# Contribution of Near Threshold States to Recombination in Plasmas

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Resonance states in atoms or ions at low energies can control the rates of important plasma processes (e.g., dielectronic recombination). We examine the role of states at negative energies just below the ionization threshold of the recombined system and find that they can contribute as much, or more, to recombination as positive energy states. In plasmas, negative energy states can be populated by three body recombination, photorecombination, or continuum lowering. Properly including these negative energy states in a theoretical treatment of plasma processes can change the thermally averaged rate coefficients and, in some cases, removes much of the sensitivity to the energy of a state.

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Low energy resonance states of atoms or ions play an important role in the total recombination rate in low temperature plasmas. In photorecombination (dielectronic plus radiative recombination), the rate is strongly enhanced at resonances because the electron spends more time near the positive ion. Low energy resonances can dominate the rate coefficient in a cold plasma because these are the only resonances that cold electrons can be captured into [1–3]. Such resonances are important in many astrophysical [4] and terrestrial situations; some astrophysical examples include x-ray photoionized active galactic nuclei [5] or planetary nebulae [6]. Low energy resonances have been observed in atomic scattering experiments. Schmidt *et al.* [7] measured total recombination rate coefficients for K-like and Ar-like Fe to be orders of magnitude larger than commonly used archived data [8], with the differences being due to resonances just above the ionization threshold of the recombined system. Fogle *et al.* [9] found that the recombination rate coefficient of $O^{4+}$ at low temperatures was dominated by a single resonance 60 meV above threshold. Schippers *et al.* experimentally found sensitivity to low energy resonances in $Mg^{8+}$ [10]. Reference [11] summarizes the experimental status of recombination for astrophysical applications.

Several atomic experimental papers have commented on the sensitivity of low temperature rate coefficients to the position of near threshold states and the problems they pose for computed rates. The sensitivity can be illustrated by considering a 0.5 eV plasma. Shifting a resonance with a 0.01 eV width from 0.05 to 0.15 eV will not drastically affect the recombination rate from this state because the population of electrons at the higher energy is only decreased by $\sim$18%. However, shifting the resonance down by 0.1 to $-0.05$ eV (i.e., 0.05 eV *below* threshold) completely removes it from participating in the dielectronic recombination (DR) process. Figure 1 shows a physical situation that demonstrates this problem; the DR of this system and the sensitivity at low temperature was emphasized in Ref. [10]. The computed positions of the $Mg^{7+}$ $1s^2 2s2p(^3P)7p$ and $7d$ states near the $Mg^{8+}$ threshold are shown.

Within the context of atomic experiments, positive energy states can contribute strongly to DR but negative energy states do not contribute at all. However, within the context of plasmas, this distinction is not sharp. Free electrons in an atomic experiment only populate positive energy states because the electron densities are low and the interaction times are short. The negative energy, Rydberg population is generated through the interplay of three-body recombination, electron-Rydberg collisions, and electron impact ionization which are relatively slow processes for storage rings. This is not true for astrophysical plasmas or some laboratory plasmas which have sufficient time to

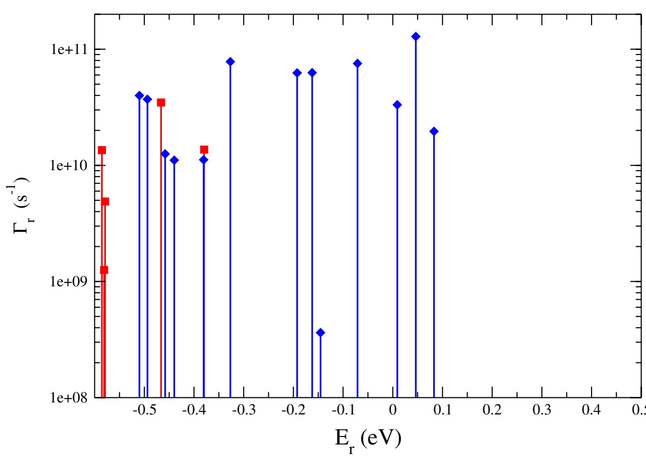


FIG. 1 (color online). The temperature-independent contribution of the $Mg^{7+}$ states to the DR rate coefficient, $\Gamma_r \equiv (2J_r + 1)/[2(2J_c + 1)][\Gamma_R \Gamma_A/(\Gamma_R + \Gamma_A)]$, as a function of energy, $E_r$, relative to the ionization threshold. The energies were obtained from the AUTOSTRUCTURE program shifting the core energies to the NIST values. The squares show the resonances belonging to the $2s2p(^3P)7p$ configuration and the diamonds show the resonances belonging to the $2s2p(^3P)7d$ configuration. Resonances belonging to the $2s2p(^3P)7\ell$ configuration with $\ell \geq 3$ are also in this energy range but have a negligible strength.

