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Collective mechanism for atomic recombination in plasmas

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A new mechanism is proposed for atomic recombination in plasmas, whereby the binding energy is carried away by a plasmon. It is suggested that this mechanism may compete with radiative and three-body modes in the case of recombination to sufficiently highly excited and perturbed states of hydrogen. A procedure for calculation of the transition rate is outlined in a model which treats the plasma oscillations by the Bohm-Pines canonical transformation and the atomic bound states by a second canonical transformation.

Two fundamental quantities in a classical plasma are the Debye screening length $\lambda_D=(k_BT/8\pi ne^2)^{1/2}$ and the (longitudinal) plasma frequency[1]

$$\omega_q \approx \omega_p(1+\tfrac{3}{2}\lambda_D^2 q^2), \quad \lambda_D q < 1 \tag{1}$$

where $\omega_p=(4\pi ne^2/m)^{1/2}$. The first term in (1) arises from the long-range correlations between electrons and the second term from their thermal motion. We consider here only the simplest, one-component model; accordingly, e and m are the electron charge and mass, respectively. Quantization gives rise to plasmons, the longitudinal analog of the usual (transverse) photons, with energies approximately $(4\times10^{-11})n^{1/2}$ eV where n, the electron number density, is in cm^{-3}.

In analogy with the case of Cherenkov photon emission, the condition for conservation of energy and momentum in the emission of a real plasmon of momentum $\hbar\mathbf{q}$ and energy $\hbar\omega_q$ by an electron of velocity $\mathbf{v}$ is[2] $\omega_q=\mathbf{q}\cdot\mathbf{v}$. Since there is a maximum plasmon wave vector[1,3] $q_c\sim\lambda_D^{-1}$, there is a critical velocity $v_c\sim\omega_p\lambda_D$ below which real plasmon emission cannot occur. The purpose of this Brief Report is to suggest and analyze briefly a new collective mechanism for atomic recombination in plasmas, whereby the binding energy is carried away by a plasmon rather than a photon or a third particle. A semiclassical picture of the process is shown in Fig. 1. An electron in an unbound (hyperbolic) orbit with respect to the given proton approaches it with a small enough impact parameter that the speed of the electron near perihelion exceeds the critical velocity v_c mentioned above, leading to emission of a real plasmon and capture of the electron into an elliptic orbit.

Consider a hydrogen plasma with $n\sim10^{18}$ cm^{-3} and $k_BT\sim1$ eV; then $\lambda_D\sim100a_0$ (a_0 is the Bohr radius of the unperturbed hydrogen atom) and $\hbar\omega_p\sim4\times10^{-2}$ eV. In zeroth approximation one may determine the perturbed hydrogen levels and wave functions by solution of the Schrödinger equation with the screened (Debye-Hückel) potential. One finds[4,5] that the 8s level has binding energy $\sim4\times10^{-2}$ eV and the 9h level (the highest screened Coulomb bound state for the given value of λ_D) $\sim8\times10^{-3}$ eV. These binding energies are an order of magnitude smaller than those of the unperturbed states, so that plasmon-mediated recombination to these levels is energetically allowed.

A correct calculation of the recombination cross section requires a quantum-mechanical treatment of at least the electrons. We shall use a simplified model consisting of a single, fixed proton at the origin immersed in a medium composed of the electrons and a uniform, immobile positive background which crudely models the other protons ("jellium"). The interactions of the electrons with each other, with the one chosen proton, and with the rigid positive background gives rise to collective plasma modes which are crucial for this mechanism of recombination. The Hamiltonian $\hat{H}$ in the Bohm-Pines representation[3] further transformed into Fock space is

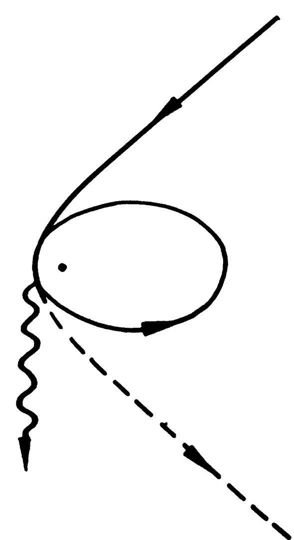

FIG. 1. Semiclassical picture of recombination by plasmon emission. The wavy line denotes the plasmon and the dashed line the "post-collision" hyperbolic orbit which would have been followed had the plasmon not been emitted.

