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Time dependence and properties of nonstationary states in the continuous spectrum of atoms

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Abstract. The recently measured Li^- $1s^22s2p\,^3P^o$ shape resonance, the Ca KLM 3d5p $^3F^o$ doubly excited autoionizing state and the long-lived He^- $1s2s2p\,^4P^o_{5/2}$ metastable level were treated as nonstationary states satisfying the time-dependent Schrödinger equation (TDSE). The lifetimes of the first two are short, of the order of 10^{-14} s, and the solution of the TDSE well into times where nonexponential decay (NED) is established, is achievable via the state-specific expansion approach (SSEA), according to which the time-dependent solution has the form $\Psi(t) = c(t)\Psi_0 + X(t)$. Ψ_0 is the square-integrable wavefunction of the localized state at $t = 0$ and $X(t)$ is composed mainly of energy normalized scattering functions with time-dependent coefficients. The coefficient $c(t)$ is related to the survival amplitude, $\alpha(t)$, by $c(t) = \alpha(t) - \langle\Psi_0|X(t)\rangle$, where the overlap matrix element appears when the function spaces are not completely orthonormal. For the diffuse Li^- $1s^22s2p\,^3P^o$ resonance, its analysis as a decaying state has as a prerequisite the calculation of a reliable Ψ_0, with correlation between the two valence electrons. This has been achieved by a special procedure and a related discussion is given. The proximity of the energy E to threshold (~ 50 meV), the closeness of the ratio E/Γ to unity (Γ is the resonance width) and the energy dependence of the bound–free matrix element, produced the result that NED should appear after only two lifetimes, when the probability of finding the system in the initial state is still non-negligible. From the exponential part of the decay curve, the width was found to be $\Gamma = 53$ meV, in agreement with the recent width of 64 ± 25 meV derived from measured cross sections in recent collision experiments (Lee *et al* 1996). The shortness of the time for which exponential decay (ED) holds and the fact that the survival probability, $P(t)$, is still significant at the beginning of the NED, does not allow the rigorous justification of the definition of the lifetime from $\tau = \frac{\hbar}{\Gamma}$, or the equivalence of this Γ with the observed energy width. Thus, we propose that a mean life, $\bar{\tau}$, should be obtained from

$$\bar{\tau} = \langle t\rangle = \frac{\int_0 t\,P(t)\,\mathrm{d}t}{\int_0 P(t)\,\mathrm{d}t}.$$

Calculation produces $\tau = 1.2 \times 10^{-14}$ s and $\bar{\tau} = 1.7 \times 10^{-14}$ s. For the Ca $^3F^o$ state, whose bound–free interaction is smooth and nearly constant from zero to about 5.5 eV, NED appears after 17 lifetimes. The lifetime of Ca $^3F^o$ is deduced from the exponential decay (ED) part of $P(t)$ to be 3.5×10^{-14} s. From our examination of the case of the He^- $^4P^o_{5/2}$ level by a number of methods based on the use of state-specific wavefunctions, we conclude that for metastable states whose lifetimes are in the range 10^{-4}–10^{-8} s, the *ab initio* calculation of $P(t)$ is, at present, prohibited by the huge requirements for computer time. Finally, having computed the amplitude $\alpha(t)$, we obtain numerically the energy distribution function, $g(E) \equiv |\langle E|\Psi_0\rangle|^2$, of the two autoionizing states. In the case of Ca it is a perfect Lorentzian.

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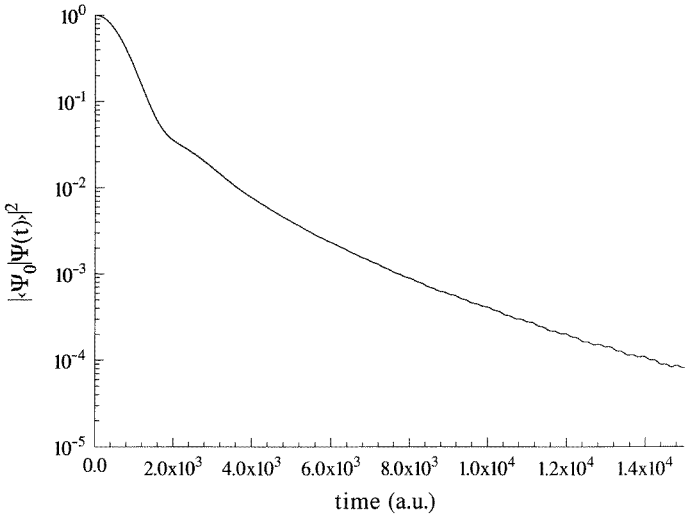

Figure 1. The survival probability (in logarithmic scale with base 10) of Li^-, initially prepared as a wavepacket of $^3P^o$ symmetry with major characteristic the $1s^2 2s\bar{p}$ configuration, as a function of time, in atomic units. The exponential decay lasts for only two lifetimes.

A reasonable generalization is to define a mean life of this state by the average

$$\bar{\tau} = \langle t \rangle = \frac{\int_0 t\, P(t)\, \mathrm{d}t}{\int_0 P(t)\, \mathrm{d}t}. \tag{6}$$

Indeed, when $P(t)$ is given by equation (5), then equation (6) gives $\bar{\tau} = \tau$.