 

establish equilibrium between the positive and negative energy states. Figure 2 shows the population of states as a function of energy for $Mg^{7+}$ in a 2.8 eV electron plasma with densities of $10^4$, $10^6$, and $10^8$ $cm^{-3}$. Reference [10] identified the temperature range of a photoionized plasma relevant for this ion to be between 2–13 eV.[12,13] Thus, the clear difference between positive and negative energy states in atomic experiments is not present in plasmas: we have found and show below that a compact state [14] just below threshold can contribute as much, or more, to the recombination rate as a state just above threshold. This conclusion only depends on the distribution of negative energy electrons and does not depend on how the negative energy Rydberg states are populated, assuming external fields or collisions with electrons and ions continually remix the $n\ell$ of the Rydberg states.

To our knowledge, all of the modeling codes that simulate atomic processes in plasmas exclude the non-Rydberg states that are just below threshold, like those shown in Fig. 1. Plasma modeling programs typically include radiative recombination (a direct recombination process) from continuum states, DR from positive energy resonances, and spontaneous decay from bound states. These programs also typically include collisional and radiative processes that redistribute the population amongst different tightly bound levels and between deeply bound states and Rydberg states. However, there is a class of doubly excited states that are compact but just below threshold that are being excluded from modeling of DR *in plasmas*. For example, astrophysical programs that model the fractional abundance of $Mg^{7+}$ will include the $2s2pn\ell$ deeply bound states and the positive energy $2s2p7\ell$ states but do not include the negative energy $2s2p7\ell$ states shown in Fig. 1.

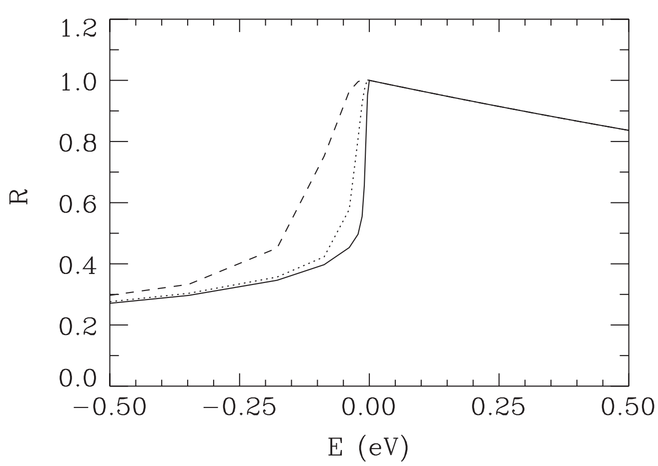


FIG. 2. The $Mg^{7+}$ relative population $R = \exp(-E/T)\zeta(E)$ for negative energy and, $R = \exp(-E/T)$ at positive energy for an electron temperature of 2.8 eV. The solid line is for a density of $10^4$ $cm^{-3}$, the dashed line is for $10^6$ $cm^{-3}$, and the dot-dashed line is for $10^8$ $cm^{-3}$. The population smoothly extends to negative energy, but has an initial decrease at negative energy which becomes sharper with decreasing density. The $1s^2 2s^2 n\ell$ Rydberg populations were calculated using the ADAS204 code [17]. In this calculation, the DR rate coefficients were taken from Ref. [19] and the rest of the radiative and collisional rates were taken from semiclassical expressions.

