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Pseudo-time Schrödinger equation with absorbing potential for quantum scattering calculations.

Arnold Neumaier[1] and Vladimir A. Mandelshtam[2]

[1] *Institut für Mathematik, Universität Wien Strudlhofgasse 4, A-1090 Wien, Austria; email: neum@cma.univie.ac.at; WWW: http://solon.cma.univie.ac.at/~neum/*

[2] *Chemistry Department, University of California at Irvine, Irvine, CA 92697, USA; email: mandelsh@uci.edu*

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Abstract

The Schrödinger equation $(H\psi)(r) = (E + u_E W(r))\psi(r)$ with an energy-dependent complex absorbing potential $-u_E W(r)$, associated with a scattering system, can be reduced for a special choice of u_E to a harmonic inversion problem of a discrete pseudo-time correlation function $y(t) = \phi^{\mathrm{T}} U^t \phi$. An efficient formula for Green's function matrix elements is also derived. Since the exact propagation up to time $2t$ can be done with only $\sim t$ real matrix-vector products, this gives an unprecedently efficient scheme for accurate calculations of quantum spectra for possibly very large systems.

Complex absorbing potentials. The spectrum of a quantum scattering system can be characterized by solving the boundary value problem associated with the Schrödinger equation,

$$(H\psi)(r) = E\psi(r). \tag{1}$$

The *bound states* then have real energies E, with solutions $\psi(r)$ exponentially localized in space. The *resonance states* (Siegert states [1]) have complex energies with $\operatorname{Im} E \leq 0$. They behave like bound states in some compact subset Ω of the configuration space, but eventually grow exponentially outside of Ω, due to the outgoing asymptotic boundary conditions.

By introduction of a so-called *optical (or absorbing) potential* $-uW(r)$ with $\operatorname{Im} u > 0$ and real $W(r) \geq 0$, that vanishes for $r \in \Omega$ and smoothly grows outside Ω, the solutions $\psi(r)$ of

$$(H\psi)(r) = (E + uW(r))\psi(r) \tag{2}$$

are damped outside Ω, the physically relevant region [2]. This forces them to behave like bound states everywhere without significantly affecting the energies E. In this framework the physically relevant part of the system is, therefore, dissipative and satisfies (1) only for $r \in \Omega$. Moreover, a general multichannel scattering problem can be considered with a numerically convenient form of $W(r)$, independent of the choice of coordinate system.

Although to satisfy $\operatorname{Im} E \leq 0$ one only needs $\operatorname{Im} u \geq 0$, traditionally one simply puts $u = i$ and gets the nonhermitian eigenvalue problem $(H - iW)\psi = E\psi$. The latter is generally much easier to handle numerically than the boundary value problem (1). As we shall see, energy-dependent choices $u = u_E$ are particularly useful.

The introduction of the absorbing potential leads to the *damped Green's function* [3–5]

$$G_W(E) := (E - H + u_E W)^{-1}. \tag{3}$$

Under suitable conditions on $u_E W(r)$, it is probably possible to prove, similar as in ref. [5] for the traditional case $u_E = i$, that $G_W(E)$ converges for any real E (and also for $\operatorname{Im} E \geq 0$) weakly to the ordinary Green's function

$$G(E) = \lim_{\varepsilon \downarrow 0} (E - H + i\varepsilon)^{-1}.$$

Practically, one usually needs to evaluate only certain matrix elements $\phi^{\mathrm{T}} G(E)\psi$, the basic numerical objects of quantum physics from which most other quantities of interest (scattering amplitudes, reaction rates, etc.) can be computed (see, e.g., refs. [3,4,6,7]). If both ϕ and ψ have support in Ω, they are well approximated by $\phi^{\mathrm{T}} G_W(E)\psi$.

Unfortunately, for very large systems with high density of states one may encounter numerical difficulties when trying to diagonalize a large nonhermitian matrix $H - u_E W$ or solve the linear system $(E - H + u_E W)X(E) = \psi$ at many values of E using general iterative techniques for nonhermitian matrices. However, one can devise alternative iterative techniques to solve (2) by exploiting the special structure of the quantum scattering problem.

From now on, we assume that the Hilbert space is discretized so that the states are vectors $\psi \in \boldsymbol{C}^K$ and H, W are real symmetric $K \times K$ matrices, W diagonal, as, e.g., in the case of a discrete variable representation [8].

