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Ionization of many-electron atoms by a quasistatic electric field

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We present a general expression for the field ionization probability of atoms and ions under a quasistatic external electric field. While the treatments available as yet are only for the case of a single electron in the outer nl subshell, the expression obtained here is applicable to atoms and ions with any number of electrons in the outer subshell and with partially filled inner subshell(s). We also present a more accurate method to determine the prefactor in the expression for the field ionization probability. Ionization probabilities are calculated using the WKB approximation; therefore, the results become exact in the weak-field limit. It is shown that in certain cases the field ionization probability depends significantly on the projection of the total orbital angular momentum in the direction of the field. A proper way to normalize the optical-electron wave-function asymptotics is explained and the difficulties in the use of Hartree-Fock routines for that purpose are discussed. The general expression obtained is used to calculate field ionization probabilities for several states of some atoms and ions that are of special interest for spectroscopic diagnostics: C I, Li I, and Ba II. We also discuss the case of a significant spin-orbit interaction, treating the ionization of the Ba II $6p$ level as an example. For the Li I $2p$ level, the present calculations disagree with previously published calculations based on the use of Hartree-Fock wave functions; possible reasons for the discrepancy are discussed. For this level and the $3d$ level of Li I, our results are compared with experimental data available in literature and are found to be in agreement. [S1050-2947(98)08208-0]

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I. INTRODUCTION

Ionization of atoms[1] by an external electric field is a fundamental atomic process that plays an important role in the formation of the charge-state distribution in plasmas under strong fields, which may occur, for example, in relatively dilute plasmas [1,2] and in shock wave fronts [3] in denser plasmas. Calculations of the field ionization (FI) probability for various atomic states are thus essential for proper modeling of the plasma charge-state composition, transport coefficients, and emission spectrum in both lines and continuum. Field ionization, studied from observations of temporal variations in the line intensities, can serve as a valuable tool for spectroscopic determination of the macroscopic-field distribution in plasmas. Since the FI probability grows rapidly with the field, it allows for an accurate determination of the electric field strength.

The FI of atoms and positive ions has been studied theoretically since 1930 [4]; however, it is still a subject of an active research [5–11]. As yet, to the best of our knowledge, the theoretical treatments have been limited to the case of atoms (ions) with a single electron in the outer nl subshell and filled inner subshells. For such systems, there is a well-known prediction for the quasistatic field ionization probability given by Smirnov and Chibisov [12]. The prefactor for this expression was later corrected by Perelomov *et al.* [13]. The expression has been derived in the framework of the WKB approximation, thus becoming exact in the limit of weak (in comparison to atomic fields) external fields. Although a single-outer-electron system is the simplest case, ionization probabilities computed numerically [9] and analytically [5,10] differ by orders of magnitude. In Sec. II we explain the likely reason for this disagreement. We also show a proper way to determine the single-electron wave-function asymptotic amplitude that appears in the prefactor in the expressions for the one-electron FI probability [12,13].

In this paper we generalize these single-electron results to the case of atoms that have several equivalent electrons in the outer nl subshell and/or holes in the inner subshell(s). The expressions we present make it possible to account for different ionization rates from different components of the LS term and into different parent terms.

We focus here on the effects of an electric field that is weak ($F \ll |E|^{3/2}$, where $|E|$ is the binding energy of optical electron in the atom under consideration and F is the external field intensity; atomic units are used throughout this work). We also assume that the electric field is quasistatic [see condition (2) below] and homogeneous over the atomic scale, i.e., this study concentrates on the FI due to macroscopic-scale fields in plasma rather than due to local fields [17]. We consider the atomic potential (as seen by the electron being removed) to be spherically symmetric and we ignore relativistic effects, unless otherwise mentioned. Con-

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[1] By ‘‘atom’’ in this study we mean a particle that is either a neutral atom or a positive ion, i.e., in which the most weakly bound electron is confined to a potential well, which for large distances has asymptotics of an attractive Coulomb potential: $V \sim r^{-1}$.

sequently, a single-electron state may be described by orbital and spin quantum numbers l,l_z,s,s_z, where z is taken in the direction of the external electric field.

The paper is structured as follows. In Sec. II we discuss the one-electron result and ways for an accurate assessment of the escaping-electron wave-function amplitude at large radii. In this section we also compare our calculations with theoretical and experimental results available in publications. In Secs. III and IV we present the generalization of the one-electron result to the case of several electrons in the outer nl subshell and give several examples of the numerical calculations using the general expression obtained.

II. THE SINGLE-ELECTRON CASE

We consider a homogeneous electric field $\mathbf{F}=-F\hat{\mathbf{z}}$ directed along the z axis; the total potential drops towards $z\to\infty$. We denote the outer classical turning point by b, i.e., $z>b$ is a classically allowed region for the electron. In the weak-field limit, the action A across the barrier is much larger than unity and the penetrability of the barrier is proportional to $\exp(-2A)$ [14], which means that the electron can only escape along the z axis, where the barrier is thinnest. In parabolic coordinates ($\xi=r+z$, $\eta=r-z$; $\eta\ll\xi$ along the escape path)

$$A=\int_{\sim 0}^{2b}|\kappa_\xi(\xi)|d\xi\simeq\sqrt{|E|}b\simeq\frac{|E|^{3/2}}{F}\gg 1, \tag{1}$$

where $b\simeq|E|/F$ is the barrier thickness and $|\kappa_\xi(\xi)|=\sqrt{\frac{1}{4}[E-V(\xi)]}$. This condition guarantees that the escaping-electron wave-function inside the barrier, far from the turning points, may be described quasiclassically. A more precise condition [condition (6)] is given below.

In the present quasistatic treatment, the characteristic frequency ω of the field fluctuation must be sufficiently low, in order for the Keldysh adiabaticity condition

$$\frac{\omega|E|^{1/2}}{F}=\gamma\ll 1 \tag{2}$$

to be fulfilled; see Refs. [15,16].

The escape rate Γ is expressed as

$$\Gamma=\int dx\,dy\,j_z(x,y,z)=\int dx\,dy\,d\sigma\,\mathrm{Im}\left\{\psi\frac{\partial}{\partial z}\psi^*\right\}, \tag{3}$$

where j_z is the flux in the direction of escape, $\psi\equiv\psi(\mathbf{r},\sigma)$ is the wave function, and σ is the spin coordinate. The escape rate Γ has a meaning of *the probability per unit time* for the atom under consideration to be ionized by the external electric field[2] (both the terms ''probability'' and ''rate''are commonly used to denote Γ).

For the case of a single electron in the outer nl subshell over closed subshells, quasiclassical calculations [12,13] yield[3]

$$\Gamma_{E,l,m}=B^2\frac{(2l+1)(l+m)!}{2^{m+1}\kappa^m m!(l-m)!}\left(\frac{2\kappa^2}{F}\right)^{2Z_P/\kappa-m-1}\times\exp\left\{-\frac{2\kappa^3}{3F}\right\}, \tag{4}$$

where $B\equiv B_{nl}$ is the amplitude of the asymptotics of the optical-electron wave function at large r, which is

$$\phi_{nl}(r)=B_{nl}r^{Z_P/\kappa-1}\exp(-\kappa r). \tag{5}$$

Here Z_P is the charge of the parent ion and $\kappa=\sqrt{2|E|}$. Expression (4) is valid for a weak electric field F that fulfills

$$F\ll\frac{\kappa^4}{2Z_P}. \tag{6}$$

Further on we denote the one-electron escape probabilities calculated using expression (4) by $\Gamma^{(1)}_{E,l,m}$.

