Properties of Rydberg autoionizing states in electric fields

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The linear-Stark-effect approximation is employed to investigate the effects of electric fields on autoionizing doubly excited atomic states corresponding to relatively large values of the outer-electron principal quantum number n. By assuming that a statistical distribution of the inner-electron magnetic sublevels has been established, simple expressions are derived which relate the autoionization and radiative transition rates in the presence of an electric field to the respective field-free rates. It is pointed out that the multiphoton laser excitation of the doubly excited states can give rise to a nonstatistical distribution of the magnetic sublevels and to complex interference terms involving transition amplitudes associated with different values of the outer-electron angular momentum quantum number l. The results of calculations are presented for the autoionization and radiative-transition rates which play the most important role in the dielectronic recombination of the Li-like Fe^{+23} ion through the $2p \rightarrow 2s$ inner-electron transition, where the contributions from large-n values are particularly important. In these calculations it is assumed that the magnetic sublevels are statistically populated and only the simple expressions for the transition rates are employed. The effects of the electric field on the dominant (inner-electron) radiative decay rate can be neglected, but the electric field mixing of the outer-electron l substates substantially increases the autoionization rates from the higher-l sublevels.

I. INTRODUCTION

The Stark energy-level structure of doubly excited autoionizing atomic states corresponding to relatively large values of the outer-electron principal and angular momentum quantum numbers n and l is expected to be analogous to that for the corresponding Rydberg bound states. The calculation of the transition rates for various spontaneous decay processes, however, represents a more complex problem for autoionizing states. In particular, the autoionization rates can be significantly altered by the field-induced mixing of the unperturbed l substates. In this investigation, we do not attempt to develop a comprehensive theory of the electric field effects, which should be capable of describing strong-field phenomena involving the mixing of outer-electron l substates corresponding to many different values of n, including the continuum states. Instead, this investigation has been limited to the development of a detailed theory based on the linear-Stark-effect approximation, which describes the electric field mixing of only the l substates corresponding to a given value of n. This approximation is expected to be valid for high l and also for high residual ionic charge Z.

The effects of electric fields on the spectral features associated with autoionizing resonances is a subject of considerable current experimental interest. The Stark-switching technique originally suggested by Freeman and Kleppner[1] has been incorporated into a three-photon laser excitation procedure by Cooke *et al.*[2] to populate the doubly excited autoionizing states of Sr corresponding to large values of l, which are normally inaccessible owing to the field-free electric-dipole optical selection rules. In a closely related experiment, Freeman and Bjorklund[3] were able to observe the effects of a static electric field on the multiphoton ionization line shapes and widths associated with Rydberg autoionizing resonances. They have given particular emphasis to the strong field dependence of the spectra for field strengths which cause a substantial mixing of l substates corresponding to different values of n. Over a limited range of field strengths, some of their spectral data may be understandable within the framework of the linear-Stark-effect approximation, in which the resonances are assumed to be well separated and the widths, although different from the field-free values, are predicted to be independent of the field.

Rydberg autoionizing states can play the most important role in the dielectronic recombination process described by Burgess,[4] which is often the dominant recombination process for multiply ionized nonhydrogenic atomic ions in high-temperature plasmas. In this process a doubly excited autoionizing state j, nl is formed by radiationless capture (the inverse of autoionization), and recombination is accomplished through a stabilizing radiative transition to a singly excited bound state by means of the inner-electron deexcitation $j \rightarrow i$. In a comprehensive monograph devoted to the broadening of atomic spectral lines by plasmas, Griem[5] points out that the radiating atomic system is subjected to a distribution of microscopic electric fields which is produced by the surrounding charged particles. The action of the quasistatic ion-produced electric microfield causes a mixing of the nearly degenerate l substates which substantially increases the radiationless capture (and the corresponding autoionization) rates for the normally inaccessible higher-l substates, which have negligible capture and autoionization rates in a field-free environment. The linear-Stark-effect approximation, which is the basis of practically all Stark-broadening profile calculations[5] which take into account ion-produced fields, has been employed[6] to investigate this effect, and a significant enhancement is predicted in the total dielectronic recombination rate obtained by adding the individual l contributions for a given n.

In this investigation, the linear-Stark-effect approximation is fully exploited in order to gain a simple physical understanding of some of the effects of a uniform static electric field on the radiative and autoionization rates which determine the resonance profiles in absorption and emission spectra. The autoionizing resonances and the adjacent continua will be treated as separate states, and the resonance-level separations will be assumed to be large in comparison with the total widths due to all spontaneous autoionization and radiative-decay processes. Seaton[7] had demonstrated that the accuracy of the isolated-resonance approximation improves with increasing Z, provided that the dominant contribution to the total width arises from autoionization. Shore[8] has shown that the total dielectronic recombination rates can be evaluated by treating those overlapping resonances with different angular momentum quantum numbers as separate states. Finally, the isolated-resonance approximation may be particularly appropriate when it is employed in conjunction with the linear-Stark-effect approximation, in which the resonance-level separations have an additional displacement which increases linearly with the field strength whereas the total widths, although different from the field-free values, are independent of the field.

In Sec. II, we present a detailed description of the electric-field-induced transformation of the field-free outer-electron states and a discussion of the various conditions which determine the validity of the linear-Stark-effect approximation. The most significant result of this investigation is presented in Sec. III, where we derive a simple expression relating the autoionization rate in the presence of an electric field to the field-free rates for the individual l substates. In this derivation, it is assumed that a statistical distribution of the inner-electron magnetic sublevels has been established. However, we also present a more general expression which is appropriate to a nonstatistical distribution of these magnetic sublevels, which can result from the multiphoton laser excitation of the autoionizing states. The radiative-transition rates in the presence of an electric field are treated in Sec. IV, and it is emphasized that the dominant radiative-decay process for the Rydberg autoionizing states involves the inner-electron transition which is unaffected by the presence of the electric field. The theory developed in this investigation is illustrated in Sec. V by presenting the results of calculations for the autoionization and radiative-transition rates which play the most important role in the dielectronic recombination of the Li-like Fe^{23+} ion through the $2p\rightarrow 2s$ inner-electron transition. In these calculations it is assumed that the magnetic sublevels are statistically populated and the autoionization rates are obtained by evaluating the simple expression. Finally, our conclusions are presented in Sec. VI.

