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Double photoionization of K- and L-shell electron pairs

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The double-photoionization probability of many-electron atoms is calculated within the independent-particle model. The sudden approximation approach and scaled hydrogenic wave functions are employed. The electron-electron interaction is effectively taken into account by screening parameters assigned to individual electrons. The interaction between the ejected electrons and other atomic electrons is described by the respective relaxation energies. The results for He and Ne agree well with the experimental data for photon energies greater than approximately twice the threshold energy.

I. INTRODUCTION

The calculated probability of ejecting two atomic electrons from an atom by a single photon depends strongly upon the choice of atomic wave functions before and after electron ejection, as well as on the correct description of the electron-electron interaction. The results obtained by using sophisticated correlated wave functions for helium[1-6] agree rather well with the corresponding experimental data. These techniques (using, e.g., creation and annihilation operators) increase in complexity when extended beyond He-like atoms. Therefore it seems worthwhile to consider less sophisticated and more approximate methods based on the simple independent-particle atomic model. The corresponding wave functions are scaled hydrogenic ones. Here we present a simple approach, where the electron-electron interaction is almost completely taken into account by screening parameters assigned to individual electrons. A similar procedure is common in the calculation of x-ray attenuation coefficients,[7] and in the plane-wave Born approximation for the ionization of atoms by light ions.[8]

The probability of ejecting two atomic electrons will be calculated in the sudden approximation first proposed by Migdal for atoms following β decay.[9] The method was elaborated by Levinger[10] and Green,[11] and extended to multiple-ionization processes by Carlson and coworkers.[12,13] In order to avoid continuum wave functions in the calculations, for the electrons from a particular shell Carlson calculated the probability w_0 of their remaining in the same shell. The difference $1-w_0$ was then the probability for transitions into the continuum, as well as into excited but bound states. Åberg[14] applied the same method for the double K-L ionization. Using Hartree-Fock wave functions, he obtained good agreement between the experimental and calculated intensities of satellite lines.[15] Later measurements of LaVilla[16] indicated that the sudden approximation results[15] are accurate to within 15%.

On the other hand, Carlson found that in the sudden approximation the probability of ejecting two electrons from the same atomic shell is considerably underestimated if independent-particle scaled hydrogenic wave functions are employed.[12] It was claimed that the main reason for this deviation is in neglecting correlation effects.

It is also the relaxation energy which significantly influences the electron ejection probability. In the present method we shall use elementary expressions for the ejection probability into the continuum and extend the $\mathbf{k}$-space integration to the region where the electron-electron interaction and relaxation effects are important.

II. THE MODEL

We shall calculate the double photoionization probability as a function of the photon energy within the fully independent particle model of the neutral, or singly and doubly ionized atom.

For a neutral atom, the Hamiltonian

$$H_0=\sum_i (p_i^2/2m - Z/r_i) + \sum_i \sum_{j>i} 1/r_{ij} \tag{1}$$

is replaced by

$$H=\sum_i (p_i^2/2m - Z_i/r_i) \ . \tag{2}$$

In this transformation, the electron-electron interaction [double sum in (1)] is approximated by a sum of central field terms. As a result, the Hamiltonian in (2) is split into the sum of single-particle scaled hydrogenic Hamiltonians, with the corresponding scaled hydrogenic wave functions and single-particle energies as solutions. The individual effective charges are given by $Z_i=Z-s_i$, with s_i the screening parameters, which can be easily calculated.[17-19]

The electrons are then treated as fully independent quasiparticles, each experiencing its own screened Coulomb-like field, forming a special kind of fermion sea. Atomic energy is given as a simple sum of independent-particle energies $W_i=-Z_i^2/n_i^2$ (in rydbergs). The difference between the model and experimental atomic energies defines the correlation energy. For He-like atoms, for instance, it is about 1 eV, almost independent of Z.

The independent-particle Hamiltonians for an atom which has lost one (say $i=1$) or two ($i=1,2$) electrons are

$$H^{*}=\sum_{i=2}(p_i^2/2m-Z_i^{*}/r_i)\ , \tag{2a}$$

$$H^{**}=\sum_{i=3}(p_i^2/2m-Z_i^{**}/r_i)\ . \tag{2b}$$

The respective effective charges and energies are Z_i^{*}, Z_i^{**} and W_i^{*}, W_i^{**}. We shall also need the ionization thresholds for ejection of one $(i=1)$ or two $(i=1,2)$ electrons, given by the difference in atomic energy before and after ionization:

$$\omega_1=\sum_{i=2}W_i^{*}-\sum_{i=1}W_i\ , \tag{3a}$$

$$\omega_2=\sum_{i=3}W_i^{**}-\sum_{i=1}W_i\ . \tag{3b}$$

The absorption of a photon of energy ω promotes a particular $(i=1)$ electron out of the fermion sea. The electron then no longer behaves as a fully independent quasiparticle deep in the fermion sea but interacts with other $(i=2)$ electrons via the $1/r_{12}$ term. This interaction is responsible for the eventual ejection (shakeoff) of the $i=2$ electron from the atom. It is also evident that the interaction term is most effective for an electron pair belonging to the same atomic shell.

