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Sum rules for collisional processes

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We derive level-to-configuration sum rules for dielectronic capture and for collisional excitation and ionization. These sum rules give the total transition rate from a detailed atomic level to an atomic configuration. For each process, we show that it is possible to factor out the dependence on continuum-electron wave functions. The remaining explicit level dependence of each rate is then obtained from the matrix element of an effective operator acting on the bound orbitals only. In a large class of cases, the effective operator reduces to a one-electron monopole whose matrix element is proportional to the statistical weight of the level. We show that even in these cases, nonstatistical level dependence enters through the dependence of radial integrals on continuum orbitals. For each process, explicit analytic expressions for the level-to-configuration sum rules are given for all possible cases. Together with the well-known J-file sum rule for radiative rates [E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (University Press, Cambridge, 1935)], the sum rules offer a systematic and efficient procedure for collapsing high-multiplicity configurations into "effective" levels for the purpose of modeling the population kinetics of ionized heavy atoms in plasma.

I. INTRODUCTION

The experimental characterization of hot plasma relies frequently on the interpretation of emission spectra. An essential tool in this analysis is the collisional-radiative model for the rate equations governing the populations N_i of atomic levels i

$$\frac{dN_i}{dt} = -N_i \sum_j P_{ij} + \sum_j N_j P_{ji} \ . \tag{1}$$

Here P_{ji} is the rate of population transfer from level j to level i. Plasma emission depends on the populations, and these depend, through the rates in Eq. (1), on the plasma conditions.

To relate level populations reliably to plasma conditions, the population transfer rates must be known with a degree of accuracy that generally requires detailed relativistic quantum-mechanical calculations. But for heavy ions in hot, dense plasma, the number of levels and transitions involved is potentially overwhelming. Recently, techniques were developed to rapidly calculate large numbers of level-to-level electron-impact excitation [1] and autoionization [2] rates in ionized atoms using the distorted-wave approximation. These techniques are based on operator recouplings and factorization theorems [1,3,4] that yield a large array of excitation cross sections from a small number of radial integrals. The method has been applied to the development of plasma diagnostics [5], x-ray laser studies [6–8] and to the calculation of resonant excitation and excitation-autoionization in charged ions [9,10]. Other workers have recently applied the method to study Z scaling of $\Delta n = 1$ collisional excitation rates in the neonlike isoelectronic sequence [11].

Further computational hardship is encountered as collisional-radiative models are enlarged to include the effects of high multiplicity autoionizing manifolds, high-lying "Rydberg" configurations, and multiple charge states. Though early applications of collisional-radiative modeling was restricted to the treatment of low-lying excited states of a single ion, and to conditions of collisional-radiative equilibrium, models have latterly been applied to the analysis of recombining and other nonequilibrium plasmas [5,7], and are used increasingly in elaborate radiation transport and hydrodynamic simulations [12]. In these time-dependent applications, though interest might be focused on a small subset of levels, the effects of autoionizing and Rydberg configurations, and of a range of charge states, must be accounted for.

At some point in the process of adding configurations to a model, it becomes necessary to adopt a procedure for treating them, and the flux of population through them, in a configuration-average approximation. A common approach is to reduce the levels belonging to a pair of configurations to a pair of "effective levels" by averaging all rates connecting them over the initial configuration and summing over the final configuration [13–15]. This approach has the collateral advantage of yielding simple analytic expressions for the average rates. The assumption underlying this approximation is that the levels within the initial configuration are populated according to their statistical weight. This configuration-configuration averaging is a consistent method, so long as it is used only to connect configuration-averaged effective levels. Indeed, models in which all levels are hydrogenically or *j-j* configuration-averaged are commonly embedded in hydrodynamic simulations, for estimating charge-state distribution and radiative energy loss. This model is obtained by summing Eq. (1) over levels $i \in C$, where C is a configuration manifold, and imposing a statistical distribution of population among levels within a configuration by setting $N_{i\,(j)} = N_{C\,(C'')}(g_{i\,(j)}/g_{C\,(C'')})$, where $g_{i\,(j)}$ and $g_{C\,(C'')}$ are the multiplicities of level i (j) and configuration C (C''), respectively:

$$\begin{aligned}\sum_i \frac{dN_i}{dt} = \frac{dN_C}{dt} &= -N_C \sum_{C''} \sum_{i \in C, j \in C''} g_i P_{ij}/g_C \\ &\quad + \sum_{C''} N_{C'} \sum_{i \in C, j \in C''} g_j P_{ji}/g_{C''} \\ &\equiv -N_C \sum_{C''} P_{CC''} + \sum_{C''} N_{C''} P_{C''C} \ . \end{aligned} \tag{2}$$

For spectroscopic applications and x-ray laser calculations, though, it is necessary to retain the detailed structure of some subset of atomic levels. A common approach to treating the population flow between these levels and a set of configuration-average effective levels is to distribute the transition rates that have been averaged over both initial and final configurations statistically among the detailed levels. This is a dicey approximation, since when local thermodynamic equilibrium does not obtain, it is unlikely that low-lying levels are statistically populated (i.e., populated in proportion to their statistical weight). It also neglects the variation in transition rates among the detailed levels, including the effects of selection rules. Evidently, a better approach would be to avoid, in the first place, averaging over configurations for which detailed level structure is to be retained. This could certainly be accomplished by the brute-force calculation of the relevant level-to-level transition rates, followed by an explicit summation over the configuration being treated as an effective level.

In this paper, we propose an efficient solution based on analytic level-to-configuration sum rules derived below. These sum rules give exactly the total transition rate,

$$P_{iC''} = \sum_{j \in C''} P_{ij} \ , \tag{3}$$

from a detailed atomic level i to an atomic configuration C'', with the sole approximation that variation in the transition energy can be neglected. Our results are similar in intention and utility to, though generally more elaborate than, the formulas obtained by averaging over both initial and final configurations. Since, after detailed balancing, the sum rules yield the reverse, configuration-to-level, transition rates $P_{C''i} = \sum_{j \in C''} g_j P_{ji}$, averaged over C'', for population flow in this direction they still embody the assumption of a statistical distribution of population in the configuration, though not for the levels that remain detailed. Furthermore, the effects of variation in transition rates among detailed levels, including selection rules, are retained. This work extends to processes involving continuum electrons, and to general mixed configuration states, techniques developed by Racah and Stein [16] in their analysis of "effective interactions" in configurations of the form l^n. (Similar techniques, based on the second quantization formalism, were applied by Bauche, Bauche-Arnoult, and Klapisch [17] to study unresolved transition arrays.)

By recoupling the interaction operator, we will show that it is possible for dielectronic capture, collisional excitation, and collisional ionization to factor out the dependence on continuum electron wave functions of the level-to-configuration rates. After summing the transition probability over $j \in C''$, as in Eq. (3), explicit dependence on the bound-state wave functions is reduced by an application of the closure theorem to the expectation value of an effective operator in the state i. Because of the continuum factorization, the expectation value can be evaluated in terms of angular recoupling coefficients and reduced matrix elements of standard n-body operators with $n \leq 3$. In a large class of cases, the operator reduces to a one-body monopole whose expectation value is proportional to the statistical weight $2J+1$, of i, and a radial factor. This simple result, however, does not imply state independence of the rates, nor justify the configuration-configuration model, since mixing coefficients and, owing to the presence of continuum electrons, the radial integrals remain level dependent. Moreover, in many cases the results are not proportional to statistical weight. For these other cases we will obtain the explicit level-to-configuration sum rules as well.

The level-to-configuration radiative transition attracted interest since the early days of atomic spectroscopy when the *J*-file sum rule was discovered [18]. The sum rules can be considered as an extension of the latter to collisional transitions where the interaction is two body and involves continuum orbitals. Like the *J*-file sum rule our results are exact for the rate at which a level is depleted, but give an average value for the population rate.

In Sec. II we present background results and notation. In Sec. III we derive the level-to-configuration sum rules for autoionization and dielectronic capture, and, in Sec. IV, we present the level-to-configuration sum rules for collisional excitation and ionization. In Sec. V we summarize and discuss our results.

II. BACKGROUND AND DEFINITIONS

The radial and angular dependences of the electrostatic operator may be completely factorized, giving [1,3,19]

$$\sum_{\substack{i,j \\ i<j}} 1/r_{ij} = \sum_{\{\alpha\beta\}\{\gamma\delta\}} \sum_t \Phi^t(\alpha\beta,\gamma\delta) \sum_{\substack{i,j \\ i \neq j}} (\mathrm{Z}_i^{(t)}(\alpha\gamma) \cdot \mathrm{Z}_j^{(t)}(\beta\delta)) \ , \tag{4}$$

where the outside sum is over *distinguishable* sets $\{\alpha\beta\} = \{\beta\alpha\}$ and $\{\gamma\delta\} = \{\delta\gamma\}$ of orbital quantum numbers $\alpha \equiv \{n_\alpha l_\alpha j_\alpha\} \equiv \mathbf{j}_\alpha$, etc. and the sum $\sum_{i,j\,(i \neq j)}$ is over electronic coordinates. Following Racah and Stein [16] we define the *j-j* unit *t*-rank tensors $\mathrm{Z}_i^{(t)}(\alpha\beta)$ by their one-particle reduced matrix elements:

$$\langle \alpha' \| \mathrm{Z}_i^{(t)}(\alpha\beta) \| \beta' \rangle = \delta_{\alpha\alpha'}\delta_{\beta\beta'} \ . \tag{5}$$

The notation $(\mathrm{Z}^{(t)} \cdot \mathrm{Z}^{(t)})$ indicates scalar product. Note that there is no parity restriction on the rank t in Eq. (4). The radial factors include both direct and exchange contributions:

$$\Phi^t(\alpha\beta,\gamma\delta) = s_1 X^t(\alpha\beta,\gamma\delta) + s_2 \sum_k (-1)^{k+t}[t] \begin{Bmatrix} \alpha & \delta & k \\ \beta & \gamma & t \end{Bmatrix} X^k(\alpha\beta,\delta\gamma) \ , \tag{6}$$

$$X^k(\alpha\beta,\delta\gamma) = \langle \alpha \| C^{(k)} \| \gamma \rangle \langle \beta \| C^{(k)} \| \delta \rangle R^k(\alpha\beta,\gamma\delta) \ , \tag{7}$$

where $C^{(k)}$ is the usual one-body tensor operator of rank k [20], $R^k(\alpha\beta,\gamma\delta)$ is the Slater integral, $[t]=2t+1$, and

$$s_1 = 1 - \delta_{\alpha\beta}\delta_{\gamma\delta}/2, \quad s_2 = (1-\delta_{\alpha\beta})(1-\delta_{\gamma\delta}) \ . \tag{8}$$

Note that if the Slater integrals involve continuum orbitals, they will depend on the continuum electron energies and thus, by conservation of energy, on the corresponding bound-bound transition energy. But for this indirect dependence, the $X^k(\alpha\beta,\delta\gamma)$ are independent of detailed level structure.

