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Ionization rate coefficients in warm dense plasmas

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We recast the atomic processes in a warm, dense plasma using Fermi-Dirac statistics and compare them to the rates of the usual Maxwell-Boltzmann approach of many collisional-radiative models. Population calculations show insignificant differences to calculations assuming nondegenerate free electrons of plasmas at solid density close to local thermodynamic equilibrium, but show departures in average ionization in the presence of strong photoionization. For example, we show that electron degeneracy affects the evolution of plasmas created by ultraviolet free electron laser interaction with solid targets.

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I. INTRODUCTION

Calculations of the degree of ionization of high density, low temperature plasmas are important in inertial fusion [1], free electron laser ablation of solids [2], and the modeling of energy flow in astrophysical bodies such as brown dwarf stars [3]. Inertial fusion seeks to isentropically compress deuterium and tritium fuel to achieve fusion using a shell ablator so that plasma material is both dense ($\gg$ solid density) and at a relatively low temperature (<1 keV). Ionization calculations have been undertaken for short wavelength (<50 nm) free electron laser interactions with solid targets where solid density (>1 g cm^{-3}) plasmas with "warm" to hot temperatures ($k_B T\ <1$ eV–1 keV) have been demonstrated [4,5]. Calculations of plasma ionization in such dense plasmas can be significantly simplified if ionization and excitation processes are balanced by recombination and deexcitation with equilibrium populations given, for example, by the Saha equation (for ionization) and Boltzmann ratios (for excited ion populations). The Saha equation can allow for effects such as free electron degeneracy and ionization potential depression important in warm dense plasmas [6,7], but is not valid when a process such as photoionization is not balanced by a recombination process. With unbalanced populating processes, it is necessary to undertake collisional-radiative calculations where all the significant populating and de-populating processes affecting ionic population densities are evaluated.

Collisional-radiative models of plasma ionization [8–11] usually employ collisional excitation, ionization and photoionization rates calculated assuming a Maxwell-Boltzmann distribution of free electrons. Collisional rates average cross sections over a Maxwell-Boltzmann distribution of electron energies, while collisional ionization and photoionization rates are calculated assuming that ionized electrons can occupy any free electron state. Such approaches are approximate and valid only at low electron density and high temperature as they neglect degeneracy effects due to the Pauli exclusion principle which states that a maximum of one electron can occupy a quantum state [12]. A plasma ionization calculation where the degeneracy of free electrons is considered has shown significant degeneracy effects can be expected for experiments using extreme ultraviolet free electron laser irradiation of solid aluminum targets [13,14].

In this article, we consider the effects of free electron degeneracy on the rates of photoionization, collisional excitation, ionization, and three-body recombination in high density, low temperature plasmas. We show that it is necessary to allow for electron degeneracy effects to stop divergent (infinitely large) calculated rates for collisional-radiative processes as electron temperatures drop towards zero. Our work shows how collisional rates (e.g., for carbon [15,16]) can be extended, in principle, to high density, low temperature ionization balance calculations. In particular, we deduce a novel accurate method to allow for three-body effects in degenerate plasmas during collisional ionization and three-body recombination. Significantly, we confirm that electron degeneracy can affect the evolution of plasmas as they are heated, particularly in extreme ultraviolet free electron laser interactions with solid targets.

II. DEGENERATE RATE COEFFICIENTS

The free electrons in a degenerate plasma may be modeled as a Fermi gas, interacting with the spatially confined bound electrons through collisional processes only. The Fermi distribution [17] for the occupation probability of a quantum state is given by

$$F(\epsilon,T_e) = \frac{1}{1+\exp\left(\frac{\epsilon-\mu}{k_B T_e}\right)}, \tag{1}$$

where μ is the chemical potential. This distribution is most familiar in its asymptotic form for $T_e = 0$, where it becomes a step function of energy. Multiplying by the density of states leads to the energy distribution

