Effects of configuration mixing on computed dielectronic-recombination rates

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We investigate qualitatively and semiquantitatively the effects on computed dielectronic-recombination rate coefficients of including mixing between basis states of two or more configurations, as opposed to the single-configuration approximation. We have made model-parameter studies for two-electron systems, and have also considered physically realistic three- and four-electron systems. We have attempted to categorize the various circumstances under which configuration-interaction effects are significant, but overall effects appear to be generally small—usually no more than 10–20 %.

I. INTRODUCTION

Dielectronic recombination (DR) is an ion-electron resonant collision process which, in the isolated-resonance approximation, can be considered to occur in two steps. First, the ion (in a level m) is excited sufficiently that the free electron can be captured into a pseudobound (doubly excited) level j; this is followed by radiative decay into a singly excited level k that is stable against autoionization. By the principle of detailed balance, the capture rate into the level j is proportional to the inverse (autoionization) rate A^a_{jm} (summed over all possible states of the ion-electron system for the ion state m). The probability of a stabilizing decay via a radiative transition to some level k, with probability rate coefficient A^r_{jk}, is given by a branching ratio with numerator A^r_{jk} and a denominator consisting of the sum of the rates for all possible autoionization and radiative-decay paths. The recombination rate for a given level j is proportional to the product of these two factors, summed over all possible transitions $j \rightarrow k$.

In a low-density plasma, only low-lying levels—normally those in the ground configuration—are populated appreciably. If we average over all levels m of the ground configuration of the ion (assumed to be populated in proportion to their statistical weights g_m) and sum over all autoionizing levels j, the DR rate coefficient for a Maxwell-Boltzmann free-electron gas at temperature T is given by[1]

$$\alpha(T)=\frac{4\pi^{3/2}a_0^3}{(kT)^{3/2}G}\sum_j g_j \sum_m A^a_{jm}\frac{\sum_k A^r_{jk}}{\sum_{m'} A^a_{jm'}\sum_{k'} A^r_{jk'}}e^{-E_{jm}/kT}, \tag{1}$$

where a_0 is the Bohr radius, $g_j=2J_j+1$ is the statistical weight of the level j, $G=\sum_m g_m$ is the total statistical weight of the ground configuration of the ion, and kT and the kinetic energy E_{jm} of the electron being captured are in rydbergs. The summation on m is over all levels of the ground configuration of the ion, and that on m' includes reionization paths to all energetically accessible levels of the ion. The summation on k is over all radiatively accessible levels of the atom that are stable against autoionization, and that on k' includes in addition any energetically accessible autoionizing levels (where it is assumed that these autoionize with unit probability, rather than decaying radiatively).

We shall consider the contribution to α of a set of levels j belonging to only two or three configurations of the recombined "atom" (which, of course, is not necessarily a neutral system). We assume that this set of levels covers an energy range small compared with kT. For given temperature, the contribution of these levels to α is then proportional to

$$F\equiv\sum_j g_j\frac{\left[\sum_m A^a_{jm}\right]\left[\sum_k A^r_{jk}\right]}{\left[\sum_{m'} A^a_{jm'}\right]+\left[\sum_{k'} A^r_{jk'}\right]}. \tag{2}$$

The question we wish to answer is how different are the values of F if we compute A^a and A^r using single-configuration wave functions versus the use of multiconfiguration wave functions that include the mixing introduced by configuration interaction (CI). This question has been considered by others in the past,[2,3] with indications that terms of Eq. (2) for individual levels j may be drastically altered, but that effects on the sum F are comparatively small. However, those results were obtained only by numerical calculations for a very limited set of specific cases. In this study we wish to investigate qualitative aspects of the problem, which hopefully will provide more general guidelines as to the types of cases in which CI effects might be most important, as well as estimates of the probable magnitude of these effects.

II. SUM RULES

There are well-known sum rules on A^a and A^r that are applicable to limiting cases in which the values of A^a are much greater than those of A^r, or vice versa. To illustrate these, let us consider a simple case of two configurations such that, in the single-configuration approximation, each can capture starting from the ground configuration of the ion and reionize *only* thereto, and such that each can decay radiatively to (and *only* to) levels of stable (singly excited) configurations; thus in Eq. (2) the summations over m and m' are identical, as are those over k and k'. An example is

$$\begin{aligned} &\mathrm{Be}^+\ 2s + e \rightleftarrows \mathrm{Be}\ 2pns \rightarrow \mathrm{Be}\ 2sns\ , \\ &\mathrm{Be}^+\ 2s + e \rightleftarrows \mathrm{Be}\ 2pnd \rightarrow \mathrm{Be}\ 2snd\ , \end{aligned} \tag{3}$$

if we neglect radiative decay of the outer electron. As a function of n, A^r is essentially constant whereas A^a decreases approximately as n^{-3}. Since A^a is much greater than A^r at small n, it is physically appropriate to consider the two cases mentioned above.