An electronic configuration C is defined by a set of electron occupation numbers $\{q_\alpha\}$ for the bound orbitals j_α of the α shell:

$$C = \prod_\alpha (\mathrm{j}_\alpha)^{q_\alpha} \tag{9}$$

and has statistical weight

$$g_c = \prod_\alpha \begin{bmatrix} 2j_\alpha + 1 \\ q_\alpha \end{bmatrix} \tag{10}$$

By restricting the orbital summation in Eq. (4) to $\{\alpha\beta\} \in A$ and $\{\gamma\delta\} \in B$, we obtain the projection of the electrostatic operator onto specific electron configurations A and B:

$$V_{A,B} = \sum_{\{\alpha\beta\} \in A, \{\gamma\delta\} \in B} \sum_t \Phi^t(\alpha\beta,\gamma\delta) \times \sum_{\substack{i,j \\ i \neq j}} (\mathrm{Z}_i^{(t)}(\alpha\gamma) \cdot \mathrm{Z}_j^{(t)}(\beta\delta)) \ , \tag{11}$$

$$\langle \psi | V_{A,B} | \psi'' \rangle = \langle \psi'' | V_{B,A} | \psi \rangle = \begin{cases} \left\langle \psi \left| \sum\limits_{\substack{i,j \\ i<j}} e/r_{ij} \right| \psi'' \right\rangle, & \psi \in A, \quad d\psi'' \in B \\ 0 \text{ otherwise} \ . \end{cases} \tag{12}$$

Note that, owing to the definition (5), nonvanishing contributions to Eq. (11) correspond to sets of orbitals $\{\alpha,\beta\}$ and $\{\gamma,\delta\}$ for which the shell occupation numbers $q_\sigma \in A$ and $q'_\sigma \in B$ obey the relation

$$q_\sigma - \delta_{\sigma\alpha} - \delta_{\sigma\beta} = q'_\sigma - \delta_{\sigma\gamma} - \delta_{\sigma\delta} \ ,$$

or, symbolically, $A - \{\alpha,\beta\} = B - \{\gamma,\delta\}$. We will refer to the orbital sets $\{\alpha,\beta\}$ and $\{\gamma,\delta\}$ as "active" orbitals with respect to A and B.

The transition rate between two atomic levels $\psi \in A$ *and* $\psi'' \in B$ (where A and B in general contain continuum electrons) is proportional to the squared matrix element $|\langle \psi | V_{A,B} | \psi'' \rangle|^2$, and the total level-to-configuration rate is related to

$$R_{\psi B} = \sum_{\psi'' \in B} \langle \psi | V_{A,B} | \psi'' \rangle \langle \psi'' | V_{B,A} | \psi \rangle \ . \tag{13}$$

As noted above, the radial part of the operator $V_{A,B}$ may depend weakly on ψ'' through continuum electron energies. In the present treatment, we will neglect the difference between $\Delta E_{\psi\psi''} = E_\psi - E_{\psi''}$ and $\Delta E_{\psi B} = E_\psi - E_B$, consistent with the goal of replacing configuration B with a single effective level. To leading order, E_B can be taken as the configuration-average energy. However, it is possible, if necessary, to improve upon this approximation by adapting the concept of "emissive zones," introduced for radiative transition arrays by Bauche, Buache-Arnoult, and Klapisch [17], and by considering higher moments of the electrostatic operator. Now, using Eq. (12), the summation in (13) can be extended to include a complete set of states and the closure theorem applied [16] to obtain

$$R_{\psi B} = \langle \psi | V_{A,B} V_{B,A} | \psi \rangle \ . \tag{14}$$

In this result, all details of the structure of configuration B have been eliminated, while the structure of A remains resolved. Besides the obvious dependence of ψ, the expectation value depends only on electron orbital quantum numbers.

The preceding development can be demonstrated using the electric dipole operator rather that the more complicated electrostatic interaction:

$$D = \sum_{\{\alpha\beta\}} P(\alpha\beta) \sum_i \mathrm{Z}_i^{(1)}(\alpha\beta) \equiv \sum_{\{\alpha\beta\}} P(\alpha\beta) \mathrm{Z}^{(1)}(\alpha\beta) \ , \tag{15}$$

where $P(\alpha\beta)$ is the dipole radial integral times $\langle \alpha \| C^{(1)} \| \beta \rangle$, and $\mathrm{Z}_i^{(1)}(\alpha\beta)$ is defined in Eq. (5). The summations here match those in Eq. (4), though with the simplification to a one-body interaction. D is projected onto configurations A and B connected by the one-electron transition $\alpha'' \Longrightarrow \beta''$, by restricting the sum in (15) to the single term $\alpha = \alpha''$, $\beta = \beta''$.

The radiative transition matrix element from $\psi \in A$ to $\psi' \in B$ is given by $d_{\psi,\psi'} \equiv |\langle \psi | D_{A,B} | \psi' \rangle|^2$ and the level-to-configuration transition rate is obtained through application of the closure theorem [16]

$$\begin{aligned} d_{\psi,B} &\equiv \sum_{\psi' \in B} \langle \psi | D_{A,B} | \psi' \rangle \langle \psi' | D_{B,A} | \psi \rangle \\ &= \langle \psi | D_{A,B} D_{B,A} | \psi \rangle \\ &= P^2(\alpha\beta) \langle \psi | \mathrm{Z}^{(1)}(\alpha\beta) \cdot \mathrm{Z}^{(1)}(\beta\alpha) | \psi \rangle \ , \end{aligned} \tag{16}$$

where

$$(\mathsf{Z}^{(1)}(\alpha\beta)\cdot\mathsf{Z}^{(1)}(\beta\alpha))=\sum_{\substack{i,j\\ i\neq j}}(\mathsf{Z}_i^{(1)}(\alpha\beta)\cdot\mathsf{Z}_j^{(1)}(\beta\alpha)) + \sum_i(\mathsf{Z}_i^{(1)}(\alpha\beta)\cdot\mathsf{Z}_i^{(1)}(\beta\alpha)) \ . \tag{17}$$

The second term in this result is the monopole operator $(-1)^{j\alpha+j\beta+1}(2j_\alpha+1)^{-1/2}\mathsf{Z}^{(0)}(\alpha,\alpha)$. The expectation value in (16) is the standard one obtained in evaluating the electrostatic interaction of the ordinary atomic Hamiltonian.

The result of this exercise is just a reformulation of the well-known J-file sum rule first derived by Condon and Shortley [18] in the case that the two-body contribution is absent. The general case was treated only recently by Bauche, Bauche-Arnoult, and Klapisch [17]. It is useful to bear in mind that the sum rules obtained below for collisional processes mediated by the electrostatic interaction are analogous to the J-file result for electric dipole transitions. It should also be noted that, when β is a continuum orbital, Eq. (16) provides the configuration-to-level radiative-recombination rate. Furthermore, since β never appears as an occupied orbital of ψ, only the monopole term survives for this process.

III. SUM RULES FOR AUGER CAPTURE AND AUTOIONIZATION

A. Definitions and sum over autoionizing states

We begin with the autoionization rate [20] from a state ψ'' to a level $\tilde{\psi}$:

$$A_{\tilde{\psi}}^{\psi''}=\sum_{\not{\varepsilon}}\sum_{J_TM_T}\left|\left\langle\tilde{\psi}(\gamma,j)\not{\varepsilon}J_TM_T\right|\sum_{\substack{i,j\\ i<j}}(e/r_{ij})\left|\psi''(\gamma'',J_T'',M_T'')\right\rangle\right|^2 . \tag{18}$$

(We will denote atomic levels with a tilde, $\tilde{\psi}$, $\tilde{\psi}'$, $\tilde{\psi}''$, etc., and its quantum states by the corresponding undecorated symbol.) Note that, since the operator is a scalar, by conservation of angular momentum only one term contributes to the sum over J_T,M_T in Eq. (18). The continuum electron is denoted by $\not{\varepsilon}$, representing the quantum numbers l,j and the energy ε, which, since the total energy is conserved, depends on ψ'' and $\tilde{\psi}$. The configuration-to-level autoionization rate from all the states ψ'' of the configuration C'' is

$$A_{\tilde{\psi}}^{C''}=(1/g_{C''})\sum_{\psi''\in C''}A_{\tilde{\psi}}^{\psi''} \ . \tag{19}$$

Using detailed balance we can write the total radiationless capture rate from an initial target state ψ (belonging to level $\tilde{\psi}$) to all states ψ'' of the level $\tilde{\psi}''$:

$$D_{\tilde{\psi}}^{\tilde{\psi}''}=(1/g)f\sum_{M_T''}A_{\tilde{\psi}}^{\psi''} , \tag{20}$$

where the statistical weight of $\tilde{\psi}$ is $g=2J+1\equiv[J]$, $A_{\tilde{\psi}}^{\psi''}$ is the autoionization rate from state ψ'' to level $\tilde{\psi}$, as given in Eq. (18), and

$$f=\tfrac{1}{2}n_e(h^2/2\pi m_ekT_e)^{3/2}\exp[-(E_{\psi''}-E_{\psi})/kT_e] \tag{21}$$

is the free-electron distribution function at temperature T_e, density n_e, and electron energy $E_{\psi''}-E_{\psi}$. Finally, the level-to-configuration dielectronic capture rate is

$$D_{\tilde{\psi}}^{C''}=(g_{C''}/g)fA_{\tilde{\psi}}^{C''} \ . \tag{22}$$

Equation (22) is the exact total capture rate from initial level $\tilde{\psi}$ into the configuration C''. On the other hand, the autoionization rate represented by Eq. (19) is only an average that assumes population is distributed amongst the levels of C'' according to their relative statistical weights.