The calculation of expression (6) using the $P(t)$ of figure 1 gives $\bar{\tau} = 1.7 \times 10^{-14}$ s, whereas $\tau = 1.2 \times 10^{-14}$ s.

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

Apart from the special cases of resonances in negative ions, it is also possible to find in existing spectra of neutral atoms autoionizing states which are relatively close to threshold. Such is the case of the doubly excited Ca 3d5p $^3F^o$ state which is included in Moore's [7] tables. It decays to the Ca^+ 4s $^2S + \varepsilon f$ $^3F^o$ continuum via Coulomb interactions. The emitted electron has an energy of about 0.24 eV [7].

The calculation of Ψ_0 focused on the electron correlation of the two valence electrons. After systematic analysis of the contributions of the various configurations, we chose as Ψ_0 the following compact representation obtained self-consistently by the MCHF method:

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

The Coulomb interaction matrix element between this Ψ_0 and the continuum Ca 4sεf, where εf are scattering solutions in the HF potential of the Ca^+ 4s ^2S configuration, is essentially constant over the physically important energy region.

After the usual convergence tests, the final results were obtained by including the continuum up to 0.1 au (2.72 eV), where the energy distance between neighbouring energy normalized scattering states was 6.7×10^{-6} au from zero up to 0.05 au and 1×10^{-5} au for the rest (i.e. the energy mesh was slightly denser in the neighbourhood of the energy of the autoionizing state which is 0.24 eV above threshold).

Figure 2 shows that ED lasts for about 25 000 atomic units of time followed by a period of oscillations. At about 35 000 au a smooth NED sets in, characterized by an inverse power dependence. The lifetime, which is deduced from the ED part of the decay curve, is 1450 au, i.e. 3.5×10^{-14} s, which is exactly what the golden-rule formula with the same Ψ_0 gives. This is a result of the smooth and nearly constant bound–free interaction characterizing this state, in contradistinction to the cases of the shape resonances $He^-\ 1s2p^2\ ^4P$ [5] and $Li^-\ 1s^22s2p\ ^3P^o$ (this work).

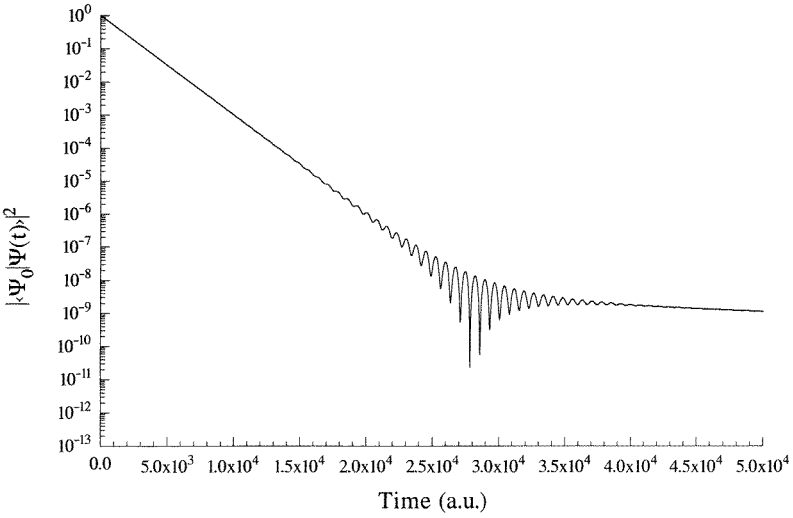

Figure 2. The same as in figure 1, but for Ca, initially prepared in the doubly excited $3d5p\ ^3F^o$ state. The exponential decay lasts for more than 17 lifetimes. The lifetime is computed to be 3.5×10^{-4} s.

3.3. The energy distribution of the autoionizing states

By inserting the unit operator $I = \int_0 \mathrm{d}E|E\rangle\langle E$ into the expression for the amplitude $\alpha(t)$ (equation (4)), ($|E\rangle$ is the exact scattering state at energy E), one obtains

$$\alpha(t) = \int_0^\infty \mathrm{d}E g(E)\mathrm{e}^{-\mathrm{i}Et} \tag{7}$$

where

$$g(E) \equiv |\langle E|\Psi_0\rangle|^2 \tag{8}$$

is the *energy distribution (or spectral) function* for the nonstationary state.

The formal theory of states decaying into the continuous spectrum shows that (e.g. [2c, p 492])

$$g(E) = \frac{1}{2\pi\,\mathrm{i}} \lim_{\varepsilon\to 0}[G^d(E - \mathrm{i}\varepsilon) - G^d(E + \mathrm{i}\varepsilon)] \tag{9}$$

where $G^d(E)$ is the diagonal Green's function.

To our knowledge, the *ab initio* accurate calculation of $G^d(E)$ for a decaying state of a polyelectronic system has not yet been done. It is only the formal approximation of the simple pole that allows the well known identification of $g(E)$ with a Lorentzian. It is