As said above, the constant B is determined from the asymptotic behavior of the radial part of the unperturbed outer-electron wave function at large distances. It is thus unique for each energy state of every species. As yet, the FI probability calculations have been performed using approximate values of B (see, for example, Ref. [5]). A way to determine B more reliably is shown in the following subsection, along with a discussion on the applicability of the form (5).

A. The asymptotic behavior of the unperturbed wave function at large radii

Sufficiently far from the core, the behavior of the unperturbed wave function is semiclassical and the potential becomes Coulombic; the radial part of the wave function is then determined by a (well-defined) value of the binding energy and thus has the form (5) precisely. The condition (6) guarantees that on such intermediate distances from the core the external electric field can still be neglected.

The purity of the angular part, on the other hand, is not completely precise due to the noncentral component of the electron-electron interaction. Therefore, one expects that there should be a small admixture of other spherical harmonics to the leading one. However, these admixtures should not affect the one-electron FI probability significantly since the dependence on the angular quantum numbers in expression (4) is sufficiently weak.

The constant B_{nl} is different for different one-electron states, but is the same for all magnetic components l_z of the state. We have calculated B_{nl} for each one-electron state of interest using the computer code ATOM, which has been de-

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[2] For simplicity, our derivations below will be performed under the assumption of a static field ($\omega\ll\Gamma$), which is stricter than condition (2). When the condition $\omega\ll\Gamma$ fails, the probability for the electron to stay in the potential well, given by $\exp(-\Gamma t)$, becomes $\exp[-\int_0^t\Gamma(t')dt']$.

[3] There are actually some inaccuracies in expressions (7) and (11) of the original paper [12]. The correct expression for a single-electron FI rate is given in Ref. [13]. Also note that the coefficient $C_{\kappa l}$ in Ref. [13] relates to B in the following way: $B=\kappa^{Z_P/\kappa+1/2}C_{\kappa l}$.

TABLE I. Coefficients (7) for the one-electron escape rates from the atomic states with a single outer electron.

Initial-state term	Z_P	l	κ	B	$C_1(m=0)$	$C_1(m=1)$	$C_2(m=0)$	$C_2(m=1)$	C_3
Ba II $6s\ ^2S$	2	0	0.85748	0.7676	2.421		-3.665		0.4203
Ba II $6p\ ^2P$	2	1	0.73508	9.917×10^{-2}	2.082×10^{-2}	5.242×10^{-2}	-4.442	-3.442	0.2648
Li I $2s\ ^2S$	1	0	0.62951	0.9313	0.2614		-2.177		0.1663
Li I $2p\ ^2P$	1	1	0.51036	0.2271	1.153×10^{-2}	4.337×10^{-2}	-2.919	-1.919	0.08862
C I $2s^22p3s\ ^1P$	1	0	0.51317	0.4036	1.271×10^{-2}		-2.897		0.09009
C I $2s^22p3s\ ^3P$	1	0	0.52722	0.4236	1.740×10^{-2}		-2.793		0.09770

veloped by Shevelko and Vainshtein [18]. The code yields the radial part of the atomic wave function,[4] the asymptotic part of which (for $r \gg Z_P/\kappa^2$) may then be fitted using expression (5) in order to find B_{nl}. We actually fitted $\ln[\phi(r)]$ rather than $\phi(r)$ to allow for a wide range of magnitudes of $\phi(r)$ at large r. Both κ and B may be fitted simultaneously, in which case κ must not differ from its table value (which is inputted into ATOM) by more than 0.1%.

It is important to mention that the ATOM code differs from the standard Hartree-Fock routines (say, the code by Cowan [19]) in its procedure. In ATOM [18,20] the energy of any term is taken from the data tables rather than calculated internally. The Schrödinger equation is then solved for the radial part of the optical-electron wave function corresponding to the term of interest. The asymptotic form of the radial part at large r is thus guaranteed to be given by expression (5) with the correct value of κ (see Sec. 5.4 in Ref. [20]), which is highly important for the FI probability calculations. On the contrary, in the standard Hartree-Fock (HF) treatments, one-electron wave functions obtained for the central part of the potential are used as a basis, which is then truncated for the feasibility of numerical calculations. The noncentral part of the potential (LS coupling) is then calculated in this truncated basis, and the eigenstates of the total Hamiltonian are found. This standard method is generally preferable for the determination of energy levels, but it yields an asymptotic result inconsistent with expression (5) due to the incomplete basis. This may give rise to a large error in the evaluation of the FI probability via the following mechanism. Instead of the form given by expression (5), the asymptotic result that the standard HF method yields is a superposition of the asymptotic forms for the one-electron states, including high-lying ones. Since the basis is incomplete, the asymptotics of high-lying states do not cancel each other properly. At sufficiently large r these high-state asymptotic tails dominate; thus, instead of the correct asymptotic result (5) that decays according to the true binding energy of the term considered, the standard treatment yields an asymptotic result that decays according to the binding energy of the highest one-electron state left in the basis. Since the FI probability is extremely sensitive to the asymptotic behavior the resulting error may be huge.

There is another subtlety in using the Hartree-Fock procedure for the calculations of the FI probability besides the problem of the basis truncation. It has been shown by Handy *et al.* [21] (see also [22–24]) that if one uses the basis of wave functions with well-defined angular parts for a general Hartree-Fock procedure, then one observes that each one-electron wave function at large distances does not have the asymptotic form (5) corresponding to its binding energy, but rather a superposition of forms (5) corresponding to binding energies of every *occupied* orbital. Since the binding energy that appears in the asymptotic form determines the exponential factor in the FI probability, this observation means that the use of such HF wave functions is expected to give a probability for the FI of the core electrons (leaving an ion with a hole in the inner shell) comparable to that for the optical electron, which is unrealistic. In reality, as already said, wave functions with well-defined angular parts are not exactly the eigenstates of the atomic Hamiltonian. An eigenstate of the total atomic Hamiltonian may be obtained only as a superposition of these basis wave functions with well-defined angular parts and such a superposition at large distances does not have the form (5). The true eigenstates of the atomic Hamiltonian have well-defined binding energies and thus, at large distances, well-defined radial asymptotics of the form (5), although they do not have well-defined angular quantum numbers. The latter may only result in corrections to the preexponent [but not to the exponential factor in expression (4)], yielding that the core electrons' escape is exponentially suppressed in comparison to that of the outer electrons, as expected.

It should also be mentioned that in the numerical estimates performed using our method, the error originating at the exponential factor is small if condition (1) is obeyed. The error originating at the preexponent (i.e., from the evaluation of B^2 and from the l,m-containing factor) depends on the purity of the leading angular component of the true eigenstate and is also small unless there is a significant mixing.

B. Numerical results for a single outer electron

We have conducted FI probability calculations for the Li I $2s$, $2p$, and $3d$ and Ba II $6s$ and $6p$ states. In all these states there is a single outer electron over closed subshells, so expression (4) is directly applicable. The coefficient B has been rigorously evaluated, as described above. Table I gives the coefficients of the one-electron escape rates from these states.

The coefficients C_1, C_2, and C_3 are parameters for the numerical evaluation of the one-electron escape rate (4):

$$\Gamma_{nlm}^{(1)} = C_1 F^{C_2} \exp\left\{-\frac{C_3}{F}\right\} \tag{7a}$$

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[4] ATOM actually outputs $P(r)=r\phi(r)$, normalized by the condition $\int_0^\infty P^2(r)dr=1$. It also uses Coulomb (rather than atomic) units.

