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REGULAR ARTICLE

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From effective Hamiltonians to fluctuation and dissipation

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Abstract Irreversible quantum dynamics is reviewed by means of projected resolvents and effective Hamiltonians. It is shown that for a particular partition the dynamical equations are formally identical to the generalized Langevin equation of non-equilibrium statistical mechanics. Three model applications underline the fundamental role played by fluctuations to study line profiles in spectroscopy and to discuss the relationship between fluctuation and dissipation. A new expression of the parameter q characterizing Fano profiles is presented.

Keywords Effective Hamiltonian · Projection techniques · Green function · Fluctuation · Dissipation · Fano profiles

1 Introduction

Projection methods are widely used in quantum chemistry to study the variables of interest while discarding the irrelevant degrees of freedom [1,2]. These methods are also of fundamental importance in non-equilibrium statistical mechanics to investigate macroscopic variables [3,4]. The comparison between theory and experiment is usually achieved through the determination of mean values. However, a deeper understanding of the phenomena may require a finer analyses in terms of fluctuations (dispersions) [5]. A typical example is the local analysis of delocalized molecular wave functions in terms of atomic charges and of their fluctuations. A similar analysis also helps to investigate spin orderings [6]. The molecular orbitals delocalized on the entire molecule are viewed as macroscopic variables (long correlation times) whereas the atomic orbitals are microscopic variables (short correlation times). Although quantum mechanics, quantum chemistry and non-equilibrium statistical mechanics are separated fields, the use of projection techniques and the perturbation theory pleads in favor of the development of a comprehensive theory. Projected resolvents and effective interactions are universal tools for investigating the dynamics. Moreover, the theory benefits from the powerful properties of analytic functions. We have already shown that the determination of small-dimensional effective Hamiltonians allows a simple description of the line profiles in spectroscopy. Fano profiles [7] are easily described in terms of interference between two resonances [8]. The theory was extended to several interacting resonances [9,10]. In this paper we continue to derive results of general relevance. The theory is recalled in Sect. 2 where various partitions of the resolvent are presented. It is shown that one of these partitions is formally identical to the Langevin equation of non-equilibrium statistical mechanics. Then, in Sect. 3, the formalism is applied to three specific problems. First, we present a form of the fluctuation–dissipation theorem based on the perturbation theory. The second application gives an expression of the q parameter of Fano profiles that contains explicitly the lifetime and the dispersion in energy of a resonance. Finally, some dynamical aspects of the ionization of the hydrogen atom are discussed.

2 Theory

Let H be the Hamiltonian of the system. The dynamics is characterized by the evolution operator

$$U(t) = \mathrm{e}^{-\mathrm{i}\,Ht/\hbar}, \tag{1}$$

the Laplace transform of which is the resolvent or Green operator

$$G(z) = \frac{1}{z-H}, \tag{2}$$

Dedicated to Jean-Paul Malrieu who advocated the analyses of molecular wave functions in terms of atomic observables and of their fluctuations.

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where z is the variable energy extended in the complex plane [11]. The evolution operator is recovered by the inverse Laplace transformation

$$U(t) = \frac{1}{2\pi\,\mathrm{i}} \int_C G(z)\, \mathrm{e}^{-\mathrm{i}\,zt/\hbar} \mathrm{d}z \quad (t > 0). \tag{3}$$

The Green operator which is unambiguously defined for $\operatorname{Im} z > 0$ is assumed to be analytically continued in the second Riemann sheet for $\operatorname{Im} z < 0$. The integration path C in the complex plane runs on the real-energy axis from $+\infty$ to $-\infty$ and is closed in the lower part ($\operatorname{Im} z < 0$) of the complex plane (see, for example, Ref. [12]).

The introduction of the resolvent in quantum mechanics applied to the many-body problem was done more than half a century ago [13–15]. Since that time resolvents and the closely related correlation functions have found extended applications in many domains ranging from atomic and molecular physics [4,11], condensed matter physics [16], chemical physics [17] to nuclear physics [18,19]. Resolvents and correlation functions play also a fundamental role in statistical mechanics [3,4,20–22]. The purpose of this paper is not to review such extended fields since there is a huge literature on these subjects. Our aim is to focus on projection methods and partitioning techniques (see, e.g., [1,10,11,23–25]) implying resonances and to show that elementary models and analytic continuation, without any reference to the many-body theory, can already provide results of general value.

