Stationarity coefficients and short-time deviations from exponential decay in atomic resonance states

Theodoros Mercouris[1,*] and Cleanthes A. Nicolaides[1,2,†]

[1]*Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation 48, Vasileos Constantinou Avenue, Athens 11635, Greece*
[2]*Physics Department, National Technical University, Athens, Greece*

By solving rigorously and accurately the time-dependent Schrödinger equation, we have obtained numerical results for the decay probability, $P(t)$, of real, multiparticle systems, in the time domain of $t \approx 0$. Three different types of atomic nonstationary states were examined, the He$^-$ $1s2p^2$ ^4P, the Ca KLM $3d5p$ $^3F^o$, and the He$^-$ $1s2s2p$ $^4P_{5/2}$, the last one being metastable and decaying via spin-spin interactions. The main results are that there is a t^2 dependence of $P(t \approx 0)$ and that a time-dependent short-time decay rate can be calculated. The computed coefficients of the t^2 term reflect the degree of stability of the state, (i.e., the degree of proximity to the notion of the standard stationary state of quantum mechanics), and are named the *stationarity coefficients*. These, together with the conventional quantity of the lifetime, corresponding to the exponential decay regime, constitute intrinsic properties of each real unstable state. For the herein studied metastable state the onset of exponential decay occurs after about 5×10^{-14} s, i.e., after a duration which is achievable experimentally with laser pulses.

I. INTRODUCTION

The excited states of polyelectronic atoms which lie in the continuous spectrum, henceforth called resonance or autoionizing states, offer a few theoretical and experimental challenges concerning the fundamentals of quantum mechanics. With regard to theory, one is the possibility of advancing and testing many-body theory to unusual and often weakly bound electronic structures, occurring in a variety of scattering and photoabsorption experiments (negative ion resonances, multiple excited states, Auger states, etc.). Another is the possibility of using them as paradigms of states where a nonseparable Hamiltonian is known, (i.e., kinetic plus Coulomb interaction operators), and where the nonstationary aspects of dissipation (decay) can be understood quantitatively from first principles, (and not in terms of models or of use of empirical data, as it has been done in other fields of physics), in order to study basic questions of quantum theory and dynamics.

As is well known, the fundamental characteristic of an isolated nonstationary state interacting with a purely continuous spectrum is its exponential decay (ED). This marks the temporary formation at $t=0$ of a localized wavepacket, Ψ_0, of energy E_0 inside the continuous spectrum. Associated with it via analytic continuation to the second Riemann sheet below the real axis is a complex eigenfunction with a complex eigenvalue, which drives the ED. The intriguing feature in this subject is that the formalism of quantum mechanics, in conjunction with model calculations, predicts the possibility of violations of the ED law, for $t \approx 0$ and for $t \gg 1/\Gamma$, where Γ is the rate of decay in the ED regime. Nevertheless,

such deviations have not been observed, and this fact agrees with calculations based on models which show that the magnitude of nonexponential decay (NED) is too small to be observable. Since the literature on this topic is considerable, we refer the reader to the treatise of Goldberger and Watson [1], to a recent review [2] and to [3–5], where a large number of references are included.

It has been argued [3,6] that when it comes to real systems, the appearance of long-time NED has to be searched in particular states, which are close to threshold. Indeed, the *ab initio* calculations of [4,5] on the nondecay (survival) probability, $P(t)$, of polyelectronic atomic resonance states, bear this out, thereby enforcing the view that it is significant to understand, formally and computationally, the sources and the magnitudes of the possible violations of the *law* of ED in real systems.

In the present paper, we apply the method for the calculation of $P(t)$ which was first presented and applied in [4,5] to the calculation of $P(t)$ very close to $t=0$. This region was excluded from analysis in our previous work, since this domain seems to be undefinable, in a rigorous sense, as regards preparation and measurement. However, given the fact that, during the past two decades, a number of calculations and arguments using models have dealt with this region, (e.g., see Refs. [2,7–14]), we thought that information coming from *ab initio* calculations on real states would shed additional insight into the issues, from a different angle. In fact, these calculations have given us the opportunity of examining the notion of stability of a decaying state and to relate it to the coefficients of the t^2 term in the $t \approx 0$ development of $P(t)$, which we name the *stationary coefficients*.

II. NONEXPONENTIAL DECAY FOR $t \approx 0$

For many decades, the theory of decaying states in all fields of physics has treated the time dependent decay dy-

---

*Email address: thmerc@eie.gr
†Email address: can@eie.gr

namics in terms of assumptions and models [1–14], and references therein. Specifically, the quantity of interest has been the $P(t)$, which at $t=0$ is one. The standard approach to its calculation and analysis has been to compute the amplitude $G(t)$, $[P(t)=|G(t)|^2]$, from the expression ($\hbar=1$),

$$G(t)=\langle\Psi_0|e^{-iHt}|\Psi_0\rangle=\int_0^\infty dE\, g(E)e^{iEt}. \qquad (1)$$

$|\Psi_0\rangle$ is the initially ($t=0$) localized state with real energy E_0, $g(E)$ is the real spectral function given by $|\langle\Psi_0|E\rangle|^2$, $|E\rangle$ is the energy normalized scattering state at energy E, and the lower bound 0 of the integral signifies the starting point of the continuous spectrum into which the nonstationary state decays. The calculation of $G(t)$ and of $P(t)$ according to Eq. (1) has been done in many publications since the 1950s, by assuming a form for $g(E)$, the best known one being the Breit-Wigner. We point out that in [3,6] it was shown that in order to account for time asymmetry as well as for the fact that the spectrum is bounded from below, (i.e., $t>0$, $E>0$), the integral for $G(t)$ must involve a complex spectral function rather than a real one. In the latter case, $G(t)$ includes the contribution from the adjoint (time reversed) states [6] since "$g(E)$ *does not differentiate between positive and negative times*" (p. 492 of [3]). In the former case, $G(t)=\langle\Psi_0|\theta(t)e^{-iHt}|\Psi_0\rangle$, where $\theta(t)$ is the step function for $t>0$.