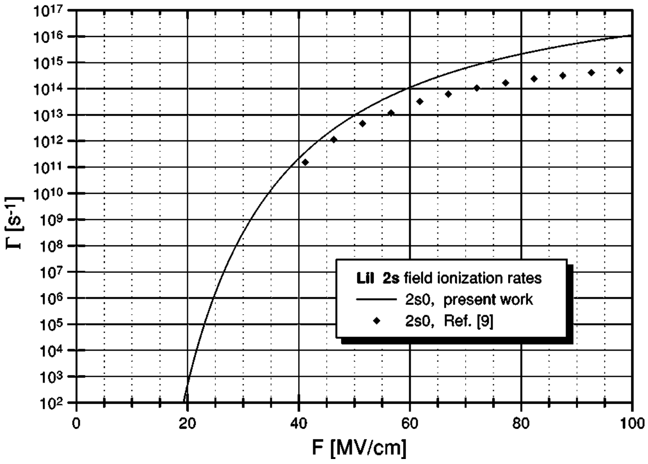

FIG. 1. Field ionization rates for the Li I 2s level.

where

$$C_1=B^2\frac{(2l+1)(l+m)!}{2^{m+1}\kappa^m m!(l-m)!}(2\kappa^2)^{2Z_P/\kappa-m-1}, \tag{7b}$$

$$C_2=-\frac{2Z_P}{\kappa}+m+1, \tag{7c}$$

$$C_3=\frac{2}{3}\kappa^3. \tag{7d}$$

The numerical results for Γ are given in atomic units (to obtain Γ in units of s^{-1} one must multiply it by 4.136 $\times 10^{16}$).

The accuracy of the calculations of Γ is limited by the terms of the next order in F (corrections to the WKB approximation and Stark corrections [17]). These terms are small as long as the applicability condition (6) is obeyed. The accuracy of B, evaluated using the ATOM code, is usually a few percent, or up to 20–30 % for atoms with a complicated structure. This determines the accuracy of Γ in the weak-field limit.

The one-electron WKB calculations found in the literature (see, for example, Ref. [10]) are also performed using the expression (4) for the FI rate. In these calculations, the coefficient B is, however, approximated by its value for hydrogen, with the quantum numbers nl substituted by their effective values n^*l^*. A comparison performed in the present study for several states of Li I shows that the values of B so derived are accurate to within a factor of 2 (i.e., giving FI probabilities accurate to within factor 4). It should be noted, however, that due to the very strong dependence of Γ on F, an error of factor 4 in the FI rate corresponds to an error of only about 20% in F, at the characteristic value $A=10$ of the action across the barrier.

Numerical results for the FI probability for the lithium atom are available in the literature [9]. Figures 1 and 2 give a comparison between the present calculation results and the results quoted in Ref. [9] for the Li I 2s and 2p levels, respectively. There is a substantial disagreement for the results for the Li I 2p level at the weaker fields.

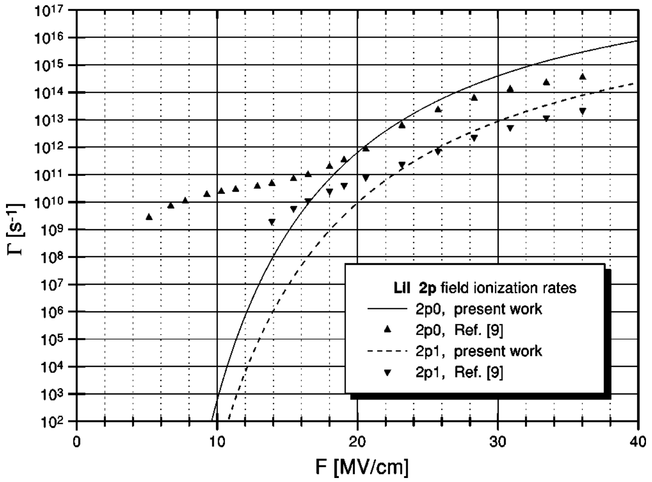

FIG. 2. Field ionization rates for the Li I 2p level components.

In Ref. [9] numerical calculations have been performed by solving the time-dependent Schrödinger equation using a truncated basis of Hartree-Fock functions. These calculations are good for stronger fields, but do not generally agree with the Gamov formula in the weak-field limit, particularly for the $m=0$ component of the 2p state. We believe that the reason for this discrepancy is the following: Since in Ref. [9] a truncated basis was used, the asymptotic form of the wave function may not be of the type (5), as we have said in the Sec. II A. In the weak-field limit the outer classical turning point is located very far from the core, so the incomplete cancellation of the weakly bound components in the Hartree-Fock wave function at large radii may lead to significantly inaccurate results, as it is explained in Sec. II A.

The Li I 2p-2s emission line has been observed by Bailey and collaborators in experiments conducted on a high-voltage ion diode [2]. The 2p-2s line emission showed no significant field ionization of the 2p level on the time scale of tens of nanoseconds for electric fields up to 10 MV/cm. Our calculations for the FI rate for the Li I 2p level show practically no FI for fields up to 13 MV/cm, consistent with this experimental finding.

The calculations in Ref. [9], however, suggest a significant FI at those fields. The FI probabilities given in [9] are about 10^{10} s^{-1} for the $2p_0$ and 10^8 s^{-1} for $2p_{\pm1}$ components. We note that these calculations, in fact, imply a FI rate for the $2p_{\pm1}$ components also comparable to 10^{10} s^{-1} due to spin-orbit-interaction mixing of the $2p_{\pm1}$ and $2p_0$ components. The fast depletion of the 2p level due to such high FI rates [in particular since the mechanisms populating the 2p level in the low-density (10^{13} cm^{-3}) plasma in that experiment are much too slow] would have reduced the 2p-2s line intensity much below the observability threshold on a time scale much shorter than the experimental time (which is tens of nanoseconds). Thus, if the FI rates given in Ref. [9] were correct, the Li I 2p-2s emission line would not have been observed, which was not the case.

As for the Li I 3d level, also considered in the present work, our calculations show that this level has a FI rate of about 10^{10} s^{-1} at 4 MV/cm field, in agreement with the calculations given in Ref. [9]. This implies the disappearance of emission lines originating at the Li I 3d level for fields exceeding this value. As pointed out by Bailey *et al.*, this is consistent with the absence of the $3d$-$2p$ line emission in the experimental observations in the high-voltage ion diode [1].

Finally, before we give the derivation of the general expression, we would like to point out that the one-electron result may also be used in some simple cases of a single electron above a nonclosed shell. The configuration $2p3s$ of C I is an example. For this configuration, the FI rate is simply $\Gamma^{(1)}_{n=3,l=0,l_z=0}$ since the escape occurs from a one-electron state $3s$. However, in this case there is a subtlety that does not occur in the case of closed lower subshells: The terms ${}^1P$ and ${}^3P$ of the initial configuration have different binding energies and thus different FI rates. The coefficients (7) for the calculation of the FI probability for the C I $2p3s\,{}^1P$ and ${}^3P$ terms are also given in Table I.

