Wave operator theory of quantum dynamics

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An energy-dependent wave operator theory of quantum dynamics is derived for time-independent and time-dependent Hamiltonians. Relationships between Green's functions, wave operators, and effective Hamiltonians are investigated. Analytical properties of these quantities are especially relevant for studying resonances. A derivation of the relationship between the Green's functions and the (t,t') method of Peskin and Moiseyev [J. Chem. Phys. **99**, 4590 (1993)] is presented. The observable quantities can be derived from the wave operators determined with the use of efficient iterative procedures. As in the theory of Bloch operators for bound states, the theory is based on a partition of the full Hilbert space into three subspaces: the model space, an intermediate space, and the outer space. On the basis of this partition an alternative definition of active spaces currently considered in large scale calculations is suggested. A numerical illustration is presented for several model systems and for the Stark effect in the hydrogen atom. [S1050-2947(98)01709-0]

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I. INTRODUCTION

The quantum theory of dynamics is a rapidly developing field. One has to deal with many time scales and a great number of degrees of freedom, corresponding to the various reversible and irreversible dynamical processes, and this leaves still many questions open. With the aim of developing different efficient computational schemes, we present here a unified description of quantum dynamics based on reduced Green's functions, energy-dependent wave operators, and effective Hamiltonians.

Much attention has been devoted to the time-dependent wave operator theory of quantum dynamics; the subject has been summarized recently in a review article [1]. Another basic approach to quantum dynamics is based on the spectral properties of the Hamiltonian. In it priority is given to energy rather than to a direct investigation of the temporal evolution of wave packets. An extended overview of the spectral computational methods can be found in a review article of Wyatt and Iung [2]. In its standard form the method of moments (Lanczos recursion algorithm) does not provide a full temporal description of the system from the initial state (see [2], p. 83) and convergence problems may appear, especially in the presence of quasicontinua or continua. However, the standard Lanczos algorithm can be improved by spectral filters, the most important one being the resolvent operator [3,4]. It is in this direction in particular that significant progress has been made in the past few years [5]. Since we are interested in restricted dynamics, e.g., in the study of a few transition amplitudes, we have to deal with restricted resolvent operators and/or with Green's functions, which are closely related to energy-dependent wave operators. All useful dynamical information is contained in these wave operators. We emphasize the role of analyticity in the complex energy plane (variable z) because our objective is to compute simultaneously dynamical events at various time scales including long-lived interacting and/or overlapping resonances.

Section II of this paper is devoted to the relationships between reduced Green's functions, wave operators, and effective Hamiltonians for time-independent and time-dependent Hamiltonians. We emphasize the unity of the formalism by using in both cases similar notations. As a by-product we obtain a derivation of the (t,t') formalism for time-dependent Hamiltonians [6].

Section III is devoted to the determination of energy-dependent wave operators by solving Bloch-type equations. As in the theory of effective Hamiltonians for bound states, the Hilbert space is divided into three subspaces: the *model space*, the *intermediate space*, and the *outer space*. The relevant dynamics is projected into the model space. The intermediate space is made up of the states that are strongly coupled to those of the model space (for example, the dressed states of a molecule submitted to a laser field). It will be suggested that the direct sum of the model space and of the intermediate space could define an *active space* [1,2]. Finally, all other states that interact weakly with the model space define the outer space treated within the framework of perturbation theory including infinite partial summations. The advantage of introducing an intermediate space for solving the Bloch equations was previously demonstrated by Malrieu *et al.* [7]. The use of an intermediate space is a powerful tool to improve the convergence properties of iterative processes towards either diabatic or adiabatic solutions. Various quasiquadratic Newton-Raphson schemes for the determination of wave operators are presented. For a discretized $N\times N$ matrix representation of the Hamiltonian, the computational effort is proportional to N^2. The usefulness of the quasiquadratic approach is demonstrated by treating several model systems, as presented in Sec. IV.

II. GREEN'S FUNCTIONS, WAVE OPERATORS, AND EFFECTIVE HAMILTONIANS

A. Time-independent Hamiltonian

The purpose of this paragraph is to introduce the basic concepts and to specify the notations. Let us consider a wave function $\psi(t)$ that fulfills the time-dependent Schrödinger equation

$$\left(H-i\hbar\frac{d}{dt}\right)\psi(t)=0. \tag{1}$$

For $t>0$, the projected wave function $\theta(t)\psi(t)$ obeys

$$\left(H-i\hbar\frac{d}{dt}\right)\theta(t)\psi(t)=-i\hbar\,\delta(t)\phi. \tag{2}$$

$\theta(t)$ is the Heaviside function. The initial condition appears as a source on the right-hand side of Eq. (2), where $\delta(t)$ is the Dirac function and $\phi=\psi(0)$. The Laplace-Fourier transformation of Eq. (2) leads to $(z-H)\phi(z)=\phi$, where $\phi(z)$ is the Laplace-Fourier transform of $\psi(t)$ associated with the initial condition $\psi(0)=\phi$ (see Appendix A). The solution of Eq. (2) leads to the Green's function

$$\phi(z)=\frac{1}{z-H}\phi. \tag{3}$$

Hereafter, the generic expression ''Green's function'' means either a function belonging to the Hilbert state as above or a matrix element of the resolvent as

$$G(z)=\left\langle\phi\left|\frac{1}{z-H}\right|\phi\right\rangle. \tag{4}$$

The z-dependent quantities in Eqs. (3) and (4), unambiguously defined for $\mathrm{Im}\,z>0$, are assumed to be analytically continued in the second Riemann sheet for $\mathrm{Im}\,z<0$. The determination of $\phi(z)$, given by Eq. (3), does not require the knowledge of the full resolvent, but only of the restricted resolvent $[1/(z-H)]P_0$, where $P_0=|\phi\rangle\langle\phi|$ is the projector onto the one-dimensional subspace spanned by the initial state ϕ. In the following, we consider the dynamics implying n initial or final states ϕ_i, $i=1,2,\ldots,n$. These states span the model space whose projector is $P_0=\Sigma_{i=1}^{n}|\phi_i\rangle\langle\phi_i|$. The projector onto the orthogonal complement is $Q_0=1-P_0$. The partition technique (see Ref. [8], p. 174) enables us to express the restricted resolvent in the form

$$\frac{1}{z-H}P_0=\left(P_0+\frac{Q_0}{z-H}H\right)\frac{P_0}{z-H^{eff}(z)}, \tag{5}$$

where

$$H^{eff}(z)=P_0\left(H+H\frac{Q_0}{z-H}H\right)P_0. \tag{6}$$

Expressions (5) and (6) can be transformed into

$$\frac{1}{z-H}P_0=\Omega(z)\frac{P_0}{z-H^{eff}(z)} \tag{7}$$

and

$$H^{eff}(z)=P_0H\Omega(z). \tag{8}$$

In Eqs. (7) and (8) we have introduced the energy-dependent wave operator $\Omega(z)$ which establishes a one-to-one correspondence between the model space and n exact Green's functions. This step is quite analogous to introducing wave operators for bound states that establish a one-to-one correspondence between n approximate solutions in the model space and n exact eigensolutions (see Appendix B). Expression (7) indicates that the poles of the Green's function, always assumed to be analytically continued, can be obtained by solving the algebraic equations

$$z=E_i(z),\quad i=1,2,\ldots,n. \tag{9}$$

The $E_i(z)$'s are the complex eigenvalues of the effective Hamiltonian given by Eq. (8). If we assume that the resonances can be identified with the poles of the Green function, solving Eq. (9) (for example, by an iterative process) provides a direct way to compute the resonance energies (see Ref. [9], p. 162).