Although we have treated the autoionizing states ψ'' as pure-configuration states, this covers the more general mixed-configuration case as well, since the sum over ψ'' can always be replaced by a sum over pure-configuration states that span the same space. On the other hand, since there is no configuration sum over capturing states ψ, their mixing must be explicitly treated. (Since we assume throughout the distorted-wave approximation, we do not consider mixing of continuum channels.) Thus, in general,

$$\psi=\sum_C\sum_{\psi_C}\alpha_{\psi_C}\psi_C ,$$

where the ψ_C are pure configuration basis states. In the general case, Eq. (19) becomes

$$A_{\tilde{\psi}}^{C''}=\sum_{C,C'}\sum_{\psi_C\psi_{C'}}\alpha_{\psi_C}\alpha_{\psi_{C'}}A^{C''}(\psi_C,\psi_{C'}) , \tag{23}$$

with the partial rate given by

$$A^{C''}(\psi_C,\psi_{C'})=(1/g_{C''})\sum_{J_T}J_T\sum_{\not{\varepsilon}}\sum_{\psi''\in C''}[\langle\psi_C(\gamma,J)\not{\varepsilon}J_TM_T|V_{\tilde{C},C''}|\psi''(\gamma'',J_T'',M_T'')\rangle \times\langle\psi''(\gamma'',J_T'',M_T'')|V_{C'',\tilde{C}'}|\psi_{C'}(\gamma',J)\not{\varepsilon}J_TM_T\rangle] , \tag{24}$$

where $\tilde{C}=C+\not{\varepsilon}$ and $\tilde{C}'=C'+\not{\varepsilon}$ and we have replaced the electrostatic operator with its projections. Using the closure theorem, the configuration-to-level autoionization rate becomes

$$A_{C''}(\psi_C,\psi_{C'})=(1/g_{\dot{C}''})\sum_{J_T}[J_T]\sum_{\not{\varepsilon}}\langle\psi_C(\gamma,J)\not{\varepsilon}J_TM_T|V_{\tilde{C},C''}V_{C'',\tilde{C}'}|\psi_{C'}(\gamma',J)\not{\varepsilon}J_TM_T\rangle \ . \tag{25}$$

Here $V_{\tilde{C},C''}V_{C'',\tilde{C}'}$ is a four body operator acting in the product space of the capturing level and the continuum electron; all explicit reference to the autoionizing states has been eliminated. Of course, $A^{C''}(\psi_C,\psi_{C'})$ still depends on the autoionizing configuration through the operator $V_{\tilde{C},C''}V_{C'',\tilde{C}'}$. Using Eq. (11), we can write

$$V_{\tilde{C}C''}=\sum_{\mathbf{j},\mathbf{j}_a,\mathbf{j}_b}\sum_{t}\sum_{\substack{i,j\\ i\neq j}}(\mathsf{Z}_i^{(t)}(\mathbf{j},\mathbf{j}_a)\cdot\mathsf{Z}_j^{(t)}(\ell,\mathbf{j}_b))\times\Phi^t(\mathbf{j},\ell,\mathbf{j}_a,\mathbf{j}_b)\ ,$$

$$V_{C'\tilde{C}'}=\sum_{\mathbf{j}',\mathbf{j}'_a,\mathbf{j}'_b}\sum_{t'}\sum_{\substack{k,l\\ k\neq l}}(\mathsf{Z}_k^{(t)}(\mathbf{j}'_b,\ell)\cdot\mathsf{Z}_l^{(t)}(\mathbf{j}'_a,\mathbf{j}'))\times\Phi^t(\mathbf{j}'_b,\mathbf{j}'_a,\ell,\mathbf{j}')\ , \tag{26}$$

and

$$V_{\tilde{C}C''}V_{C''\tilde{C}'}=\sum_{\mathbf{j},\mathbf{j}_a,\mathbf{j}_b,\mathbf{j}',\mathbf{j}'_a,j'_b}\ \sum_{tt'}\Phi^{tt'}Z^{tt'}\ , \tag{27}$$

where $\mathbf{j}_a,\mathbf{j}_b,\mathbf{j}'_a,\mathbf{j}'_b\in C''$, $\mathbf{j}\in C$, and $\mathbf{j}'\in C'$. The radial factor (which still depends on the energies of ψ and $\psi_{C''}$) is

$$\Phi^{tt'}(\mathbf{j},\mathbf{j}',\mathbf{j}_a,\mathbf{j}'_a,\mathbf{j}_b,\mathbf{j}'_b,\ell)=\Phi^t(\mathbf{j},\ell,\mathbf{j}_a,\mathbf{j}_b)\Phi^t(\mathbf{j}'_b,\mathbf{j}'_a,\ell,\mathbf{j}') \tag{28}$$

and the angular operator is

$$Z^{tt'}(\mathbf{j},\mathbf{j}',\mathbf{j}_a,\mathbf{j}'_a,\mathbf{j}_b,\mathbf{j}'_b,\ell)=\sum_{\substack{i,j,k,l\\ i\neq j,\ k\neq l}}(\mathsf{Z}_i^{(t)}(\mathbf{j},\mathbf{j}_a)\cdot\mathsf{Z}_j^{(t)}(\ell,\mathbf{j}_b))\times(\mathsf{Z}_k^{(t')}(\mathbf{j}'_b,\ell)\cdot\mathsf{Z}_l^{(t')}(\mathbf{j}'_a,\mathbf{j}'))\ . \tag{29}$$

B. Active electrons and the factorization of the continuum

In autoionization from configuration C'' to C, an electron in orbital $\mathbf{j}_b\in C''$ is ejected into the continuum, while an electron in $\mathbf{j}_a\in C''$ makes a radiationless transition to orbital $\mathbf{j}\in C$. With this in mind, the set of active electrons (or orbitals) with respect to C and C'' is $\mathbf{j}_a$, $\mathbf{j}_b$, and $\mathbf{j}$. When mixing between configurations C and C' is accounted for, the set is doubled to include $\mathbf{j}'_a$, $\mathbf{j}'_b$ and $\mathbf{j}'$. Except in very rare cases the set of active electrons $\mathbf{j},\mathbf{j}_a,\mathbf{j}_b,\mathbf{j}',\mathbf{j}'_a\mathbf{j}'_b$ is unique and, owing to Eq. (5), when its expectation value is taken, the sum over orbitals in $V_{\tilde{C}C''}V_{C''\tilde{C}'}$ reduces to a single term.

A couple of examples can help clarify the identification of active electrons. (To simplify notation, the orbital j quantum numbers are omitted in the examples that follow.) For an autoionizing configuration $C''=3d^94p4f$, and final states that are a mixture of $C=3d^{10}$ and $C'=3d^94d$, the only active electrons are

$$\mathbf{j}_a=\mathbf{j}'_a=4p,\quad \mathbf{j}_b=\mathbf{j}'_b=4f,\quad \mathbf{j}=3d,\quad \mathbf{j}'=4d$$

and

$$\begin{aligned}\langle\psi_C|V_{\tilde{C},C''}V_{C',\tilde{C}''}|\psi_{C'}\rangle&=\sum_{\mathbf{j}\in C,\mathbf{j}_a,\mathbf{j}_b,\mathbf{j}'_a,\mathbf{j}'_b\in C'',\mathbf{j}'\in C'}\ \sum_{t,t'}\Phi^t(\mathbf{j},\ell,\mathbf{j}_a,\mathbf{j}_b)\Phi^{t'}(\mathbf{j}'_b,\mathbf{j}'_a,\ell,\mathbf{j}')\\&\qquad\times\sum_{i\neq j,\ k\neq l}\langle\psi_C|(\mathsf{Z}_i^{(t)}(\mathbf{j},\mathbf{j}_a)\cdot\mathsf{Z}_j^{(t)}(\ell,\mathbf{j}_b))(\mathsf{Z}_k^{(t')}(\mathbf{j}'_b,\ell)\cdot\mathsf{Z}_1^{(t')}(\mathbf{j}'_a,\mathbf{j}'))|\psi_{C'}\rangle\\&=\sum_{t,t'}\Phi^t(3d,\ell,4p,4f)\Phi^{t'}(4f,4p,\ell,4d)\\&\qquad\times\sum_{i,k}\langle\psi_C|(\mathsf{Z}_i^{(t)}(3d,4p)\cdot\mathsf{Z}_k^{(t)}(\ell,4f))(\mathsf{Z}_k^{(t')}(4f,\ell)\cdot\mathsf{Z}_i^{(t')}(4p,4d))|\psi_{C'}\rangle\ .\end{aligned} \tag{30}$$

An instance where $\mathbf{j}_a\neq\mathbf{j}'_a$ and $\mathbf{j}_b\neq\mathbf{j}'_b$ is $C=3d^{10}4s4d$, $C'=3d^{10}4p4f$, and $C''=3d^94s4p4d4f$, then, necessarily, $\mathbf{j},\mathbf{j}_a,\mathbf{j}_b=3d,4p,4f$ and $\mathbf{j}',\mathbf{j}'_a,j'_b=3d,4s,4d$.

In Appendix A, it is shown that $Z^{tt'}$ factorizes into operators that act independently on the bound and continuum electrons:

$$Z^{tt'}=(-1)^{j_b+\ell+t+t'}\sum_{x,x',T}(-1)^{x+x'+T}[x,T][x']^{1/2}\begin{Bmatrix}j_{b'}&\ell&x'\\ t&x&j_b\end{Bmatrix}\begin{Bmatrix}j_b{}'&\ell&x'\\ T&t'&\ell\end{Bmatrix}[\mathsf{Y}^{tt'(x,x',T)}\times\mathsf{Z}^{(T)}(\ell,\ell)]^{(0)}\ . \tag{31}$$

$\mathsf{Y}^{tt'(x,x',T)}$ is a combination of one-, two-, and three-body operators (see Appendix A) acting only on bound electrons, and given in terms of irreducible tensor operators as

$$\mathsf{Y}^{tt'(x,x',T)}=\sum_{i,j,k}[[\mathsf{Z}_i^{(t)}(\mathbf{j},\mathbf{j}_a)\times\mathsf{Z}_j^{(x)}(\mathbf{j}'_b,\mathbf{j}_b)]^{(x')}\times\mathsf{Z}_k^{(t')}(\mathbf{j}'_a,\mathbf{j}')]^{(T)}-\delta_{j'_bj_b}\delta_{x,0}\delta_{x',t}[j_b]^{1/2}\sum_{i,k}[\mathsf{Z}_i^{(t)}(\mathbf{j},\mathbf{j}_a)\times\mathsf{Z}_k^{(t')}(\mathbf{j}'_a,\mathbf{j}')]^{(T)}\ . \tag{32}$$

The electronic indices i,j,k in Eq. (32) run independently over all bound electrons, and

$$\mathsf{Z}^{(t)}(\mathbf{j}_1,\mathbf{j}_2)=\sum_i\mathsf{Z}_i^{(t)}(\mathbf{j}_1,\mathbf{j}_2)\ . \tag{33}$$

To evaluate the configuration-to-level autoionization rate of Eq. (25), we use (27) and (31), and the standard reduction for the scalar product of two operators acting on different systems [20,21]. The summation over J_T yields a $\delta_{T,0}$ factor and (see Appendix A)

$$A^{C''}(\psi_C,\psi_{C'})=(1/g_{C''})\sum_{\mathbf{j},\mathbf{j}_a\mathbf{j}_b}\ \sum_{\mathbf{j}',\mathbf{j}'_a,\mathbf{j}'_b}\ \sum_{t,t'}(-1)^{j_b+j'_b+t+t'+1}[J]^{1/2}\sum_x(-1)^x[x]\langle\psi_C(\gamma,J)\|\mathrm{Y}^{tt'(x,x,0)}\|\psi_{C'}(\gamma',J)\rangle$$
$$\times\sum_{\mathscr{j}}\begin{Bmatrix} j_{b'} & \mathscr{j} & t' \\ t & x & j_b \end{Bmatrix}\Phi^{tt'} . \tag{34}$$

Note that the remaining reduced matrix element is independent of the continuum orbital.

