Modified resonance amplitudes with strongly correlated channels

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A modification of resonance amplitudes is proposed that takes into account violent inner-shell processes accompanied by correlated multielectron transitions. For light ions with electrons in high Rydberg states, the conventional expression for the total widths of the resonance states given in terms of the Auger and radiative transition probabilities is not adequate. The present terms introduced to the widths can be very large and can seriously affect dielectronic recombination and resonance excitation; all the earlier calculations have been reexamined. Implications of this change on future calculations and on other related processes, such as photoionization plus Auger ionization, excitation-autoionization, multiple ionization, and similar processes in ion-atom collisions are also discussed.

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Resonance processes in atomic (and nuclear) collisions are ordinarily described by amplitudes of Breit-Wigner form [1,2], where the energy denominators specify the positions and widths of the resonance states. The total width is given by a sum of decay probabilities to all the open channels that are allowed by conservation laws and selection rules.

It is proposed here that the conventional resonance theory must be modified, sometimes drastically, to incorporate the simultaneous multielectron processes, such as the shake-off and shake-up processes that lead to additional ionization and excitations. These effects are important for "violent" Auger and radiative decays and their inverses where the effective inner-shell core charge changes by one or more units, as in the inner-shell excitation and ionization, irrespective of the way such holes are produced or annihilated. They can occur in electron-ion collisions as well as in photoexcitations and photoionizations, and also in ion-atom collisions. We have found specific cases, to be described below, in which the correlated channels dominate and the existing resonance theory totally breaks down.

In the conventional treatment of the inner-shell processes, the outer-shell spectator electrons are generally assumed to remain in the "same" orbitals, as long as the change of the core is not too violent. That is, the new orbitals of the spectator electrons are adjusted to the Hartree-Fock fields of the new configuration with modified energies, but the numbers of nodes in the wave functions and the angular momenta are held fixed at the values assumed in the old configuration. For violent collisions, however, the change can be large enough to shake one or more outer-shell electrons to upper levels (with different $n'l'$) or to continuum states, resulting in extra channels for the resonant state configuration to decay. This has been neglected in all the previous dielectronic-recombination (DR) and resonant-excitation (RE) calculations [3,4]. It is therefore crucial to determine under what conditions such new channels become important and to reexamine the existing data for their validity. We emphasize that the shake effect is not the same as the usual configuration interaction between closed channels represented by square-integrable wave functions; it not only distorts the states involved, but can also introduce new excitation and ionization channels which are open and involve one or more continuum electrons. Of course, this latter aspect of the shake effect is of interest here.

The shake process was studied earlier [5,6] in the determination of final charge-state distribution of atoms as a result of nuclear beta decays, and in photoionization and excitation of inner-shell electrons. More recently, the shake effect was incorporated [7] into the simple radiative-Auger-cascade model in explaining the final charge-state distribution of Ne, Mg, and Ar ions with one or more inner-shell holes. It was found that the shake effect during the initial formation of the inner-shell holes was crucial in explaining the production of high charge states observed in experiments [8,9]. The subsequent cascade decay of the inner-shell holes also required shake corrections, at the level of 5–10 % overall, although some individual Auger transitions were accompanied by as much as 30% corrections. Only the low-lying excited states were involved in this study, however, and the present paper extends the treatment to those states with high-Rydberg-state electrons [10] in light ions where the effect is greatly magnified.

In electron-ion collisions, the resonant excitation and dielectronic recombination processes are described as [3,4]

$$e + A^{z+}(i) \rightarrow (A^{(z-1)+})(d) \rightarrow \begin{cases} A^{z+}(j)+e', & \text{(RE)} \\ A^{(z-1)+}(f)+x & \text{(DR)} . \end{cases} \tag{1}$$