II. ELECTRIC FIELD TRANSFORMATION

In this section we describe the application of quantum-mechanical perturbation theory techniques to investigate the effects of a uniform static electric field $\vec{F}$ on the doubly excited autoionizing states j, nlm. Particular emphasis will be given to relatively large values of the outer-electron principal quantum number n. It is well known that the angular momentum l is no longer a good quantum number, because the presence of the electric field destroys the spherical symmetry. However, the projection m, which is defined with respect to the direction of the electric field, remains a good quantum number. We note that the nonzero values of m give rise to a twofold (Kramers) degeneracy of the outer-electron states which is in addition to the twofold degeneracy associated with the electron spin. The excited state j of the residual ion is assumed to be a low-lying state which is practically unaffected by the presence of the electric field.

In the present investigation we will take into account the electric-field-induced mixing of only the nearly degenerate outer-electron l substates corresponding to a given value of n. The appropriate transformation of the field-free l substates has the form

$$|n\lambda m\rangle = \sum_{l=|m|}^{n-1} |nlm\rangle\langle nlm|n\lambda m\rangle , \quad (1)$$

where the quantum number λ, which replaces l

in the presence of the electric field, can have the integer values from 0 to $n-|m|-1$. The transformation coefficients $\langle nlm|n\lambda m\rangle$ together with the Stark energy eigenvalues $E(n\lambda m)$ are to be determined by solving the set of homogeneous linear equations[9]

$$\sum_{l=|m|}^{n-1}\{\langle nl'm|-\vec{D}\cdot\vec{F}|nlm\rangle - [E(n\lambda m)+Z^2E_H(n-\Delta_{lm})^{-2}]\delta(l',l)\}\times\langle nlm|n\lambda m\rangle=0,\quad l'=|m|,\; n-1, \tag{2}$$

where E_H is the hydrogen ground-state ionization energy and $\vec{D}$ denotes the electric-dipole moment operator.

The field-free states nlm are eigenstates of a single-electron Hamiltonian which describes the motion of the outer electron in the potential associated with the residual ion in the excited state j. This potential, which is not spherically symmetric, is usually approximated by a function of only the radial coordinate, and the departure of the field-free energy eigenvalues $E(nlm)$ from their nonrelativistic hydrogenic values is conventionally taken into account through the inclusion of the quantum defect Δ_l which is independent of m. However, the multiphoton laser excitation procedure employed in recent experiments[2,3] results in a nonstatistical distribution of the inner-electron magnetic sublevels for which the ionic-core potential cannot be represented by a spherically symmetric function. A noncentral potential prevents the separation of the wave equation in spherical coordinates and introduces into Eq. (2) matrix elements which are nondiagonal in both l and m. We have taken into account only the diagonal matrix element of the ionic-core potential by including the quantum defects Δ_{lm} which depend on m as well as on l.

The nonrelativistic contribution to the quantum defect Δ_{lm} decreases as $1/Z$ with increasing residual ionic charge Z and falls off very rapidly with increasing l. Accordingly, a good first approximation for large Z and l is obtained by neglecting the quantum defects and approximating the matrix elements of the dipole interaction by the hydrogenic values, which are given by

$$\langle nlm|-\vec{D}\cdot\vec{F}|nl'm\rangle=ea_0|\vec{F}|\delta(l',l\pm1)\times\tfrac{3}{2}\left(\frac{n}{Z}\right)(n^2-l_>^2)^{1/2}\left(\frac{l_>^2-m^2}{4l_>^2-1}\right)^{1/2}, \tag{3}$$

where $l_>$ denotes the larger of l and l'. The assumption of complete degeneracy with respect to l and m leads to the well-known linear Stark effect for which the matrix eigenvalue problem given by Eq. (2) has an exact solution. It is now convenient to introduce the electric quantum number q which is related to the quantum number λ by $q=n-2\lambda-|m|-1$ and to the parabolic quantum numbers n_1 and n_2 (defined by Bethe and Salpeter[10]) by $q=n_1-n_2$.

The transformation coefficients may be expressed in terms of the Wigner 3-j symbols by means of the relationship[11]

$$\langle nlm|n\lambda m\rangle=(-1)^{\frac{1+m-q-n}{2}}(2l+1)^{1/2}\times\begin{pmatrix}\frac{n-1}{2} & \frac{n-1}{2} & l\\ \frac{m-q}{2} & \frac{m+q}{2} & -m\end{pmatrix}. \tag{4}$$

The energy eigenvalues are given by the expression[10]

$$E(n\lambda m)=-Z^2E_H n^{-2}+\tfrac{3}{2}(n/Z)\,qea_0\,|\vec{F}| \tag{5}$$

and are independent of m. In the linear-Stark-effect approximation, the electric field causes a splitting of the n^2 degenerate outer-electron sublevels into $2n-1$ Stark sublevels which is linearly proportional to the field strength and produces a mixing of the unperturbed l substates which is independent of the field.

The linear-Stark-effect approximation is expected to become a valid description of the electric field mixing when the Stark displacement which is obtained from second-order perturbation theory exceeds $\frac{1}{2}$ the field-free separations between the neighboring l sublevels. The second-order (quadratic-Stark) shift $\Delta E^{(2)}(nlm)$ may be estimated in this field-strength region by retaining in the summation over intermediate unperturbed eigenstates only the two adjacent opposite-parity eigenstates corresponding to $l'=l\pm1$. If the dipole matrix elements are approximated by their hydrogenic values, we obtain the well-known Unsold formula[10]

$$\Delta E^{(2)}(nlm)=-\frac{9}{4}\frac{n^2}{Z^2}e^2a_0^2|\vec{F}|^2\left(\frac{[n^2-(l+1)^2][(l+1)^2-m^2][4(l+1)^2-1]^{-1}}{E(nlm)-E(n,l+1,m)}+\frac{[n^2-l^2][l^2-m^2][4l^2-1]^{-1}}{E(nlm)-E(n,l-1,m)}\right). \tag{6}$$

The desired lower limit on $|\vec{F}|$, above which the linear-Stark-effect approximation is expected to be valid, is obtained from the condition

$$\Delta E^{(2)}(nlm) \geq \tfrac{1}{2}\,|E(n, l+1, m) - E(nlm)|$$

$$\sim \left(\frac{Z^2}{2n^3}\right)\left(\frac{e^2}{a_0}\right)|\Delta_{lm} - \Delta_{l+1,m}| \,. \qquad (7)$$