III. GENERAL EXPRESSION FOR THE FIELD IONIZATION PROBABILITY

In this section we generalize the treatment for a single electron to the case of an atom of an arbitrary electronic structure. To do so, we have to consider a many-electron wave function [14,25] describing all the electrons in the atom, instead of a one-electron wave function that was used in previous considerations. The approximation of independent electrons still applies, so we present our many-electron wave function as a linear combination of products of single-electron wave functions corresponding to all occupied one-electron states in the atom. It is rather obvious that the result (4) could have been derived using a many-electron wave function too for an atomic configuration in which there is a single electron in the outermost subshell and no holes in the lower subshells. A simple way to show this is given in the Appendix. We now use the approach we show in the Appendix for the case of several electrons in the outer nl subshell and fractional parentage. All the lower closed subshells may be ignored, and thus we may present (see, for example, [26]) the wave function (A5) of K electrons in the outer subshell in the form

$$\begin{aligned}\Phi^{L_zS_z}_{LS}(\mathbf{r}_1\sigma_1\cdots\mathbf{r}_K\sigma_K)&\equiv|(nl)^KLL_zSS_z\rangle\\&=\sum_{S^P,L^P}G^{SL}_{S^PL^P}(-1)^{K-1}\sum_{S^P_zs_z,}\sum_{L^P_z,l_z}\begin{bmatrix}S^P & 1/2 & S\\ S^P_z & s_z & S_z\end{bmatrix}\\&\quad\times\begin{bmatrix}L^P & l & L\\ L^P_z & l_z & L_z\end{bmatrix}|(nl)^{K-1}L^PL^P_zS^PS^P_z\rangle|(nl)^1ll_z\tfrac{1}{2}s_z\rangle.\end{aligned}\tag{8}$$

Here $|(nl)^{K-1}L^PL^P_zS^PS^P_z\rangle$ is a parent wave function, $|(nl)^1ll_z\frac{1}{2}s_z\rangle\equiv\psi^{l_zs_z}_{nl\frac{1}{2}}(\mathbf{r}_1\sigma_1)$ is the one-electron wave function, and the square brackets denote Clebsh-Gordan coefficients. $G^{SL}_{S^PL^P}$ are the fractional parentage coefficients; tables for them are given in Ref. [27] along with detailed explanations.

Having established this, we have also automatically established the norm

$$\begin{aligned}&\langle(nl)^{K-1}L^{P\prime}L^{P\prime}_zS^{P\prime}S^{P\prime}_z|(nl)^{K-1}L^PL^P_zS^PS^P_z\rangle\\&\quad=\delta_{L^PL^{P\prime}}\ \delta_{L^P_zL^{P\prime}_z}\ \delta_{S^PS^{P\prime}}\ \delta_{S^P_zS^{P\prime}_z},\end{aligned}$$

which allows us to calculate the integral (A4) given in the Appendix. We first evaluate the expression (A3)

$$\begin{aligned}\Gamma^{LL_zSS_z}_{\mathbf{r}_1}&=\int dx_1dy_1d\sigma_1\int d\mathbf{r}_2d\sigma_2\cdots\int d\mathbf{r}_Nd\sigma_N\mathrm{Im}\left\{\Phi(\mathbf{r}_1\sigma_1\cdots\mathbf{r}_N\sigma_N)\frac{\partial}{\partial z_1}\Phi^*(\mathbf{r}_1\sigma_1\cdots\mathbf{r}_N\sigma_N)\right\}_{z_1>b}\\&=\sum_{S^P,L^P}\ \sum_{S^P_z,s_z}\ \sum_{L^P_z,l_z}\ \sum_{S'^P,L'^P}\ \sum_{S'^P_z,s'_z}\ \sum_{L'^P_z,l'_z}\int dx_1dy_1d\sigma_1\mathrm{Im}\left\{\psi^{l_zs_z}_{nl\frac{1}{2}}(\mathbf{r}_1\sigma_1)\frac{\partial}{\partial z_1}\psi^{*l'_zs'_z}_{nl\frac{1}{2}}(\mathbf{r}_1\sigma_1)\right\}_{z_1>b}\\&\quad\times G^{SL}_{S^PL^P}\begin{bmatrix}S^P & 1/2 & S\\ S^P_z & s_z & S_z\end{bmatrix}\begin{bmatrix}L^P & l & L\\ L^P_z & l_z & L_z\end{bmatrix}G^{SL}_{S'^PL'^P}\begin{bmatrix}S'^P & 1/2 & S\\ S'^P_z & s'_z & S_z\end{bmatrix}\begin{bmatrix}L'^P & l & L\\ L'^P_z & l'_z & L_z\end{bmatrix}\\&\quad\times\langle(nl)^{N-1}L'^PL'^P_zS'^PS'^P_z|(nl)^{N-1}L^PL^P_zS^PS^P_z\rangle\\&=\sum_{S^P,L^P}(G^{SL}_{S^PL^P})^2\sum_{S^P_z}\sum_{L^P_z}\sum_{s_z}\sum_{l_z}\begin{bmatrix}S^P & 1/2 & S\\ S^P_z & s_z & S_z\end{bmatrix}\begin{bmatrix}L^P & l & L\\ L^P_z & l_z & L_z\end{bmatrix}\sum_{s'_z}\sum_{l'_z}\begin{bmatrix}S^P & 1/2 & S\\ S^P_z & s'_z & S_z\end{bmatrix}\begin{bmatrix}L^P & l & L\\ L^P_z & l'_z & L_z\end{bmatrix}\\&\quad\times\int dx_1dy_1d\sigma_1\mathrm{Im}\left\{\psi^{l_zs_z}_{nl\frac{1}{2}}(\mathbf{r}_1\sigma_1)\frac{\partial}{\partial z_1}\psi^{*l'_zs'_z}_{nl\frac{1}{2}}(\mathbf{r}_1\sigma_1)\right\}_{z_1>b}.\end{aligned}$$

The Clebsh-Gordan coefficient $[{}^{J^{(1)}}_{J^{(1)}_z}\,{}^{J^{(2)}}_{J^{(2)}_z}\,{}^{J}_{J_z}]$ is nonzero only if $J_z=J^{(1)}_z+J^{(2)}_z$; thus the double summations on s_z,s'_z and l_z,l'_z are removed ($s_z=s'_z$ and $l_z=l'_z$). We are then left with

$$\Gamma_{\mathbf{r}_1}^{LL_zSS_z} = \sum_{S^P,L^P} (G^{SL}_{S^PL^P})^2 \sum_{S_z^P}\sum_{L_z^P}\sum_{s_z}\sum_{l_z} \left(\begin{bmatrix} S^P & 1/2 & S\\ S_z^P & s_z & S_z\end{bmatrix}\right)^2 \left(\begin{bmatrix} L^P & l & L\\ L_z^P & l_z & L_z\end{bmatrix}\right)^2$$

$$\times \int dx_1 dy_1 d\sigma_1 \mathrm{Im}\left\{ \psi^{l_z s_z}_{nl\frac{1}{2}}(\mathbf{r}_1\sigma_1)\frac{\partial}{\partial z_1}\psi^{*l_zs_z}_{nl\frac{1}{2}}(\mathbf{r}_1\sigma_1)\right\}_{z_1>b}$$

$$= \sum_{S^P,L^P} (G^{SL}_{S^PL^P})^2 \sum_{S_z^P}\sum_{L_z^P}\sum_{s_z}\sum_{l_z} \left(\begin{bmatrix} S^P & 1/2 & S\\ S_z^P & s_z & S_z\end{bmatrix}\right)^2 \left(\begin{bmatrix} L^P & l & L\\ L_z^P & l_z & L_z\end{bmatrix}\right)^2 \Gamma^{(1)}_{nll_z},$$

where

$$\Gamma^{(1)}_{nll_z} \equiv \int dx\ dy\ d\sigma\ \mathrm{Im}\{\psi^{l_zs_z}_{nl(1/2)}(\mathbf{r}\sigma)(\partial/\partial z)\psi^{*l_zs_z}_{nl\frac{1}{2}}(\mathbf{r}\sigma)\}_{z>b}.$$