In the case of a one-dimensional model space, the inverse Laplace-Fourier transformation provides the probability amplitude of survival of the initial state (autocorrelation function)

$$\langle\phi|\psi(t)\rangle=\frac{1}{2\pi i}\int_C dz\,\frac{1}{z-E(z)}\exp\left(\frac{-izt}{\hbar}\right), \tag{10}$$

where

$$E(z)=\langle\phi|H\Omega(z)|\phi\rangle \tag{11}$$

and the integration path in the complex plane is indicated in Appendix A. Similarly, for an n-dimensional model space, one can recover the state-to-state probability amplitudes

$$U_{fi}(t)=\frac{1}{2\pi i}\int_C dz\left\langle\phi_f\left|\frac{P_0}{z-H^{eff}(z)}\right|\phi_i\right\rangle\exp\left(\frac{-izt}{\hbar}\right). \tag{12}$$

The initial state ϕ_i and the final state ϕ_f are assumed to belong to the model space. The effective Hamiltonian in Eq. (12) is given by Eq. (8). Expressions (10) and (12) emphasize the major role played by the wave operator from which the useful transition amplitudes can be obtained immediately.

B. Time-dependent Hamiltonian

With obvious notation Eq. (2) becomes

$$\left(H(t)-i\hbar\frac{d}{dt}\right)\theta(t)\psi(t)=-i\hbar\,\delta(t)\phi. \tag{13}$$

It can be checked immediately that the square-integrable wave function with respect to time $\phi(t)=\exp(-\epsilon t/\hbar)\theta(t)\psi(t)$ fulfills

$$\left(H(t)-i\hbar\frac{d}{dt}-i\epsilon\right)\phi(t)=-i\hbar\,\delta(t)\phi$$

$$= \frac{1}{2\pi i}\int_{-\infty}^{+\infty} dE\ \exp\left(\frac{iEt}{\hbar}\right)\phi, \tag{14}$$

where ϵ is a small positive number. The linearity of Eq. (14) suggests to look for elementary energy and time-dependent solutions $\phi(E,t)$, which obey

$$\left(H(t) - i\hbar\frac{d}{dt} - i\epsilon\right)\phi(E,t) = \exp\left(-\frac{iEt}{\hbar}\right)\phi. \tag{15}$$

Multiplying both sides of Eq. (15) by $\exp(iEt/\hbar)$ leads to

$$\left[E + i\epsilon - \left(H(t) - i\hbar\frac{d}{dt}\right)\right]\phi(E,t) = \phi. \tag{16}$$

After introducing the time-dependent operator

$$\mathcal{H}(t) = H(t) - i\hbar\frac{d}{dt} \tag{17}$$

and $z = E + i\epsilon$, Eq. (16) can be written as

$$[z - \mathcal{H}(t)]\phi(z,t) = \phi, \tag{18}$$

the formal solution of which is

$$\phi(z,t) = \frac{1}{z-\mathcal{H}}\phi. \tag{19}$$

The time-dependent wave function $\phi(t)$ can be recovered by means of the inverse Laplace-Fourier transformation (see Appendix A). Expressions (3) and (19) look quite similar. However, in Eq. (3) H acts in the usual Hilbert space, whereas in Eq. (19) $\mathcal{H}$ acts in the *generalized* Hilbert space that is the vectorial product of the usual Hilbert space by the vectorial space arising from the variable t. In this extended Hilbert space the inner product implies an integration with respect to t. Box normalization can be used ($0 \leqslant t \leqslant T$), in which T is the time period in the case of a time-periodic Hamiltonian; alternatively it can be identified with the finite duration of an electromagnetic interaction for nonperiodic cases [1]. Expressions (18) and (19) generalize in the most direct way expressions (3) and (4), which are valid for time-independent Hamiltonians. The price that one has to pay for passing from Eqs. (3) and (4) to Eqs. (18) and (19) is to add the variable time in the full vectorial space. It is interesting to establish a link between the function $\phi(z,t)$ in Eq. (19) and the (t,t') formalism introduced by Peskin and Moiseyev [6]. The inverse Laplace-Fourier transformation performed on Eq. (18) with respect to the variable z gives

$$\left(i\hbar\frac{d}{dt'} - \mathcal{H}(t)\right)f(t',t) = i\hbar\,\delta(t')\phi. \tag{20}$$

By exchanging the variables t and t' and using Eq. (17) one obtains

$$\left[i\hbar\left(\frac{d}{dt} + \frac{d}{dt'}\right) - H(t)\right]f(t,t') = i\hbar\,\delta(t)\phi. \tag{21}$$

Equation (21) shows that $f(t,t')$ is identical to the Peskin-Moiseyev wave function $\psi(t',t)$. Thus we have established a direct connection between the Green's function $\phi(z,t)$, which depends on energy and time, and the (t,t') formalism. It is interesting to note that the temporal information with respect to the initial condition included in $\delta(t)\phi$ on the right-hand side of Eq. (14) has been lost in Eq. (15): it contains an exponential term fully delocalized in time. There are other ways to expand $\delta(t)$ in source terms in Eq. (14), e.g., by means of a Fourier series, which makes the initial condition periodic. This direction is important for numerical applications but it will be not pursued here anymore.

If we enlarge the dynamics to a set of n states ϕ_i ($i = 1,2,\ldots,n$), Eqs. (7) and (8) become

$$\frac{1}{z-\mathcal{H}}P_0 = \Omega(z)\frac{P_0}{z - H^{eff}(z)}, \tag{22}$$

$$H^{eff}(z) = P_0\mathcal{H}\Omega(z). \tag{23}$$

The similarity between Eqs. (7) and (8) and Eqs. (22) and (23) is not only formal. The discretization of the variable t and the use of finite sets of square-integrable time-dependent functions lead to finite representations of H and $\mathcal{H}$. Consequently, the same computational schemes can be applied in both cases (see Sec. III) and the transition amplitudes can be easily expressed in terms of $\Omega(z)$ and $H^{eff}(z)$. Let us assume that the generalized Hilbert space is spanned by the orthonormal basis set

$$|k,n\rangle\rangle = |\phi_k\rangle \cdot f_n(t), \quad \langle\langle k,n|k',n'\rangle\rangle = \delta_{kk'}\delta_{nn'}. \tag{24}$$

Hereafter the notations $|\ \rangle\rangle$ and $\langle\langle\ |\ \rangle\rangle$ will be used for vector and scalar products in the generalized Hilbert space. By introducing into Eq. (22) the closure relation in the generalized Hilbert space, the probability amplitude for passing from the initial state ϕ_i to the final state ϕ_f at time t can be written in the form

$$U_{fi}(t) = \sum_n U_{fi,n}(t) f_n(t). \tag{25}$$

$U_{fi,n}(t)$ is the inverse Laplace-Fourier transform of $\hat{U}_{fi,n}(z)$ (see Appendix A):

$$U_{fi,n}(t) \leftrightarrow \hat{U}_{fi,n}(z) = \left\langle\left\langle f,n\left|\frac{1}{z-\mathcal{H}}\right|\phi_i\right\rangle\right\rangle. \tag{26}$$

Using a harmonic temporal basis set, Eqs. (25) and (26) become

$$U_{fi}(t) = \sum_n c_{fi,n}(t)\cdot e^{in\omega t} \tag{27}$$

and

$$c_{fi,n}(t) \leftrightarrow \hat{c}_{fi,n}(z) = \left\langle\left\langle f,n\left|\frac{1}{z-\mathcal{H}}\right|i,0\right\rangle\right\rangle. \tag{28}$$

In Eq. (27) $c_{fi,n}(t)$ is the nth Fourier component of the transition amplitude. If $|i,0\rangle\rangle$ and $|f,n\rangle\rangle$ belong to the model space, $\hat{c}_{fi,n}(z)$ can be derived from the effective Hamiltonian

$$\hat{c}_{fi,n}(z)=\left\langle\left\langle f,n\left|\frac{P_0}{z-H_{eff}(z)}\right|i,0\right\rangle\right\rangle. \tag{29}$$

The advantage in deriving the relevant dynamical quantities from the matrix elements of $H^{eff}(z)$ is that they can be determined by using the same techniques as for bound states. An application to the determination of a survival amplitude will be presented in Sec. III.