Evaluation of the operator $\mathrm{Y}^{tt'(x,x,0)}$, and further reduction of $A^{C''}(\psi_C,\psi_{C'})$, depends on whether or not the active orbitals $\mathbf{j}_a,\mathbf{j}_b$ ($\mathbf{j}'_a,\mathbf{j}'_b$) with respect to C'' and C (C') are equivalent to electrons in C' (C). The several possible cases are treated separately in Sec. III C.

C. "New" orbitals and reduction of the level-to-configuration rates

To evaluate $Y^{tt'(x,x,0)}$ we generalize the concept of "new" electrons, introduced by Racah and Stein [16], to the general mixed-configuration case. An occupied orbital of C'' will be called "new" if it is active with respect to C and does not appear in C' *or* if it is active with respect to C' and does not appear in C.

Case 1: Both active electrons of C'' occupy "new" orbitals. An example is autoionization from the doubly excited sodiumlike configuration $C''=2p^5n'sn''p$ into a neonlike state ψ, which is a mixture of $C=2p^6$ and $C'=2p^5n'p$. The active orbitals $n's$ and $n''p$ do not appear in C' and are thus "new" orbitals. The final orbitals of the radiationless transition are $\mathbf{j}=2p$ and $\mathbf{j}'=n'p$ for C and C', respectively.

In this case, owing to Eq. (5), the matrix element of Y vanishes except for contributions when the electronic indices i,j,k are all equal and $\mathbf{j}'_b=\mathbf{j}_a$, $\mathbf{j}'_a=\mathbf{j}_b$. Only the one-body part of Y contributes and the configuration-to-level partial autoionization rate reduces to the following monopole interaction (see Appendix A):

$$A^{C''}(\psi_C,\psi_{C'})=(1/g_{C''})([J]/[j])^{1/2}\delta_{j,j'}\delta_{l,l'}\langle\psi_C(\gamma,J)\|Z^{(0)}(\mathbf{j},\mathbf{j}')\|\psi_{C'}(\gamma',J)\rangle$$
$$\times\sum_{\mathscr{j}}\sum_{t,t'}\left[\left[\delta_{\mathbf{j}_a\mathbf{j}_b}(-1)^{t+t'}\begin{Bmatrix} j_a & t' & \mathscr{j} \\ j_a & t & j \end{Bmatrix}+\delta_{t,t'}[t]^{-1}\right]\Phi^{t}(\mathbf{j},\mathscr{j};\mathbf{j}_a,\mathbf{j}_b)\Phi^{t'}(\mathbf{j}',\mathscr{j};\mathbf{j}'_a,\mathbf{j}'_b)\right] , \tag{35}$$

where we have used the identities following from Eq. (6)

$$\Phi^{t'}(\mathbf{j}'_b,\mathbf{j}'_a,\mathscr{j},\mathbf{j}')\equiv(-1)^{\xi}\Phi^{t'}(\mathbf{j}',\mathscr{j};\mathbf{j}'_a,\mathbf{j}'_b) , \tag{36}$$

with $\xi=j'_a-\mathscr{j}+j'_b-j'$, and

$$\Phi^{tt'}\equiv(-1)^{\xi}\sum_{t,t'}\Phi^{t}(\mathbf{j},\mathscr{j};\mathbf{j}_a,\mathbf{j}_b)\Phi^{t'}(\mathbf{J}',\mathscr{j};\mathbf{j}'_a,\mathbf{j}'_b) . \tag{37}$$

Note that the Kronecker δ functions restrict configuration mixing in this case to contributions with $n\neq n'$, $l=l'$, $j=j'$.

For $C=C'$, $Z^{(0)}(\mathbf{j},\mathbf{j})$ is just the number operator for shell $\{n_{\mathrm{j}}l_{\mathrm{j}}j\}$:

$$\langle\psi_C(\gamma,J)\|Z^{(0)}(\mathbf{j},\mathbf{j}')\|\psi_C(\gamma,J)\rangle=q_{\mathrm{j}}([J]/[j])^{1/2} , \tag{38}$$

and

$$A^{C''}(\psi_C,\psi_C)=(1/g_{C''})q_{\mathrm{j}}([J]/[j])$$
$$\times\sum_{\mathscr{j}}\sum_t[t]^{-1}[\Phi^t(\mathbf{j},\mathscr{j};\mathbf{j}_a,\mathbf{j}_b)]^2 . \tag{39}$$

Note that the sole angular dependence in this result is the statistical weight $[J]=2J+1$.

This strikingly simple result is superficially reminiscent of the J-file sum rule [17,18], which also yields a simple statistical level dependence for the configuration-to-level rate. It might also be cited as justification, at least for this fairly broad class of transitions, for the practice of assuming a statistical distribution of transition strength when using configuration-to-configuration rates in level-to-level models.

However, in contrast with the bound-bound radiative case covered by the J-file rule, the radial factor in (39), through the continuum orbital, retains a dependence on the energy of each level, in addition to the explicit dependence on $2J+1$. This dependence is not negligible, though it is smooth, and an interpolation scheme can be applied in analogy to that of Bar-Shalom, Klapisch, and Oreg [1]. Moreover, when configuration mixing is accounted for, the mixing coefficients are level dependent, and introduce a nontrivial departure from the simple statistical dependence suggested by Eq. (39).

Case 2: One active orbital in C'' is "new," one is not. An example of this case is autoionization from the highly excited state of the zinclike ion $C''=(3d)^9(4d)^2n''l''$ to a final copperlike state consisting of $C=(3d)^{10}4d$ mixed with $C'=(3d)^94d^2$. The orbitals that are active between C'' and C are clearly $\mathbf{j}_a=4d$, $\mathbf{j}_b=n''l''$, and $\mathbf{j}=3d$. Since the $4d$ orbital is occupied also C', it is not "new," while $n''l''$ is. The active orbitals with respect to C' are not unique, since the internal transition of either a $4d$ or $3d$ electron contributes to the matrix element of $V_{\bar{C}C''}V_{C''\bar{C}'}$ in Eq. (27), and $\mathbf{j}'=4d$ or $3d$.

In this case contributions to $Z^{tt'}$ vanish unless the electron indices j and l in Eq. (32) are equal. When $i=k$ as well, we again obtain a monopole contribution to $A^{C''}(\psi_C,\psi_{C'})$. The total rate (including $i\neq k$) is

$$A^{C''}(\psi_C,\psi_{C'})=(1/g_{C''})[J]^{1/2}\sum_{\mathbf{j},\mathbf{j}',\mathbf{j}_a,\mathbf{j}'_a}\sum_t [t]^{-1}\left\langle\psi_C(\gamma,J)\left|\left|\left|\left[(-1)^{j'-j_{a'}}\sum_{\substack{i,j\\ i\neq j}}(\mathbf{Z}_i^{(t)}(\mathbf{j},\mathbf{j}_a)\cdot\mathbf{Z}_j^{(t)}(\mathbf{j}'_a,\mathbf{j}'))\right.\right.\right.\right.\right.$$
$$\left.\left.\left.\left.\left.+\delta_{t,0}\delta_{\mathbf{j}_a\mathbf{j}'_a}[j]^{-1/2}\mathbf{Z}^{(0)}(\mathbf{j},\mathbf{j}')\right]\right|\right|\right|\psi_{C'}(\gamma',J)\right\rangle$$
$$\times\sum_{\mathscr{j}}\Phi^t(\mathbf{j},\mathscr{j};\mathbf{j}_a,\mathbf{j}_b)\Phi^t(\mathbf{j}',\mathscr{j};\mathbf{j}'_a,\mathbf{j}'_b)\ . \tag{40}$$

The two-body term that augments the monopole here is proportional to the standard matrix element of the electrostatic interaction, calculable by standard computer routines [22].

Case 3: No new orbitals in C''. This last case is the most general, but rarely occurs. An example is $C=(2p)^6n'p'$, $C'=(2p)^5(n'p')^2$, and $C''=(2p)^5(n'p')^3$. The active orbitals of C'' with respect to C and C', respectively, are $\mathbf{j}_a=\mathbf{j}_b=n'p'$. Since they appear in both C and C', neither orbital is new. None of the contributions to (32) vanish identically in this case and the results include three-, two-, and one-body contributions,

$$A^{C''}(\psi_C,\psi_{C'})=(1/g_{C''})\sum_{\mathbf{j},\mathbf{j}_a,\mathbf{j}_b,\mathbf{j}',\mathbf{j}'_a,\mathbf{j}'_b}\sum_{\mathscr{j}}\sum_{tt'}\Phi^{tt'}\langle\psi_C(\gamma,J)||\zeta^{tt'}||\psi_{C'}(\gamma',J)\rangle\ , \tag{41}$$

where $\zeta^{tt'}=\overline{A}+\overline{B}+\overline{\Gamma}$. $\overline{A}$, $\overline{B}$, and $\overline{\Gamma}$, the one-, two-, and three-body contribution, respectively, are defined in Appendix A, Eqs. (A29)–(A32).

IV. SUM RULES FOR COLLISIONAL TRANSITIONS

In the collisional-radiative model, the population of autoionizing states and high-lying Rydberg levels is controlled by dielectronic capture, autoionization, radiative decay, collisional excitation, and collisional ionization. We have covered the first two processes in the preceding sections, deriving sum rules for "level-to-configuration" averaging that permit the detailed states of an autoionizing configuration to be collapsed into a single, effective level. The third process, radiative decay, as well as radiative recombination, is covered by the J-file sum rule. To complete this work, we derive below analogous sum rules for collisional excitation and ionization. Of course, as with the J-file result, these will be applicable not just to transitions from singly excited to autoionizing levels, but for any level-to-configuration transition array.