Regardless of the adopted form of $g(E)$, or, if time asymmetry is considered, of the form of a complex spectral function, the *law* of exponential decay (ED), which is expressed by $P(t)=e^{-\Gamma t}$, where Γ is the rate of decay in the ED region, is not satisfied for $t\approx0$ and for $t\gg1/\Gamma$. Yet, a variety of measurements have not uncovered any violation of ED of fundamental origin in an isolated quantum state dissipating into a purely continuous spectrum. A testimony to this fact is a comment on the law of ED by Greenland [15], who, following the null results of the careful measurements on unstable nuclei by Norman *et al.* [16], conjectured: "*The correct combination of circumstances does not seem to arise naturally to produce deviations from exponential decay, which is why it is such an accurately fulfilled law, even out to 45 half-lives.*"

In two relatively recent publications [4,5], we presented a theory for the *ab initio* solution of the time-dependent Schrödinger equation (TDSE) in the case of polyelectronic atomic resonance states decaying into the continuous spectrum of the kinetic energy of the free electron. It is based on the state specific expansion of the time dependent $\Psi(t)$, with $\Psi(0)=\Psi_0$, in terms of accurate representations of bound and energy normalized scattering wave functions (see below). The choice of the states that were studied in [4,5] followed from the earlier prediction [3,6] that, in real multiparticle systems, in order for the magnitude of the long time NED to become non-negligible after only a few ED lifetimes, the resonance state must be very close to threshold. (As with every generally accepted rule (law) of physics, possible violations may occur only in exceptional cases.) We reported results for the long time NED, which turned out to be considerably enhanced for states of negative

ions (He$^-$ $1s2p^2\,^4P$,Li$^-$ $1s\,^22s2p\,^3P^o$) as well as of atoms (Ca $KLM\,3d5p\,^3F^o$). These states, except Li$^-$$1s^22s2p\,^3P^o$, have also been used as the examples for the present work on the $t\approx0$ NED regime.

For $t\approx0$, i.e., in the preexponential short time regime,

$$P(t)\approx1-(\Delta E)^2t^2+\cdots, \qquad (2)$$

where

$$(\Delta E)^2=\langle\Psi_0|(H-\langle H\rangle)^2|\Psi_0\rangle=\delta, \qquad (3)$$

$$\langle H\rangle=\langle\Psi_0|H|\Psi_0\rangle=E_0. \qquad (4)$$

The extensively discussed expression (2) is obtained directly from the expansion of the operator e^{-iHt} in Eq. (1). Although it is model independent, several investigations have also considered models for $g(E)$ where the short t dependence is different, e.g., [7–11,14]. It is then significant to understand, formally and computationally, the sources and the magnitudes of the possible violations in real systems. Specifically, we have asked the question: How does the $P(t)$ of a true atomic decaying state behave for $t\approx0$? If we fit this short time $P(t)$ to a polynomial in t, which term dominates and with what coefficient?

Before we proceed with the *ab initio* calculation, in the following section we draw from earlier work [17] in order to discuss a concept about stationarity of excited states.

III. DEGREE OF STATIONARITY OF UNSTABLE STATES

It has been argued [3,17,18], with examples of highly excited states, that the crucial concept in the theory of decaying states is the existence and computation of a multiparticle localized wavepacket in the continuous spectrum, Ψ_0, having a real energy E_0. Assuming loss of memory of the excitation process, this causes the breakdown of time continuity of the Schrödinger equation at $t=0$, and, through its interaction with the open channels, and, possibly, with other localized wavepackets via the open channels, it produces, for $t>0$, the observable information about its intrinsic properties. $|\Psi_0\rangle$ is square integrable but is not an eigenfunction of the full Hamiltonian H, since it does not represent a discrete, stationary state. Instead, it represents a nonstationary state at $t=0$ without whose existence, concepts such as poles of the scattering matrix, complex eigenvalue Schrödinger equation, rapid phase shift changes and peaks in a reaction cross section, cannot be justified.

The proximity, due to $|\Psi_0\rangle$, of the concept of a decaying state to that of a stationary state, implies that, formally, the time domain of $t\approx0$ might reveal information about the degree of stationarity of the nonstationary state, $|\Psi(t)\rangle$. Following the arguments of [17], we define the vector for $t\approx0$,

$$|u(t)\rangle=|\Psi(t)\rangle-|\Psi_0\rangle. \qquad (5)$$

Equation (5) implies that $G(t)\sim1$, since, for all t, $|\Psi(t)\rangle$ is formally given by $G(t)|\Psi_0\rangle+|\hat{u}(t)\rangle$, where $|\hat{u}(t)\rangle$ signifies the decayed products.