(a) $A^a \ll A^r$ (large n). In this case, the summations over k and k' having been assumed identical, Eq. (2) reduces to

$$F \cong \sum_j g_j \sum_m A^a_{jm} = \sum_J (2J+1) \sum_{j'} \sum_m A^a_{j'm}\ , \tag{4}$$

where the summation over j' is over all levels of the two configurations that have a given value J of the total angular momentum. Now, each value of $A^a_{j'm}$ in the usual perturbation method of calculation is proportional to the square of the corresponding (bound-continuum) element of the Hamiltonian matrix.[4] It is well known that the sum of the squares of all elements of a given J matrix is invariant under an orthogonal transformation; it is easily seen as a special case that the sum of the squares of the bound-continuum elements is invariant under an orthogonal transformation that mixes bound states together but not bound states with continua. It follows from Eq. (4) that F is invariant with respect to the degree of bound-bound CI mixing (and also with respect to the degree of departure from pure LS coupling within the bound states).

(b) $A^a \gg A^r$ (small n). In this case, the summations over m and m' having been assumed identical, Eq. (2) reduces to

$$\begin{aligned} F &\cong \sum_J (2J+1) \sum_{j'} \sum_k A^r_{j'k} \\ &\propto \sum_J (2J+1) \sum_{j'} \sum_k (E_{j'k})^3 S_{j'k}\ , \end{aligned} \tag{5}$$

where $S_{j'k}$ is the line strength for the radiative transition $j' \rightarrow k$ and $E_{j'k}$ is the energy of this transition. If all transitions have nearly the same energy, then $(E_{j'k})^3$ can be factored out of the double summation, and the well-known sum rule for line strengths indicates that F is again invariant (or nearly so) under CI (and intermediate-coupling) mixings.

(c) $A^a \cong A^r$ (intermediate n). When neither the A^a nor the A^r clearly dominate, the above sum rules do not apply. However, it is worth considering a hypothetical situation in which the ratio of radiative to autoionization decay rates is independent of the doubly excited level j,

$$\sum_k A^r_{jk} = c \sum_m A^a_{jm}\ . \tag{6}$$

Then Eq. (2) becomes

$$\begin{aligned} F &= \sum_j g_j \frac{c \left[\sum_m A^a_{jm} \right]^2}{(1+c) \left[\sum_{m'} A^a_{jm'} \right]} \\ &= \frac{c}{(1+c)} \sum_j g_j \sum_m A^a_{jm}\ , \end{aligned}$$

where we have again assumed that the summations over m and m' (and over k and k') are identical. Assuming c to be unaffected by CI, this is again invariant, from Eq. (4). Thus we might anticipate that in physical cases, where Eq. (6) is only very roughly satisfied, the value of F would nonetheless be rather insensitive to CI and intermediate-coupling effects. The most serious departures from (6) occur in the case of levels for which radiative selection rules make $c=0$, or for which autoionization selection rules make $c^{-1}=0$. Even very small intermediate-coupling or CI mixings may then open up new decay channels, making c or c^{-1} nonzero, respectively, and thus make F unusually sensitive to the effects we are considering.

Of course, the summation over k' in Eq. (2) may [in cases more highly excited than the example (3)] include terms representing radiative decay to doubly excited levels that quickly autoionize, and hence are not to be included in the summation over k; the summations over k and k' then do not cancel to produce the result (4). The sum rule will, however, still indicate F to be insensitive to the degree of CI mixing to the extent that the ratio of the summations over k and k' is independent of j and independent of the degree of mixing. Similarly, the summation over m' in (2) may include terms representing autoionization to excited ion-core configurations, so that the summations over m and m' do not cancel in the case of Eq. (5). Effects will be particularly large if the alternative decay channels are opened only as a result of configuration mixings. These types of sensitive cases will be considered in more detail later on.

III. MODEL CALCULATION I

To verify some of the above considerations, we have performed a number of model calculations in which the strength of configuration mixing is varied for each of the three cases (a), (b), (c) above. All numerical calculations were made using the computer program RCG (Mod 9), which contains a built-in facility for the calculation of F and an easy means of varying the CI strength.[5] The calculations were done in intermediate coupling, spin-orbit as well as Coulomb interactions being included.

