Classical numerical integrators for wave-packet dynamics

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(Received 8 September 1995; accepted 2 November 1995)

Gray and Verosky have recently studied the reformulation of the N-state matrix representation of the time-dependent Schrödinger equation as an N-degrees of freedom classical Hamiltonian system. This opens the possibility of using in quantum dynamics numerical integrators originally devised for classical mechanics. When the Hamiltonian matrix is time-dependent, Gray and Verosky suggest the use of a Magnus approximation before reducing the quantum system to its classical format. We show that Magnus approximations are not necessary and suggest an alternative technique. With the new technique it is possible to obtain simple integrators of arbitrarily high orders of accuracy that can be applied to all matrix Schrödinger problems with a, possibly time-dependent, real Hamiltonian matrix. The connection between the new approach and high-order split-operator methods is studied. © *1996 American Institute of Physics.* [S0021-9606(96)01306-7]

I. INTRODUCTION

Gray and Verosky[1] have recently studied in detail the reformulation of the N state matrix representation of the time-dependent Schrödinger equation as an N-degree of freedom classical Hamiltonian system. This reformulation has several interesting implications; for instance, it makes possible to use in quantum dynamics numerical integrators originally devised for classical mechanics, including symplectic integrators.[2] However, when the Hamiltonian matrix in the quantum problem is time-dependent, the resulting classical Hamiltonian system is not separated and explicit symplectic integrators cannot be directly applied. Gray and Verosky suggest the use a Magnus approximation[3–5] before rewriting the quantum system in its classical format. In this paper, we show that Magnus approximations are not really necessary and suggest an alternative technique. With the new technique it is possible to obtain simple integrators of arbitrarily high orders of accuracy that can be applied to all matrix Schrödinger problems with a, possibly time-dependent, real Hamiltonian matrix.

Section II describes the new technique. Section III is devoted to a numerical illustration concerning a diatomic molecule in a strong laser field. The new technique is found to vastly outperform the Magnus approximation approach. There is a connection between the techniques suggested here and (high-order) split-operator integrators;[6,7] this connection is explored in Sec. IV.

II. SYMPLECTIC PARTITIONED RUNGE–KUTTA METHODS FOR SCHRÖDINGER EQUATIONS

In matrix form, the time-dependent Schrödinger equation is

$$i\hbar \frac{d}{dt}\mathbf{c}(t)=\mathbf{H}(t)\mathbf{c}(t), \tag{1}$$

where $\mathbf{c}(t)$ is a column vector with N complex components and the Hamiltonian $\mathbf{H}(t)$ is an $N\times N$ Hermitian matrix. Equation (1) arises when describing a system with N interacting states, with $\mathbf{c}(t)$ representing the coefficients in a basis set expansion. Also (1) results from discretization of the spatial variables in the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t}\psi(t)=\hat{H}(t)\psi(t), \tag{2}$$

[$\hat{H}(t)$ is the Hamiltonian operator]; then the entries of $\mathbf{c}(t)$ are values of the wave function $\psi(t)$ at the nodes of the spatial grid. Gray and Verosky[1] (see also references therein) introduce two real N component vectors

$$\mathbf{p}(t)=\sqrt{2\hbar}\ \mathrm{Im}\ \mathbf{c}(t), \quad \mathbf{q}(t)=\sqrt{2\hbar}\ \mathrm{Re}\ \mathbf{c}(t) \tag{3}$$

and point out that they obey the classical Hamilton equations of motion[8]

$$\frac{d}{dt}\mathbf{p}=-\frac{\partial H}{\partial \mathbf{q}}, \quad \frac{d}{dt}\mathbf{q}=+\frac{\partial H}{\partial \mathbf{p}} \tag{4}$$

corresponding to the real-valued Hamiltonian function

$$H(\mathbf{p},\mathbf{q},t)=\frac{1}{2\hbar}(\mathbf{q}^T-i\mathbf{p}^T)\mathbf{H}(t)(\mathbf{q}+i\mathbf{p}). \tag{5}$$

In this way the quantum problem (1) may be seen as a particular instance of the classical equations (4).

The main feature of any classical system of the form (4) is[8] that its solutions preserve the Poincaré invariants, or, in more up-to-date (but equivalent) terms, that its solution operator is symplectic. When classical systems of the form (4) are numerically integrated, it is often advisable to use a symplectic integrator,[2] i.e., an integrator that also preserves the Poincaré invariants. Most symplectic integrators are implicit and require, at each time step, the solution of a system of algebraic equations. Explicit symplectic integrators are possible for separated Hamiltonian functions H of the form

$$H(\mathbf{p},\mathbf{q},t)=H_1(\mathbf{p})+H_2(\mathbf{q},t). \tag{6}$$

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 0021-9606/96/104(6)/2349/7/$10.00