C. Resonances

The systematic use of the wave operator $\Omega(z)$ (variable z) is especially relevant in the study of resonances. For long-lived resonances, much attention must be paid to the unavoidable spurious reflections that result from the use of finite grids or of a finite number of square-integrable functions. Some smoothing, or filtering, or an averaging procedure is needed to perform analytical continuation. Many techniques have been developed for this purpose. One can make complex the dissociative continuous nuclear and/or electronic variables [10–14]. This approach is very efficient to determine the poles of a Green's function, but it does not provide directly the full Green's function. Another possibility is to add an optical potential to the Hamiltonian [15–17]. In the following, we will assume that the Hamiltonian under study contains all the ingredients needed to investigate resonances (optical potentials, rotated coordinates, etc.). We will keep the unique notation H for any real or complex Hamiltonian. Therefore, Eqs. (7) and (8) will be our two basic equations.

III. DETERMINATION OF THE WAVE OPERATOR

Hereafter it will be assumed that all operators are represented by finite matrices. The discretization comes from the use of finite square-integrable functions associated with the molecular electronic and nuclear coordinates and with the variable time. Multiplying on the left Eq. (7) by $z-H$ and on the right by $z-H^{eff}$ gives

$$(z-H)\Omega(z)=P_0[z-H^{eff}(z)]. \tag{30}$$

Equation (30) indicates that the term on the right-hand side acts as a source term containing the information about the initial state. Multiplying both sides of Eq. (30) by the projector Q_0 into the orthogonal complementary space gives

$$Q_0(z-H)\Omega(z)=0. \tag{31}$$

Using Eqs. (5) and (7), the solution of Eq. (31) can be written in the form

$$\Omega(z)=P_0+X(z), \tag{32}$$

where $X(z)$ is the reduced wave operator

$$X(z)=\frac{Q_0}{z-H}HP_0. \tag{33}$$

This expression is rather formal since $X(z)$ has to be continued into the second Riemann sheet. This can be done by transforming H into a complex rotated Hamiltonian or by adding an optical potential to the Hamiltonian as discussed in Sec. II C. Since all the information concerning the dynamics projected in the model space is contained in the wave operators, we need efficient methods for their determination. The methods of moments such as filter diagonalization [18] or harmonic inversion [5] are well adapted to the discrete variable representation of the Hamiltonian, which is far from being diagonal. On the contrary, many problems lead to almost diagonal representations. A good example is the Floquet theory of dressed molecules in laser fields. For usual laser fields the perturbative approach is the most convenient. In the following, we present perturbation-iteration schemes that can be considered as generalizations of the recursive distorted-wave approximation and the single-cycle method [19–21]. These generalizations have two main features. First, as mentioned above, they rely on the partition of the full Hilbert space into three subspaces (the model, intermediate, and outer spaces) instead of two subspaces (the model and outer spaces). Second, these generalizations are well-defined quasiquadratic approximations of the exact quadratic Newton-Raphson scheme.

A. Model space, intermediate space, and outer space

In order to extract the relevant information from large degenerate or quasidegenerate matrix representations of the Hamiltonian, we divide the orthogonal space, complementary to the model space, into two orthogonal subspaces: an intermediate space and its complementary space, the outer space. This partitioning has been proved useful in quantum chemistry for determining the many-electron wave functions of bound states (see Appendix B). The intermediate space includes all states that interact notably or in certain cases strongly with the model space. Let us denote by P_1 and P_2 the orthogonal projectors into the intermediate and the outer space, respectively: $Q_0=P_1+P_2$. The reduced wave operator can be split into two terms

$$X(z)=X_1+X_2, \quad X_1=P_1X(z), \quad X_2=P_2X(z). \tag{34}$$

The localization of the matrix elements of X_1 and X_2 is indicated in Fig. 1. Multiplying Eq. (31) on the left by the projectors P_1 and P_2 and using Eqs. (32) and (34) leads to the two basic equations (see Appendix C)

$$X_1=\frac{P_1}{z-H}V(1+X_2)P_0 \tag{35}$$

and

$$X_2=\frac{P_2}{z-H_0}V(1+X_1+X_2)P_0. \tag{36}$$

Equations (35) and (36) look perturbative. All quantities in these expressions can be easily evaluated since the inversion of $P_1(z-H)P_1$ is feasible in the intermediate space and the unperturbed Hamiltonian H_0 is diagonal in the outer space. We could try to solve simultaneously Eqs. (35) and (36) by a first-order iterative process, which would lead to at best lin-

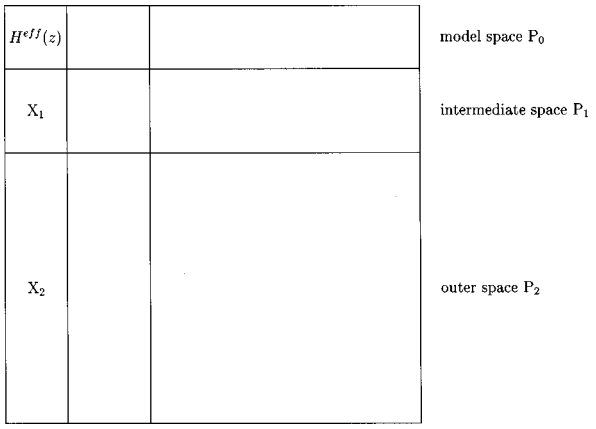

FIG. 1. Matrix localization of the effective Hamiltonian $H^{eff}(z)$ and of the projected reduced wave operator X_1 and X_2. $X=X_1+X_2$, $Q_0=P_1+P_2$, and $P_0+Q_0=1$.

ear convergence. Experience shows that the procedure generally fails for large matrices, especially when one increases the number of basis function and/or the number of points in grids for discrete variable representations. The Newton-Raphson scheme can be conveniently used to solve Eqs. (35) and (36). The approximate solution $X=X_1+X_2$ is incremented by the quantities ΔX_1 and ΔX_2 given in Appendix C. The linearity of Eqs. (35) and (36) ensures that the exact expressions for X_1 and X_2 could be obtained in one step. Obviously, this procedure cannot be used for practical calculations since it would imply the inversion of large matrices; this would require, however, a computational effort as extensive as determinating the full resolvent operator. The number of multiplications would be proportional to N^3, N being the dimension of the Hamiltonian matrix. In Appendix C it is shown how quasiquadratic Newton-Raphson schemes can be obtained, which require a number of multiplications proportional to $n\cdot N^2$, n being the dimension of the model space.

B. Discussion

The principal aim of the wave operator theory of quantum dynamics, which includes long-lived events such as resonances, is to reduce the dimension of the vector space participating in the dynamics. Such a subspace is generally called an active space. There is extensive literature concerning the definition and the determination of active spaces [1,2,22,23]. It must be emphasized that the concept of active space is more computational than physical. The size of an active space depends strongly on the choice of the representation of the Hamiltonian. In this article, the states that participate mainly in the dynamics belong either to the model space or to the intermediate space. Whatever the selection procedure of the intermediate space might be (based on some energy criteria or obtained from the first steps of an iterative solution of the Bloch equation [2]) we suggest to define the active space as the direct sum of the model and of the intermediate space. With such a definition all usual diagonalizations and inversions of operators can be carried out easily on a workstation.

