

Physical constraints on nonstationary states and nonexponential decay

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For the understanding of irreversibility at the quantum level, the formation and decay of transient (unstable) states play a fundamental role. If the system is treated within Hermitian quantum mechanics, the resulting energy distribution of the resonance state, whose Fourier transform yields the time-dependent probability of decay, $P(t)$, is real. The physical constraint of the lower bound in the energy spectrum introduces “memory,” and causes nonexponential decay (NED) to set in after $t \gg \tau$, where τ is the lifetime defined by exponential decay. The closer to threshold the decaying state is, the earlier NED appears. Apart from the constraint of $E \geq 0$, the constraint of $t \geq 0$ must be accounted for at the same time. It results from the discontinuity at $t=0$ of the solution of the time-dependent Schrödinger equation, which breaks the unitarity associated with the S matrix and gives rise to a complex energy distribution, as a manifestation of the non-Hermitian property of the decaying states. For a narrow isolated resonance state, for which the self-energy is essentially energy-independent, analytic results for $P_{\text{NED}}(t)$ obtained from semiclassical path-integral calculations agree with the quantum-mechanical ones when both physical constraints $E > 0$ and $t > 0$ are taken into account. As an example of the difference in the magnitude of the $P_{\text{NED}}(t)$ when using a real and a complex energy distribution, application is made to the decay of the unstable $\text{He}_2^{2+} \ ^1\Sigma_g^+$ ground molecular state.

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I. RESONANCES AS DECAYING STATES

Resonances that appear during a large variety of reactions and excitations of quantum systems can be interpreted as being caused by intermediate transient states in the course between reactants at $t = -\infty$ (stationary states) and final products at $t = +\infty$ (stationary states). These transient states are formed at, say, $t=0$, as localized wave packets, Ψ_0 . They exist on the average much longer than the excitation time and then decay irreversibly into a purely continuous spectrum of the total Hamiltonian. Although the bulk of the published literature on such resonances has looked at them from a time-independent point of view, giving emphasis on observations that measure energy-dependent quantities (e.g., cross sections), it is also significant to analyze them from a time-dependent point of view. This means use of the time-dependent Schrödinger equation (TDSE) when the formalism employs wave functions and Hamiltonians (as in this work), or of the Liouville–von Neumann equation when statistical ensembles are involved.

A treatise on the quantum mechanics of resonance (decaying) states within both time-independent and time-dependent frameworks is the book of Goldberger and Watson [1]. In developing the arguments of this paper, I will refer to their results. Samples of volumes dedicated to the issues of resonance states and irreversibility are the proceedings of a satellite Nobel symposium entitled “*Resonances and Microscopic Irreversibility*,” edited by Brändas [2], and the collection of articles edited by Prigogine and Rice [3], under the title “*Resonances, Instability and Irreversibility*.”

Our recent work on the theory and calculation from first

principles of the $P(t)$ of nonstationary states in real atomic systems [4] has brought to my attention three papers on time-dependent properties of decaying states [5–7]. The first two [5,6] refer explicitly to earlier work by Nicolaides and Beck [8,9]. The third [7], having as title “*Asymmetric Quantum Mechanics*,” defines resonance states in terms of “rigged Hilbert spaces” and discusses their connection to the discontinuity of the TDSE at $t=0$, an issue which also concerned the work of [8,9].

The present contribution was written in view of these articles and of the continuing interest in the fundamental properties of decaying states. Its purpose is to emphasize that in the rigorous treatment of the issue of the time dependence of decaying states, which is described, as usual, by the nondecay (survival) probability $P(t)$, and of their role in microscopic irreversibility, two physical constraints must be accounted for simultaneously, regardless of the degree of energy dependence of the “self-energy” of the unstable state. These constraints are that the energy integrations must be in the range $0 \leq E < \infty$, rather than $-\infty < E < \infty$, and that the relevant quantities must correspond only to $t \geq 0$. Both of the above constraints have consequences as regards the appearance and magnitude of $P(t)$ in the regime of very long times, where exponential decay (ED) formally changes into nonexponential decay (NED), with probability denoted here by $P_{\text{NED}}(t \rightarrow \infty)$.

