)^{\frac{1}{2(p-1)}}. \tag{41}$$

The above expression for $t_{\max}$ is exact within the tridiagonal approximation. Before we proceed further, we need certain clarifications. We first note that the approximant for $\mathbf{C}(t)$ defined below is a $p$ term series.

$$\mathbf{C}(t) \simeq \sum_{k=0}^{(p-1)} \frac{(-it/\hbar)^k}{k!} \{H_p\}^k \mathbf{C}_0. \tag{42}$$

The $p$th term of the above series is the term

$$\mathbf{C}(t)_p = \frac{(-it/\hbar)^{(p-1)}}{(p-1)!} \{H_p\}^{(p-1)} \mathbf{C}_0. \tag{43}$$

Let us denote the approximant for $\mathbf{C}(t)$ minus the last term $\mathbf{C}(t)_p$ by $\mathbf{A}$

$$\mathbf{A} = \sum_{k=0}^{(p-2)} \frac{(-it/\hbar)^k}{k!} \{H_p\}^k \mathbf{C}_0. \tag{44}$$

For a *convergent series approximation*, the norm of the last term of the series must be made small when compared to the norm of the sum of the previous $(p-1)$ terms of the approximant for $\mathbf{C}(t)$. Hence the criterion

$$\left\| \mathbf{C}(t)_p \right\|^2 \simeq \epsilon \tag{45}$$

must be replaced by the correct criterion

$$\left( \frac{\|\mathbf{C}(t)_p\|}{\|\mathbf{A}\|} \right)^2 \simeq \epsilon. \tag{46}$$

However for real time evolution since $H_p$ is Hermitian, $e^{-\frac{itH_p}{\hbar}}$ is unitary. Hence we get

$$\|\mathbf{A}\| = \left\| \sum_{k=0}^{(p-2)} \frac{(-it)^k}{k!} \{H_p\}^k \mathbf{C}_0 \right\| \simeq \left\| \sum_{k=0}^{\infty} \frac{(-it)^k}{k!} \{H_p\}^k \mathbf{C}_0 \right\| = \left\| e^{-\frac{itH_p}{\hbar}} \mathbf{C}_0 \right\| = 1. \tag{47}$$

Thus for real time propagation, the error criterion does not need any modification. But if the propagation time is purely imaginary, say $t = -i\tau$, where $\tau$ is real then $e^{-\frac{itH_p}{\hbar}}$ is no longer unitary. In this case $H_p = U H_{pd} U^\dagger$ implies the following relation

$$e^{-\frac{itH_p}{\hbar}} = e^{-\frac{\tau H_p}{\hbar}} = U e^{-\frac{\tau H_{pd}}{\hbar}} U^\dagger = U \begin{bmatrix} e^{-\tau\lambda_1/\hbar} & 0 & \dots & 0 \\ 0 & e^{-\tau\lambda_1/\hbar} & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots \\ 0 & \dots & \dots & e^{-\tau\lambda_1/\hbar} \end{bmatrix} U^\dagger. \tag{48}$$

Hence we have

$$\|\mathbf{A}\| \simeq \left\| e^{-\frac{itH_p}{\hbar}} \mathbf{C}_0 \right\| = \left\| U e^{-\frac{\tau H_{pd}}{\hbar}} U^\dagger \mathbf{C}_0 \right\| = \left\| e^{-\frac{\tau H_{pd}}{\hbar}} U^\dagger \mathbf{C}_0 \right\| \simeq \sqrt{e^{-2\tau\lambda_1/\hbar}|u_{11}|^2 + e^{-2\tau\lambda_2/\hbar}|u_{12}|^2 + \cdots + e^{-2\tau\lambda_p/\hbar}|u_{1p}|^2}. \tag{49}$$

Hence instead of the error criterion for the real time step,

$$t_{\max} = \hbar \left( \epsilon \left[ \frac{(p-1)!}{\|\mathbf{Y}\|} \right]^2 \right)^{\frac{1}{2(p-1)}} \tag{50}$$

we have the following modified criterion for the imaginary time step

$$\tau = \hbar \left( \epsilon \left[ \frac{(p-1)!\|\mathbf{A}\|}{\|\mathbf{Y}\|} \right]^2 \right)^{\frac{1}{2(p-1)}}. \tag{51}$$

The time step for real time is an explicit expression. On the other hand, for the purely imaginary time, the quantity $\|\mathbf{A}\|$ too has a dependence on $\tau$. Hence in this case, the maximum time step, $\tau$, has to be found by an iterative method like the Newton–Raphson scheme. The iterations however converge very rapidly. Finally let all the eigenvalues and the time step satisfy the following property.

