Quantum time evolution in time-dependent fields and time-independent reactive-scattering calculations via an efficient Fourier grid preconditioner

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A numerical scheme is suggested for accurate large-scale quantum dynamics simulations. The time-dependent Schrödinger equation with finite time-dependent interaction terms is replaced by an inhomogeneous equation with imaginary boundary operators applied along the time axis. This equation is solved globally for a finite time interval using recent Krylov subspace-based iterative methods that are accelerated by a Fourier grid preconditioner. The same scheme is applied also to time-independent reactive-scattering calculations with absorbing boundary operators where the operation of the Green’s function is carried out by solving an inhomogeneous time-independent equation. The scheme is economic in terms of both memory requirement and computation time. It is especially favorable when high grid densities are required, e.g., for representation of highly oscillatory fields or high-energy wave functions. Illustrative applications are given for representative models of bound and dissociative systems driven by time-dependent pulsed fields, and for time-independent calculations of the cumulative reaction probability for the generic reaction \( H + H_2 \) at high collision energies. © 1995 American Institute of Physics.

I. INTRODUCTION

The quantum dynamics of nuclei on potential energy surfaces provide the most detailed description of chemical reactions. Efficient computational methods for solving the time-dependent Schrödinger equation with scalability to large systems are therefore desired for a rigorous study of chemical reactions. When large molecular systems (\( \geq \) three or four atoms) are studied, the matrix representation of the Hamiltonian is typically too large to be stored and manipulated directly, so that propagation (or iterative) methods that only require successive operations of the Hamiltonian onto a vector must be applied. Among the numerous methods of this type, global polynomial approximations of the time-evolution operator \( \exp(-i\hat{H}t/\hbar) \) have been found to be most stable\textsuperscript{2,3} since the error involved is not accumulated (as is typical for a stepwise integration), but rather is uniformly distributed along the entire time interval and therefore can be reduced \textit{globally} with increasing numerical effort.

When the molecular system is driven by an external time-dependent field (e.g., a laser field) the system’s Hamiltonian is explicitly time-dependent, and the Schrödinger equation reads

\[
i\hbar \frac{\partial}{\partial t} \psi = \hat{H}(t) \psi. \tag{1.1} \]

Historically, global time propagators have not been applied in this case because of the well-known “time-ordering” problem associated with Dyson’s series.\textsuperscript{4,5} Recently,\textsuperscript{6,7} though, it was shown that this problem is avoided when a time coordinate \( (t') \) is added to the system coordinate space.\textsuperscript{8} By applying global polynomial approximations of the exponential time-evolution operator in the \textit{extended} coordinate space, \( \exp[-i(\hat{H}(t') - i\hbar / \partial t') t/\hbar] \), the time-dependent Schrödinger equation with time-dependent Hamiltonians was solved with accuracy and stability that were only reached before for time-independent Hamiltonians.\textsuperscript{9,10} However, for optimal performance, polynomial approximations require “long” recurrences\textsuperscript{2} (successive Hamiltonian operations), and their efficiency decreases whenever the detailed “step-by-step” dynamical evolution is required (e.g., within iterative schemes for optimal laser control of chemical processes\textsuperscript{11}).

In the present work, we suggest a numerical scheme for a global solution of the Schrödinger equation with finite-range time-dependent Hamiltonians that demonstrates stability and exponential convergence, characteristic of global polynomial approximations, and yet enables one to significantly reduce the required numerical effort (by an order of magnitude, for the studied cases). The scheme is based on the reactive-scattering theory for time-dependent Hamiltonians that was introduced in Ref. 12: The time-dependent Schrödinger equation is converted into a boundary-value problem on a finite time interval by adding time-dependent imaginary boundary operators to the Hamiltonian. Practically, the exponential operation in the extended coordinate space, \( \exp[-i(\hat{H}(t') - i\hbar / \partial t') t/\hbar] \) can be replaced by a single operation of the Green’s operator, \( [E + i\hbar / \partial t' - \hat{H}(t') + i\hat{t}(t')]^{-1} \). The latter is most efficiently carried out by solving the following inhomogeneous equation:

\[
\frac{\partial}{\partial t} \psi(t) = \hat{H}(t) \psi(t) - \lambda \psi(t),
\]

where \( \lambda \) is an imaginary boundary parameter.

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The differential operators dominate the spectral range, which provides the full time evolution of the system.

There are numerous advantages in replacing the homogeneous Schrödinger equation [Eq. (1.1)] by the inhomogeneous equation [Eq. (1.2)]. First, one can make use of recent advances in the development of efficient iterative (Krylov-subspace-based) methods for solving non-Hermitian linear systems (see, e.g., Ref. 13). Second, iterative solvers can be significantly accelerated by applying physically motivated preconditioners, which reduce the spectral range of the left-hand-side operator in Eq. (1.2).

An essential part of the iterative solution is the representation (discretization) of the Hamiltonian operation. The Fourier grid method has been shown to be especially suitable for accurate quantum-mechanical calculations because of the balanced representation of coordinate and momentum spaces and the highly efficient transformation [the fast Fourier transform (FFT) algorithm] between them.14,15 Below, we exploit another important advantage of this representation: Since both the local (coordinate-space) and nonlocal (differential) operators are applied in a diagonal form, economic diagonal preconditioners can be applied simultaneously (within a single iteration) in the two spaces, providing remarkable acceleration of the iterative solvers, especially when the differential operators dominate the spectral range of the Hamiltonian (i.e., when a high-density grid is required).

The suggested scheme is not limited, of course, to the extended coordinate space and to time-dependent Hamiltonians. The operation of the Green’s function, i.e., the solution of the corresponding inhomogeneous time-independent equation

$$[E - \hat{H} + i \hat{\epsilon}] \chi = \varphi,$$  

is the main computational task in most stationary reactive-scattering calculations, where \( \hat{\epsilon} \) is a boundary operator that imposes the scattering boundary conditions on a finite configuration space.16-21 As we demonstrate below, the Fourier grid preconditioner provides an efficient way to solve Eq. (1.3) and thus to accelerate standard reactive-scattering calculations.