Freeman and Kleppner[1] have investigated the relative importance of various contributions to the quantum defects for high-angular-momentum bound states of alkali atoms. They pointed out that the leading relativistic term, which is approximately $\alpha^2 Z^2/2l$, can play a more important role for large l than the long-range second-order dipole interaction term, which decreases as l^{-5}. Rydberg autoionizing states corresponding to a non-S ionic-core state represent a more complex problem, because additional long-range contributions can occur in first-order perturbation theory. The first-order quadrupole contribution associated with the single-electron core state $j = n_j l_j m_j$ is found to be given by

$$\Delta_{lm}^{(ql)} = Z\left(\frac{3m^2 - l(l+1)}{(l)(l+1)(2l+1)(2l+3)(2l-1)}\right) \times \left(\frac{n_j^2}{2Z_j^2}\right)\frac{[5n_j^2+1-3l_j(l_j+1)][3m_j^2 - l_j(l_j+1)]}{(2l_j+3)(2l_j-1)} \qquad (8)$$

and is the leading nonvanishing first-order contribution to Δ_{lm}. This contribution vanishes when averaged over either m_j or m but will be nonvanishing whenever a nonstatistical distribution of the magnetic sublevels is excited. In the multiphoton excitation of the doubly excited states by laser light which is linearly polarized along the electric field direction, only the substate for which both m_j and m are zero can be populated. The nonvanishing first-order quadrupole contribution, which decreases only as l^{-3} with increasing l, may be more important for large l than the second-order dipole term.

An upper limit on $|\vec{F}|$ is obtained from the condition

$$\tfrac{3}{2}\left(\frac{n}{Z}\right)(n - |m| - 1)\, e a_0\, |\vec{F}| \leq \left(\frac{Z^2}{2n^3}\right)\left(\frac{e^2}{a_0}\right), \qquad (9)$$

which follows from the requirement that the largest linear Stark shift must not exceed $\frac{1}{2}$ the separation between sublevels belonging to different values of n. This criterion was introduced by Inglis and Teller[12] in connection with the merging of the higher members of a spectral line series which results from the action of the quasistatic electric microfields in a plasma. For field strengths exceeding the critical value, the mixing of substates corresponding to different values of n can no longer be neglected. Equations (6)–(9) suggest that the validity region of the linear-Stark-effect approximation for a given n increases with increasing Z and l.

A well-known phenomena, which is associated with the breakdown of the linear-Stark-effect approximation, is field-induced ionization. According to classical mechanics, field-induced ionization can occur when the outer-electron level lies above the potential barrier in the field direction. This barrier is lower than the field-free ionization threshold by the amount $2e(|\vec{F}|\, eZ)^{1/2}$. The threshold for field-induced ionization is well defined, because the quantum-mechanical tunneling effect[13] is usually significant only over an extremely narrow range of field strengths. If the Stark shifts are now ignored, the effective threshold for field-induced ionization is found to be given by

$$|\vec{F}| = (Z^3/16n^4)(e/a_0^2)\,, \qquad (10)$$

which is above the Inglis-Teller limit for $n > 5$. This argument indicates that field-induced ionization can be neglected within the validity region of the linear-Stark-effect approximation.

A closely related phenomena, which is also associated with the breakdown of the linear-Stark-effect approximation, is the anomalous field-induced ionization of certain Stark states of sodium observed by Littman *et al.*[14] and attributed to the mixing of sublevels corresponding to different n values.

The discussion given in this section is based on the assumption that the field strength is sufficiently large to break down the coupling between the outer-electron angular momentum l and that of the ionic core. In the following sections, the transition rates from the doubly excited states d will therefore be evaluated in the uncoupled representation $d = j, n\lambda m$.

III. AUTOIONIZATION RATES

In this section, we employ the linear-Stark-effect approximation discussed in Sec. II in order to derive an expression for the rate of the radiationless transition from the Stark doubly excited state $d = j, n\lambda m m_s$ to the continuum state $i, \vec{k}_i m_{s_i}$ having the same energy. The outer-electron continuum state is specified by giving the ejected electron momentum vector $\vec{k}_i$, which is associated with the formation of the residual ion in the deexcited state i, and the electron spin-projection m_{s_i}. For completeness, we have now introduced the outer-electron spin-projection quantum numbers m_s and m_{s_i}. According to first-order perturbation theory, the radiationless transition rate is given by

$$A_a(d\to i,\vec{k}_i m_{s_i})=\frac{2\pi}{\hbar}\left|\langle j,n\lambda m m_s|V|i,\vec{k}_i m_{s_i}\rangle\right|^2, \qquad (11)$$

where V is the electrostatic interaction between the outer electron and the ionic-core electrons.

The ionic-core eigenstates will be specified in the LS-coupling representations

$$i=\gamma_i L_i M_{L_i} S_i M_{S_i}, \qquad (12)$$

$$j=\gamma_j L_j M_{L_j} S_j M_{S_j}, \qquad (13)$$

where γ_i and γ_j are used to denote all additional quantum numbers, including the principal quantum numbers and the parities. The core eigenstates will be assumed to be sufficiently low-lying states for which the effects of the electric field can be neglected.

In the case of the lowest-lying excited state j, the final state i which is formed in the autoionization process must be the ground state of the residual ion. For more highly excited states j, autoionization into a lower excited state i is energetically allowed and may be the most probable autoionization process. The inclusion of autoionization into an excited state of the recombining ion has been found[15] to result in a substantial reduction in the dielectronic recombination rates for certain ionization stages, because radiationless capture from excited states i can almost always be neglected. This point is brought up in order to emphasize the importance of giving consideration to all energetically allowed final ionic states in the determination of the total contribution to the width due to autoionization.

