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Nonexponential decay in autoionization near threshold

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A general upper bound is obtained for the nonexponential contribution to the time-dependent occupation amplitude $G(t)$ for an autoionizing state just above the continuum threshold in the limit of narrow widths. This upper bound is shown to be inconsistent with some recently published results predicting new observable nonexponential effects in $|G(t)|^2$, but is consistent with earlier long-accepted theory. It is also shown how some nonexponential contibutions to the decay might, in principle, still occur as a consequence of close proximity between the autoionizing state and the ionic threshold, although these contributions now have a different form than those recently proposed.

The problem of determining the time dependence for the occupation of an isolated initially populated state coupled to a continuum has a long history, and the theory of "virtual states" of this kind, including effects arising from the absence of continuum states below some critical threshold energy, is summarized, for example, by Goldberger and Watson (GW).[1] Possible effects arising from the existence of a continuum threshold have been reexamined by Nicolaides and Beck (NB)[2] who conclude that the occupation probability should obey the law

$$|G(t)|^2 = e^{-\Gamma t/\hbar} + \frac{\hbar^2}{(4E_0^2+\Gamma^2)\pi^2 t^2} \tag{1}$$

in the limit of long times t, where Γ is the width characterizing the coupling to the continuum, E_0 is the energy above threshold, and G is the occupation amplitude of the isolated state. In particular, NB predict that for realizably small values of Γ, the second term in (1) should produce observable nonexponential decay (NED) contributions to $|G(t)|^2$ at large times t. It should also be noted that the nonexponential part of Eq. (1) fails to exhibit the intuitively reasonable behavior of approaching zero as Γ/E_0 approaches zero, also in contrast with the results of GW. This behavior is crucial since NB assume the width Γ to be very small. NB attribute the disagreement between their results and those of GW to their different choice of integration contour, emphasizing that the relevant integral over energies should be evaluated starting only from the continuum threshold.

To the extent that the particular integration contour controls the predicted time dependence, the contour to be used is not subject to choice on the basis of intuition, but is subject to restrictions following logically from the initial model assumptions, and it becomes useful to employ an alternative derivation which avoids any apparent ambiguity about the integration contour. This derivation leads to an upper bound for the NED contribution and allows reexamination of the prediction regarding observable deviations from exponential decay in autoionization. Although some functional forms of NED (such as t^{-n} dependence) require, in principle, that NED be the dominant surviving contribution at very large t, a small enough upper bound would allow NED to dominate only after the total excitation probability is no longer of physical significance; furthermore, our upper bound substantially reduces the estimates of NB by at least a factor of order $(\Gamma/E_0)^2$.

The time dependence of the occupation probability for a state $|\Phi_I\rangle$ given that $|\Phi_J\rangle$ was initially occupied, where $|\Phi_I\rangle$ and $|\Phi_J\rangle$ are members of a set of sparsely spaced states coupled to each other and to a quasicontinuum of discrete states $\{|\Psi_i\rangle\}$, has already been shown[3] to be given by $|\alpha_{IJ}(t)|^2$, where α_{IJ} has the form

$$\alpha_{IJ}(t) = -\frac{1}{2\pi i}\oint [\hat{F}^{-1}(z)]_{IJ}\exp(izt/\hbar)\,dz \quad . \tag{2}$$

The closed integration contour in Eq. (2) includes within it all of the (real) energies $E_i^{(0)}$ of the quasicontinuum states and the real energies E_I of the sparse states, and the elements of the matrix $\hat{F}$ are given by

$$\hat{F}_{IJ}(z) = (z-E_I)\delta_{IJ} + (1-\delta_{IJ})V_{IJ} - \int_{-\infty}^{\infty} \frac{\langle v_{Ii}v_{Ji}\rangle_{\mathscr{E}}}{z-\mathscr{E}}\,d\mathscr{E} \tag{3}$$