The outline of this article is as follows. In Sec. II, the inhomogeneous time-dependent equation with imaginary boundary operators is discussed in some detail. Iterative Krylov subspace methods for solving linear systems are briefly reviewed in Sec. III, and the Fourier grid preconditioner is introduced in Sec. IV. Applications for benchmark problems of field-driven bound and dissociative systems are given in Sec. V, where the numerical properties of the presented scheme are demonstrated. In Sec. VI, the Fourier grid preconditioner is applied to a time-independent reactive-scattering calculation of the cumulative reaction probability for a generic hydrogen-exchange reaction at high collision energies. Concluding remarks are given in Sec. VII.

**II. THE INHOMOGENEOUS TIME-DEPENDENT SCHRODINGER EQUATION**

A key step in obtaining global solutions of the time-dependent Schrödinger equation is the conversion of the first-order initial-value problem [Eq. (1.1)] into a boundary-value problem on a finite time interval \( t \), where \(-T/2 < t < T/2\).

In the \((t,t')\) propagators,6,7,9 this problem is solved by replacing Eq. (1.1) with a first-order equation in two time variables. An alternative solution is obtained by adding imaginary operators to the Hamiltonian in the extended space, which explicitly impose two boundary conditions. Then, the homogeneous Eq. (1.1) can be replaced by an inhomogeneous equation in a single time variable, whose unique solution satisfies the boundary conditions. This approach was applied in the reactive-scattering formulation for time-dependent Hamiltonians in Ref. 12, and is briefly summarized below.

Without loss of generality, let us consider the case of a one-dimensional system, coupled to a time-dependent field. (The generalization to higher spatial dimensions is straightforward.) The time-dependent Schrödinger equation [Eq. (1.1)] thus reads

$$i\hbar \frac{\partial}{\partial t} \psi(x,t) = \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x,t) \right] \psi(x,t).$$  

We assume a typical situation in which the interaction is composed of a field-free molecular term and a finite time-dependent interaction term, i.e.,

$$V(x,t) = V_M(x) + \mu(x,t),$$

where

$$\mu(x,t) \rightarrow 0 \quad \text{as} \quad t \rightarrow \pm T/2.$$  

For simplicity, we also assume that the molecular system is initially in a stationary state of the field-free Hamiltonian, \( e^{-iE_i \hat{t}} \phi_E(x) \), i.e.,

$$e^{iE_i \hat{t}} \psi(x,t) \rightarrow \phi_E(x) \quad \text{as} \quad t \rightarrow -T/2,$$

where

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V_M(x) \phi_E(x) = E \phi_E(x).$$

Equations (2.1) and (2.3) define a unique time evolution. However, in any global-grid or basis-set representation of functions on the finite interval, inherent boundary conditions are imposed also as \( t \rightarrow T/2 \). For example, when a discrete variable representation (DVR) is used (as in Ref. 12), the sampled functions decay to zero, while the functions are periodic in time if a Fourier grid or basis set is used.5,7,9 In general, a solution of the homogeneous Schrödinger equation [Eq. (2.1)] that satisfies both boundary conditions will not exist.22 However, within a given finite representation, a well-behaved approximation \( \Psi(x,t) \) to the solution \( \psi(x,t) \) can be obtained by imposing explicitly the boundary values in terms of “smooth” imaginary boundary operators.12

$$\epsilon(t) = \epsilon_i(t) + \epsilon_f(t).$$  

(2.4)
\[ \varepsilon_i(t) \to 0 \text{ for all intermediate "physically interesting" times, and imposes the physical initial condition by rising asymptotically as } t \to -T/2. \]  
\[ \varepsilon_i(t) \text{ rises from zero as } t \to T/2, \text{ and smoothly imposes the "artificial" (final) boundary condition.} \]

The inhomogeneous Schrödinger equation that corresponds to Eqs. (2.1) and (2.3) reads

\[
E + \frac{i\hbar}{\partial t} \frac{\partial}{\partial t} + \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} V(x,t) + i\varepsilon(t) \left[ e^{iE/t} \Psi(x,t) \right] = i\varepsilon_i(t) \phi_f(x) + i\varepsilon_f(t) \phi_b(x). \tag{2.5}
\]

Because of the inclusion of the imaginary boundary operator \( \varepsilon_i(t) \), the operator on the left-hand side is regular, and thus the equation has a unique solution. At initial times \( t = -T/2 \), both \( \mu(x,t) \) and \( \varepsilon_i(t) \) vanish. From Eqs. (2.3) and (2.5), it follows that \( \Psi(x,t) \) satisfies the desired initial condition

\[ e^{iE/t} \Psi(x,t) \to \phi_E(x) \text{ as } t \to -T/2. \tag{2.6} \]

At intermediate times, \( \varepsilon_i(t) \) and \( \varepsilon_f(t) \) vanish, so that Eq. (2.5) for \( \Psi(x,t) \) coincides with the homogeneous Schrödinger equation for \( \psi(x,t) \) [Eq. (2.1)]. The error \[ |\Psi(x,t) - \psi(x,t)| \] is therefore significant only at positive asymptotic times where \( \varepsilon_f(t) \) is switched on. Rather than approximating \( \psi(x,t) \), \( \Psi(x,t) \) smoothly approaches the boundary value at \( T/2 \), which is determined by the choice of \( \phi_b(x) \) in Eq. (2.5). For example, in Ref. 12, a DVR with absorbing boundary conditions \( [\phi_b(x) = 0] \) was applied. For this choice, it follows that

\[ e^{iE/t} \Psi(x,t) \to 0 \text{ as } t \to T/2. \tag{2.7} \]

In the present work, we apply the Fourier grid method, which explicitly imposes periodic boundary conditions on the time interval,\(^{14,15}\) and so we set

\[ \phi_b(x) = \phi_f(x), \tag{2.8a} \]

so that the artificial boundary condition is

\[ e^{iE/t} \Psi(x,t) \to \phi_E(x) \text{ as } t \to T/2. \tag{2.8b} \]

Our strategy is to solve the inhomogeneous Eq. (2.5) rather than the homogeneous Eq. (2.1). Equation (2.5) can be rewritten as a standard linear system of the type

\[
\hat{A} \chi(x,t) = \psi(x,t), \tag{2.9}
\]

with a known input function representing the boundary conditions [Eqs. (2.6) and (2.8)]

\[ \psi(x,t) = i\varepsilon(t) \phi_f(x), \tag{2.10} \]

a regular non-Hermitian differential operator

\[
\hat{A} = E - \hat{p}_t - \frac{1}{2m} \hat{p}_x^2 - \hat{V} + i\hat{\varepsilon}
\]

\[
= E + i\hbar \frac{\partial}{\partial t} + \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} V(x,t) + i\varepsilon(t), \tag{2.11}
\]

and an output

\[ \chi(x,t) = e^{iE/t} \Psi(x,t), \tag{2.12} \]

where \( \Psi(x,t) \) approximates the exact time evolution of the physical system, \( \psi(x,t) \).