The desired expression for the autoionization rate in the presence of an electric field can be conveniently derived without unnecessary approximations by employing general symmetry relationships. The derivation is accomplished by expanding the initial and final states of the combined system in terms of eigenstates of the total orbital angular momentum operator $\vec{L}$ and of the total spin angular momentum operator $\vec{S}$. If the ejected electron state is first expanded in terms of its partial-wave components and the additions of the various angular momenta are expressed in terms of the Wigner 3-j symbols, the final continuum-state expansion is obtained in the form[16]

$$|i,\vec{k}_i m_{s_i}\rangle=\sum_{LM_L}\sum_{SM_S}\sum_{l_i m_i}\exp\left[i\left(\frac{l_i\pi}{2}-\sigma(l_i)\right)\right]Y^*_{l_i m_i}(\vec{k}_i)(-1)^{l_i-L_i-M_L+1/2-S_i-M_S}[(2L+1)(2S+1)]^{1/2}$$
$$\times\begin{pmatrix}L_i & l_i & L\\ M_{L_i} & m_i & -M_L\end{pmatrix}\begin{pmatrix}S_i & \frac{1}{2} & S\\ M_{S_i} & m_{s_i} & -M_S\end{pmatrix}|\gamma_i L_i S_i, k_i l_i, LSM_L M_S\rangle, \qquad (14)$$

where $\sigma(l_i)$ is the Coulomb phase shift. At very large distances between the ejected electron and the residual ion, the wave functions associated with the total angular momentum eigenstates $\gamma_i L_i S_i, k_i l_i, LSM_L M_S$ have the asymptotic form corresponding to the incoming spherical-wave boundary condition,[17] which is expressed in terms of the adjoint of the scattering matrix describing the multichannel electron-ion collision problem. These wave functions are assumed to be normalized per unit electron energy interval with functions corresponding to different continuum channels being orthogonal. In the linear-Stark-effect approximation described in the preceding section, the analogous expansion for the initial doubly excited state $d=j, n\lambda m m_s$ is given by

$$|j,n\lambda m m_s\rangle=\sum_{LM_L}\sum_{SM_S}\sum_{l}\langle nlm|n\lambda m\rangle(-1)^{l-L_j-M_L+1/2-S_j-M_S}[(2L+1)(2S+1)]^{1/2}$$
$$\times\begin{pmatrix}L_j & l & L\\ M_{L_j} & m & -M_L\end{pmatrix}\begin{pmatrix}S_j & \frac{1}{2} & S\\ M_{S_j} & m_s & -M_S\end{pmatrix}|\gamma_j L_j S_j, nl, LSM_L M_S\rangle. \qquad (15)$$

After the expansions (14) and (15) have been introduced into the expression for the autoionization rate, the Wigner-Eckart theorem can be employed to separate the dependences on the angular momentum projection quantum numbers. We will derive an expression for the total autoionization rate, which is defined by performing an integration over the ejected electron angles $\vec{k}_i$ and summations over the final-state projection quantum numbers M_{L_i}, M_{S_i}, and m_{s_i}. It is customary to assume that a statistical distribution of the magnetic sublevels in the initial doubly excited state has been established and to carry out an average over the corresponding projection quantum numbers M_{L_j}, M_{S_j}, m, and m_s. In order to describe autoionization following the multiphoton laser excitation of a nonstatistical distribution of the initial magnetic sublevels, it will be necessary to retain the dependences on M_{L_j} and m (autoionization will be assumed to occur before the polarization acquired in optical excitation can be altered by spin-orbit interactions, so that the averages over M_{S_j} and m_s can still be performed).

The autoionization rate from the doubly excited state with definite values of the projection quantum numbers M_{L_j} and m can be expressed in terms of the reduced matrix elements

$$(\gamma_j L_j S_j, nl, LS \| V \| \gamma_i L_i S_i, k_i l_i, LS)$$

in the form

$$\begin{aligned} A_a(\gamma_j L_j M_{L_j} S_j, n\lambda m \to \gamma_i L_i S_i, k_i) = \frac{2\pi}{\hbar} \sum_{l} \sum_{l'} \sum_{l_i} \sum_{\Lambda} \sum_{L} \sum_{S} (2\Lambda+1)(-1)^{L+\Lambda+M_{L_j}+m} \langle nlm | n\lambda m\rangle \langle nl'm | n\lambda m\rangle^* \\ \times \begin{pmatrix} l & l' & \Lambda \\ m & -m & 0 \end{pmatrix} \begin{pmatrix} L_j & L_j & \Lambda \\ -M_{L_j} & M_{L_j} & 0 \end{pmatrix} \begin{Bmatrix} L_j & l & L \\ l' & L_j & \Lambda \end{Bmatrix} \\ \times (\gamma_j L_j S_j, nl, LS \| V \| \gamma_i L_i S_i, k_i l_i, LS) \\ \times (\gamma_j L_j S_j, nl', LS \| V \| \gamma_i L_i S_i, k_i l_i, LS)^* , \end{aligned} \tag{16}$$

where the 6-j symbol is obtained from the use of a standard angular momentum recoupling relationship and the asterisk denotes the complex conjugate. It is apparent that the coherent excitation of the initial magnetic sublevels introduces a complex interference between transition amplitudes associated with different values of l.

If the average over M_{L_j} is now performed, a particularly simple relationship between the autoionization rates $A_a(\gamma_j L_j S_j, n\lambda m \to \gamma_i L_i S_i, k_i)$ in the presence of an electric field and the field-free values $A_a(\gamma_j L_j S_j, nl \to \gamma_i L_i S_i, k_i)$ is obtained in the form

$$\begin{aligned} A_a(\gamma_j L_j S_j, n\lambda m \to \gamma_i L_i S_i, k_i) \\ = \sum_{l=|m|}^{n-1} |\langle nlm | n\lambda m\rangle|^2 A_a(\gamma_j L_j S_j, nl \to \gamma_i L_i S_i, k_i) , \end{aligned} \tag{17}$$

which is independent of the field strength. This field independence is the result of the linear-Stark-effect approximation for the outer electron in the doubly excited state and also the neglect of the electric field effects on the continuum electron in the final state. The discussion at the end of Sec. II suggests that the neglect of the electric field effects on the continuum states is consistent with the linear-Stark-effect approximation. At field strengths for which the linear-Stark-effect approximation is no longer valid, significant effects are expected to occur due to the influence of the electric field on the continuum states.

The field-free autoionization rates are more generally evaluated in the coupled angular momentum representation $\gamma_d L_d S_d$, in which the ionic-core angular momenta L_j and S_j are coupled to the respective outer-electron angular momenta to form the total orbital and spin angular momenta L_d and S_d. The field-free autoionization rates in the uncoupled representation can be evaluated by employing the relationship

$$\begin{aligned} A_a(\gamma_j L_j S_j, nl \to \gamma_i L_i S_i, k_i) = \frac{1}{2(2l+1)(2S_j+1)(2L_j+1)} \\ \times \sum_{L_d} \sum_{S_d} (2L_d+1)(2S_d+1) A_a(\gamma_d L_d S_d \to \gamma_i L_i S_i, k_i) , \end{aligned} \tag{18}$$

which is analogous to the relationship[18] between the partial-wave cross sections for the closely related electron-impact excitation process and the multichannel collision S-matrix elements which are defined in the coupled representation.