For $t \approx 0$, one intuitively would expect that

$$\left\| \lim_{t \to 0} u(t) \right\| = \left\| \lim_{t \to 0} [\exp(-iHt) - \exp(-iH_0 t)] |\Psi_0\rangle \right\| = \min, \quad (6)$$

where

$$H_0 = |\Psi_0\rangle \langle \Psi_0 H |\Psi_0\rangle \langle \Psi_0|$$

and

$$\langle \Psi_0 | H | \Psi_0 \rangle = E_0 = \langle \Psi_0 | H_0 | \Psi_0 \rangle. \quad (7)$$

Also,

$$\lim_{t \to 0} [\exp(-iHt)] = 1 - iHt,$$

$$\lim_{t \to 0} [\exp(-iH_0 t)] = 1 - iH_0 t. \quad (8)$$

From Eqs. (6) through (8) we obtain the result that for the nonstationary state, the optimal $|\Psi_0\rangle$ is such that the variance δ of Eq. (3) is minimum [17]

$$\delta = \min. \quad (9)$$

The use of Eq. (9), and its non-Hermitian extension which allows the optimization of trial wave functions for the calculation of widths, has been demonstrated in actual calculations of resonance states [17,19–22]. Here, its usefulness is taken to be conceptual. It signifies the degree of the deviation from stationarity, before exponential decay sets in. In this work we will call δ the *stationarity coefficient*. Its definition implies that it depends only on $|\Psi_0\rangle$ and the first two moments of H. In this work, we will compute it from the solution of the TDSE, for the first time for real multiparticle systems.

We point out that the moments of H, i.e., $\langle \Psi_0 | H^n | \Psi_0 \rangle$, are related, in the limit of $t \to 0$, to the derivatives of the nondecay amplitude, $G(t)$, by (Appendix C of [3] corrected for misprints):

$$\langle \Psi_0 | H^n | \Psi_0 \rangle (-i)^n = (-i)^n \langle \Psi(t) | H^n | \Psi(t) \rangle \quad (10a)$$

$$= (-i)^n \int dE \, E^n g(E) \quad (10b)$$

$$= \left. \frac{\partial^n G(t)}{\partial t^n} \right|_{t=0}. \quad (10c)$$

As is well known, if the computation of δ is to be done directly from its definition, Eq. (3), then this requires that the evaluation of expressions (10a) and (10b) for $n = 2$ produce a finite result. However, there are distributions, such as the Lorentzian, for which (10a) and (10b) yield an infinite result. On the other hand, a time dependent calculation such as the one described below, can always produce $[\partial^n G(t)]/\partial t^n|_{t=0}$, from which the related moments, and in particular, the $n = 2$ case, can be obtained.

IV. METHOD OF INTEGRATION OF THE TDSE

The dynamics of decay is given by the solution of the TDSE,

$$i \frac{\partial}{\partial t} \Psi(t) = H \Psi(t), \quad (11)$$

where H is the polyelectronic Hamiltonian and $\Psi(t=0)$ ($\equiv \Psi_0$), is the initially localized wave function of the resonance, whose energy E_0, [see Eq. (4)], is embedded in the continuous spectrum.

Our approach to the solution of the TDSE for this problem has been to expand $\Psi(t)$ in terms of state specific N electron wave functions, calculated by advanced methods which account for the electronic structure of each participating state, and solve for the time-dependent coefficients. The details of the method have been given in previous publications [4,5], and therefore, only the essentials are given below.

The expansion over the stationary states involves Ψ_0 and other square-integrable wave functions, Ψ_n, representing other resonances possibly contributing, indirectly, to the decay dynamics, and the scattering functions, $U(\epsilon)$, representing the continuous spectrum. Thus, the form of this expansion is

$$\Psi(t) = \sum_{n=0}^{N} \alpha_n(t) \Psi_n + \int_0^{\infty} b(\epsilon,t) U(\epsilon) \, d\epsilon \quad (12)$$

with the initial condition $\alpha_0(t=0) = 1$ and $\alpha_n(0) = b(\epsilon,0) = 0$, for $n \neq 0$.

In our previous work [4,5] as well as in the present one, Ψ_n were obtained numerically as multiconfigurational Hartree-Fock (MCHF) wave functions. The wave functions of the continuous spectrum have the structure

$$U(\epsilon) = \Psi_{\text{core}} \otimes \epsilon l, \quad (13)$$

where the continuum orbitals ϵl are energy normalized and are obtained, numerically, for each value of the energy ϵ from a scattering calculation where the potential is fixed by the structure and the symmetry of the core state. The wave function of this core state is also obtained numerically at the MCHF level.

As the next step, we substitute $\Psi(t)$ of Eq. (12), into (11). The following system of integrodifferential equations is produced:

$$i \frac{d}{dt} \alpha_n(t) + i \int_0^{\infty} \frac{d}{dt} b(\epsilon,t) S_n(\epsilon) d\epsilon$$

$$= E_n \alpha_n(t) + \int_0^{\infty} b(\epsilon,t) V_n(\epsilon) d\epsilon, \quad n = 0,1, \ldots, N,$$

$$i \frac{d}{dt} b(\epsilon,t) + i \sum_{m=0}^{N} \frac{d}{dt} \alpha_m(t) S_m(\epsilon) d\epsilon$$

$$= (E_{\text{th}} + \epsilon) b(\epsilon,t) + \sum_{m=0}^{N} \alpha_m(t) V_m(\epsilon). \quad (14)$$

The overlap, $S_n(\epsilon)$, and interaction, $V_n(\epsilon)$, matrix elements are given by

$$S_n(\epsilon) = \langle \Psi_n | U(\epsilon) \rangle, \quad V_n(\epsilon) = \langle \Psi_n | H | U(\epsilon) \rangle. \quad (15)$$

The existence and the magnitude of $S_n(\epsilon)$ depends on the electronic structure of initial and final states and on the function spaces used to represent them. For shape (single particle) resonances (see below), this overlap is, in general, significant and must be included.