$$0 < |\lambda_i|\tau/\hbar \ll 1; \quad i = 1, 2, \dots, p. \tag{52}$$

Then we have

$$e^{-2\tau|\lambda_i|/\hbar} \simeq 1; \quad i = 1, 2, \dots, p. \tag{53}$$

As a result

$$\|\mathbf{A}\| \simeq \sqrt{e^{-2\tau\lambda_1}|u_{11}|^2 + e^{-2\tau\lambda_2}|u_{12}|^2 + \cdots + e^{-2\tau\lambda_p}|u_{1p}|^2} \simeq \sqrt{|u_{11}|^2 + |u_{12}|^2 + \cdots + |u_{1p}|^2} = 1. \tag{54}$$

Thus in this case, the criteria for the real and imaginary time steps are the same.

## 4. Bounds on the time step

The time steps that we have derived are *exact* within the tridiagonal approximation. They involve the eigenvalues and first component of each eigenvector of the tridiagonal matrix $H_p$. This is unlike the one given by Park and Light which involves just the off diagonal elements $\beta_1, \beta_2, \dots, \beta_p$. Before we compare these two time steps we examine the applicability of the classical Gershgorin theorem [8,9] for further simplification of the estimates we have derived.

**Gershgorin's theorem.** *Every eigenvalue $\lambda$ of the n by n matrix B with elements $b_{ij}$ lies in at least one of the circles*

$$|z - b_{ii}| \leqslant \sum_{j \neq i}^{n} |b_{ij}| \quad (i = 1, 2, \dots, n). \tag{55}$$

Let us denote by $X_k$ the sum of the magnitudes of all the elements of the $k$th row of the tridiagonal matrix $H_p$. Let $X$ be the maximum of the numbers $X_1, X_2, \ldots, X_p$.

$$X_k = |\alpha_k| + |\beta_k| + |\beta_{k-1}|, \tag{56}$$

$$X = \mathrm{Max}(X_1, X_2, \ldots, X_p). \tag{57}$$

Then Gershgorin's theorem implies that

$$|\lambda|_{\max} \leqslant X. \tag{58}$$

For the real time case, the expression for the maximum time step is given by

$$t_{\max} = \hbar\left(\epsilon\left[\frac{(p-1)!}{\|\mathbf{Y}\|}\right]^2\right)^{\frac{1}{2(p-1)}}, \tag{59}$$

where $\|\mathbf{Y}\|$ is given by

$$\|\mathbf{Y}\| = \sqrt{{\lambda_1}^{2(p-1)}|u_{11}|^2 + {\lambda_2}^{2(p-1)}|u_{12}|^2 + \cdots + {\lambda_p}^{2(p-1)}|u_{1p}|^2}. \tag{60}$$

In order to get a practical bound for the real time case, we need approximations for the quantity $\|\mathbf{Y}\|$. We notice that the following inequality is true

$$\lambda_1^{2(p-1)}|u_{11}|^2 + \lambda_2^{2(p-1)}|u_{12}|^2 + \cdots + \lambda_p^{2(p-1)}|u_{1p}|^2 \leqslant \lambda_{\max}^{2(p-1)}\left[|u_{11}|^2 + |u_{12}|^2 + \cdots + |u_{1p}|^2\right] = \lambda_{\max}^{2(p-1)} \leqslant X^{2(p-1)}. \tag{61}$$

Also,

$$\lambda_1^{2(p-1)}|u_{11}|^2 + \lambda_2^{2(p-1)}|u_{12}|^2 + \cdots + \lambda_p^{2(p-1)}|u_{1p}|^2 \geqslant \lambda_{\min}^{2(p-1)}\left[|u_{11}|^2 + |u_{12}|^2 + \cdots + |u_{1p}|^2\right] = \lambda_{\min}^{2(p-1)}. \tag{62}$$

Thus we see that

$$\hbar\left(\epsilon\left[\frac{(p-1)!}{\lambda_{\min}^{(p-1)}}\right]^2\right)^{\frac{1}{2(p-1)}} \geqslant t_{\max} \geqslant \hbar\left(\epsilon\left[\frac{(p-1)!}{\lambda_{\max}^{(p-1)}}\right]^2\right)^{\frac{1}{2(p-1)}} \geqslant \hbar\left(\epsilon\left[\frac{(p-1)!}{X^{(p-1)}}\right]^2\right)^{\frac{1}{2(p-1)}}. \tag{63}$$

Thus Gershgorin's theorem enables us to get a lower bound for the maximum time step for the real time case, purely in terms of the row sums of the tridiagonal matrix. This is not useful from a practical point of view since we need as large a time step as possible, compatible with the error criterion. However, Eq. (63) indicates that the maximum allowed real time step is sandwiched between two bounds involving the minimum and maximum eigenvalues of the tridiagonal matrix.