For many applications it is convenient to investigate the Green operator by means of perturbative approaches using partitioning techniques. The space of the states is divided into a small n-dimensional *model* (or inner) space and its orthogonal complement the *outer* space. The projectors onto the model space and the outer space are P_0 and Q_0, respectively, ($P_0 + Q_0 = 1$). The projector into the model space can be written as

$$P_0 = \sum_{i=1}^{n} |i\rangle\langle i|; \quad \langle i|j\rangle = \delta_{ij}; \quad i, j = 1, 2 \cdots n. \tag{4}$$

If we are interested in the dynamics in the model space, the relevant information is provided by the projected resolvent

$$P_0 \frac{1}{z - H} P_0 = \frac{P_0}{z - H^{\mathrm{eff}}(z)}. \tag{5}$$

Equation (5) defines an energy-dependent effective Hamiltonian

$$H^{\mathrm{eff}}(z) = P_0 H P_0 + R(z);$$
$$R(z) = P_0 H \frac{Q_0}{z - H} H P_0. \tag{6}$$

$P_0 H P_0$ is the Hamiltonian projected in the model space and $R(z)$ is an energy-shift operator [11]. In Eq. (6) and hereafter, we shall use the abbreviated notation $Q_0/(z - H)$ instead of $Q_0/(z - Q_0 H Q_0)$ which means the inversion of $Q_0(z - H)Q_0$ within the outer space. A more general partition of the resolvent (see appendix A) is

$$\frac{1}{z - H} P_0 = \frac{P_0}{z - H^{\mathrm{eff}}(z)} + \frac{Q_0}{z - H} H \frac{P_0}{z - H^{\mathrm{eff}}(z)}. \tag{7}$$

It results from Eq. (7) that the Laplace transform of the time derivative of the evolution operator projected, on the right, in the model space can be expressed as

$$\frac{H}{z - H} P_0 = \frac{H^{\mathrm{eff}}(z)}{z - H^{\mathrm{eff}}(z)} + \frac{Q_0}{z - H} H \frac{P_0}{z - H^{\mathrm{eff}}(z)} z. \tag{8}$$

Equations (7) and (8) assume that the resolvent has been partitioned according to (36) in appendix A. Another form of Eq. (8) is derived in appendix A from the partition (42):

$$\frac{H}{z - H} P_0 = \frac{1}{z - H} H^{\mathrm{eff}}(z) + \frac{Q_0}{z - H} H P_0. \tag{9}$$

The above expressions underline the importance of discussing the reduced dynamics arising from an initial state belonging to the model space in terms of effective Hamiltonians. The formal connection with the Langevin equation is established in Appendix A.

The aim of the theory is to provide effective Hamiltonians which depend as little as possible on the energy. This can be achieved by extending the model space. The choice of the states defining the model space is crucial. These states are generally long-lived states, for example, resonances or quasi-bound states [2]. However, the model space can also include short-lived states which produce asymmetric line profiles in spectroscopy (Fano profiles). This is similar to non-equilibrium statistical mechanics where both slow and fast variables are required for passing from the microscopic world (short correlation times) to the macroscopic world (long correlation times). From an effective Hamiltonian the dynamics in the model space is provided by the inverse Laplace transformation

$$|\phi(t)\rangle = \frac{1}{2\pi\,\mathrm{i}} \int_C \frac{P_0}{z - H^{\mathrm{eff}}(z)} |\phi\rangle\, \mathrm{e}^{-\mathrm{i}\,zt/\hbar}\, \mathrm{d}z. \tag{10}$$

$|\phi(t)\rangle$ is the projection of the exact solution in the model space and ϕ is the initial state. The probability of remaining in the initial state (survival probability) at time t is

$$P(t) = |\, \langle\phi|\phi(t)\rangle\, |^2. \tag{11}$$

Other observables are the line shapes (or line profiles) characterized by the intensity

$$I(E) = -\frac{1}{\pi} \operatorname{Im} G(E); \quad G(E) = \langle\phi| \frac{P_0}{E - H^{\mathrm{eff}}(E)} |\phi\rangle. \tag{12}$$

E is the energy and it is always assumed that the system was prepared at the initial time $t = 0$ in a discrete state $|\phi\rangle$ coupled to a continuum. We aim to investigate the exact solution $\psi(t) = \exp(-\mathrm{i}\,Ht/\hbar)|\phi\rangle$ that can be expanded as

$$|\psi(t)\rangle = |\phi\rangle - \mathrm{i}\frac{t}{\hbar} H|\phi\rangle - \frac{t^2}{2\hbar^2} H^2|\phi\rangle \cdots \tag{13}$$