A. Collisional excitation

The collisional excitation sum rule is especially straightforward since, in a previous work, the factorization of the continuum electron was obtained for the level-to-level cross section, and the collision strength reduced to a one-body operator [1]. We begin with the definition of the collision strength:

$$\Omega_{01}=8\sum_{\mathscr{j},\mathscr{j}'}\Omega_{01}(\mathscr{j},\mathscr{j}')\ ,$$
$$\Omega_{01}(\mathscr{j},\mathscr{j}')=\sum_{J_T,M_T}\left|\left\langle\psi_0(\Gamma_0,J_0)\mathscr{j}J_TM_T\left|\sum_{\substack{i,j\\ i<j}}(1/r_{ij})\right|\psi_1(\Gamma_1,J_1)\mathscr{j}'J_TM_T)\right\rangle\right|^2\ , \tag{42}$$

where $\mathscr{j},\mathscr{j}'$ designate partial waves of the incident and outgoing continuum electron. It is shown by Bar-Shalom, Klapisch, and Oreg [1] that

$$\Omega_{01}=8\sum_t\sum_{\mathbf{j}_0,\mathbf{j}_1}\sum_{\mathbf{j}'_0,\mathbf{j}'_1}\langle\psi_0||Z^{(t)}(\mathbf{j}_0,\mathbf{j}_1)||\psi_1\rangle$$
$$\times\langle\psi_0||Z^{(t)}(\mathbf{j}'_0,\mathbf{j}'_1)||\psi_1\rangle$$
$$\times Q^t(\mathbf{j}_0,\mathbf{j}_1;\mathbf{j}'_0,\mathbf{j}'_1)\ . \tag{43}$$

Here ψ_0 and ψ_1 are the mixed-configuration initial and final levels of the transition and $\mathbf{j}_0,\mathbf{j}_1$ and $\mathbf{j}'_0,\mathbf{j}'_1$ are the active orbitals involved. In the pure configuration case $\mathbf{j}_0=\mathbf{j}'_0$ and $\mathbf{j}_1=\mathbf{j}'_1$, and, for transitions between different configurations, only one term contributes to the sum over $\mathbf{j}_0,\mathbf{j}_1$ in Eq. (43). The radial factor Q^t is a sum over continuum partial waves, includes both the direct and exchange parts of the cross section, and depends implicitly on the transition energy. It is defined and discussed in detail in Ref. [1].

We will obtain the level-to-configuration collision strength by summing over states ψ_1 belonging to configuration C_1. In so doing, we shall again assume that the average energy of C_1 can be used to evaluate the radial factor accurately enough for our purpose, and factor it out. As before, we can sum over pure configuration states without loss of generality. Allowing for configuration mixing in the remaining detailed level ψ_0, we obtain

$$\Omega_0^{C_1}=\sum_{C_0,C'_0}\sum_{\psi\in C_0,\psi'\in C'_0}\alpha_\psi\alpha_{\psi'}\Omega^{C_1}(\psi,\psi')\ ,$$

where ψ and ψ' are pure configuration states of ψ_0, and

$$\Omega^{C_1}(\psi,\psi')=8\sum_{\mathbf{j}_0,\mathbf{j}_1}\sum_{\mathbf{j}'_0,\mathbf{j}'_1}\sum_t Q^t(\mathbf{j}_0,\mathbf{j}_1;\mathbf{j}'_0,\mathbf{j}')X^t_{\psi\psi'} \tag{44}$$

and

$$X^{t}_{\psi\psi'}=(-1)^{J_0-J_1+J'_1-J'_0}\sum_{\psi_{C_1}\in C_1}\langle\psi\|\mathrm{Z}^{(t)}(\mathrm{j}_0,\mathrm{j}_1)\|\psi_{C_1}\rangle\langle\psi_{C_1}\|\mathrm{Z}^{(t)}(\mathrm{j}'_1,\mathrm{j}'_0)\|\psi'\rangle$$

$$=(-1)^{J'_1-J'_0}[j_0]^{1/2}\langle\psi\|(\mathrm{Z}^{(t)}(\mathrm{j}_0,\mathrm{j}_1)\cdot\mathrm{Z}^{(t)}(\mathrm{j}'_1,\mathrm{j}'_0))\|\psi'\rangle\ . \tag{45}$$

Using Eq. (33), the two-body operator in Eq. (50) can be rewritten as

$$(\mathrm{Z}^{(t)}(\mathrm{j}_0,\mathrm{j}_1)\cdot\mathrm{Z}^{(t)}(\mathrm{j}'_1,\mathrm{j}'_0))$$

$$=\sum_{\substack{i,j\\ i\neq j}}(\mathrm{Z}^{(t)}_i(\mathrm{j}_0,\mathrm{j}_1)\cdot\mathrm{Z}^{(t)}_j(\mathrm{j}'_1,\mathrm{j}'_0))$$

$$+\delta_{\mathrm{j}_0,\mathrm{j}'_1}(-1)^{J_0+J_1+1}[J_0]^{-1/2}Z^{(0)}(\mathrm{j}_0,\mathrm{j}'_0)\ . \tag{46}$$

Thus, the $t=1$ contribution to Eq. (43) is identical in form to the J-file sum rule for the level-to-configuration radiative rate. Indeed, as shown by Bar-Shalom, Klapisch, and Oreg [1] collisional excitation can be represented by a one-electron multipole transition operator multiplied by a radial factor varying smoothly with the transition energy.

Note that for transitions between different configurations, i.e., when j_1 (j'_1) is "new" [does not occur in C_0 (C'_0)], the first term in Eq. (46) vanishes, and the level-to-configuration collision strength is given by the simple one-body monopole operator, $\mathrm{Z}^{(0)}$ alone. Following the same line of argument as in Sec. III we can conclude that, for this class of transitions, as long as the level dependence of the radial factor in (44) can be neglected, collisional transition rates from a configuration into a level depend only on the statistical weight $[J]$.

B. Collisional ionization and three-body recombination

The rates for collisional ionization and for its inverse, three-body recombination, derive from the collisional ionization strength [20].

$$I_{\psi_0\psi_1}\equiv 8\sum_{\mathscr{j}_0,\mathscr{j}_1,\mathscr{j}_2}\sum_{J_T,M_T,J_a}\left|\left\langle\psi_0(\Gamma_0,J_0)\mathscr{j}_0J_TM_T\left|\sum_{\substack{i,j\\ i<j}}(1/r_{ij})\right|\psi_1(\Gamma,J_1)\mathscr{j}_2,J_a,\mathscr{j}_1J_TM_T\right\rangle\right|^2, \tag{47}$$

where ψ_0 and ψ_1 are, respectively, the target (initial) and ionized (final) mixed configuration bound states, $\mathscr{j}_0$ stands for the continuum orbital of the incident free electron, and $\mathscr{j}_2\mathscr{j}_1$ represent the outgoing electron orbitals. The continuum electrons can be factorized as in the previous processes. The steps are presented in Appendix B with the result [cf. Eq. (B5)]

$$I_{\psi_0\psi_1}=8\sum_{\mathrm{j},\mathrm{j}'}\langle\psi_0\|a^{\dagger}_{\mathrm{j}}\|\psi_1\rangle\langle\psi_0\|a^{\dagger}_{\mathrm{j}'}\|\psi_1\rangle Q(\mathrm{j},\mathrm{j}')\ , \tag{48}$$

where

$$Q(\mathrm{j},\mathrm{j}')=\sum_{\mathscr{j}_0,\mathscr{j}_1,\mathscr{j}_2}\sum_{t}[t]^{-1}\Phi^{t}(\mathrm{j},\mathscr{j}_0;\mathscr{j}_2,\mathscr{j}_1)\Phi^{t}(\mathrm{j}',\mathscr{j}_0;\mathscr{j}_2,\mathscr{j}_1)\ . \tag{49}$$

As for other processes, this radial factor depends on transition energy. Assuming that the average energy of C_0 can be used, the following results for the level-to-configuration recombination and ionization strengths are obtained:

$$I_{C_0\psi_1}\equiv\sum_{\psi'_0\in C_0}I_{\psi'_0\psi_1}=8\sum_{t}\sum_{\mathrm{j},\mathrm{j}'\in C_0}([J_1]/[j])^{1/2}\delta_{j,j'}\delta_{l,l'}$$

$$\times\{\delta_{\mathrm{j},\mathrm{j}'}([J_1][j])^{1/2}-\langle\psi_1\|Z^{(0)}(\mathrm{j},\mathrm{j}')\|\psi_1\rangle\}Q(\mathrm{j},\mathrm{j}') \tag{50}$$

and

$$I_{\psi_0C_1}\equiv\sum_{\psi'_1\in C_1}I_{\psi_0\psi'_1}=8\sum_{t}\sum_{\mathrm{j},\mathrm{j}'\in C_1}([J_0]/[j])^{1/2}\delta_{j,j'}\delta_{l,l'}\langle\psi_0\|Z^{(0)}(\mathrm{j},\mathrm{j}')\|\psi_0\rangle\}Q(\mathrm{j},\mathrm{j}')\ . \tag{51}$$

In Eqs. (50) and (51) ψ'_0 and ψ'_1 are pure configuration states, but ψ_0 and ψ_1 are in general mixed. But, since the result is a monopole operator, which connects configurations differing only in principal quantum number, it is a good approximation to neglect all configuration interaction. Then the results simplify to the highly intuitive expressions

$$I_{C_0\psi_1}=8([J_1]/[j])(2j+1-q^{(C_1)})Q(\mathrm{j},\mathrm{j}') \tag{52}$$

and

$$I_{\psi_0C_1}=8([J_0]/[j])q^{(C_0)}Q(\mathrm{j},\mathrm{j}')\ , \tag{53}$$

where in Eqs. (52) and (53), j denotes the active orbital in

C_0, and $q^{(C_0)}$ is the occupation number of that orbital.

Again, the level-to-configuration rates are distributed statistically among levels. For ionization also the variation of the radial factor $Q(\mathbf{j},\mathbf{j})$ with energy is smooth but not necessarily small; factors of 2 can be expected. However, if this variation is neglected, the statistical distribution of level-to-configuration collisional ionization is not restricted to a class of common cases, but is rather a general rule.

V. SUMMARY AND DISCUSSION

We have presented in this paper level-to-configuration sum rules for autoionization, dielectronic capture, collisional excitation, and collisional ionization and recombination. These sum rules express the total transition rate from a specific multiconfigurational atomic level into a configuration in terms of the expectation value of an effective operator in that level. Our results follow from factorizing from each cross section the dependence on free-electron wave functions. The expectation value multiplies radial integrals that include all explicit dependence on the continuum orbitals, and that usually depend on transition energy.

The sum rules derived here are natural extensions of the J-file sum rule for level-to-configuration radiative transitions, and of the work of Racah and Stein [16] for "effective interactions," to processes involving continuum electrons. In many cases, our results further suggest the J-file rule by reducing to the matrix element of a one-body, monopole operator, yielding an apparently statistical distribution of configuration-to-configuration transition strength among levels. But because continuum orbitals enter the radial factors, a residual dependence on transition energy spoils the simple statistical outcome. Thus our results do not justify the practice of assuming statistical distributions of transition strength, but rather isolate the source of deviations from this rule, the better to evaluate its accuracy.