The fact that the continuous spectrum is bounded from below ($0 < E < \infty$) may have an effect on the evolution of quantum systems when passing through a resonance (decaying) state. Its manifestation is the formal appearance of $P_{\text{NED}}(t \rightarrow \infty)$, regardless of whether the energy distribution is real or complex [8–10], a property that is connected to the nature of quantum-mechanical irreversibility (see below).

The second constraint, $t > 0$, is a consequence of the fact

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that there is a singularity in the solution of the TDSE at $t = 0$ when considering a decaying state. This singularity breaks unitarity, and theory must select only one of the two complex eigenfunctions (eigenvalues) resulting from it, namely the decaying (and not the “growing”) state. The corresponding energy distribution is now complex, whereas the real energy distribution, here denoted by $g(E)$, is the result of the unitary structure of S -matrix quantum mechanics, via which the formalism incorporates the contribution of time-reversed states.

The above remarks raise the issue of the nature of the energy distribution in the description of irreversibility at the quantum level, and its possible manifestation. In this paper it is emphasized that, although the ED part of $P(t)$, in terms of which the normal definition of unstable states is made, cannot distinguish the effect of $g(E)$ from that of the corresponding complex energy distribution, the NED part of $P(t)$ does so. The arguments are supported by analytic results of two different types of treatment: Application of the formal theory of decaying states and application of the semiclassical theory of path integrals to model potentials appropriate for the description of tunneling phenomena, such as α -particle emission and autodissociation of extraordinary molecular ground states (e.g., $\text{He}_2^{2+} \ ^1\Sigma_g^+$).

II. REMARK ON THE CATEGORIES OF THEORIES AND COMPUTATIONS OF THE $P(t)$ OF DECAYING STATES

The general description of the dynamics of irreversible decay is characterized by the law of ED, $P(t) = e^{-\Gamma t}$ ($\hbar = 1$), where $P(t)$ is defined by $P(t) = |\langle \Psi_0 | \Psi(t) \rangle|^2$. $\Psi(t)$ is the solution of the appropriate TDSE and $\Psi_0 [\equiv \Psi(0)]$ is a many-particle (in general) localized wave packet representing the nonstationary state at $t=0$. It is worth stressing that the assumption of existence and the possibility of accurate computation of Ψ_0 as a square-integrable wave function, regardless of whether it can be interpreted as corresponding to a “Feshbach” or a “shape” resonance, is fundamental to the theory of decaying states. It is usually introduced formally as an eigenfunction of a zero-order operator H_0 , where the interaction causing the decay has been excluded. However, when the Hamiltonian is nonseparable, the explicit form of a local operator H_0 is impossible, since the decay-causing interaction is part of an interparticle operator (e.g., Coulomb), unless it is caused by the application of an external field. Therefore, the construction of Ψ_0 for real many-particle systems, such as atoms, molecules, or nuclei, must engage advanced theory and special methods, since interparticle correlations may be strong and at the same time the state lies in the continuous spectrum with an energy, $E_0 = \langle \Psi_0 | H | \Psi_0 \rangle$, that is only a local minimum with respect to variations of linear or nonlinear parameters in the trial wave function. In atomic physics, this problem has been solved in the framework of the *state-specific* theory (e.g., [11,12] and references therein), whereby the polyelectronic wave functions are made up of suitably chosen and optimized function spaces that are compact as well as physically transparent, and can be used in rather complex calculations, such as the recent deter-

mination of basic properties of attosecond dynamics [13].

The constant Γ above is the rate of exponential decay, or $1/\tau$, where τ is the corresponding lifetime. In the rare case that NED becomes physically significant, a different concept of lifetime must be considered, and computed as $\bar{\tau} = \int_0^t P(t) dt / \int_0^\infty P(t) dt$ [4].

Apart from the formal analysis on the deviations from ED, such as the ones discussed in this paper, the existence of quantum-mechanical NED is confirmed by numerical computation. For example, the essential phenomenology was obtained decades ago via the direct numerical solution of the TDSE with a model one-dimensional potential [14]. On the other hand, for states of real systems treated in terms of many-particle wave functions, the *ab initio* calculation of $P(t)$ for decaying states has been achieved only recently, via the transformation of the TDSE into a large system of coupled integrodifferential equations which are solved numerically [4]. A number of results were obtained, pertaining to the ED and to the $t \approx 0$ and long-time NED regimes. The TDSE for the calculations in [4,14] did not include the δ -function inhomogeneity imposed by the singularity at $t = 0$ [see Eq. (10)].

