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Unified treatment of radiative and dielectronic recombination

G. Alber, J. Cooper, and A. R. P. Rau*
Joint Institute for Laboratory Astrophysics, University of Colorado and National Bureau of Standards, Boulder, Colorado 80309

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A coupled-channel analysis of electron-positive ion recombination is carried out, with full treatment of the coupling between radiation and autoionization continua. The cross section for this process reduces in the appropriate limits to the expressions for radiative and dielectronic recombination. The coupling to the radiation continuum leads to a modified Fano profile for the autoionizing resonances. The more complete, combined expressions derived here may be of interest for recent experimental studies of recombination and their comparison with theoretical results.

The process of electron-positive-ion recombination is of considerable interest, particularly in laboratory and astrophysical plasmas.[1] Conventionally, this process is viewed as occurring through two different mechanisms. One is the direct transition from the initial continuum state to a bound state of the resulting neutral atom or positive ion, accompanied by radiation of a photon. This process, called radiative recombination (RR), dominates for capture into the ground and low-lying excited states, but becomes negligible for capture into highly excited states.[2] Here, a second process, which proceeds through quasibound doubly excited autoionizing states of the electron-ion system, is considered to play the dominant role. Termed dielectronic recombination (DR), the initial continuum electron is viewed as being captured by inverse autoionization into the doubly excited configuration which then radiatively stabilizes to end up as a bound, highly excited Rydberg state.[3]

In the past year, the study of dielectronic recombination has seen a flurry of excitement because, for the first time, direct experimental measurements have been made of the rate of this process.[4-7] Obtained by different laboratories for different ionic species, the measured rates have generally been larger than calculations, sometimes by half an order of magnitude or more. The discrepancy has been puzzling because different methods, using extensive and sophisticated computations, generally closely agree on the theoretical estimates.[8,9] At the same time, the discrepancy has been disturbing, because such calculations carried out over the past two decades form the basis of one set of diagnostics for temperature and number densities of ions in both laboratory and astrophysical plasmas. Among the mechanisms being studied to account for enhancements of DR rates are the effects of external electric fields.[10,11]

In this Rapid Communication, we do not consider the above questions of DR rates and enhancement mechanisms for capture into the highly excited states. Rather, we develop an analysis that considers RR and DR in a unified way. Both physically and operationally, there is no distinction between the two processes and viewing them as two distinct ones is artificial. Instead, by considering the coupling between *all* the channels involved, we develop the theory of electron-ion recombination so as to give a simple expression for the rate which, in appropriate limits of neglecting certain couplings, reduces to the RR and DR rates. Some of the recent DR experiments have shown, besides enhancements in the region of very highly excited states, larger cross sections also at a lower energy range[7] where, in fact, both DR and the enhancements being currently considered give essentially negligible contributions. We identify, through our analysis, the circumstances under which appreciable rates may be found in this energy range.

The arrangement of this paper is as follows. First, we give a brief sketch of the basic DR expression. We then go on to a full multichannel analysis of the recombination. For concreteness, and as an illustrative example, we consider throughout $e+\mathrm{Ca}^+$ recombination for incident electron energies between 0 and 3.14 eV. The ground state of Ca^+ is a $4s\ ^2S$ state and 3.14 eV above it lies the excited $4p\ ^2P$ state. In the region where the doubly excited configurations $4pnl$ of Ca lie, direct capture from a continuum $4s\epsilon l'$ state with $l'=l\pm1$ (ϵ is the kinetic energy of the incident electron) to a bound excited state $4snl$, competes with the alternative route of capture into the doubly excited state $4pnl$, followed by radiative stabilization when the $4p$ electron of the ion decays to the ground $4s$ state. The energy of the emitted photon is $\simeq 3.14$ eV. In a complete calculation of $e+\mathrm{Ca}^+$ recombination, coupling to states of the intermediate $\mathrm{Ca}^+(3d)$ level will also need to be considered.[12]

