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⁵⁴The results are too clumsy to give here.

Two-Photon Emission of X Rays

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(Received 26 January 1973)

Two-photon emission from heavy elements with a single *K*-shell vacancy (e.g., Cu^+) is considered. Simple closed-form expressions are given for the spontaneous, singly stimulated, and doubly stimulated two-photon emission rates. The material parameters relevant to these two-photon processes are shown to be the one-photon absorption cross sections and oscillator strengths.

I. INTRODUCTION

We describe here a simple theory of the decay of a *K*-shell vacancy in heavy elements such as Cu by the process of two-photon emission.¹ Spontaneous, singly stimulated, and doubly stimulated processes are considered. We show that with suitable approximations the matrix elements describing the material parameters important to the two-photon emission process can be obtained from those describing one-photon emission and absorption. This permits us to obtain simple closed-form expressions which contain only known material parameters. The close relationship between corresponding linear (one-photon) and nonlinear (two-photon) processes is similar to that found previously,^{2–4} and appears to be characteristic of the x-ray region. Since the two-photon emission rate is found to be comparatively intense, $\sim 10^{-6}$ the one-photon rate, there exists the possibility of experimentation.

Two-photon absorption and emission by atomic hydrogen⁵ and by heavy hydrogenic ions⁶ have received very considerable attention. Although inner-shell electrons are often considered to be hydrogenic in nature, this important body of work—which provides the necessary background to our present treatment—cannot simply be applied to many-electron ions. The reason is that the sets of intermediate states available to an *L*-shell electron

in atomic hydrogen, for example, are very different from those which are available in Cu. These distinctions are made more apparent later when the similarities and differences between the two kinds of systems are discussed.

The model we use here is that of a single electron moving in some effective spherical potential. It is supposed that this potential reproduces the set of energy levels which are available to the electron. Such a description considers only the existence of single-particle excitations and is thus equivalent to a representation of the wave function in terms of a single Slater determinant. We explicitly neglect electron spin, since we assume that two-photon emission accompanied by a spin flip is a weaker process than one in which no spin flip is required.⁷

In order to be specific, we treat the case of a Cu^+ ion with a single *K*-shell vacancy, and consider the process of two-photon emission by an *L*-shell electron dropping down to fill this vacancy. The initial state of the system is thus an electron in the *L* shell and a hole in the *K* shell, while in the final state the position of the electron and hole are reversed. The energy levels available to the electron are shown in Fig. 1. While we treat an isolated ion, we consider our results to be applicable to solid copper. The reason for this is that the deep *K*- and *L*-shell electrons are not much affected by the presence of other atoms, while the

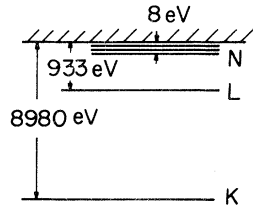


FIG. 1. Energy levels of the one-electron model used (not to scale). The binding energies are listed in electron volts for Cu. In the initial state the electron is in the L shell; in the final state it is in the K shell. The first empty excited state is the N shell. Note the small spread of the excited bound states, ~ 8 eV, relative to the large L - and K -shell binding energies.

specific properties of the empty bound states do not, as we show later, enter explicitly. The continuum states might be expected to be very different for the free ion and for the solid, but, except near the absorption edge, the one-photon photoionization coefficients, which are dependent upon the properties of these states, are known to be approximately independent of the chemical composition of the sample. This implies that the same is true for the wave functions, probably because an electron in the continuum "sees" mainly the screened spherical potential of the heavy hole it left behind. We expect, therefore, that the gross features of two-photon emission by a heavy ion will be a characteristic of the ion and only secondarily dependent upon its environment.

In the following sections we treat first the matrix elements describing the material parameters and then the spontaneous and stimulated transition rates.

II. MATRIX ELEMENTS

The matrix elements describing the transition of an electron between a state of higher energy $|h\rangle$ and one of lower energy $|l\rangle$, with the simultaneous emission or absorption of two photons, were first given by Göppert-Mayer.⁸ Although in her work she employs the dipole approximation, which is inappropriate for the x-ray region, her results are easily modified to permit inclusion of the complete vector potential.⁹⁻¹¹ With the wave vector \vec{k}_i and unit polarization vector \vec{u}_i of the output field at frequency ω_i , we may write the matrix elements as

$$\mathfrak{M}_i^h(\omega_1, \omega_2, \vec{k}_1, \vec{k}_2, \vec{u}_1, \vec{u}_2) = M_i^h(\vec{A} \cdot \vec{A}) + M_i^h((\vec{p} \cdot \vec{A})^2). \quad (1)$$

Here $M(\vec{A} \cdot \vec{A})$ arises in first-order perturbation theory from the A^2 term in the interaction Hamiltonian and is given by

$$M_i^h(\vec{A} \cdot \vec{A}) = \hat{u}_1 \cdot \hat{u}_2 \langle h | e^{i(\vec{k}_1 + \vec{k}_2) \cdot \vec{r}} | l \rangle. \quad (2)$$

$M((\vec{p} \cdot \vec{A})^2)$ arises in second-order perturbation theory and is given by

$$M_i^h((\vec{p} \cdot \vec{A})^2) = (\hbar/m)(1 + \pi_{1,2}) \sum_p [\langle h | (\hat{u}_1 \cdot \vec{\nabla}) e^{i\vec{k}_1 \cdot \vec{r}} | p \rangle \times \langle p | (\hat{u}_2 \cdot \vec{\nabla}) e^{i\vec{k}_2 \cdot \vec{r}} | l \rangle / (\Omega_{pl} - \omega_2)], \quad (3)$$

where the operator $\pi_{1,2}$ permutes the subscripts 1 and 2, and Ω_{pl} is the frequency of the transition from the intermediate state $|p\rangle$ to the lower state. In keeping with our model, we have suppressed the sums over one-electron operators in Eqs. (2) and (3).