## 5. Wave packet in harmonic oscillator potential

We present two examples below. In the first example, we handle a very simple test problem, a Gaussian wave packet oscillating in a simple harmonic potential $kx^2/2$. With $x_0$ as the initial displacement, the initial wave packet and the exact probability density are given by [10]

$$\psi(x,0) = \frac{\alpha^{1/2}}{\pi^{1/4}} e^{-\alpha^2(x-x_0)^2/2}, \tag{64}$$

$$\left\|\psi(x,t)\right\|^2 = \frac{\alpha}{\sqrt{\pi}} e^{-\alpha^2[x - x_0\cos(\omega_c t)]^2}, \tag{65}$$

$$\alpha = [mk/\hbar^2]^{1/4}; \qquad \omega_c = (k/m)^{1/2}. \tag{66}$$

The Hamiltonian was constructed by a discrete variable representation (DVR) scheme [11]. The basis functions are given by

$$\phi_j(x) = \left[2/(b-a)\right]^{1/2} \sin\left[j\pi(x-a)/(b-x)\right]; \quad j = 1, 2, \ldots, (N-1);\ x \in [a,b]. \tag{67}$$

For a symmetric choice of width $a$ on either side, the basis functions and the grid points are given by

$$\phi_j(x) = (1/a)^{1/2} \sin\left[j\pi(x+a)/(2a)\right], \tag{68}$$

$$x_i = -a + (2a/N)i. \tag{69}$$

With $N$ set to 120, a 119 by 119 DVR Hamiltonian matrix was chosen. The subspace dimension, $p$, was chosen as 22. Other values were tested and good results were obtained. The error tolerance parameter $\epsilon$ was taken as $10^{-14}$ as an extreme application of the error bound. The wave packet was evolved for 50 fs and Table 1 gives the comparison of the probability densities at various positions calculated by the Lanczos method using the Park and Light time step and the time step indicated by the present method. In order to evolve the wave packet for 50 fs = 2067 au, Park and Light time step method needs 6 iterations with time steps 392.86, 392.85,

Table 1
Results of harmonic oscillator test problem with a 119 by 119 DVR Hamiltonian

| $x$ | Prob. density (Exact) | Prob. density (Park) | Prob. density I | Prob. density II |
|---|---|---|---|---|
| 12 | 0.931823044974D−02 | 0.93182512853665D−02 | 0.93182241817208D−02 | 0.93182091762780D−02 |
| 23 | 0.890725084140D−02 | 0.89072658257629D−02 | 0.89072403438205D−02 | 0.89072288859009D−02 |
| 45 | 0.667370901062D−02 | 0.66737593537479D−02 | 0.66737029563028D−02 | 0.66737104609287D−02 |
| 65 | 0.407997717359D−02 | 0.40799511575690D−02 | 0.40799868240726D−02 | 0.40799918957181D−02 |

Parameter values are given in atomic units. Wave number $= (1/\lambda) = 60$; semi system width (a) $= 520$; $x_0 = 10$; $p = 22$; $\epsilon = 10^{-14}$; time $= 50$ fs.

392.85, 393.12, 393.29 and 392.84 au. The present method employing the time steps given by Eqs. (59), (60), needs 4 iterations with time steps 545.34, 559.68, 564.25 and 588.64 au. The time step of the present method is about 1.4 times the time step of the Park and Light method, thus giving more efficient time evolution. These results are presented in the third column of Table 1. It must be noted that the DVR Hamiltonian we employ has an inherent error essentially stemming from the various approximations while constructing the matrix elements of the Hamiltonian operator [11]. The quantities obtained by time evolution by employing this approximant to the exact Hamiltonian operator will also have a corresponding error component. Hence it is appropriate to solve the evolution equation given by Eq. (5) by direct diagonalization and the probability density obtained via this process is presented as "Exact" in the first column of Table 1 instead of the analytical solution provided by Eq. (65). A comparison of the second and third columns of Table 1 also reveals the values obtained by using the present time step expression is slightly superior.

