Distorted-wave calculations of dielectronic recombination as a function of electric field strength

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The effects of external electric fields on dielectronic recombination have been studied in the distorted-wave approximation. The eigenvectors for the doubly excited Rydberg states were determined by diagonalizing a Hamiltonian matrix which includes the internal electrostatic and spin-orbit terms, as well as the Stark matrix elements. Calculations were performed for the dielectronic recombination transitions associated with the $2s \rightarrow 2p$ excitation in the Li-like ions B^{2+} , C^{3+} , and O^{5+} ; and the $3s \rightarrow 3p$ excitation in the Na-like ions P^{4+} , S^{5+} , and CI^{6+} . The results for the Na-like ions are compared with recent merged-beam measurements, and the differences between the two sequences with respect to the enhancement of dielectronic recombination as a function of electric field strength are discussed.

I. INTRODUCTION

Dielectronic recombination (DR) can be thought of as a two-step process. In the first step, a free electron collisionally excites an N-electron ion and is simultaneously captured into a doubly excited autoionizing state of the (N+1)-electron ion:

$$e^{-} + X_i(Z,N) \longrightarrow X_i^{**}(Z,N+1) . \tag{1}$$

It can then autoionize back to the initial state i, or to an excited state k of the N-electron ion:

$$X_{j}^{**}(Z, N+1) \rightarrow X_{k}^{*}(Z, N) + e^{-}$$
 (2)

However, it can also emit a photon and decay to an excited state f of the (N + 1)-electron ion:

$$X_{i}^{**}(Z, N+1) \rightarrow X_{f}^{*}(Z, N+1) + h\nu$$
 (3)

If this state is below the first ionization limit of the (N+1)-electron ion, it will be stable, and the DR process will be complete.

In this paper, we shall consider DR transitions associated with $\Delta n = 0$ excitations. For such transitions within high-temperature plasmas, recombination through the multitude of doubly excited Rydberg states with very high principle quantum numbers will normally dominate the total DR process. Therefore, the cross section will be very sensitive to the existence of external electric fields, which surely are present in plasmas and electron-ion beam experiments. First of all, such fields can ionize electrons in high Rydberg states and thereby decrease the DR rate. Secondly, electric fields redistribute the angular momentum among the doubly excited Rydberg states which tends to open up more recombination channels and enhance the rate of dielectronic recombination.

Several approximate methods have been developed for estimating the enhancement of the DR process due to field mixing.¹⁻³ They all employ the configurationaverage approximation in which the rates for recombination, autoionization, and radiation are averaged over all the states of a given doubly excited configuration. Furthermore, they attempt to estimate the onset of the linear Stark region where doubly excited configurations containing Rydberg electrons with the same value of n but different values of l are degenerate; in this region, the fieldmixed DR cross section or rate coefficient may be calculated by making a simple transformation from the spherical to the parabolic basis.

Recently, LaGattuta⁴ has developed an approximate diagonalization technique for calculating field-mixing effects on DR, which is based on the configuration-average approximation. This method employs eigenvectors for the doubly excited Rydberg states determined by diagonalizing a Hamiltonian matrix for which the diagonal components consist of the average Hartree-Fock energy of a given configuration plus an average-quadrupole term between the outermost electrons, and the off-diagonal terms consist of the Stark matrix elements between the Rydberg electrons within the doubly excited configurations. This may prove to be an efficient way of estimating fieldmixing effects as a function of field strength, and represents an improvement over earlier techniques. However, it is difficult to evaluate its accuracy since it does not take into account the mixing between individual levels within the doubly excited configurations. The separation between such levels is a critical parameter in determining the amount of mixing at a given field strength. In an earlier study,^{5,6} we examined the systematics of

In an earlier study,^{5,6} we examined the systematics of field mixing in dielectronic recombination in the Li and Na isoelectronic sequences by employing the configuration-average and linear Stark approximations. This provided physical insight into field-mixing effects and enabled us to determine the maximum field enhancement of DR cross sections as a function of ionization stage. In this paper, we present the results of extensive distortedwave calculations of dielectronic recombination as a function of electric field strength. The intermediate-coupled, field-mixed eigenvectors used to represent the doubly excited Rydberg states were determined by diagonalizing a Hamiltonian which includes the spin-orbit, internal electrostatic, and Stark matrix elements. These calculations then take into account the mixing between individual dou-