The integrals in Eq. (14) are performed by the trapezoidal rule and the solution for the coefficients is tested for convergence with respect to two parameters: the number of scattering states and the extent of the continuous spectrum. The time dependent coefficients are advanced in time via the Taylor series expansion technique [4] that has proven efficient in solving systems of tens of thousands of coupled equations.

V. RESULTS ON THE SHORT-TIME EVOLUTION OF NONSTATIONARY STATES

We chose to study three resonance states belonging to different categories as regards their decay mechanism and their lifetimes. The first two, He$^-$ $1s2p^2$ ^4P and Ca KLM $3d5p$ $^3F^\circ$, fall into the category of short-lived states (lifetime of 10^{-14}–10^{-13} s) with decaying mechanisms involving one and two electron nonrelativistic operators. The third one, He$^-$ $1s2s2p$ $^4P_{5/2}$, is a long-lived metastable state (lifetime of about 350 μs) that decays via relativistic spin-spin interactions.

A. The He$^-$ $1s2p^2$ ^4P shape resonance

This state is a shape (single particle) resonance, lying about 11 meV above threshold and decaying into the He$^-[1s2p\,^3P^o + \epsilon p]^4P$ continuum [4]. For the purpose of the present study, the correlated localized part Ψ_0 of the resonance wave function was computed in terms of a MCHF expansion, containing the five most important components [4]:

$$\Psi_0 = 0.916\psi(1s2p^2) - 0.383\psi(1s3p^2) + 0.118\psi(1s3d^2)$$
$$+ 0.010\psi(1s4p^2) + 0.005\psi(1s4d^2).$$

Its calculated energy is 12.7 meV, while its experimental one [23] is 10.8 meV. One might think that such a small difference would play an insignificant role in the overall calculation. However, we found that for such a state, and probably also for other shape resonances very close to threshold, the calculation is sensitive to the value of E_0 and its position relative to the distribution of the interaction. In this work, we adopted the experimental value. The system (14) was solved for very short times and for $n=0$ only, since the other four roots of the MCHF solution, which represent higher lying resonance states, do not affect the substance of the physics of the decay of He$^-$ $1s2p^2$ ^4P.

Figure 1 depicts $P(t)$ for short times as a function of t^2. The main contribution to $P(t)$ is expected to come from the quadratic term of the expansion
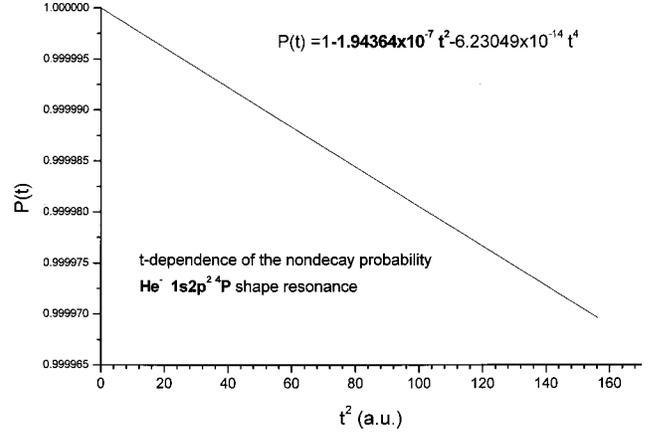

FIG. 1. He$^-$ $1s2p^2$ ^4P shape resonance. Short time nondecay probability $P(t) = |\alpha_0(t)|^2$ as a function of t^2, see also Eq. (1). One atomic unit of time $= 2.418 \times 10^{-17}$ s.

$$P(t) = 1 + \sum_n a_n t^n. \quad (16)$$

Indeed, this is what Fig. 1 demonstrates. The slope of the straight line is the stationarity coefficient. In practice, by fitting polynomials of increasing order to the calculated $P(t)$, we found that the coefficient a_2, which is the stationarity coefficient δ of Eqs. (3) and (9), is by far the dominant one in the expansion (16). Specifically, its value is -1.9×10^{-7}.

In addition to the above, we define a *time-dependent rate* by considering the *logarithmic* derivative of $P(t)$:

$$\Gamma(t) = -\frac{d}{dt}[P(t)]/P(t), \quad (17a)$$

which, for short times, $(P(t) \approx 1)$, is

$$\Gamma(t) \approx -a_1 - 2a_2 t - \cdots. \quad (17b)$$

This time-dependent rate is shown in Fig. 2 for a wide range of values of t. For sufficiently large times (relatively speak-
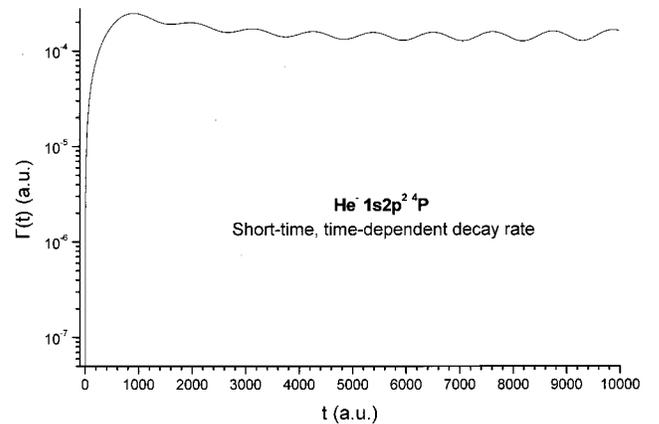