We also found that, when equivalent electrons are involved in transitions, or configuration mixing occurs, statistical dependence (i.e., state independence) does not obtain, even neglecting variations in transition energy. In these cases, where the "active" electrons are not "new," our results involve one-, two-, and three-body multipole operators. With the exception of the three-body operators that can be encountered in dielectronic capture from excited states, the matrix elements we have obtained can be calculated by standard computer routines [23] based on the method of Fano [24]. An extension of the Fano method to three-body operators will be presented elsewhere.

Aside from their mathematical interest and their bearing on the assumption of state-independent atomic transition rates, the sum rules have important practical applications in collisional-radiative modeling. These applications will be systematically explored in further reports: here we will only summarize the potential utility of the present results.

In the Introduction, we partially motivated this work by describing several generic problems encountered in collisional-radiative modeling, related to the proliferation of atomic levels, and the averaging of atomic configurations and population flux. The sum rules, including the J-file rule, provide a consistent and computationally efficient procedure for collapsing configurations into effective levels, and describing the flux of population through them. This procedure shares the computational simplicity of using configuration-average rates (i.e., those averaged over initial and final configurations), but avoids the assumption of state independence when connecting a configuration and a level. As we have seen, this assumption breaks down when configuration mixing is taken into account, or equivalent electrons are involved in a transition. In the context of collisional-radiative modeling, the application of configuration-average rates to level-to-configuration transitions also assumes that the levels are statistically populated. The level-to-configuration sum rules are distinctly preferable in applications where it is necessary to retain the detailed structure of a subset of atomic levels, while including the effects of a large number of surrounding configurations. The sole approximation involved is the assumption of a statistical population distribution in the averaged configuration. Note, in particular, that the sum rules are exact when describing the flux of population from an individual level into a configuration.

In addition, we expect the sum rules to be useful in evaluating rates for dielectronic recombination and similar multistep processes. These transitions involve summing over many pathways connecting one level to another through transitions to and from intermediate configurations. The product of rates for each intermediate transition and branching ratios that are the inverse of the total depletion rate for each intermediate state, must be summed over all intermediate states. The use of sum rules can expedite this calculation in two ways. First, they yield an exact, computationally simple expression for the branching ratio into a specific configuration. Exact, total branching ratios can thus be obtained by sums over configurations, rather than levels. Second, if the levels in an intermediate configuration are populated according to their statistical weight (or assumed to be), then the sum over intermediate states of a given configuration is easily seen to reduce to a product of sum-rule transition rates, divided by the configuration-average branching ratio. Of course, the assumption of statistical populations is highly problematic, and the use of configuration averages in evaluating dielectronic recombination, though common [13–15,25] is known to be fraught with danger [26], at least in the zero-density limit. Still, level-to-configuration sum rules improve upon the usual configuration-average treatments by retaining the structure of initial and final states. In addition, the preferred approach to calculating rate coefficients for two-step processes [9,10,26,27], which involves weighting intermediate states by fluorescent yield rather than multiplicity, breaks down at high densities owing to the neglect of collisional mixing. Thus we expect that, particularly for high-lying autoionizing configurations that are near equilibrium with the continuum, a density regime exists where the sum rules can yield the most accurate transition rates. In all events, since the method of weighting by fluorescence yield cannot be reduced to analytic expressions, the sum rules provide a far simpler calculation, while at the same time improving on the accuracy of existing configuration average treatments.

The results obtained here, and their possible utility, suggest new applications and development directions for the theory of atomic transition arrays. One is related to the need to choose an "average" configuration energy to evaluate a sum rule. We have already alluded to the possibility of improving upon this approximation by adapting the concept of "emissive zones," introduced for radiative transition arrays by Bauche, Bauche-Arnoult, and Klapisch [17] to obtain a shift in the configuration-average energy difference. In fact, by considering higher moments of the transition arrays for processes treated here, it ought to be possible to systematically correct for the neglect of transition energy variation. Another direction is suggested by the recently expounded super-transition-array (STA) theory [28], which considers transitions between groups of configurations (super configurations). In the context of the STA paradigm, sum rules can be expected to yield the means to reduce superconfigurations to effective levels.

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APPENDIX A

Decoupling of the continuum for autoionization

The angular part of the effective operator for the configuration-to-level autoionization rate is

$$Z^{tt'}=\sum_{\substack{i,j,k,l\\ i\neq j,\ k\neq l}}(\mathrm{Z}_i^{(t)}(\mathbf{j},\mathbf{j}_a)\cdot\mathrm{Z}_j^{(t)}(\mathscr{j},\mathbf{j}_b))\times(\mathrm{Z}_k^{(t')}(\mathbf{j}'_b,\mathscr{j})\cdot\mathrm{Z}_l^{(t')}(\mathbf{j}'_a,\mathbf{j}'))\ . \tag{A1}$$

Terms with $i=j$ or $k=l$ vanish since the continuum orbital $\mathscr{j}$ is orthogonal to all bound orbitals. Thus we can extend the sum to obtain

$$\begin{aligned}Z^{tt'}&=\sum_{i,j,k,l}(\mathrm{Z}_i^{(t)}(\mathbf{j},\mathbf{j}_a)\cdot\mathrm{Z}_j^{(t)}(\mathscr{j},\mathbf{j}_b))(\mathrm{Z}_k^{(t')}(\mathbf{j}'_b,\mathscr{j})\cdot\mathrm{Z}_1^{(t')}(\mathbf{j}'_a,\mathbf{j}'))\\&\equiv(-1)^{t+t'}[t,t']^{1/2}[[\mathrm{Z}^{(t)}(\mathbf{j},\mathbf{j}_a)\times\mathrm{Z}^{(t)}(\mathscr{j},\mathbf{j}_b)]^{(0)}\times[\mathrm{Z}^{(t')}(\mathbf{j}'_b,\mathscr{j})\times\mathrm{Z}^{(t')}(\mathbf{j}'_a,\mathbf{j}')]^{(0)}]^{(0)}\ ,\end{aligned} \tag{A2}$$

where the scalar product is related to the zero-rank tensor product by

$$(\mathrm{Z}_i^{(t)}(\mathbf{j},\mathbf{j}_a)\cdot\mathrm{Z}_j^{(t)}(\mathbf{j}'_a,\mathbf{j}'))=(-1)^t[t]^{1/2}[\mathrm{Z}^{(t)}(\mathbf{j},\mathbf{j}_a)\times\mathrm{Z}^{(t)}(\mathbf{j}'_a,\mathbf{j}')]^{(0)}\ .$$

In second quantized notation,

$$\mathrm{Z}^{(t)}(\mathbf{j},\mathbf{j}')\equiv\sum_i\mathrm{Z}_i^{(t)}(\mathbf{j},\mathbf{j}')=-[t]^{-1/2}\{a_{\mathbf{j}}^{\dagger},a_{\mathbf{j}'}\}^{(t)}\ , \tag{A3}$$

where $a_{\mathbf{j}}^{\dagger}$ and $a_{\mathbf{j}'}$ are tensorial creation and annihilation operators [1,29]. Substituting (A3) where the continuum electron appears in (A2) yields

$$Z^{tt'}=(-1)^{t+t'}[[\mathrm{Z}^{(t)}(\mathbf{j},\mathbf{j}_a)\times\{a_{\mathscr{j}}^{\dagger},a_{\mathbf{j}_b}\}^{(t)}]^{(0)}\times[\{a_{\mathbf{j}'_b}^{\dagger},a_{\mathscr{j}}\}^{(t')}\times\mathrm{Z}^{(t')}(\mathbf{j}'_a,\mathbf{j}')]^{(0)}]^{(0)}\ . \tag{A4}$$

By recoupling the angular momenta, and using the anticommutation relation [29]

$$\{a_{\mathbf{j}'},a_{\mathbf{j}}^{\dagger}\}^{(t)}=\delta_{\mathbf{j}'\mathbf{j}}\delta_{t,0}[j]^{1/2}+(-1)^{j+j'-t+1}\{a_{\mathbf{j}}^{\dagger},a_{\mathbf{j}'}\}^{(t)}\ , \tag{A5}$$

we can rearrange the operators in the following order:

$$\{[(\mathrm{Z}^{(t)}(\mathbf{j},\mathbf{j}_a)\times\{a_{\mathbf{j}'_b}^{\dagger},a_{\mathbf{j}_b}\}^{(x)})^{(x')}\times\mathrm{Z}^{(t')}(\mathbf{j}'_a,\mathbf{j}')]^{(T)}\times\{a_{\mathscr{j}}^{\dagger},a_{\mathscr{j}}\}^{(T)}\}^{(0)}\ .$$

The recoupling coefficient in this case is [30]

$$\begin{aligned}&((\mathbf{j},\mathbf{j}_a)t,(\mathscr{j},\mathbf{j}_b)t;0{:}(\mathbf{j},\mathbf{j}_a)t,(\mathscr{j},\mathbf{j}_b)t;0|(\mathbf{j},\mathbf{j}_a)t,(\mathbf{j}'_b,\mathbf{j}_b)x;x'(\mathbf{j}'_a,\mathbf{j}');T{:}(\mathscr{j},\mathscr{j});T)^{(0)}\\&\qquad=(-1)^{j_b+x+x'-T+j+1}[x,x',T]^{1/2}\begin{Bmatrix}j_{b'}&\mathscr{j}&x'\\t&x&j_b\end{Bmatrix}\begin{Bmatrix}j_{b'}&\mathscr{j}&x'\\T&t'&\mathscr{j}\end{Bmatrix}\ .\end{aligned} \tag{A6}$$

The scalar part of the anticommutation relation contributes an additional three-body contribution when $\mathbf{j}_b=\mathbf{j}'_b$:

$$\delta_{\mathbf{j}_{b'},\mathbf{j}_b}\delta_{x,0}\delta_{x',t}[j_b]^{1/2}\{[(\mathrm{Z}^{(t)}(\mathbf{j},\mathbf{j}_a)\times\{a_{\mathbf{j}_{b'}}^{\dagger}a_{\mathbf{j}_b}\}^{(x)})^{(x')}\times\mathrm{Z}^{(t')}(\mathbf{j}'_a,\mathbf{j}')]^{(T)}\times\{a_{\mathscr{j}}^{\dagger},a_{\mathbf{j}}\}^{(T)}\}^{(0)}$$

$$=\delta_{\mathbf{j}_{b'},j_b}\delta_{x,0}\delta_{x',t}[j_b]^{1/2}\{[\mathrm{Z}^{(t)}(\mathbf{j},\mathbf{j}_a)\times\mathrm{Z}^{(t')}(\mathbf{j}'_a,\mathbf{j}')]^{(T)}\times\{a_{\mathscr{j}}^{\dagger}a_{\mathscr{j}}\}^{(T)}\}^{(0)}\ . \tag{A7}$$