$$f_{FD}(\epsilon,T_e) = \frac{G}{n_e}\sqrt{\epsilon}F(\epsilon,T_e), \tag{2}$$

where n_e is the electron density and $G = 4\pi(2m_e/h^2)^{3/2}$, where the constants have their usual meanings. The chemical potential is calculated for a Fermi gas as a normalization factor through the relation $\int_0^\infty f_{FD}(\epsilon,T_e)d\epsilon = 1$. At $T_e = 0$, the chemical potential takes the value of the Fermi energy $\mu(0) = E_F = (3n_e/2G)^{2/3}$; beyond this, μ decreases monotonically with T_e. We calculate that μ remains positive and hence the plasma is degenerate when the electron density is high ($n_e \gtrsim 10^{22}$ cm^{-3}) and temperature is low ($k_B T_e < 20$ eV).

For $\mu/k_BT_e \ll -1$, Eq. (2) reduces to the usual Maxwell-Boltzmann distribution.

Using the Fermi-Dirac distribution requires that we take account of the probability that the electrons involved in photoionization and in collisions can occupy a free electron state after the collision, via so-called blocking factors given by

$$\tilde{F}(\epsilon,T_e) = 1 - F(\epsilon,T_e). \tag{3}$$

We show that the additional computation in assuming a Fermi-Dirac distribution is needed for high density, low temperature ionization rate calculations.

The photoionization coefficient is normally independent of plasma conditions, with the exception of modifications of the ionization potential. However, Pauli blocking factors, dependent on both free electron density and temperature, can lower the rate of photoionization [18]: for a photon energy E_γ and ionization potential E_i, photoionized electrons must emerge with an energy of $E_\gamma - E_i$ into an unoccupied quantum state. We model the energy distribution of the photons in a laser beam by a delta function, leading to a departure from the photoionization cross section σ_0^γ due to electron degeneracy compared to an atom in free space, given by $\sigma_{FD}^\gamma = \sigma_0^\gamma \tilde{F}(E_\gamma - E_i,T_e)$, where $\tilde{F}$ are blocking factors. The change in cross section is plotted as a function of temperature for differing photon energies in Fig. 1(a). Likewise, the integrals used to calculate the rates of free-free absorption and emission are modified by a similar factor; after carrying out the integrals, there is no longer a simple relation between inverse rates, unlike in the Maxwell-Boltzmann case where their ratio is given by the black-body spectrum through detailed balance. We have for the free-free absorption coefficient in units of cm^{-1}

$$\kappa_{FD}^{\text{free-free}} = 1.462\times10^{-15}\sum_{i=1}^{Z}\frac{N_i i^2}{E_\gamma^3}\exp(E'_\gamma) \times\left[k_BT_e\ln\left(\frac{\exp(E'_\gamma-\mu')+1}{\exp(2E'_\gamma-\mu')+1}\right)+E_\gamma\right], \tag{4}$$

where E_F is the Fermi energy, energies are measured in eV, and the primed quantities denote division by k_BT_e. Degeneracy effects may lead to an increase in the free-free absorption coefficient compared with the usual Maxwell-Boltzmann expression, if the absorbed photon energy is large compared with the chemical potential, and hence the absorbing electron may freely transition to a higher energy state.

In order to calculate the collisional rates for atomic processes involving one or more of both incoming and outgoing electrons, we use the standard approach [19,20] of integrating over the incoming and outgoing particle energies (here ϵ_0 and ϵ_1) and appropriate quantum-mechanical cross sections; microreversibility relations can be used to obtain the cross section of an inverse process. The definite integrals in these definitions of collisional rates are not analytic in the case of the Fermi-Dirac electron distribution, unlike the Maxwell-Boltzmann.