This format is quite common for classical systems, but, as discussed below, does not arise when studying time-dependent quantum systems. The simplest examples of explicit, symplectic numerical methods for separated Hamiltonian systems (6) are given by partitioned Runge–Kutta (PRK) methods.[2,9–11] Each explicit, symplectic PRK method is specified by two arrays of real coefficients

$$(b_1,b_2,\ldots,b_s)[B_1,B_2,\ldots,B_s]. \tag{7}$$

If the steplength is k, then a step $t_n \mapsto t_{n+1}=t_n+k$ of the PRK method (7) applied to the system with Hamiltonian (6) is given by

$$\mathbf{Q}_{n,0}=\mathbf{q}_n,$$

$$\mathbf{P}_{n,1}=\mathbf{p}_n,$$

for $i=1,\ldots,s$,

$$\begin{aligned}\mathbf{Q}_{n,i}&=\mathbf{Q}_{n,i-1}+kB_i\frac{\partial H_1}{\partial \mathbf{p}}(\mathbf{P}_{n,i}),\\ \mathbf{P}_{n,i+1}&=\mathbf{P}_{n,i}-kb_i\frac{\partial H_2}{\partial \mathbf{q}}(\mathbf{Q}_{n,i},t_n+C_ik),\end{aligned} \tag{8}$$

$$\mathbf{q}_{n+1}=\mathbf{Q}_{n,s},$$

$$\mathbf{p}_{n+1}=\mathbf{P}_{n,s+1}.$$

Here $\mathbf{Q}_{n,i},\mathbf{P}_{n,i}$ are intermediate stages and

$$C_i=B_1+B_2+\cdots+B_i.$$

The whole algorithm only requires the storage of two N-dimensional real vectors (one for the p variables and one for the q variables). The coefficients in (7) are chosen to increase the order of accuracy r defined by $\mathbf{p}_n=\mathbf{p}(t_n)+O(h^r)$, $\mathbf{q}_n=\mathbf{q}(t_n)+O(h^r)$ and to reduce the size of the error constants implied in the $O(h^r)$ symbol. By increasing s, and therefore the work per step, it is possible to reach arbitrarily high orders of accuracy. The intermediate stages $\mathbf{Q}_{n,i}$ may be viewed as approximations to $\mathbf{q}(t_n+C_ik)$ and the stages $\mathbf{P}_{n,i}$ may be viewed as approximations to $\mathbf{p}(t_n+c_ik)$ with

$$c_i=b_1+b_2+\cdots+b_{i-1}$$

($c_1=0$). However the stages should not be used to output solution values at off-step points t_n+C_ik, t_n+c_ik, because the approximations they provide are of an order of accuracy lower than the order r achieved at the step-points t_n.

Gray and Verosky[1] integrate the Schrödinger equation (1) by first rewriting it, via (3), in the classical form (4), (5) and then integrating the classical equations with a symplectic integrator. They focus on the case where the matrix $\mathbf{H}$ in (1) is real valued. Then the classical Hamiltonian function (5) is

$$H(\mathbf{p},\mathbf{q},t)=\frac{1}{2\hbar}[\mathbf{p}^T\mathbf{H}(t)\mathbf{p}+\mathbf{q}^T\mathbf{H}(t)\mathbf{q}]. \tag{9}$$

If, furthermore, $\mathbf{H}$ does not depend on t explicitly, then the classical Hamiltonian function (9) possesses the separated format (6) with

$$H_1=\frac{1}{2\hbar}\mathbf{p}^T\mathbf{H}\mathbf{p},\quad H_2=\frac{1}{2\hbar}\mathbf{q}^T\mathbf{H}\mathbf{q}$$

and, as pointed out above, explicit symplectic integrators are applicable. In particular the application of (7)–(8) leads to the algorithm

$$\mathbf{Q}_{n,0}=\mathbf{q}_n,$$

$$\mathbf{P}_{n,1}=\mathbf{p}_n,$$

for $i=1,\ldots,s$,

$$\begin{aligned}\mathbf{Q}_{n,i}&=\mathbf{Q}_{n,i-1}+\frac{kB_i}{\hbar}\mathbf{H}\mathbf{P}_{n,i},\\ \mathbf{P}_{n,i+1}&=\mathbf{P}_{n,i}-\frac{kb_i}{\hbar}\mathbf{H}\mathbf{Q}_{n,i},\end{aligned} \tag{10}$$

$$\mathbf{q}_{n+1}=\mathbf{Q}_{n,s},$$

$$\mathbf{p}_{n+1}=\mathbf{P}_{n,s+1}.$$

This provides a simple integrator for (1) ($\mathbf{H}$ real and time independent) that, per step, only requires the computation of $2s$ N-dimensional real matrix-vector products $\mathbf{HP}_{n,i},\mathbf{HQ}_{n,i}$. This algorithm is particularly appealing[1] when the problem is so big that memory limitations matter or when the problem is so small that programming a more efficient, but more complicated, algorithm is not worthwhile. Also note that (10) is well suited to vector machines. In most other circumstances, for time-independent $\mathbf{H}$, more sophisticated propagators such as the short iterative Lanczos algorithm and especially the Chebyshev propagator should be used.[12]