Combining these contributions, and factoring the common dependence on the continuum, we have

$$Z^{tt'}=(-1)^{j_b+\mathscr{j}+t+t'}\sum_{x,x',T}(-1)^{x+x'+T}[x,T][x']^{1/2}\begin{Bmatrix} j_{b'} & \mathscr{j} & x' \\ t & x & j_b \end{Bmatrix}\begin{Bmatrix} j_{b'} & \mathscr{j} & x' \\ T & t' & \mathscr{j} \end{Bmatrix}[\mathrm{Y}^{(x,x',t)}\times\mathrm{Z}^{(T)}(\mathscr{j},\mathscr{j})]^{(0)}\ , \tag{A8}$$

where

$$\mathrm{Y}^{(x,x',T)}=\sum_{i,j,k}[[\mathrm{Z}_i^{(t)}(\mathbf{j},\mathbf{j}_a)\times\mathrm{Z}_j^{(x)}(\mathbf{j}'_b,\mathbf{j}_b)]^{(x')}\times\mathrm{Z}_k^{(t')}(\mathbf{j}'_a,j')]^{(T)}$$

$$-\delta_{\mathbf{j}'_b\mathbf{j}_b}\delta_{x,0}\delta_{x',t}[j_b]^{1/2}\sum_{i,k}[\mathrm{Z}_i^{(t)}(\mathbf{j},\mathbf{j}_a)\times\mathrm{Z}_k^{(t')}(\mathbf{j}'_a,\mathbf{j}')]^{(T)}\ . \tag{A9}$$

The partial rate of Eq. (24) is

$$A^{C''}(\psi_C,\psi_{C'})=\sum_{\mathbf{j},\mathbf{j}_a,\mathbf{j}_b,\mathbf{j}'\mathbf{j}'_a,\mathbf{j}'_b}\ \sum_{t,t'}\Phi^{tt'}\sum_{J_T}[J_T]\sum_{\mathscr{j}}\langle\psi_C(\gamma,J)\mathscr{j}J_TM_T|Z^{tt'}|\psi_{C'}(\gamma',J)\mathscr{j}J_TM_T\rangle\ . \tag{A10}$$

From Eq. (A9), Eq. (3.35) of Judd [21], and the identity

$$\sum_{J_T}[J_T](-1)^{J+\mathscr{j}+J_T}\begin{Bmatrix} J & \mathscr{j} & J_T \\ \mathscr{j} & J & T \end{Bmatrix}=\delta_{T,0}[J,\mathscr{j}]^{1/2}\ , \tag{A11}$$

we obtain

$$\sum_{J_T}[J_T]\sum_{\mathscr{j}}\langle\psi_C(\gamma,J)\mathscr{j}J_TM_T|\mathrm{Z}^{tt'}|\psi_{C'}(\gamma',J)\mathscr{j}J_TM_T\rangle$$

$$=\langle\psi_C(\gamma,J)\|\zeta^{tt'}\|\psi_{C'}(\gamma',J)\rangle\ , \tag{A12}$$

where

$$\zeta^{tt'}=(-1)^{j_b+j'_b+t+t'+1}[J]^{1/2}$$

$$\times\sum_x(-1)^x[x]\begin{Bmatrix} j_{b'} & \mathscr{j} & t' \\ t & x & j_b \end{Bmatrix}\mathrm{Y}^{(x,x,0)} \tag{A13}$$

and

$$\mathrm{Y}^{(x,x,0)}=\sum_{i,j,k}\mathrm{Y}_{i,j,k}^{(x,x,0)}-\delta_{\mathbf{j}_{b'},\mathbf{j}_b}\delta_{x,0}\delta_{t',t}[j_b]^{1/2}$$

$$\times\sum_{i,k}[\mathrm{Z}_i^{(t)}(\mathbf{j},\mathbf{j}_a)\times\mathrm{Z}_k^{(t)}(\mathbf{j}'_a,\mathbf{j}')]^{(0)}\ , \tag{A14}$$

$$\mathrm{Y}_{i,j,k}^{(x,x,0)}=[[\mathrm{Z}_i^{(t)}(\mathbf{j},\mathbf{j}_a0\times\mathrm{Z}_j^{(x)}(\mathbf{j}'_b,\mathbf{j}_b)]^{(x')}\times\mathrm{Z}_k^{(t')}(\mathbf{j}'_a,\mathbf{j}')]^{(0)}\ . \tag{A15}$$

The order of coupling here is arbitrary since the triple product in (A15) is associative. The independent sum over electronic indices i,j,k in (A14) gives rise to one three-body operator

$$\Gamma=\sum_{\substack{i,j,k\\ i\neq j\neq k}}\mathrm{Y}_{i,j,k}^{(x,x,0)}\ , \tag{A16}$$

three two-body operators

$$B_1=\sum_{\substack{i,j,k\\ i=j\neq k}}\mathrm{Y}_{i,j,k}^{(x,x,0)}\ ,$$

$$B_2=\sum_{\substack{i,j,k\\ j=k\neq i}}\mathrm{Y}_{i,j,k}^{(x,x,0)}\ , \tag{A17}$$

$$B_3=\sum_{\substack{i,j,k\\ i=k\neq j}}\mathrm{Y}_{i,j,k}^{(x,x,0)}\ ,$$

and a one-body operator

$$A_1=\sum_{\substack{i,j,k\\ i=j=k}}\mathrm{Y}_{i,j,k}^{(x,x,0)}\ . \tag{A18}$$

The second term in Eq. (A14) gives rise to a two-body operator

$$B_4=-\delta_{\mathbf{j}'_b\mathbf{j}_b}\delta_{x,0}\delta_{t',t}[j_b]^{1/2}$$

$$\times\sum_{\substack{i,k\\ i\neq k}}[\mathrm{Z}_i^{(t)}(\mathbf{j},\mathbf{j}_a)\times\mathrm{Z}_k^{(t)}(\mathbf{j}'_a,\mathbf{j}')]^{(0)}\ , \tag{A19}$$

and a one-body operator

$$A_2=-\delta_{\mathbf{j}'_b\mathbf{j}_b}\delta_{x,0}\delta_{t',t}[j_b]^{1/2}$$

$$\times\sum_i[\mathrm{Z}_i^{(t)}(\mathbf{j},\mathbf{j}_a)\times\mathrm{Z}_i^{(t)}(\mathbf{j}'_a,\mathbf{j}')]^{(0)}\ . \tag{A20}$$

Thus

$$\zeta^{tt'}=(-1)^{j_b+j'_b+t+t'+1}[J]^{1/2}$$

$$\times\sum_x(-1)^x[x]\begin{Bmatrix} j_{b'} & \mathscr{j} & t' \\ t & x & j_b \end{Bmatrix}$$

$$\times(A_1+A_2+B_1+B_2+B_3+B_4+\Gamma)$$

$$\equiv\overline{A}_1+\overline{A}_2+\overline{B}_1+\overline{B}_2+\overline{B}_3+\overline{B}_4+\Gamma\ . \tag{A21}$$

By recoupling operators carrying the same electron index, and using the relation

$$[\mathrm{Z}_i^{(t)}(\alpha\gamma)\times\mathrm{Z}_i^{(t')}(\beta\delta)]^{(T)} =\delta_{\beta\gamma}(-1)^{j_\alpha+j_\delta+T}[T]^{1/2}\begin{Bmatrix} t & T & t' \\ j_\alpha & j_\beta & j_\delta \end{Bmatrix}\mathrm{Z}_i^{(T)}(\alpha\delta)\;, \tag{A22}$$

we obtain

$$\bar{B}_1=\delta_{\mathbf{j}_a\mathbf{j}_b'}(-1)^{t+t'+j_b'-\mathscr{j}}[J]^{1/2}\begin{Bmatrix} j_b' & t' & \mathscr{j} \\ j_b & t & j \end{Bmatrix} \times\sum_{\substack{i,k\\ i\neq k}}(\mathrm{Z}_i^{(t')}(\mathbf{j},\mathbf{j}_b)\cdot\mathrm{Z}_k^{(t')}(\mathbf{j}_a',\mathbf{j}'))\;, \tag{A23}$$

$$\bar{B}_2=\delta_{\mathbf{j}_b\mathbf{j}_a'}(-1)^{t+t'+j_b-\mathscr{j}}[J]^{1/2}\begin{Bmatrix} j_b & t & \mathscr{j} \\ j_b' & t' & j' \end{Bmatrix} \times\sum_{\substack{i,j\\ i\neq j}}(\mathrm{Z}_i^{(t')}(\mathbf{j},\mathbf{j}_a)\cdot\mathrm{Z}_j^{(t')}(\mathbf{j}_b',\mathbf{j}'))\;, \tag{A24}$$

$$\bar{B}_3=\delta_{\mathbf{j}_a\mathbf{j}_a'}(-1)^{j+j'+j_b'+j_b+1}[J]^{1/2} \times\sum_x[x]\begin{Bmatrix} j_b' & \mathscr{j} & t' \\ t & x & j_b \end{Bmatrix}\begin{Bmatrix} t' & x & t \\ j & j_a & j' \end{Bmatrix} \times\sum_{\substack{i,j\\ i\neq j}}(\mathrm{Z}_i^{(x)}(\mathbf{j},\mathbf{j}')\cdot\mathrm{Z}_j^{(x)}(\mathbf{j}_b',\mathbf{j}_b))\;, \tag{A25}$$

$$\bar{B}_4=\delta_{\mathbf{j}_b\mathbf{j}_b'}(-1)^{j_b+\mathscr{j}+1}[J]^{1/2}[t]^{-1} \times\sum_{\substack{i,j\\ i\neq j}}(\mathrm{Z}_i^{(t)}(\mathbf{j},\mathbf{j}_a)\cdot\mathrm{Z}_j^{(t)}(\mathbf{j}_a',\mathbf{j}'))\;, \tag{A26}$$

$$\bar{A}_1=\delta_{\mathbf{j}_b\mathbf{j}_a'}\delta_{\mathbf{j}_a\mathbf{j}_b'}(-1)^{t+t'+j_b+j_a+j+\mathscr{j}}[J/j]^{1/2} \times\begin{Bmatrix} j_b' & t' & \mathscr{j} \\ j_b & t & j \end{Bmatrix}\mathbf{Z}^{(0)}(\mathbf{j},\mathbf{j}')\;, \tag{A27}$$

$$\bar{A}_2=\delta_{\mathbf{j}_b\mathbf{j}_b'}\delta_{\mathbf{j}_a\mathbf{j}_a'}\delta_{tt'}(-1)^{j_b'+j_a+j+\mathscr{j}} \times[J/j]^{1/2}[t]^{-1}\mathbf{Z}^{(0)}(\mathbf{j},\mathbf{j}')\;. \tag{A28}$$

Rearranging these expressions, we obtain the following results.