Obviously, $\Gamma^{(1)}_{nll_z}$ cannot depend on S_z^P and L_z^P, and in the nonrelativistic limit it also does not depend on s_z. Thus the summation on s_z may be explicitly performed, to yield the final expression for the ionization probability

$$\Gamma^{LL_zSS_z}_{total} = K\Gamma^{LL_zSS_z}_{\mathbf{r}_1}$$

$$= K\sum_{S^P,L^P} (G^{SL}_{S^PL^P})^2 \sum_{L_z^P}\sum_{l_z} \left(\begin{bmatrix} L^P & l & L\\ L_z^P & l_z & L_z\end{bmatrix}\right)^2 \Gamma^{(1)}_{nll_z}. \tag{9}$$

Note that $\Gamma^{(1)}_{nll_z}$ depends (via the binding energy) on S^P and L^P. The total FI probability $\Gamma^{LL_zSS_z}_{total}$ does not depend on S_z (the projection of the total spin).

IV. APPLICATIONS OF THE GENERAL RESULT

Let us first note that the general expression (9) becomes identical to $\Gamma^{(1)}_{nll_z}$ for a single outer electron ($K=1$) and closed inner subshells ($S^P=0$, $L^P=0$), i.e., for the single-electron case. For a single electron above a partially-filled subshell, like the C I $2p3p$ configuration, one should obviously apply the result (9) to find the ionization probability of the state with a certain projection L_z of the total orbital angular momentum, and the expression (4) to find the ionization probability of the state with a certain projection l_z of the orbital angular momentum of the optical electron. In the absence of fractional parentage, expression (9) turns into a simple angular component weighting rule

$$\Gamma^{LL_zSS_z}_{total} = K\sum_{L_z^P}\sum_{l_z} \left(\begin{bmatrix} L^P & l & L\\ L_z^P & l_z & L_z\end{bmatrix}\right)^2 \Gamma^{(1)}_{nll_z}. \tag{10}$$

In particular, for the closed outer subshell, the general result (9) gives

$$\Gamma^{closed\ \ subshell}_{total} = 2(2l+1)\sum_{L_z^P}\sum_{l_z} \left(\begin{bmatrix} L^P=l & l & 0\\ L_z^P & l_z & 0\end{bmatrix}\right)^2 \Gamma^{(1)}_{nll_z}$$

$$= 2(2l+1)\sum_{l_z} \left(\begin{bmatrix} l & l & 0\\ -l_z & l_z & 0\end{bmatrix}\right)^2 \Gamma^{(1)}_{nll_z}$$

$$= 2(2l+1)\sum_{l_z} \left(\frac{1}{\sqrt{2l+1}}\right)^2 \Gamma^{(1)}_{nll_z}$$

$$= 2\sum_{l_z} \Gamma^{(1)}_{n,l,l_z} \equiv \sum_{l_z,s_z} \Gamma^{(1)}_{nll_z}.$$

This is an intuitively expected result that simply follows from the fact that the escape probability for any one electron does not involve its correlations with the others.

A result similar to expression (9) also follows for the jl (alias $j\mathcal{K}$) coupling scheme. In this case there is one optical electron $|(nl)ll_z\frac{1}{2}s_z\rangle$ over a parent ion state $|(n^Pl^P)^{N^P}L^PS^PJ^PJ_z^P\rangle$. For jl coupling $(n^Pl^P)\neq(nl)$; thus it is essentially a one-electron escape case. Denoting $\mathcal{K}=\mathbf{J}^P+\boldsymbol{l}$, we may present the total wave function in the form

$$|(n^Pl^P)^{N^P}J^P(nl)\mathcal{K}K_zs_z\rangle$$

$$= \sum_{J_z^P}\sum_{l_z} \begin{bmatrix} J^P & l & \mathcal{K}\\ J_z^P & l_z & \mathcal{K}_z\end{bmatrix}$$

$$\times |(n^Pl^P)^{N^P}L^PS^PJ^PJ_z^P\rangle|(nl)ll_z\tfrac{1}{2}s_z\rangle.$$

Here the radial part of $|(nl)ll_z\frac{1}{2}s_z\rangle$ depends implicitly (via the binding energy) on J^P, but does not depend on $\mathcal{K}$, i.e., one should use the specific binding energy for each value of J^P, averaged over all $\mathcal{K}$ possible for that J^P. The FI rate is then

TABLE II. Coefficients (7) for the one-electron escape rates from the ground configuration terms of the neutral carbon atom.

Initial-state term	Z_P	l	κ	B	$C_1(m=0)$	$C_1(m=1)$	$C_2(m=0)$	$C_2(m=1)$	C_3
C I $2s^22p^2\ {}^1D$	1	1	0.857 30	0.839	1.766	1.402	−1.3329	−0.3329	0.4201
C I $2s^22p^2\ {}^3P$	1	1	0.909 87	1.033	2.931	1.946	−1.1981	−0.1981	0.5022
C I $2s^22p^2\ {}^1S$	1	1	0.794 11	0.711	1.080	1.078	−1.5185	−0.5185	0.3338

$$\Gamma^{J^P\mathcal{K}\mathcal{K}_z}=\sum_{J_z^P}\sum_{l_z}\left(\begin{bmatrix} J^P & l & \mathcal{K} \\ J_z^P & l_z & \mathcal{K}_z \end{bmatrix}\right)^2\Gamma^{(1)}_{nll_z}, \tag{11}$$

where s_z is omitted from the notation since it has no effect on the FI probability.

We now give numerical examples for the FI probability calculations using the general result (9). For all calculations, the expression (4) for one-electron escape rates $\Gamma^{(1)}_{nll_z}$ is used. The constants B_{nl} are determined as discussed in Sec. II A. The binding energies are taken from atomic data tables given in Refs. [28–30].

A. Application to a few species of interest for spectroscopy

1. The C I $2s^2 2p^2$ *configuration: Occasional discrimination of certain* L$_z$ *components*

Here we are using expression (10) to calculate the FI probabilities. First we would like to emphasize the following interesting feature: In some cases, a certain L_z component of the term should ionize much slower than the others. The reason for that is as follows: The one-electron FI probability $\Gamma^{(1)}_{nll_z}$ is highest for the smallest $m\equiv|l_z|$, i.e., for $l_z=m=0$. The one-electron FI probability for certain value of m is roughly $(|E|^{3/2}/F)^m$ times smaller than for $m=0$. Thus, if in expression (10) the Clebsh-Gordan coefficient $\left[\begin{smallmatrix} L^P & l & L \\ L_z & 0 & L_z \end{smallmatrix}\right]$ is zero, then the entire component $^{2S+1}L_{L_z}$ ionizes $|E|^{3/2}/F$ times more slowly than the others. Thus a discrimination may occur between the components of a certain term (e.g., the components of the C I $2p^2\ {}^3P$ term, as illustrated below). In dilute plasmas (in which a probability of collision-induced transition between components of the same term is low) under static electric fields this effect may be manifested by higher relative abundance of the components that field ionize more slowly.