For short times the dynamics is supported by the states $H^k|\phi\rangle$; ($k = 0, 1, \ldots$) which generate the basis of the method of moments [26]. Since these states are non-orthogonal, the Gram–Schmidt procedure applied to $|\phi\rangle$, $H|\phi\rangle$, $H^2|\phi\rangle \ldots$ defines in the model space an orthogonal basis $|i\rangle$; ($i =$

$1, 2, \ldots, n$). In this paper we shall consider only two- and three-dimensional model spaces ($n = 2, 3$). The associated matrix representations are

$$\mathbf{H}^{\text{eff}}(z) = \begin{bmatrix} E_1 & \Delta E \\ \Delta E & E_2 + R_2(z) \end{bmatrix} \tag{14}$$

and

$$\mathbf{H}^{\text{eff}}(z) = \begin{bmatrix} E_1 & \Delta E & 0 \\ \Delta E & E_2 & H_{23} \\ 0 & H_{23} & E_3 + R_3(z) \end{bmatrix}, \tag{15}$$

where $R_2(z) = \langle 2|R(z)|2\rangle$ and $R_3(z) = \langle 3|R(z)|3\rangle$. The matrix representations (14) and (15) are not universal. In fact, they are specific to the case when the model space is generated from an arbitrary initial state $|\phi\rangle$ and the successive action of H on it. The energy-shift operator is represented by a unique non-zero element only under these assumptions (see, e.g., [21] chapter 14). The advantage of using an orthonormal basis is to provide matrix representations whose elements have a clear meaning: energies on the diagonal and extra-diagonal energy dispersions. Thus $\Delta E = [\,\langle 1|H^2|1\rangle - \langle 1|H|1\rangle^2\,]^{1/2}$ represents the fluctuation of the energy in the initial state. Matrices (14) and (15) are exact. Unfortunately, their determination for actual systems is a difficult task. Nevertheless, we will show that simple matrix representations, such as (14) and (15), can provide general results in many domains ranging from line profiles (Fano profiles) to the fundamentals of fluctuation and dissipation. From a mathematical point of view the success is founded on the basic properties of analytic functions, mainly on analytic continuation.

The purpose of the elementary applications that are presented in the next section is to illustrate the relevance of the approach.

3 Applications

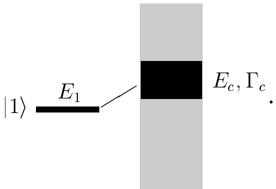
3.1 Fluctuation and dissipation

We start from the matrix representation (14) and consider a simplified model of a resonance which may be weakly or strongly coupled to a continuum. It is assumed that there are no other resonances imbedded in the continuum. Then one can neglect the dependence of $R_2(z)$ on z (see complement C_3 in Ref [11]) for a flat continuum approximation and a graphical construction of the Green function to understand the time evolution of the system. Separating the real and imaginary parts of $R_2(z)$ provides

$$R_2(z) \simeq \Delta_c - i\frac{\Gamma_c}{2} \tag{16}$$

which allows to transform (14) into the energy-independent effective Hamiltonian

$$\mathbf{H}^{\text{eff}} = \begin{bmatrix} E_1 & \Delta E \\ \Delta E & E_c - \mathrm{i}\frac{\Gamma_c}{2} \end{bmatrix}. \tag{17}$$



$E_c = E_2 + \Delta_c$ and Γ_c are the energy and the width of the effective part of the continuum (doorway state) [19,27]. The spectral decomposition of the effective Hamiltonian reads

$$H^{\text{eff}} = |\phi_1\rangle\langle\tilde{\phi_1}|\,\mathcal{E}_1 + |\phi_2\rangle\langle\tilde{\phi_2}|\,\mathcal{E}_2. \tag{18}$$

The eigenenergies $\mathcal{E}_1$ and $\mathcal{E}_2$ are complex; $\langle\tilde{\phi_1}|$ and $\langle\tilde{\phi_2}|$ are the duals of $|\phi_1\rangle$ and $|\phi_2\rangle$ [8]. The application of the Cauchy theorem in Eq. (10) leads to the time-dependent wave function

$$\phi(t) = \tilde{c}_1 \exp(-\mathrm{i}\frac{\mathcal{E}_1}{\hbar}t)|\phi_1\rangle + \tilde{c}_2 \exp(-\mathrm{i}\frac{\mathcal{E}_2}{\hbar}t)|\phi_2\rangle, \tag{19}$$

where

$$\tilde{c}_1 = \langle\tilde{\phi_1}|\phi\rangle; \qquad \tilde{c}_2 = \langle\tilde{\phi_2}|\phi\rangle. \tag{20}$$