with $\langle v_{Ii}v_{Ji}\rangle_{\mathscr{E}}$ an average (over many quasicontinuum states in the neighborhood of $\mathscr{E}$) involving the coupling v_{Ii} between sparse state $|\Phi_I\rangle$ and quasicontinuum state $|\Psi_i\rangle$, and with V_{IJ} the coupling between $|\Phi_I\rangle$ and $|\Phi_J\rangle$. The corresponding problem involving sparse states coupled to a true continuum can correctly be regarded as merely the idealized limit of the discrete-state problem, since any actual quantum system always has finite spatial extent and therefore possesses only a discrete spectrum. The derivation of (2) and (3), which leaves no ambiguity whatsoever in the allowable choice of contour, is obtained by expanding the true eigenstates of the system as linear combinations of the zero-order states $\{|\Phi_I\rangle\}$ and $\{|\Psi_i\rangle\}$, and by assuming that a quasicontinuum spacing, small compared with h/Γ, allows replacement of certain sums by integrals.[3] The reader interested in this derivation and in a more extensive discussion of the assumptions involved is referred to Ref. 3.

Consider therefore the special case of one initially populated state coupled to a dense quasicontinuum, so that the occupation probability of the discrete state at energy E_0 is

$$G(t)=\frac{1}{2\pi i}\int_{-\infty}^{\infty}\left[\frac{1}{E-E_0-w_{(-)}(E)}-\frac{1}{E-E_0-w_{(+)}(E)}\right]\times e^{-iE/\hbar}dE \ , \tag{4}$$

where

$$w_{(\pm)}(E)=\lim_{z\to E\pm i\epsilon}\int_{-\infty}^{\infty}\frac{\rho(\mathscr{E})\langle v_i^2\rangle_{\mathscr{E}}}{z-\mathscr{E}}d\mathscr{E}$$
$$=\left[\mathrm{P}\int\frac{\rho(\ )\langle v_i^2\rangle_{\mathscr{E}}}{E-\mathscr{E}}d\mathscr{E}\right]\pm i\pi\rho(E)\langle v_i^2\rangle_E \ , \tag{5}$$

with the integration contour (infinitesimally close to the real axis) illustrated in Fig. 1(a). Of course, we assume $\rho(\mathscr{E})\langle v_i^2\rangle_{\mathscr{E}}$ to be nonzero only from $\mathscr{E}=0$ to E_b, where the limit $E_b\to\infty$ will ultimately be assumed. The coupling Γ of the autoionizing state (which differs from the Γ of Ref. 3) is defined to be some mean value of $\pi\rho(E)\langle v_i^2\rangle_E$ which need not be specified precisely for our purposes; 2Γ is an actual width when $\pi\rho\langle v_i^2\rangle$ is only weakly dependent on energy, so that the line shape for excitation of the discrete state coupled to a nonabsorbing continuum would be Lorentzian.

We now assume that $w(z)$ in the continuum limit is regular everywhere except on the real-axis segment $[0,E_b]$, and except possibly for isolated poles elsewhere, this behavior being suggested before the continuum limit is taken. The discontinuous change in the imaginary part of $w(z)$ across the real-axis segment suggests that $[0,E_b]$ is a branch line. It is possible to show that no poles of $[z-E-w(z)]^{-1}$ occur on the first sheet, except possibly for (at most two) solutions of

$$E-E_0-\int_0^{E_b}\frac{\rho(\mathscr{E})\langle v_i^2\rangle_{\mathscr{E}}}{E-\mathscr{E}}d\mathscr{E}=0 \ , \tag{6}$$

along the real axis below E_a and above E_b [as illustrated, respectively, by P_1 and P_2 in Fig. 1(b)]. These real solutions do not give exponential decay, and will be considered later. There might (and generally will) be at least one complex pole on a second Riemann sheet reached by analytic continuation of $w_{\mathrm{I}}(z)$ [$w(z)$ on sheet I] across the branch cut. We therefore deform the contour in stages as illustrated in Fig. 1(c), where P_{II} denotes the complex pole on sheet II. The final step is to let E_b approach ∞, so that the contributions associated with the E_b contour integrals are assumed to go to zero. Then $G(t)$ has a contribution $G_a(t)$ from the contour (on sheets I and II) associated with the