To simplify the following equations we further assume without loss of generality that the discretized Hamiltonian is shifted and scaled so that $|\langle H\rangle_\psi| \leq 1$ for any state ψ, where we have defined the expectation value as $\langle H\rangle_\psi := \psi^* H\psi/\psi^*\psi$ and * denotes conjugate transposition. Such scaling is implemented routinely in the framework of the Chebyshev polynomial expansion.

We now consider the special choice

$$u_E = E + i\sqrt{1-E^2}, \quad \text{or} \quad E(u) = \frac{1+u^2}{2u}, \tag{4}$$

which after insertion into (2) gives a nonlinear eigenvalue problem for $u = u_E$, more useful than (2):

$$H\psi = \frac{1+u^2 D}{2u}\psi \quad \text{with} \quad D = 1 + 2W. \tag{5}$$

We may think of this equation as an eigenvalue problem

$$H\psi = E(u)\psi \tag{6}$$

involving an operator-valued u-dependent energy

$$E(u) = \frac{1+u^2 D}{2u} \tag{7}$$

that reduces in Ω (where $D(r) = 1$) to the constant (4).

In ref. [9] a similar nonlinear eigenvalue problem with $E(u) = (D^{-1} + u^2 D)/2u$ was implicitly encountered leading to a numerical scheme to compute, e.g., the complex resonance energies by *harmonic inversion* of a "discrete-time" correlation function, generated by a damped Chebyshev recursion. Here, related results are derived rigorously and in a more general framework. In particular, a *pseudo-time Schrödinger equation* is derived that allows one to achieve a substantial numerical saving compared to the previous works.

The eigenpairs (u_k, ψ_k) of (5) can be used to evaluate the physically interesting quantities (e.g., the complex resonance energies E_k, scattering amplitudes, etc.). However, because of the nonlinearity they have somewhat different properties from those of the regular nonhermitian eigenvalue problem, which we now proceed to derive.

Theorem 1: Completeness and Orthogonality. The nonlinear eigenvalue problem (5) has at most $2K$ distinct eigenvalues u_k. Thus, there are at most K physical eigenvalues E_k of (2) with $\mathrm{Im}\, E_k \geq 0$.
If there are $2K$ distinct eigenvalues $u_1, \ldots, u_{2K}$ with associated eigenvectors ψ_k satisfying (5), then for any vector $\phi_\alpha \in \boldsymbol{C}^K$ there is a set of $2K$ numbers $\theta_{\alpha k}$ satisfying the *completeness relations*

$$\phi_\alpha = \sum_{k=1}^{2K} \theta_{\alpha k}\psi_k, \quad 0 = \sum_{k=1}^{2K} \theta_{\alpha k} u_k \psi_k. \tag{8}$$

Furthermore, ψ_k satisfy the *orthogonality relations*

$$\psi_j^{\mathrm{T}}(1 - u_j u_k D)\psi_k = \delta_{jk} \tag{9}$$

for all $j \neq k$. If the eigenvectors can be normalized such that (9) also holds for $j = k$, then (8) holds with

$$\theta_{\alpha k} = \psi_k^{\mathrm{T}} \phi_\alpha \tag{10}$$

Proof. Let

$$U = \begin{pmatrix} 0 & I \\ -D^{-1} & D^{-1}(2H) \end{pmatrix}.$$

where I denotes the $K \times K$ unit matrix. The ordinary eigenvalue problem

$$U\hat{\psi} = u\hat{\psi} \tag{11}$$

yields, with $\hat{\psi} = \binom{\psi}{\psi'}$,

$$\psi' = u\psi, \quad D^{-1}\psi + u^2\psi - uD^{-1}(2H)\psi = 0.$$

After multiplication by $D/2u$, we find (5). In particular, the eigenpairs $(u_k, \hat{\psi}_k)$ of U satisfy

$$\hat{\psi}_k = \begin{pmatrix} \psi_k \\ u_k\psi_k \end{pmatrix}, \tag{12}$$

where (u_k, ψ_k) is an eigenpair of (5). Since conversely, any such eigenpair determines an eigenpair of U, the nonlinear eigenvalue problem (5) has at most $2K$ distinct eigenvalues. If there are $2K$ distinct eigenvalues $u_1, \ldots, u_{2K}$, the matrix U is diagonalizable, and there is a basis $\hat{\psi}_1, \ldots, \hat{\psi}_{2K}$ of eigenvectors of the form (12). Therefore, we may write

$$\begin{pmatrix} \phi_\alpha \\ 0 \end{pmatrix} = \sum_{k=1}^{2K} \theta_{\alpha k}\hat{\psi}_k = \begin{pmatrix} \sum \theta_{\alpha k}\psi_k \\ \sum \theta_{\alpha k} u_k \psi_k \end{pmatrix}$$

with uniquely determined coefficients $\theta_{\alpha k}$. This gives (8).