Equation (19) allows us to compute the survival probability (11). The line shape can be expressed as

$$I(E) = -\frac{1}{\pi}\,\mathrm{Im}\left(\frac{f_1}{E-\mathcal{E}_1} + \frac{f_2}{E-\mathcal{E}_2}\right); \qquad f_i = \langle\phi|\phi_i\rangle\langle\tilde{\phi_i}|\phi\rangle;\ (i = 1, 2). \tag{21}$$

The survival probabilities and the associated line shapes are represented in Fig. 1 for three values of Γ_c. From (a) to (c) one passes from an irreversible decay of the survival probability to Rabi-like reversible oscillations. These results were obtained from the exact diagonalization of the effective Hamiltonian. However, it is illuminating to proceed by perturbation in order to provide new insights in the relationship between fluctuation and dissipation. Assuming that the diagonal terms are dominant in (17), the perturbation theory provides the eigenenergies

$$\mathcal{E}_1 = E_1 + \frac{(\Delta E)^2}{E_1 - E_c + \mathrm{i}\frac{\Gamma_c}{2}} + \cdots; \qquad \mathcal{E}_2 = E_c - \mathrm{i}\frac{\Gamma_c}{2} + \frac{(\Delta E)^2}{E_c - E_1 - \mathrm{i}\frac{\Gamma_c}{2}} + \cdots \tag{22}$$

In addition, if we assume that $|E_c - E_1| \ll \Gamma_c$, Eq. (22) reduces to

$$\mathcal{E}_1 = E_1 - \mathrm{i}\frac{\Gamma}{2} + \cdots, \qquad \mathcal{E}_2 = E_c - \mathrm{i}\frac{\Gamma_c}{2} + \mathrm{i}\frac{\Gamma}{2} + \cdots \tag{23}$$

where

$$\boxed{\Gamma = 4\frac{(\Delta E)^2}{\Gamma_c}}. \tag{24}$$

Equation (24) provides a particular form of the *fluctuation–dissipation* theorem which relates spectral densities of fluctuation to dissipation functions. Here the fluctuation in energy ΔE is related to the dissipation coefficient Γ appearing in the exponential decay of $P(t) \simeq \exp(-\frac{\Gamma}{\hbar}t)$. This means that only zero-frequency components are considered. In addition no trace was taken over a reservoir (Fig 1). However, the same expression (24) was derived by Cohen-Tannoudji et al. from a “coarse grained” expression of the rate

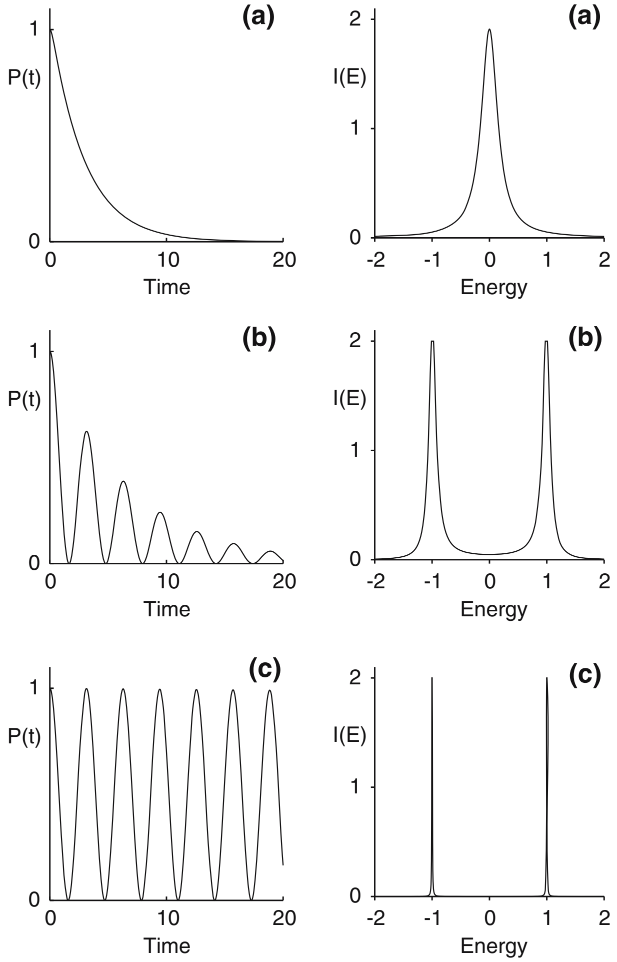


Fig. 1 Dissipation and oscillations. From weak to strong coupling. The effective Hamiltonian is given by Eq. (17). $E_1 = E_c = 0, \Delta E = 1$. The dynamics (*on the left*) and the line shapes (*on the right*) are presented for three values of Γ_c (a) $\Gamma_c = 12$, (b) $\Gamma_c = 0.3$, (c) $\Gamma_c = 0.001$. The system was prepared in the initial state $|1\rangle$. (arbitrary units)