$$\hat{H}=\hat{T}_e+\hat{H}_{\rm pl}+\hat{V}_{e-e}+\hat{V}_{e-p}+\hat{V}_{e-\rm pl}+\hat{V}_{p-\rm pl}+N\Delta\ ,$$

$$\hat{T}=\sum_k(\hbar^2k^2/2m)\hat{e}_k^\dagger\hat{e}_k\ ,$$

$$\hat{H}_{\rm pl}=\sum_{\substack{q\\ q<q_c}}\hbar\omega_q(\hat{c}_q^\dagger\hat{c}_q+\tfrac{1}{2})\ ,$$

$$\hat{V}_{e-e}=\tfrac{1}{2}\Omega^{-1}\sum_{\substack{q\\ q>q_c}}\sum_{kk'}(4\pi e^2/q^2)\hat{e}^\dagger_{k+q}\hat{e}^\dagger_{k'-q}\hat{e}_{k'}\hat{e}_k\ ,$$

$$\hat{V}_{e-p}=-\Omega^{-1}\sum_{\substack{q\\ q>q_c}}\sum_{k}(4\pi e^2/q^2)\hat{e}^\dagger_{k-q}\hat{e}_k\ , \tag{2}$$

$$\hat{V}_{e-\rm pl}=\Omega^{-1}\sum_{\substack{q,k,k'\\ q<q_c\\ k'>q_c}}\left[\frac{4\pi e^2}{(k')^2}\right]\left[\frac{2\pi e^2\hbar\omega_q}{\Omega}\right]^{1/2}(\hbar q)^{-1}\xi_{qkk'}$$

$$\times(\hat{c}_q^\dagger\hat{e}^\dagger_{k+k'-q}\hat{e}_k+\text{H.c.})\ ,$$

$$\hat{V}_{p-\rm pl}=-\sum_{\substack{q\\ q<q_c}}(2\pi e^2\hbar\omega_q/q^2\Omega)^{1/2}(\hat{c}_q^\dagger+\hat{c}_q)\ ,$$

$$\Delta=-\sum_{\substack{q\\ q<q_c}}(2\pi e^2/q^2\Omega)=-\pi^{-1}e^2q_c\ .$$

Here $\hat{e}_k$ and $\hat{e}_k^\dagger$ annihilate and create electrons with momentum $\hbar\mathbf{k}$, $\hat{c}_q$ and $\hat{c}_q^\dagger$ annihilate and create plasmons with momentum $\hbar\mathbf{q}$ and energy $\hbar\omega_q$, q_c is a wave-vector cutoff $\sim\lambda_D^{-1}$, Ω is the volume of the system (periodic boundary conditions), $N=n\Omega$ is the number of electrons, and

$$\xi_{qkk'}=(\omega_q-\hbar\mathbf{q}\cdot\mathbf{k}/m)^{-1}-[\omega_q-(\hbar/m)\mathbf{q}\cdot(\mathbf{k}+\mathbf{k}')]^{-1}\ . \tag{3}$$

In (3) we have neglected terms of order q^2 for $q<q_c$; these represent pure quantum effects and are very small (less than 1% of ω_q for $n\sim10^{18}$ and $k_BT\sim1$ eV). In (2) $\hat{T}_e$ represents the free electron kinetic energy, $\hat{H}_{\rm pl}$ the free plasmons, $\hat{V}_{e-e}$ a screened electron-electron interaction, $\hat{V}_{e-p}$ the corresponding screened electron-proton interaction, $\hat{V}_{e-\rm pl}$ the electron-plasmon interaction representing emission and absorption of single plasmons by electrons in the field of the proton, $\hat{V}_{p-\rm pl}$ the absorption and emission of virtual plasmons by the proton, and Δ a constant negative-energy shift which results from the long-range correlations between the electrons.[6]

A few remarks are in order: (a) If we had considered a proton at $\mathbf{r}_0$ with velocity $v_0>v_c$, then $\hat{V}_{p-\rm pl}$, containing a factor $\exp(-i\mathbf{q}\cdot\mathbf{r}_0)$, would describe Cherenkov-like emission of real plasmons by the fast proton. (In fact, this was the original motivation of Pines[3].) In the present case the proton is at rest and the proton emits and absorbs only virtual plasmons, which will be found to give a negative-energy shift. (b) In the original work of Pines[3] $\hat{V}_{e-\rm pl}$ was neglected compared to the leading term giving real plasmon emission by the proton. In the present case, since $\hat{V}_{p-\rm pl}$ gives only a constant energy shift, $\hat{V}_{e-\rm pl}$ is the leading term for the dynamics of real plasmon emission by *electrons* in the field of the proton. (c) In coordinate space $\hat{V}_{e-p}$ can be represented to a good approximation[3,7] by the potential

$$-\sum_i(e^2/r_i)e^{-q_cr_i}\ , \tag{4}$$

where r_i is the distance between the proton and the ith electron. (d) The derivation of (2) and (3) is rather lengthy and is given in the Bohm-Pines papers and a forthcoming paper on the details of the plasmonic recombination mechanism.