The autoionization rates in the coupled angular momentum representation are given in terms of the reduced matrix elements of the electrostatic interaction V by the expression

$$A_a(\gamma_d L_d S_d \to \gamma_i L_i S_i, k_i) = \frac{2\pi}{\hbar} \frac{1}{(2S_d+1)(2L_d+1)} \sum_{l_i} |(\gamma_j L_j S_j, nl, L_d S_d \| V \| \gamma_i L_i S_i, k_i l_i, L_d S_d)|^2 . \tag{19}$$

For large values of n, the autoionization rates can be obtained from the threshold ($k_j^2=0$) values of the partial-wave cross sections $\sigma(\gamma_i L_i S_i, k_i l_i \to \gamma_j L_j S_j, k_j l_j)$ describing the electron-impact excitation process $X^{+(Z)}(i)+e^-(k_i l_i) \to X^{+(Z)}(j)+e^-(k_j l_j)$. The relationship obtained from quantum defect theory by Seaton[7] may be expressed in the form

$$A_a(\gamma_j L_j S_j, nl \to \gamma_i L_i S_i, k_i) = \left(\frac{E_H}{\hbar}\right)\left(\frac{2Z^2}{\pi n^3}\right)\frac{(2S_i+1)(2L_i+1)}{2(2S_j+1)(2L_j+1)(2l+1)}\left(\frac{E_j-E_i}{E_H}\right)\sum_{l_i}\frac{\sigma(\gamma_i L_i S_i, k_i l_i \to \gamma_j L_j S_j, k_j l_j)}{\pi a_0^2}\bigg|_{k_j^2=0} . \tag{20}$$

If the collisional excitation process is assumed to occur primarily as a result of the dipole part of the electrostatic interaction, the threshold partial-wave cross sections may be expressed in terms of the transition oscillator strengths $f(\gamma_i L_i S_i \to \gamma_j L_j S_j)$ in the form

$$\sigma(\gamma_i L_i S_i, k_i l_i \to \gamma_j L_j S_j, k_j l_j)\,|_{k_j^2=0} = \frac{8\pi^2 a_0^2}{\sqrt{3}}\left(\frac{E_H}{E_j-E_i}\right)^2 f(\gamma_i L_i S_i \to \gamma_j L_j S_j)\, g(k_i l_i, k_j l_j)\,|_{k_j^2=0} . \tag{21}$$

The well-known n^{-3} dependence of the autoionization rates is directly revealed by Eq. (20). A rapid decrease with increasing l is also anticipated, but the precise form of the l dependence is more difficult to derive. The derivation of the l dependence may be attempted in the long-range dipole (Bethe) approximation, in which the effective free-free partial-wave Gaunt factor $g(k_i l_i, k_j l_j)$ is defined in terms of the continuum-electron radial wave functions $F_{k_i l_i}(r)$ by

$$g(k_i l_i, k_j l_j) = \frac{2\sqrt{3}}{\pi} l_> \delta(l_j, l_i \pm 1) \times \left| \int_0^\infty \frac{dr}{r^2} F_{k_i l_i}(r) F_{k_j l_j}(r) \right|^2 . \tag{22}$$

In the case of a $\Delta n_i=0$ transition of the ionic core, the radial integral can be evaluated in the Coulomb approximation by setting $k_i^2=k_j^2$. This approximation leads to the result[19]

$$g(k_i l_i, k_j l_j)\,|_{k_i^2=0} = \frac{2\sqrt{3}}{\pi} l_> \delta(l_j, l_i \pm 1)\left(l_>^2 + \frac{Z^2 E_H}{E_j - E_i}\right)^{-1} , \tag{23}$$

which predicts a much slower decrease with l than distorted-wave calculations[20] in which the complete dipole contribution is evaluated.

IV. RADIATIVE-DECAY RATES

It has been pointed out by Shore[8] that the total radiative-decay rate from the doubly excited state can be written as the sum of the rates describing the radiative decay of the inner- and outer-electron states. In the presence of an electric field, it is advantageous to further subdivide the outer-electron decay processes according to the importance of the electric field effect on the final state. Because of the rapid n^7 increase of the quadratic Stark displacements with increasing n, we can neglect the effect of the electric field on those final states f of the combined electron-ion system which correspond to the decay of the outer electron into a low-lying state. Because of the dependence of the radiative-decay rate on the third power of the transition frequency, these processes are almost always more probable than those involving transitions between the neighboring Stark sublevels of the outer electron.

The total radiative-decay rate $A_r(d)$ from the doubly excited state $d=j, n\lambda m m_s$ is, therefore, expressed as the sum of three different contributions in the form

$$A_r(d) = \sum_i A_r(j, n\lambda m m_s \to i, n\lambda m m_s) + \sum_f A_r(j, n\lambda m m_s \to f) + \sum_{n'\lambda' m'} A_r(j, n\lambda m m_s \to j, n'\lambda' m' m_s) . \tag{24}$$

The decay rates $A_r(j, n\lambda m m_s \to i, n\lambda m m_s)$ describe the spontaneous radiative transitions between the low-lying ionic-core states, which are assumed to be unaffected by the presence of the electric field. The radiative-transition frequency is slightly shifted from the position of the ionic-core transition $j \to i$ due to the presence of the outer electron, and in the absence of the electric field this shift is expressible in terms of the difference between the quantum defects associated with the initial and final ionic-core states. However, this effect can be neglected in the evaluation of the radiative-decay rate. We will therefore make the customary approximation

$$A_r(j, n\lambda m m_s \to i, n\lambda m m_s) = A_r(j \to i) , \tag{25}$$

in which the presence of the outer electron is ignored. In contrast to the outer-electron radiative-decay rates which decrease as n^{-3} with increasing n, the inner-electron radiative-decay rate is independent of n. Accordingly, the dominant radiative-decay process for the Rydberg autoionizing states corresponding to large values of n is expected to be the inner-electron transition, which is unaffected by the presence of the electric field.