of variation of the density matrix (operator) describing a statistical mixture of states (see §D in chapter IV of Ref. [11]). Since expression (24) was derived by perturbation, the conditions of validity of the perturbation theory must be satisfied. The eigenfunctions associated with $\mathcal{E}_1$ and $\mathcal{E}_2$ are

$$|\phi_1\rangle = |1\rangle + 2\,\mathrm{i}\frac{\Delta E}{\Gamma_c}|2\rangle + \cdots ,$$
$$|\phi_2\rangle = |2\rangle - 2\,\mathrm{i}\frac{\Delta E}{\Gamma_c}|1\rangle + \cdots , \tag{25}$$

the validity of which requires

$$\Delta E \ll \Gamma_c. \tag{26}$$

Let us define two correlation and dissipation times by

$$\tau_c = \frac{\hbar}{\Gamma_c}; \quad \tau = \frac{\hbar}{\Gamma}. \tag{27}$$

Then condition (26) can be transformed into

$$\tau_c \ll \tau \tag{28}$$

which means that the microscopic correlation time must be much shorter that the macroscopic correlation time. Condition (28) can also be transformed into

$$\Delta E \cdot \tau \gg \frac{\hbar}{2} \tag{29}$$

which is compatible with the energy–time uncertainty relation.

Thus, we have not only established an expression of the fluctuation–dissipation theorem but have also predicted its range of validity in the framework of the standard perturbation theory. The results which were derived from effective Hamiltonians and wave functions could be easily generalized to effective Liouvillians and density matrices when the initial state is not a pure state. In many cases it is easier to apply the perturbation theory in the complex plane (energy or frequency) than to investigate directly the time-dependent observables (time-dependent perturbation theory, coarse graining, etc.).

3.2 Fano profiles

The above derivation of the fluctuation–dissipation theorem was based on a simple model Hamiltonian. We employ it again to investigate asymmetric profiles in spectroscopy implying quantum interferences with the continuum. Instead of using the perturbation theory we shall determine the exact Green function associated with the initial state

$$|\phi\rangle = \cos\theta\,|1\rangle + \sin\theta\,|2\rangle. \tag{30}$$

The probabilities of exciting the resonance and of exciting the continuum at the initial time are $\cos^2\theta$ and $\sin^2\theta$, respectively (Fig 2). Assuming $E_1 = E_c = 0$, the direct calculation of the Green function (12) gives

$$G(E) = \frac{E + \Delta E \sin 2\theta + \mathrm{i}\frac{\Gamma_c}{2}\cos^2\theta}{E\,(E + \mathrm{i}\frac{\Gamma_c}{2}) - (\Delta E)^2} \tag{31}$$

and the intensity

$$I(E) = \left| \frac{E \sin\theta + \Delta E \cos\theta}{E\,(E + \mathrm{i}\frac{\Gamma_c}{2}) - (\Delta E)^2} \right|^2 \frac{\Gamma_c}{2\pi}. \tag{32}$$

It allows the direct determination of the Fano q parameter (see Eq. (20) in Ref. [9])

$$\boxed{q = 2\,\frac{\Delta E}{\Gamma} \cdot \cot\theta}. \tag{33}$$

This expression is exact and new. It should have a large range of validity irrespective of the type of spectroscopy (dipolar electric, magnetic…). It is the product of two factors. The first one is the ratio of the dissipation in energy of the resonance ΔE over its lifetime Γ. The second factor is the ratio of the probability amplitudes of exciting the resonance ($\cos\theta$) or the continuum ($\sin\theta$) at the initial time. The parameter q appears in the celebrated Fano's expression of the line shape. It characterizes the asymmetry of the profile (see Eq. (21) in Ref. [7]). Expression (33) may appear rather formal since