The description given above of two alternative routes for recombination, constitutes the usual picture of RR and DR. The RR probability is proportional to $|\langle 4snl|z|4s\epsilon l'\rangle|^2$, z being the photon operator in the usual electric dipole approximation. On the other hand, the energy averaged DR probability is given in terms of the radiative rate Γ_R for $4pnl \rightarrow 4snl$, and the autoionization rate Γ_A for the capture $4s\epsilon l' \rightarrow 4pnl$ by[13]

$$W_{\mathrm{DR}} = \left(2\pi\frac{\Gamma_A}{\Delta\epsilon/\hbar}\right)[\Gamma_R/(\Gamma_R+\Gamma_A)] \ , \tag{1}$$

as long as Γ_R and Γ_A are much smaller than the frequency spacing between adjacent resonances $\Delta\epsilon/\hbar$.[14] This expression has a ready interpretation, the first factor expressing the probability of capture into $4pnl$ and the second, the probability that this state goes to the final $4snl$, given the alternative branchings into the autoionization (or electron) continuum and the radiative (or photon) continuum. The result in Eq. (1) is basic to the DR literature, and has been derived in a variety of ways.[1,3,15] The result, itself, exemplifies that a common element in all these approaches is that the alternative branchings of the $4pnl$ closed channel are seen as independent, with neglect of the coupling between the resulting electron and photon continua. Yet, these continua are themselves coupled, the coupling being essentially the one involved in RR, where the $4snl$ state and $4s\epsilon l'$ are connected by the photon operator.

The neglect of coupling between the two continua involved is not serious when n is large, because the coupling is then indeed small, as evidenced by the negligible RR rates for high n. However, for small values of n (typically $n \simeq 4$–8 in the Ca example), the coupling can become significant. (Note that for these same small values of n, the other assumption of DR, wherein Γ_R is identified essentially as the $4p \rightarrow 4s$ radiative rate of the Ca^+ ion, the outer nl electron being regarded as a spectator, can also be expected to break down, necessitating the inclusion of correlations between the two electrons.) With reference to Fig. 1, it is clear that the complete process of electron-ion recombination is really one of three coupled channels, the $4s\epsilon l'$ electron continuum, the $4snl$ photon continuum, and the $4pnl$ state of the closed channel. [There are, in general, really two electron continua with $l' = l \pm 1$ but, to a first approximation, coupling between them can be ignored. Also the channel with $l' = l + 1$ is generally the dominant one because the dipole matrix elements involved for $l \rightarrow l+1$ are usually much larger (often by an order of magnitude) than for $l \rightarrow l-1$.[16]]

We now turn to a multichannel scattering treatment of electron-ion recombination. Such a treatment was given by Davies and Seaton,[13] who considered the coupled pair of equations between a structured electron continuum (that is, one including embedded autoionizing states such as $4pnl$ in a background $4s\epsilon l'$ continuum) and the photon continuum built on the final bound state.

In particular, we consider a transition of the form $|\gamma JM\epsilon\rangle \rightarrow |bJ_fM_f, \vec{k}\vec{\lambda}\rangle$. J and J_f are the total angular momenta of the colliding electron-ion system and the recombined system, M and M_f are the corresponding magnetic quantum numbers, ϵ is the kinetic energy of the colliding electron, and $\vec{k}$ and $\vec{\lambda}$ are the wave vector and polarization of the emitted photon. γ and b stand for all other quantum numbers uniquely specifying the initial and final states. In the approximation where the transition amplitude to only one set of final states (b,J_f) is appreciable, we finally find, with the procedure of Davies and Seaton[13] for the transition probability $W_R(\gamma J\epsilon \rightarrow bJ_f)$ integrated over the wave vector of the emitted photon and summed over its polarizations as