The width of the resonance state d contains transition probabilities for all Auger (a) and radiative (r) decay channels. The DR and RE amplitudes are thus defined as

$$\begin{aligned} M^{\mathrm{DR}}_{i,df} &= \langle f|D|d\rangle [E - E_d + i\Gamma(d)/2]^{-1} \langle d|V|i\rangle , \\ M^{\mathrm{RE}}_{i,dj} &= \langle j|V|d\rangle [E - E_d + i\Gamma(d)/2]^{-1} \langle d|V|i\rangle , \end{aligned} \tag{2}$$

in the isolated resonance approximation [3], for example. The operators D and V are the electron-radiation and electron-electron couplings, respectively. The width $\Gamma(d)$ is given by

$$\Gamma(d)=\Gamma_a(d)+\Gamma_r(d) , \tag{3}$$

where

$$\Gamma_a(d)=\sum_j A_a(d\rightarrow j)=2\pi\sum_j |\langle j|V|d\rangle|^2 ,$$

$$\Gamma_r(d)=\sum_f A_r(d\rightarrow f)=2\pi\sum_j |\langle f|D|d\rangle|^2 .$$

Amplitudes for other resonance processes are similarly defined. The energy averaged cross sections [3] (in units of πa_0^2) over the energy bin Δe_c are given by

$$\sigma_{i,d}^{\mathrm{DR}}=(4\pi\mathcal{R}^2/e_c\Delta e_c)V_a(i\rightarrow d)w(d) , \tag{4a}$$

$$\sigma_{i,dj}^{\mathrm{RE}}=(4\pi\mathcal{R}^2/e_c\Delta e_c)V_a(i\rightarrow d)z(d\rightarrow j) , \tag{4b}$$

where $w(d)=\Gamma_r/\Gamma(d)$ and $z(d\rightarrow j)=A_a(d\rightarrow j)/\Gamma(d)$ are the total fluorescence yield and partial Auger yield, respectively, and $\mathcal{R}$ is the Rydberg constant.

Since the shake effects cannot exist independently of the violent a and r (or their inverse) processes, each shake width must be associated with the corresponding a or r transition. Estimates of the shake widths require a careful evaluation of the correlated vertices of the types *VGV*, *VGVGV*, and *VGD*, *VGVGD*, etc., where only the off-energy shell part of the Green's function G is to be retained. The on-shell parts of G must be excluded, because they correspond to the cascade Auger and radiative transitions, which are included separately in the cascade theory. This point is essential in order to avoid the double-counting problem.

Instead of the above complicated and least-developed procedure, we follow the earlier work by Carlson [5] and by Carlson and Krause [6] and adopt a simple method of estimating the shake contribution, employing the sudden approximation. The method has been refined [7] recently by incorporating a cascade part, and applied [8,9] to the multiple photoionization of Ar. Thus the shake transition probabilities associated with the particular Auger transition $d\rightarrow j$ may be defined by

$$A_{as}(d\rightarrow j;N_s)$$
$$\simeq A_a(d\rightarrow j)[P_s(d\rightarrow j;N_s)/P_s(d\rightarrow j;N_s=0)] , \tag{5}$$

where N_s denotes the number of electrons which are removed by the shake. A_{rs} associated with the radiative transitions are similarly defined. The shake-off probabilities P_s are calculated simply in terms of the overlap integrals as

$$P_s(d\rightarrow j;N_s)=\sum_k \prod_{n,l} \binom{N_{nl}}{M_{nlk}} P_{nl}(d\rightarrow j;k)^{M_{nlk}} , \tag{6}$$

$$P_{nl}(d\rightarrow j;k)=1-|\langle d,nl|j,nl\rangle|^2 - \sum_{n',l'} |\langle d,nl|j,n'l'\rangle|^2 . \tag{6a}$$

In Eq. (6), we have the constraint in selecting N_s electrons from different orbitals, i.e., $N_s=\sum_{n,l} M_{nl,k}$ for each selection mode k. The last sum in the expression for P_{nl} in (6a) is the Pauli correction [5,6]. The overlaps defined by (6a) describe only the radial correlations and cannot treat possible angular correlations. The approach may overestimate the effect, but is sufficiently reliable for our purpose when $P<0.3$.