To obtain a physically realistic starting point for the case $A^a \cong A^r$, we considered CI between

$$\mathrm{Fe}^{22+}\ 1s^2 3p5s \text{ and } \mathrm{Fe}^{22+}\ 1s^2 3p5d\ ;$$

except for $3p5s$-$2s\varepsilon f$, these configurations capture from and autoionize to

$$1s^2 2s\varepsilon p \quad \text{and} \quad 1s^2 2s\varepsilon f$$

(where the kinetic energy ε of the free electron is about 64 Ry), and decay radiatively to

$$1s^2 2s5s \quad \text{and} \quad 1s^2 2s5d \ ,$$

respectively. In this model calculation we ignored radiative decay to $1s^2 3s5s$ and $1s^2 3s5d$ (which have much smaller decay rates) so as to satisfy the assumptions of Sec. II. For the present, we ignore also the decay of $5s$ and $5d$ to $2p$, as well as to higher np.

Starting from Hartree-Fock (HF) results for this case, we scaled the single-configuration Coulomb and spin-orbit radial integrals F^k, G^k, and ζ down by a factor 0.3 to reduce the energy spread in each configuration (to about 15 kK$\equiv$15 000 cm^{-1}). The center-of-gravity energy of the $3p5s$ configuration was rounded from the calculated value of 9396 to 10 000 kK, and the calculated value of 9449 for $3p5d$ was changed to 8000, 9900, 10 100, and 12 000 kK for the four model calculations of this study.

The HF values of the bound-bound configuration-interaction integrals $R^k(3p5s,3p5d)$ were increased by a factor 10 for $E_{\rm av}(3p5d)$=9900 and 10 100 kK, and by an additional factor of 20 for $E_{\rm av}(3p5d)$=8000 and 12 000 kK. Calculations were then made for a series of R^k values, scaled from zero up to these modified values. (Since the energy separations of $3p5d$ from $3p5s$ have been modified to about 2 and 40 times the HF separation of 53 kK, the use of the true HF separations and configuration-mixing strengths would correspond to the use of a scale factor of about 0.2 in these model calculations.) The $^1P_1$ and $^3P_1$ levels of the two configurations showed CI mixings of 2%, 7%, and 21% at scale factors of 0.2, 0.4, and 1.0, respectively.

Calculations of this type were made using the HF values for the bound-free CI integrals that determine the capture and autoionization rates, and for the radial dipole integrals that determine the radiative-decay rates. Decay branching ratios (for zero bound-bound CI) ranged from 0.39 to 0.63 for the four levels of $3p5s$, and from 0.49 to 0.96 (averaging 0.80) for the eight autoionizing (P and F) levels of $3p5d$; these ratios are sufficiently close to the desired case $A^a \cong A^r$ (Branching ratios of one-half). To investigate the cases $A^a \gg A^r$ and $A^a \ll A^r$, we made identical sets of calculations, except with the bound-free CI integrals multiplied by factors of 10^3 and 10^{-3} relative to the HF values (A^a values multiplied by 10^6 and 10^{-6}, respectively).

Computed results as a function of the degree of $3p5s$-$3p5d$ mixing are shown in Fig. 1. As expected from the discussion of sum rules, the effects of CI mixings are practically nil in the two extreme cases, and over the range considered are less than 10% even in the case $A^a \cong A$. The strong variation of F with the center-of-gravity energy of $3p5d$ in the case $A^a \gg A^r$ is, of course, a consequence of the factor $(E_{j'k})^3$ in Eq. (5).[6] The effect of the factor $(E_{j'k})^3$ is, of course, smaller for the case $A^a \cong A^r$, and disappears completely in the case $A^a \ll A^r$ where F depends only on A^a.