We have examined the possibility of using the time steps employing the largest and smallest eigenvalues. Obviously the use of the *largest* eigenvalue will yield a *smaller* time step. The use of the *smallest* eigenvalue may yield an unduly large time step. Hence, we take the *geometric mean* $\lambda_{\text{geo}}$ of all the eigenvalues $\lambda$ which satisfy the criterion $|\lambda/\lambda_{\max}| \geqslant 2 \times 10^{-16}$. The number $2 \times 10^{-16}$ corresponds to the machine precision in double precision accuracy. This $\lambda_{\text{geo}}$ is used to calculate the maximum time step instead of either $\lambda_{\max}$ or $\lambda_{\min}$ in Eq. (63). The geometric mean of eigenvalues bears resemblance to Park and Light's parameter $(\prod_k^{p-1} \beta_k)^{1/(p-1)}$. However, our use of the geometric mean is based on the rigorous analysis presented above. This results in a time step that is mostly larger than the previous time steps. For a 50 ps time evolution, only two 2 iterations are needed with time steps 2014.52 and 167.72 au. These results are presented in the last column of Table 1. These results show that the choice of the geometric mean of the eigenvalues for calculating a good approximation of $\|\mathbf{Y}\|$ holds promise.

## 6. Reactive scattering in Eckart barrier

In the next example, we see that the situation is reversed. That is, the present method indicates a *shorter* time step compared to the one given by Park and Light. The problem considered is the wave packet evolution for an Eckart potential barrier. The potential is given by

$$V(x) = V_0 \operatorname{sech}^2(x); \qquad V_0 = 0.0114 \text{ au}. \tag{70}$$

Using the theory of Miller, Schwartz and Tromp [12], the exact quantal reaction rate constant $k$ is given by the time integral of the flux auto correlation function $c(\tau)$ as [13]

$$kQ = \lim_{t\to\infty} \operatorname{Re} \int_0^t c(\tau)\, \mathrm{d}\tau, \tag{71}$$

$$c(\tau) = \frac{(-\hbar^2)}{2m^2} \operatorname{Tr}\big\{\big[(\partial/\partial s)\delta(s) + \delta(s)\partial/\partial s\big]U(-t_c^*)\big\}\big\{\big[(\partial/\partial s)\delta(s) + \delta(s)\partial/\partial s\big]U(t_c)\big\}, \tag{72}$$

$$U(t_c) = e^{-iHt_c/\hbar}; \qquad t_c = \tau - i\hbar\beta/2; \qquad \beta = 1/(k_B T). \tag{73}$$

Here $Q$ is the translational partition function per unit length for reactants. $U(t_c)$ is the propagator for the complex time and $T$ is the temperature. Here $Tr$ denotes the quantum mechanical trace and $s$ represents the reaction coordinate, with $s = 0$ defining the transition surface separating the reactants and products. In a discrete real-valued, zero-order orthonormal basis, the correlation function $c(\tau)$ and the matrix element $U_{mn}$ are given by

$$c(\tau) = (-1/2)(\hbar/m)^2 \sum_{i,j,k=1}^{N} \phi_i(0)\phi_j'(0)U_{jk}(-t_c^*)\big[\phi_k(0)\phi_l'(0) - \phi_l(0)\phi_k'(0)\big]U_{li}(t_c), \tag{74}$$

$$U_{mn} = \langle \phi_m | e^{-iHt_c/\hbar} | \phi_n \rangle. \tag{75}$$

We use the DVR Hamiltonian and the basis functions $\phi_j(x)$ defined earlier. With $N = 40$ (39 basis functions), each basis function is first evolved through a purely imaginary time $(-i\hbar\beta/2)$ and then evolved over a real time of 40 fs in steps of 1 fs. Thus $e^{-iHt_c/\hbar}|\phi_n\rangle$

Table 2
Comparison of maximum and minimum time steps for the Park and Light and present schemes

| | Real time step | | Imag. time step | |
|---|---|---|---|---|
| | Park and Light | Present | Park and Light | Present |
| Maximum | 3972 | 450.64 | 3614 | 227.08 |
| Minimum | 2087 | 124.08 | 2177 | 121.92 |
| $N_R$ | 1560 | 1560 | | |
| $N_I$ | | | 39 | 116 |

$N_R$ is the total number of iterations to evolve all 39 the basis functions through a period of 40 fs. $N_I$ is the number of iterations to evolve all the 39 basis functions through an imaginary time, $(-i\hbar\beta/2)$ where $T = 1/k_B\beta = 500$ K.

and hence $U_{mn}$ are calculated at intervals of 1 fs. Then by using Eq. (75), we evaluate $c(\tau)$ and the final required quantity $kQ$. The area under the curve of the plot of $c(\tau)$ against time gives the value $kQ$.