The bulk of the numerous papers on the subject have employed the Fourier-Laplace transform relation between the energy and the time domains, using assumptions and models for the choice of the energy distribution. Such approaches to the calculation of $P_{\text{NED}}(t \rightarrow \infty)$ deal with phenomenology, and can be divided into two categories.

In the first, the calculation has proceeded by *assuming* a form for the real $g(E)$ with a pole structure (e.g., [10,15–20]), from which $G(t) \equiv \langle \Psi_0 | \Psi(t) \rangle$ is obtained via Fourier transformation [see Eq. (1) below]. The case in which the self-energy is energy-independent, as is reasonable to expect for narrow isolated resonances, $g(E)$ is derived to be the Lorentzian (e.g., [9] and below).

In the second, which, as I will argue, is more appropriate, the calculation starts by connecting the decay amplitude for $t > 0$ to the corresponding Green’s function, $G_>(E + i0)$, given by the diagonal matrix element of the resolvent operator, $R(z) = (z - H)^{-1}$. $R(z)$ is a bisectionally analytic function above and below the real energy axis of the continuous spectrum, whose discontinuity for $E \geq 0$ is $g(E)$. This connection leads to the construction of a Fourier integral of a complex energy distribution, which, for the case of an isolated resonance, has a complex pole below the real axis [1,8,9]. When this integral is truncated so as to account for the lower bound of the continuous spectrum, the result for $P_{\text{NED}}(t \rightarrow \infty)$ contains the effect of $E \geq 0$ as well as of $t \geq 0$ [8,9] and herein.

III. THE REAL ENERGY DISTRIBUTION $g(E)$ AND ITS USE FOR THE CALCULATION OF THE SURVIVAL AMPLITUDE, $G(t)$

The concept of a decaying state starts with the formation at $t=0$ inside the continuous spectrum of a square-integrable Ψ_0 which is not a discrete stationary state of the total Hamiltonian H . For a time-independent H , the formal solution of the TDSE is $\Psi(t) = \exp[(-i/\hbar)Ht]|\Psi_0\rangle$ with $t > 0$ or $t < 0$.

Assuming loss of memory of the excitation mechanism, something which is acceptable when the lifetime of the state associated with Ψ_0 is much longer than the duration of excitation, the survival amplitude $G(t)$ can be written as ($\hbar = 1$) (see, however, the discussion that follows)

$$\begin{aligned} G(t) &\equiv \langle \Psi_0 | \Psi(t) \rangle \\ &= \langle \Psi_0 | \exp(-iHt) | \Psi_0 \rangle \\ &= \int_0^\infty dE g(E) e^{-iEt}. \end{aligned} \quad (1)$$

$g(E)$ is the energy distribution of the resonance state, given by the real and positive function $|\langle \Psi(E) | \Psi_0 \rangle|^2$, and $|\Psi(E)\rangle$ are the exact scattering stationary states of the continuous spectrum with Dirac normalization, $\langle \Psi(E') | \Psi(E) \rangle = \delta(E' - E)$. An elegant formalism for the calculation of $\Psi(E)$ in the presence of resonances, in the framework of the Hermitian, standing-wave properties of the reaction (K) matrix, has been presented by Fano [21] in his analysis of photoabsorption in regions where autoionizing states exist. The last term of Eq. (1) results from the insertion of the unit operator $I = \int dE |\Psi(E)\rangle \langle \Psi(E)|$, which is Hermitian. The lower limit of the continuous spectrum is set at zero.

It is very difficult to compute accurately $g(E)$ for real systems, the level of difficulty depending on the degree of complexity of the Hamiltonian and of the related many-body problem. [A calculation of the $g(E)$ of a polyelectronic autoionizing state was produced in [4(c)], by first computing Ψ_0 and $\Psi(t)$.] Instead, as already mentioned, in the overwhelming majority of the publications on $G(t)$, $g(E)$ is introduced by *assuming* an analytic form. Hence, the results are necessarily phenomenological. For example, the Lorentzian form, which is the example adopted here, has been used in [6,8–10,15] for the study of aspects of NED. Different forms, such as those chosen in [16–19], have been used for discussions on unstable states of nuclear and particle physics and on the so-called “Zeno” effect. A generalized Lorentzian was used recently in connection with random matrix models [20].