When $\mathbf{H}$ is real valued but depends explicitly on t, the classical Hamiltonian function H in (9) is not separated and the PRK algorithm (8) is not directly applicable. To circumvent this difficulty, Gray and Verosky use the Magnus approximation,[3–5] i.e., for $t_n\leq t\leq t_{n+1}$, they replace (1) by a problem

$$i\hbar\frac{d}{dt}\bar{\mathbf{c}}(t)=\bar{\mathbf{H}}_n^{(\rho)}\bar{\mathbf{c}}(t), \tag{11}$$

where the time-independent matrix $\bar{\mathbf{H}}_n^{(\rho)}$ (the Magnus approximation of order $\rho\geq 2$) is such that the solution operator $\exp[-i(t_{n-1}-t_n)\bar{\mathbf{H}}_n^{(\rho)}/\hbar]$ of (11) approximates the true solution operator $\Phi(t_{n-1},t_n)$ of (1) [$\Phi(t_{n-1},t_n)$ is the complex $N\times N$ matrix that maps $\mathbf{c}(t_n)$ into $\mathbf{c}(t_{n-1})$]. For the Magnus approximation of order ρ,

$$\exp[-i(t_{n+1}-t_n)\bar{\mathbf{H}}_n^{(\rho)}/\hbar]=\Phi(t_{n-1},t_n)+O(k^{\rho+1}).$$

The lowest ($\rho=2$) Magnus approximation is simply given by the average

$$\bar{\mathbf{H}}_n^{(\rho)}=\frac{1}{k}\int_{t_n}^{t_{n+1}}\mathbf{H}(t)dt; \tag{12}$$

higher-order Magnus approximations involve the computation of integrals of commutators of $\mathbf{H}(t)$ and may be rather messy in realistic problems. By applying the PRK method (7) to the classical Hamiltonian system arising from (11), Gray and Verosky obtain the integrator

$$\mathbf{Q}_{n,0}=\mathbf{q}_n,$$

$$\mathbf{P}_{n,1}=\mathbf{p}_n,$$

for $i=1,\ldots,s$,

$$\mathbf{Q}_{n,i}=\mathbf{Q}_{n,i-1}+\frac{kB_i}{\hbar}\bar{\mathbf{H}}_n^{(\rho)}\mathbf{P}_{n,i},$$

$$\mathbf{P}_{n,i-1}=\mathbf{P}_{n,i}-\frac{kb_i}{\hbar}\bar{\mathbf{H}}_n^{(\rho)}\mathbf{Q}_{n,i}, \tag{13}$$

$$\mathbf{q}n+1=\bar{Q}n.s,$$

$$\mathbf{p}_{n+1}=\mathbf{P}_{n,s+1},$$

which reduces to (10) in the particular case where $\mathbf{H}$ is time independent. Clearly (13) has order of accuracy $\min(r,\rho)$, where r is the order of (7) and ρ the order of the Magnus approximation being used. If, as in Ref. 1, one chooses for simplicity $\rho=2$, then the order of accuracy of (13) is at most 2, even if a high-order PRK formula is being used. In fact, Table I in Ref. 1 reports results corresponding to PRK methods with $r=2$ and $r=3$ which show that, when k is reduced, the errors behave as $O(k^2)$. Numerical results reported in Ref. 1 show that (13) may be competitive with other techniques for the integration of (1) with time-dependent $\mathbf{H}$. Note that in this case the Chebyshev method is not applicable (but see Refs. 13 and 14).

Here we suggest an alternative to (13) that does not require Magnus approximations and retains the order of accuracy r of the underlying PRK method (7).

We consider the time-dependent Hamiltonian function with $(N+1)$-degrees of freedom given by

$$\tilde{H}(\mathbf{p},\mathbf{q};\mathcal{T},\mathcal{Q};t)=\frac{1}{2\hbar}[\mathbf{p}^T\mathbf{H}(\mathcal{T})\mathbf{p}+\mathbf{q}^T\mathbf{H}(t)\mathbf{q}]-\mathcal{Q}, \tag{14}$$

where $\mathcal{T}$ is a momentum like variable and $\mathcal{Q}$ is the conjugate coordinate. The equation of motion of $\mathcal{T}$ is

$$\frac{d\mathcal{T}}{dt}=-\frac{\partial\tilde{H}}{\partial\mathcal{Q}}=1,$$

which shows that, if initially $\mathcal{T}(t_0)=t_0$, then $\mathcal{T}\equiv t$. Therefore, for the $\mathbf{p}$ and $\mathbf{q}$ variables, the equations of motion arising from (14) are the same as the equations of motion arising from (9). The advantage is that (14) is separated, with

$$\tilde{H}=\tilde{H}_1+\tilde{H}_2,$$

$$\tilde{H}_1=\frac{1}{2\hbar}\mathbf{p}^T\mathbf{H}(\mathcal{T})\mathbf{p},\quad \tilde{H}_2=\frac{1}{2\hbar}\mathbf{q}^T\mathbf{H}(t)-\mathbf{q}-\mathcal{Q},$$