33 3124

bly excited states with the same value of n but different values of l due to the presence of an external electric field. However, as in earlier studies, we do not include mixing between Rydberg states with different values of n, and we ignore the effect that the electric field may have on the incoming continuum electron; this latter effect is presently being investigated in the context of DR at Los Alamos." Finally, we have not incorporated any correlation effects in these calculations. One such effect is core polarization, in which the presence of the Rydberg electron tends to polarize the core and thereby distort the electrostatic potential of the Rydberg electron. For Rydberg states for which $l \neq 0$, this effect can be approximated by including the term $\frac{1}{2}\alpha r^{-4}$ in the single-configuration Hamiltonian, where α is the dipole polarizability of the core.⁸ For high values of *l*, where this term will have its greatest validity and its largest effect on the diagonalization, it is smaller than both the spin-orbit term of the core and the direct electron-electron electrostatic term, especially for higher stages of ionization. Although this as well as other correlation effects are worthy of further investigation, they have not been included here.

In Sec. II we outline the theoretical methods and calculational procedures used in our work. In Sec. III, results of calculations for the Na-like ions P^{4+} , S^{5+} , and Cl^{6+} and the Li-like ions B^{2+} , C^{3+} , and O^{5+} are presented and compared with available measurements. Finally, in Sec. V, we conclude by discussing the implications of these results.

II. THEORETICAL METHODS AND CALCULATIONAL PROCEDURES

The Hamiltonian for an (N+1)-electron ion in an external electric field (in Hartree atomic units) is given by

$$H = \sum_{t=1}^{N+1} \left[-\frac{1}{2} \nabla_t^2 - \frac{Z}{r_t} + \xi(r_t) l_t \cdot \mathbf{s}_t + \mathbf{F} \cdot \mathbf{r}_t + \sum_{u < t} \frac{1}{|\mathbf{r}_t - \mathbf{r}_u|} \right], \qquad (4)$$

where $\xi(r_t)$ is the radial part of the spin-orbit interaction and F is the electric field strength.

For the doubly excited configurations considered here, involving two outer electrons above a closed subshell, it is convenient to evaluate the matrix elements of the above Hamiltonian using a basis set in which the two outer electrons are coupled according to the jK scheme,⁹ $|n_j l_j \frac{1}{2} j_j n l K_j \frac{1}{2} J_j M_j \rangle$. In this notation, n_j , l_j , and j_j are the principle, orbital angular momentum, and total angular momentum quantum numbers for the first excited electron, respectively; n and l are the principle and orbital angular momentum quantum numbers of the Rydberg electron, respectively. In the absence of an electric field, this representation becomes quite pure as the principle quantum number n of the Rydberg electron increases and the electrostatic interactions and the spin-orbit interaction for the Rydberg electron decrease. The Stark matrix elements cannot mix states with different values of j_i ; thus, for sufficiently high values of n, it is quite accurate to diagonalize the matrices for each value of j_i separately. Using standard methods of Racah angular algebra, it is a straightforward procedure^{9,10} to evaluate expressions for the matrix elements in this basis in terms of 3-i and 6-isymbols and radial electrostatic, spin-orbit, and dipole parameters. Diagonalization of the resulting matrix for given values of n and M_i yields eigenvectors for the doubly excited states of the form

$$|n_{j}l_{j}n\gamma_{j}M_{j}\rangle = \sum_{j_{j}lK_{j}J_{j}}Y_{jj}^{n_{i}l_{j}n\gamma_{j}M_{j}}|n_{j}l_{j}j_{j}nlK_{j}J_{j}M_{j}\rangle, \quad (5)$$

where γ_j is simply a serial number used to specify completely a particular eigenvector.

The dielectronic recombination cross section from a state of the initial level *i* of an *N*-electron ion through a particular doubly excited state *j* of the (N + 1)-electron ion to all possible bound states of that ion is given in the isolated-resonance approximation by the equation

$$\sigma = \frac{8\pi^2}{k_{\epsilon}^3} \frac{1}{2g_i} \sum_{l_{\epsilon}K_i J_i M_i} \left| \left\langle n_j l_j n \gamma_j M_j \right| \sum_{m=1}^{N} \frac{1}{r_{N+1,m}} \left| n_i l_i j_i k_{\epsilon} l_{\epsilon} K_i J_i M_i \right\rangle \right|^2 \\ \times \frac{\sum_{f} A_r(j \to f)}{\sum_{k} A_a(j \to k) + \sum_{f'} A_r(j \to f')} L_{\Gamma_j}(E_i + k_{\epsilon}^2/2 - E_j) .$$
(6)

In the above expression, k_{ϵ} is the linear momentum and l_{ϵ} is the angular momentum of the continuum electron; g_i is the statistical weight of the initial level of the *N*-electron ion; the factor of 2 in the denominator is the intrinsic statistical weight of the continuum electron; n_i , l_i , and j_i are the principal, orbital angular momentum, and total angular momentum quantum numbers, respectively, of the singly occupied open subshell in the initial *N*-electron ion; the initial states, including the continuum electron, are designated in jK coupling; and the continuum um normalization is one multiplied by a sine function.