The total escape probabilities for the terms of the C I $2p^2$ configuration are derived from the one-electron escape probabilities using expression (10):

$$\Gamma^{^1D_{\pm 2}}_{total}=2\Gamma^{(1)^1D}_{2p_1},$$

$$\Gamma^{^1D_{\pm 1}}_{total}=\Gamma^{(1)^1D}_{2p_0}+\Gamma^{(1)^1D}_{2p_1},$$

$$\Gamma^{^1D_0}_{total}=\frac{4}{3}\Gamma^{(1)^1D}_{2p_0}+\frac{2}{3}\Gamma^{(1)^1D}_{2p_1},$$

$$\Gamma^{^3P_{\pm 1}}_{total}=\Gamma^{(1)^3P}_{2p_0}+\Gamma^{(1)^3P}_{2p_1},$$

$$\Gamma^{^3P_0}_{total}=2\Gamma^{(1)^3P}_{2p_1},$$

$$\Gamma^{^1S_0}_{total}=\frac{2}{3}\Gamma^{(1)^1S}_{2p_0}+\frac{4}{3}\Gamma^{(1)^1S}_{2p_1}.$$

It is seen, as said above, that $\Gamma^{^1D_{\pm 2}}_{total}\ll\Gamma^{^1D_{0,\pm 1}}_{total}$ since $\Gamma^{(1)^1D}_{2p_1}\ll\Gamma^{(1)^1D}_{2p_0}$ and $\Gamma^{^3P_0}_{total}\ll\Gamma^{^3P_{\pm 1}}_{total}$ since $\Gamma^{(1)^3P}_{2p_1}\ll\Gamma^{(1)^3P}_{2p_0}$. The coefficients (7) for the calculation of the one-electron escape probabilities $\Gamma^{(1)}$ are given in Table II. The total FI probabilities are presented in Fig. 3.

2. The C I $2s2p^3$ *configuration: Features of the case of a fractional parentage*

The configuration $2s2p^3$ produces the following terms: $^5S^o$, $^3S^o$, $^3P^o$, $^1P^o$, $^3D^o$, and $^1D^o$. We will now consider $^5S^o$ and $^3D^o$; the rest are autoionizing.

The $^3D^o$ term of $2s2p^3$ is actually a $^2D^o$ term of the $2p^3$ configuration over a vacancy $2s\ {}^2S$. The $2s$ electron does not participate in the escape, so all that is required to be known is the probability of the FI of the $2p^3\ {}^2D^o$ term components into the $2p^2\ {}^1D$ and ^3P parent terms. Hence all the angular factors are the same for the $2s2p^3\ {}^3D^o$ and $^1D^o$ terms; they both ionize[5] like $2p^3\ {}^2D^o$. Their binding energies are different, however; thus κ and B must be evaluated for the $^3D^o$ and $^1D^o$ terms independently. There is also another subtlety we would like to emphasize in particular: Due to the exchange interaction, all the true parent terms $2s2p^2\ {}^2D$, ^2P, and ^4P have different binding energies. This means that in the present calculations different κ should be used for different parents, even though *the same* initial term is ionized.

The FI probabilities for the components of $2p^3\ {}^2D^o$ (and thus for the $2s2p^3\ {}^3D^o$ and $^1D^o$ terms) are calculated directly from the general expression (9). For the sake of simplicity, $2s2p^2\ {}^2P$ and ^4P are considered to have the same energy. The result is

$$\Gamma^{^\sigma D^o_{\pm 2}}_{total}=3(G^{^2D}_{^3P})^2\Gamma^{(1)^\sigma D\rightarrow {}^{2,4}P}_{2p_1}+(G^{^2D}_{^1D})^2\{2\Gamma^{(1)^\sigma D\rightarrow {}^2D}_{2p_0}+\Gamma^{(1)^\sigma D\rightarrow {}^2D}_{2p_1}\},$$

$$\Gamma^{^\sigma D^o_{\pm 1}}_{total}=\frac{3}{2}(G^{^2D}_{^3P})^2\{\Gamma^{(1)^\sigma D\rightarrow {}^{2,4}P}_{2p_0}+\Gamma^{(1)^\sigma D\rightarrow {}^{2,4}P}_{2p_1}\}+\frac{1}{2}(G^{^2D}_{^1D})^2\{\Gamma^{(1)^\sigma D\rightarrow {}^2D}_{2p_0}+5\Gamma^{(1)^\sigma D\rightarrow {}^2D}_{2p_1}\},$$

$$\Gamma^{^\sigma D^o_0}_{total}=(G^{^2D}_{^3P})^2\{2\Gamma^{(1)^\sigma D\rightarrow {}^{2,4}P}_{2p_0}+\Gamma^{(1)^\sigma D\rightarrow {}^{2,4}P}_{2p_1}\}+3(G^{^2D}_{^1D})^2\Gamma^{(1)^\sigma D\rightarrow {}^2D}_{2p_1},$$

where $\sigma=1$ or 3. $G^{^2D}_{^3P}=1/\sqrt{2}$ is a fractional parentage coefficient for $np^{3\,2}D\rightarrow np^{2\,3}P$ and $G^{^2D}_{^1D}=-1/\sqrt{2}$ is a fractional parentage coefficient for $np^{3\,2}D\rightarrow np^{2\,1}D$. Note that, as discussed in Sec. IV A 1, a discrimination (lower FI rate) of certain term components occurs also here: for $^{1,3}D^o_{\pm 2}$ ionization into the $^{2,4}P$ parent term and for $^{1,3}D^o_0$ ionization into the ^2D parent term.

The calculation for the terms $^5S^o$ and $^3S^o$ is simpler since there is no fractional parentage. Both terms ionize as $2p^3\ {}^4S^o$ into $2p^{2\,3}P$. Thus it is readily observed that

$$\Gamma^{^\sigma S^o_0}_{total}=\Gamma^{(1)^\sigma S\rightarrow {}^{2,4}P}_{2p_0}+2\Gamma^{(1)^\sigma S\rightarrow {}^{2,4}P}_{2p_1},$$

---

[5] This is simply an illustration. In reality, the C I $2s2p^3\ {}^1D^o$ term is autoionizing and there is very little sense in assessing its FI probability.

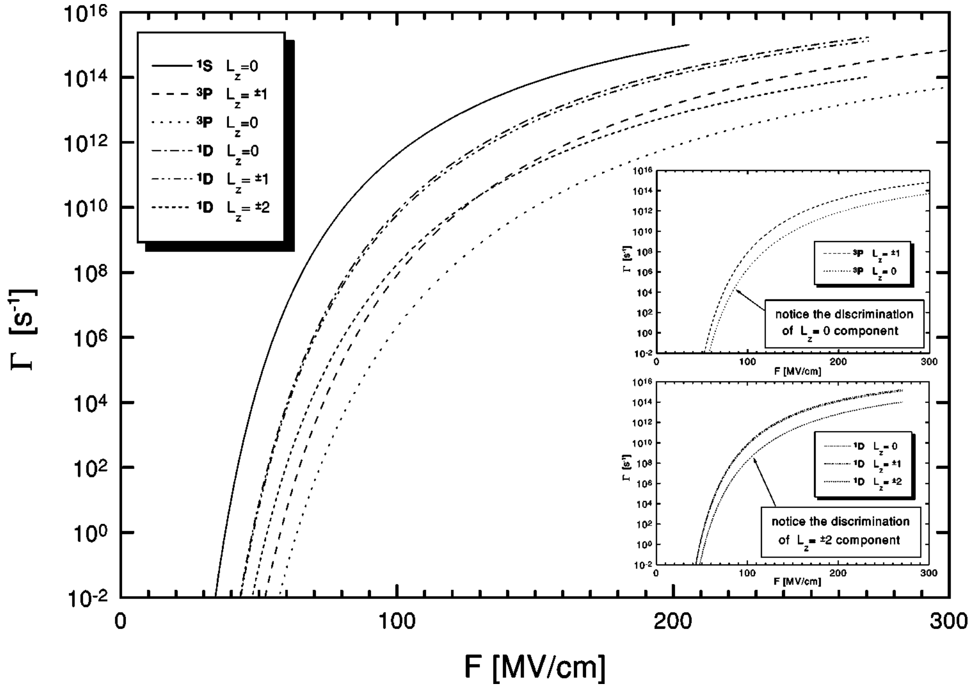

FIG. 3. Field ionization rates for the terms of the C I $2s^22p^2$ configuration. The insets emphasize the discrimination (lower field ionization rates) of the $L_Z=0$ component of the ^3P term and of the $L_Z=\pm 2$ component of the ^1D term.