FIG. 2. He$^-$ $1s2p^2$ ^4P shape resonance. Short time, time-dependent decay rate $\Gamma(t)$ (in a.u., logarithmic scale), from Eq. (17a).
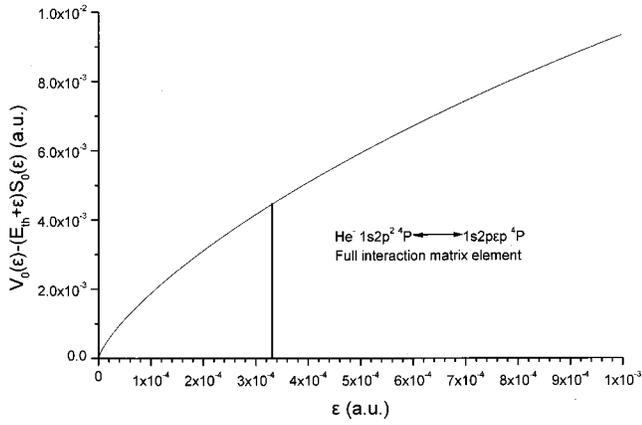
FIG. 3. He$^-$ $1s2p^2$ ^4P shape resonance. Full interaction matrix element $V_0(\epsilon)-(E_{\text{threshold}}+\epsilon)S_0(\epsilon)$ (in a.u.) as a function of the energy ϵ (in a.u.) above threshold. The thick vertical line indicates the position E_0 of the resonance.

FIG. 4. As in Fig. 1, but for the Ca $3d5p$ $^3F^o$ autoionizing state.

ing) ($t \geqslant 700$ a.u.), $\Gamma(t)$ acquires an essentially time-independent value that coincides with the autoionization rate. On the other hand, for short times, $\Gamma(t)$ varies linearly with t and the concomitant slope is, as expected, equal to $-2a_2$.

The special value of the present work and approach is that it produces results on the dynamics of decay of real, multiparticle systems starting from first principles. This fact allows the possibility of comparison with previous work which has been carried out by assuming models of decay of unstable states. Two such comparisons are made below. The first involves the possible relationship between the energy spread, $\Delta E=\delta^{1/2}$, and the lifetime, τ, of a nonstationary state. The second involves the details of initial time $P(t)$ and its connection to the position and interaction with the continuum of Ψ_0.

An immediate answer to the first issue is provided by the time–energy uncertainty relationship, $\Delta E \Delta t \geqslant \frac{1}{2}$. A stricter condition has been proposed by Gislason, Sabelli, and Wood, [9]

$$\Delta E \tau \geqslant 3\pi 5^{1/2}/25 = 0.843. \tag{18}$$

For the shape resonance under study, we obtained $\Delta E = (1.9 \times 10^{-7})^{1/2}$. In addition, the calculation of the lifetime in [4] yielded $\tau \approx 5200$ a.u. From these *ab initio* results, the first of their kind, we indeed confirm the condition of Gislason *et al.* [9], since $\Delta E \tau \approx 2.3 > 0.843$.

The second issue regards the oscillatory behavior of $\Gamma(t)$ which appears after its initial linear variation with t, around the value of the autoionization rate. Such behavior has been seen in model calculations of Levitan [10] who studied, analytically, the time dependent rate in the second order of an unstable quantum system using a model interaction of the exponential type [$V_n(\epsilon)$ of Eq. (15)]. He concluded that, if the interaction decreases slowly as a function of energy so that contributions from energies higher than E_0 are included, then the quadratic mode is followed by an oscillating period before ED. This conclusion is in harmony with our findings. Indeed, Fig. 3 shows that the full interaction drops slowly
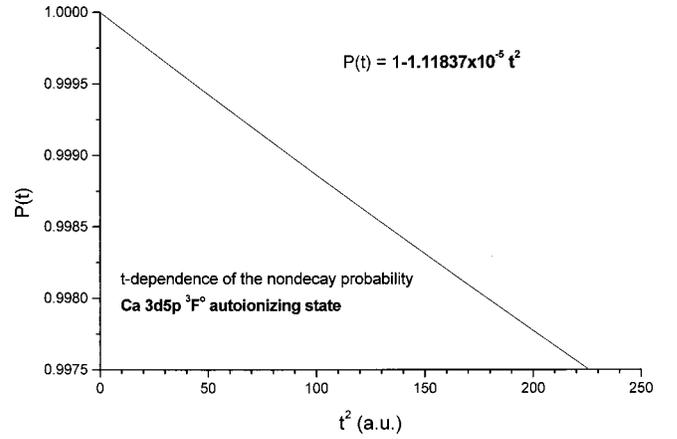
with energy. [The full interaction matrix element in calculations of decay of real states of multielectron systems is given by $V_0(\epsilon)-(E_{\text{threshold}}+\epsilon)S_0(\epsilon)$, where the symbols are defined in Eq. (15). The individual behavior as a function of ϵ of each matrix element is different. For example, in He$^-$ $1s2p^2$ ^4P the values of $V_0(\epsilon)$ are positive for all ϵ and those of $S_0(\epsilon)$ are negative.] The thick line shows the position of the resonance, which is at about 3.3×10^{-4} a.u. The curve reaches a maximum at about $\epsilon = 0.1$ a.u. and then starts dropping slowly. (Not possible to include it within the scale of this figure.) Its value reaches 2×10^{-3} a.u. at about $\epsilon = 1$ a.u.