and (8) is directly applicable. The use of (8) gives equations for advancing not only $\mathbf{p},\mathbf{q}$, but also $\mathcal{T}$ and $\mathcal{Q}$. The equations for $\mathcal{Q}$ can be safely discarded because the variable $\mathcal{Q}$ does not feature in the equations for the variables $\mathbf{p}$ and $\mathbf{q}$ we are interested in. The equations for $\mathcal{T}$ simply say that the intermediate stage values of $\mathcal{T}$ coincide with corresponding values of t. After dropping the $\mathcal{T}$ and $\mathcal{Q}$ variables/equations, we obtain the following algorithm

$$\mathbf{Q}_{n,0}=\mathbf{q}_n,$$

$$\mathbf{P}_{n,1}=\mathbf{p}_n,$$

for $i=1,\ldots,s$,

$$\mathbf{Q}_{n,i}=\mathbf{Q}_{n,i-1}+\frac{kB_i}{\hbar}\mathbf{H}(t_n+c_ik)\mathbf{P}_{n,i},$$

$$\mathbf{P}_{n,i-1}=\mathbf{P}_{n,i}-\frac{kb_i}{\hbar}\mathbf{H}(t_n+C_ik)\mathbf{Q}_{n,i}, \tag{15}$$

$$\mathbf{q}_{n+1}=\mathbf{Q}_{n,s},$$

$$\mathbf{p}_{n+1}=\mathbf{P}_{n,s+1}.$$

This integrator, which as (13) reduces to (10) if $\mathbf{H}$ is time independent, does not require computing averages of $\mathbf{H}$ or higer-order Magnus approximations. The storage is limited to $2N$-dimensional real vectors and, per step, $2s$ N-dimensional real matrix-vector products are needed.

The idea of introducing an "artificial" time $\mathcal{T}$ to reduce nonautonomous problems to autonomous problems is of course well known in mathematics and classical mechanics, see, e.g., Ref. 2. A similar device has recently been used[13,14] in the quantum context; however in these references the artificial time plays the role of a new spatial independent variable in the Schrödinger equation, while here the artificial time is a new dependent variable.

III. NUMERICAL RESULTS

As in Ref. 1 we use as a test problem the Walker and Preston[15] model of a diatomic molecule in a laser field. The Hamiltonian operator $\hat{H}$ in (2) is (assuming units for which $\hbar=1$)

$$\hat{H}=-\frac{1}{2\mu}\frac{\partial^2}{\partial x^2}+V(x)+Ax\cos(\omega t), \tag{16}$$

with $V(x)$ a Morse potential $V(x)=D(1-\exp(-\alpha x))^2$. For an HF molecule, $D=0.2251$ a.u., $\alpha=1.1741$ a.u., $\mu=1745$ a.u. As in Ref. 1, we take $A=0.011\,025$ a.u. and $\omega=0.017\,87$ a.u. The initial condition corresponds to the HF molecule in its ground Morse oscillator vibrational state. The wave packet $\psi(x,t)$ is replaced by its amplitudes $c_j(t)=\psi(x_j,t)(\Delta x)^{1/2}$ at N uniformly spaced points $x_j=x_0+j\Delta x$. We use $N=64$, $x_0=-0.8$ a.u. and $\Delta x=0.08$ a.u., which guarantees that the amplitudes C_0 and C_N are negligible and periodic boundary conditions may be assumed. This yields a matrix equation of the form (1) with

$$\mathbf{H}(t)=\mathbf{H}_{\text{mol}}+A\mathbf{X}\cos(\omega t)=\mathbf{T}+\mathbf{V}+A\mathbf{X}\cos(\omega t), \tag{17}$$

where $\mathbf{V}$ and $\mathbf{X}$ are diagonal matrices with diagonal entries $V(x_j)$ and x_j respectively and $\mathbf{T}$ is the kinetic energy matrix. The application of the algorithms (13) or (15) requires products of known vectors $\mathbf{P}$ or $\mathbf{Q}$ with the matrices $\mathbf{V}$, $\mathbf{X}$, and $\mathbf{T}$. For the diagonal matrices $\mathbf{V}$ and $\mathbf{X}$, each such a product requires N real multiplications. The products $\mathbf{TP}$ or $\mathbf{TQ}$ are cheaply evaluated by FFT techniques; each of them requires a real→complex FFT transform, N multiplications in transformed space and a complex→real inverse FFT transform.