The radiative rate $A_r(j \rightarrow f)$ from a particular doubly excited state j to all states of a lower level f in the (N+1)-electron ion is given by the equation

$$A_{r}(j \rightarrow f) = \frac{4\omega_{jf}^{3}}{3c^{3}} \sum_{M_{f}} \left| \left\langle \gamma_{f} J_{f} M_{f} \left| \sum_{m=1}^{N+1} \mathbf{r}_{m} \left| n_{j} l_{j} n \gamma_{j} M_{j} \right\rangle \right|^{2}, \right.$$

$$(7)$$

where ω_{jf} is the transition frequency, c is the speed of light, γ_f is used to designate all quantum numbers other

(13)

(14)

than J_f and M_f which are needed to specify the final state in intermediate coupling, and we employ the dipolelength form of the electromagnetic interaction. In Eq. (6), we use f to designate bound levels only, while f' is used to signify any lower level, including autoionizing levels. By including radiative transitions to autoionizing levels in the denominator, and not in the numerator, one can correct approximately for the effect of cascading among the autoionizing levels. Such final autoionizing levels can decay with the emission of another photon to yet another autoionizing level or to a bound level; however, they will more likely autoionize and not contribute to the DR cross section. The inclusion of these additional radiative terms significantly complicates an already complex calculation, and usually leads to relatively small corrections.¹¹ For these reasons, they are omitted from the present work.

The autoionizing rate $A_a(j \rightarrow k)$ from a particular doubly excited state j of the (N + 1)-electron ion to all states of a level k of the N-electron ion is given by the expression

$$A_{a}(j \rightarrow k) = \frac{4}{k_{\epsilon}} \sum_{l_{\epsilon}K_{k}J_{k}M_{k}} \left| \left\langle n_{k}l_{k}j_{k}k_{\epsilon}l_{\epsilon}K_{k}J_{k}M_{k} \right| \sum_{m=1}^{N} \frac{1}{r_{N+1,m}} \left| n_{j}l_{j}n\gamma_{j}M_{j} \right\rangle \right|^{2}.$$

$$(8)$$

Finally, the Lorentzian profile $L_{\Gamma_i}(E_i + k_{\epsilon}^2/2 - E_j)$ is given by the equation

$$L_{\Gamma_j}(E_i + k_{\epsilon}^2/2 - E_j) = \frac{1}{2\pi} \frac{\Gamma_j}{(E_i + k_{\epsilon}^2/2 - E_j)^2 + \Gamma_j^2/4} ,$$
(9)

where E_i and E_j are the energies of the initial level *i* of the N-electron ion and the doubly excited state j of the (N+1)-electron ion, respectively, Γ_i is the full width at half maximum of the doubly excited resonance state j, which with the approximations used here is given by

$$\Gamma_j = \sum_k A_a(j \to k) + \sum_f A_r(j \to f) .$$
⁽¹⁰⁾

Atomic units are employed in all of the above expressions.

Since we assume nonoverlapping resonances, we follow Hahn and collaborators (see, for example, Ref. 3) and define an energy-averaged cross section $\overline{\sigma}$:

$$\overline{\sigma} = \frac{1}{\Delta \epsilon} \int_{\epsilon - \Delta \epsilon/2}^{\epsilon + \Delta \epsilon/2} \sigma(\epsilon) d\epsilon , \qquad (11)$$

where ϵ is the electron energy ($\epsilon = k_{\epsilon}^2/2$) and $\Delta \epsilon$ is an energy bin width larger than the largest resonance width Γ_i . We also see by comparing Eqs. (6) and (8) that the cross section can be written entirely in terms of autoionizing and radiative rates. Finally, we assume that the energy spread within the initial configuration is small (of course, for the $s \rightarrow p$ transitions considered in this paper there is only a single initial level) and we determine an average cross section from a state within the initial configuration through a particular state within a doubly excited configuration:

$$\bar{\sigma} = \frac{2\pi^2}{\Delta\epsilon k_{\epsilon}^2} \frac{1}{2G_I} \frac{\sum_i A_a(j \to i) \sum_f A_r(j \to f)}{\sum_k A_a(j \to k) + \sum_f A_r(j \to f)} , \quad (12)$$

where G_I is the total statistical weight of the initial configuration. It is important to note that in Eq. (12) \sum_{i} designates a sum over the levels of the initial N-electron configuration only, while \sum_k signifies a sum over all lower levels of the N-electron ion.