B. The Ca $3d5p$ $^3F^o$ autoionizing state

This state, which is found experimentally at 0.24 eV above threshold, has two valence electrons, whose interaction constitutes the dominant cause of the decay into the Ca$^+[4s$ $^2S+\epsilon f]^3F^o$ continuum via Coulomb interactions.
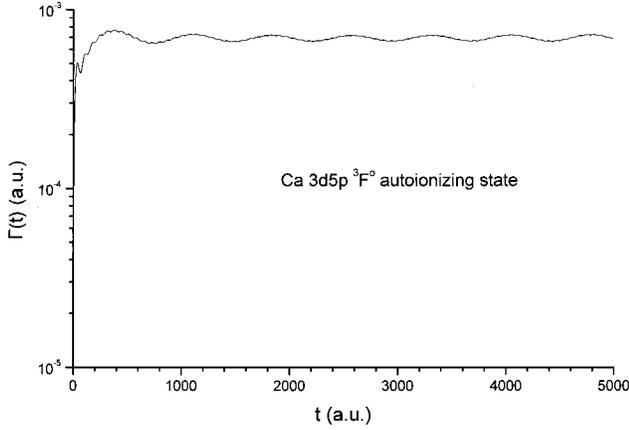
The analysis of the contributions of the various correlating configurations resulted in a three-term compact wave function Ψ_0, which was obtained self-consistently by the MCHF method,

$$\Psi_0(\text{Ca } 3d5p \ ^3F^o) = 0.994\psi(3d5p) - 0.103\psi(4d4p)$$
$$+ 0.013\psi(4d4f).$$

Details of the long-time decay curve of this state were given in [5]. Also in [5], by Fourier transforming the time-dependent amplitude of decay, we obtained for the first time for a real autoionizing state its spectral function, $g(\epsilon)$ of Eq. (1).

Figure 4 shows the survival probability as a function of t^2, for short times. From the slope of the straight line we obtain the stationarity coefficient $\delta = -a_2 = -1.12 \times 10^{-5}$. Now, $\Delta E = (1.12 \times 10^{-5})^{1/2}$ and the lifetime which was calculated in [5], $\tau \approx 1450$ a.u. Therefore, $\Delta E \tau \approx 4.8 > 0.843$, that again satisfies the form of the uncertainty relation (18), proposed in [9].

As in the previous case of He$^-$ $1s2p^2$ ^4P, the time-dependent rate $\Gamma(t)$ provides us with a_2 and with the region of time where exponential decay sets in. Indeed, from Fig. 5
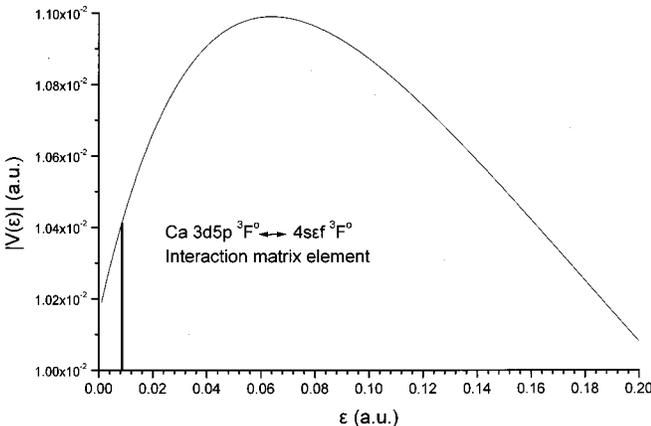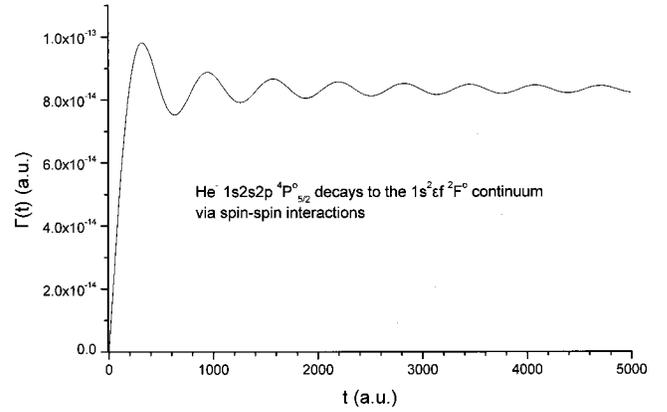
FIG. 5. As in Fig. 2, but for the Ca $3d5p$ $^3F^o$ autoionizing state.

FIG. 7. As in Fig. 5, but for the He$^-$ $1s2s2p$ $^4P^o_{5/2}$ metastable state.

one sees that for $t \geqslant 400$ a.u. ED has essentially taken over. On the other hand, for short times the slope of the linearly varying $\Gamma(t)$ is equal to $-2a_2$.