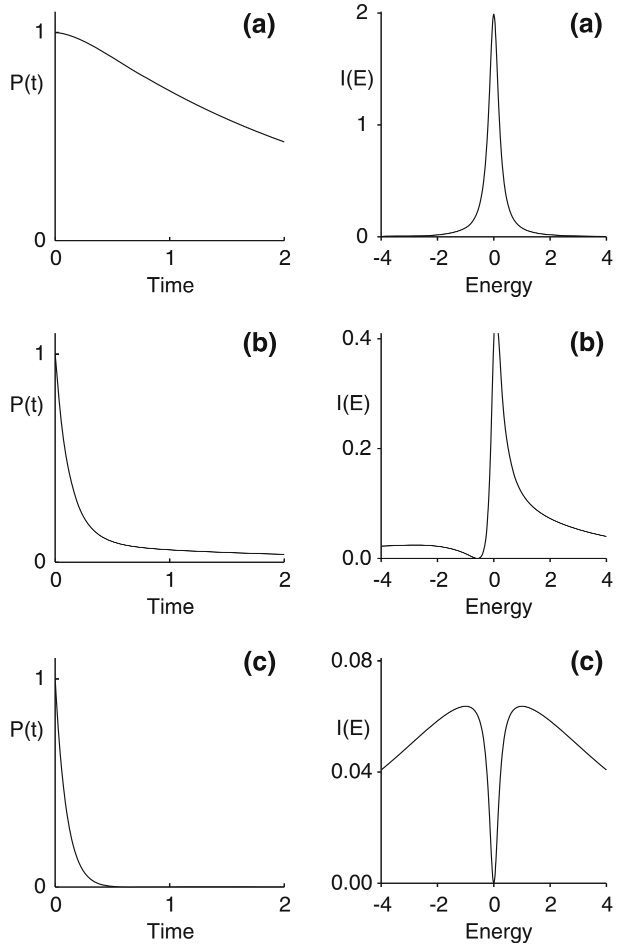


Fig. 2 Fano profiles. The effective Hamiltonian is given by (17), $E_1 = E_c = 0$, $\Delta E = 1$ and $\Gamma_c = 10$. The survival probabilities $P(t)$ Eq. (11) (*on the left*) and the line shapes $I(E)$ Eq. (12) (*on the right*) are represented for the initial state $|\phi\rangle = \cos\theta\,|1\rangle + \sin\theta\,|2\rangle$. (a) $\theta = 0$, $q = \infty$, (b) $\theta = \pi/3$, $q = 5/\sqrt{3}$, (c) $\theta = \pi/2$, $q = 0$. (arbitrary units)

ΔE and $\cot\theta$ are not measurable. However, the essence of this expression is to express the observable quantities q and Γ in terms of the dispersion in energy ΔE and $\cot\theta$ which govern the excitation of the continuum at the initial state, thus providing a microscopic explanation of their origin.

Expression (33) is the second important result of this paper after the derivation of the formula (24) of the fluctuation–dissipation theorem. Note again the role played by the fluctuation ΔE in the expression (33).

3.3 Ionization of the hydrogen atom

A hydrogen atom is subjected to a static electric field of amplitude $\mathcal{E}$. As soon as the atom is exposed to the field it becomes a resonance and the atom begins to ionize. We assume that the atom is in the ground state at the initial time. Many analytical and accurate numerical studies have been already devoted to this system (see, for example, Ref. [28] and references therein). Here we focus on models (14) and (15) which provide an elementary description of the energy and of the dynamical properties in terms of the energy dispersion ΔE of the resonance. If the electric field is weak ($\mathcal{E} \ll 0.01$ a.u), the isolated resonance decays following approximatively an exponential law. The Hamiltonian of the system in atomic units (a.u.) is

$$H = -\frac{\Delta}{2} - \frac{1}{r} + \mathcal{E} r \cos\theta. \tag{34}$$

The matrix elements of the representations (14) and (15) are easily computed. One finds (a.u.)

$$E_1 = -0.5, \qquad E_2 = 0, \qquad E_3 = \frac{5 + (186/25)\mathcal{E}^2}{1 + (996/25)\mathcal{E}^2},$$
$$H_{23} = \frac{1}{2\sqrt{3}}\left(1 + \frac{996}{25}\mathcal{E}^2\right)^{\frac{1}{2}}. \tag{35}$$