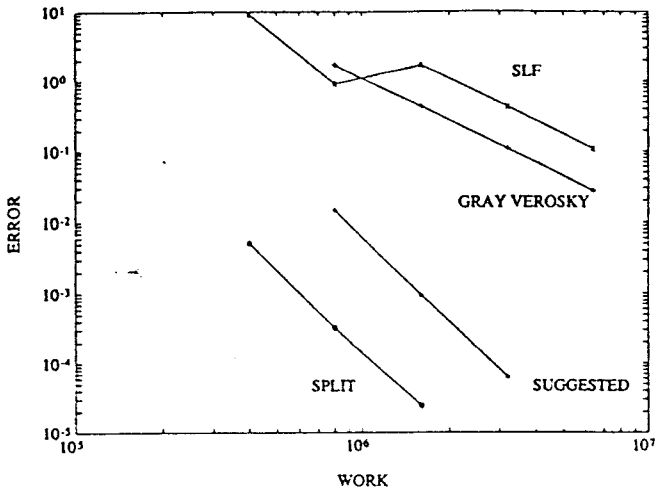

FIG. 1. Efficiency comparison. The horizontal axis corresponds to work measured by number of pairs of FFT/inverse FFT transforms on N-dimensional real vectors. The vertical axis is the percent error in the molecular energy at the final time $100[E_{\text{numerical}}(1000\tau)-E_{\text{exact}}(1000\tau)]/E_{\text{exact}}(1000\tau)$. The Gray–Verosky algorithm (13) is run with steplengths $k=\pi/100$, $\pi/200$, $\pi/400$, $\pi/800$ ($\pi/50$ is unstable). The algorithm (15) suggested here is run with steplengths $k=\pi/100$, $\pi/200$, $\pi/400$ ($\pi/50$ is unstable). The SLF method has $k=\pi/200,\ldots,\pi/3200$ ($\pi/100$ is unstable). For the split-operator algorithm (25), $k=\pi/50$, $\pi/100$, $\pi/200$ ($\pi/25$ is unstable).

In our experiments we use a PRK method (7) of order $r=4$ with five stages, $s=5$. It is possible, in a unique way, to construct a fourth-order PRK method with only four stages, but the resulting formula, discovered independently by Forest/Ruth[16] and Candy/Rozmus,[17] has very large error constants and is very inefficient.[2] The method used here has been suggested by McLachlan[18] and uses the extra stage so as to reduce the error constant. The coefficients are given by

$$b_1=\tfrac{6}{11},\quad b_2=\tfrac{1}{2}-b_1,\quad b_3=b_2,\quad b_4=b_3,$$
$$b_5=0,\quad B_1=\frac{642+\sqrt{471}}{3924},\quad B_2=\tfrac{121}{3924}(12-\sqrt{471}),$$
$$B_3=1-2(B_1+B_2),\qquad (18)$$
$$B_4=B_2,\quad B_5=B_1.$$

Note the symmetry in the coefficients that implies the time reversibility of the algorithm. Note also that the last b_i vanishes, leading to computational savings. First of all, there is no need to compute $\bar{H}_n^{\rho}\mathbf{Q}_{n,5}$ in (13) or $H(t_n+c_5k)\mathbf{Q}_{n,5}$ in (15). Furthermore, $\mathbf{P}_{n+1,1}=\mathbf{p}_{n+1}=\mathbf{P}_{n,6}=\mathbf{P}_{n,5}$ and thus in (15) the first product $\mathbf{H}(t_{n+1})\mathbf{P}_{n+1,1}$ in the i-loop of the step $t_{n+1}\to t_{n+2}$ coincides with the last product $\mathbf{H}(t_n+c_5k)\mathbf{P}_{n,5}$ found in the preceding step (FSAL, first same as last, property[2]). When using (13) the first product $\bar{H}_{n+1}^{\rho}\mathbf{P}_{n+1,1}$ does not quite coincide with the last $\bar{H}_n^{\rho}\mathbf{P}_{n,5}$, because the Magnus matrix $\bar{H}$ changes with n; however this change does not affect the matrix $\mathbf{T}$ that is the only requiring FFTs. Therefore, with the coefficients (18), the algorithms (13) and (15) only require eight FFT/inverse FFT pairs per step (four to advance the $\mathbf{p}$'s and four to advance the $\mathbf{q}$'s).

We have implemented the Gray–Verosky algorithm (13), with the weights (18) and the lowest-order Magnus approximation (12) and also the suggested algorithm (15) with the same weights. A natural time unit for the problem is $\tau=2\pi/\omega=351.6$ a.u. or 8.505 fs. The integration is carried out for $0\leq t\leq 1000\tau$ and the accuracy is measured by monitoring the errors in the molecule energy $E(t)=\langle c(t)|T+V|c(t)\rangle$ at the final time 1000τ. Figure 1 is an efficiency plot; the novel algorithm (15), that is simpler than the Magnus algorithm (13), is also much more efficient, yielding errors three to five orders of magnitude smaller for a given computational cost. The Magnus algorithm only achieves second-order accuracy in spite of using the fourth-order coefficients (18). Higher-order Magnus approximations could of course be employed, but they would be messy in realistic problems. Also note that no matter how large ρ is chosen, there is an error associated with the replacement of (1) by the Magnus system (11) that is required by (13). For this reasons, we believe that (15) is to be preferred to (13) in all cases. We emphasize that our technique is not confined to the weights (18) but rather any explicit, symplectic PRK can be used. The literature[2,18] contains examples of coefficients of orders up to 8.

As a further reference integrator, we have used the symplectic leapfrog (SLF) scheme.[1] This is given by (13) with $\rho=2$, $s=2$ and the weights

$$b_1=1,\quad b_2=0,\quad B_1=B_2=\tfrac{1}{2}. \qquad (19)$$

Since $b_s=0$, an FSAL property holds and, per step 2 transform pairs are required. After comparing in Fig. 1 the SLF results with those of the algorithms that use the coefficients (18) the advantages of high-order coefficients are clear.