IV. NUMERICAL ILLUSTRATION

We have selected for our study a few model systems containing both quasicontinua and true continua. They illustrate several key points important for understanding and computing the wave operators and their associated effective Hamiltonians. We begin by revisiting the Fano model, which contains the basic ingredients illustrating reversible and irreversible dynamics (resonances). This model emphasizes the importance of the choice of the model space: It is one-dimensional for an irreversible evolution (weak coupling) or at least two-dimensional for a reversible dynamics (strong coupling). The second model, a driven oscillator whose solutions are known, possesses a true continuum. The infinite matrix representation of its Hamiltonian is truncated in order to check the accuracy and the convergence properties of the quasiquadratic scheme described in Appendix C. The influence of the size of the intermediate space is discussed. Finally, a hydrogen atom put in a static electric field (Stark effect) provides a good example of the efficiency of our approach to investigate simultaneously the two almost degenerate resonances originating from the first excited states of the hydrogen atom ($2s$ and $2p_0$ orbitals).

A. The Fano model

The infinite matrix representation of the Fano model [24,8] can be written in the form

$$\begin{pmatrix} 0 & v & v & v & \cdots \\ v & 0 & 0 & 0 & \\ v & 0 & -\delta & 0 & \\ v & 0 & 0 & +\delta & \\ \vdots & & & & \ddots \end{pmatrix}. \tag{37}$$

The energy of the discrete state ϕ coupled to the quasicontinuum is taken as the origin of the energies. δ is the constant energy difference between the levels of the quasicontinuum and v is the strength of the interaction between the discrete state and the quasicontinuum states $|k\rangle$, $k=0,\pm1,\pm2,\ldots$. The above notation as well as the exact solution of this model can be found in the complement C_1 of Ref. [8]. The physical results are obtained at the limit $\delta\to0$ while v^2/δ remains constant. The transition rate Γ to the continuum is equal to

$$\Gamma=\frac{2\pi^2}{\hbar\delta}. \tag{38}$$

We will consider successively two dynamics: an irreversible dynamics corresponding to a weak coupling ($\delta/v\ll1$) and a reversible dynamics corresponding to a strong coupling ($\delta/v\gg1$). In both cases the initial state is ϕ.

1. Irreversible dynamics (weak coupling)

The dynamics is projected into the one-dimensional model space ($n=1$) spanned by ϕ. For times $t\ll2\pi\hbar/\delta$ the initial state ϕ decays into the quasicontinuum whereas for larger times recurrences may appear. The unique matrix term $E(z)$ representing $H^{eff}(z)$ [defined by Eq. (11)] is given by the exact expression

$$E(z)=-i\frac{\Gamma\hbar}{2}\times i\cot\left(\frac{\pi z}{\delta}\right). \tag{39}$$

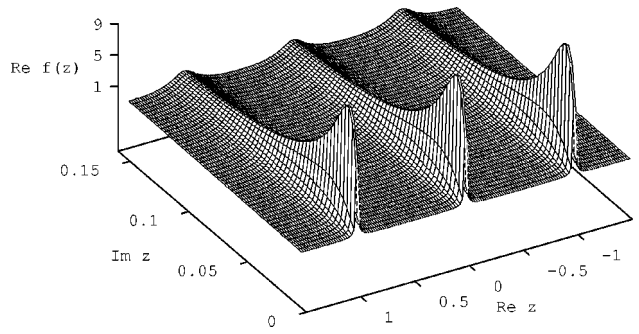

FIG. 2. Representation of the real part of $f(z)=i\cot(\pi z/\delta)$ as a function of z for $\delta=1$. This quantity tends to 1 when Imz tends to ∞; it tends to ∞ for the real values $z=k\delta$ $(k=0,\pm1,\pm2,\ldots)$.

The real part of $i\cot(\pi z/\delta)$ is shown in Fig. 2. It is quite remarkable that all information needed to compute the survival amplitude $\langle\phi|\psi(t)\rangle$ (autocorrelation function) is contained in $E(z)$ as given by Eq. (39). Note that this information is highly singular near the real energy axis, where distributions appear for the values $k\delta$ $(k=0,\pm1,\pm2,\ldots)$.

In order to obtain the first terms of the temporal evolution of the autocorrelation function, from the initial time $t=0$, we expand $E(z)$ in the Fourier series

$$E(z)=-i\frac{\Gamma\hbar}{2}-i\Gamma\hbar\sum_{k=1}^{\infty}\exp\left(\frac{2\pi ikz}{\delta}\right). \tag{40}$$

Then $1/[z-E(z)]$ is expanded in power of $x=E(z)+i\Gamma\hbar/2$ in the neighborhood of $z=-i\Gamma\hbar/2$,

$$\frac{1}{z-E(z)}=\frac{1}{z+i\Gamma\hbar/2}+\frac{x}{(z+i\Gamma\hbar/2)^2}+\frac{x^2}{(z+i\Gamma\hbar/2)^3}+\cdots. \tag{41}$$

The inverse Laplace-Fourier transformation of Eq. (41) and the use of the theorem of residues leads to the autocorrelation function

$$\langle\phi|\psi(t)\rangle=\exp\left(-\frac{\Gamma t}{2}\right)-\sum_{k=1}^{N}\theta(t-t_k)P_k[\Gamma(t-t_k)]\times\exp\left(-\frac{\Gamma(t-t_k)}{2}\right). \tag{42}$$

In Eq. (42) N is a positive integer. The polynomial P_k is defined by

$$P_k(x)=\sum_{l=1}^{k}(-1)^{l+1}\frac{\binom{l-1}{k-1}}{l!}x^l,\quad t_k=\frac{2\pi\hbar k}{\delta}.$$

The $\binom{l-1}{k-1}$ are the binomial coefficients. Expression (42) is exact when N approaches infinity. Figure 3 represents the survival probability $|\langle\phi|\psi(t)\rangle|^2$ as a function of t. It can be immediately checked that, as expected, the first recurrences correspond to the values $k=1,2,3,\ldots$ in Eq. (42).