In the next section, we briefly discuss the recent advances in developing iterative Krylov subspace-based methods to solve non-Hermitian linear systems of the Eq. (2.9) type.

### III. ON KRYLOV SUBSPACE METHODS FOR SOLVING NON-HERMITIAN LINEAR SYSTEMS

When a linear system of the type \( \hat{A} \chi = \phi \) is very large, direct methods for solving the system may exceed the available computer storage or require too much computation time. In this case, iterative methods can be applied to find an approximate solution \( \chi_k \) with a residue \( r_k = \phi - \hat{A} \chi_k \). If \( \hat{A} \) has a structure that makes its operation onto a vector economical, then iterative methods that only demand this operation repeatedly are a preferable choice. Most of today’s best iterative methods belong to the large class of Krylov subspace methods where, at the \( k \)th step, the space of the approximant is spanned by the Krylov subspace

\[ \chi_k - \chi_0 = \underbrace{\mathcal{K}_k(r_0, \hat{A})}_{\text{span} \{ r_0, \hat{A} r_0, \hat{A}^2 r_0, \ldots, \hat{A}^{k-1} r_0 \}}. \tag{3.1} \]

When \( \hat{A} \) is Hermitian, there are two dominant Krylov methods: the Lanczos method\(^{23}\) and the conjugate gradient (CG) method.\(^{24}\) In the Lanczos method, an orthonormal basis for \( \mathcal{K}_k(r_0, \hat{A}) \) is created by using the Gram–Schmidt orthogonalization, which reduces to a three-term recursion. The basis vectors created have to be saved for the final construction of the approximate solution. The Lanczos method makes \( r_k \) orthogonal to \( \mathcal{K}_k(r_0, \hat{A}) \) and therefore minimal in this space. The CG method is a well-established Krylov method with optimal minimization and computational properties for the case that \( \hat{A} \) is Hermitian and positive definite. The fact that the basis vector \( v_{k+1} \) is parallel to the residue \( r_k \) is used to calculate the approximate solution \( \chi_k \) recursively without the need to save the basis vectors as in the original Lanczos case. In the CG method, the norm of \( r_k \) is explicitly minimized.

For non-Hermitian \( \hat{A} \), many attempts have been made to maintain the ideas of the CG and Lanczos methods. While in the Hermitian case the construction of an orthonormal basis for the Krylov space can be reduced to a three-term recursion, this is not the case for non-Hermitian matrices, where the Gram–Schmidt orthogonalization gives rise to long-term recurrences, e.g., by the Arnoldi algorithm.\(^{25}\) In the generalized minimal residual (GMRES) algorithm,\(^{26}\) the Arnoldi process is coupled to a least-squares minimization of the residual norm in every step. The result is a very robust method, but with the drawback of a linear growth in the storage and computational effort with the dimension of the Krylov space, since \( k \)-orthogonal-basis vectors are needed to construct the approximate solution \( \chi_k \).

An ideal solver for the non-Hermitian problem that has a rigorous minimization property and is based on short recurrences is theoretically possible only for a very narrow class of operators, as was shown in Refs. 27 and 28. One is therefore led to consider one of the following strategies:

1. Maintain the Hermitian property by solving the normal equation \( \hat{A}^\dagger \hat{A} \chi = \hat{A}^\dagger \phi \) (see, e.g., Ref. 29).
(2) Try to minimize the cost of GMRES by using restarts, preferably adaptive restarts, or some hybrid-GMRES method using GMRES to gain knowledge of the system, replacing it finally with some optimal polynomial in $\hat{A}$. 

(3) Use short-term recursive methods based on a generalized (complex) inner product without a rigorous residual minimization but with “look-ahead” strategies to avoid possible breakdowns.

In practice, the latter strategy seems to be the most successful for a large class of problems. The CG method is extended to the biconjugate gradient (BCG) method, where two biorthogonal sequences of residuals are created using coupled two-term recurrences. This is guaranteed to work well as long as the method does not break down because of accidental zero coefficients in the algorithm. Conjugate gradient squared (CGS) is an extension of the BCG method in which the symmetry of the bilinear form (constructing the biorthogonal sequences of residuals) is used so that the operation $\hat{A}^\dagger$ on a vector is replaced by an extra operation of $\hat{A}$ in each iteration. When the operation of $\hat{A}$ on a previous residual vector results in its contraction, a double effect is possible when $\hat{A}$ operates twice. However, like the BCG method, CGS does not include any explicit minimization property.

Recently, Freund and Nachtigal introduced the quasiminimal residual (QMR) algorithm. QMR is based on adding a quasiminimization property to the BCG method with an efficient look-ahead version to avoid most breakdowns and loss of orthogonality. This results in smoother convergence behavior and in a “safer” algorithm but also in complicated coding and analysis especially because of the look-ahead algorithm. Freund introduced the transposed free quasiminimal residual (TFQMR) algorithm, where a quasiminimization property is added to the CGS method. An implementation of a look-ahead version for TFQMR is under construction. The quasikernel polynomial formulation of QMR and TFQMR in Refs. 39 and 40 provides a deeper understanding of the Krylov-subspace methods, especially of the quasiminimal-residue algorithms. Upper bounds for the QMR and TFQMR iterates have been derived in Ref. 39, showing that QMR and TFQMR are expected to have a convergence rate similar to that of GMRES.