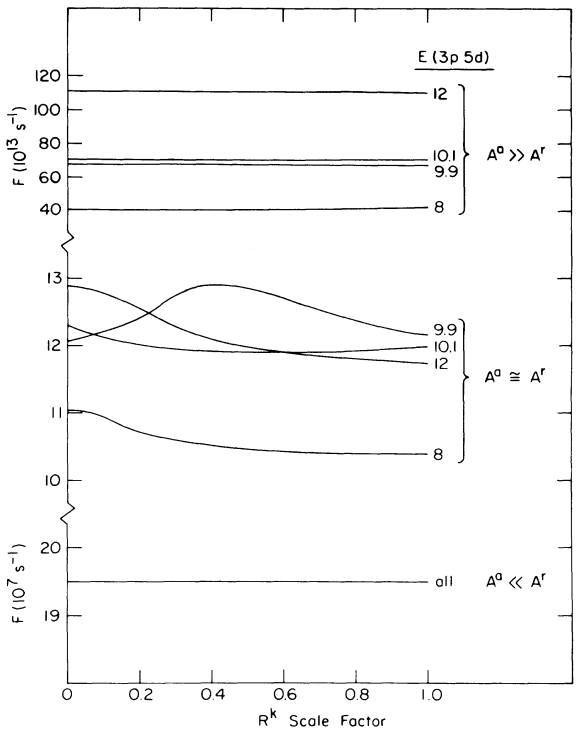

FIG. 1. Model-calculation dependence of F on bound-bound configuration-interaction strength for $2s5s+2s5d-3p5s+3p5d+2s\varepsilon l$, for three different autoionization strengths and for $E_{\rm av}(3p5d)$=8, 9.9, 10.1, and 12 (in units of 10^6 cm^{-1}). The bound-bound CI strength for recombination of Fe^{23+} to Fe^{22+} corresponds to an R^k scale factor of about 0.2.

The extreme flatness of the curves for the case $A^a \gg A^r$ is actually the result of the near equality of the two values of the radial dipole integral $\langle 2s\|r\|3p\rangle$ for the two transition arrays. We have neglected radiative decay of the outer $5s$ and $5d$ electrons (to $2p$), which is important for highly ionized systems, and the dipole integrals for these two decays are not equal. To simulate this, we made calculations for various values of the $2s5d$-$3p5d$ dipole integral. When this value was doubled, then with increasing Cl, F increased for E_{3p5d}=8000 kK and decreased for E_{3p5d}=12 000 kK. The opposite behavior was seen when this dipole integral was halved, but when cut another factor of 2, F increased in both instances; the reason for this behavior will be seen in Sec. IV. In all cases, the variation in F from zero to full CI was less than 5%.

IV. MODEL CALCULATION II

In Sec. V we shall encounter a case in which one of the interacting configurations can (in the single-configuration approximation) decay radiatively only to autoionizing levels, and therefore contribute little or not at all to DR. It is instructive to mock up this case in the model of Sec. III by deleting the configuration $2s5d$; computed results are

shown in Fig. 2. Again, variation of F with CI mixings over the range considered was less than 10%, except for the lowest set of curves, where at very small values of the R^k scale factor the condition $A^a \ll A^r$ is not fulfilled for the levels of $3p5d$. (Violation of this condition for some of the levels even at large scale factor accounts for the computed small variation of F with both scale factor and E_{3p5d}.)

An interesting feature of the results for the case $A^a \gg A^r$ is that CI mixings increase F for $E_{3p5d}=8000$ kK, whereas transfer of line strength from the $2s5s$-$3p5s$ array ($\Delta E=10\,000$ kK) to the $2s5s$-$3p5d$ array ($\Delta E=8000$ kK) would from Eq. (5) be expected to decrease F. It turns out that the CI-induced upward perturbations of the $3p5s$ levels increase the $2s5s$-$3p5s$ transition energies enough to more than offset this effect. On the other hand, downward perturbation of the $3p5s$ levels in the case $E_{3p5d}=12\,000$ kK is insufficient to offset line-strength transfer to the $2s5s$-$3p5d$ array, because of the larger value of $(\Delta E)^3$ for the latter array in this case (12^3, versus only 8^3 in the first case).

These results can be seen analytically from a perturbation calculation for the mixing of two levels at unperturbed energies E_1 and E_2 (corresponding to $3p5s$ and $3p5d$, respectively). If the configuration mixing is a fraction x ($0 \leq x < 0.5$), then the line-strength transfer is also a fraction x. The perturbed energies E' can be found by eliminating the off-diagonal matrix element E_{12} between the two eigenvalue equations $E_1c_1+E_{12}c_2=E'c_1$ and $E_{12}c_1+E_2c_2=E'c_2$, and by then using the normalization condition $c_1^2+c_2^2=1$ and setting first $x=c_2^2$ and next $x=c_1^2$. In order to be able to see more clearly the dependence on x, we expand the exact expressions in power series, and find to second order that

$$E_1' = \frac{E_1-(E_1+E_2)x}{(1-2x)} \cong E_1+(x+2x^2)(E_1-E_2)$$

and (7)

$$E_2' = \frac{E_2-(E_1+E_2)x}{(1-2x)} \cong E_2-(x+2x^2)(E_1-E_2)\ .$$

If the line strength of the unperturbed transition array is S, and $\sum A^r$ therefore proportional to SE_1^3 (the energy of $2s5s$ being chosen as zero), then with CI

$$\sum A^r \propto \frac{(1-x)S}{(1-2x)^3}[E_1-(E_1+E_2)x]^3+\frac{xS}{(1-2x)^3}[E_2-(E_1+E_2)x]^3 \tag{8}$$