The sum over autoionizing rates is given by the expression

)

$$\begin{split} \sum_{k} A_{a}(j \rightarrow k) &= \frac{4}{k_{\epsilon}} (2l_{j}+1) \sum_{n_{k}l_{k}} (2l_{k}+1) \sum_{l_{\epsilon}} (2l_{\epsilon}+1) \sum_{j_{k}K_{k}J_{k}M_{k}} \\ &\times \delta_{M_{j},M_{k}} \left[\sum_{l_{j_{j}}K_{j}J_{j}} \delta_{J_{j},J_{k}} Y_{jjlK_{j}J_{j}}^{n_{j}l,n\gamma_{j}M_{j}} \left[\delta_{K_{j},K_{k}} \sum_{\lambda_{d}} r_{d}^{\lambda_{d}} (l_{k}j_{k}l_{\epsilon}K_{k};l_{j}j_{j}lK_{j})R^{\lambda_{d}} (n_{k}l_{k}k_{\epsilon}l_{\epsilon};n_{j}l_{j}nl) \\ &+ \sum_{\lambda_{e}} r_{e}^{\lambda_{e}} (l_{k}j_{k}l_{\epsilon}K_{k}J_{k};l_{j}j_{j}lK_{j}J_{j})R^{\lambda_{e}} (k_{\epsilon}l_{\epsilon}n_{k}l_{k};n_{j}l_{j}nl) \right] \right]^{2}, \end{split}$$

where the angular coefficient of the direct term is given by

$$r_{d}^{\lambda_{d}}(l_{k}j_{k}l_{\epsilon}K_{j};l_{j}j_{j}lK_{j}) = (-1)^{K_{j}-1/2} [(2l+1)(2j_{j}+1)(2j_{k}+1)]^{1/2} \begin{bmatrix} l_{k} & \lambda_{d} & l_{j} \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} l_{\epsilon} & \lambda_{d} & l \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} l_{j} & \frac{1}{2} & j_{j} \\ j_{k} & \lambda_{d} & l_{k} \end{bmatrix} \begin{bmatrix} j_{j} & l & K_{j} \\ l_{\epsilon} & j_{k} & \lambda_{d} \end{bmatrix},$$

and the angular coefficient of the exchange term is

$$r_{e}^{\lambda_{e}}(l_{k}j_{k}l_{e}K_{k}J_{j};l_{j}j_{j}lK_{j}J_{j}) = (-1)^{K_{k}-1/2+J_{j}}[(2l+1)(2j_{j}+1)(2j_{k}+1)(2K_{j}+1)(2K_{k}+1)]^{1/2} \begin{bmatrix} l_{e} & \lambda_{e} & l_{j} \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} l_{k} & \lambda_{e} & l \\ 0 & 0 & 0 \end{bmatrix} \\ \times \sum_{j=l-1/2}^{l+1/2} (2j+1) \begin{bmatrix} j_{j} & l & K_{j} \\ \frac{1}{2} & J_{j} & j \end{bmatrix} \begin{bmatrix} j & l_{j} & K_{k} \\ \frac{1}{2} & J_{j} & j \end{bmatrix} \begin{bmatrix} j & l_{j} & K_{k} \\ l_{k} & \lambda_{e} & l_{k} \end{bmatrix} \begin{bmatrix} j & l_{j} & K_{k} \\ l_{e} & j_{k} & \lambda_{e} \end{bmatrix} .$$
(15)

 $R^{\lambda_d}(n_k l_k k_{\epsilon} l_{\epsilon}; n_j l_j n l)$ and $R^{\lambda_e}(k_{\epsilon} l_{\epsilon} n_k l_k; n_j l_j n l)$ are the direct and exchange Slater parameters, respectively.

In considering the expressions for the sum over radiative rates, we must distinguish between three different cases. The first case involves a transition between configurations which differ only in the first open subshell:

$$n_i l_i n l \to n_f l_f n l . \tag{16}$$

We refer to these as type-1 transitions. The second case involves a transition between configurations which differ only in the second open, or Rydberg electron, subshell:

$$n_i l_i n l \to n_j l_j n_f l_f . \tag{17}$$

We refer to these as type-2 transitions. Finally, the third case involves a transition in which the electron in the second open subshell drops to the first open subshell:

$$n_j l_j n l \to n_j l_j^2 . \tag{18}$$

We also refer to these as type-2 transitions, although the expression for the radiative rate is quite different. Type-2 transitions are often ignored in calculations of DR rate coefficients and cross sections but can be quite important near threshold, especially in high stages of ionization.