In the present work, TFQMR from Ref. 38 was used to solve the inhomogeneous linear equations. While the scaling of the number of iterations with the problem was similar to that of GMRES (with no restarts), TFQMR seems to be more promising in studying large systems. Unlike GMRES, it requires only a linear (order-$N$) increase in the storage and algorithm operations with the size of the system, $N$. Thus, the computational task in a single iteration reduces essentially to the operation $\hat{A}$ itself (which, in most current representations, scales as $N \log N \sim N^2$).

**IV. THE FOURIER GRID PRECONDITIONER**

We now focus on the basic operator $\hat{A}$. As an example, we discuss the inhomogeneous time-dependent equation [see Eqs. (2.9)–(2.12)]. The generalization of the following discussion to systems of higher dimensions or to the stationary reactive-scattering case [Eq. (1.3)] is straightforward. Within the Fourier grid method, the operator $\hat{A}$ is grouped into local operators, which are diagonal in time-coordinate $(x,t)$ representation, and differential operators, which are diagonal in the canonically conjugate momentum representation $(p_x,p_t)$. The operation of the local operators, $[E - V(x,t) + i\epsilon(t)]$, onto a function $\chi(x,t)$ is obtained by direct multiplication on a discretized grid:

\[
\begin{align*}
\frac{d}{dt} x_i &= -\frac{L}{2} + (i-1) \frac{L}{N_x}; \quad i = 1, \ldots, N_x, \\
\frac{d}{dt} t_i &= -\frac{T}{2} + (i-1) \frac{T}{N_t}; \quad i = 1, \ldots, N_t.
\end{align*}
\]

(4.1)

The operation of the differential operator, $(-\hat{p}_x - \hat{p}_t^2/2m)$, is obtained by transforming $\chi(x,t)$ to its momentum (energy) representation $\chi(p_x,p_t)$, multiplying it by $(-\hat{p}_x - \hat{p}_t^2/2m)$ on the discretized momentum energy grid:

\[
\begin{align*}
p_{x,i} &= -\frac{\pi \hbar N_x}{L} + (i-1) \frac{2 \pi \hbar}{L}; \quad i = 1, \ldots, N_x, \\
p_{t,i} &= -\frac{\pi \hbar N_t}{T} + (i-1) \frac{2 \pi \hbar}{T}; \quad i = 1, \ldots, N_t,
\end{align*}
\]

(4.2)

and back transforming to coordinate-time representation. The transformations between the discrete $(x,t)$ and $(p_x,p_t)$ representations are most efficiently performed by the FFT algorithm, where periodic boundary conditions are imposed on the intervals

\[-L/2 < x < L/2; \quad -T/2 < t < T/2.\]

Once the operation of $\hat{A}$ has been well defined, it can be used iteratively to generate the Krylov subspace for the approximation solution. However, the iterative solvers can be accelerated by applying preconditioners, i.e., an approximate solution to the equation $\hat{A}_0 \chi(x,t) = \varphi(x,t)$ can be obtained faster by solving $\hat{A}^{-1}_0 \hat{A}_0 \chi(x,t) = \hat{A}^{-1}_0 \varphi(x,t)$. Although the two equations are equivalent, the corresponding finite Krylov subspaces are different, and so are the residual (error) functions obtained in the $k$th iteration. One wishes to choose a preconditioner $\hat{A}_0$ that reduces the number of iterations without increasing significantly the computational cost of a single iteration. To reduce the number of iterations, the preconditioner should approximate $\hat{A}$, so that $\hat{A}_0^{-1} \hat{A} \approx I$ in some sense.

As an approximation to the full dynamical system defined by $\hat{A}$, we chose the free-evolution problem, characterized by $\hat{A}_0$,

\[
\hat{A}_0 = E - \hat{p}_x - \frac{\hat{p}_t^2}{2m} - V_0 + i\epsilon_0,
\]

(4.3)

where the kinetic (differential) terms in $\hat{A}$ [Eq. (2.11)] are included explicitly and the local operators are approximated as constants. This resembles the choice of Zhang and coworkers, who used the kinetic-energy operator as a zero-order Hamiltonian within an interaction picture of the Schrödinger equation. This choice is particularly useful when the Fourier grid method is used to represent the differential operators, as discussed below.
Clearly, \( \hat{A} \approx \hat{A}_0 \) when the kinetic terms dominate its spectral presentation. Physically, this situation is typical of dynamics in highly oscillatory driving fields and/or of high translational energies in the molecular system (highly oscillatory wave functions). The extent to which \( \hat{A}_0 \) approximates \( \hat{A} \) is reflected in the clustering of the spectrum of \( \hat{A}_0^{-1}\hat{A} \) around \((1,0)\) in the complex plane. A typical example for the clustering is presented in Fig. 1 for the driven-oscillator model discussed below.

Within the Fourier grid representation, the “kinetic”-preconditioner operation involves no additional computational effort while the number of iterations is reduced. The kinetic-preconditioned system is defined as

\[
\hat{B}\chi(x,t) = \hat{A}_0^{-1}\chi(x,t),
\]

where

\[
\hat{B} = \hat{A}_0^{-1}\hat{A} = \hat{I} + \hat{A}_0^{-1}(\hat{A} - \hat{A}_0).
\]

The task in operating \( \hat{B} \) on a function \( \chi(x,t) \) is first to multiply the function by the local operator \((\hat{A} - \hat{A}_0)\) on the grid defined in Eq. (4.1), then to transform the result to \((p_x,p_t)\) representation, multiply by the inverse of \( \hat{A}_0 \), \((E - p_x^2/p_t^2/2m + i\epsilon_0 - V_0)^{-1} \), on the grid defined in Eq. (4.2), and transform back to \((x,t)\) representation. Since both the local and the differential operators are diagonal in the corresponding representations, the inverse operation becomes trivial, and the main computational effort reduces to the direct and inverse Fourier transformations, just like when the nonpreconditioned \( \hat{A} \) is applied.