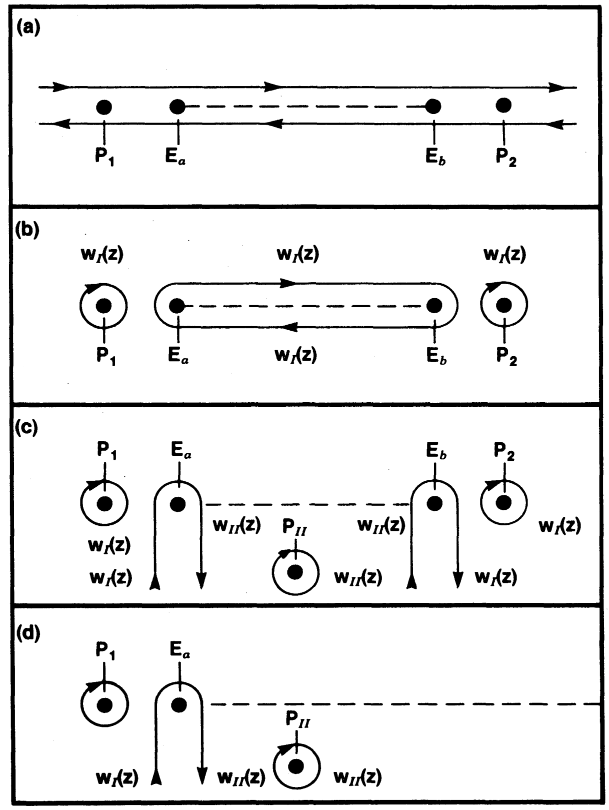

FIG. 1. Deformation of the integration contour used in the text.

continuum edge at $E\equiv E_a=0$, a possible contribution $G_1(t)$ associated with the possible pole P_1 along the real axis, and a contribution $G_p(t)$ associated with the complex pole on sheet II. The contribution $G_p(t)$ should by itself give simple exponential decay [if only a single pole contributes to $G_p(t)$] and, under idealized circumstances of a continuum unbounded at both ends, this would be the only contribution that need be considered. Our primary concern, however, is with the contributions $G_a(t)$ and $G_1(t)$ produced by the continuum edge. For any arbitrary functional form of $w(z)$, let

$$w(z)=Cu(z) \ ,$$

where $u(z)$ is dimensionless and where the scaling factor C has units of energy. We adjust the width Γ by adjusting C with $u(z)$ held fixed. Then $G_a(t)$ is given by

$$2\pi iG_a(t)=C\int_{-i\infty}^{0}\exp\left(\frac{izt}{\hbar}\right)\frac{u_{\mathrm{I}}(z)-u_{\mathrm{II}}(z)}{[z-E_0-Cu_{\mathrm{I}}(z)][z-E_0-Cu_{\mathrm{II}}(z)]}dz \ . \tag{7}$$

As Γ is decreased by decreasing C, $|G_a(t)|^2$ approaches zero, in disagreement with the results of NB. If we make the slightly restrictive assumption that $|u_{\mathrm{I}}(z)|$ and $|u_{\mathrm{II}}(z)|$ are bounded along the relevant part of the contour and consider $|Cu|$ small compared with $|E_0|$ over the relevant integration region, expansion of the integrand to the lowest order in C/E_0 gives

$$2\pi G_a(t)=\frac{C}{E_0}\int_{-i\infty}^{0}\exp\left(\frac{-iE_0\xi t}{\hbar}\right)\frac{u_{\mathrm{I}}(\xi E_0)-u_{\mathrm{II}}(\xi E_0)}{(\xi-1)^2}d\xi \ . \tag{8}$$