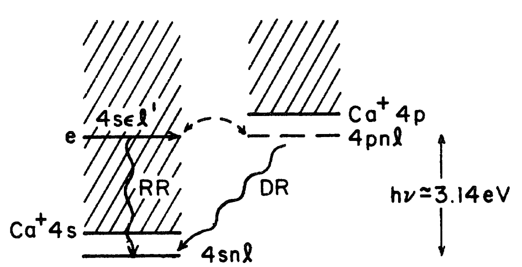

FIG. 1. Electron-ion recombination, illustrated in the Ca atom. Two alternative pathways for radiating a photon of energy $\simeq 3.4$ eV are shown. These are termed radiative (RR) and dielectronic (DR) recombination, the latter involving an intermediate doubly excited state. The dotted arrow represents the electron-electron interaction between the $4s\epsilon l'$ continuum and the (closed) $4pnl$ channel.

well as the magnetic quantum numbers M_f of the final states,

$$W_R(\gamma J\epsilon \rightarrow bJ_f) = \frac{\Gamma(\epsilon)}{|1+Z(\epsilon)|^2} \quad . \tag{2a}$$

Here, we have defined

$$\Gamma(\epsilon) = 2\pi\hbar |\langle \gamma J\epsilon || r || bJ_f\rangle|^2 \frac{4\omega^3\alpha}{(2J+1)3c^2}\bigg|_{\hbar\omega=\epsilon-\epsilon_b} \tag{2b}$$

as the transition probability in lowest-order perturbation theory from the *structured* $|\gamma J\epsilon\rangle$ continuum (with energy normalized continuum functions) to the final bound state $|bJ_f\rangle$ with energy ϵ_b. $\alpha = e^2/4\pi\epsilon_0\hbar c$ is the fine-structure constant. The expression involving

$$Z(\epsilon) = -\frac{i}{4\pi}\int d\epsilon' \frac{\Gamma(\epsilon')}{\epsilon'-\epsilon-i\eta} \tag{2c}$$

accounts for the higher-order field corrections inherent in the spontaneous decay of the structured continuum.

When the autoionizing resonances are well separated, as in the range of n values we are focusing on (e.g., $4p4d$, $4p5d$, $4p6d$ in Ca), the radial matrix element in Eq. (2b) may be represented by a Beutler-Fano profile,[17] giving rise to the following energy dependence of the lowest-order transition probability

$$\Gamma(\epsilon) = W_{\mathrm{RR}}\frac{(q+\xi)^2}{1+\xi^2} \quad . \tag{3}$$

The radiative recombination probability W_{RR} is defined by an expression like Eq. (2b), in which the structured continuum $|\gamma J\epsilon\rangle$ is replaced by the corresponding *bare* continuum state. The scaled detuning ξ from the energy of the autoionizing state ϵ_A is defined as $\xi = (\epsilon - \epsilon_A)/(\frac{1}{2}\hbar\Gamma_A)$, where Γ_A is the autoionization rate. The Fano-q parameter[17] is related to the spontaneous radiative decay rate of the autoionizing state $|aJ\rangle$

$$\Gamma_R = |\langle aJ || r || bJ_f\rangle|^2 \frac{4\omega^3\alpha}{(2J+1)3c^2}\bigg|_{\hbar\omega=\epsilon_A-\epsilon_b} \tag{4a}$$

by

$$q^2 = \frac{\Gamma_R}{\frac{1}{2}\Gamma_A \frac{1}{2} W_{\mathrm{RR}}} \quad . \tag{4b}$$

With reference to Fig. 1, q is a ratio of the matrix elements involved in connecting the lower state $|bJ_f\rangle$ (or $4snl$) to the closed $|aJ\rangle$ (or $4pnl$) directly and through the alternative route involving the continuum $|\gamma J\epsilon\rangle$ (or $4s\epsilon l'$).