The operator \( \hat{B} \) can be further preconditioned with no significant extra effort by using a standard diagonal preconditioner in the coordinate \((x,t)\) representation. The diagonal preconditioner improves the clustering of the eigenvalues [see, e.g., Fig. 1] when the matrix representation of \( \hat{B} \) is diagonally dominant. The diagonal part of \( \hat{B} \) [Eq. (4.5)] in the \((x,t)\) representation is given by

\[
\text{diag}(\hat{B}) = \hat{I} + \text{diag}(\hat{A}_0^{-1})(\hat{A} - \hat{A}_0),
\]

where \( \text{diag}(\hat{A}_0^{-1}) \) in the coordinate representation is a constant given by the average value of \((E - p_x^2/p_t^2/2m + i\epsilon_0 - V_0)^{-1} \) on the discrete grid [Eq. (4.2)]. The diagonal-preconditioned system is therefore defined as

\[
\hat{C}\chi(x,t) = \text{diag}(\hat{B})^{-1}\hat{A}_0^{-1}\chi(x,t),
\]

where \( \hat{C} \) is explicitly given by

\[
\hat{C} = \text{diag}(\hat{B})^{-1}\hat{B} = [\hat{I} + \text{diag}(\hat{A}_0^{-1})(\hat{A} - \hat{A}_0)]^{-1}[\hat{I} + \hat{A}_0^{-1}(\hat{A} - \hat{A}_0)].
\]

The diagonal-preconditioner operation requires only an extra vector multiplication (which scales as \( N \)) and is thus of negligible extra numerical effort with respect to the operation \( \hat{B} \) (or \( \hat{A} \)) which scales as \( \text{const}\times N \log N \).

![Figure 1](image_url)

**FIG. 1.** (a) Discretized spectrum of the operator \( \hat{A} \) for the pulsed-driven harmonic oscillator model. The model and grid parameters are given in Table I. A matrix representation was obtained by operating \( \hat{A} \) on a basis of unit vectors in the discrete time-coordinate representation, and the eigenvalues were obtained by diagonalization. (b) The spectrum after the kinetic-preconditioner operation (diagonalizing \( \hat{B} \)). (c) The spectrum after the kinetic-preconditioner operation followed by a diagonal preconditioner (diagonalizing \( \hat{C} \)).

**V. APPLICATIONS: TIME EVOLUTION IN TIME-DEPENDENT FIELDS**

**A. Bound systems: A pulsed-driven oscillator**

First, we consider field-induced processes in bound systems. As a representative model, we choose the pulsed-
driven harmonic oscillator.\textsuperscript{9,12,46,47} Since analytical results are available, this model enables a careful study of the properties and performances of the present approach. The potential consists of the field-free harmonic term and a linear coupling term to a time-dependent field

\[
V(x,t) = \frac{m\Omega^2}{2} x^2 + xf(t),
\]  

which is modeled as

\[
f(t) = \lambda e^{-t^2/2\sigma^2} \cos(\omega t),
\]  

where \(\lambda, \omega, \) and \(\sigma\), respectively, characterize the pulse intensity, the carrier frequency, and the width. In the simulations below, the oscillator is assumed to be initially in its ground stationary state so that

\[
E = \frac{1}{2} \hbar \Omega
\]  

and

\[
\phi_{\epsilon}(x) = \left(\frac{m\Omega}{\pi\hbar}\right)^{1/4} e^{-m\Omega x^2/2\hbar}. 
\]  

To impose the boundary conditions on a finite grid \((-T/2 < t < T/2)\), imaginary boundary operators are added to the Hamiltonian,\textsuperscript{12}

\[
\epsilon(t) = \epsilon_i(t) + \epsilon_f(t),
\]

\[
\epsilon_i(t) = \epsilon_{\text{max}} e^{-(t+T/2)^2/2\tau_u},
\]

\[
\epsilon_f(t) = \epsilon_{\text{max}} e^{-(t-T/2)^2/2\tau_u},
\]  

where \(\epsilon_{\text{max}}\) and \(\epsilon_u\) characterize the strength and the relative width, respectively, of the boundary operators.

In Fig. 2(a), a driving pulse is presented as a function of time along with the imaginary boundary functions. The calculated average displacement of the oscillator in phase space \([\langle x(t)\rangle, \langle p_x(t)\rangle]\) following the pulse excitation is plotted in Fig. 2(b) (the model and computational parameters are given in Table I). The time evolution \([\Psi(x,t)]\) was obtained by substituting the interaction term, the boundary operators, and the initial condition [Eqs. (5.1)–(5.5)] into the inhomogeneous Schrödinger equation [Eqs. (2.9)–(2.11)] and solving iteratively the linear system [or its preconditioned versions, Eqs. (4.4) and (4.7)] using the TFQMR algorithm.\textsuperscript{38} The position and momentum expectation values are defined as

\[
\langle x(t_i) \rangle = \frac{1}{N_x} \sum_{j=1}^{N_x} |\Psi(x_j,t_i)|^2 x_j, 
\]

\[
\langle p(x,t_i) \rangle = \frac{1}{N_x} \sum_{j=1}^{N_x} -i\hbar \Psi^*(x_j,t_i) \Psi'(x_j,t_i), 
\]  

where \(\Psi'(x,t)\) is obtained by differentiating \(\Psi(x,t)\) with respect to \(x\) on the Fourier grid. The absolute error in the position and momentum calculations with respect to the exact (analytical) solution is plotted in Fig. 2(c). The error is shown to be uniformly distributed along the physically relevant time interval, which is typical of global propagators. The error at asymptotic times, \(t \to T/2\) is large, illustrating the deviation of the solution of the inhomogeneous equation 

\(\Psi(x_j,t_i)\) from the exact solution, because of the finite-interval representation.