$$\cong (1-x)S[E_1+(x+2x^2)(E_1-E_2)]^3+xS[E_2-x(E_1-E_2)]^3$$

$$\cong SE_1^3+S[(x+3x^2)(2E_1^3-3E_1^2E_2)+3x^2E_1E_2^2]+S[(x+3x^2)E_2^3-3x^2E_1E_2^2] \tag{9}$$

$$=SE_1^3+(x+3x^2)S[(2E_1^3-3E_1^2E_2)+(E_2^3)]\ . \tag{10}$$

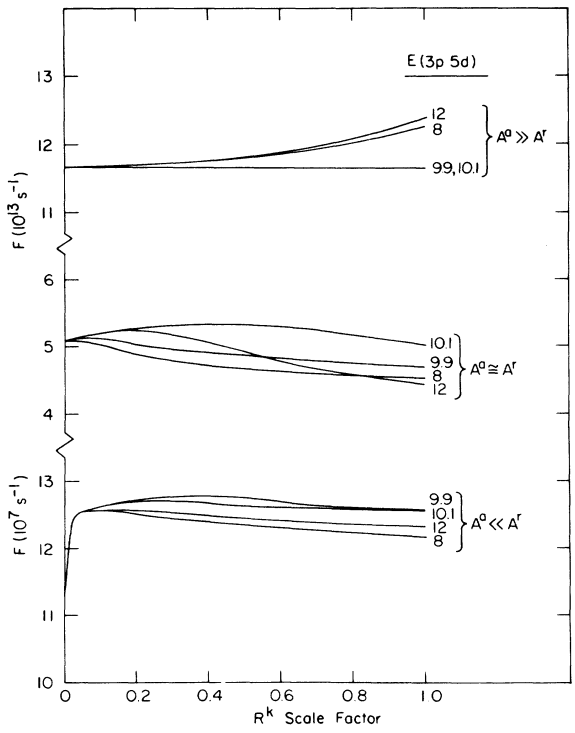

FIG. 2. Same as Fig. 1, except with $2s5d$-$3p5d$ radiative decay deleted.

As a function of E_2, both (8) and (10) are easily seen to have positive curvature, with minimum at $E_2=E_1$. For E_2 up to somewhat greater than $2E_1/3$ (depending on the value of x), the first term of (9) in brackets is positive, so that the upward perturbation of $3p5s$ is alone sufficient to offset the line strength lost to $3p5d$; for larger E_2 (including $E_2>E_1$), the line strength acquired by $3p5d$ [represented by the final bracketed term of (8) or (9)] must be included to obtain an increase over the $x=0$ value.

V. A THREE-ELECTRON EXAMPLE

We next consider two physically realistic examples that are more complex than the model calculations discussed above. The first is depicted in Fig. 3. We consider basically the configuration Ar^{5+} $3s3p12s$, produced by electron capture from the continua $3s^2\varepsilon p$ based on the ground configuration $3s^2$ of Ar^{6+}, and then either autoionizing back to $3s^2\varepsilon p$ or decaying radiatively to $3s^212s$. Interacting with $3s3p12s$, we consider the configuration $3p3d12s$, which in the absence of CI can neither capture from $3s^2\varepsilon p$ (since the Coulomb interaction is only a two-electron operator) nor decay radiatively in one step to states stable against autoionization (because electric-dipole transitions involve only a one-electron operator).

With CI included, $3p3d12s$ acquires some $3s3p12s$ nature [though only 3.8% for the $3p3d\,(^1P)12s\ ^2P$ levels, and much less for the others], and to that extent is able to