The interaction of the initially localized state with the underlying continuum is shown in Fig. 6. Here, because of the two-electron rearrangement and the ionic core, the overlap $S(\epsilon)$, which is defined by Eq. (15), is zero. The thick vertical line indicates the position E_0 of Ψ_0. The same conclusion with the case of He$^-$ $1s2p^2$ ^4P regarding the origin of the oscillations holds.

C. The He$^-$ $1s2s2p$ $^4P^o_{5/2}$ metastable state

This is a metastable state that decays to the $1s^2 \epsilon f$ $^2F^o$ underlying continuum via spin-spin interactions. Its lifetime is about 350 μs (see Ref. [5]). Because of this very long lifetime, the determination of the full time-dependent curve of decay has proven to be impossible within certain constraints of computer speed and of length of duration of the computation [5]. The calculation of wave functions and of relativistic matrix elements in the Breit-Pauli approximation follows from the 1980s work of Aspromallis and Nicolaides [24].
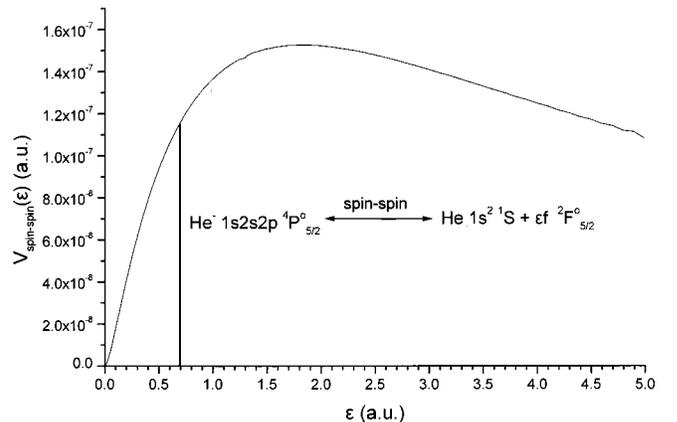
On the other hand, it is indeed possible to compute the short-time rate $\Gamma(t)$. Figure 7 depicts $\Gamma(t)$ as a function of t. It is revealed that ED sets in for $t \geqslant 2000$ a.u., while from the slope of the linearly varying $\Gamma(t)$, for very short times, we obtain $a_2 = -2.7 \times 10^{-16}$. For this case the product $\Delta E \tau$ is equal to 2×10^5, which, of course, also satisfies inequality (18).

The spin-spin interaction of Ψ_0 with the continuum, which causes the decay, is shown in Fig. 8. As in the previous case, the overlap $S(\epsilon)$ is zero. The vertical line indicates the position E_0, which is 0.69 eV above threshold. The explanation of the oscillatory structure of $\Gamma(t)$ in Fig. 7 is as before, and verifies again the results that emerged from the model calculations of Levitan [10].

VI. DISCUSSION AND CONCLUSION

The phenomenon of decay of unstable quantum mechanical states involves irreversible fragmentation into a purely continuous spectrum of a multiparticle system which initially ($t=0$) is represented by a localized wave function, Ψ_0, whose energy E_0 is embedded in the continuous spectrum of the kinetic energy of the emitted articles. The physics of this

FIG. 6. Ca $3d5p$ $^3F^o$ autoionizing state. Absolute value of the interaction matrix element, $V(\epsilon)$ (in a.u.), as a function of energy ϵ (in a.u.) above threshold.

FIG. 8. He$^-$ $1s2s2p$ $^4P^o_{5/2}$ metastable state. The spin-spin interaction (in a.u.) of Ψ_0 with the $1s^2 \epsilon f$ $^2F^o$ continuum, as a function of the energy ϵ (in a.u.) above threshold.

phenomenon is of fundamental interest and has been discussed in a number of papers over many decades. In the overwhelming majority of these works, the main interpretative and computational tool has been Eq. (1) and equivalent forms, and the use of models and assumptions about the form and properties of the function $g(E)$. This approach has produced qualitative and phenomenological information about the existence of nonexponential decay (NED) for short times, $t \approx 0$, and for very long times, $t \gg 1/\Gamma$.

In recent publications [4,5], as well as in the present investigation, we showed that it is possible to obtain quantitatively from first principles, for all times covering the exponential decay (ED) regime and the two NED regimes, the survival probability $P(t)$ [or any quantity for which the time-dependent wave function, $\Psi(t)$, is needed], for real, polyelectronic unstable atomic states, by solving numerically the time-dependent Schrödinger equation (TDSE). This is achieved by using a physically appropriate expansion of $\Psi(t)$ over accurately computed state-specific polyelectronic wave functions representing localized states (square-integrable wave functions) and fragmented states (energy-normalized scattering wave functions). $P(t)$ is obtained numerically for each state of interest. Furthermore, by obtaining numerically the interaction matrix elements and other quantities, such as the energy dispersion, it is possible to compare with previous results based on models and formalism. (See the discussion in the text related to Refs. [9] and [10].)

The theory and calculations of [4,5] focused on the exponential and long-time NED regime. In the work presented in this paper we focused on the pre-exponential, short-time NED regime, using as prototypical examples, three atomic autoionizing (autodetaching) states: $He^- \, 1s2p^2 \, {}^4P$, which is a single particle shape resonance for which the change of the self-consistent field as well as the two-electron operators contribute to $P(t)$, Ca $KLM \, 3d5p \, {}^3F^o$, which autoionizes predominantly via the two-electron Coulomb interaction, and $He^- \, 1s2s2p \, {}^4P^o_{5/2}$ which decays slowly via relativistic spin–spin interactions.