Based on the specific cases to be discussed below, we propose a modification of (3) for the total widths of the resonance states d as

$$\Gamma(d)=\Gamma_a(d)+\Gamma_r(d)+\Gamma_s(d) , \tag{7}$$

where the new term Γ_s represents the shake effect and is given by

$$\Gamma_s(d)=\Gamma_{as}(d)+\Gamma_{rs}(d) , \tag{8}$$

where, using (5),

$$\Gamma_{as}(d)=\sum_j A_{as}(d\rightarrow j) ,$$

$$\Gamma_{rs}(d)=\sum_f A_{rs}(d\rightarrow f) .$$

Presumably, the resonance energies are also shifted by a magnitude comparable to that of the widths, but the simple procedure adopted here cannot predict such shifts.

To illustrate the need for the modification as suggested by Eqs. (7) and (8), we consider the dielectronic-recombination and resonance-excitation processes that involve specific excitation-capture states. The examples we give below were found by many trial calculations and searches, and show the region in the Z and n parameter space where the shake effect becomes dominant and the theory using (3) breaks down.

We first consider the modification of the widths, as given by (7) and (8), for the DR and RE cross sections, specifically for the initial state $i=1s^22s$ of C IV being excited by electron impact, in which a $1s$ hole is created. Previous study of the DR process showed that the dominant intermediate states are $d=1s2s2pnp$, with $n\geq 2$. We concentrate here on the configurations with $n=3$, 4, and 5, where the shake effect is not too large ($P<0.2$), so that the modification suggested above [Eq. (5)] is expected to be valid. The calculation was carried out in the angular-momentum-average [3] representation to simplify the discussion. Figure 1 gives the total DR and RE cross sections for the C III target, with and without the shake contribution. Three different Auger decay modes of state d are shown for the RE process. Note that when the shake effect is included, the cross sections are reduced by a factor of 2 at $n=6$, and become rapidly smaller for higher n. The n dependence of the effect is strong, increasing roughly as n^3. Obviously, the standard procedure of summing the high-Rydberg-state contribution to DR by a simple extrapolation from the low-n states is no longer valid and requires caution. In Fig. 2, the shake probabilities P for Be I and C III of the Li isoelectronic sequence are summarized, showing the domain in which the conventional theory may break down; $n>5$ for C IV and $n>3$ for Be II, as indicated by the arrow in the figure. The Z dependence is equally dramatic; the shake

effect becomes rapidly small for high charge states. It suggests that for ions with $Z < 10$ and $n > 5$, the conventional procedure of calculating the resonance cross sections using (3) may no longer be acceptable. For C IV with $n > 7$, the shake effect becomes too large to be treated in terms of the A_{as} suggested by Eq. (5), and a total cutoff of the contribution to DR and RE from such states may be advisable.

The modification of the widths using (7) improves the treatment of the decay part of the resonance cross sections, but the formation part (V_a) of the reaction in (4) must also be reexamined. Consider again the C IV target ion when the $1s$ hole is created on configuration i. The $2s$ electron in the i configuration may be shaken up and leave the $2s$ orbital into another configuration $d = 1s2s2p3p$, for example. The overlap integral $\langle i,2s|d,2s\rangle$ provides an estimate of having the $2s$ electron raised to $3s$, $4s$, $5s$, etc., to the new states $d_s = 1s2p3s3p$, $1s2p4s3p$, etc. which are created with the total probability of $P = 0.011$. This, of course, happens during the creation of state d. (We note, however, that for low-charged-state ions, the shake is mainly to the continuum, about 60% of the time, while for highly charged ions, excitations to bound upper levels dominate, increasing roughly linearly with Z.) Since V_a is calculated in the distorted-wave Born approximation, the probability of formation of d is not affected by this. We therefore estimate the cross sections for the formation of state d_s to be $\sigma^{\mathrm{DRS}} \simeq 0.01\sigma^{\mathrm{DR}}$. With additional field mixing of high Rydberg states, the shake-driven DR cross section (DRS) may be enhanced. Obviously, such a process should occur at somewhat higher collision energies than that without the shake because of the extra energies needed for shake, and become small for higher-charge ions. The mechanism suggested here may be relevant [11] to a recent experiment [12] on resonant-transfer excitation followed by x-ray stabilization involving F^{6+}. New processes with V_{as} and $z_s = A_{as}/\Gamma$, and with V_{rs} and $w_s = A_{rs}/\Gamma$ are also possible.