For $T = 500$ K, the correct reported values of $c(0)$ and $kQ$ are 1.51 ps$^{-2}$ and $9.8 \times 10^{-3}$ ps$^{-1}$, respectively [13]. The calculated $c(0)$ and $kQ$ values are 1.501275 ps$^{-2}$ and the $9.832 \times 10^{-3}$ ps$^{-1}$, respectively, employing either the Park and Light or the present time step criteria. The time steps are however different. For the real times of 1 fs time interval, the maximum and minimum time steps by the Park and Light scheme are 3972 and 2087 au. The corresponding maximum and minimum time steps are 450.64 and 124.08 au for the present method. Thus the time steps for the present method are much smaller. However since each 1 fs time interval correspond to 41.34 au, the minimum time intervals of both the time step methods (2087 and 124.08 au) exceed this. Hence the total number of iterations for real time evolution is the same for both the methods. On the other hand, the magnitude of the imaginary time is 315.77 au. The maximum and minimum time steps by the Park and Light method are 3614 and 2177 au, respectively. The corresponding quantities for the present method are 227.08 and 121.92 au, respectively. The Park and Light time step criterion needs 39 iterations to evolve all the basis functions while the present method requires 116 iterations to perform the same evolution. Thus for both the real and imaginary time propagation, the Park and Light time step criterion yields time steps that are much *larger* than the exact time step admissible under the tridiagonal approximation. Table 2 summarizes the above results.

Some final comments regarding the maximum time steps via the Park and Light method and the present method are needed. The starting point for both the methods is the norm of the last vector $H_p^{p-1}\mathbf{c}(0)$ in the finite sequence of linearly independent vectors $\{\mathbf{c}(0), H_p\mathbf{c}(0), H_p^2\mathbf{c}(0), \ldots, H_p^{p-1}\mathbf{c}(0)\}$. Thus, the strict validity of both the time step bounds is guaranteed in the space spanned by the vectors $\{\mathbf{c}(0), H_p\mathbf{c}(0), H_p^2\mathbf{c}(0), \ldots, H_p^{p-1}\mathbf{c}(0)\}$. On the other hand, the solution of the time evolution equation

$$\frac{\partial \mathbf{C}}{\partial t} = (-i/\hbar) H_p \mathbf{C}$$

is obtained by resorting to the diagonalization of $H_p$. That is, the solution vector $C(t)$ is sought in the basis consisting of the eigenvectors of $H_p$. This basis, namely, the eigenvectors of $H_p$ and the second basis, made up of the vectors $\{\mathbf{c}(0), H_p\mathbf{c}(0), H_p^2\mathbf{c}(0), \ldots, H_p^{p-1}\mathbf{c}(0)\}$ are *not* the same. Hence we recognize that the time step bounds of both Park and Light and the present methods are in some sense guide line values rather than strict bounds when the solution procedure adopted is diagonalization. This helps to understand why one does not observe serious errors due to numerical instability during the imaginary time propagation when the exact time step bounds indicated by us are exceeded by the use of Park and Light prescription. The maximum and minimum time steps through the Park and Light scheme are 3614 and 2177 au, respectively. These values are much higher than the corresponding values, 227.08 and 121.92 au, which are the exact bounds within the basis set consisting of the vectors $\{\mathbf{c}(0), H_p\mathbf{c}(0), H_p^2\mathbf{c}(0), \ldots, H_p^{p-1}\mathbf{c}(0)\}$.

## 7. Conclusions

We have presented a comprehensive derivation of the upper and lower bounds for the time steps, for the unitary quantum time evolution using the Lanczos method. The time step expressions we have derived are exact within the basis set consisting of the vectors $\{\mathbf{c}(0), H_p\mathbf{c}(0), H_p^2\mathbf{c}(0), \ldots, H_p^{p-1}\mathbf{c}(0)\}$. The values of the time steps obtained via these expressions differ significantly from the ones obtained by using the corresponding expression of Park and Light. The judicious use of the geometric mean of the eigenvalues yields a new time step which may turn out to be very economical. This point warrants further numerical experimentation for a variety of problems, and it will be addressed in a future work.

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