The results of our calculations showed that, by fitting $P(t)$ to a polynomial in t, Eq. (16), the short-time NED is overwhelmingly dominated by the t^2 term, in agreement with the formal expansion of Eq. (2). It was argued that the computed coefficient of the t^2 term, $\delta = a_2$ which we named the

stationarity coefficient, is a physically meaningful property of each real state, analogous to the lifetime associated with the regime of ED, and reflects the degree of the states stability. We also showed that it is possible to define and compute for short times a time-dependent rate, Eq. (17a), whose expansion reveals that δ is half the coefficient of the linear term in t [Eq. (17b)].

As we mention in Secs. I and II, the clear-cut observation of NED for an isolated unstable quantum state remains elusive. Regarding the long-time NED, Nicolaides and Beck [3,6] argued, via formal and numerical demonstrations, that the magnitude of this type of violation of the law of ED can be enhanced considerably in multiparticle states whose energy is very close to the threshold of the continuum into which they decay, even when the energy dependence of the interaction is weak. The choice of the $He^- \, 1s2p^2 \, {}^4P$ and the Ca $KLM \, 3d5p \, {}^3F^o$ nonstationary states and the related applications which were presented in [4,5] were made for this reason. Indeed, the suggestion of [3,6] was confirmed in the first principles computations of [4,5]. It remains to be seen whether such deviations can be clocked experimentally. A possible scheme may involve pump-probe synchronization with femtosecond laser pulses in the process

$$He^- \; 1s2s2p \; {}^4P^o_{5/2} \xrightarrow{h\nu} He^- \; 1s2p^2 \; {}^4P$$

$$\xrightarrow{h\nu'} He \; 1s2p \; {}^3P^o + e^-.$$
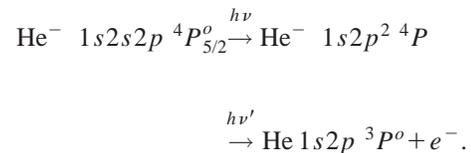
The population of $1s2p^2 \, {}^4P$ is time dependent (since the state is nonstationary) and this dependence ought, in principle, to be recordable in the intensity of the photoelectrons.

When it comes to the question of observing the short-time NED we opined [3,4] that the $t=0$ point is not well defined since it depends on the excitation wave packet and on the detection setup. On the other hand, it appears that the possibility of its observation should depend primarily on the duration of this pre-exponential NED regime. By choosing to investigate the metastable state $He^- \, 1s2s2p \, {}^4P^o_{5/2}$, we explored the possibility that the duration of the pre-exponential NED regime is sufficiently long to be clocked experimentally. Indeed, this duration for this state is about 5×10^{-14} s, which is within the femtosecond range of available laser pulses.

[1] M. L. Goldberger and K. M. Watson, *Collision Theory* (Wiley, New York, 1964).

[2] H. Nakazato, M. Namiki, and S. Pascazio, Int. J. Mod. Phys. B **10**, 247 (1996).

[3] C. A. Nicolaides and D. R. Beck, Int. J. Quantum Chem. **14**, 457 (1978).

[4] C. A. Nicolaides and Th. Mercouris, J. Phys. B **29**, 1151 (1996).

[5] Th. Mercouris and C. A. Nicolaides, J. Phys. B **30**, 811 (1997).

[6] C. A. Nicolaides and D. R. Beck, Phys. Rev. Lett. **38**, 683 (1977); addendum: **38**, 1037 (1977).

[7] C. B. Chiu, E. C. G. Sudarshan, and B. Misra, Phys. Rev. D **16**, 520 (1977).

[8] A. Peres, Ann. Phys. (N.Y.) **129**, 33 (1980).

[9] E. A. Gislason, N. H. Sabelli, and J. W. Wood, Phys. Rev. A **31**, 2078 (1985).

[10] J. Levitan, Phys. Lett. A **129**, 267 (1988).

[11] J. G. Muga, G. W. Wei, and R. F. Snider, Europhys. Lett. **35**, 247 (1996).

[12] P. Facchi and S. Pascazio, Phys. Lett. A **241**, 139 (1997).

[13] K. Unnikrishnan, Phys. Rev. A **60**, 41 (1999).

[14] I. Antoniou, E. Karpov, G. Pronko, and E. Yarevsky, Phys.

Rev. A **63**, 062110 (2001).

[15] P. T. Greenland, Nature (London) **335**, 298 (1988).

[16] E. B. Norman, S. B. Gazes, S. G. Crane, and D. A. Bennett, Phys. Rev. Lett. **60**, 2246 (1988).

[17] C. A. Nicolaides and D. R. Beck, Phys. Rev. A **15**, 1787 (1977).

[18] C. A. Nicolaides, Phys. Rev. A **6**, 2078 (1972).

[19] P. Froelich and E. Brändas, Phys. Rev. A **12**, 1 (1975).

[20] I. Ôksüz, Phys. Rev. A **13**, 1507 (1976).

[21] C. A. Nicolaides and D. R. Beck, Phys. Lett. A **65**, 11 (1978).

[22] C. A. Nicolaides and H. J. Gotsis, J. Phys. B **25**, L171 (1992).

[23] C. W. Walter, J. A. Seifert, and J. R. Peterson, Phys. Rev. A **50**, 2257 (1994).

[24] G. Aspromallis and C. A. Nicolaides, J. Phys. B **19**, L13 (1986).