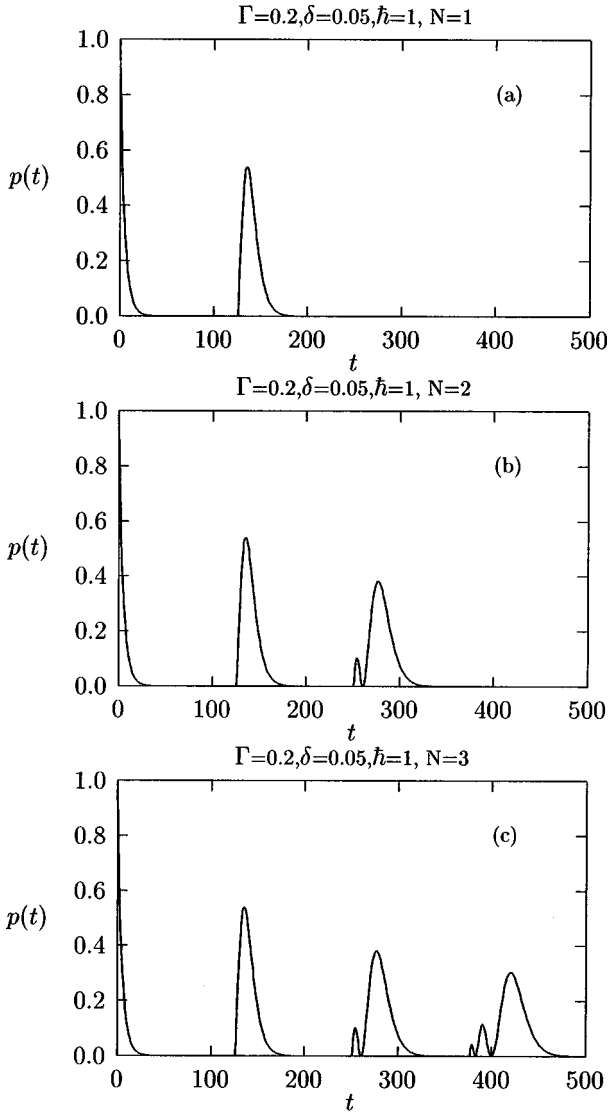

FIG. 3. Representation of the irreversible survival probability $p(t)=|\langle\phi|\psi(t)\rangle|^2$ as a function of t. Recurrences occur at times $t_k=2\pi k\hbar/\delta(k=1,2,\ldots$ and $\delta=1)$. The three first recurrences in (a), (b), and (c) come from the values $N=1$, 2, and 3 in expression (42) (arbitrary units).

2. Reversible dynamics (strong coupling)

The dynamics is now dominated by the reversible exchange that occurs inside the two-dimensional model space between the initial state $|\phi\rangle$ and the state $|0\rangle$ belonging to the quasicontinuum. The exact matrix representation of the two-dimensional effective Hamiltonian is given by

$$H^{eff}(z)=\begin{bmatrix}\epsilon & v\\ v & 0\end{bmatrix}, \tag{43}$$

where $\epsilon=E(z)-v^2/z$ is a small quantity with respect to v. It can be written in the form $\epsilon=-i\Gamma\hbar/2\times i[\cot(\pi z/\delta)-(\pi z/\delta)^{-1}]$. The representation of the real part of $i[\cot(\pi z/\delta)-(\pi z/\delta)^{-1}]$ is given in Fig. 4. It can be checked that ϵ is regular at $z=0$. The analytic continuation of $H^{eff}(z)$ can be obtained by expanding $H^{eff}(z)$ in a Taylor series near $z=0$, which leads to

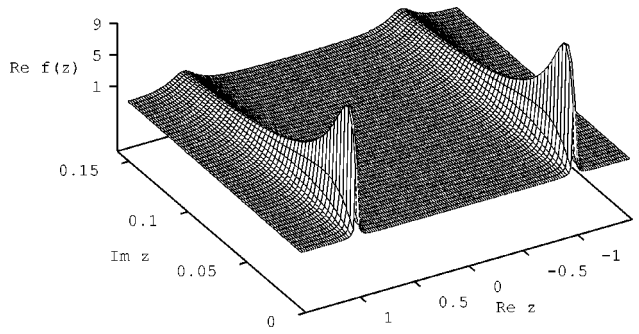

FIG. 4. Representation of the real part of $f(z)=i[\cot(\pi z/\delta)-(\pi z/\delta)^{-1}]$ as a function of z for $\delta=1$. Note the disappearance of the singularity at the origin $z=0$.

$$\left\langle \phi \left| \frac{P_0}{z-H^{eff}(z)} \right| \phi \right\rangle = \frac{z}{(z^2-v^2)} + \frac{z^2}{(z^2-v^2)^2}\epsilon + \frac{z^3}{(z^2-v^2)^3}\epsilon^2 + \cdots, \quad (44)$$

In Eq. (44)

$$\epsilon = z\left(\pi\frac{v}{\delta}\right)^2 \sum_{k=1}^{\infty} (-1)^k \frac{4^k}{(2k)!} B_{2k}\left(\frac{\pi z}{\delta}\right)^{2(k-1)}. \quad (45)$$

The B_{2k} are the Bernoulli numbers ($B_0=1, B_2=\frac{1}{6}, \ldots$). The inverse Laplace-Fourier transformation of Eq. (44) leads to the expansion of the autocorrelation function in powers of $(v/\delta)^2$

$$\langle \phi|\psi(t)\rangle = \cos\left(\frac{vt}{\hbar}\right) - \frac{1}{3}\left(\frac{\pi v}{\delta}\right)^2\left[\cos\left(\frac{vt}{\hbar}\right) - \frac{vt}{2\hbar}\sin\left(\frac{vt}{\hbar}\right)\right] + \cdots. \quad (46)$$

Figure 5 shows that the dynamics is not significantly modified by the addition of the first correcting term in $(v/\delta)^2$. The same conclusion would be achieved for higher-order terms.

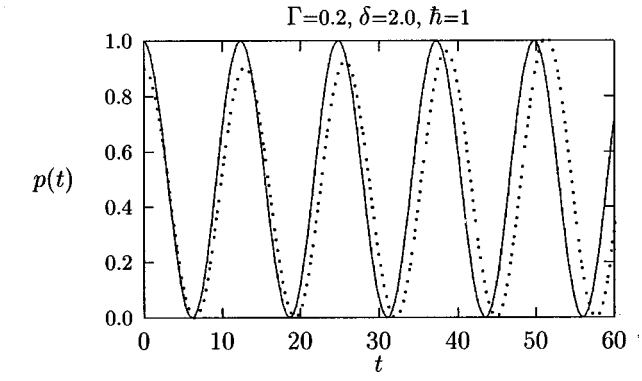

FIG. 5. Representation of the reversible survival probability $p(t)=|\langle\phi|\psi(t)\rangle|^2$ as a function of t. The full line corresponds to $\langle\phi|\psi(t)\rangle=\cos(vt/\hbar)$; the dotted line corresponds to $\langle\phi|\psi(t)\rangle$ given by Eq. (46) (arbitrary units).

B. Driven harmonic oscillator

The electric dipolar interaction between an electromagnetic wave and a harmonic oscillator can be approximated by the time-dependent Hamiltonian (see [25], pp. 204 and 205)

$$H=\hbar\omega a^\dagger a + \hbar[f(t)a + f^*(t)a^\dagger]. \quad (47)$$

If the oscillator is in its ground state $|0\rangle$ at the initial time, it develops into a coherent state. We will consider a resonant interaction and chose $f(t)$ in the form $f(t)=\alpha\exp(i\omega t)$. The exact solution is given by

$$|\psi(t)\rangle = \sum_{n=0}^{\infty} \frac{(-i\alpha)^n}{\sqrt{(n!)}} t^n \exp\left(-\frac{1}{2}\alpha^2 t^2\right) e^{-in\omega t}|n\rangle. \quad (48)$$

The probability amplitude and the occupation numbers of the various states follow an irreversible evolution. In particular, for the ground state, the autocorrelation function and the survival probability are exactly given by

$$\langle 0|\psi(t)\rangle = \exp\left(-\frac{\alpha^2 t^2}{2}\right), \quad p(t)=e^{-\alpha^2 t^2}. \quad (49)$$

The survival probability has to be compared with the probability law $p(t)=\exp(-\Gamma t)$ that characterizes the temporal evolution of a Breit-Wigner resonance. The Green's function corresponding to the autocorrelation function given in Eq. (49) is known (see Appendix A)

$$G(z) = -\frac{i\sqrt{\pi}}{\sqrt{2}\hbar\alpha}\exp^{-[1/2(z/\hbar\alpha)^2]}\operatorname{erfc}\left(-\frac{iz}{\sqrt{2}\hbar\alpha}\right). \quad (50)$$