The demonstration that $\hat{V}_{p-\rm pl}$ gives rise to a negative-energy shift proceeds as in other Bose quasiparticle theories by carrying out a canonical transformation to cancel the terms $\hat{V}_{p-\rm pl}$ linear in plasmon operators $\hat{c}_q$ and $\hat{c}_q^\dagger$. The required (unitary) transformation is

$$\hat{S}^{-1}\hat{c}_q\hat{S}=\hat{c}_q+(2\pi e^2/\Omega q^2\hbar\omega_q)^{1/2}\ ,$$

$$\hat{S}^{-1}\hat{c}_q^\dagger\hat{S}=(\hat{S}^{-1}\hat{c}_q\hat{S})^\dagger \tag{5}$$

and leads to a negative shift Δ identical with (2)

$$\hat{S}^{-1}(\hat{H}_{\rm pl}+\hat{V}_{p-\rm pl})\hat{S}=\hat{H}_{\rm pl}+\Delta\ . \tag{6}$$

As in similar fixed-source theories, this shift is interpreted as the energy of virtual zero-point plasmons absorbed and emitted by the proton. The only other term in the Hamiltonian (2) affected by the transformation (5) is the term $\hat{V}_{e-\rm pl}$ which is transformed into $\hat{V}_{e-\rm pl}+\hat{V}'_{e-p}$, where

$$\hat{V}'_{e-p}=\Omega^{-2}(2\hbar)^{-1}\sum_{\substack{q,k,k'\\ q<q_c k'>q_c}}\left[\frac{4\pi e^2}{q^2}\right]\left[\frac{4\pi e^2}{(k')^2}\right](\xi_{qkk'}+\xi_{-q,k+k'-q,-k'})\hat{e}^\dagger_{k+k'-q}\hat{e}_k\ , \tag{7}$$

which can be regarded as a dynamical correction to the static screened Coulomb proton-electron interaction $\hat{V}_{e-p}$. Inserting the explicit expression (3), one sees that the summand tends to cancel between regions with opposite alignments of the relevant vectors, whereas $(4\pi e^2/q^2)$ in $\hat{V}_{e-p}$ is isotropic. It is therefore within the spirit of the random-phase-approximation to neglect $\hat{V}'_{e-p}$ compared to $\hat{V}_{e-p}$, and we shall do so here. Indeed, if one neglects $\mathbf{q}$ compared to $\mathbf{k}'$ (since $q<q_c, k'>q_c$) and neglects $(\hbar q^2/2m)$ compared to ω_q as was done in (3), then for fixed $\mathbf{k}$ and $\mathbf{k}'$ the summand is an odd function of $\mathbf{q}$, so that $\hat{V}'_{e-p}$ vanishes in this approximation.

At this point it is interesting to compare our result with the Ecker-Weizel (EW) potential[8,9]

$$V_{\mathrm{EW}}(r)=-e^2[(1/r)e^{-r/\lambda_D}+(1/\lambda_D)] \tag{8}$$

between electrons and protons in a plasma, which has been used to interpret the plasma shifts of the discrete and continuous spectra of hydrogen. If we use the Debye-Hückel potential for the screened interaction $\hat{V}_{e-p}$ in coordinate space and add the negative shift 2Δ [one Δ from the proton energy shift, Eq. (6), and another Δ from the energy shift of each electron, Eqs. (1) and (2)], then we obtain an effective potential

$$V_{\mathrm{eff}}(r)=-e^2[(1/r)e^{-r/\lambda_D}+(0.7/\lambda_D)] , \tag{9}$$

which is very similar to (8).