Since the $1/r_{12}$ term in (1) no longer contributes to the formation of average independent-particle fields, its contribution to the effective charges Z_i has to be excluded. Transforming the remaining i/r_{ij} terms within the central field approximation we define a new model Hamiltonian

$$H'=\sum_{i=1}(p_i^2/2m-Z_i'/r_i)+1/r_{12}\ . \tag{4}$$

The promotion of a particular electron therefore leads to a sudden change of the individual effective charges from $Z_i=Z-s_i$ to $Z_i'=Z-s_i'$ and hence to the sudden change of the respective electron states.

In the lowest-order approximation, the probability for the ejection of the shakeoff electron is given by

$$w=\int|\langle\mathbf{k}|0\rangle|^2d\mathbf{k}\ . \tag{5}$$

Here $|0\rangle$ denotes the initial state of the shakeoff electron experiencing nuclear charge $Z-s_2$, while $|\mathbf{k}\rangle$ represents the final state of the same electron experiencing the effective nuclear charge $Z-s_2'$. These states, being eigenstates of different independent-particle Hamiltonians (2) and (4), are not fully orthogonal which makes the matrix element $\langle\mathbf{k}|0\rangle$ different from zero.

The **k** space over which the integration (5) extends depends not only upon the photon energy transfer but also upon the available range of energy t_1 of the ejected photoelectron. To express their dependence, we first consider the one-electron photoeffect. There the matrix element is obviously calculated for the energy

$$t_i=\omega+W_1\ . \tag{6}$$

Here ω is the photon energy and W_1 the hydrogenic independent-particle energy of the photoelectron. The single ionization threshold ω_1 (3a) is, however, lower than $-W_1$ due to the post-photoeffect relaxation of all other electrons in the atom. It can be expressed as

$$\omega_1=-W_1+\sum_{i=2}(W_i^{*}-W_i)\ . \tag{7}$$

Since $Z_i^{*}>Z_i$, the sum in (7) is negative. Its absolute value represents the relaxation energy due to the ejection of the $i=1$ electron. It is convenient to include ω_1 in (6):

$$t_1=\omega-\omega_1+\sum_{i=2}(W_i^{*}-W_i)\ . \tag{8}$$

The energy t_1 is therefore negative for photon energies close to the threshold. However, to attain positive states, the energy missing is supplied later through collisions with other $(i>1)$ electrons at the expense of the relaxation energy.

For the two-electron photoeffect, the energy relation required for the calculation of the matrix element (5) is a generalization of Eq. (6):

$$t_1+t_2=\omega+W_1'+W_2'\ . \tag{9}$$

The sum t_1+t_2 is fixed for a given ω but the available ranges of individual values of t_1 and t_2 may be considerable. In the following we shall determine the range of t_2, which in turn defines the integration limits in (5). We expect that Eq. (9) is valid when the interaction term $1/r_{12}$ is strong in comparison with the mean electron-electron interaction. This condition is obviously fulfilled if both ejected electrons are from the same shell, but not otherwise. The case where the two electrons are ejected from different shells will therefore not be considered in the present study.

We shall first determine the lowest possible values of t_1 and t_2. For photon energies approaching the threshold, the respective ranges of t_1 and t_2 gradually decrease until they finally converge into single values. Since the double photoeffect is then just possible, these limiting values of t_1 and t_2 are also the lowest possible.

With the threshold energy ω_2 (3b), Eq. (9) is rewritten as

$$\begin{aligned} t_1+t_2=\omega-\omega_2+&\sum_{i=3}(W_i^{**}-W_i)\\ &+(W_1'-W_1)+(W_2'-W_2)\ . \end{aligned} \tag{10}$$

The absolute value of the sum in (10) is evidently the relaxation energy available after the ejection of $i=1,2$ electrons. The last two terms represent the contribution of the interaction between the $i=1,2$ electrons.