A Fermi-Dirac rate for collisional excitation in units of s^{-1}, with cross section denoted by $\Sigma^\uparrow$, can be calculated through the formula

$$J_{FD}^\uparrow(E_j,T_e,\mu) = N_i G\sqrt{\frac{2}{m_e}}\int_{E_j}^{\infty}\Omega(\epsilon_0/E_j) \times F(\epsilon_0,T_e)\tilde{F}(\epsilon_0-E_j,T_e)d\epsilon_0, \tag{5}$$

with E_j the excitation energy, G defined for Eq. (2), Ω the collision strength of the particular transition, and N_i the density of ions in units of cm^{-3}. The collision strength is typically of the form

$$\Omega\left(\frac{\epsilon_0}{E_j}\right) = B_0\ln\left(\frac{\epsilon_0}{E_j}\right)+\sum_{k=1}B_k\left(\frac{\epsilon_0}{E_j}\right)^{-(k-1)}, \tag{6}$$

where B_k are constants [16]. The microreversibility relation[19] for the collisional deexcitation and excitation cross sections, respectively, are

$$\Sigma^\downarrow(\epsilon_0) = \frac{g}{g^*}\frac{\epsilon_0+E_j}{\epsilon_0}\Sigma^\uparrow(\epsilon_0+E_j), \tag{7}$$

with g/g^* the ratio of degeneracies. Substituting this into the integral for the rate of collisional deexcitation, we see that the rate can be calculated by repeating the process for excitation while effectively shifting the chemical potential by the excitation energy and multiplying by the ratio of degeneracies to give

$$J_{FD}^\downarrow(E_j,T_e,\mu) = \frac{g}{g^*}J_{FD}^\uparrow(E_j,T_e,\mu+E_j). \tag{8}$$

A full calculation of the rate of collisional ionization using Fermi-Dirac statistics requires knowledge of the differential cross section $d\sigma/d\epsilon_1$—in effect the energy distribution of the outgoing electrons after an inelastic collision. We have for the collisional ionization rate in units of s^{-1}

$$K_{FD}^\uparrow = N_i G\sqrt{\frac{2}{m_e}}\int_{E_i}^{\infty}\int_0^{\epsilon_0-E_i}\epsilon_0\frac{d\sigma^\uparrow}{d\epsilon_1}F(\epsilon_0,T_e) \times\tilde{F}(\epsilon_1,T_e)\tilde{F}(\epsilon_0-\epsilon_1-E_i,T_e)d\epsilon_0 d\epsilon_1. \tag{9}$$

The microreversibility relation [19] for the three-body recombination and differential collisional ionization cross sections, respectively, are

$$\sigma_\downarrow(\epsilon_1,\epsilon_2) = \frac{g}{g^*}\sqrt{\frac{m_e}{2}}\frac{1}{G}\frac{\epsilon_0}{\epsilon_1\epsilon_2}\frac{d\sigma_\uparrow(\epsilon_0)}{d\epsilon_1}. \tag{10}$$

Substituting this and the energy conservation condition $\epsilon_0 = \epsilon_1+\epsilon_2+E_i$ into the integral for three-body recombination, we obtain

$$K_{FD}^\downarrow = N_i\frac{g}{g^*}G\sqrt{\frac{2}{m_e}}\int_{E_i}^{\infty}\int_0^{\epsilon_0-E_i}\epsilon_0\frac{d\sigma^\uparrow}{d\epsilon_1}F(\epsilon_1,T_e) \times F(\epsilon_0-\epsilon_1-E_i,T_e)\tilde{F}(\epsilon_0,T_e)d\epsilon_0 d\epsilon_1. \tag{11}$$

The usual Maxwell-Boltzmann expressions emerge from Eqs. (5)–(11) if the energy distribution is set to $F(\epsilon,T_e) = n_e[2/G\sqrt{\pi}(k_BT_e)^{3/2}]\exp(-\epsilon/k_BT_e)$ and $\tilde{F}=1$. To calculate the rates of collisional ionization and three-body recombination, we have used a version of the Mott differential cross section [21,22], modified to be consistent with established