$G(z)$ can be expressed [26] in the form of an infinite continuous fraction

$$G(z)=\frac{1}{z-E(z)}, \quad E(z)=\cfrac{(\hbar\alpha)^2}{z-\cfrac{2(\hbar\alpha)^2}{z-\cfrac{3(\hbar\alpha)^2}{z-\cdots}}}. \quad (51)$$

Again, the information concerning the autocorrelation function is contained in $E(z)$. In order to illustrate the efficiency of the computational scheme presented in Sec. III A and in Appendix C, we have used a finite matrix representation of the time-dependent operator $\mathcal{H}(t)$ [defined by Eq. (17)]. Since $\mathcal{H}(t)$ is periodic [$\mathcal{H}(t+T)\equiv\mathcal{H}(t)$, $T=2\pi/\omega$], the calculations were done within the framework of the Floquet theory [27]. The use of the moment method applied to $\mathcal{H}$ provides the relevant basis set in the generalized Hilbert space

$$|n\rangle\rangle = \frac{1}{\sqrt{T}}|n\rangle e^{-in\omega t}. \quad (52)$$

The matrix representation of $\mathcal{H}$ in this basis is given in Fig. 6(a). Note that this matrix representation is identical except for a multiplicative factor with the matrix representation of the position operator $(a+a^\dagger)$ acting in the standard basis of the unperturbed harmonic oscillator.

	$\|0\rangle\rangle$	$\|1\rangle\rangle$	$\|2\rangle\rangle$	$\|3\rangle\rangle$	$\|4\rangle\rangle$
$\langle\langle 0\|$	0	1	0	0	0
$\langle\langle 1\|$	1	0	$\sqrt{2}$	0	0
$\langle\langle 2\|$	0	$\sqrt{2}$	0	$\sqrt{3}$	0
$\langle\langle 3\|$	0	0	$\sqrt{3}$	0	$\sqrt{4}$
$\langle\langle 4\|$	0	0	0	$\sqrt{4}$	0

(a)

	$\|0\rangle\rangle$	$\|1\rangle\rangle$	$\|2\rangle\rangle$	$\|3\rangle\rangle$	$\|4\rangle\rangle$
$\langle\langle 0\|$	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	0	0
$\langle\langle 1\|$	$\frac{1}{\sqrt{2}}$	$-\sqrt{2}$	0	$-\frac{\sqrt{3}}{2}$	$-\frac{\sqrt{3}}{2}$
$\langle\langle 2\|$	$\frac{1}{\sqrt{2}}$	0	$\sqrt{2}$	$\frac{\sqrt{3}}{2}$	$\frac{\sqrt{3}}{2}$
$\langle\langle 3\|$	0	$-\frac{\sqrt{3}}{2}$	$\frac{\sqrt{3}}{2}$	$-\sqrt{4}$	0
$\langle\langle 4\|$	0	$-\frac{\sqrt{3}}{2}$	$\frac{\sqrt{3}}{2}$	0	$\sqrt{4}$

(b)

FIG. 6. Matrix representation of $\mathcal{H}=H-i\hbar\,(d/dt)$. H is the Hamiltonian of the driven harmonic oscillator given by Eq. (47) ($\hbar\omega=\alpha=1$). (a) basis $|n\rangle\rangle$ given by Eq. (52) and (b) rotated basis given by Eqs. (53).

Hereafter, it will be assumed that $|0\rangle\rangle$ spans a one-dimensional model space. The iterative determination of the reduced wave operator X cannot be obtained directly from the matrix representation in Fig. 6(a) since all its diagonal elements are zero. This highly degenerate representation has to be at least partially diagonalized. This was done by considering the matrix representation of $\mathcal{H}$ in Fig. 6(b) in the rotated basis

$$|i)\rangle=\begin{cases}\dfrac{1}{\sqrt{2}}[|i\rangle\rangle-|i+1\rangle\rangle], & i=1,3,\ldots\\[2ex] \dfrac{1}{\sqrt{2}}[|i+1\rangle\rangle+|i\rangle\rangle], & i=2,4,\ldots.\end{cases}\tag{53}$$

Although the new representation is very far from being diagonal, the iterative process described in Appendix C is very efficient. As expected, the convergence properties of the procedure depend strongly on the size of the intermediate space and on the number of terms used in the expansion of $P_0/(1-A_{22})$ (see Appendix C). The number of iterations required to obtain approximatively seven digits on the components of the wave operator is given in Table I. The calculations were carried out using a matrix representation of dimension $N=100$. The overall results were found to be in excellent agreement with the exact values (seven exact figures). The real and imaginary parts of $E(z)$ are represented in Figs. 7(a) and 7(b) for Im $z=0.5$ and 4.0, respectively. All dynamical information concerning the survival amplitude is contained in these dispersion curves, which are representative of an irreversible processes. The numerical results were found to be stable and the convergence properties quite similar by extending the size of Hamiltonian matrix ($N=200$).

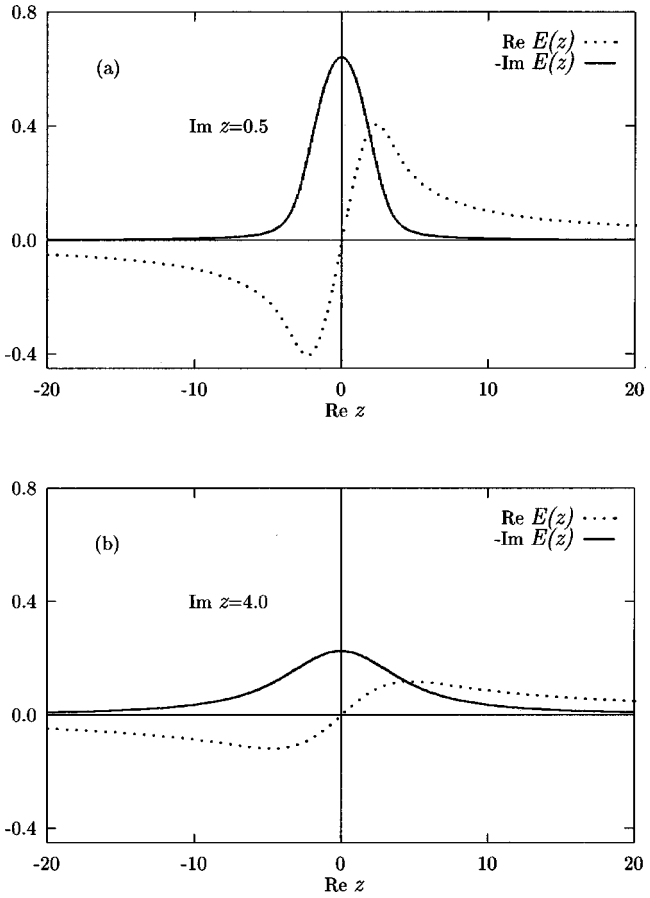

FIG. 7. Real and imaginary parts of $E(z)$ as a function of $E=\mathrm{Re}\,z$. (a) Im $z=0.5$ and (b) Im $z=4.0$.

C. Stark effect in the hydrogen atom

We have chosen to study this well-documented system because its spectrum possesses a true continuum. Moreover, there is no simple analytical solution and the hydrogen atom has been frequently used as a representative benchmark for testing resonance methods using a finite basis set of square-integrable (L^2) functions [28].

The Hamiltonian in spherical coordinates and in atomic units (a.u.) is given by

TABLE I. Number of iterations required for obtaining approximately seven figures in the components of the wave operator ($\epsilon=10^{-7}$) (see Appendix C) as a function of the dimension m of the intermediate space and of the number k of terms used in the expansion of $P_2/(1-A_{22})$.