It is reasonable that the lowest value of t_1 is close to that for single photoeffect and therefore to the respective single-photoeffect relaxation energy. This implies that the relaxation energy in (10) is approximately equally shared between the two electrons. Introducing the relaxation energy sharing factor α and using (3b), the lowest value of t_1 can be expressed as

$$t_1\rightarrow\alpha\sum_{i=3}(W_i^{**}-W_i)=\alpha(\omega_2+W_1+W_2)\ . \tag{11}$$

We shall further assume that the relaxation energy experienced by a particular electron is proportional to the respective relaxation energy for the single photoeffect. The values of α are thus typically $\frac{1}{2}$, though they may be significantly different for an electron pair belonging to different subshells. Equation (11) also shows that t_1 may extend to negative values, but not for He-like atoms where the corresponding relaxation energy is zero. We find the lower limit for t_2 from the lowest value of t_1+t_2 as follows from (9) by setting $\omega \rightarrow \omega_2$ and inserting (11):

$$t_2 \rightarrow (1-\alpha)(\omega_2+W_1+W_2)+(W_1'-W_1)+(W_2'-W_2) \ . \tag{12}$$

The absolute value of the first term in (12) is now the relaxation energy available to the shakeoff electron and obviously vanishes for He-like atoms. The last two terms, as in (10), take into account the interaction between the ejected electrons.

The upper limit of t_2 also depends on the lowest possible value for t_1. As follows from Eqs. (10) and (11), it is given by an expression similar to (12), except that ω_2 is restored to ω. Since the matrix element in (5) is a rapidly decreasing function of t_2, an accurate value for the upper limit is not so important.

III. THE CALCULATION

By expanding the Coulomb wave function in (5) into partial waves and realizing that contributions other than monopole vanish, we obtain for the K-shell shakeoff process:

$$\langle \mathbf{k}|0\rangle = 8\pi \frac{(Z-s)^{3/2}}{(Z-s')^3} \int R_{k0}(kr)e^{-pr}r^2 dr \ . \tag{13}$$

The screening parameters for the bound state $|0\rangle$ and for the final state $|\mathbf{k}\rangle$ are s and s', respectively. The parameter p is defined as $(Z-s)/(Z-s')$.

The Coulomb function in (13) is normalized as $R_{k0}(kr, k\rightarrow\infty)=\sin(kr)/kr$. Integration was performed using the method of Zernik[20] (note the different normalization there). Formulas given in Refs. 1 and 3 might also be used, though in Ref. 3 the dependence of the probability w on s and p is not so explicit.

The derivation of (13) for the L-shell shakeoff process is analogous and can therefore be omitted here. Multiplying (13), or the corresponding formulas for the L-shell, by the density of available states we find general expression for the shakeoff process from the K or L shell:

$$w = 4p^3(p-1)^2 \times \int_{k^2_{\text{min}}}^{k^2_{\text{max}}} A(p,k) \frac{e^{-4\arctan(nk/p)/k}}{(1-e^{-2\pi/k})(p^2/n^2+k^2)^{2(n+1)}} d(k^2) \tag{14}$$

$$A(p,k) = \begin{cases} 8 \quad \text{for } K \text{ shell} \\ 1-p^2/4+k^2 \quad \text{for } L_1 \text{ shell} \\ p^2(1+k^2)/3 \quad \text{for } L_{2,3} \text{ shell} \ , \end{cases}$$

with $n=1$ and 2 for the K and L shells, respectively.

Integration limits, as follow from (12), are

$$\begin{aligned} k^2_{\text{min}} &= (1-\alpha)\omega_2/(Z-s')^2+2(\alpha p^2-1)/n^2 \ , \\ k^2_{\text{max}} &= (\omega-\omega_2)/(Z-s')^2+k^2_{\text{min}} \ . \end{aligned} \tag{15}$$

Here we have used the rydberg as the energy unit and the Bohr radius divided by $Z-s'$ as the length unit.

The values of k^2 are negative at the lower end of the integration interval. According to Ref. 8, the normalization factor $1-\exp(-2\pi/k)$ is then set equal to 1. For arctan of the complex argument we use the identity $\arctan(ix)=i\,\text{arctanh}(x)$.

In the limit of high photon energies, the probability w scales as $(p-1)^2=[(s-s')/(Z-s')]^2$, in qualitative agreement with previous results.[10,12] For low photon energies and $p\approx 1$ we obtain for the K shell:

$$w = 32e^{-4}(p-1)^2(\omega-\omega_2)/Z^2 \ . \tag{16}$$

This result agrees well with those of Wannier[21] and Rau[22] where the behavior of w close to the threshold is proportional to $(\omega-\omega_2)^r$, the power r being slightly greater than 1 due to the electron-electron interaction in the final state.