Neglecting the direct radiative recombination ($W_{\mathrm{RR}} \rightarrow 0$) leads to an infinite value of q^2 and corresponds to the case of pure dielectronic recombination. q^2 therefore represents a measure of the relative importance of RR and DR. In Eq. (3), q, Γ_A, and W_{RR} may be assumed energy independent over the energy range of one resonance. Typically, q varies from a small value at low n to very large values for the highest states near the ionization limit.

With $\Gamma(\epsilon)$ as given by Eq. (3), the electron-ion recombination probability in Eq. (2a) can be evaluated as

$$W_R(\gamma J\epsilon \rightarrow bJ_f) = W_{\mathrm{RR}}\frac{(q+\xi)^2}{\psi^2[\xi + (2\Gamma_R/\Gamma_A q\psi)]^2 + (1+\Gamma_R/\Gamma_A)^2} \quad ; \tag{5a}$$

with $\psi = 1 + (\Gamma_R/\Gamma_A q^2)$; an intermediate step in this derivation has

$$1 + Z(\epsilon) = 1 + \left(\frac{\Gamma_R}{\Gamma_A q^2}\right)\frac{(q+\xi)^2}{1+\xi^2} + i\left(\frac{\Gamma_R}{\Gamma_A q^2}\right)\frac{(q^2-1)\xi - 2q}{1+\xi^2} \quad . \tag{5b}$$

Davies and Seaton,[13] in their application of this formalism to DR, have taken $q^2 \rightarrow \infty$ so that they obtain the corresponding limit of Eq. (5a),

$$W_{\rm DR}(\epsilon) = 4\frac{\Gamma_R/\Gamma_A}{\xi^2 + (1+\Gamma_R/\Gamma_A)^2} \quad . \tag{6}$$

This Lorentzian, with total width $\Gamma_R + \Gamma_A$, leads upon integration over $d\epsilon/\Delta\epsilon$ [the separation $\Delta\epsilon$ between resonances is taken to be $>> (1/2)\hbar\Gamma_A$ according to our assumption of well-separated resonances] to the $W_{\rm DR}$ in Eq. (1).

Equation (5a) represents a modified Fano profile. The closed-channel resonance at energy ϵ_A and with width $\hbar\Gamma_A$, is shifted in position by an amount $\hbar\Gamma_R/(q\psi)$ and broadened to $(\Gamma_R + \Gamma_A)/\psi$ as a result of the coupling to the radiation continuum. Precisely, such a profile has been derived in the quantum optics literature for states that can decay by both electron and photon emission.[18] The average recombination probability (Gailitis average[19]) for an isolated resonance can be obtained upon integrating Eq. (5a),

$$\begin{aligned}\langle W\rangle &= \frac{1}{\Delta\epsilon}\int_{-\Delta\epsilon/2}^{\Delta\epsilon/2} W_R(\gamma J\epsilon \rightarrow bJ_f)d\epsilon \\ &= 4\frac{\Gamma_R}{\Gamma_A q^2\psi^2} + 2\pi\frac{\hbar\Gamma_A}{\Delta\epsilon}\frac{\Gamma_R}{\Gamma_R+\Gamma_A} \\ &\quad \times \frac{1}{\psi}\left(1 - \frac{[1+(\Gamma_R/\Gamma_A)]^2 + 4(\Gamma_R/\Gamma_A)}{q^2\psi^2}\right) \quad . \end{aligned}\tag{7}$$

This is the central result of our paper, giving the averaged electron-ion recombination probability. The first term in Eq. (7), which is independent of $(\hbar\Gamma_A/\Delta\epsilon)$, is the contribution of the pure electron continuum and is the RR probability $W_{\rm RR}$, as in Eq. (4b). (For typical electron-ion recombination, one has $\psi \simeq 1$.) This term drops out when $q^2 \rightarrow \infty$. The second term in Eq. (7) represents the effect of the closed-channel state. In the limit $q^2 \rightarrow \infty$, this term reduces to the DR contribution $W_{\rm DR}$ in Eq. (1). In between, for finite, nonzero values of q^2, Eq. (7) gives the full contribution to recombination of RR, DR, and "cross terms" between them, representing interferences between the involved amplitudes. When $\hbar\Gamma_A/\Delta\epsilon << 1$ and q^2 is not too large, the first term in Eq. (7) becomes dominant.