For type-1 transitions, we assume that neither the transition frequency nor the radial dipole moment are affected by the presence of the Rydberg electron. Calculations have shown that this is a good approximation. The sum over radiative rates then reduces to a rather simple expression:

$$\sum_{f} A_{r}(j \to f) = \frac{4}{3c^{3}} \sum_{n_{f}l_{f}} \omega_{jf}^{3} \frac{l_{>}}{(2l_{j}+1)} (d_{n_{f}l_{f},n_{j}l_{j}})^{2} , \qquad (19)$$

where $l_{>} = \max(l_j, l_f)$, and the radial dipole moment is given by

$$d_{n_{f}l_{f},n_{j}l_{j}} = \int_{0}^{\infty} P_{n_{f}l_{f}} r P_{n_{j}l_{j}} dr . \qquad (20)$$

We employ the transition frequencies and radial dipole moments calculated for the transitions $n_j l_j \rightarrow n_f l_f$ in the *N*-electron ion.

For type-2 transitions of the kind depicted in Eq. (17), we ignore the variation in the transition frequency over the levels of the final configuration, and then obtain the following expression for the sum over radiative rates:

$$\sum_{f} A_{r}(j \to f) = \frac{4}{3c^{3}} \sum_{n_{f}l_{f}} \omega_{jf}^{3} \sum_{l} \frac{l_{>}}{(2l+1)} (d_{n_{f}l_{f},nl})^{2} \times \sum_{j_{j}K_{j}J_{j}} (Y_{jj}^{n_{j}l_{n}n_{j}}M_{j})^{2} .$$
 (21)

Finally, for type-2 transitions of the kind shown in Eq. (18), we make the same approximation as for Eq. (21) to obtain the equation

$$\begin{split} \sum_{\gamma_{f}J_{f}M_{f}} A_{r}(j \rightarrow f) &= \frac{8\omega_{jf}^{2}}{3c^{3}} \sum_{ll'} \sqrt{l} d_{n_{j}l_{j},nl} \sqrt{l'} d_{n_{j}l_{j}nl'} \\ &\times \sum_{\substack{j_{j}K_{j}J_{j}\\ j_{j}K_{j}}} Y_{jjK_{j}J_{j}}^{n_{j}l_{j}n\gamma_{j}M_{j}} Y_{jj'K_{j}J_{j}}^{n_{j}l_{j}n\gamma_{j}M_{j}} (-1)^{l_{>}+l'_{>}-j_{j}-j_{j}'+1} [(2j_{j}+1)(2j_{j}'+1)(2K_{j}+1)(2K_{j}+1)]^{1/2} \\ &\times \sum_{L_{j}} (2L_{j}+1) \left[\frac{l}{\frac{1}{2}} K_{j} \ j_{j} \right] \left[\frac{l'}{\frac{1}{2}} K_{j} \ j_{j} \right] \\ &\times \sum_{L_{j}} (2L_{j}+1) \left[\frac{l}{\frac{1}{2}} K_{j} \ j_{j} \right] \left[\frac{l'}{\frac{1}{2}} K_{j} \ j_{j} \right] \\ &\times \sum_{(L_{f}+S_{f} \ \text{even})} (2L_{f}+1) \left[\frac{l_{j}}{\frac{1}{2}} L_{f} \ l_{j} \ L_{j} \ l_{j} \ L_{j} \ k_{j} \right] \\ &\times (2S_{f}+1) \left[\frac{L_{j} \ \frac{1}{2}} J_{j} \ S_{f} \right] \left[L_{j} \ \frac{1}{2} K_{j} \ l_{j} \ S_{f} \right], \end{split}$$

$$(22)$$

where $l_{>} = \max(l, l_{j})$ and $l'_{>} = \max(l', l_{j})$. The complexity of this equation arises from the restriction on L_{f} and S_{f} for equivalent electrons; if it were not for this, it would reduce to the form of Eq. (21).