	$z=4i$										$z=10+4i$			
$k \backslash m$	2	4	6	8	10	12	14	16	18	20	2	4	6	8
0	18	16	14	12	10	7	5	3	2	1	5	3	2	1
1	8	7	7	6	5	4	3	2	2	1	3	2	2	1
2	10	9	8	7	6	5	4	3	2	1	3	2	2	1
4	7	6	5	5	4	3	3	2	2	1	2	2	2	1
8	4	4	4	3	3	3	2	2	2	1	2	2	2	1

TABLE II. Poles in atomic units (a.u.) of the Green's function $\langle 1s|1/(z-H_\theta)|1s\rangle = 1/[z-E(z)]$ for the ground state of the hydrogen atom in the dc field $\mathcal{E}=0.1$ a.u. obtained by the iterative solution of Eq. (56); $\theta=0.4$.

Iteration	E(k)
0	-0.5
1	-0.526876-$i0.007936$
2	-0.527427-$i0.007290$
3	-0.527419-$i0.007269$
4	-0.527418-$i0.007269$
Ref. [28]	-0.527419-$i0.007268$
Ref. [29]	-0.527418-$i0.007269$

$$H=-\frac{\Delta}{2}-\frac{1}{r}-\mathcal{E}r\cos\theta, \tag{54}$$

where $\mathcal{E}$ is the amplitude of the electric field and $z=r\cos\theta$ is the z coordinate of the electron. Since we limit our numerical investigation to the energy of the resonances, assumed to correspond to the poles of the analytically continued Green's function, it is useful to work with the complex rotated Hamiltonian [14]

$$H_\theta=-\frac{\Delta}{2}e^{2i\theta}-\frac{e^{-i\theta}}{r}-\mathcal{E}r\cos\theta e^{i\theta}. \tag{55}$$

We have used for the ground and for the first excited state a basis set of Slater orbitals with angular symmetries up to $l=7$, as in Ref. [28]. The radial parts for the l symmetry were chosen in the form const$\times r^{l+k}e^{-r}$, $k=0,1,\ldots,9$.

1. Ground state

The exact $1s$ wave function spans the model space. We have considered a diagonal matrix representation of H_θ within each angular symmetry. This required the diagonalization of eight small 10×10 matrices. The iterative procedure in determining the wave operator was found to be very efficient to obtain the values of $E(z)$. From the knowledge of $E(z)$, the poles of the Green's function were easily found by solving the equation

$$z=E(z). \tag{56}$$

For this well-isolated resonance, which is almost a bound state, it is expected that the first-order iterative procedure $z^{(k+1)}=E(z^{(k)})$, $k=0,1,2,\ldots$, should converge in a few iterations [9]. The results are given in Table II. As expected, the convergence is very fast and the converged values are in excellent agreement with those found by Nicolaides and Themelis [28] and Silverman and Nicolaides [29].

2. First excited state

Since the two resonances are almost degenerate, it is relevant to use the two-dimensional model space spanned by the $2s$ and $2p_0$ wave functions. We have slightly extended the flexibility of the basis used for the ground state. This was done by adding to the previous basis two orbitals of s symmetry with radial parts proportional to $\exp(-r/2)$ and $r\exp(-r/2)$ and one orbital of p symmetry with a radial part proportional to $r\exp(-r/2)$. With this basis we have reproduced exactly the $2s$ and $2p_0$ energies of the isolated atom. The same procedure as above led to a two-dimensional z-dependent effective Hamiltonian whose eigenvalues were denoted $E_1(z)$ and $E_2(z)$. The iterative solution of the two equations $z=E_i(z)$, $i=1,2$, led to the two resonance energies. The values obtained at various iterations are given in Table III. Again, they are in excellent agreement with those previously reported [30,28].

V. CONCLUSION

Up to now, the theory of effective Hamiltonians for molecular quantum mechanics was based mainly on the time-dependent wave operator $\Omega(t)$ [1]. In this paper we adopt the spectral point of view in which a special importance is ascribed to the variable energy [2]. This approach is especially relevant for investigating long-lived events, such as quantum resonances. We have defined energy-dependent wave operators $\Omega(z)$ that arise naturally from either time-independent or time-dependent Hamiltonians. We have established the link between our approach and the (t,t') theory of Peskin and Moiseyev [6]. With the aim of solving large-scale molecular dynamics, Bloch-type equations were solved by an iterative procedure based on a partition of the full Hilbert space into a model space, an intermediate space, and

TABLE III. Complex eigenvalues $E_1(z)$ and $E_2(z)$, in atomic units, for the first excited state of the hydrogen atom in the dc field $\mathcal{E}=0.01$ a.u. of the effective Hamiltonian $H^{eff}(z)$ obtained at various iterations; $\theta=0.4$.

Iteration	$2s-2p_0$ state	$2s+2p_0$ state
0	-0.125	-0.125
1	-0.160063-$i0.01161$	$-0.103143i0.00194$
2	-0.166166-$i0.005351$	-0.103830-$i0.001783$
3	-0.166088-$i0.005446$	-0.103899-$i0.001673$
4	-0.166088-$i0.005446$	-0.103894-$i0.001650$
5		-0.103890-$i0.001647$
6		-0.103889-$i0.001647$
Ref. [30]	-0.16609-$i0.005442$	-0.10389-$i0.001637$
Ref. [28]	-0.166088-$i0.005446$	-0.103888-$i0.001632$

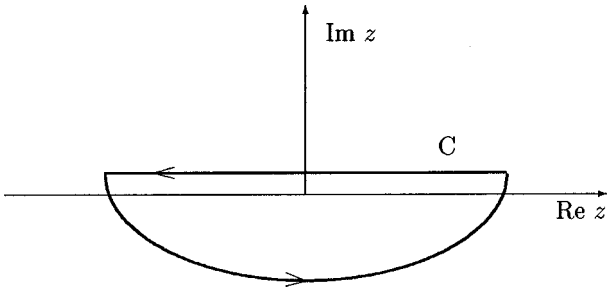

FIG. 8. Integration path C in the complex plane.

an outer space. The investigation of a few model examples has shown that the concepts of model space, energy-dependent wave operators, and effective Hamiltonians are useful for understanding both dynamics and effective computation. In the Fano model one- or two-dimensional model spaces were required for describing irreversible or reversible evolutions, respectively. Although our numerical investigation was purposely limited to small matrices, the iterative procedure presented in this paper is intended to perform large-scale dynamic calculations. Recently, the procedure has been successfully applied to the accurate determination of the lifetimes of many electronically and vibrationally excited states of the LiH molecule decaying through vibronic interactions [31].

APPENDIX A: THE LAPLACE-FOURIER TRANSFORMATION

The formulas below were adapted to quantum mechanics from Refs. [32] and [26]. The Laplace-Fourier transform of a function $f(t)$ is defined by

$$\hat{f}(z)=\frac{1}{i\hbar}\int_0^\infty dt\ f(t)e^{izt/\hbar}. \tag{A1}$$

For $t>0$ the function $f(t)$ can be recovered by integration in the complex plane (see Fig. 8):

$$f(t)=\frac{1}{2\pi i}\int_C dz\ \hat{f}(z)e^{-izt/\hbar}. \tag{A2}$$

The Laplace-Fourier transforms are

$$f(t)\leftrightarrow\hat{f}(z),$$

$$e^{-\epsilon t/\hbar}f\leftrightarrow\hat{f}(z+i\epsilon),$$

$$f(t-t_0)\leftrightarrow e^{izt_0/\hbar}\hat{f}(z),$$

$$i\hbar\,\delta(t)\leftrightarrow 1,$$

$$\frac{d^n f}{dt^n}\leftrightarrow\frac{1}{(i\hbar)^n}z^n\hat{f}(z),$$

$$t^n f(t)\leftrightarrow(-i\hbar)^n\frac{d^n\hat{f}(z)}{dz^n},$$

$$\theta(t)\leftrightarrow\frac{1}{z}$$

[$\theta(t)$ is the Heaviside function],

$$\theta(t)e^{-\epsilon t/\hbar}\leftrightarrow\frac{1}{z+i\epsilon},$$

$$\theta(t)e^{-\epsilon^2t^2/\hbar^2}\leftrightarrow\frac{\sqrt{\pi}}{2i\epsilon}e^{-z^2/4\epsilon^2}\mathrm{erfc}\left(-\frac{iz}{2\epsilon}\right),$$

$$\theta(t)\psi(t)\leftrightarrow\frac{1}{z-H}\phi$$

(the time-independent Hamiltonian).