Using (5) and the symmetry of H and D we may compute $\psi_j^{\mathrm{T}} H \psi_k$ in two different ways:

$$\psi_j^{\mathrm{T}} H \psi_k = \psi_j^{\mathrm{T}} \frac{1 + u_k^2 D}{2u_k}\psi_k = \psi_k^{\mathrm{T}} \frac{1 + u_j^2 D}{2u_j}\psi_j.$$

For $j \neq k$, by assumption $u_j \neq u_k$. Thus, we may take difference, multiply by $2u_j u_k/(u_k - u_j)$, and find (9). For $j = k$, we may achieve (9) by normalizing the eigenvectors, provided that the left hand side of (9) does not vanish. Using (9) and (8) we find (10):

$$\begin{aligned}
\theta_{\alpha k} &= \textstyle\sum_j \theta_{\alpha j}\delta_{jk} = \sum_j \theta_{\alpha j}\psi_j^{\mathrm{T}}(1 - u_j u_k D)\psi_k \\
&= \left(\textstyle\sum \theta_{\alpha j}\psi_j\right)^{\mathrm{T}} \psi_k - u_k \left(\textstyle\sum \theta_{\alpha j} u_j \psi_j\right)^{\mathrm{T}} D\psi_k \\
&= \phi_\alpha^{\mathrm{T}}\psi_k = \psi_k^{\mathrm{T}}\phi_\alpha.
\end{aligned}$$

We now consider an eigenpair (u, ψ) of (5) with $\psi^*\psi \neq 0$. Multiplying (5) by $2u\psi^*$ gives the quadratic equation

$$u^2\langle D\rangle_\psi - 2u\langle H\rangle_\psi + 1 = 0. \tag{13}$$

The solutions of (13) are

$$u = \frac{\langle H\rangle_\psi \pm i\sqrt{\langle D\rangle_\psi - \langle H\rangle_\psi^2}}{\langle D\rangle_\psi}. \tag{14}$$

Since $\langle D\rangle = 1 + 2\langle W\rangle_\psi \geq 1$ and $|\langle H\rangle_\psi| \leq 1$, the square root is real and

$$|u|^2 = \frac{\langle H\rangle_\psi^2 + \langle D\rangle_\psi - \langle H\rangle_\psi^2}{\langle D\rangle_\psi^2} = \frac{1}{\langle D\rangle_\psi} \leq 1. \tag{15}$$

Thus, u is a complex number lying in the unit disk. Moreover, $|u| = 1$ iff $\langle W\rangle_\psi = 0$, i.e., iff ψ has support in Ω, which is the case for the bound states. The states with $|u| \sim 1$ correspond to the narrow resonances. Due to (14) the solutions of (5) come in complex conjugate pairs (u, ψ) and $(\bar{u}, \bar{\psi})$. The physically relevant eigenenergies with $\operatorname{Im} E \leq 0$ come from u with $\operatorname{Im} u \geq 0$.

Note that a similar analysis of a quadratic eigenvalue problem was carried out in ref. [10], arising from the use of the Bloch operator L, rather than an absorbing potential. There, equation (6) is considered with $E(u) = (iuL + u^2 I)/2$, and u is a momentum variable close to the real axis, instead of a number close to the unit circle. However, this equation can only be used for less general, single-channel scattering problems and, besides, it is hard to solve efficiently using iterative techniques.

Reduction to a harmonic inversion problem. Consider the *pseudo-time Schrödinger equation* defined by the recurrence

$$\phi(t) = D^{-1}(2H\phi(t-1) - \phi(t-2)) \quad (t = 2, 3, ...) \tag{16}$$

with $\phi(0) = \phi_0$ and $\phi(1) = 0$. (This choice of initial conditions is most convenient, although other initial conditions with $\phi(1) \neq 0$ yield analogous results. A similar 3-term-recurrence with another choice of special initial conditions leading to "modified Chebyshev recurrence" was considered in refs. [9,11].) Since D is diagonal and matrix-vector products $H\phi$ are usually cheap to form, $\phi(0), \ldots, \phi(T)$ are computable using $O(KT)$ operations and a few vectors stored at a time. If the initial vector ϕ_0 is real, only real arithmetic is needed.