Therefore, if B is an upper bound for $|u_{\mathrm{I}}|$ and $|u_{\mathrm{II}}|$ along the contour, $G_a(t)$ satisfies

$$|G_a(t)|\le\frac{CB}{\pi E_0}\left|\int_{-\infty}^{0}\exp\left(\frac{E_0ty}{\hbar}\right)\frac{dy}{|1-iy|^2}\right|$$
$$\le\frac{CB}{\pi E_0}\int_0^{\infty}\exp\left(\frac{-E_0ty}{\hbar}\right)dy$$

or

$$|G_a(t)|^2\le\frac{\Gamma^2}{\pi^2E_0^2}\frac{\hbar^2}{E_0^2t^2} \ , \tag{9}$$

where we identify CB with Γ. This identification is justified by the meaning of Γ as a representative value of $\pi\rho\langle v_l^2\rangle$. Equation (9) gives an upper bound for $|G_a(t)|^2$ under the general conditions of small Γ/E_0 for all times $t>0$ (and not merely asymptotically for large values of t as in NB and GW). This upper bound is inconsistent with the results of NB [being much smaller than the results presented in Fig. 2 of NB and smaller by order $(\Gamma/E_0)^2$ than Eq. (16) of NB] but is consistent with the results of GW. Examination of the final contour in Fig. 1(d) furthermore shows it to be equivalent to that employed by GW, but not to the contour employed by NB. The small value of our upper bound arises in Eq. (7) from cancellation between corresponding points of the continuum-edge contour on sheets I and II; the NB choice of contour omits the sheet-I contribution, making cancellation impossible.

As seen graphically in Fig. 2, the solution to Eq. (6) (and therefore the real pole P_1) might or might not exist, depending on the specific functional form of $\rho(\mathscr{E})\langle v_l^2\rangle_{\mathscr{E}}$ and possibly on the value of E_0. When the pole exists, $G_1(t)$, given by

$$G_1(t)=e^{iE_0t/\hbar}\Big/\left|1-\frac{d}{dE}\int\frac{[\rho(\mathscr{E})\langle v_l^2\rangle_{\mathscr{E}}]}{(E-\mathscr{E})}d\mathscr{E}\right| , \tag{10}$$

leads to an additional nonexponential contribution to $G(t)$. The weaker the coupling in comparison with E_0, however, the greater is the magnitude of the slope of

$$-\int\frac{\rho(\mathscr{E})\langle v_l^2\rangle_{\mathscr{E}}}{E-\mathscr{E}}d\mathscr{E} \tag{11}$$

at the intersection point in Fig. 2, and the smaller is the contribution of the pole, for small enough coupling Γ/E_0. The previous conclusions about G_a therefore apply also to G_1, at least semiquantitatively.

It is also necessary to consider the possibility of additional complex poles on the second sheet. If $\rho(\mathscr{E})\langle v_l^2\rangle_{\mathscr{E}}$ is essentially constant over the width of the state (as expected for narrow widths), and therefore constant over the part of the original contour [Fig. 1(a)] contributing significantly to the integral, replacement of $\rho\langle v_l^2\rangle$ by this constant value eliminates the problem of continuation onto a second Riemann sheet and leads to simple exponential decay (arising from G_p alone), again consistent with the previous results for the other possible contributions to $G(t)$.

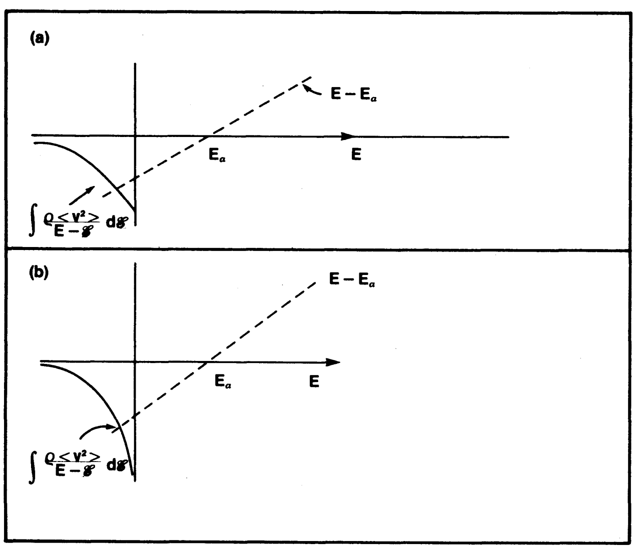

FIG. 2. Graphical illustration of the solution of Eq. (6) to find the real pole P_1, (a) for a case in which solutions might sometimes not exist, and (b) for a $\pi\rho\langle v_l^2\rangle$ dependence on energy that always yields a solution.