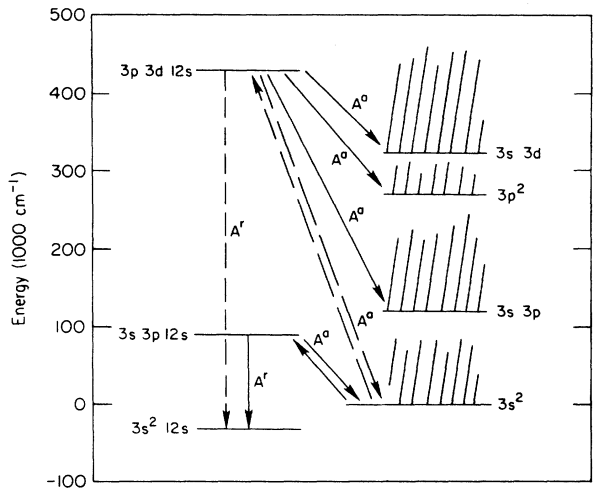

FIG. 3. Schematic energy-level diagram for center-of-gravity energies of Ar^{5+} $3s^2 12s - 3s3p12s + 3p3d12s +$ continua based on Ar^{6+} $3s^2$, $3s3p$, $3p^2$, and $3s3d$. In the single-configuration approximation, the solid arrows illustrate that $3s3p12s$ can decay radiatively to $3s^2 12s$, and can capture from and autoionize to continuum states based on the ion configuration $3s^2$; on the other hand, $3p3d12s$ cannot decay radiatively to states stable against autoionization, nor can it capture from nor ionize to continuum states based on $3s^2$. The dashed arrows show the additional processes made possible by configuration admixture of $3s3p12s$ into $3p3d12s$. (For clarity, the capture and ionization arrows are shown connected to the ion-core configurations, but, of course, the continuum states involved are actually ones having the same energy as the pseudo-bound autoionizing states. Electron capture into $3p3d12s$ from excited configurations of the ion are physically possible, but the corresponding arrows have been omitted because we have assumed these configurations to be essentially unoccupied.)

both capture from $3s^2\varepsilon p$ and radiatively decay to $3s^2 12s$. However, the $3p3d12s$ states can also autoionize to continua based on the $3s3p$, $3p^2$, and $3s3d$ configurations of the ion. These alternative decay paths make the summation over m' in (2) much larger than the summation over m (1.78×10^{13} s^{-1} versus 0.056×10^{13} s^{-1}), so that the corresponding terms in the summation over j are very small. Thus the line strength transferred by CI from $3s3p12s$ to $3p3d12s$ is largely lost so far as DR is concerned. In all cases, A^a is much greater than A^r, so that the situation corresponds qualitatively to the case described by Eq. (8) or (9), with the final term in brackets deleted. We would expect a decrease in F relative to the zero-CI case, and this is confirmed by the detailed numerical calculations summarized in Table I.

The above qualitative remarks can be elaborated on quantitatively. The only levels that we need consider are $3s3p\,(^1P)12s\,^2P$ and $3p3d\,(^1P)12s\,^2P$ because these are the only ones that have appreciable probability of radiative decay to $3s^2(^1S)12s\,^2S$; the unperturbed energies were computed to be $E_1=174.7$ and $E_2=507.2$ kK above $3s^2 12s$, and the perturbed values were $E_1'=161.0$ and $E_2'=520.9$ kK. Avoiding the series-expansion approximations involved in Eqs. (7)–(10), we find the ratio of perturbed to unperturbed DR rate to be

$$\begin{aligned} F'/F &= (1-x)(E_1'/E_1)^3 + x(E_2'/E_1)^3(0.056/1.78) \\ &= 0.962\times0.783 + 0.038\times26.5\times0.031 \\ &= 0.753 + 0.031 = 0.784 \,. \end{aligned} \tag{11}$$

This is in full agreement with the detailed numerical results given in Table I, where for the full CI calculation $F'/F=4.97/6.33=0.785$.

Several points concerning (11) are worth emphasizing.

(a) The dominant term is appreciably less than unity not so much because of the loss of line strength [the factor $(1-x)$], but because the perturbed transition energy E_1' is significantly smaller than the unperturbed value E_1; this perturbation is in turn large, in spite of the small-CI mixing, because the energy difference E_2-E_1 is large compared with E_1 [see Eqs. (7)].

(b) The second term of (11) is as small as it is because it is really proportion to x^2; that is, the number 0.056×10^{13} is x times the zero-CI autoionization rate 1.48×10^{13} for the $3s3p\,(^1P)12s\,^2P$ levels.

(c) The second term is not completely negligible mainly because E_2' is so much larger than E_1. If capture to levels of the upper configuration had been possible in the single-configuration approximation, this term would have been larger by an order of magnitude; i.e., by a factor of roughly x^{-1}. The second term would also have been much larger if the alternate autoionization channels from

TABLE I. Effect of CI mixing on dielectronic-recombination rate coefficients, for CI strengths scaled from zero up to the HF values. (a) $3s^2 4d12s$ omitted. (b) $3s^2 4d12s$ and $3s^2 4s\varepsilon l$ omitted. (c) $3s^2 4s\varepsilon l$ omitted. Numbers in square brackets are powers of ten, e.g., 2[5] is 2×10^5.