The efficiency of the TFQMR algorithm with a Fourier
grid preconditioner is demonstrated in Fig. 3, comparing its performance to the recent \((t, t')\) Newton–Chebyshev method by Peskin, Kosloff, and Moiseyev. The convergence of the simulation (Fig. 2) with increasing numerical effort is demonstrated by plotting a measure of the global error on the “physically interesting” interval (where the pulse is “on”) versus the number of iterative operations [number of Fourier transformations \((x, t) \rightarrow (p_x, p_t) \rightarrow (x, t)\)]. Like the Newton interpolation scheme, the TFQMR algorithm exhibits exponential convergence. However, TFQMR requires fewer iterations to obtain any given accuracy, where a special acceleration (by an order of magnitude) is obtained when the Fourier grid preconditioner is applied. The latter is consistent with the clustering of the spectrum of the preconditioned system (see Fig. 1). Note that the \((t, t')\) Newton–Chebyshev scheme is far from its optimal performance since the detailed time evolution requires a frequent truncation of the polynomial interpolation, so that only short recurrences \((\approx 20)\) are applied at each time \((t)\) step. This situation is typical in cases where the detailed dynamics is of interest, e.g., in iterative schemes for controlling chemical processes by “tailored” light fields.

Figure 4 demonstrates an increase in the preconditioner efficiency with an increase in the number of sampling points along the time interval. This is a highly desirable feature, since any discrete representation requires increasingly dense grids for higher accuracy. As the grid density \(N_x / N_t\) increases, the discrete spectral range of the operator \(p_t\) increases according to Eq. (4.2). The “bad news” is the overall increase in the spectral range of the basic operation \(\hat{A}\) (or the extended Hamiltonian in the Newton–Chebyshev scheme). The “good news” is that this increase is compensated by a more efficient kinetic preconditioner, since the differential terms become more dominant \((\hat{A} \rightarrow \hat{A}_0)\).

The promising scaling of the number of iterations with the grid density provides an efficient treatment of systems with highly oscillatory fields. In particular, it provides a possible solution to the important problem of dynamics with different time scales, e.g., when a driven field includes a broad envelope and high carrier frequencies.

While the present scheme seems to be accurate as well as economical, it contains nonphysical parameters that may affect the accuracy and/or the required numerical effort and that, in principle, should be optimized. In Fig. 5(a), the “saturated” degree of accuracy is plotted for different parameters of the boundary operators. Accurate results are obtained over four orders of magnitude in \(\epsilon_{\text{max}}\). This high stability is not typical in standard applications of absorbing boundary potentials to the time-independent Schrödinger equation. We attribute this enhanced stability to the fact that the Schrödinger equation is first-order in the time variable and therefore the absorbing boundary does not induce reflections that are typical of the second-order (wave) equation (see Ref. 12 for a more detailed discussion of this issue).

In Fig. 5(b), the sensitivity of the TFQMR iterative solver to the parameters of the Fourier grid preconditioner is illustrated. On a logarithmic scale, the numerical effort associated with obtaining a given global accuracy is only slightly dependent on the choice of \(\epsilon_0\) and \(V_0\) within a broad region. Since \(V_0\) approximates the interaction potential \(V(x, t)\) over the entire grid, a reasonable rule of thumb for its optimal selection is a measure of the effective potential energy during the time evolution, i.e.,

\[V_0 \approx \frac{1}{N_x N_t} \sum_{j=1}^{N_x} \sum_{t_i=1}^{N_t} |\Psi(x_j, t_i)|^2 V(x_j, t_i).\]

Since \(\Psi(x, t)\) is a priori unknown, any educated guess for \(V_0\) could be applied, based on physical approximations or low-accuracy calculations. \(\epsilon_0\) should be chosen to be large enough that the preconditioner \(\hat{A}_0\) is not singular, i.e., larger than the typical spacings in the discrete representation of the kinetic operators, and yet small enough so that it does not
change significantly the spectral range of $\hat{A}_0$, i.e., much smaller than the range of the discrete kinetic spectrum.

**B. Dissociative systems: A nonsymmetric Eckart well**

Dissociative systems are not only more interesting from a practical point of view, since they relate to bond-breaking reactions, but they also provide an extra challenge for stable and accurate quantum-dynamics simulations, since, at least for one coordinate (the reaction coordinate), the exact wave function “stretches” to infinity. A way to overcome this difficulty is to solve the time-dependent Schrödinger equation with absorbing boundary conditions for the scattering coordinate. The circles, squares, and diamonds correspond to $V_0=1.5, 0.5$, and $-0.5$ a.u., respectively.

As a model system for field-induced dissociation, we choose the nonsymmetric Eckart potential well, coupled to a time-dependent field via a local dipole interaction

$$V(x,t) = V_M(x) + \mu(x)f(t).$$

The nonsymmetric Eckart well, plotted in Fig. 6(a), is given by

$$V_M(x) = e^{2\alpha x} \left( \frac{v_0 - v_1}{1 + e^{2\alpha x}} - \frac{(\sqrt{v_0} + \sqrt{v_1})^2}{(1 + e^{2\alpha x})^2} \right),$$

where the dipole interaction is modeled as

$$\mu(x) = \frac{4v_0x}{(e^{\alpha x} + e^{-\alpha x})^2}.$$

The driving field $f(t)$ is given in Eq. (5.2). The initial state was taken as the ground state of the field-free Hamiltonian [see Fig. 6(a)], which was obtained numerically by solving

$$\left[ \frac{\hat{p}^2}{2m} + V_M(x) \right] \phi_E(x) = E \phi_E(x),$$

and the ground-state energy is

$$E = -0.6007035 \text{ a.u.}$$

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As before, the interaction terms, the initial condition, and the boundary operators [Eq. (5.5)] were substituted in the inhomogeneous Schrödinger equation [Eqs. (2.9)–(2.12)], and the equation was solved using preconditioned TFQMR to obtain the time evolution of the dissociating system. A contour plot of the probability density evolution $|\Psi(x,t)|^2$ is given in Fig. 6(b) (the computational parameters are summarized in Table II).