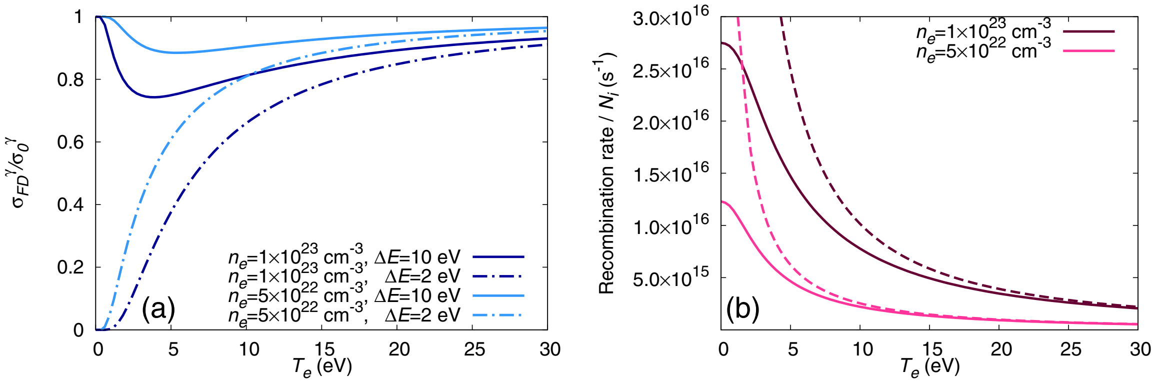

FIG. 1. (Color online) (a) Ratio of the photoionization cross section of atoms in a dense plasma with Pauli blocking factors from the value of a free atom. Here $\Delta E = E_\gamma - E_i$ and electron densities are as indicated. (b) Comparison of the three-body recombination rate of singly ionized carbon, with electron densities as indicated, of Maxwell-Boltzmann (dashed line) to Fermi-Dirac (solid line) statistics.

collisional ionization cross sections of the form

$$\sigma^{\uparrow} = \frac{1}{E_i \epsilon_0}\left[C_0 \ln\left(\frac{\epsilon_0}{E_i}\right) + \sum_{k=1} C_k \left(\frac{\epsilon_0 - E_i}{\epsilon_0}\right)^k\right], \tag{12}$$

where C are constants [16]. Keeping only the first term results in the usual Lotz formula [23]. Taking the same functional form as the Mott cross section and requiring that $\int_0^{\epsilon_0 - E_i} \frac{d\sigma^{\uparrow}}{d\epsilon_1} d\epsilon_1 = \sigma^{\uparrow}$, we propose for a reduced differential cross section, in units of cm^2 eV^{-1} with energies in eV,

$$\frac{d\sigma^{\uparrow}}{d\epsilon_1} = \frac{1}{2E_i\epsilon_0}\left[\frac{C_0 E_i}{(\epsilon_0 - \epsilon_1 - E_i + a)(\epsilon_0 - \epsilon_1 - E_i + b)} + \frac{C_0 E_i}{(\epsilon_1 + a)(\epsilon_1 + b)} + \sum_{k=1} k C_k \frac{\epsilon_1^{k-1} + (\epsilon_0 - \epsilon_1 - E_i)^{k-1}}{\epsilon_0^k}\right], \tag{13}$$

where the quantities

$$a = \frac{1}{2}\left(\sqrt{\epsilon_0^2 + 4E_i^2} - \epsilon_0\right),$$
$$b = a + E_i.$$

The functional form of this differential cross section, consistent with the accurately verified total cross section, has been compared to Mott's in Fig. 2. The main feature of this differential cross section, where one electron is likely to emerge from the collision with the majority of the kinetic energy, is maintained. Assuming the differential cross section to be independent of outgoing electron energy[8] may lead to a significant error in the calculation of the rates.

We have compared the rates in Eq. (11), using cross section data from [16], to the rate from Maxwell-Boltzmann statistics in Fig. 1(b); they deviate at low temperatures as expected. In particular, the Fermi-Dirac rate does not diverge as the Maxwell-Boltzmann rate, but tends to a finite value at zero temperature despite a divergent recombination cross section, due to the limited occupation at low energies. The Fermi-Dirac rate is no longer linearly dependent on the free electron density for a given temperature.