Gray and Verosky[1] also report results for this test problem when using the short iterative Lanczos algorithm and the split operator algorithm. Those results compare unfavorably with the results obtained with the algorithm suggested here.

IV. PRK METHODS AND SPLIT-OPERATOR INTEGRATORS

There is a useful relation between the methods considered above and split-operator integrators. Let us consider a system of (real or complex) differential equations

$$\frac{d\mathbf{y}}{dt}=\mathbf{f}(\mathbf{y})+\mathbf{g}(\mathbf{y}), \qquad (20)$$

whose right-hand side has been written as the sum of two contributions. Assume that the partial systems

$$\frac{d\mathbf{y}}{dt}=\mathbf{f}(\mathbf{y}),\quad \frac{d\mathbf{y}}{dt}=\mathbf{g}(\mathbf{y}), \qquad (21)$$

can be explicitly integrated, so that their corresponding solution operators $\exp(t\mathbf{f})$ and $\exp(t\mathbf{g})$ are known. Then, given the array of coefficients (7), we can construct the following split-operator integrator for (20)

$$\mathbf{y}_{n+1}=\exp(b_s k\mathbf{f})\exp(B_s k\mathbf{g})\cdots\exp(b_1 k\mathbf{f})\exp(B_1 k\mathbf{g})\mathbf{y}_n. \qquad (22)$$

where, over a step of length k, the simultaneous evolution under f and g that takes place in (20) is replaced by successive evolutions under g and f over substeps of lengths $B_1k, b_1k, \ldots, B_sk, b_sk$. If f and g are linear, $f(y)=Ly$, $g(y)=My$, (L and M are matrices), then

$$\exp(t\mathrm{f})=I+tL+\frac{t^2}{2}L^2+\cdots,$$

$$\exp(t\mathrm{g})=I+tM+\frac{t^2}{2}M^2+\cdots,$$

so that the evolution operators $\exp(t\mathrm{f})$ and $\exp(t\mathrm{g})$ are *bona fide* exponentials. For nonlinear f and g, the interpretation of solution operators as exponentials is via Lie operators[2] and is not needed to understand what follows. By using the BCH (Baker–Campbell–Hausdorff) formula,[2,18] the exponentials in (22) can be combined into a single exponential

$$\mathrm{y}_{n+1}=\exp(\alpha k\mathrm{f}+\beta k\mathrm{g}+\gamma k^2[\mathrm{f},\mathrm{g}]+\delta k^3[\mathrm{f},[\mathrm{f},\mathrm{g}]]+\epsilon k^3[\mathrm{g},[\mathrm{g},\mathrm{f}]]+\cdots)\mathrm{y}_n, \tag{23}$$

where $\alpha,\beta,\gamma,\delta,\epsilon$ are polynomials in the coefficients b_i, B_i (for instance $\alpha=b_1+\cdots+b_s$, $\beta=B_1+\cdots+B_s$) and square brackets denote the Lie–Poisson bracket, i.e., $[\mathrm{f},\mathrm{g}]$ is the vector-valued function of y whose jth component is

$$\sum_i\left(\mathrm{f}_i\frac{\partial \mathrm{g}_j}{\partial \mathrm{y}_i}-\mathrm{g}_i\frac{\partial \mathrm{f}_j}{\partial \mathrm{y}_i}\right)$$

(subscripts denote components) [if f and g are linear and given by matrices L and M, then their bracket is also linear and given by the negative $-(LM-ML)$ of the commutator of the matrices]. By comparing (23) with the true evolution

$$\mathrm{y}(t_{n+1})=\exp(k(\mathrm{f}+\mathrm{g}))\mathrm{y}(t_n),$$

we see that (22) is of order $r\geq 1$ if $\alpha=\beta=1$ (i.e., $\Sigma_i b_i=\Sigma_i B_i=1$), of order $r\geq 2$ if in addition $\gamma=0$, of order $r\geq 3$ if furthermore $\delta=\epsilon=0,\ldots$. In this way, given a target order of accuracy r, it is possible to derive a system of polynomial equations that the coefficients b_i and B_i have to satisfy for (22) to be of order r regardless of the specific f and g. The coefficients in (18) have $r=4$; the coefficients in (19) have $r=2$ and identify the splitting integrator associated with Strang's name[19] and often used in applications.[12] A very important recent contribution to the theory of splitting methods is Ref. 18.

The system (20) has been assumed to be autonomous (i.e., f and g do not explicitly depend on t). Nonautonomous systems may be integrated with the integrator (22): All that is required is to first rewrite the system one wishes to integrate in autonomous form by considering $\mathcal{T}\equiv t$ as a new dependent variable to be appended to y. This will be illustrated in the examples that follow.