A detailed description of the dissociation dynamics as plotted in Fig. 6(b) requires a linear increase in the grid size $L$ with the sampled time interval $T$ due to the asymptotic free evolution. To decrease $L$, we apply imaginary coordinate-dependent operators as $x \to \pm L/2$, which absorb outgoing flux at the grid boundaries. The effect is demonstrated in Fig. 7, where a snapshot of the probability density at $t=5\pi$ a.u. is plotted. Figures 7(a) and 7(b) correspond to a time evolution on a truncated grid (see Table II) where the wave function is strongly distorted near the grid boundary $x \to -L/2$. When imaginary boundary operators are added to the Hamiltonian [Fig. 7(c)],

$$\hat{\epsilon}(x) = \hat{\epsilon}_R(x) + \hat{\epsilon}_L(x),$$

$$\hat{\epsilon}_R(x) = \epsilon_{max} e^{-(x+L/2)^2/L^2},$$

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the wave function decays to zero as $x \to -L/2$, while the interior part is recovered and approximates the correct solution.

Note that by using the reactive-scattering formulation of Ref. 12, one can obtain the entire time evolution (for asymptotic $x$ and $t$), although a finite-grid representation is used. The asymptotic evolution is fully determined by the scattering matrix elements in the extended $(x,t)$ space, which are readily obtained from the solution of the inhomogeneous equation on the grid, $\Psi(x,t)$.12

Also note in Figs. 7(a) and 7(b) that the addition of $\hat{\epsilon}(x)$ to the Hamiltonian does not involve a significant increase in the numerical effort when the preconditioned TFQMR is used. The $(t,t')$ Newton–Chebyshev scheme, which is far more expensive before imaginary boundaries are applied, would require a significant additional numerical effort when the spectral domain of the Hamiltonian expands to the complex plane due to the inclusion of the imaginary boundary operators.

VI. APPLICATIONS: REACTIVE SCATTERING

The Fourier grid preconditioner is readily applicable also to stationary (time-independent) scattering calculations involving time-independent Hamiltonians. The main computational task in calculating state-to-state, partial-state-resolved, or cumulative reaction probabilities is the evaluation of the Green’s operation on a finite grid in coordinate space, where the finite-grid boundaries are imposed, e.g., in terms of imaginary boundary operators. The Green’s operator is defined as

$$\hat{G}(E) = \left[\hat{H} + i\hat{\epsilon}\right]^{-1},$$

where $\hat{H}$ is the molecular time-independent Hamiltonian and $\hat{\epsilon} = \hat{\epsilon}_r + \hat{\epsilon}_p$

includes the boundary operators in the reactants $r$ and products $p$ regions.

A realization of the Green’s operator enables direct calculations of the cumulative reaction probability $N(E)$, avoiding the need to perform state-to-state calculations. Among the several methods suggested in the past few years, we have chosen that of Manthe and Miller,19 which expressed $N(E)$ as a trace of a low-rank Hermitian operator,

$$N(E) = \text{tr}[\hat{P}(E)],$$

where

$$\hat{P}(E) = 4\hat{\epsilon}_r^{1/2}\hat{G}(E)\hat{\epsilon}_p\hat{G}^*(E)\hat{\epsilon}_r^{1/2}.$$  

The trace can be most efficiently evaluated in this case by constructing a Krylov-basis representation of $\hat{P}(E)$, using the Lanczos algorithm (with or without full orthogonalization). For an initial normalized vector in coordinate space, $|v_1\rangle$, a sequence of orthonormal-basis vectors $\{|v_k\rangle\}$ is constructed recursively as

$$|v_k\rangle = \frac{1}{C_k} \left(1 - \sum_{j=1}^{k-1} |v_j\rangle\langle v_j|\right)\hat{P}|v_{k-1}\rangle.$$  

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<th>Fig.</th>
<th>$\lambda$</th>
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<th>$\omega$</th>
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<td>0.05</td>
<td>1.5, 0.5, −0.5</td>
<td>1–10</td>
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TABLE II. Parameters for the dissipative unsymmetric Eckart model, $\hbar=m=1$ (all in a.u.).
and the process can be stopped when \(N(E)\) converges within a certain tolerance. Each iteration of the operator \(\hat{P}(E)\) involves two successive Green’s operations and thus two iterative solutions of a linear system, as follows. First, a vector \(|u\rangle\) is obtained by
\[
[E - \hat{H} - i\hat{\epsilon}]|u\rangle = \epsilon_{\text{max}}^{(1/2)}|v_{k-1}\rangle;
\] (6.7)
then \(|w\rangle\) is obtained by
\[
[E - \hat{H} + i\hat{\epsilon}]|w\rangle = \epsilon_{\text{min}}^{(1/2)}|u\rangle;
\] (6.8) finally, the operation of \(\hat{P}(E)\) is obtained by
\[
\hat{P}(E)|v_{k-1}\rangle = 4\epsilon_{\text{max}}^{(1/2)}|w\rangle.
\] (6.9)

**A. Cumulative reaction probabilities for the collinear \(H+H_2\) reaction**

As a model system, we choose the collinear \(H+H_2\) reaction in the bond-length coordinates \((x, y)\), with the LSTH potential energy surface \(^{52}\) (applying a “cutoff” energy of 8.5 eV),
\[
\hat{H} = -\frac{\hbar^2}{m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} - \frac{\partial}{\partial x}\frac{\partial}{\partial y}\right) + V_{\text{LSTH}}(x,y),
\] (6.10)
on a finite grid
\[
x_i = L_0 + (i - 1) \frac{L_1 - L_0}{N_x}; \quad i = 1,...,N_x,
\] (6.11)
\[
y_i = L_0 + (i - 1) \frac{L_1 - L_0}{N_y}; \quad i = 1,...,N_y.
\] (6.11)

Note that the kinetic-coupling term (the mixed second derivative) induces no extra complications when the Fourier grid method is used because of the diagonal representation of the differential operators.