In all such cases, it becomes clear that $G(t)$ is determined not only by the pole structure of $g(E)$, which provides the celebrated exponential decay, but also by the model-independent behavior of $\Psi(t)$ for $t \approx 0$ [via the first-order expansion of the evolution operator, $\exp(-iHt) \approx 1 - iHt$], by the possible energy dependence of $g(E)$ beyond the Lorentzian, and by the energy lower bound at $E=0$, where the continuous spectrum starts, features that cause NED.

I now make two comments regarding $g(E)$ and NED. The first is that, as Khalfin [10] first demonstrated by applying a theorem of functional analysis, since $g(E)$ is real and positive, the existence of the lower bound forbids the satisfaction of ED for all t . A simple mathematical proof of the same argument was given in [9]. The degree of violation of ED for long times, i.e., the comparative magnitudes of $P_{\text{NED}}(t \rightarrow \infty)$ and of $e^{-\Gamma t}$, depends on the proximity of the energy of the decaying state to the threshold of the continuous spectrum, regardless of the form of $g(E)$ [8,9,4].

The second comment has to do with the choice of the form for $g(E)$. For an isolated resonance state, $g(E)$ is characteristic of Ψ_0 and of its interaction with the continuous spectrum. Fano’s theory of the mixing of discrete with scattering states [21] or the formal theory of decaying states, e.g., [9], shows that

$$g(E)dE = \frac{1}{2\pi} \frac{\Gamma(E)}{[E - E_0 - \Delta(E)]^2 + \frac{\Gamma^2(E)}{4}} dE, \quad (2)$$

where the energy-dependent functions $\Gamma(E)$ (the width) and $\Delta(E)$ (the energy shift from E_0) are given in terms of matrix elements $\langle \Psi_0 | H | \varphi(E) \rangle$, $\varphi(E)$ being the scattering wave functions of the continuum in the absence of the effective bound-discrete interaction, that are mixed with Ψ_0 to form $\Psi(E)$. On the other hand, the theory of decaying states [1,9] also leads to an alternative equation for $g(E)$, expressing its relation to Hermitian quantum mechanics, where unitarity is preserved and information from time-reversed states is included. The derivation is based on the analytic properties of the resolvent operator, $R(z) = (z - H)^{-1}$, and leads to

$$g(E) = (1/2\pi i) [G_<(E - i0) - G_>(E + i0)] \quad (3a)$$

$$= \mp (1/\pi) \text{Im} G(E \pm i0) = \langle \Psi_0 | \delta(E - H) | \Psi_0 \rangle, \quad (3b)$$

where

$$\begin{aligned} G(z) &= \langle \Psi_0 | R(z) | \Psi_0 \rangle \quad \text{and} \quad G(z^*) = [G(z)]^\dagger, \\ z &= E + i0. \end{aligned} \quad (3c)$$

z is a complex variable with units of energy. $[G(z)]^\dagger$ is the adjoint of $G(z)$.

The functions $G(E \pm i0)$ are the diagonal matrix elements $\langle \Psi_0 | (E - H \pm i0) | \Psi_0 \rangle$ and the symbols $>$ or $<$ are added to label the contribution to $G(t)$ for $t > 0$ and for $t < 0$, respectively, when the Fourier transform is evaluated. Equation (3b) shows explicitly that $g(E)$ represents the discontinuity of $\langle \Psi_0 | R(z) | \Psi_0 \rangle$ on the real axis of the continuous spectrum. The significance of Eq. (3) for the present issue will be discussed in the next section. Suffice it to add here that the reality of $g(E)$ is secured by both forms, Eqs. (2) and (3). However, it becomes immediately obvious from Eq. (3a) that if only one of the Green’s functions is kept, say $G_>(E + i0)$, which corresponds to the decaying state for $t > 0$, then the energy distribution becomes complex (Sec. IV). I recall that the analytic continuation through the cut to the second Riemann sheet below the real axis reveals one complex pole close to E_0 , which is the complex eigenvalue of the decaying state, whose eigenfunction is not square-integrable.