In addition to field-mixing effects, electric fields will ionize electrons in high Rydberg states. In the case of the merged-beam experiments on DR with which we will be comparing our calculations, the recombined ions, after radiative relaxation, will be field ionized as they move at high velocities through the field of the analyzing magnet. One should properly calculate the probability of an electron in a high Rydberg state of the (N + 1)-electron ion surviving the motional electric field due to the analyzer and being detected. We are now investigating ways of incorporating various hydrogenic field ionization formulas into the present formalism. In the interim, our preliminary work with such hydrogenic approximations indicates that the semiclassical formula^{12,13}

$$n_{\rm max} = (6.2 \times 10^{10} q^3 / v_i B)^{1/4} \tag{23}$$

gives a reasonable estimate of the maximum principle quantum number n_{max} of states for ions which survive the analyzer, where q is the charge of the ion before recombination, v_i is the ion velocity in m/s, and B is the magnetic field in tesla. Thus, we presently incorporate field ionization due to the analyzer by simply calculating the DR cross section for all doubly excited states up to n_{max} . This is legitimate since only type-1 transitions are appreciable for high values of n, and therefore, the values of nare the same for the doubly excited and final states at high n. The electric field due to space charge in the interaction region, which of course is the source of field mixing, is orders of magnitude smaller than the field in the analyzer; thus it cannot cause any field ionization for ions in those states which after radiative relaxation will survive the analyzer and be detected.

A new program DRFEUD (for dielectronic recombination field enhanced using diagonalization) has been developed which employs the above expressions to calculate the intermediate-coupled, energy-averaged DR cross sections for a given field in the interaction region. The energies, radial wave functions, and radial electrostatic and spin-orbit parameters for the doubly excited configurations of the (N+1)-electron ion; the energies, radial wave functions, and potential functions for the configurations of the N-electron ion; and the energies and radial wave functions for the final bound-state configurations of the (N+1)-electron ion are generated using the radialwave-function code developed by Cowan.⁹ The wave functions are solutions to the Hartree-Fock equations with relativistic modifications,¹⁴ which include the massvelocity and Darwin corrections within modified differential equations. The continuum wave functions are calculated in a local distorting potential constructed using the direct part of the Hartree-Fock potential plus the semiclassical exchange approximation of Riley and Truhlar.¹⁵ These continuum wave functions are also corrected for relativistic effects by including the mass-velocity correction in the distorting potential.

It is not feasible to generate Hartree-Fock orbitals for all the configurations needed in the calculation of the total DR cross section. Therefore the many radial parameters used to determine the energy-level structures and autoionizing and radiative rates are extended to high values of n using various extrapolation formulas. Where necessary, hydrogenic wave functions are used to generate these parameters for high values of l.

Since a diagonalization must be performed for each value of n and M_i , the program had to be designed for efficiency. All angular coefficients and radial parameters for the Hamiltonian matrix elements and autoionizing and radiative rates are first determined and stored. Then for each value of n and M_i , the program generates the matrix elements, diagonalizes the Hamiltonian, and finally uses the eigenvectors to determine the rates and cross sections. The full energy matrix is diagonalized up to about n = 30; from n = 30 to n = 40 or 50 (depending on the ion), the matrices for each value of j_i are diagonalized separately. This is legitimate, since for n = 30 and above there is essentially no mixing between states with different values of j_i . In most cases for *n* above 40 or 50, the matrix is diagonalized for only the lower of the two j_j values. Unless additional autoionizing decay channels open up, the ratio of the cross sections for the two values of j_j becomes nearly a constant at high n. Thus, the cross section for the lower j_i alone can be used to determine the total cross section for this last group of n values. Even with these simplifications, block tridiagonal matrices as large as 400×400 had to be diagonalized for some of the cases considered in this paper. The number of energy matrices that have to be included is reduced by the fact that the cross section falls off rather rapidly with M_i , and it is legitimate to exclude matrices for $|M_i|$ greater than 10 to 14, again depending on the ion.

In order to make comparisons between theory and the results of the merged-beam experiments, one must take into account the velocity distribution of the electrons in the rest frame of the ions. In fact, the electron distribution is so wide that it is impossible to determine an experimental cross section as a function of energy. Instead, these experiments measure what amounts to electron speed multiplied by the cross section convoluted with an electron distribution function-a sort of rate coefficient which is a function of electron energy. However, one must be careful not to confuse this with the more commonly defined rate coefficient as a function of electron temperature. The magnitude of the relatively small component of velocity perpendicular to the ion beam is believed to be distributed in a highly asymmetric fashion, while the velocity distribution parallel to the ion beam is thought to be symmetric; this results in an overall distribution as a function of energy which is asymmetric.¹⁶ As a final step, our program combines the experimentally determined distribution function and the theoretical cross sections to produce this rate coefficient as a function of energy.