To impose the boundary conditions, the following boundary operators were applied along the nonsymmetric stretch (the reaction) coordinate, \(Q(x,y) = (x-y)/\sqrt{2}\),
\[
\epsilon_p(x,y) = \epsilon_{\text{max}}\epsilon_{\text{env}}\left[(Q(x,y) - Q(L_1,L_0))/2\right]^2(\epsilon_{\text{env}}(Q(L_1,L_0) - Q(L_1,L_1))]
\] (6.12)
\[
\epsilon_x(x,y) = \epsilon_{\text{max}}\epsilon_{\text{vib}}\left[(Q(x,y) - Q(L_0,L_1))/2\right]^2(\epsilon_{\text{vib}}(Q(L_0,L_0) - Q(L_0,L_1))]
\] (6.12)

To calculate \(N(E)\), Eqs. (6.5) and (6.6) were iterated starting from a uniform vector \(|v_{1}\rangle\), until convergence of the trace within an absolute error of \(10^{-3}\). In each iteration, the operation \(\hat{P}(E)\) was applied according to Eqs. (6.7)–(6.9), with \(\hat{H}\) and \(\hat{\epsilon}\) from Eqs. (6.10)–(6.12). Each linear system (Eqs. (6.7 and 6.8)) was solved iteratively using Fourier grid preconditioned TFQMR \(^{38}\) (see Sec. IV) with a tolerance of \(10^{-6}\). The results are plotted in Fig. 8. The dots correspond to converged values for the computational parameters in Table III within the tolerance of the iterative solution. The relative error in the calculated \(N(E)\), estimated according to the sensitivity of the result to the choice of the absorbing potentials, is 2% for most energies. However, a larger error is associated with the results at the threshold energies (the vibrational levels of \(H_2\), as marked on the plot), where larger grids are required for higher accuracy.

In Fig. 9, the gain in using the Fourier grid preconditioner is demonstrated for the energy \(E = 4\hbar\omega\) (four times the reaction barrier height). The principal trend that was ob-

**FIG. 7.** Snapshot of the dissociating wave function \(|\Psi(x,t=5\pi)|^2\). The solid lines correspond to an accurate result (obtained on a larger grid) and the dashed lines correspond to an approximate calculation on a truncated grid. Each plot was converged to within an absolute accuracy of \(10^{-3}\), and the corresponding number of iterations is marked on the plot. (a) A Newton–Chebyshev propagation (Ref. 11). (b) TFQMR with a Fourier grid preconditioner. (c) TFQMR with a Fourier grid preconditioner and imaginary coordinate-dependent operators \(\hat{\epsilon}(x)\).
well as for a global solution of the time-dependent Schrödinger equation with time-dependent Hamiltonians (involving the Green’s operator) as well as for a global solution of the time-dependent Schrödinger equation with time-dependent Hamiltonians (involving the Green’s operator in the extended time-coordinate space).

The promising scaling of the method with increasing grid density suggests that it should be especially useful for accurate large-scale simulations involving high grid densities. Among the various applications of this type are quantum evolution in highly oscillatory pulsed driving fields, involving different time scales, and high-energy quantum-scattering calculations.

While the models studied so far show promising results, a few questions are still left for further study and investigation. First, one may wish for a better class of preconditioners, based on the Fourier grid methods. One possible generalization would be the application of polynomial preconditioners, which is equivalent to approximating the inverse of $\hat{A}$ by a truncated “Born series” in each iteration. Another direction could be adaptive preconditioning in which the preconditioner parameters are optimized within the iterative solutions. Other physically motivated preconditioners can also be applied that are based on diagonalizing a zero-order Hamiltonian and using its diagonal representation as a preconditioner. In fact, the Fourier grid preconditioner can be regarded as an application of this idea where the zero-order Hamiltonian includes only the (shifted) kinetic-energy terms. It is important to note, however, that while a “better” choice of the zero-order Hamiltonian is likely to reduce the number of iterations, the diagonalization transformations are likely to increase the cost of a single iteration. The Fourier grid is especially appealing because of the highly efficient transformations (the FFT algorithm).

Finally, we point out a similarity between the Fourier grid preconditioner as introduced here and the interaction-picture method of Zhang, Tannor, and coworkers for solving the time-dependent Schrödinger equation. Within the interaction picture, the generator of motion $\hat{H} = \hat{H}_0 + \hat{V}$ is replaced by $\hat{H}_I = e^{i\hat{H}_0 t} \hat{V} e^{-i\hat{H}_0 t}$. Chosing $\hat{H}_0$ as the kinetic-energy operator, the spectral range of $\hat{H}_I$ is determined by the interaction-potential operator $\hat{V}$. For finite-range potentials, this enables a compact and efficient grid representation in the coordinate space and a significant reduction in the

![FIG. 8. Dots represent calculated cumulative reaction probabilities for the collinear $H + H_2$ as a function of energy in units of the reaction barrier height, $v_0=0.425$ eV. The corresponding computational parameters are summarized in Table III. Triangles represent the vibrational (threshold) energy levels of $H_2$.](image1)

![FIG. 9. Average number of iterations required for solving the linear systems [Eqs. (6.7) and (6.8)] as a function of the number of grid points (the grid density). Circles represent TFQMR with no preconditioner. Diamonds represent TFQMR with the Fourier grid preconditioner. The average number of iterations corresponds to a relative tolerance of $10^{-6}$ for the TFQMR algorithm. Each $N(E)$ calculation required six to eight “external” Lanczos iterations for an absolute accuracy of $10^{-7}$.](image2)

<table>
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<th>Fig.</th>
<th>$E/v_0$</th>
<th>$N_x$</th>
<th>$N_y$</th>
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<th>$L_1$</th>
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<th>$\epsilon_{\nu}$</th>
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<td>64</td>
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<td>10</td>
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<td>0.1</td>
<td>0.5×E</td>
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<tr>
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<td>6–7.5</td>
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<td>72</td>
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<td>10</td>
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<td>0.5×E</td>
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<tr>
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<td>100</td>
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<tr>
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computational cost. Although the interaction-picture wave function $e^{iHt} \psi(x, t)$ is less detailed and contains less information than the Schrödinger wave function $\psi(x, t)$, it is sufficient for obtaining most relevant dynamic observables.\(^{44,45,53}\) A drawback of the interaction representation is that for a time-independent Hamiltonian, the generator of motion becomes time-dependent. When the Schrödinger Hamiltonian is implicitly time-dependent, this involves no extra complication, and this method can be used as an alternative to, or in combination with, the method presented here in order to manipulate the spectral range of the Hamiltonian. This has not been tried yet and is beyond the scope of the present work.

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