Another change of representation is useful for extracting from $\hat{V}_{e-\mathrm{pl}}$ the term representing free-bound electron transitions with plasmon emission. The required canonical transformation in the simplest case where the bound state is a single-particle state (the proton being treated here as a fixed force center) is effected by a unitary operator $\hat{U}$ given by[10,11]

$$\hat{U}=\exp\left[\frac{\pi}{2}\hat{F}\right], \quad \hat{F}=\sum_\nu (\hat{A}_\nu^\dagger \hat{a}_\nu-\hat{a}_\nu^\dagger \hat{A}_\nu) , \tag{10}$$

where $\hat{A}_\nu$ and $\hat{A}_\nu^\dagger$ are the (Fermi) annihilation and creation operators for electrons bound in (here perturbed) hydrogen orbitals centered on the proton at the origin:

$$\hat{A}_\nu^\dagger=\sum_k \tilde{\phi}_\nu(k)\hat{e}_k^\dagger, \quad \hat{A}_\nu=(\hat{A}_\nu^\dagger)^\dagger . \tag{11}$$

The index ν stands for (nlm) (and the spin z-component s, which will be suppressed here); $\tilde{\phi}_\nu$ is the (perturbed) hydrogen momentum wave function, the Fourier transform of the perturbed spatial wave function $\phi_\nu(x)$. The new bound-state Fermi annihilation and creation operators $\hat{a}_\nu$ and $\hat{a}_\nu^\dagger$ introduced by this transformation anticommute with the original (plane-wave) electron operators $\hat{e}_k$ and $\hat{e}_k^\dagger$ (although the $\hat{e}_k$ and $\hat{A}_\nu^\dagger$ do *not* anticommute) and they commute with the plasmon operators $\hat{c}_q$, and $\hat{c}_q^\dagger$. The canonical transformation effected by (10) is

$$\hat{U}^{-1}\hat{e}_k\hat{U}=\hat{e}_k-\sum_{k,k'}\Delta_{kk'}\hat{e}_{k'}+\sum_\nu \tilde{\phi}_\nu(k)\hat{a}_\nu , \tag{12}$$

where $\Delta_{kk'}$ is the bound-state kernel

$$\Delta_{kk'}=\sum_\nu \tilde{\phi}_\nu(k)\tilde{\phi}_\nu^*(k') . \tag{13}$$

Insertion of (12) into $\hat{V}_{e-\mathrm{pl}}$, Eq. (2), yields several terms; the one describing the plasmonic recombination and the inverse ionization process is

$$\hat{V}(\text{electron} \rightleftharpoons \text{atom}+\text{plasmon})=\sum_{\substack{k,q,\nu\\ q<q_c}}(\hat{c}_q^\dagger \hat{a}_\nu^\dagger (q\nu\,|\,V\,|\,k)\hat{e}_k+\text{H.c.}) , \tag{14}$$

with

$$(q\nu\,|\,V\,|\,k)=\Omega^{-3/2}\left[\frac{2\pi e^2\hbar\omega_q}{q^2}\right]^{1/2}\sum_{\substack{k'\\ k'>q_c}}\left[\frac{4\pi e^2}{(k')^2}\right]\left[\tilde{\phi}_\nu^*(k+k'-q)\xi_{qkk'}-\sum_{k''}\tilde{\phi}_\nu^*(k''+k'-q)\xi_{qk''k'}\Delta_{k''k}\right] . \tag{15}$$

The effect of the subtraction term involving $\Delta_{k''k}$ is to orthogonalize the k dependence of the matrix element to the bound electron subspace. This is physically correct since $\hat{e}_k$ annihilates an unbound electron. An equivalent point of view is to regard $\hat{e}_k$ as the annihilation operator for an orthogonalized plane wave rather than a (Born-approximation) free plane wave.

The physics of the emission in the matrix element (15) is contained in $\xi_{qkk'}$. Interpreting $\mathbf{v}_k=\hbar\mathbf{k}/m$ as the random (classical) velocity of the electrons in the plasma, one sees that the first term in (3) has a singularity at $\omega_q=\mathbf{q}\cdot\mathbf{v}_k$. This is the previously mentioned condition for real plasmon emission. Because of the constraint $q<q_c$ only the few electrons in the high-velocity tail of the Maxwellian distribution will be able to satisfy this condition. For this reason Bohm and Gross[1] neglected the singularity in getting the dispersion relation (1); we continue using this approximation here. Things are different for the second term in (3), where the singularity occurs at

$$\omega_q=\mathbf{q}\cdot[\mathbf{v}_k+(\hbar\mathbf{k}'/m)] . \tag{16}$$

The term $\hbar\mathbf{k}'/m$ represents the increase in velocity of the electrons produced by the short-range ($k' > q_c$) attractive interaction with the proton; it is crucial for the mechanism in which we are interested because now electrons with any velocity in the field of the proton are potentially able to produce real plasmon emission. The reason is that the sum on k' appearing in (15) ensures that for any $\mathbf{v}_k$ there is always a $\mathbf{k}'$ such that (16) is satisfied. This is consistent with the semiclassical picture of Fig. 1, according to which an electron starting with a low velocity $\mathbf{v}_k$ can increase its velocity until it emits a plasmon and becomes bound to the proton.