The double ionization of helium is of particular interest for the present approach, since comparison with other theoretical[1-6] and experimental data[12,23-25] is possible. From the experimental binding energy and the relaxation energy $Z^2-(Z-s)^2$ for the one-electron photoeffect, we find the screening constant $s=0.296$. For He-like atoms, $s'=0$, $\omega_2=W_1+W_2$, and the lower integration limit simplifies to

$$k^2_{\text{min}} = 2(p^2-1) \ . \tag{17}$$

Values of w for different photon energies were calculated by numerical integration of (14). In the present approximation, w is equal to the ratio of the double- to total-ionization cross section. The ratio of double- to single-ionization cross section σ^{++}/σ^{+} is then given by $w/(1-w)$. Figure 1 shows that the present results agree well with the experimental data, and with the calculations of Carter and Kelly[5] and Tiwary[6] for photon energies greater than approximately twice the threshold energy. For lower photon energies, however, the sudden approximation method evidently yields too-steep behavior. It might be argued that the change of screening should be effectively smaller than $s-s'$ since the photoelectron escapes from the atom with a velocity which is small compared to the shell velocity.

For high photon energies, the cross section ratio is 4.98% which seems reasonable in Fig. 1. It should be noted that choosing the screening constant as $s=\frac{5}{16}$–as follows from the variational procedure as well as from the

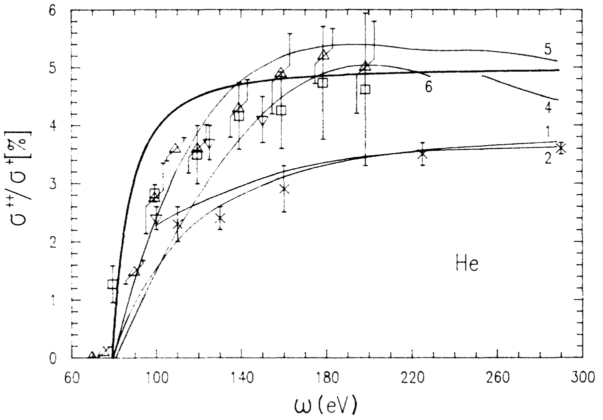

FIG. 1. Double- to single-ionization cross-section ratio for He. Present results are shown by a bold line; the numbers on thin curves are the same as in the list of references. Experimental data: ×, Carlson (Ref. 12); ∇, Schmidt *et al.* (Ref. 23); △, Wight and Van der Wiel (Ref. 24); □, Holland *et al.* (Ref. 25).

independent-particle model in the completely uncorrelated case–would make the high-energy limit 5.87%. This value exceeds the maximum of the corresponding values reported in Refs. 5 and 6 by 10%. The high-energy limit should probably be reduced by a factor of 2 for very high (but not relativistic) energies according to the asymptotic calculation of Åberg[3] and Amusia *et al.*[4] As shown in Ref. 4, at very high energies events prevail where each of the ejected electrons receives half of the photon energy. Momentum conservation requires that the electrons quit the atom in opposite directions. These processes indicate gradual breakdown of the shakeoff model for very high photon energies.

For the double L-shell ionization, we can compare our results with the experimental[12,23–27] and theoretical data[28–30] on neon. This example also demonstrates the importance of assumption (11), since setting $t_1 \rightarrow 0$ would lead to singularity in w.

The total probability for the L-shell shakeoff process was obtained from the sum of statistically weighted probabilities for particular subshells. The relative single-ionization cross sections for $2s$ and $2p$ subshells were taken from the work of Chang and Olsen.[31] The energies ω_2 were calculated using the Dirac-Fock values of Maurer and Watson[32] and the experimental binding energies of Sevier.[33]

The factors α (11) for an $L_1 - L_{2,3}$ electron pair were 0.42 and 0.58, respectively, and 0.5 otherwise. Due to the uncertainties in α, our results are uncertain not more than a few percent, since the uncertainties in partial shakeoff probabilities tend to be mutually canceled out.