APPENDIX B: THE BLOCH WAVE OPERATOR FOR BOUND STATES (FROM REFS. [33] AND [2])

The full Hilbert space is the direct sum of a finite n-dimensional model space and of its orthogonal complement, the outer space. The orthogonal projectors associated with the model space and the outer space are P_0 and Q_0, respectively,

$$P_0+Q_0=1. \tag{B1}$$

The theory is based on the Bloch wave operator Ω, which establishes a one-to-one correspondence between n projected solutions in the model space and n exact solution in the full Hilbert space. The wave operator obeys the basic nonlinear equation [34,35]

$$H\Omega=\Omega H\Omega, \tag{B2}$$

where H is the Hamiltonian of the system. Equation (B2) can be split into two parts and written in the form

$$H\Omega=\Omega H^{eff}, \tag{B3}$$

$$H^{eff}=P_0H\Omega. \tag{B4}$$

Equation (B3) is a natural generalization of the time-independent Schrödinger equation for one energy level. The eigenvalues of the effective Hamiltonian defined by Eq. (B4) provide n exact eigenvalues of H and the corresponding eigenfunctions are the projections in the model space of n exact solutions. An advantage of the wave operator approach is that it makes it possible to investigate simultaneously a small finite number of almost degenerate states. The diagonalization of a low-dimensional effective Hamiltonian provides exact energies by means of a numerically stable procedure. Another advantage of the Bloch wave operator approach for bound states is that it is quite similar to the wave operator formalism of scattering theory [36] in which the Møller operators fulfill the wave operator equation

$$H\Omega_\pm=\Omega_\pm H_0. \tag{B5}$$

The zeroth-order Hamiltonian describes usually noninteracting particles. Equations (B3) and (B5) possess quite similar linear structures.

APPENDIX C: DETERMINATION OF WAVE OPERATORS FOR GREEN'S FUNCTIONS

We assume that the full Hilbert space has been discretized and that the Hamiltonian of the system is represented by a finite-dimensional $N\times N$ matrix. Since we intend to investigate systems up to $N\simeq 10^6$, it would be impossible to invert or to diagonalize the corresponding large matrices. Therefore, we have to look for iterative schemes. This requires a computational effort proportional to N^2 instead of N^3 for the direct inversion or the full diagonalization of large matrices. In the present approach we extend a computational scheme previously developed within the theory of effective Hamiltonians for bound states [7]. The full N-dimensional Hilbert space is split into three subspaces: the *model space* (dimension n), the *intermediate space* (dimension m), and the *outer space* (dimension N-n-m). Typically, we could have $n\simeq 10$, $m\simeq 10^2$, and $N>10^4$. Diagonalization and inversions can easily be done within the intermediate space, which interacts strongly with the model space, whereas the weak influence of the outer space can be treated by perturbation. The orthogonal projectors associated with the model space, the intermediate space, and the outer space are P_0, P_1, and P_2, respectively,

$$P_0+P_1+P_2=1, \quad P_1+P_2=Q_0, \quad P_0+Q_0=1. \tag{C1}$$

We assume that the full Hamiltonian $H=H_0+V$ is divided into an unperturbed Hamiltonian H_0, diagonal in its matrix representation, and a perturbation V. From the definition (33), the reduced wave operator $X(z)$ is a solution of

$$(z-H)X(z)=Q_0HP_0. \tag{C2}$$

Let us split $X(z)$ into two terms

$$X(z)=X_1+X_2,$$

where

$$X_1=P_1X(z), \quad X_2=P_2X(z). \tag{C3}$$

Multiplying both sides of Eq. (C2) on the left by P_1 leads to

$$X_1=\frac{P_1}{z-H}V(1+X_2)P_0. \tag{C4}$$

Multiplying both sides of Eq. (C2) on the left by P_2 leads to

$$X_2=\frac{P_2}{z-H_0}V(1+X_1+X_2)P_0. \tag{C5}$$

Equations (C4) and (C5) can be written in the form

$$X_1=f_1, \quad X_2=f_2, \tag{C6}$$

where

$$f_1=\frac{P_1}{z-H}V(1+X_2)P_0, \tag{C7}$$

$$f_2=\frac{P_2}{z-H_0}V(1+X_1+X_2)P_0. \tag{C8}$$

One can expand Eqs. (C6) in the neighborhood of the exact solution in terms of two small increments ΔX_1 and ΔX_2 (Newton-Raphson scheme):

$$X_1+\Delta X_1=f_1+A_{12}\Delta X_2, \tag{C9}$$

$$X_2+\Delta X_2=f_2+A_{21}\Delta X_1+A_{22}\Delta X_2, \tag{C10}$$

where

$$A_{12}=\frac{P_1}{z-H}VP_2,$$

$$A_{21}=\frac{P_2}{z-H_0}VP_1, \tag{C11}$$

$$A_{22}=\frac{P_2}{z-H_0}VP_2.$$

Whatever might be approximate values of X_1 and X_2, the exact Newton-Raphson scheme would lead to the exact solution in one iteration. After some elementary algebra, the solution of the system of linear Eqs. (C9) and (C10) is given by

$$\Delta X_1=-\frac{P_1}{1-A_1}\left[(X_1-f_1)+A_{12}\frac{P_2}{1-A_{22}}(X_2-f_2)\right], \tag{C12}$$

$$\Delta X_2=-\left[1+\frac{P_2}{1-A_{22}}A_2\right]\frac{P_2}{1-A_{22}}[A_{21}(X_1-f_1)+(X_2-f_2)], \tag{C13}$$

where

$$A_1=A_{12}\frac{P_2}{1-A_{22}}A_{21}, \quad A_2=A_{21}\frac{P_1}{1-A_1}A_{12}. \tag{C14}$$

Since the operator $1-A_{22}$, which is defined in the outer space, cannot be inverted directly, approximate inversion schemes are required. Quasi-Newton procedures can be obtained by expanding $P_2/(1-A_{22})$:

$$\frac{P_2}{1-A_{22}}=1+A_{22}+(A_{22})^2+\cdots. \tag{C15}$$

The series converges if all the eigenvalues λ_i of A_{22} have $|\lambda_i|<1$. This can be obtained by using a large intermediate space. If there are eigenvalues $|\lambda_i|>1$, one can use a procedure based on Chebyshev polynomials or on more general polynomial expansions of the form

$$\frac{P_2}{1-A_{22}}=c_0+c_1A_{22}+c_2(A_{22})^2+\cdots \tag{C16}$$

(see [37], p. 99). In our program, the iterative process stops when the quantity (Euclidian norm)

$$\frac{1}{\sqrt{n(N-n)}}\|X-f_1-f_2\| \tag{C17}$$

becomes smaller than $\epsilon=10^{-p}$; p provides approximately the number of exact figures of the components of X_1 and X_2.

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