Finally, it should be noted that the values $E_0=10^{-3}$ eV and $\Gamma=10^{-5}$ eV considered by NB, when applied to the illustrative example discussed by GW,[4] give a branch-point contribution G_a equal in magnitude to the exponential-decay contribution G_p only after 41 lifetimes, at which point experimental observation of the decay would be extremely difficult. (If 10^{15} atoms could be excited, as suggested, the excitation would be depleted completely at about 35 lifetimes for simple exponential decay.) The numerical estimates considered by NB,[2] on the other hand, give a NED contribution 10^4 times larger than our upper bound.

The model thus far considered ignores the bound states of negative energy converging to the ionization threshold and therefore strictly applies, not to atomic ionization, but to such phenomena as the decay of an impurity state into a band of continuum states in a solid. When the bound states are included (for atomic autoionization) $w(z)$ takes the form

$$w(z)=\sum_l{}'\frac{v_l^2}{z-E_l^{(0)}}+\int_0^\infty\frac{\pi\rho\langle{}_l^2\rangle_{\mathscr{E}}}{z-\mathscr{E}}d\mathscr{E} , \tag{12}$$

where the first contribution is a summation over the zero-order bound states (i.e., for negative $E_l^{(0)}$). Coupling to the autoionizing state shifts the bound-state energies to values E_ν that are solutions of the secular equation

$$E-E_0=w(E) \tag{13}$$

{as seen by generalizing Eq. (7) of Ref. 3, or Eq. (3) of Ref. 5, to include a continuum above the threshold, or by recognizing that the new eigenvalues must be poles of $[z-E_0-w(z)]^{-1}$}. It can easily be seen graphically that each interval $(E_l^{(0)},E_{l+1}^{(0)})$ between successive zero-order bound-state energies then contains exactly one eigenvalue E_ν. Therefore every neighborhood of the branch point at threshold contains arbitrarily many poles of $[z-E_0-w(z)]^{-1}$ (corresponding to the eigenvalues E_ν), making it difficult to evaluate the $G_a(t)$ contour integral along the small semicircular arc around the branch point. A possible solution to this difficulty involves considering only the case in which v_l^2 approaches zero as the branch point is approached from below the origin; in this case, however, all of our results presented earlier for the behavior of $G_a(t)$ are recovered.

In summary, the results presented here impose an upper bound on the possible nonexponential contributions to $G(t)$ arising from the existence of an ionization threshold, showing that these contributions approach zero as Γ/E_0 becomes small for coupling width Γ and energy E_0 of the autoionizing state above threshold. Our upper bound is inconsistent with some recently published predictions[2,3] but consistent with earlier long-accepted results.[1] We attribute this inconsistency to the arbitrary choice of an integration contour (in the more recent work[2]) that is inconsistent with requirements imposed by mathematical considerations. Our analysis nevertheless does identify a number of other sources for deviation from simple exponential decay which might be of significance in certain physical applications. The overlapping of several states, close compared with their widths, can also provide an additional mechanism.[3] It should be noted, in particular, that simple exponential decay is not a universal law, and that deviations from this law have, for example, been observed experimentally in the corresponding molecular radiationless decay problem in a number of instances.[6]

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[1]M. L. Goldberger and K. M. Watson, *Collision Theory* (Wiley, New York, 1964), Chap. 8.

[2]C. A. Nicolaides and D. R. Beck, Phys. Rev. Lett. 38, 683 (1977); 38, 1037 (1977); Int. J. Quantum Chem. 14, 457 (1978).

[3]S. D. Druger, J. Chem. Phys. 68, 5250 (1978).

[4]Reference 1 , p. 450, Eq. (116).

[5]S. D. Druger, J. Chem. Phys. 67, 3249 (1977).

[6]G. E. Busch, P. M. Rentzepis, and J. Jortner, Chem. Phys. Lett. 11, 437 (1971); J. Chem. Phys. 56, 361 (1971); A. E. W. Knight and C. S. Parmenter, Chem. Phys. 15, 85 (1976); R. Van der Werf, D. Zeverhuijzer, and J. Kommandeur, Chem. Phys. Lett. 27, 325 (1974).