Equation (2) suggests immediately that the approximation of $\Gamma(E) \approx \Gamma(E_0) \equiv \Gamma$, $\Delta(E) \approx \Delta(E_0) \equiv \Delta$, which is very reasonable for narrow resonances, leads to the Lorentzian (Breit-Wigner) form

$$g^L(E)dE = \frac{1}{2\pi} \frac{\Gamma(E_0)}{[E - E_0 - \Delta(E_0)]^2 + \frac{\Gamma^2(E_0)}{4}} dE. \quad (4)$$

The constants Γ and Δ can also be evaluated at E_r , where $E_r = E_0 + \Delta(E_r)$ is the exact position of the resonance state. However, the corresponding very small difference as regards the present discussion is totally irrelevant.

It is the Lorentzian that was adopted by Khalfin [10] to obtain an expression for $G(t)$ in the NED regime [Eq. (3.20) of [10]], which he obtained under the assumption of $(t/\hbar)(E_r^2 + \Gamma^2)^{1/2} \gg 1$ [his Eq. (3.17)]. It was also adopted by Sluis and Gislason [6] [their Eq. (23)], who used the formulas given in [9] for the evaluation of the integral (1) [Eq. (8.37) of [9] as compared with Eq. (19) of [6]]. It was shown in [9] [Eq. (8.54), corrected here for a misprint], that the use of $g^L(E)$ in Eq. (1), derived from the pole approximation to $g(E)$ of Eq. (3a), produces the analytic result for $P_{\text{NED}}(t \rightarrow \infty)$ of

$$P_{\text{NED}}(t \rightarrow \infty) \approx \frac{\hbar^2 \Gamma^2}{4\pi^2 (E_r^2 + \Gamma^2/4)^2 t^2}. \quad (5)$$

This is the result that corresponds to the amplitude derived by Khalfin [Eq. (3.20) of [10]].

It was demonstrated explicitly in [9], pp. 494–498, that Eq. (5) is the result of two conditions on E and on t , within the simple pole approximation of energy-independent Γ and Δ . It is obtained for the case represented by $g^L(E)$ and Eq. (1), namely $E \geq 0$ and $\infty > t > -\infty$, as well as for the symmetric case of $t \geq 0$ and $\infty > E > -\infty$, represented by the choice of only $(-1/2\pi i) G_>(E + i0)$ in Eq. (3a). The first case is the one chosen implicitly by Khalfin [10], since as already stated, the real $g(E)$ “does not differentiate between positive and negative times” (p. 492 of [9]). The second case is the one corresponding to the treatment of [1], where the crucial expression is their Eq. (40d) on p. 434,

$$\Psi(t) = (1/2\pi i) \int_{-\infty}^{\infty} dE e(-iEt) G^+(E) X_a \quad (6)$$

[Eq. (40d) of [1], p. 434]. The functions $G^+(E) = G_>(E + i0)$ and $X_a = \Psi_0$. As Goldberger and Watson state (p. 434 of [1]), “The wave function $\Psi(t)$ contains a complete description of the system for $t > 0$.” However, Eq. (6) does not consider the fact that the continuous spectrum has a lower bound. The integration for the corresponding survival amplitude $G_>(t)$ was done in [1] via the contour of Fig. 8.3 on p. 447. This contour shows that the contribution to NED comes from integration for negative imaginary values along two directions, from $-i\infty$ to 0 and from 0 to $-i\infty$. Thus, the integral of Eq. (108) on p. 448 of [1] is equivalent to the integral 8.30 of [9] (case of $t \geq 0, \infty > E > -\infty$), and to the integral 8.39 of [9] (case of $E \geq 0$ and $\infty > t > -\infty$).

IV. THE SINGULARITY AT $t=0$, COMPLEX ENERGY DISTRIBUTION, AND $P_{\text{NED}}(t \rightarrow \infty)$

The use of real $g(E)$ is in accordance with Hermitian structures and has characterized most of the calculations of $G(t)$. Its origin lies in the use of the unit operator $I = \int dE |\Psi(E)\rangle \langle \Psi(E)|$, an expansion that is part of the foundations of the quantum mechanics of stationary states and of unitarity.