The decay rates $A_r(j, n\lambda m m_s \to f)$, which describe the spontaneous radiative transitions of the outer electron into a low-lying final state f of the combined electron-ion system, become negligible in comparison with the inner-electron transition rate for large n. However, the dielectronic recombination processes corresponding to the outer-electron radiative transitions of the type $1s2pnp \to 1s^2 2p$ with $n=3$ and 4 give rise to particularly prominant satellites near the higher-n $1snp \to 1s^2$ resonance lines of the helium like ions of high-Z elements in plasmas.[21] In order to evaluate the intensities of these satellite lines in dense plasmas, where they are often comparable to those of the associated higher-n resonance emission lines, an expression for the outer-electron radiative-decay rate will be required. The expression for the outer-electron radiative-decay rate can be derived in LS coupling through the use of Eq. (15) together with the Wigner-Eckart theorem. Assuming that a statistical distribution of the initial magnetic sublevels M_{L_j}, M_{S_j}, and m_s has been excited, the average radiative-decay rates $A_r(\gamma_j L_j S_j, n\lambda m \to \gamma_f L_f S_f)$ in the presence of an electric field are given in terms of the field-free rates $A_r(\gamma_j L_j S_j, nl \to \gamma_f L_f S_f)$ by the expression

$$A_r(\gamma_j L_j S_j, n\lambda m \to \gamma_f L_f S_f)\,, \\ = \sum_{l=|m|}^{n-1} |\langle nlm | n\lambda m\rangle|^2 A_r(\gamma_j L_j S_j, nl \to \gamma_f L_f S_f)\,, \quad (26)$$

which is analogous to the result expressed by Eq. (17) for the autoionization rates. The field independence of this expression is the result of the linear-Stark-effect approximation for the outer electron in the doubly excited state and the neglect of the Stark shift in the emitted-photon frequency. Although the Stark shift associated with the radiative decay of the outer electron can be neglected in the evaluation of the decay rate, its effect on the emitted-photon spectrum is expected to be more important than the effect of the very small shift associated with the radiative decay of the inner electron.

The field-free radiative transition rates $A_r(\gamma_j L_j S_j, nl \to \gamma_f L_f S_f)$, like the corresponding autoionization rates, are more generally evaluated in terms of the radiative-decay rates $A_r(\gamma_d L_d S_d \to \gamma_f L_f S_f)$ describing transitions between eigenstates of the combined system which are specified in the coupled angular-momentum representation. The transition rates $A_r(\gamma_j L_j S_j, nl \to \gamma_f L_f S_f)$, which are defined in the uncoupled angular-momentum representation, are then obtained by using the relationship

$$A_r(\gamma_j L_j S_j, nl \to \gamma_f L_f S_f) \\ = \frac{1}{2(2l+1)(2S_j+1)(2L_j+1)} \\ \times \sum_{L_d} \sum_{S_d} (2L_d+1)(2S_d+1) A_r(\gamma_d L_d S_d \to \gamma_f L_f S_f)\,. \quad (27)$$

In the electric-dipole approximation, the radiative-transition rates which are defined in the coupled angular-momentum representation are related to the reduced matrix elements $(\gamma_d L_d S_d \| \vec{D} \| \gamma_f L_f S_f)$ of the dipole-moment operator $\vec{D}$ by the well-known result

$$A_r(\gamma_d L_d S_d \to \gamma_f L_f S_f) = \frac{4}{3} \frac{\omega^3}{\hbar c^3} \frac{1}{(2L_d+1)} \\ \times |(\gamma_d L_d S_d \| \vec{D} \| \gamma_f L_f S_f)|^2 \, \delta(S_d, S_f)\,, \quad (28)$$

where ω is the emitted-photon frequency.

The contribution to $A_r(d)$ arising from radiative decays to neighboring Stark levels of the outer electron is expected to be the least important of the three contributions owing to the relatively small energy differences associated with such transitions. These transitions connect the different doubly excited levels which are associated with a given excited state j of the ionic core. An adequate treatment of these transitions is expected to be obtained by using the single-electron approximation

$$A_r(j, n\lambda m m_s \to j, n'\lambda' m' m_s) = A_r(n\lambda m m_s \to n'\lambda' m' m_s)\,, \quad (29)$$

in which the influence of the ionic-core electrons may be taken into account only through the inclusion of the associated quantum defects Δ_{lm} in the determination of the Stark-transformation coefficients and frequency shifts. If the linear-Stark-effect approximation is employed for both the initial and the final outer-electron states, the required electric-dipole matrix elements can be evaluated by using the expression given by Bethe and Salpeter.[10] The field-free dipole selection rule $\Delta l = \pm 1$ is no longer valid in the presence of an electric field, and the only remaining rigorous selection rule is $\Delta m = 0, \pm 1$.

V. CALCULATIONS

In this section we apply the theory developed in the preceding sections to calculate the autoionization and radiative-decay rates from doubly excited

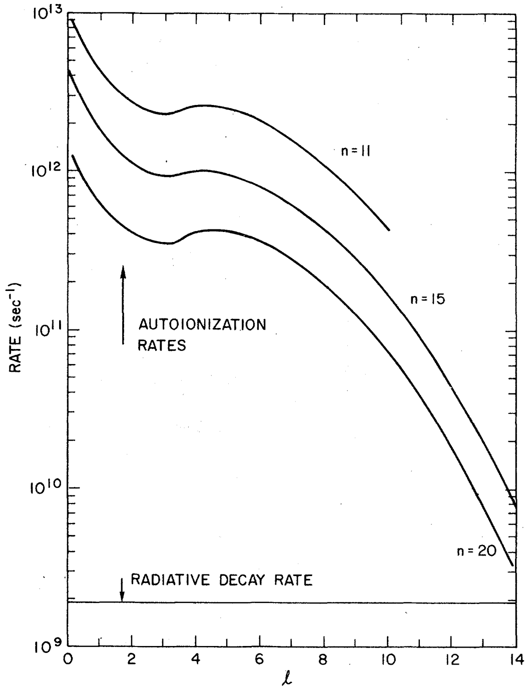

FIG. 1. Autoionization rates and the inner-electron radiative-decay rate from the field-free doubly excited states $1s^2 2p$, nl of Fe^{22+}.