Depending on the plasma density and temperature, there are different paths for the $Mg^{8+}$ ion to *temporarily* capture an electron into a high Rydberg state. Figure 2 shows the electron energy population attached to $Mg^{7+}$ ions in different density plasmas. One way to think of this figure is that an electron's energy in the plasma is not constant. Collisions cause the energy to vary with a thermal distribution; the negative energy population is a natural extension of the positive energy Maxwell-Boltmann distribution. If the electron is in a Rydberg state with the right energy and angular momentum, it can mix through configuration interaction (CI) with a compact doubly excited state of $A^{q-1}$. These states typically have much larger radiative decay rates than the Rydberg states. For example, using the data of Fig. 1, Rydberg states of $Mg^{7+}$ with $n \sim 76$ will CI mix with the states at $-0.15$ eV; because the compact state radiates more strongly than the Rydberg state, the mixing allows the Rydberg state to radiate much more quickly to the ground state. Thus, the presence of the compact negative energy state greatly increases the radiative decay rate of Rydberg states which stabilizes $q - 1$ ions that otherwise would have later been reionized by a collision.

We will first examine the case where the compact doubly excited state is mixed with Rydberg states of several $n$ manifolds and does not strongly perturb the population; this sample case allows for a simple connection between the treatment of positive and negative energy states. We use atomic units except where explicitly stated otherwise. When a single state is embedded in a continuum or Rydberg series, Eq. (84) of Ref. [15] showed that the short range $S$ matrix has the property

$$1 - |S_{11}(E)|^2 = \frac{\Gamma_R \Gamma_A}{(E - E_r)^2 + [(\Gamma_R + \Gamma_A)/2]^2} \qquad (1)$$

where $E_r$ is the energy of the compact state (which can be positive or negative), $\Gamma_R$ is the radiative decay rate of the state and $\Gamma_A$ is related to the CI coupling between the state and the channel (it is the autoionization rate when $E_r > 0$ and is related to the number of Rydberg states perturbed by the state when $E_r < 0$). The nonunitarity of the $S$ matrix is a result of treating the photon emission as a loss channel. The important point is that this form does not depend on whether $E_r$ is positive or negative.

If the resonance is at positive energy, the nonunitarity of the $S$ matrix can be used to obtain the energy averaged collision rate coefficient for this resonance from a thermal distribution

$$\langle v\sigma \rangle = \left(\frac{2\pi}{T}\right)^{3/2} \frac{2J_r + 1}{2(2J_c + 1)} \frac{\Gamma_R \Gamma_A}{\Gamma_R + \Gamma_A} e^{-E_r/T} \qquad (2)$$

where $T$ is the temperature ($T \gg \Gamma_R + \Gamma_A$), $J_r$ is the angular momentum of the resonance, and $J_c$ is the angular momentum of the core; compare to Eq. (15) of Ref. [16]. If the resonance is at negative energy, the probability to be in an $n$ manifold with total angular momentum $J_r$ and core electron(s) with angular momentum $J_c$ is

$$P(n, J_r) = \left(\frac{2\pi}{T}\right)^{3/2} \frac{2J_r + 1}{2(2J_c + 1)} \exp(-E_n/T)\zeta(E_n) \quad (3)$$

where $E_n = -Z^2/(2n^2)$ is the energy of the $n$ manifold and $\zeta(E_n)$ is the Saha-Boltzman deviation factor [17] which is the ratio of the actual electron distribution to a purely thermal distribution. The function $\zeta(E_n)$ depends on the plasma temperature and density. To get the photon emission rate coefficient at negative energy, we use the fact that Eq. (1) is the probability that a photon is emitted during one interaction with the core and the fact that the bound electron returns to the core once during every Rydberg period $\tau = 2\pi/(\Delta E/\Delta n)$ with the change in energy given by $\Delta E/\Delta n = E_{n+1/2} - E_{n-1/2}$. Thus, the photon emission rate coefficient from the negative energy states is

$$\langle v\sigma \rangle = \sum_n \frac{\Delta E/\Delta n}{2\pi}[1 - |S_{11}(E_n)|^2]P(n, J_r) \quad (4)$$

which can be thought of as the extra contribution to the recombination rate coefficient due to the state perturbing the Rydberg series. This equation can be derived more formally using Eqs. (84–86) of Ref. [15] and has an error inversely proportional to $n$. When the energy width of the perturbation extends over several $n$ manifolds, the sum over $n$ can be simplified by converting to an integral over energy

$$\langle v\sigma \rangle \simeq \left(\frac{2\pi}{T}\right)^{3/2} \frac{2J_r + 1}{2(2J_c + 1)} \frac{\Gamma_R \Gamma_A}{\Gamma_R + \Gamma_a} e^{-E_r/T} \zeta(E_n) \quad (5)$$

which is the same expression as that for when $E_r > 0$ except for the factor of $\zeta(E_n)$.