The integral (1) over $g(E)$ can be done either for real E or in the complex energy plane [1,6,8–10,15–20]. This is evident from the structure of Eqs. (2)–(4). When this is done, the term of ED emerges from the pole below the real axis. In addition, either the participation of both directions along the imaginary axis or the contribution of two poles, z_0 and its conjugate z_0^* , corresponding to the adjoint Green’s functions $G_>(E + i0)$ and $G_<(E - i0)$, gives rise to NED [1,9,10]. If the approximation of energy-independent self-energy is made, the Fourier integral that must be evaluated is the sum of contributions from $1/(z - z_0)$ and from $1/(z - z_0^*)$ and integration must go from 0 to ∞ . The integration can be done exactly in terms of exponential integrals (shown to be valid for complex variables as well) and retention of the leading term. The result for $P_{\text{NED}}(t \rightarrow \infty)$ is Eq. (5) [9].

The theory and calculations of [8,9] argued that in order for the arrow of time to be accounted for together with the basic characteristic of the energy spectrum, the rigorous treatment of $P(t)$ must account for both constraints, $E \geq 0$ and $t \geq 0$. The former constraint introduces “memory” into the evolution process, regardless of the form of the energy distribution, and eventually causes a slowing down of the decay from its exponential form (see the Appendix of [4b]). The latter constraint expresses the initial conditions at (step function) the $t=0$ singularity, which is caused by the momentary formation of the nonstationary state. This singularity of the solution of the TDSE breaks, in principle, a basic feature of Hermitian quantum mechanics, namely unitarity, by separating the decaying state, $t > 0$, from its adjoint, $t < 0$. As a result, instead of $g(E)$, the energy distribution associated with irreversibility at the microscopic level is complex. In [8,9], the use of the approximation of the energy-independent self-energy $[\Delta - (i/2)\Gamma]$ allowed the derivation of analytic results for $P_{\text{NED}}(t \rightarrow \infty)$, both in terms of $G^L(E)$ (real function) and in terms of the corresponding (unnormalized) complex Green’s function,

$$G^L(E) \approx -[E - E_r + (i/2)\Gamma]^{-1}, \quad E > 0 = 0, \quad E \leq 0. \quad (7)$$

The arguments and calculations of [8,9] aimed at introducing and demonstrating two main ideas.

(i) The association of a resonance state with a simple pole and with the concomitant ED is a function of the ratio E_r/Γ . Given the lower bound at $E=0$, as this ratio approaches $O(1)$ while threshold is reached, the violation of ED at long times is enhanced, since the effects of memory are accumulated faster. Therefore, the search for the discovery of nonstationary states where NED is observable should focus on

exceptional cases, i.e., on resonance states very close to the threshold (see also [4(b) and 4(c)]).

(ii) For the rigorous treatment of irreversible decay, both the $E \geq 0$ and the $t \geq 0$ restrictions must be considered. The latter implies that the real function $g(E)$ should be replaced by the complex function $G_{>}(E+i0)$ of Eq. (3a), which, upon continuation through the cut of the real energy axis into the second sheet, reveals the decaying state pole at $z_0 = E_0 + \Delta - (i/2)\Gamma$.

Conditions (ii) above imply that only one pole, z_0 , and its corresponding complex eigenfunction are used for the description of the physics of decay. For energy-independent $[\Delta - (i/2)\Gamma]$, the result for $G_{>}(t)$ is [8,9]

$$\begin{aligned} G_{>}(t) &= \frac{1}{2\pi i} \oint \frac{\exp(-izt)}{z-z_0} dz \\ &= \exp(-iz_0 t) \left[1 - \frac{1}{2\pi i} E_1(-iz_0 t) \right], \end{aligned} \quad (8)$$

where $E_1(x)$ is the exponential integral. The first term is due to the pole. The second originates from the contour integration along the imaginary axis in one direction only. By taking the first term of the asymptotic form of $E_1(x)$ and by omitting the interference terms, the result for $P_{\text{NED}}(t \rightarrow \infty)$ is [8,9]

$$P_{\text{NED}}(t \rightarrow \infty) \approx \frac{\hbar^2}{4\pi^2(E_r^2 + \Gamma^2/4)t^2}. \quad (9)$$

Equation (9) has the same dependence on t as Eq. (5), but the coefficients are different.