Note that Eq. (7) is the mean recombination probability for electrons of energy ϵ to a specific bound state $|bJ_f\rangle$. This is the desired expression for experiments[5,7] in which the radiated photon of energy around $\epsilon - \epsilon_b$ is detected in coincidence with the recombined atom. For other applications in plasma physics, when the total recombination probability of electrons with ϵ to all possible final states without regard to the energy of the emitted photon is of interest, this expression will have to be summed over all these contributions.

We have not made an explicit application in this paper of Eq. (7) to a specific atom. We make a few comments, however, on the e-Ca^+ system. A recent experiment on this recombination so as to yield $\simeq 3.14$ eV photons shows, among other things, a measurable cross section down to low kinetic energies of the electron.[7] At $\epsilon \simeq 2.2$ eV, the cross section is $\simeq 5\times10^{-18}\ {\rm cm}^2$. DR calculations from Eq. (1) essentially give zero in this region of energies.[9,12] We note that the energy 2.2 eV corresponds to the location of the $4p4d\ ^1P$ doubly excited state of Ca (the similar $4p5d$ lies at 2.6 eV and $4p6d$ at 2.8 eV). The contribution of these states, therefore, needs to be taken into account through Eq. (7) to compare with the experimental cross sections in this region of energies. This will require, as major input, the q values for these states from the singly excited $4s4d$-$4s6d$ states of Ca. Such values are not currently available. We note that from photoionization calculations[20] from the ground $4s^2$ state of Ca, we estimate, through detailed balancing,[2] that the RR cross section for $\epsilon \simeq 2.2$ eV is $\simeq \frac{1}{2}\times10^{-21}\ {\rm cm}^2$. Another system in which unexplained large cross sections have been observed at low electron energies is C^{3+}. At energies $\simeq 1.8$–3 eV, the calculated DR cross sections lie much lower than experiment,[6] and it has been pointed out that the RR cross section is of comparable magnitude in this energy region.[9] Clearly, it is the combined expression (7) that should be used to compare with experiment. Note that RR increases with increasing charge of the ion so that the enhancements from Eq. (7) are likely to be more important for recombination in highly stripped ions.

Finally, we note that by focusing on fairly small values of n, we have been able to legitimately use the approximation of isolated resonances. For extension to higher n, the treatment has to be generalized to allow for overlapping resonances ($\hbar\Gamma_A \gtrsim \Delta\epsilon$) and particularly radiation smearing of the resonances when $\hbar\Gamma_R >> \Delta\epsilon$, where $\Delta\epsilon$ is the separation between the $4pnl$ resonances. Such a treatment through multichannel quantum-defect theory has recently been given by Seaton[21] for the case of negligible radiative recombinations ($q^2 \rightarrow \infty$). The final result is to replace Eq. (1) by

$$W_{\rm DR} = \frac{2\pi\Gamma_A}{\Delta\epsilon/\hbar}\frac{\exp(2\pi\hbar\Gamma_R/\Delta\epsilon) - 1}{\exp(2\pi\hbar\Gamma_R/\Delta\epsilon) - 1 + (2\pi\hbar\Gamma_A/\Delta\epsilon)} \tag{8}$$

for the energy averaged DR probability. Γ_A is thereby a generalized autoionization rate allowing also for effects due to strongly overlapping resonances. Extension of this result, by retaining a finite value for q as in this paper instead of taking the $q^2 \rightarrow \infty$ limit, should provide the full treatment of electron-ion recombination, valid also for overlapping resonances.

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*1983–1984 JILA Visiting Fellow. Permanent address: Department of Physics and Astronomy, Louisiana State University, Baton Rouge, Louisiana 70803.

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