(i) Three-body contribution:

$$\Gamma=(-1)^{j_b+j_b'+t+t'+1}[J]^{1/2}\sum_x(-1)^x[x]\begin{Bmatrix} j_b' & \mathscr{j} & t' \\ t & x & j_b \end{Bmatrix} \times\sum_{\substack{i,j,k\\ i\neq j\neq k}}[[\mathrm{Z}_i^{(t)}(\mathbf{j},\mathbf{j}_a)\times(\mathrm{Z}_j^{(x)}(\mathbf{j}_b',\mathbf{j}_b)]^{(x)}\times\mathrm{Z}_k^{(t')}(\mathbf{j}_a',\mathbf{j}')]^{(0)}\;. \tag{A29}$$

(ii) Two-body contribution:

$$\bar{B}_1+\bar{B}_2+\bar{B}_3+\bar{B}_4=[J]^{1/2}\sum_x\sum_\alpha(\delta_{\mathbf{j}_a\mathbf{j}_b'}\delta_{\mathbf{j}_\alpha\mathbf{j}_b}\delta_{\mathbf{j}_\alpha'\mathbf{j}_a'}\delta_{xt'}\beta_1+\delta_{\mathbf{j}_a\mathbf{j}_a'}\delta_{\mathbf{j}_\alpha\mathbf{j}_b}\delta_{\mathbf{j}_\alpha'\mathbf{j}_b'}\beta_2+\delta_{\mathbf{j}_b\mathbf{j}_a'}\delta_{\mathbf{j}_\alpha\mathbf{j}_a}\delta_{\mathbf{j}_\alpha'\mathbf{j}_b'}\delta_{xt}\beta_3+\delta_{\mathbf{j}_b\mathbf{j}_b'}\delta_{\mathbf{j}_\alpha\mathbf{j}_a}\delta_{\mathbf{j}_\alpha'\mathbf{j}_a'}\delta_{x,t}\beta_4) \times\sum_{\substack{i,j\\ i\neq j}}(\mathrm{Z}_i^{(x)}(\mathbf{j},\mathbf{j}_\alpha)\cdot\mathrm{Z}_j^{(x)}(\mathbf{j}_\alpha',\mathbf{j}'))\;, \tag{A30}$$

where

$$\beta_1=(-1)^{t+t'+j_b'-\mathscr{j}}\begin{Bmatrix} j_b' & t' & \mathscr{j} \\ j_b & t & j \end{Bmatrix}\;,$$

$$\beta_2=(-1)^{j_a+j_b+j_b'+j+j'+\mathscr{j}+t+t'+x} \times\begin{Bmatrix} \mathscr{j} & j_a & x \\ j & j_b & t \end{Bmatrix}\begin{Bmatrix} \mathscr{j} & j_a & x \\ j' & j_b' & t' \end{Bmatrix}\;,$$

$$B_3=(-1)^{j_b'-\mathscr{j}+t+t'}\begin{Bmatrix} j_b & t & \mathscr{j} \\ j_b' & t' & j' \end{Bmatrix}\;,$$

$$\beta_4=(-1)^{j_b'+\mathscr{j}+t+t'}\delta_{tt'}[t]^{-1}\;. \tag{A31}$$

(iii) One-body contribution:

$$\bar{A}_1+\bar{A}_2=(-1)^{t+t'+j_b+j_a+j+\mathscr{j}}[J/j]^{1/2} \times\delta_{j,j'}\left[\delta_{\mathbf{j}_b\mathbf{j}_a'}\delta_{\mathbf{j}_a\mathbf{j}_b'}\begin{Bmatrix} j_b & t & \mathscr{j} \\ j_b' & t' & j' \end{Bmatrix} +\delta_{\mathbf{j}_b\mathbf{j}_b'}\delta_{\mathbf{j}_a\mathbf{j}_a'}\delta_{tt'}[t]^{-1}\right]\mathbf{Z}^{(0)}(\mathbf{j},\mathbf{j}')\;. \tag{A32}$$

The symmetry $\mathbf{j}_a\leftrightarrow\mathbf{j}_b$, $\mathbf{j}_a'\leftrightarrow\mathbf{j}_b'$ is hidden in these results since, by our definition, we have chosen $\mathbf{j}_b$ and $\mathbf{j}_b'$ as the orbitals that are coupled to the continuum in the direct contribution to Eq. (25).

APPENDIX B

The collisional ionization strength is

$$I_{\psi_0\psi_1} \equiv 8 \sum_{\mathscr{j}_0,\mathscr{j}_1,\mathscr{j}_2} \sum_{J_T M_T J_a} \left| \left\langle \psi_0(\Gamma_0,J_0)\mathscr{j}_0 J_T M_T \,\middle|\, \sum_{\substack{i,j\\ i<j}} (1/r_{ij}) \,\middle|\, \psi_1(\Gamma_1,J_1)\mathscr{j}_2,J_a,\mathscr{j}_1 J_T M_T \right\rangle \right|^2 . \quad \text{(B1)}$$

We apply the representation in Eq. (4) and factorize the orbitals $\mathscr{j}_0,\mathscr{j}_1$ using Eq. (3-38) of Ref. [21]. This step is identical to the factorization of the continuum in the collisional excitation process [1], and leads to the result related to Eq. (44),

$$I_{\psi_0\psi_1} = 8 \sum_{J_a\mathscr{j}_2} \sum_{\mathbf{j}_0,\mathbf{j}_0'} \sum_t Q^t(\mathbf{j}_0,\mathscr{j}_2;\mathbf{j}_0',\mathscr{j}_2') \langle \psi_0 \| Z^{(t)}(\mathbf{j}_0,\mathscr{j}_2) \| \psi_1 \mathscr{j}_2 J_a \rangle \langle \psi_0 \| Z^{(t)}(\mathbf{j}_0',\mathscr{j}_2') \| \psi_1 \mathscr{j}_2 J_a \rangle , \quad \text{(B2)}$$

$$Q^t(\mathbf{j}_0,\mathscr{j}_2;\mathbf{j}_0',\mathscr{j}_2') = [t]^{-1} \sum_{\mathscr{j}_0,\mathscr{j}_1} \Phi^t(\mathbf{j}_0,\mathscr{j}_0;\mathbf{j}_2,\mathscr{j}_1) \Phi^t(\mathbf{j}_0',\mathscr{j}_0;\mathbf{j}_2,\mathscr{j}_1) . \quad \text{(B3)}$$

Using Eq. (A6), and Eqs. (3-35) of Ref. 21, and the relation [29]

$$\langle 0 \| a_{\mathscr{j}_2} \| \mathscr{j}_2 \rangle = [\mathscr{j}_2]^{1/2} , \quad \text{(B4)}$$

we obtain

$$\langle \psi_0 \| Z^{(t)}(\mathbf{j}_0,\mathscr{j}_2) \| \psi_1 \mathscr{j}_2 J_a \rangle = (-1)^{j_0+J_a+J_0+\mathscr{j}_2+1} [J_a]^{1/2} \begin{Bmatrix} J_a & t & J_0 \\ j_0 & J_1 & \mathscr{j}_2 \end{Bmatrix} \langle \psi^0 \| a_{\mathbf{j}_0}^\dagger \| \psi_1 \rangle . \quad \text{(B5)}$$

Substituting Eq. (B5) in (B2) and summing over J_a yields the fully factorized result

$$I_{\psi_0\psi_1} \equiv 8 \sum_{\mathbf{j},\mathbf{j}'} \langle \psi_0 \| a_{\mathbf{j}}^\dagger \| \psi_1 \rangle \langle \psi_0 \| a_{\mathbf{j}'}^\dagger \| \psi_1 \rangle Q(\mathbf{j},\mathbf{j}') , \quad \text{(B6)}$$

where

$$Q(\mathbf{j},\mathbf{j}') = \sum_{\mathscr{j}_0\mathscr{j}_1,\mathscr{j}_2} \sum_t [t]^{-1} \Phi^t(\mathbf{j},\mathscr{j}_0;\mathscr{j}_2,\mathscr{j}_1) \Phi^t(\mathbf{j}',\mathscr{j}_0;\mathscr{j}_2,\mathscr{j}_1) . \quad \text{(B7)}$$

The level-to-configuration result is obtained by using the relation [29]

$$\langle \psi_0 \| a_{\mathbf{j}}^\dagger \| \psi_1 \rangle = (-1)^{J_0-j-J_1} \langle \psi_1 \| a_{\mathbf{j}} \| \psi_0 \rangle \quad \text{(B8)}$$

and summing over the target states ψ_0 in configuration C_0 in Eq. (B6). The result is

$$I_{C_0\psi_1} \equiv 8 \sum_t \sum_{\mathbf{j},\mathbf{j}' \in C_0} ([J_1]/[j])^{1/2} \delta_{j,j'} \langle \psi_1 \| \{a_{\mathbf{j}},a_{\mathbf{j}'}^\dagger\}^{(0)} \| \psi_1 \rangle Q(\mathbf{j},\mathbf{j}') \quad \text{(B9)}$$

and, from (A3) and (A5),

$$\{a_{\mathbf{j}},a_{\mathbf{j}'}^\dagger\}^{(0)} = \delta_{\mathbf{j}'\mathbf{j}}([J_1][j])^{1/2} - Z^{(0)}(\mathbf{j},\mathbf{j}') . \quad \text{(B10)}$$

In the same way, summing over $\psi_1 \in C_1$ in Eq. (B6) yields

$$\begin{aligned} I_{\psi_0 C_1} &= 8 \sum_t \sum_{\mathbf{j},\mathbf{j}' \in C_1} ([J_1]/[j])^{1/2} \delta_{j,j'} \langle \psi_0 \| -\{a_{\mathbf{j}}^\dagger,a_{\mathbf{j}'}\}^{(0)} \| \psi_0 \rangle Q(\mathbf{j},\mathbf{j}') \\ &= 8 \sum_t \sum_{\mathbf{j},\mathbf{j}' \in C_1} ([J_1]/[j])^{1/2} \delta_{j,j'} \langle \psi_0 \| Z^{(0)}(\mathbf{j},\mathbf{j}') \| \psi_0 \rangle Q(\mathbf{j},\mathbf{j}') . \end{aligned} \quad \text{(B11)}$$

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