In zeroth approximation the wave functions $\tilde{\phi}_\nu(k)$ in (15) can be taken to be the eigenstates of the screened Coulomb potential satisfying

$$(\hbar^2 k^2/2m)\tilde{\phi}_\nu(\mathbf{k}) - \Omega^{-1} \sum_{\substack{q \\ q > q_c}} (4\pi e^2/q^2)\tilde{\phi}_\nu(\mathbf{k}+\mathbf{q}) = \varepsilon_\nu \tilde{\phi}_\nu(\mathbf{k}) . \quad (17)$$

With the above choice one neglects the imaginary part of the atomic self-energy, i.e., the finite lifetime of the perturbed atomic state. In particular, the simplified model considered herein neglects the Stark broadening due to the other positive ions[12] since they are treated as a uniform background. The Stark broadening due to the electrons is, in principle, included if one uses the appropriate generalized Schrödinger equation[13] and this broadening is expected to be comparable[12] to that due to the positive ions at the densities and temperatures considered herein ($n \sim 10^{18}$ cm^{-3}, $k_B T \sim 1$ eV). We intend to generalize the treatment to a two-component plasma (both protons and electrons treated dynamically) in subsequent work.

The leading approximation to the transition rate for plasmon-mediated recombination is

$$W(q\nu \mid k) = (2\pi/\hbar^2) \mid (q\nu \mid T \mid k) \mid^2 \times \langle \hat{N}_k (1+\hat{N}_q)(1-\hat{N}_\nu) \rangle \delta(\varepsilon_{fi}) , \quad (18)$$

where

$$\begin{aligned} \varepsilon_{fi} &= \hbar\omega_q + \varepsilon_\nu - (\hbar^2 k^2/2m) , \\ \hat{N}_k &= \hat{e}_k^\dagger \hat{e}_k , \\ \hat{N}_q &= \hat{c}_q^\dagger \hat{c}_q , \\ \hat{N}_\nu &= \hat{a}_\nu^\dagger a_\nu . \end{aligned} \quad (19)$$

The expression (18) is the product of the standard expression for the transition rate of a reaction in vacuum by a statistical factor $\langle \cdots \rangle$ expressing the effects of occupancy of the initial and final states. In thermal equilibrium

$$\langle \cdots \rangle \approx \langle \hat{N}_k \rangle (1 + \langle \hat{N}_q \rangle)(1 - \langle \hat{N}_\nu \rangle) . \quad (20)$$

This is the standard statistical factor for a transition in a medium. Since the model only allows formation of a single atom (only one proton at the origin, all others a "smeared background") and $\langle \hat{N}_\nu \rangle$ is the mean occupation of level ν before formation of an atom in this state, we may take $\langle \hat{N}_\nu \rangle = 0$ and replace the Fermi blocking factor $(1 - \langle \hat{N}_\nu \rangle)$ by unity. The mean number $\langle \hat{N}_q \rangle$ of plasmons at each given q is also $\ll 1$ in the density-temperature regime under consideration (nondegenerate plasmon gas). Then (18) reduces to

$$W(q\nu \mid k) \approx (2\pi/\hbar) \mid (q\nu \mid T \mid k) \mid^2 f_k \delta(\varepsilon_{fi}) , \quad (21)$$

where f_k is the electron distribution function $\langle \hat{N}_k \rangle$ of the plasma, nearly Maxwellian in the given regime. In leading order the T matrix $(q\nu \mid T \mid k)$ reduces to the Hamiltonian matrix element $(q\nu \mid V \mid k)$ for the given reaction. Although this has the appearance of a Born approximation, it is expected to be much better than the usual "bare Born" approximation. In the first place, the atomic wave function is the screened Coulomb one, which takes into account in zeroth order the strong perturbation due to the plasma environment. In the second place, the matrix element (15) includes the orthogonalization correction which is neglected in the usual Born approximation. A similar orthogonalization term has been proposed previously as a correction to Born-approximation photoionization matrix elements.[14] In the present formulation this term arises naturally as a consequence of the canonical transformation (12).

The numerical evaluation of the plasmonic recombination rate and a comparison with the radiative rate is underway; this, together with a more detailed description of the representations used herein, will be given in a subsequent publication. We also plan to generalize the theory to the more realistic two-component plasma case.

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