	F (s^{-1})			
Bound-bound R^k scale factor	Ar^{5+}	Si I (a)	Si I (b)	Si I (c)
0.0	6.33 [10]	1.13 [11]	1.46 [11]	1.47 [11]
0.05	6.33 [10]	1.13 [11]	1.48 [11]	1.48 [11]
0.2	6.26 [10]	1.13 [11]	1.53 [11]	1.53 [11]
0.4	6.05 [10]	1.16 [11]	1.61 [11]	1.60 [11]
0.6	5.74 [10]	1.20 [11]	1.70 [11]	1.68 [11]
0.8	5.36 [10]	1.25 [11]	1.79 [11]	1.74 [11]
1.0	4.97 [10]	1.31 [11]	1.89 [11]	1.80 [11]

$3p3d12s$ had not been present; we would then have had $F'/F = 0.753 + 0.038 \times 26.5 = 1.76$.

(d) Finally, the result (11) is pertinent to DR only for an electron gas of infinite temperature. If, for example, kT were equal to the energy difference $E'_2 - E'_1$, then the Boltzmann factor in (1) would make the second term of Eq. (8) or (11) less important in DR by a factor e^{-1}.

VI. A FOUR-ELECTRON EXAMPLE

Our final example is shown in Fig. 4 for DR from Si^+ to neutral Si. The configurations $3s3p^2 12s$, $3s^2 3d\,12s$, and $3s^2 4d\,12s$ can all capture from the continua $3s^2 3p\varepsilon l$ based on the ground configuration of Si^+, and can all decay radiatively to $3s^2 3p\,12s$. Coulomb interactions among the electrons $3s3p^2$ produce the very large energy splittings shown in the figure. (The much smaller splittings arising from the interaction of $12s$ with $3s3p^2$ are not shown.) In Si^+, $3s(3p^2\,{}^1D)\,{}^2D$ interacts very strongly with $3s^2 3d\,{}^2D$, and more weakly with higher members of the $3s^2 nd\,{}^2D$ Rydberg series. Correspondingly, the $3s(3p^2\,{}^1D)({}^2D)12s\,{}^{1,3}D$ levels mix strongly (25%) with the $3s^2 3d\,12s\,{}^{1,3}D$ levels, and less strongly (3%) with the $3s^2 4d\,12s\,{}^{1,3}D$ levels; CI mixings for other levels of $3s3p^2 12s$ are negligible (because of the close approximation to pure LS coupling and the LS selection rule for CI). Even for the levels that decay radiatively most strongly, A^r values are less than 1% of A^a, so that we are again dealing with the case $A^a \gg A^r$.

Computed values of F as a function of the degree of CI mixing (scaled from zero up to the full HF values just mentioned) are shown in Table I for three cases. (Limitations of the computer program—which originally was written to handle DR calculations only for configurations with small energy spreads—prevented proper inclusion of all configurations simultaneously.) Comparison of columns (b) and (c) of the table shows that inclusion of the $3s^2 4d\,12s$ configuration is relatively unimportant, as one would expect from the small degree of mixing. Comparison of column (a) with column (b) shows the somewhat more important effect of including the alternative autoionization channel from $3s^2 3d\,12s$ into $3s^2 4s\varepsilon l$; even so, this effect is only 25–30% because the $3d\,12s$ levels provide a relatively small portion of the total DR rate. The *increase* of F with CI results from the fact that phase relations are such as to produce a strong transfer of line strength from the $3s^2 3p\,12s - 3s3p^2({}^2D)12s$ lines to the $3s^2 3p\,12s - 3s^2 3d\,({}^2D)12s$ lines, the latter having greater transition energies than the former. The magnitude of the CI effect in the best calculation [case (a)] is only 16%.

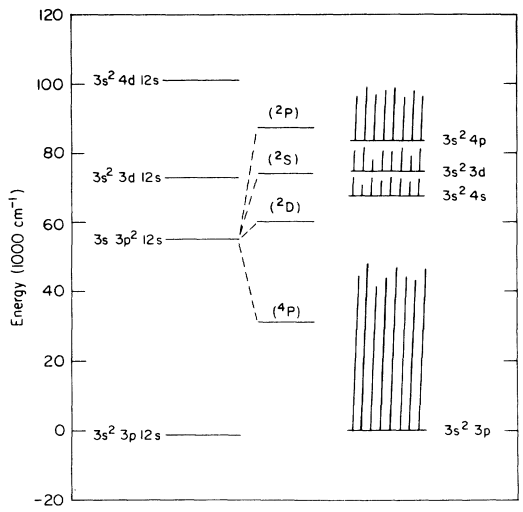

FIG. 4. Schematic energy-level diagram for Si I $3s^2 2p\,12s - 3s3p^2 12s + 3s^2 3d\,12s + 3s^2 4d\,12s$ + continua based on Si^+ $3s^2 3p$, $3s^2 4s$, $3s^2 3d$, and $3s^2 4p$. The energies drawn are for configuration centers of gravity, except for the indicated Coulomb splittings of $3s3p^2$ in Si I $3s3p^2 12s$; the parenthetical labels represent the terms of $3s3p^2$. Even in the single-configuration approximation, $3s3p^2 12s$, $3s^2 3d\,12s$, and $3s^2 4d\,12s$ can all decay radiatively to $3s^2 3p\,12s$, and can all capture from and autoionize to continuum states based on the ion-core configuration $3s^2 3p$.