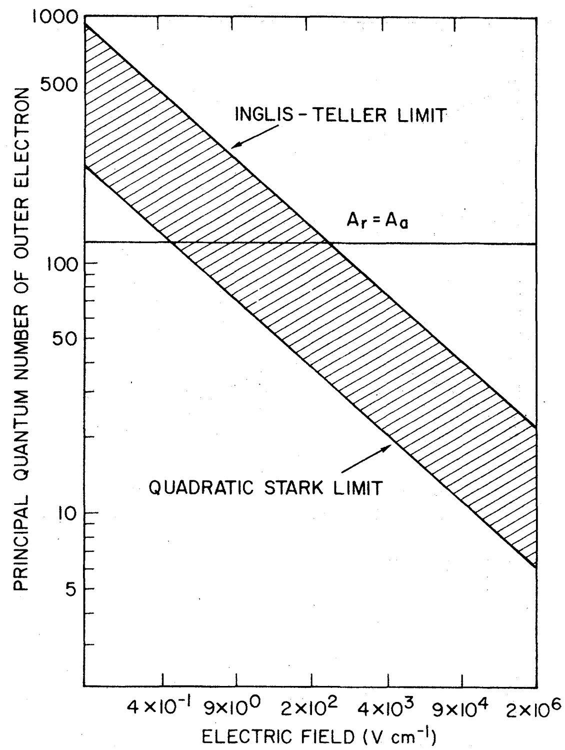

FIG. 2. Range of n value for which the linear-Stark-effect approximation is valid for the doubly excited states $1s^2 2p$, nl of Fe^{22+}.

states of the beryllium like ion Fe^{22+} in the presence of a uniform static electric field. The field strength will be assumed to be within a range for which the linear-Stark-effect approximation is valid.

The field-free autoionization rates $A_a(2p, nl \to 2s)$, which describe the radiationless transition

$$Fe^{22+}(1s^2 2p, nl) \to Fe^{23+}(1s^2, 2s) + e^- , \qquad (30)$$

have been evaluated by using Eq. (20) together with distorted-wave results[20] for the partial-wave cross sections describing the electron-impact excitation process

$$Fe^{23+}(1s^2 2s) + e^- \to Fe^{23+}(1s^2 2p) + e^- . \qquad (31)$$

The l dependence of the field-free autoionization rates is illustrated for three representative values of n in Fig. 1. The horizontal line corresponds to the rate for the inner-electron radiative transition

$$Fe^{22+}(1s^2 2p, nl) \to Fe^{22+}(1s^2 2s, nl) + \hbar\omega , \qquad (32)$$

which is the predominant radiative decay process for $n > 10$. The autoionization rates for the $\Delta n_j = 0$ $2p \to 2s$ ionic-core transition decrease much more rapidly with increasing l than is predicted by Eq. (23). However, the decrease is much less rapid than for the $\Delta n_j = 1$ $3p \to 2s$ ionic-core transition, for which radiative decay becomes comparable to autoionization when $n > 3$. The fact that radiative decay becomes comparable to autoionization only for relatively large values of n ($n \sim 100$) in the $2p \to 2s$ transition is the reason for the importance of the Rydberg autoionizing states in dielectronic recombination through a $\Delta n_j = 0$ transition of the recombining ion.

The range of n values for which the linear-Stark-effect approximation is valid can be determined for a given field strength from the conditions expressed by Eqs. (7) and (9). This range clearly depends on l and m. The representative range of n values which is shown as a function of the field strength in Fig. 2 has been determined by choosing $l = 4$ and taking the m average of the quadratic Stark shift, given by Eq. (6), which enters into the determination of the lower limit on n. The quadrupole contributions to the quantum defects, which are needed in the evaluation of the quadratic Stark shifts, were evaluated for $m_j = -1$ using Eq. (8). The importance of the Rydberg autoionizing states which are associated with the $2p$ ionic-core state is emphasized by the horizontal line at $n = 123$, for which the radiative-decay rate becomes equal to the field-free autoionization rate.

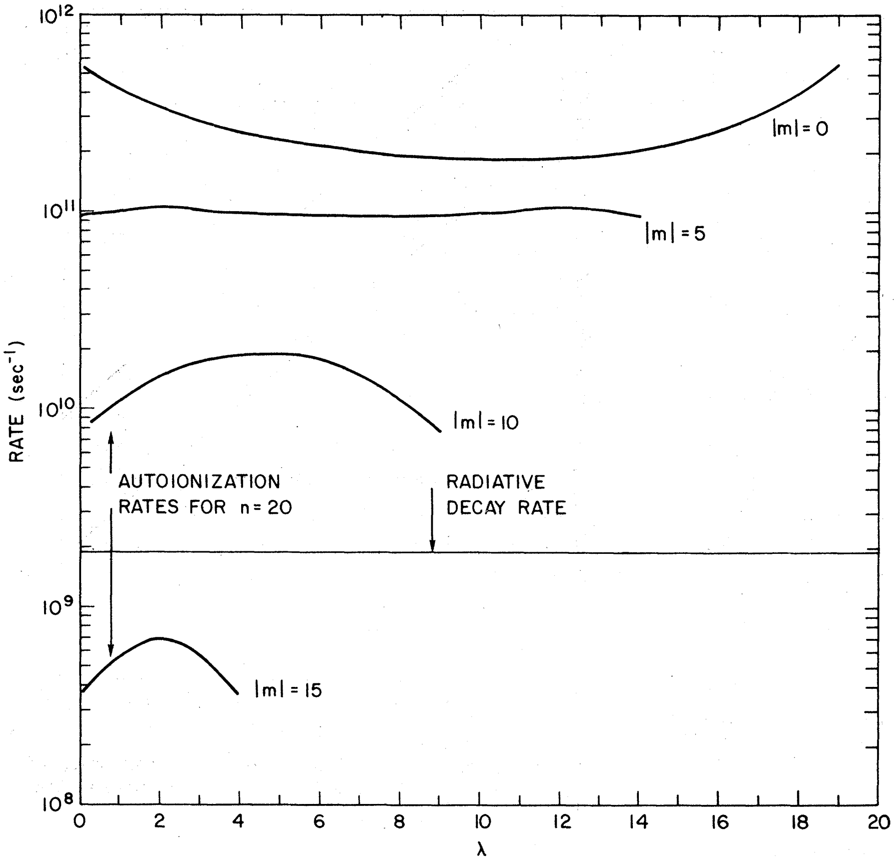

FIG. 3. Autoionization rates and the inner-electron radiative-decay rate from the doubly excited Stark states $1s^2 2p$, $n\lambda m$ of Fe^{22+} with $n=20$.