In general, the shake effect is relatively small, at the 5–10% level in the total cross sections and rates when the outer-shell electrons are in low-lying states of highly charged ions, but can be large for processes involving high Rydberg states of lightly charged ions. The reactions which are expected to be least affected by the shake are the following: (i) The outer-shell DR and RE with

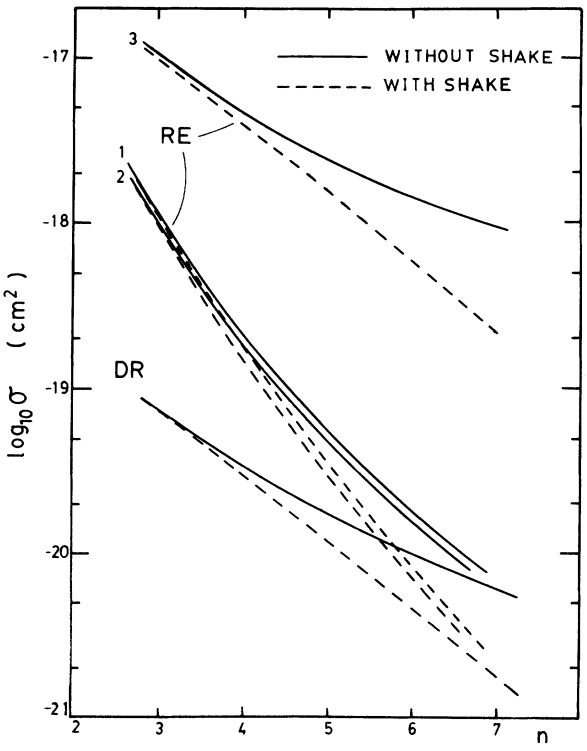

FIG. 1. The DR and RE cross sections for the $1s2s2pnp$ with $n = 3$, 4, and 5 of C III, with (— — —) and without (——) the shake effect. Note the drastic n dependence of both the DR and RE cross sections. All the transition probabilities are calculated in the angular-momentum average representation. $\Delta e_c = 0.01$ Ry was used. RE 1, 2, and 3 correspond to the three final excitation channels, $2s \rightarrow 2s$, $2p$, and np, respectively.

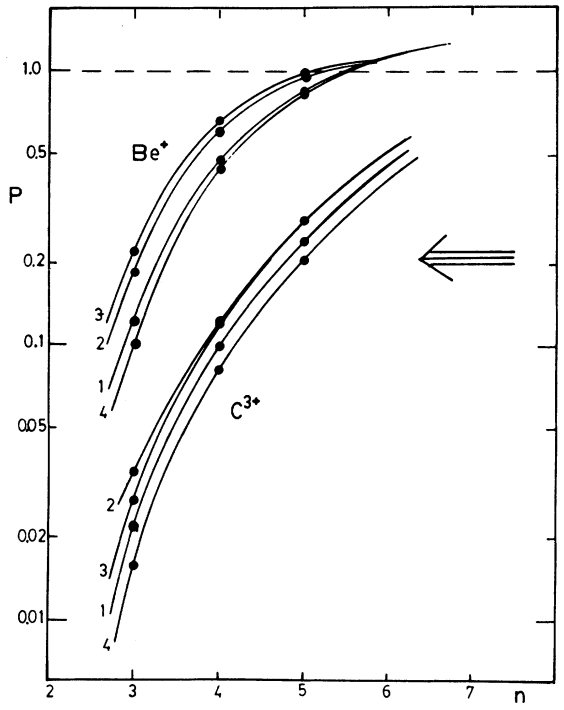

FIG. 2. The shake-off probabilities P associated with the Be II and C IV ions (before the excitation capture) vs n are obtained using the nonrelativistic Hartree-Fock wave functions and evaluating the appropriate overlap integrals in accordance with the sudden approximation. Note the drastic Z dependence. The dominant Auger transitions are the $2s2p \rightarrow 1s$ plus continuum. For $P < 0.2$, the method employed here using (5) and (6) may be reliable, but for $P > 0.2$, as marked by an arrow in the figure, the method breaks down, and a totally new approach may be required. The numbers 1–4 denote the different overlaps between the various configurations: (1) the ns orbital overlap between the configurations $1s2sns$ and $1s^2ns$, (2) the np overlap between $1s2s2pnp$ and $1s^2np$, (3) the np overlap between $1s^2np$ and $1s2s^2np$, and finally (4) the ns overlap between $1s^2ns$ and $1s2s^2ns$.