As a first example, consider an N-degrees of freedom time-dependent Hamiltonian system (4) with a separated Hamiltonian function (6). We wish to integrate this system with the method (22) for a given choice of coefficients (7). To rewrite the system in autonomous Hamiltonian form we introduce the $(N+1)$-degrees of freedom time-independent Hamiltonian function

$$H^*(\mathrm{p},\mathrm{q};\mathcal{P},\mathcal{T}_q)=H(\mathrm{p},\mathrm{q},\mathcal{T}_q)+\mathcal{P}=[H_1(\mathrm{p})+\mathcal{P}]+[H_2(\mathrm{q},\mathcal{T}_q)]=H_1^*+H_2^*, \tag{24}$$

where $\mathcal{T}_q$ is a coordinatelike variable (hence the subscript q) and $\mathcal{P}$ is the canonically conjugate momentum. In the equations of motion,

$$\frac{d\mathcal{T}_q}{dt}=\frac{\partial H^*}{\partial \mathcal{P}}=1,$$

so that $\mathcal{T}_q\equiv t$, provided that initially $\mathcal{T}_q(t_0)=t_0$. The Hamiltonian system associated with (24) can be decomposed as

$$\frac{d}{dt}\begin{bmatrix}\mathrm{p}\\ \mathrm{q}\\ \mathcal{P}\\ \mathcal{T}_q\end{bmatrix}=\begin{bmatrix}-\dfrac{\partial H_2^*}{\partial \mathrm{q}}\\ 0\\ -\dfrac{\partial H_2^*}{\partial \mathcal{T}_q}\\ 0\end{bmatrix}+\begin{bmatrix}0\\ \dfrac{\partial H_1^*}{\partial \mathrm{p}}\\ 0\\ \dfrac{\partial H_1^*}{\partial \mathcal{P}}\end{bmatrix}.$$

The partial systems (21) are given by

$$\frac{d}{dt}\begin{bmatrix}\mathrm{p}\\ \mathrm{q}\\ \mathcal{P}\\ \mathcal{T}_q\end{bmatrix}=\begin{bmatrix}-\dfrac{\partial H_2^*}{\partial \mathrm{q}}\\ 0\\ -\dfrac{\partial H_2^*}{\partial \mathcal{T}_q}\\ 0\end{bmatrix}$$

and

$$\frac{d}{dt}\begin{bmatrix}\mathrm{p}\\ \mathrm{q}\\ \mathcal{P}\\ \mathcal{T}_q\end{bmatrix}=\begin{bmatrix}0\\ \dfrac{\partial H_1^*}{\partial \mathrm{p}}\\ 0\\ \dfrac{\partial H_1^*}{\partial \mathcal{P}}\end{bmatrix},$$

and they are also Hamiltonian: they are the systems associated with the Hamiltonians H_2^* and H_1^* respectively. In the evolution under H_1^* the momentumlike variables p and $\mathcal{P}$ remain constant and q and $\mathcal{T}_q$ vary linearly with t; such an evolution is sometimes called a shear flow. In the evolution under H_2^* the coordinatelike variables q and $\mathcal{T}_q$ remain constant and p and $\mathcal{P}$ vary linearly. Once the solution of the partial systems has been found in closed form we may apply (22). After dropping the auxiliary variables $\mathcal{T}_q$ and $\mathcal{P}$, the result is none other than the algorithm (8). In this way, each split-operator integrator induces a PRK method for separated (possibly nonautonomous) classical Hamiltonian systems.

As a second example, consider now the application of (22) to the Hamiltonian system with time-dependent Hamiltonian function (14) with $N+1$-degrees of freedom [this

Hamiltonian arose when bringing (9) into separated form]. We now introduce the time-independent Hamiltonian with $N+2$-degrees of freedom

$$\tilde{H}^*(\mathbf{p},\mathbf{q},\mathcal{I},\mathcal{Q},\mathcal{I}_q)=\left[\frac{1}{2\hbar}\,\mathbf{p}^T\mathbf{H}(\mathcal{I})\mathbf{p}+\mathcal{I}\right]+\left[\frac{1}{2\hbar}\,\mathbf{q}^T\mathbf{H}(\mathcal{I}_q)\mathbf{q}-\mathcal{Q}\right],$$

which is divided into a part independent of the coordinates and a part independent of the momenta, so that the partial systems are readily integrable in terms of shear flows. By applying (22) to this splitting of the differential system, we obtain the algorithm (15). Therefore rewriting the quantum system (1) (H real) in classical form (4) and introducing the auxiliary (14) can be seen as devices whereby *any* quantum system with time-dependent Hamiltonian can be brought within the scope of *any* chosen split-operator integrator (22), possibly of high order.

In some cases the given quantum system (1) is already amenable to the application of splitting integrators; this happens, for instance, for grid representations of the Schrödinger equation (2) with an operator of the form [cf. (16)]

$$\hat{H}=-\frac{1}{2\mu}\frac{\partial^2}{\partial x^2}+V(x,t).$$

In these cases, given a set of coefficients (7), one may either go to the classical Hamiltonian system and use the PRK algorithm (15) or apply directly the split-operator scheme (22) to the quantum system (1). The use in quantum problems of the Strang splitting (19) is well known. Higher-order splittings have also been used[6,7] (note that the Ref. 7 uses the terms "symplectic integrator" to refer to split-operator methods for the quantum system, this is at variance with our terminology where symplectic methods are integrators of classical Hamiltonian problems). We illustrated the use of quantum splittings in the particular case of the test example (16) used in Sec. III.