The treatment of the previous paragraph shows that the photorecombination rate coefficient is a continuous function of the energy of the state, even at threshold. Thus, the current theoretical and conceptual treatment of threshold resonances can be substantially flawed when applied to plasmas. To take the example from the second paragraph, moving a resonance to below threshold does *not* remove this state from participating in DR, and, in fact, the radiative rate coefficient from the state might be greater just below threshold. An important side benefit is that the extreme sensitivity of the calculated rate coefficient to the energy position of the resonance is reduced; now the size of the error to the DR rate coefficient comes from the change in the energy distribution with energy and density.

We have applied this simple formulation to the states in Fig. 1 using the populations shown in Fig. 2. The results are shown in Fig. 3. We performed the atomic calculation using the AUTOSTRUCTURE code[16] with the thresholds attached to the $2s2p$ and $2p^2$ cores shifted to the NIST energies. The lines show the contribution only from positive energies. The solid line is from the experiment of Ref. [10]. The dashed line is from the AUTOSTRUCTURE calculation. If we artificially moved all of the resonances between 0 and 70 meV down in energy by 90 meV to just below threshold, we obtain the dash-dotted line which is a substantially reduced DR rate coefficient for low temperatures because the resonances that have been shifted to negative energies no longer count for DR in the usual calculation of DR rates. At a temperature of 1 eV there is a factor of ~4 suppression of the rate and at 2.8 eV there is a factor of ~2 suppression. Note the sensitivity of the calculation: a shift in resonance energy of 2.5% of the thermal energy gave a factor of 2 change in the DR rate. Another important feature is that the realistic calculation does not match the experimental rate at low temperatures. At 2 eV, the experimental rate is a factor of ~2.5 smaller than our calculation. This illustrates how difficult it is to reproduce the experimental rate coefficient when there are near threshold resonances.

The main result on Fig. 3 are the symbols at temperatures of 2.8 and 5 eV which show the recombination when the negative energy states are included. The symbols are for plasmas with a density of either $10^4$ or $10^8$ cm$^{-3}$ and for the calculation with the states at the correct energies

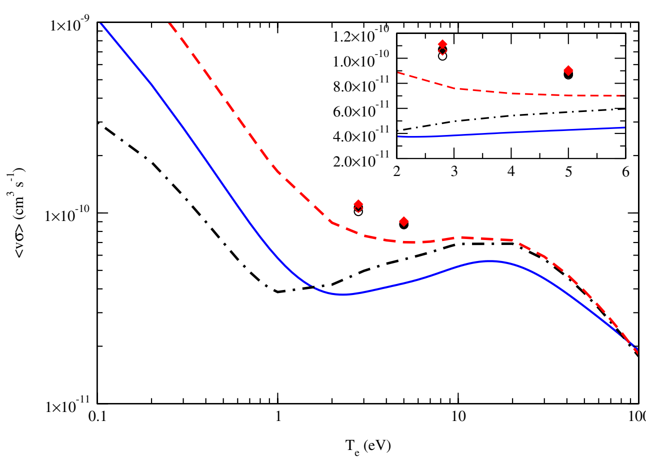


FIG. 3 (color online). The radiative recombination rate coefficient as a function of the electron temperature. The lines only use positive energy states: the solid (blue) line is from experiment [10], the dashed (red) line is from the AUTOSTRUCTURE calculation described in the text, the dash-dotted (black) line is when the positive energy states below 70 meV are shifted to just below threshold. The symbols include the negative energy states. Open symbols are for a density of $10^4$ cm$^{-3}$ and closed symbols are for $10^8$ cm$^{-3}$. The diamonds are for the correct AUTOSTRUCTURE calculation and the circles are when the positive energy states below 70 meV are shifted to just below threshold. Because the data for negative energy states varies little, some of the symbols are not clearly visible.