V. ANALYSIS AND DISCUSSION

Sluis and Gislason [6] commented on the results of [8,9], suggesting, as Druger and Samuel [5] did before them, that the evaluation of $G(t)$ was done improperly, and that the result of Eq. (9) is incorrect. The objections of [5,6] seem to have missed the point made in [8,9] and here. The results (8) and (9) were obtained under physical constraints that account for time asymmetry as well as for the spectral lower bound. In order to produce them, the Fourier integration over $1/(E - z_0)$ can be done for real E from 0 to ∞ . (See the numerical results of [8,9] and Appendix B of [9].) Of course, it can also be done in the complex energy plane. The corresponding contour of integration chosen in [8,9], and criticized in [5], is shown in Fig. 1. It does not enclose the positive real axis in both directions from 0 to ∞ . This means that use is not made of the unit operator [Eq. (1)] over the stationary states of Hermitian quantum mechanics. Instead, it deals directly with $G_{>}(E+i0)$ of Eq. (3a) and goes along only one direction of the imaginary energy axis, accounting for the lower bound in the energy spectrum and expressing the fact that the system becomes non-Hermitian owing to the imposed boundary conditions of the time arrow at the singularity, $t=0$.

In fact, subsequent results of Holstein [22] on the $P(t)$ of α -particle decay, obtained via semiclassical path-integral calculations with a model potential consisting of a spherically

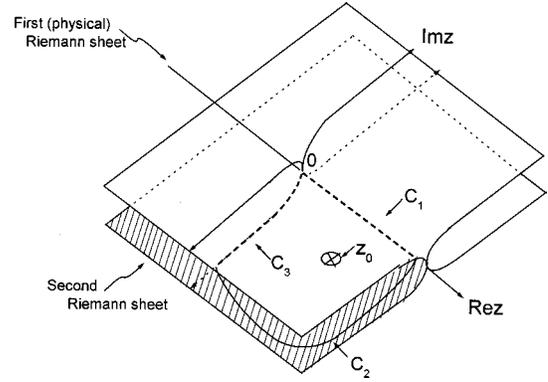


FIG. 1. Contour of integration chosen in [8,9] for the evaluation of the survival amplitude of an isolated decaying state with energy-independent self-energy. It accounts for the physical constraints of $E \geq 0$ and $t \geq 0$. The contour on the arc C_2 is zero as $z \rightarrow \infty$. The pole z_0 is put on the second Riemann sheet.

symmetric square well and a Coulomb repulsion, led exactly to Eq. (9) [Eq. (29) of [22]]. In the path-integral formulation, the direction $(x_1, t_1) \rightarrow (x_2, t_2)$, $t_2 > t_1$, comes in naturally, and therefore the corresponding propagator $G(t)$, $t = t_2 - t_1$, must incorporate only the $t > 0$ contribution. Actually, using the path-integral formalism for the determination of the semiclassical Green's function, $G_{\text{sc}}(E)$, and the subsequent evaluation of $G_{>}(t)$ via a truncated Fourier transform, Douvropoulos and the author [23] have shown that the same results hold as well for even more realistic model potentials with a local minimum supporting nonstationary states. $G_{\text{sc}}(E)$ consists of a summation over the complex poles corresponding to the resonance states that the potential can support, multiplied by quantities that can be calculated semiclassically. The complex eigenvalue of interest appears with a negative imaginary part, thereby contributing to $t > 0$ decay only.

In conclusion, the “memory” introduced into the decay of an unstable state by the existence of the lower limit of the continuous spectrum breaks the Markovian nature of time evolution and results in NED, regardless of the type of energy distribution [10,9]. However, there is a difference of fundamental importance when the arrow of time introduced by the singularity in the solution of the TDSE at $t=0$ is considered. In this case, the energy distribution driving the decay is complex. The use of a real energy distribution implies the contribution to $G(t)$ from “adjoint time-reversed states” as well (p. 684 of [8], p. 492 of [9]). In other words, the use of $g(E)$ is in accordance with Hermitian quantum mechanics, but the problem of decaying states is intrinsically non-Hermitian. The conclusion is that, together with $E \geq 0$, the calculation must express the result of the replacement of the time-evolution operator, $T(t) = e^{-iHt}$, which is unitary over the domain $(-\infty < t < +\infty)$, by $\theta(t)e^{-iHt}$, where $\theta(t)$ is the step function for $t > 0$. The corresponding time-asymmetric TDSE is then [Eq. (3.4) of [9]]