The lifetimes of the states $|2\rangle$ and $|3\rangle$ are much shorter than the lifetime of the resonance 1s, so it is justified to assume that the energy shifts $R_2(z)$ and $R_3(z)$ in (14) and (15) are complex constants. In our model they were chosen in such a way that one of the eigenvalues of the energy-independent effective Hamiltonian (Markovian approximation) coincides exactly with the pole of the Green function corresponding to the resonance 1s. The direct diagonalization of (14) and (15) allows us to compute the survival probability of remaining in the initial state at the time t. Figure 3 shows that the simplest models $n = 2$ and $n = 3$ (dashed and dotted lines, respectively) provide already good approximations of the exact dynamics (full lines). The same is true for the line shapes on the right of Fig. 3. We see that the solution improves from $n = 2$ to $n = 3$. The more extended the model space is, the better the solution. The exact solution would require $n = \infty$ but this cannot be done within the method of moments which fails from $n = 3$ because of the appearance of Dirac functions. Thus the general statement concerning the relationship between fluctuation and dissipation (see above) is well illustrated on the simplest actual system possessing only one electron.

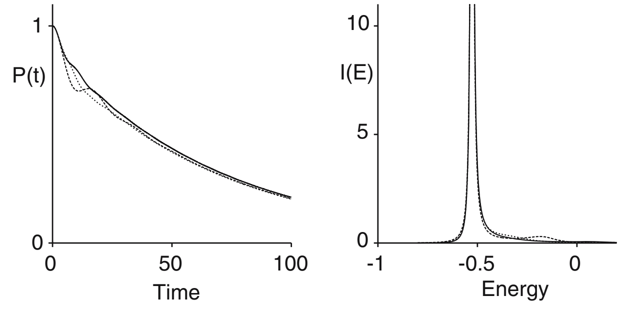


Fig. 3 Ionization of the hydrogen atom in a static electric field. $\mathcal{E} = 0.1$ a.u. *Full lines* exact calculation; *dashed lines* model Hamiltonian $n = 2$; *dotted lines* model Hamiltonian $n = 3$. The survival probability $P(t)$ and the intensity $I(E)$ are defined by Eqs. (11) and (12) (atomic units).

4 Conclusion

We have reviewed the theory of quantum dynamics based on the determination of projected resolvents and energy-dependent effective Hamiltonians. A similar approach for irreversible statistical physics would require the determination of energy-dependent effective Liouvillians. We have pointed out the partition needed for deriving projected equations of the dynamics which are formally identical to the generalized Langevin equation. We have presented a new formulation of the relationship between fluctuation and dissipation when the initial state is a pure state. For that purpose, a two-dimensional effective Hamiltonian was especially useful since the perturbation theory in the complex plane allowed us to express the width of the resonance in terms of a much larger width of a doorway state. The derivation of a new expression of the parameter q in Fano profiles is an illustration of how the theory can bring generic results since the Green function formalism can be extended to time-dependent Hamiltonians (see [12]). Another extension of the formalism including mixed initial states (thermal averages) is being investigated. It should open new ways to pass from the microscopic world (short correlation times) to the macroscopic world (long correlation times) and provide a better understanding of the roots of irreversibility.

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Appendix

A Partitioning technique

The partition of the resolvent may be written as [2,11]

$$\begin{aligned}\frac{1}{z-H} = {} & \frac{P_0}{z-H^{\mathrm{eff}}(z)} \\ & + \frac{Q_0}{z-H} H \frac{P_0}{z-H^{\mathrm{eff}}(z)} + \frac{P_0}{z-H^{\mathrm{eff}}(z)} H \frac{Q_0}{z-H} \\ & + \frac{Q_0}{z-H} + \frac{Q_0}{z-H} H \frac{P_0}{z-H^{\mathrm{eff}}(z)} H \frac{Q_0}{z-H},\end{aligned} \tag{36}$$

where

$$H^{\mathrm{eff}}(z) = P_0 H P_0 + R(z); \quad R(z) = P_0 H \frac{Q_0}{z-H} H P_0. \tag{37}$$

The effective Hamiltonian $H^{\mathrm{eff}}(z)$ is the sum of a projected Hamiltonian and of a level-shift operator [11]. For any initial state belonging to the model space, the relevant information is contained in the resolvent (36) projected, on the right, in the model space:

$$\frac{1}{z-H} P_0 = \frac{P_0}{z-H^{\mathrm{eff}}(z)} + \frac{Q_0}{z-H} H \frac{P_0}{z-H^{\mathrm{eff}}(z)}. \tag{38}$$