By Theorem 1, we can write (16) as

$$\begin{pmatrix} \phi(t) \\ \phi(t+1) \end{pmatrix} = U^t \begin{pmatrix} \phi_0 \\ 0 \end{pmatrix} = \sum_{k=1}^{2K} \theta_{0k} u_k^t \begin{pmatrix} \psi_k \\ u_k\psi_k \end{pmatrix}$$

and, therefore,

$$\phi(t) = \sum_{k=1}^{2K} \theta_{0k} u_k^t \psi_k. \tag{17}$$

This *power expansion* is very important, and is analogous to the (physical time) expansion $\phi(t) = e^{-itH}\phi(0) = \sum_{k=1}^{K} \theta_k e^{-itE_k}\psi_k$ for the solutions of the standard time-dependent Schrödinger equation. It allows one to reap all the benefits of time-dependent methods (see, e.g., refs. [12,13,6]) without having to deal with the time-dependent Schrödinger equation, which is hard to solve accurately at long times t in the case of nonhermitian Hamiltonian. Instead, only the much more benign and numerically very stable equation (16) must be solved.

By (17), the pseudo-time cross-correlation function

$$y_\alpha(t) := \phi_\alpha^{\mathrm{T}}\phi(t) \quad (t = 0, 1 \dots) \tag{18}$$

of a state ϕ_α has the form

$$y_\alpha(t) = \sum_{k=1}^{2K} d_{\alpha k} u_k^t \tag{19}$$

with

$$d_{\alpha k} = \phi_0^{\mathrm{T}}\psi_k\psi_k^{\mathrm{T}}\phi_\alpha = \theta_{0k}\theta_{\alpha k}. \tag{20}$$

This reduces the nonlinear eigenvalue problem (5) to solving the *harmonic inversion problem*, i.e., to finding the spectral parameters $(u_k, d_{\alpha k})$ $(k = 1, \dots, 2K)$ satisfying (19) for the sequence $y_\alpha(t)$ computed by (16) and (18). Since by (15) the sequence $y_\alpha(t)$ is bounded and the spectral mapping (4) moves the physically relevant eigenvalues u_k close to the unit circle, this is an efficiently tractable problem, even in very large dimensions [14,9].

Time doubling of an autocorrelation function. As is well known, a true time autocorrelation function at time t can be computed by solving the time-dependent Schrödinger equation up to time $t/2$, since one can use

$$C(t) := \phi^{\mathrm{T}} e^{-iHt}\phi = (e^{-iHt/2}\phi)^{\mathrm{T}}(e^{-iHt/2}\phi).$$

For the Chebyshev autocorrelation function $c(t) := \phi_\alpha^{\mathrm{T}}\phi(t)$, based on (16) with $D = I$ and the initial conditions $\phi(0) = \phi_0$, $\phi(1) = H\phi_0$, a factor of two saving is also well known (see, e.g., the discussion in ref. [9]):

$$c(2t) = 2\phi(t)^{\mathrm{T}}\phi(t) - c(0), \quad c(2t+1) = 2\phi(t)^{\mathrm{T}}\phi(t+1) - c(1).$$

This expression was used in [15] for resonance computation implementing a damped Chebyshev recursion. However, being approximate, it only worked for sufficiently narrow resonances. In the present framework, we can write the pseudo-time cross-correlation function as

$$y_\alpha(t) = \begin{pmatrix}\phi_\alpha\\0\end{pmatrix}^{\mathrm{T}} U^{t+s}\begin{pmatrix}\phi_0\\0\end{pmatrix} = \left\{\begin{pmatrix}\phi_\alpha\\0\end{pmatrix}^{\mathrm{T}} U^t\right\}\left\{U^s\begin{pmatrix}\phi_0\\0\end{pmatrix}\right\},$$

which suggests that an exact doubling scheme exists. This is now derived for the autocorrelation function as only ϕ_0 is propagated.