The system (1) with H given by (17) is first rewritten in autonomous form (we assume units for which $\hbar=1$)

$$\frac{d}{dt}\begin{bmatrix}\mathbf{c}\\ \mathcal{I}\end{bmatrix}=\begin{bmatrix}-i\mathbf{H}(\mathcal{I})\mathbf{c}\\ 1\end{bmatrix}$$

and partitioned as

$$\frac{d}{dt}\begin{bmatrix}\mathbf{c}\\ \mathcal{I}\end{bmatrix}=\begin{bmatrix}-i\mathbf{T}\mathbf{c}\\ 1\end{bmatrix}+\begin{bmatrix}-i(\mathbf{V}+A\mathbf{X}\cos(\omega\mathcal{I}))\mathbf{c}\\ 0\end{bmatrix}.$$

Then, (22) is applied and, after elimination of the auxiliary variable $\mathcal{I}$, we obtain the algorithm

$\mathbf{C}_{n,0}=\mathbf{c}_n$,

for $i=1,\ldots,s$,

$$\mathbf{C}_{n,2i-1}=\exp(-iB_ik(\mathbf{V}+A\mathbf{X}\cos(\omega(t_n+c_ik))))\times\mathbf{C}_{n,2i-2},$$

$$\mathbf{C}_{n,2i}=\exp(-ib_ik\mathbf{T})\mathbf{C}_{n,2i-1},$$

$$\mathbf{c}_{n+1}=\mathbf{C}_{n,2s}. \tag{25}$$

This requires the storage of an N-dimensional complex vector; (15) needed two N-dimensional *real* vectors, which is of course equivalent. The matrices $\exp(-iB_ik(\mathbf{V}+A\mathbf{X}\cos(\omega(t_n+c_ik))))$ are diagonal with diagonal entries $\exp(-iB_ik(V(x_j)+Ax_j\cos(\omega(t_n+c_ik))))$ and therefore $\mathbf{C}_{n,2i-1}$ is easily computed. The computation of $\mathbf{C}_{n,2i}$ requires FFT techniques to diagonalize $\exp(-ib_ik\mathbf{T})$. Hence (25) demands, per step, s FFT/inverse FFT pairs on N-dimensional complex vectors. By comparison, (15) requires $2s$ transform pairs but deals with real vectors, so that the cost is equivalent. When $b_s=0$ (FSAL property) there are computational savings: (25) only needs $s-1$ transform pairs.

For the weights (18), we have implemented (25) on the test problem of Sec. III. The results can be seen in Fig. 1. The advantages of splitting the quantum system over going to the classical system [i.e., over using (15)] are obvious. However we emphasize that splitting the quantum system is only possible when the system possesses a particular structure; going to the classical system and applying (15) is always possible provided that the Hamiltonian matrix H is real valued. The superiority of (25), when applicable, over (15) is no doubt due to the following. In (15) the true solution with an exponential-like behavior is approximated by a sequence of shear flows, while in (25) is approximated by a sequence of true quantum solutions.

We finish this section with some observations. The algorithm (25) is unitary: $\mathbf{c}_{n-1}$ has, if round-off is ignored, the same length as $\mathbf{c}_n$. This is because each of the fractional steps multiplies C by a matrix of the form $\exp(-i\mathbf{M})$, where M is a real symmetric matrix. Also, if we recover the real vectors p, q via (3), then (25) implies a symplectic integrator for the classical system. This happens because a unitary linear transformation in N-dimensional complex space is always symplectic when regarded as a transformation of the $2N$-dimensional real space. On the other hand, for (15) the quantity $2\hbar|\mathbf{c}|^2=|\mathbf{p}|^2+|\mathbf{q}|^2$ is not exactly conserved as the simulation proceeds. However, it is well known[2] that symplectic integrators do a very good job at accurately conserving any invariants of motion the system being integrated may have and we do not expect significant changes in the length of c. In Fig. 1, for (15) with the coarsest stepsize $k=\pi/100$, the length of c at the final time 1000τ deviates from the initial length in less than 5×10^{-9} percent. Therefore, in our opinion, the fact that PRK methods are not exactly unitary is not a serious problem.

V. CONCLUSIONS

A technique has been suggested that, in tandem with the reduction to classical Hamiltonian form suggested in Ref. 1, allows the construction of simple integrators of arbitrarily high order applicable to all matrix Schrödinger problems with a real, possibly time-dependent Hamiltonian matrix. Each array of splitting coefficients (7) with order r leads to such a generally applicable Schrödinger integrator of the same order. However, for those Hamiltonians that are di-

rectly amenable to (quantum) splitting, the classical reformulation is not advantageous and one should directly split the quantum problem.

Clearly much additional numerical experimentation is needed before a definite assessment of the merit of the new techniques can be made. In particular a comparison on realistic problems with the approaches in Refs. 13 and 14 should definitely be carried out.

ACKNOWLEDGMENTS

J.M.S.S. has been supported by Grant No. DGICYT PB92-254. We are most thankful to Dr. S. K. Gray for bringing this problem to our attention.

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