III. CALCULATIONS FOR Na- AND LI-LIKE IONS

We now present the results of calculations for the Nalike ions P^{4+} , S^{5+} , and Cl^{5+} and the Li-like ions B^{2+} , C^{3+} , and O^{5+} . The first three ions were chosen because the new measurements on these cases have been reported,¹⁶ and the latter three were included since the new measurements on these ions have been made and will be reported soon.¹⁷

For the Na-like ions, the DR process is initiated with the recombination transition of the form

$$e^{-} + X^{q+}(3s) \rightarrow X^{(q-1)+}(3pnl)$$
, (24)

followed by the radiative transition of the form

$$X^{(q-1)+}(3pnl) \rightarrow X^{(q-1)+}(3snl) + h\nu$$
 (25)

or

$$X^{(q-1)+}(3pnl) \rightarrow X^{(q-1)+}(3pn'l') + hv$$
. (26)

The competing autoionizing transitions are

$$X^{(q-1)+}(3pnl) \rightarrow X^{q+}(3s) + e^{-}$$
 (27)

or

$$X^{(q-1)+}(3p_{3/2}nl) \to X^{q+}(3p_{1/2}) + e^{-}.$$
⁽²⁸⁾

The second intercombination autoionizing transition only occurs when the $3p_{3/2}nl$ states are above the $3p_{1/2}$ ionization limit. Because our program employs a *jK* basis set for the doubly excited Rydberg states, it is quite natural to include such intercombination transitions in the calculations. However, whether or not they will contribute depends on the value of n_{max} . For the Na-like ions, the values of n_{max} for the merged-beam experiment¹⁶ are above the point where these transitions begin. However, only Cl⁶⁺ has a high enough value of n_{max} that they produce a measurable effect in the total cross sections, and even there it is quite small.

The result of our calculation of the energy-averaged DR cross section as a function of electron energy for P^{4+} with no field in the interaction region is shown in Fig. 1. The energy bin width used in all the cases reported here is 0.005 hartrees or 0.136 eV; this is larger than the largest



FIG. 1. Energy-averaged dielectronic recombination cross section for P^{4+} in the absence of an electric field. The calculation includes all resonances up to $n_{max} = 63$ and the energy bin width is equal to 0.136 eV.



FIG. 2. Theoretical values of the dielectronic recombination rate coefficients for P^{4+} (as measured in the electron-ion merged-beam experiment) as a function of electron energy for five different electric fields in the interaction region. . . . , F=0 V/cm; --, F=5 V/cm; -, -, F=25 V/cm; -, F=25 V/cm; -, F=625 V/cm. The calculations include all resonances up to $n_{max}=63$. Also shown are the results of the zero-field (••••) and maximum-field (----) calculations using the configuration-average approximation (Refs. 5 and 6). These are marked as CA in the figure. The solid circles (•) are the experimental data from Ref. 16.

resonance width, and yet much smaller than the experimental energy spread. As we shall see, the narrow resonances at low energy will be completely washed out by the electron distribution function appropriate to the mergedbeam experiments.

Our theoretical results for the three Na-like ions of the



FIG. 3. Dielectronic recombination rate coefficients for S^{5+} . $n_{max} = 63$. All notation is the same as that for Fig. 2.



FIG. 4. Dielectronic recombination rate coefficients for Cl^{6+} . $n_{max} = 76$. All notation is the same as that for Fig. 2.

rate coefficient (as measured in the merged-beam experiment) as a function of electron energy for five different electric fields from 0 to 625 V/cm are shown in Figs. 2-4. In all three cases, the field enhancement turns on rather slowly with field strength, and the agreement between experiment and theory is quite good for a field of 25 V/cm. This is pleasing since the space-chargeproduced electric field in these experiments is expected to be close to this value. Also shown in Fig. 2 are the results of the zero-field and maximum-field calculations for P⁴⁺, using the configuration-average (CA) approximation.^{5,6} As expected, the CA approximation overestimates the rate coefficient. For no field, the CA calculation is 22% above the intermediate-coupling calculation, and the CA maximum field result is also 22% above the 625-V/cm intermediate-coupling result. Nevertheless, the CA approximation does provide a reasonable estimate for the range of possible DR rate coefficients or cross sections in the presence of an electric field. The discrepancy between the calculated values and the experimental points at high energy is an indication of an error in the assumed shape of the electron distribution function.