If we are only interested in the dynamics projected in the model space, the relevant information is contained in the fully projected resolvent

$$P_0 \frac{1}{z-H} P_0 = \frac{P_0}{z-H^{\mathrm{eff}}(z)}. \tag{39}$$

The above expressions refer to the evolution operator. Similar projections of its time derivative will provide expressions related to the Langevin equation of statistical mechanics. By using (38) and (48), the Laplace transform of the time derivative of the evolution operator (52) projected, on the right, in the model space is

$$\frac{H}{z-H} P_0 = \frac{H^{\mathrm{eff}}(z)}{z-H^{\mathrm{eff}}(z)} + \frac{Q_0}{z-H} H \frac{P_0}{z-H^{\mathrm{eff}}(z)} z \tag{40}$$

and its full projection is

$$P_0 \frac{H}{z-H} P_0 = \frac{H^{\mathrm{eff}}(z)}{z-H^{\mathrm{eff}}(z)}. \tag{41}$$

Equations (38), (39), (40) and (41) emphasize the relevance of the effective Hamiltonians for understanding the irreversible dynamics. In statistical physics, the Langevin equation is not derived from Eq. (36) but from another partition of the resolvent. The identity

$$\frac{1}{z-H} Q_0 = \frac{Q_0}{z-H} + \frac{1}{z-H} P_0 H \frac{Q_0}{z-H} \tag{42}$$

allows to transform Eq. (40) into

$$\begin{aligned}\frac{H}{z-H} P_0 &= \frac{1}{z-H} P_0 H P_0 + \frac{1}{z-H} R(z) + \frac{Q_0}{z-H} H P_0 \\ &= \frac{1}{z-H} H^{\mathrm{eff}}(z) + \frac{Q_0}{z-H} H P_0.\end{aligned} \tag{43}$$

Using Eq. (51) and Eq. (53), the inverse Laplace transformation of Eq. (43) provides the dynamical equation

$$\mathrm{i}\hbar \frac{\mathrm{d}U}{\mathrm{d}t} P_0 = U(t) P_0 H P_0 + \frac{1}{\mathrm{i}\hbar} \int_0^t U(t-\tau) R(\tau) \mathrm{d}\tau + F(t), \tag{44}$$

where the "memory" operator $R(\tau)$ is the inverse Fourier transform of $R(z)$. $F(t) = \exp(-\mathrm{i}\, Q_0 H Q_0\, t/\hbar)\, H P_0$ is a "random" or "fluctuating" force. Equation (44) looks like a generalized Langevin equation [3]. Notice, however, that it refers to probability amplitudes whereas Langevin equations refer to densities.

B Laplace transformation

In this paper the Laplace transformation of a function $f(t)$ is defined by

$$f(z) = \frac{1}{i\hbar} \int_0^\infty \mathrm{d}t\, f(t)\, \mathrm{e}^{izt/\hbar}. \tag{45}$$

For $t > 0$, $f(t)$ is recovered by the inverse transformation

$$f(t) = \frac{1}{2\pi i} \int_C \mathrm{d}z\, f(z)\, \mathrm{e}^{-izt/\hbar}. \tag{46}$$

In Eq. (46) z represents the energy extended in the complex plane. The integration path in the complex plane is counterclockwise (see, for example, Ref. [12]). The advantage of our definition is that it allows to recover $f(t)$ by using the standard properties of analytical functions (Cauchy theorem). Some useful properties adapted from Ref. [29] are

$$f(t) \longleftrightarrow f(z) \tag{47}$$

$$\mathrm{i}\hbar \frac{\mathrm{d}f}{\mathrm{d}t} \longleftrightarrow zf(z) - f(t=0) \tag{48}$$

$$\mathrm{i}\hbar\, \delta(t) \longleftrightarrow 1 \tag{49}$$

$$\theta(t) \longleftrightarrow \frac{1}{z} \tag{50}$$

$$U(t) = \mathrm{e}^{-\mathrm{i}\frac{H}{\hbar}t} \longleftrightarrow \frac{1}{z-H} \tag{51}$$

$$\mathrm{i}\hbar \frac{\mathrm{d}U}{\mathrm{d}t} \longleftrightarrow \frac{H}{z-H} \tag{52}$$

$$\frac{1}{\mathrm{i}\hbar} f(t) \star g(t) \longleftrightarrow f(z) \cdot g(z). \tag{53}$$

The convolution product is defined by

$$f(t) \star g(t) = \int_0^t f(\tau)\, g(t-\tau)\, \mathrm{d}\tau = \int_0^t f(t-\tau)\, g(\tau)\, \mathrm{d}\tau. \tag{54}$$

In (54) $\delta(t)$ is the Dirac function, $\theta(t)$ is the Heaviside function, and H is the Hamiltonian operator.

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