Screening parameters were calculated according to the simple model[17] which does not distinguish between $2s$ and $2p$ electrons. From the total energy of the neutral Ne atom calculated from the tables,[32,33] we obtained $s = 4.11$ for the initial state. For the final state, the screening parameter was calculated from the independent-particle part of the Hamiltonian (4). The $1/r_{12}$ term was treated as a perturbation and therefore neglected. According to the models,[17,18] the total L-shell energy E_L' in (4) is given by

$$E_L' = 2(Z - 2\kappa - 6\lambda)^2/4 + 6(Z - 2\kappa - 7\lambda)^2/4 \ . \qquad (18)$$

Here the first term represents the energy of $i = 1,2$ atomic electrons and the second term the energy of the remaining six. The parameters κ and λ are contributions of a distinct K and L electron, respectively, to the L-shell screening parameter. Since the interaction term in (4) was assumed to be small, E_L' can be set equal to the corresponding Dirac-Fock value obtained from the tables.[32,33] With $\kappa = 0.95$ deduced from the energies[32] we find $s' = 2\kappa + 6\lambda = 3.866$.

The cross-section ratio σ^{++}/σ^{+} as a function of the photon energy is shown in Fig. 2. The present calculation gives–as in the He case–values which are too large for low photon energies. The high-energy values seem to be overestimated according to the measurements of Holland *et al.*,[25] but less than the corresponding values of Refs. 28-30. The kink at 87 eV, also indicated in the measurement of Samson and Haddad,[27] is the $L_1 - L_3$ threshold.

The sudden approximation method being sufficiently efficient in the case of helium and neon, can be used further to calculate the double to single ionization cross section ratio for heavier elements as well. Results for the double K-shell ionization are shown in Fig. 3. The screening parameters $s = 0.3$ and $s' = 0$ were used for the elements heavier than He. The energies ω_2 up to Ne were calculated according to the atomic model.[19] For heavier elements, the energies ω_1 from the tables[33] were used and

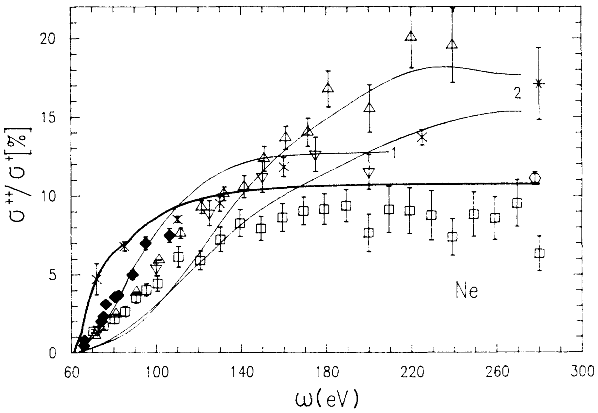

FIG. 2. Double- to single-ionization cross-section ratio for Ne. Bold line, present results; hexagon, calculation of Chang *et al.* (Ref. 28); 1, calculation of Chang and Poe (Ref. 29); 2, calculation of Carter and Kelly (Ref. 30), dipole length (upper curve) and dipole velocity approximation (lower curve). Experimental data as in Fig. 1; asterisk, Lightner *et al.* (Ref. 26); closed diamond, Samson and Haddad (Ref. 27).

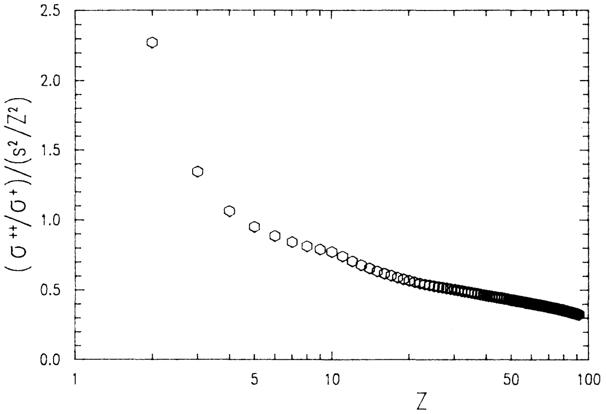

FIG. 3. High energy limit of σ^{++}/σ^{+}, normalized to $(s-s')^2/Z^2$, as a function of Z.

a simple approximation for the energy difference $\omega_2-2\omega_1$ was introduced.

Photon-induced hypersatellite spectra measured for several elements from Ti to Ni (Ref. 34) and the absorption measurements on Cu (Ref. 35) yield the *K*-shell double ionization probability which is by an order of magnitude higher than the corresponding values in Fig. 3. The difference is due to the parallel ionization-excitation process (shakeup) which for these measurements cannot be distinguished from the proper double ionization into the continuum.

IV. CONCLUSION

The independent-particle atomic model provides a useful estimate for the two-electron photoeffect. Based on simple principles it yields results which (in case of helium and neon) are comparable to those of more rigorous calculation. The use of independent-particle wave functions suggests that the concept of screening accounts well for the many-body effects in the atom.

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