III. EFFECTS ON MACROSCOPIC PROPERTIES

We have compared the steady state ionization fraction of carbon calculated using the Fermi-Dirac to the Maxwell-Boltzmann rates calculated as discussed above, assuming ionization potential depression using the Stewart-Pyatt formula [24] (itself derived using Fermi-Dirac statistics) in

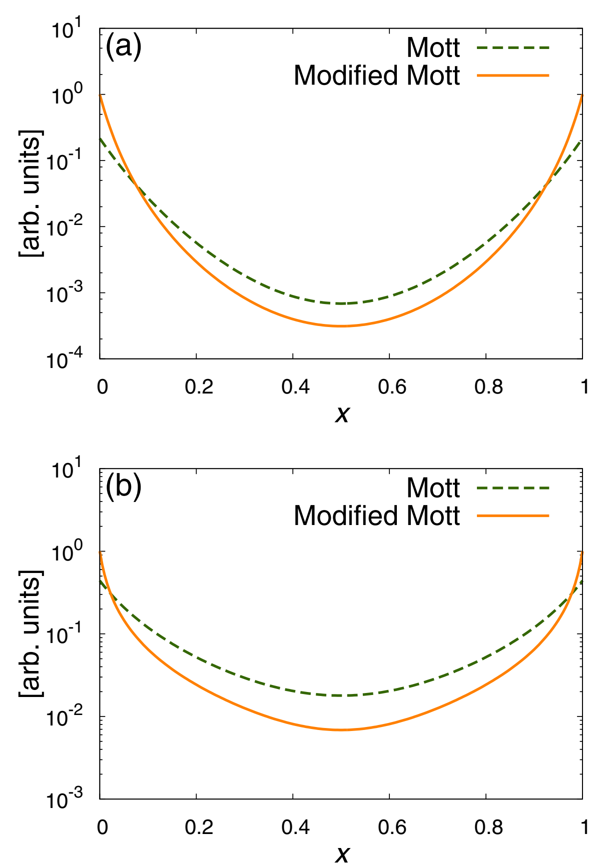

FIG. 2. (Color online) Comparison of the differential collisional ionization cross section due to Mott (dashed) to the modified Mott used in this work (solid) plotted as a function of the fraction of its domain $x = \epsilon_1/(\epsilon_0 - E_i)$ for the first ionization stage of carbon and (a) $\epsilon_0 = 50$, (b) $\epsilon_0 = 100$.

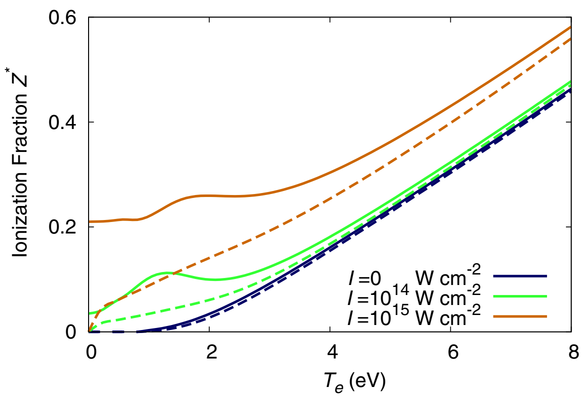

FIG. 3. (Color online) Comparison of the steady state ionization fraction of a carbon plasma (density of 2.23 g cm^{-3}, corresponding to graphite) for Fermi-Dirac (solid) and Maxwell-Boltzmann (dashed) statistics, irradiated by 50 eV photons at intensities indicated.