(diamonds) or with the resonances between 0 and 70 meV shifted below threshold (circles). This figure demonstrates the effect on the recombination rate coefficient when the negative energy states of Fig. 1 are included. There are two important features. The first is that the magnitude of the DR rate has increased by a factor of $\sim 2$ at 2.8 eV and a factor of $\sim 1.6$ at 5.0 eV compared to the calculation using only the positive energy states that more nearly matches the experiment (black dash-dotted line). This demonstrates that the negative states can strongly affect the recombination rate in a plasma. The second important feature is that the calculation with the correct energies and with shifted energies gave very similar rates when the negative energy states were included; this is in contrast with the calculation that only used positive energy states which showed extreme sensitivity to the energies of the states. This figure shows that the atomic experiments which only probe positive energies can miss a substantial part of the recombination rate coefficient in plasmas for some cases.

The effect of weakly bound states on recombination has already been seen although the *general* importance of the observation was not noted. In Ref. [18], a measurement and calculation of fluorescence in a neutral, ultracold plasma consisting of cold electrons and $Ca^+$ ions found anomalous dependence of the fluorescence on the density; the temperature of the plasma was tens of K and the density was in the range of $10^8$–$10^9$ $cm^{-3}$. The explanation given in Ref. [18] was that the bound, compact $3d^2$ and $3d5s$ states that perturb the $4snd$ Rydberg series were strongly contributing to the fluorescence for some of the plasma parameters.

A final point is that this idea presents a novel challenge for atomic experiments. In recent years, several papers have presented experimental results that have been suggested to be the benchmark for DR (for example, Ref. [11]). However, these experiments do not include the resonances just below threshold so that in some situations the results are not complete. New developments in atomic experiments should be pursued to explore the role of these states. It is also a challenge to plasma modelers to include this new mechanism and investigate its full importance.

In summary, we have found that some negative energy states, often neglected in the simulation of ion evolution in plasmas, can have a strong effect on photorecombination rate coefficients. We presented a simplified theoretical treatment that shows that the sensitivity to computational errors can be strongly reduced by including these states. Also, we have given a compact expression for how a resonance state can be included in plasma diagnostic programs. It should be possible to include the effect of these states through minor modifications of current plasma simulation programs. A general theory for incorporating the interaction between states from different Rydberg series seems to be more difficult but might not be important in practice. The role of near threshold negative energy states is not limited to dielectronic recombination and might be important in other processes that occur in low temperature plasmas.

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[1] H. Nussbaumer and P. J. Storey, Astron. Astrophys. **99**, 177 (1981).
[2] N. R. Badnell, J. Phys. B **21**, 749 (1988).
[3] D. W. Savin *et al.*, Astrophys. J. Lett. **489**, L115 (1997).
[4] D. E. Osterbrock and G. J. Ferland, *Astrophysics of Gaseous Nebulae and Active Galactic Nuclei* (University Science Books, Sausalito, CA, 2005).
[5] M. Sako *et al.*, Astron. Astrophys. **365**, L168 (2001).
[6] L. H. Allen and C. D. Keyes, Astrophys. J. **65**, 405 (1987).
[7] E. W. Schmidt *et al.*, Astron. Astrophys. **492**, 265 (2008).
[8] M. Arnaud and J. Raymond, Astrophys. J. **398**, 394 (1992).
[9] M. Fogle *et al.*, Astron. Astrophys. **442**, 757 (2005).
[10] S. Schippers *et al.*, Astron. Astrophys. **421**, 1185 (2004).
[11] S. Schippers, J. Phys. Conf. Ser. **163**, 012001 (2009).
[12] T. Kallman and M. Bautista, Astrophys. J. Suppl. Ser. **133**, 221 (2001).
[13] C. B. Tarter *et al.*, Astrophys. J. **156**, 943 (1969).
[14] By "compact state," we mean a state with a much smaller spatial extent than the Rydberg series that it perturbs [e.g., $2s2p(^3P)7d$ is compact compared to the $2s^2(^1S)66f$ state at nearly the same total energy].
[15] F. Robicheaux *et al.*, Phys. Rev. A **52**, 1319 (1995).
[16] N. R. Badnell *et al.*, J. Phys. B **19**, 3827 (1986).
[17] H. P. Summers *et al.*, Plasma Phys. Controlled Fusion, **48**, 263 (2006).
[18] S. D. Bergeson and F. Robicheaux, Phys. Rev. Lett. **101**, 073202 (2008).
[19] J. Colgan *et al.*, Astron. Astrophys. **412**, 597 (2003).