$$(i\partial_t - H)T(t) = i\delta(t). \quad (10)$$

Although there are no first-principles computations on real systems based on Eq. (10), it follows from the equivalent

results of the integral formulation that although the inhomogeneity does not change the lifetime in the regime of exponential decay, it does affect $P_{\text{NED}}(t \rightarrow \infty)$, as demonstrated by the difference between Eqs. (5) and (9). In this context, one might object that the results (5) and (9) are specific to the approximation of energy-independent Γ and Δ . Nevertheless, it is the fact that they are different in magnitude that has value regarding the understanding of the violation of quantum-mechanical time symmetry caused by the formation of resonance states. If, in the future, it becomes possible to measure with great accuracy the NED of an isolated unstable state, for which accurate calculations of the same quantity could also exist within the two frameworks discussed in this paper (real and complex energy distributions), significant information as to the physical relevance of long-time NED should emerge. A proposal for an experiment in atomic physics is presented in [4(a)].

VI. APPLICATION TO THE $\text{He}_2^{2+} 1\sigma_g^2 1\Sigma_g^+$ MOLECULAR AUTODISSOCIATING STATE

Because of the smallness of the possible quantum-mechanical effects in the regime of long-time NED, when it comes to computation or measurement it is preferable to consider well-defined isolated states with unperturbed decay channels. Such cases, involving polyelectronic atomic resonance states, were studied in [4] via the numerical solution of the TDSE from first principles.

Another type of physical situation where there is a narrow, well-defined initially localized nonstationary state decaying into a single open channel of free particles is represented by the extraordinary ground state of the He_2^{2+} molecule, the $1\sigma_g^2 1\Sigma_g^+$. The fact that this state exists in a local potential-energy minimum inside the continuous spectrum of $\text{He}^+ + \text{He}^+$ was first discovered and interpreted by Pauling in 1933 [24]. The form of this potential implies the

existence of vibrational levels as shape resonances. Viewed from a different angle, this system, as well as similar molecular ground states [25,26], can store large amounts of energy that can be easily released as kinetic energy of $\text{He}^+ + \text{He}^+$. The crucial element in such a consideration is the degree of stability of the vibrational levels toward autodissociation (tunneling) [25]. The energy of the $v=0$ vibrational level of the $\text{He}_2^{2+} 1\sigma_g^2 1\Sigma_g^+$ state is about 1.3 eV below the top of the barrier and about 8.9 eV above the energy of the dissociated product, $\text{He}^+ + \text{He}^+$. Using semiclassical WKB formulas for tunneling, its lifetime was calculated to be about 220 min [25]. Semiclassical results of such widths were subsequently confirmed by quantum-mechanical calculations [27,28].

The analysis of [23] has shown that the tunneling vibrational levels of the $\text{He}_2^{2+} 1\sigma_g^2 1\Sigma_g^+$ state can be subjected to the NED treatment discussed here. In general, when the level is not near the top of the tunneling barrier, in which case the width is broad and may be energy-dependent (apart from the possibility of resonance overlap), $P_{\text{NED}}(t \rightarrow \infty)$ is given exactly by Eq. (9). Therefore, the quantum theory of decaying about the nature of the energy distribution and the limits of integration in the calculation of $P(t)$ ($t \geq 0, E \geq 0$) is confirmed again using path integrals, where the arrow of time is intrinsic to the formalism.

Finally, it is instructive to see the result of the application of formulas (5) and (9) to the lowest vibrational resonance level of $\text{He}_2^{2+} 1\sigma_g^2 1\Sigma_g^+$, when the energy and the width calculated in [25] are used. A significant difference is observed, even though the magnitude of $P_{\text{NED}}(t \rightarrow \infty)$ relative to $e^{-\Gamma t}$ is too small for this system, since the ratio E_r/Γ is large and the level is far from threshold [8,9]. Specifically, when the result from the use of the real energy distribution is applied [Eq. (5)], NED starts dominating after about 193 exponential lifetimes. When Eq. (9) is applied, NED dominates after about 102 exponential lifetimes.

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