VII. SUMMARY

The examples considered above are rather limited in scope, but point to the following tentative conclusions.

The case $A^a \ll A^r$ shows the least variation of F with CI mixing [because radiative transition energies are not involved—in contrast to the case $A^a \gg A^r$, Eq. (5)]. However, the case $A^a \ll A^r$ is usually a minor contributor to total DR rates, and so is of minimal physical interest.

The case $A^a \gg A^r$ provides the dominant contribution to DR rates for weakly ionized systems. The effects of CI mixing tend to be largest when the mixing configurations have appreciably different energies, because of the conservation of line strength together with the cubic dependence of A^r on the radiative decay energy, Eq. (5). Effects will also be largest if CI causes line strength to be transferred to levels having alternate autoionization channels (resulting in a decrease of DR rate). In highly ionized systems, CI is significant mainly among levels of the same complex (configurations having not only the same parity, but also the same set of principal quantum numbers). Also, the dominant contributions to DR rates usually come from $\Delta n \neq 0$ excitations. All energies then are much the same, so that the effects just described are minimized.[7]

The case $A^a \cong A^r$ is difficult to analyze in quantitative fashion, but contributes predominantly to DR only for very highly ionized systems, where A^r values are comparable with A^a values even for the lowest energetically pertinent n of the outer electron. We would expect no large effects of CI mixings; no significant energy effects nor opening of new autoionization channels would be expected because of the reasons given in the preceding paragraph. Likewise, opening of new radiative decay channels is unlikely, because of the presence of large spin-orbit mixings. (Indeed, it is in general probably more important to take into account intermediate-coupling departures from pure-LS-couping conditions than it is to include CI effects.)

On a more quantitative note, CI mixings between two

configurations are necessarily less than 50%. In most cases they are unlikely to exceed 25% percent, and then for only a few of the levels of each configuration. Since the line strength that is transferred is seldom lost to DR (and sometimes adds to it rather than subtracting from it), we would expect the large majority of cases to show CI effects on DR rates of no more than 10–20%. This is especially true of *total* DR rates, obtained by summing over all possible contributing configurations, because many of these configurations will show only minor effects, and some pairs will show an increase with CI whereas others will show a decrease. Furthermore, the effects should be especially small for highly ionized systems, which are precisely those for which no experimental data exist, and for which one must depend completely on theoretical values. This conclusion is consistent with the 2–3% effect computed by Roszman and Weiss[2] for the DR of Fe^{23+} to Fe^{22+}, and with the 5% effect computed by McLaughlin and Hahn[3] for dielectronic recombination of other lithiumlike ions.

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[1]See, for example, R. D. Cowan, *The Theory of Atomic Structure and Spectra* (University of California Press, Berkeley, 1981), Sec. 18-11.

[2]L. J. Roszman and A. W. Weiss, J. Quant. Spectrosc. Radiat. Transfer **30**, 67 (1983).

[3]D. J. McLaughlin and Yukap Hahn, Phys. Rev. A **29**, 712 (1984).

[4]Cowan, Ref. 1, Eq. (18.65).

[5]Cowan, Ref. 1, Secs. 16-1 and 16-2.

[6]In the case $A^a \gg A^r$, the ratio of the DR rates for the highest to the lowest curve is about 2.8, which is less than a factor $(\frac{12}{8})^3 = 3.38$, because the line strength of the $2s5d$-$3p5d$ transition array is only $\frac{5}{6}$ of the total line strength of the two arrays ($\frac{5}{6}$ being the ratio of the statistical weight of $3p5d$ to the total statistical weight of $3p5d$ and $3p5s$).

[7]D. C. Griffin and M. S. Pindzola, Phys. Rev. A **35**, 2821 (1987), have made calculations for the contribution to DR of Fe^{15+} from the capture processes $3s\varepsilon l \rightarrow 4l'4l''$ (all possible l, l', and l'' of given parity), and found values with CI that are greater than the single-configuration values by 7.6% for even parity and 5.7% for odd parity.