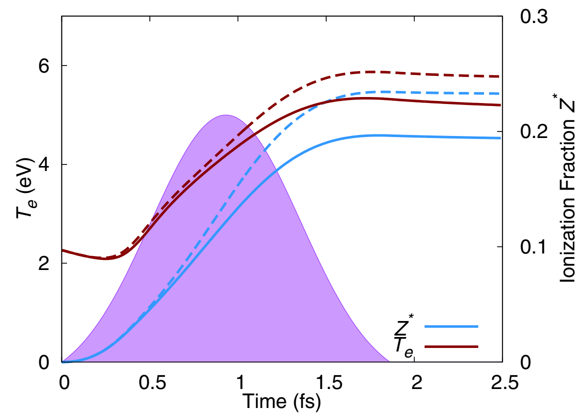

FIG. 4. (Color online) Evolution of the electron temperature and ionization fraction of carbon (density of 3.53 g cm^{-3}, corresponding to diamond) irradiated by a laser beam with photon energies of 14 eV and Gaussian intensity as shown shaded with a full-width half maximum of 1 fs and peak intensity of 10^{14} W cm^{-2} with Maxwell-Boltzmann (dashed line) and Fermi-Dirac (solid line) statistics as indicated.

Fig. 3 for various incident laser intensities with $E_\gamma = 50$ eV. The ionization fractions calculated in the Fermi-Dirac case are nearly identical to that from Maxwell-Boltzmann in the absence of radiation. However, we see a significant difference in the two corresponding ionization fractions in the presence of photoionizing radiation; the steady state ionization fraction does not vanish as $T_e \to 0$, because the Fermi-Dirac three-body recombination rate remains finite.

In practice a constant temperature cannot be maintained in the presence of such high intensities, as given in Fig. 3, due to a rise in thermal energy from free-free absorption. Nonetheless, if the plasma temperature is raised by a flux of photons of these energies and intensities to the range in Fig. 3, steady state calculations can provide a reasonable approximation to the transient plasma conditions during the heating. Even if a laser pulse is expected to heat a plasma far beyond the temperature range where degeneracy effects are important, the initial deviation from Maxwell-Boltzmann statistics may affect subsequent evolution.

We have performed a dynamic simulation, using a previously developed collisional-radiative code [11], of a carbon plasma irradiated by 14 eV photons with the electron temperature and density, resulting from a calculation of appropriate heat capacities and assuming free electrons instantly equilibrate to Fermi-Dirac or Maxwell-Boltzmann statistics as indicated, plotted in Fig. 4. The simulation begins with the absence of free electrons, leading the first electrons to be emitted with energies of $E_\gamma - E_1$, where E_1 is the first ionization energy. As a result, the temperature is initially high and begins to drop as further electrons are collisionally ionized. The early temperatures differ due to the differences in heat capacity between the two models, which converge as the temperature rises; the difference in final temperature is due to different overall absorption coefficients. The discrepancy in temperature between the two models is lower in the case of covalently bonded carbon, modeled initially as neutral, compared to studies of metallically bonded aluminum [13,14], which begins with an established large density of valence electrons. We have neglected any heating of the ions, as the time scale for this is significantly longer than the present simulation.

IV. CONCLUSION

We have introduced formulas for collisional-radiative rates consistent with Fermi-Dirac statistics, which form a low temperature correction to the rates usually calculated with a Maxwell-Boltzmann distribution. We have suggested a differential collisional ionization cross section, required to calculate ionization rates when the Pauli exclusion principle has a significant effect on free electrons in a plasma. We have calculated the ionization fraction of a degenerate plasma and hence shown that degeneracy effects are important for ion densities close to solid only with unbalanced processes such as external ionizing radiation, but small otherwise. The chemical potential of electrons rises with their density, and hence degeneracy effects are more important for dense, compressed plasmas.

This work has a relevance to plasmas produced by lasers with photon energies just above an ionization potential, which maximizes their photoionization cross section, with high electron densities and low temperatures. It also has implications for capsule compression in inertial fusion, where carbon ablator material may mix with fuel during compression [25]; the resulting difference in radiation absorption coefficient between the Fermi-Dirac and Maxwell-Boltzmann models may be significant.