where $\sigma=3$ or 5. It is important to note that although the C I $2s2p^3$ $^5S^o$ and $^3D^o$ terms are not autoionizing, they can still undergo a forced autoionization [31]. The results presented here are only for direct field ionization; therefore, they should be treated as partial decay rates into the C II $2s2p^2$ configuration (while forced autoionization produces the C II ground-state configuration $2s^22p$).

Table III gives the coefficients (7) for the one-electron escape probabilities $\Gamma^{(1)}$ for the terms $^5S^o$ and $^3D^o$ of the C I $2s2p^3$ configuration. The total FI rates for the terms C I $2s2p^3$ $^5S^o$ and $^3D^o$ are presented in Fig. 4.

3. Ba II 6p: The case of a significant spin-orbit interaction

For atoms with a high nuclear charge the spin-orbital interaction becomes significant. In this case, since l_z is no longer conserved, it is not appropriate to consider the rates of FI from l_z components of the level nl occupied by the optical electron. The FI rates in this case must be evaluated for jj_z components of the level nl, where j equals $l-\frac{1}{2}$ or $l+\frac{1}{2}$ unless $l=0$.

To evaluate the one-electron FI rates $\Gamma^{(1)}_{lsjj_z}$ from jj_z components of the level nl, we start again from expression (3), and take the one-electron wave function in the form

$$\psi_{lsjj_z}(\mathbf{r},\sigma)=\sum_{l_z,s_z}\begin{bmatrix} l & \frac{1}{2} & j \\ l_z & s_z & j_z \end{bmatrix}\psi_{lsl_zs_z}(\mathbf{r},\sigma).$$

The operator $\partial/\partial z$ commutes with both l_z and s_z, so expression (3) immediately yields

$$\Gamma^{(1)}_{lsjj_z}=\sum_{l_z,s_z}\left(\begin{bmatrix} l & \frac{1}{2} & j \\ l_z & s_z & j_z \end{bmatrix}\right)^2\Gamma^{(1)}_{nll_z}, \tag{12}$$

where, for consistency, the FI rates $\Gamma^{(1)}_{nll_z}$ from l_z-components of the level nl must all be evaluated with an average binding energy of the level nl rather than with the specific binding energies of the j components.

The Ba II $6p$ level may serve as an example for such a case. For this level, the splitting between the $j=\frac{1}{2}$ and $j=\frac{3}{2}$ components is approximately 5×10^{13} s^{-1}, which means that for FI rates comparable to or lower than that, mixing between l_z components is important and expression (12) must be used.

One may also notice that $\Gamma^{(1)}_{l=1,j=3/2,j_z=\pm3/2}=\Gamma^{(1)}_{l=1,l_z=\pm1}\ll\Gamma^{(1)}_{l=1,l_z=0}$ and thus the $(j=\frac{3}{2},j_z=\pm\frac{3}{2})$ component should

TABLE III. Coefficients (7) for the one-electron escape rates from the terms ^3D and ^5S of the C I configuration $2s2p^3$. In the fractional parentage case, the arrow points to the final term of the C II $2s2p^2$ configuration.

Initial-state term	Z_P	l	κ	B	$C_1(m=0)$	$C_1(m=1)$	$C_2(m=0)$	$C_2(m=1)$	C_3
C I $2s2p^3$ $^3D\rightarrow{}^{2,4}P$	1	1	0.916 83	0.8517	2.010	1.304	−1.181	−0.1814	0.5138
C I $2s2p^3$ $^3D\rightarrow{}^2D$	1	1	0.962 47	1.154	3.884	2.178	−1.078	−0.0780	0.5944
C I $2s2p^3$ ^5S	1	1	0.955 08	1.215	4.275	2.453	−1.094	−0.0941	0.5808

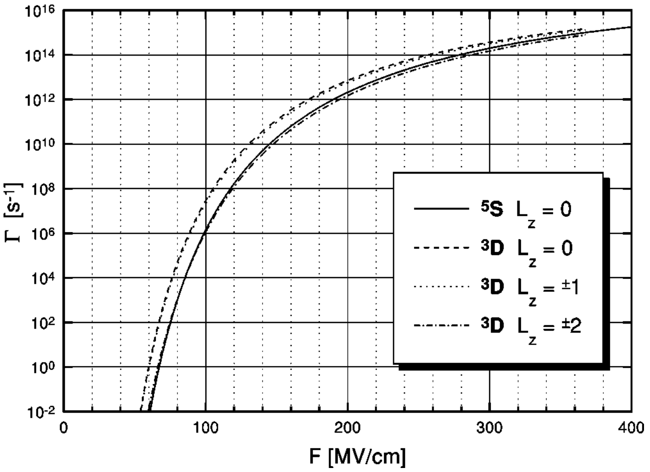

FIG. 4. Field ionization rates for the nonautoionizing terms of the C I $2s2p^3$ configuration.

ionize much more slowly than the $(j=\frac{3}{2}, j_z=\pm\frac{1}{2})$ and $(j=\frac{1}{2}, j_z=\pm\frac{1}{2})$ components. The coefficients (7) for the evaluation of $\Gamma^{(1)}_{nll_z}$ for the Ba II $6p$ level are given in Table I.

V. SUMMARY AND CONCLUSIONS

As yet, the probability of ionization by an electric field could only be calculated for the outer electron of atoms (ions) that have a single electron in their outer nl subshell and no inner-subshell vacancies. In this study, a general expression is presented for the probability of field ionization of atoms (ions) with an arbitrary electron configuration. In the limit of a single outer electron over closed nl subshells, the present expression for the FI probability coincides with published results [13]. In addition, we have given a recipe for a more accurate determination of the amplitude B of the single-electron wave-function asymptotics at large radii, which appears in the prefactor of the expressions for the FI probability. We have also pointed out the need for cautiousness in the application of the Hartree-Fock method of atomic structure modeling for the determination of the FI rates. The general expression we present predicts a nontrivial dependence of the FI probability on L_z (the projection of the total orbital angular momentum in the direction of external field). Furthermore, we point out the subtlety arising from possible FI into different terms of the parent ion in the fractional parentage case and show the way to account for it. The case of significant spin-orbit interaction is also analyzed.

In our treatment we use the WKB approximation; thus our expression is exact in the weak-external-field limit. However, calculating the FI probability under this limit is sufficient for most of the practical purposes since the ionization of atoms and ions, for fields within this limit, is already fast relative to the time scales of the radiative processes and of most of the plasma experiments.