Theorem 2: The Doubling Scheme. For vectors $\phi(t)$ and $\phi(s)$ satisfying the pseudo-time Schrödinger equation (16) with initial conditions $\phi(0) = \phi_0$, $\phi(1) = 0$, the autocorrelation function $y_0(t) := \phi_0^{\mathrm{T}}\phi(t)$ satisfies

$$y_0(s+t) = \phi(s)^{\mathrm{T}}\phi(t) - \phi(s+1)^{\mathrm{T}}D\phi(t+1) =: z(s,t).$$

Proof: This follows from the power expansion (17) and the orthogonality relations (9):

$$\begin{aligned} z(s,t) &= \sum_{j,k=1}^{2K} \theta_{0j}\theta_{0k}u_j^s u_k^t(\psi_l^{\mathrm{T}}\psi_k - u_j u_k \psi_l^{\mathrm{T}} D\psi_k) \\ &= \sum_{k=1}^{2K} \theta_{0k}^2 u_k^{s+t} = y_0(s+t). \end{aligned}$$

Hardly any additional storage will be needed if the sequence $y_0(t)$ $(t = 0, ..., 2T-2)$ is generated by

$$y_0(2t) = z(t,t), \quad y_0(2t-1) = z(t,t-1), \tag{21}$$

concurrently with the computation of $\phi(t)$ using $t = 0, ..., T$. In exact arithmetic the harmonic inversion of the doubled sequence $y_0(t)$ will give the exact results if $T > 2K$, thus, using only $T \sim 2K$ of matrix-vector products. However, this is impractical as it would formally require to solve a $T \times T$ eigenvalue problem. To reduce the computational burden and to maintain numerical stability the eigenvalues are extracted very efficiently in a small Fourier subspace by the *Filter Diagonalization Method* [14,9]. In this case, the required length $2T$ of the doubled sequence needed to converge an eigenenergy E_k (cf. Eq. 4) will be defined by the locally averaged density of states $\rho(E)$ for $E_k \sim E$ [9].

Theorem 3: The Green's function matrix elements. Under the assumptions of Theorem 1, let $\phi(t)$ be a solution of the pseudo-time Schrödinger equation (16) with initial conditions $\phi(0) = \phi_0$, $\phi(1) = 0$. Then the matrix elements of the damped Green's function (3) with $u_E = E + i\sqrt{1-E^2}$ are

$$\phi_\beta^{\mathrm{T}} G_W(E)\phi_\alpha = \sum_{k=1}^{2K} \frac{d_{\beta k}d_{\alpha k}}{d_{0k}} \frac{2u_E u_k}{u_k - u_E}, \tag{22}$$

where the three sets of spectral parameters $\{d_{\beta k}, u_k\}$, $\{d_{\alpha k}, u_k\}$ and $\{d_{0k}, u_k\}$ (with identical eigenvalues u_k) satisfy the harmonic inversion problem (19) for the cross-correlation functions $y_\beta(t)$, $y_\alpha(t)$ and $y_0(t)$, respectively.

Proof. For an eigenpair (u_k, ψ_k) of (5) we can write

$$(E - H + u_E W)\psi_k = \frac{u_k - u_E}{2u_k u_E}(1 - u_k u_E D)\psi_k.$$

Then (8) and (10) imply

$$(E - H + u_E W) \sum_k \frac{2u_E u_k \theta_{\alpha k}}{u_k - u_E} \psi_k$$
$$= \sum_k \theta_{\alpha k} \psi_k - u_E D \left(\sum_k \theta_{\alpha k} u_k \psi_k \right) = \sum_k \theta_{\alpha k} \psi_k = \phi_\alpha.$$

Multiplying this by $\phi_\beta^{\rm T}(E - H + u_E W)^{-1}$ and using $\theta_{\beta k} = \phi_\beta^{\rm T} \psi_k$ we obtain

$$\phi_\beta^{\rm T} G_W(E) \phi_\alpha = \sum_{k=1}^{2K} \theta_{\beta k} \theta_{\alpha k} \frac{2u_E u_k}{u_k - u_E}, \tag{23}$$

Now replacement of $\theta_{\beta k}\theta_{\alpha k}$ by $d_{\beta k} d_{\alpha k}/d_{0k}$ gives (22).

Note that (23) also gives an explicit expression for the damped Green's function in terms of the eigenpairs:

$$G_W(E) = \sum_{k=1}^{2K} \frac{2u_E u_k}{u_k - u_E} \psi_k \psi_k^{\rm T}, \tag{24}$$

A formula similar to (22) was obtained (without a rigorous derivation) in ref. [16], in the framework of the damped Chebyshev recursion in place of (16). However, here, due to the doubling scheme (21), only half the number of matrix-vector products will be needed to obtain the same amount of information.

Thus, we have a very efficient and stable method to extract the complete spectral and dynamical information of a general (multichannel) quantum scattering system using a minimal number of matrix-vector products. This will be demonstrated numerically in a forthcoming publication.

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