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[1] A. E. Turrell, M. Sherlock, and S. J. Rose, J. Comput. Phys. **249**, 13 (2013).
[2] B. I. Cho, K. Engelhorn, S. M. Vinko, H.-K. Chung, O. Ciricosta, D. S. Rackstraw, R. W. Falcone, C. R. D. Brown, T. Burian, J. Chalupsky, C. Graves, V. Hajkova, A. Higginbotham, L. Juha, J. Krzywinski, H. J. Lee, M. Messersmidt, C. Murphy, Y. Ping, N. Rohringer *et al.*, Phys. Rev. Lett. **109**, 245003 (2012).
[3] J. P. Cox and R. T. Giuli, *Principles of Stellar Structure Volume II: Applications to Stars* (Gordon and Breach Science Publishers, New York, 1968).
[4] S. M. Vinko, O. Ciricosta, B. I. Cho, K. Engelhorn, H.-K. Chung, C. R. D. Brown, T. Burian, J. Chalupsky, R. W. Falcone, C. Graves, V. Hajkova, A. Higginbotham, L. Juha, J. Krzywinski, H. J. Lee, M. Messerschmidt, C. D. Murphy, Y. Ping, A. Scherz, W. Schlotter *et al.*, Nature (London) **482**, 59 (2012).
[5] E. Galtier, F. B. Rosmej, T. Dzelzainis, D. Riley, F. Y. Khattak, P. Heimann, R. W. Lee, A. J. Nelson, S. M. Vinko, T. Whitcher, J. S. Wark, T. Tschentscher, S. Toleikis, R. R. Faustlin, R. Sobierajski, M. Jurek, L. Juha, J. Chalupsky, V. Hajkova, M. Kozlova *et al.*, Phys. Rev. Lett. **106**, 164801 (2011).
[6] V. G. Molinari, D. Mostacci, F. Rocchi, and M. Sumini, Phys. Lett. **316**, 247 (2003).
[7] B. J. B. Crowley, High Energy Density Phys. **13**, 84 (2014).
[8] H.-K. Chung, M. H. Chen, W. L. Morgan, Y. Ralchenko, and R. W. Lee, High Energy Density Phys. **1**, 3 (2005).
[9] J. J. MacFarlane, I. E. Golovkin, and R. R. Woodruff, J. Quant. Spectrosc. Radiat. Transfer **99**, 381 (2006).
[10] O. Peyrusse, J. Phys. B **33**, 4303 (2000).
[11] V. Aslanyan and G. J. Tallents, Phys. Plasmas **21**, 062702 (2014).
[12] W. Pauli, Science **103**, 213 (1946).
[13] B. Deschaud, O. Peyrusse, and F. B. Rosmej, Europhys. Lett. **108**, 53001 (2014).
[14] B. Deschaud, O. Peyrusse, and F. B. Rosmej, High Energy Density Phys. **15**, 22 (2015).
[15] D. H. Sampson and H. L. Zhang, Phys. Rev. A **45**, 1556 (1992).
[16] H. Suno and T. Kato, At. Data Nucl. Data Tables **92**, 407 (2006).
[17] C. Kittel, *Introduction to Solid State Physics*, 8th ed. (Wiley, New York, 1996).
[18] A. F. Nikiforov, V. G. Novikov, and V. B. Uvarov, *Quantum-Statistical Models of Hot Dense Matter* (Birkhauser, Basel, 2005), p. 165.
[19] J. Oxenius, *Kinetic Theory of Particles and Photons: Theoretical Foundations of Non-LTE Plasma Spectroscopy* (Springer-Verlag, Berlin, 1986).
[20] D. Salzmann, *Atomic Physics in Hot Plasmas* (Oxford University Press, New York, 1997).
[21] N. Oda, Radiat. Res. **64**, 80 (1975).
[22] H. Ehrhardt, K. Jung, G. Knoth, and P. Schlemmer, Z. Phys. D. **1**, 3 (1986).
[23] W. Lotz, Z. Phys. **232**, 101 (1970).
[24] J. Stewart and K. Pyatt, Astrophys. J. **144**, 1203 (1966).
[25] P. A. Bradley, Phys. Plasmas **21**, 062703 (2014).
[26] See http://dx.doi.org/10.13140/RG.2.1.2203.4088.