In a thermal (nonturbulent) plasma, the microscopic electric fields produced by equal concentrations of electrons and hydrogen ions can be estimated by employing the quasistatic approximation originally developed by Holtsmark,[22] who assumed that the time variation of the electric microfields can be neglected during the radiative lifetime of the emitting ion in its excited state. This simplified theory, which provides a much better approximation for ions than for electrons, predicts[5] that the mean field strength $\langle|\vec{F}|\rangle$ is related to the electron density N_e by $\langle|\vec{F}|\rangle = 2 \times 10^{-6} N_e^{2/3}$ V/cm. The electron-density range which corresponds to the field-strength range in Fig. 2 is 10^6–10^{18} cm^{-3}. The Rydberg autoionizing states, which play a particularly important role in the dielectronic recombination process associated with the $\Delta n_j = 0$ $2p \to 2s$ ionic-core transition, occur within the validity region of the linear-Stark-effect approximation in solar-flare and Tokamak plasmas with densities approaching 10^{14} cm^{-3}.

The autoionization rates $A_a(2p, n\lambda m \to 2s)$ in the presence of an electric field have been computed from the field-free values in Fig. 1 by means of Eq. (17), which is appropriate to a statistical distribution of the initial magnetic sublevels. The results for $n=20$ are shown as functions of λ for four representative values of $|m|$. The reflection symmetry exhibited by the curves in Fig. 3 is a consequence of the symmetry properties of the Stark transformation coefficients, given by Eq. (4), which require that the autoionization rates for the Stark states must be unaltered by the transformation $q \to -q$ (and also $m \to -m$). Recall that the electric quantum number q is related to λ by the relationship $q = n - 2\lambda - |m| - 1$. These symmetry properties have been discussed in connection with the hydrogenic radiative-decay rates by Herrick,[23] who has also given sum rules for Stark expansions of the same type as Eqs. (17) and (26). The horizontal line in Fig. 3 corresponds to the dominant (inner-electron) radiative-decay rate, which is unaffected by the presence of the electric field.

The most important property of the Stark autoionization rates in Fig. 3 is the rapid decrease with increasing $|m|$. This behavior can be understood in terms of the limitation $l \geq |m|$ in the Stark expansion, given by Eq. (17), and the rapid decrease with increasing l which is displayed by the field-free values in Fig. 1. For low values of $|m|$, the higher-l substates, which have relatively small field-free autoionization rates, can undergo field-induced autoionization due to the admixture in the Stark wave function of the lower-l substates, for which the autoionization rates are relatively large. The phenomena of field-induced autoionization, which is treated in this investigation within the framework of the linear-Stark-effect approximation, has been studied previously by us[24] using the quadratic-Stark-effect approximation.

The rate of radiationless capture in the dielectronic recombination process is related to the rate for the inverse autoionization process by means of a detailed balance relationship. Field-induced capture into the normally inaccessible higher-l substates is expected to accelerate the rate of dielectronic recombination, because these states have large statistical weights and relatively low field-free rates for the competing autoionization process. In a previous investigation,[6] we have reported a substantial amplification in the dielectronic recombination rates associated with the higher-n manifolds of outer (recombining) electron states.

VI. CONCLUSIONS

Within the framework of the linear-Stark-effect approximation, a detailed theory has been developed which describes the effects of an electric field on autoionization and radiative-decay processes from doubly excited states corresponding to relatively large values of the outer-electron principal quantum number n. The linear-Stark-effect approximation is expected to be valid for high l and also for high residual ionic charge Z. Particularly simple expressions have been derived for the average transition rates by assuming that a statistical distribution fo the inner-electron magnetic sublevels has been established. A treatment has also been given for nonstatistical distributions of the magnetic sublevels, which can occur in the multiphoton laser excitation of the doubly excited states. The linear Stark effect on the autoionization rates from the Rydberg doubly excited states is found to have important consequences for dielectronic recombination. The extension of this investigation to the strong-field region, in which levels corresponding to different n values begin to overlap, is complicated by the need to take into account field-induced autoionization due to tunneling.

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[1]R R. Freeman and D. Kleppner, Phys. Rev. A 14, 1614 (1976).
[2]W. E. Cooke, T. F. Gallagher, S. A. Edelstein, and R. M. Hill, Phys. Rev. Lett. 40, 178 (1978).
[3]R. R. Freeman and G. C. Bjorklund, Phys. Rev. Lett. 40, 118 (1978).
[4]A. Burgess, Astrophys. J. 139, 776 (1964).
[5]H. R. Griem, *Spectral Line Broadening by Plasmas* (Academic, New York, 1974).
[6]V. L. Jacobs, J. Davis, and P. C. Kepple, Phys. Rev. Lett. 37, 1390 (1976).
[7]M. J. Seaton, J. Phys. B 2, 5 (1969).
[8]B. W. Shore, Astrophys. J. 158, 1205 (1969).
[9]I. I. Sobelman, *Introduction to The Theory of Atomic Spectra* (Pergamon, New York, 1974).
[10]H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two- Electron Atoms* (Academic, New York, 1957).
[11]D. L. Park, Z. Phys. 159, 155 (1960).
[12]D. R. Inglis and E. Teller, Astrophys. J. 90, 439 (1939).
[13]J. R. Oppenheimer, Phys. Rev. 31, 66 (1928).
[14]M. G. Littman, M. L. Zimmerman, and D. Kleppner, Phys. Rev. Lett. 37, 486 (1976).
[15]V. L. Jacobs, J. Davis, P. C. Kepple, and M. Blaha, Astrophys. J. 211, 605 (1977).
[16]V. L. Jacobs, J. Phys. B 6, 1461 (1973).
[17]G. Breit and H. A. Bethe, Phys. Rev. 93, 888 (1954).
[18]M. J. Seaton, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic, New York and London, 1962).
[19]K. Alder, A. Bohr, T. Huus, B. Mottelson, and A. Winther, Rev. Mod. Phys. 28, 432 (1956).
[20]J. Davis, P. C. Kepple, and M. Blaha, J. Quant. Spectrosc. Radiat. Transfer 16, 1043 (1976).
[21]P. G. Burkhalter (private communication).
[22]J. Holtsmark, Ann. Phys. (Leipz.) 58, 577 (1919).
[23]D. R. Herrick, Phys. Rev. A 12, 1949 (1975).
[24]J. Davis and V. L. Jacobs, Phys. Rev. A 12, 2017 (1975).