In Fig. 5 we show the theoretical energy-averaged cross section for Cl^{6+} as a function of *n* for the same five values of electric field. We see from this curve that the low electric fields affect the cross sections only at high values of *n*, and the cross sections from n = 10 to 30 are enhanced significantly only by the 125- and 625-V/cm fields. The small dip in the cross section at n = 46, which is most apparent in the 625-V/cm curve, is due to the $3p_{3/2}nl$ to $3p_{1/2}$ intercombination autoionizing transition which begins at this point. As can be seen, it has a relatively small effect on the total cross section.

The results of our calculations of the rate coefficients as a function of energy for the DR transitions associated with the $2s \rightarrow 2p$ excitation in the Li-like ions B^{2+} , C^{3+} , and O^{5+} are shown in Figs. 6–8. An inspection of these curves shows that the field enhancement turns on relatively rapidly with field strength, in contrast with the corresponding curves in the Na-like ions. This is due to the fact that the energy separation between doubly excited levels with the same n and adjacent values of l is smaller for these ions than in the case of the Na isoelectronic sequence; thus the electric field is more effective in the Lilike ions in producing a redistribution of angular momentum and a corresponding enhancement of dielectronic recombination. The experimental results for these cases have not yet been reported and therefore cannot be shown here. At this point it is sufficient to say that the experimental points lie on, or slightly above, the 625-V/cm curves,¹⁵ which implies that the 25-V/cm curves are 25-30 % below experiment. Since the field in the interac-



FIG. 5. Energy-averaged dielectronic recombination cross sections for Cl^{6+} as a function of the principle quantum number n for five different fields in the interaction region. The notation for each of the curves with respect to field strength is the same as in Fig. 2. The energy bin width is equal to 0.136 eV.



FIG. 6. Dielectronic recombination rate coefficients for B^{2+} . $n_{max} = 32$. All notation is the same as that for Fig. 2.



FIG. 7. Dielectronic recombination rate coefficients for C^{3+} . $n_{max} = 44$. All notation is the same as that for Fig. 2.

tion region should be the same in all these cases, this appears to be a relatively small but real discrepancy between theory and experiment. It may be due to a number of factors, including the method used here for estimating the effects of field ionization. Nevertheless, the experimental results are consistent with the theoretical prediction that the field enhancement should be larger in the Li-like ions than in the Na-like ions with the same relatively small electric field.

Finally, in Fig. 9, we show the energy-averaged cross section for O^{5+} as a function of *n*. In comparison to the case of Cl^{6+} , we see that small electric fields are much more effective in enhancing the cross section even for values of *n* between 10 and 30. This serves as further



FIG. 8. Dielectronic recombination rate coefficients for O^{5+} . $n_{max} = 63$. All notation is the same as that for Fig. 2.



FIG. 9. Energy-averaged dielectronic recombination cross section for O^{5+} as a function of *n*. The energy bin width is equal to 0.136 eV. All notation is the same as in Fig. 5.

confirmation of the discussion in the last paragraph. There is no dip in this curve since the $2p_{3/2}nl$ to $2p_{1/2}$ intercombination autoionizing transition does not begin until n = 72 for O⁵⁺, which is beyond the value of n_{max} for which field ionization should occur in the merged-beam experiment.¹⁶ This same situation exists for all the Li-like ions considered here.

IV. CONCLUSIONS

A new program has now been developed which, for the first time, will calculate intermediate-coupled, distortedwave dielectronic recombination cross sections as a function of electric field. At the present time, the program is restricted to cases for which the doubly excited, intermediate states involve only two open singly occupied subshells. However, this restriction is based on the size of the Hamiltonian matrix that must be diagonalized, rather than any inherent limitations in the methods employed, and we plan to modify the code shortly so that it will handle He-like ions involving three open singly occupied subshells in the doubly excited states. In addition, we soon hope to incorporate in this program recent work that we have done on field ionization, so that our results no longer depend on the semiclassical formula. The program does not include any influence that the electric field may have on the incoming continuum electron, and it ignores configuration mixing in the intermediate states; furthermore, it ignores the effects of overlapping resonances. However, with present restrictions on the size and the speed of computers, this method may represent a practical limit to the complexity of the calculations that may be performed on the total dielectronic recombination cross section in an electric field.

Our results for selected ions in the Na and Li isoelectronic sequences appear to agree reasonably well with measurements from recent electron-ion merged-beam experiments. The calculations indicate that the cross section increases with electric field more rapidly in the Li-like ions than in the Na-like ions, and this prediction seems to be consistent with experiment.

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