The general expression derived was used to calculate the field ionization probability of several atoms and ions that are of interest for spectroscopic investigations, namely, for the ground and excited states of neutral carbon and lithium, and of singly ionized barium. Our results for the Li I $2p$ and $3d$ levels were found to be in agreement with results available from experiments on high-voltage ion diodes [1,2].

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APPENDIX

We write down an N-electron wave function as a Slater determinant:

$$\Phi=\frac{1}{\sqrt{N!}}\sum_{i=1}^{N!}(-1)^i\tilde{P}_i\{\psi_{\alpha_1}\cdots\psi_{\alpha_N}\}[(\mathbf{r}_1\sigma_1)\cdots(\mathbf{r}_N\sigma_N)], \tag{A1}$$

where $\tilde{P}$ is a permutation operator acting on the array $\alpha_1\cdots\alpha_N$ of one-electron wave functions. These one-electron wave functions are orthonormal:

$$\int d\mathbf{r}\, d\sigma\ \psi_{\alpha_1}\psi^*_{\alpha_2}=\delta_{\alpha_1,\alpha_2}. \tag{A2}$$

Any one of the electrons at $\mathbf{r}_1\cdots\mathbf{r}_N$ has a finite probability to escape. The escape probability of the electron at $\mathbf{r}_1$, for example, is

$$\Gamma_{\mathbf{r}_1}=\int dx_1dy_1d\sigma_1\mathrm{Im}\left\{\int d\mathbf{r}_2d\sigma_2\cdots\int d\mathbf{r}_Nd\sigma_N \times\Phi(\mathbf{r}_1\sigma_1\ldots\mathbf{r}_N\sigma_N)\frac{\partial}{\partial z_1}\Phi^*(\mathbf{r}_1\sigma_1\ldots\mathbf{r}_N\sigma_N)\right\}_{z_1>b}. \tag{A3}$$

The total FI rate is therefore

$$\begin{aligned}\Gamma&=\int dx_1dy_1J(x_1y_1z_1)+\int dx_2dy_2J(x_2y_2z_2)+\cdots\\&\quad+\int dx_Ndy_NJ(x_Ny_Nz_N)\\&=\int dx_1dy_1d\sigma_1\mathrm{Im}\left\{\int d\mathbf{r}_2d\sigma_2\cdots\int d\mathbf{r}_Nd\sigma_N\right.\\&\quad\left.\times\Phi(\mathbf{r}_1\sigma_1\cdots\mathbf{r}_N\sigma_N)\frac{\partial}{\partial z_1}\Phi^*(\mathbf{r}_1\sigma_1\cdots\mathbf{r}_N\sigma_N)\right\}_{z_1>b}+\cdots\\&\quad+\int dx_Ndy_Nd\sigma_N\mathrm{Im}\left\{\int d\mathbf{r}_1d\sigma_1\cdots\int d\mathbf{r}_{N-1}d\sigma_{N-1}\right.\\&\quad\left.\times\Phi(\mathbf{r}_1\sigma_1\cdots\mathbf{r}_N\sigma_N)\frac{\partial}{\partial z_N}\Phi^*(\mathbf{r}_1\sigma_1\cdots\mathbf{r}_N\sigma_N)\right\}_{z_N>b}.\end{aligned} \tag{A4}$$

We can regroup Φ to separate the part corresponding to the electron with the coordinates $\mathbf{r}_1\sigma_1$, i.e.,

$$\begin{aligned}
&\Phi(\mathbf{r}_1\sigma_1\cdots\mathbf{r}_N\sigma_N)\\
&\quad=\frac{1}{\sqrt{N!}}\sum_{i=1}^{N!}(-1)^i\tilde{P}_i\{\psi_{\alpha_1}\cdots\psi_{\alpha_N}\}[(\mathbf{r}_1\sigma_1)\cdots(\mathbf{r}_N\sigma_N)]\\
&\quad=\frac{1}{\sqrt{N!}}\sum_{k=1}^{N}(-1)^k\psi_{\alpha_k}(\mathbf{r}_1\sigma_1)\\
&\qquad\times\sum_{j=1}^{(N-1)!}(-1)^j\tilde{P}_j\{\psi_{\alpha_1}\cdots\psi_{\alpha_{k-1}}\psi_{\alpha_{k+1}}\cdots\psi_{\alpha_N}\}\\
&\qquad\times[(\mathbf{r}_2\sigma_2)\cdots(\mathbf{r}_N\sigma_N)]. \qquad\qquad (\mathrm{A5})
\end{aligned}$$

Let us now consider this expression for large z_1. As already said in Sec. II, only the optical electron wave function ψ_{opt} has a non-negligible amplitude outside the barrier (i.e., only such an electron may escape). Therefore, for $z_1>b$, only one term α_k, the term proportional to $\psi_{opt}\,(r_1,\sigma_1)$, survives out of all the terms. Thus, for large z_1,

$$\begin{aligned}
&\Phi(\mathbf{r}_1\sigma_1\cdots\mathbf{r}_N\sigma_N;z_1>b)\\
&\quad=\frac{1}{\sqrt{N!}}(-1)^{k_{opt}}\psi_{opt}(\mathbf{r}_1\sigma_1)\\
&\qquad\times\sum_{j=1}^{(N-1)!}(-1)^j\tilde{P}_j\{\psi_{p_1}\cdots\psi_{p_{N-1}}\}\\
&\qquad\times[(\mathbf{r}_2\sigma_2)\cdots(\mathbf{r}_N\sigma_N)], \qquad\qquad (\mathrm{A6})
\end{aligned}$$

where ψ_{p_n} is the nth one-electron parent wave function.

We can now calculate (A3), i.e., the first term in expression (A4):

$$\begin{aligned}
\Gamma_{\mathbf{r}_1}&=\int dx_1dy_1d\sigma_1\mathrm{Im}\left\{\int d\mathbf{r}_2d\sigma_2\cdots\int d\mathbf{r}_Nd\sigma_N\Phi(\mathbf{r}_1\sigma_1\cdots\mathbf{r}_N\sigma_N)\frac{\partial}{\partial z_1}\Phi^*(\mathbf{r}_1\sigma_1\cdots\mathbf{r}_N\sigma_N)\right\}_{z_1>b}\\
&=\frac{1}{N!}\int dx_1dy_1d\sigma_1\mathrm{Im}\left\{\psi_{opt}(\mathbf{r}_1\sigma_1)\frac{\partial}{\partial z_1}\psi^*_{opt}(\mathbf{r}_1\sigma_1)\right\}\\
&\quad\times\int d\mathbf{r}_2d\sigma_2\cdots\int d\mathbf{r}_Nd\sigma_N\left|\sum_{j=1}^{(N-1)!}(-1)^j\tilde{P}_j\{\psi_{p_1}\cdots\psi_{p_{N-1}}\}[(\mathbf{r}_2\sigma_2)\cdots(\mathbf{r}_N\sigma_N)]\right|^2\\
&=\frac{1}{N!}\int dx_1dy_1d\sigma_1\mathrm{Im}\left\{\psi_{opt}(\mathbf{r}_1\sigma_1)\frac{\partial}{\partial z_1}\psi^*_{opt}(\mathbf{r}_1\sigma_1)\right\}(N-1)!=\frac{1}{N}\Gamma^{(1)}.
\end{aligned}$$

The other $N-1$ terms in expression (A4) will yield precisely the same result; thus

$$\Gamma=N\Gamma_{first\ \ term}\equiv\Gamma^{(1)}.$$

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