$\Delta n = 0$ (intrashell) excitation and capture. The shake corrections are negligible. (ii) The $\Delta n > 0$ processes (intershell excitation and capture) involving only the outermost-shell electrons. The shake is minimal here also. (iii) The inner-shell $\Delta n > 0$ processes with large enough $Z_{\text{eff}} = (Z_c + Z_I - N_{\text{core}})/2 > 10$ and small $n < 5$. Here, Z_c is the nuclear bare core charge, Z_I is the initial charge of the target ion, and N_{core} is the number of closed-shell core electrons which are inert spectators. We surveyed all the past work [3,4] on DR and resonant-transfer excitation [13]. Luckily, most of the currently available data are not affected much by the shake effect because of the above reasons (i)–(iii).

On the other hand, the present study shows that reactions which are most affected by the shake process are the following: (a) The Auger and radiative (and their inverse) transitions in which Z_{eff} of the core changes by one or more units, where $Z_{\text{eff}} < 10$. (b) The resonance states with at least one electron in high-Rydberg-state electrons, $n > 4$.

In fact, (a) and (b) above are inter-related. We expect the shake contribution to be large ($> 20\%$) when the effective Z is such that the level spacing between the two adjacent n's of the Rydberg electron is comparable to the change in the nth level due to an increase in Z by one unit, i.e., $Z \simeq n$ in the case of the $1s$ vacancy.

Several experimental verifications of the shake effect are suggested: (1) Study of the Auger (and x-ray) spectra produced in the decay of resonance states of Be I, B^+, and C^{2+}, where the resonance states contain a hole in $1s$ and an electron in high Rydberg states (with $n > 3$). Similar experiments may be set up for Mg^+ and Al^{2+}, with an initial L-shell hole. Suppression of the Auger lines is expected for low Z_I ions. The n dependence of the data is also of interest in order to test the behavior shown in Figs. 1 and 2. (2) Final charge-state distributions of decay products of hollow ions formed in a DR or RE process. We expect an enhanced production of more highly charged ions in the final decayed states of the residual ion, as the target core charge Z is lowered. (3) New, broader Auger lines and their satellites must be emitted as a result of the shake effect, some of which are red-shifted from the original lines. (4) Production of sizable number of low-energy continuum shake electrons as well as low energy radiations [14].

The shake effect is not limited to electron-ion resonance processes of DR and RE: (a) The resonant ionization (and double and triple autoionizations) may be significantly modified by the shake, leading to multiple ionization. (b) The shake-on contribution to ion-atom double- and triple-charge exchanges can be sizable, with or without the accompanying A_{as} and A_{rs}. (c) Photoionization plus Auger ionization and excitation processes have to be reexamined in light of the shake feature. We note that in general the shake processes associated with the radiative transitions are found to be smaller [7] than those associated with Auger transitions.

In summary, we have shown that important modifications of the resonance formulas for DR and RE, and other resonant inner-shell processes, are required to take into account the strongly correlated multielectron channels. The total widths of the resonance levels are supplemented by the addition of the shake widths Γ_s, as shown by Eq. (7). All the previous works on DR and RE were reexamined, and we found that, because of reasons (i)–(iii) above, the total cross sections and rate coefficients are not affected much by the shake effect, to within $5-10\%$ accuracy. The present study alerts one to the importance of the shake effect in future work on DR and RE and related resonant processes involving inner-shell electrons, where the theory must take into account this modification when appropriate. The procedure adopted here is crude but is sufficient to show qualitatively the importance of the effect. Much more work is needed to treat correctly the phenomena in terms of the correlated interaction vertices.

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