We obtain initial estimates of Eqs. (2) and (3) by noting that even in the x-ray region an expansion of the exponentials is frequently permissible. If a is the radius of the K shell, it is easily seen that $ka \approx \frac{1}{2} \alpha Z$, where α is the fine-structure constant and Z the atomic number. For Cu we have $ka \approx 0.11$. For $M(\vec{A} \cdot \vec{A})$ one obtains by inspection

$$M_i^h(\vec{A} \cdot \vec{A}) \approx i(ka) - (ka)^2 + \dots, \quad (4)$$

so that only the term linear in k need be retained. $M((\vec{p} \cdot \vec{A})^2)$ may be estimated by noting that when $\omega_1 \approx \omega_2 = \omega$, ω is less than $\frac{1}{2}$ the smallest possible Ω_{pl} , so that the approximation $\Omega_{pl} - \omega \approx \Omega_{pl}$ appears reasonable. Here the leading term is independent of k and is

$$M_i^h((\vec{p} \cdot \vec{A})^2) \approx \langle h | z \frac{\partial}{\partial z} | l \rangle \approx \frac{1}{3}, \quad (5)$$

while the next-higher-order term is smaller by a factor of order ka .

When only leading terms are retained, Eq. (2) contributes only to the $2p-1s$ two-photon transition and Eq. (3) contributes only to the $2s-1s$ transition. This division, however, is valid only if one of the frequencies, e. g., ω_1 , is not too small. When ω_1 is very small compared to all allowed values for Ω_{pl} and Ω_{ph} , it may be seen that

$$\lim_{\omega_1 \rightarrow 0} M_i^h(\vec{A} \cdot \vec{A}) = - \lim_{\omega_1 \rightarrow 0} M_i^h((\vec{p} \cdot \vec{A})^2). \quad (6)$$

This is an exact result, so that in this limit the contributions of $M(\vec{A} \cdot \vec{A})$ and $M((\vec{p} \cdot \vec{A})^2)$ become mixed together. Since \mathfrak{M} goes to zero with ω_1 , we will not concern ourselves to any great extent with this low-frequency limit, except to point out how the effects of Eq. (6) differ for the present problem and for the case of a hydrogenic system.

For Cu, the condition $\omega_1 \rightarrow 0$ is satisfied if ω_1 is small compared to the frequency of the L -absorption edge at ~ 933 eV. For a hydrogenic system, however, the near degeneracy of the $2s$ and $2p$ levels, for example, requires a very much smaller value for ω_1 . For such systems the limiting form for \mathfrak{M} is easily obtained.¹² If the splitting of the upper state $|h\rangle$ and its near-degenerate partner $|\phi_h\rangle$ is δ_h , then

$$\mathfrak{M}_i^h(\omega_1 \rightarrow 0) = \frac{-\omega_1}{\omega_1 + \delta_i} \langle h | \hat{u}_1 \cdot \vec{r} | \phi_h \rangle \\ \times \langle \phi_h | (\hat{u}_2 \cdot \vec{\nabla}) e^{i\vec{k}_2 \cdot \vec{r}} | l \rangle, \quad (7)$$

while, when the lower state is degenerate,

$$\mathfrak{M}_i^h(\omega_1 \rightarrow 0) = \frac{\omega_1}{\omega_1 - \delta_i} \langle h | (\hat{u}_2 \cdot \vec{\nabla}) e^{i\vec{k}_2 \cdot \vec{r}} | \phi_l \rangle \\ \times \langle \phi_l | \hat{u}_1 \cdot \vec{r} | l \rangle. \quad (8)$$

Because of this property, the two-photon emission spectrum for hydrogenic systems^{5(c)} falls to zero much more slowly with ω_1 than does the spectrum of the many-electron systems of interest here.

Returning to the problem at hand, retaining only leading terms, and writing θ for the angle between \vec{k}_1 and \vec{k}_2 , we have

$$\langle | M_{1s}^{2p}(\vec{A} \cdot \vec{A}) |^2 \rangle_{\text{polarizations}} = \left(\frac{1 + \cos^2 \theta}{2} \right) g_{2p,1s} \\ \times \left(\frac{\hbar \Omega_{2p,1s}}{2mc^2} \right) \frac{\omega_1^2 + \omega_2^2 + 2\omega_1\omega_2 \cos \theta}{\Omega_{2p,1s}^2}, \quad (9)$$

where $g_{2p,1s}$ is the oscillator strength of the one-photon $2p-1s$ transition. In writing Eq. (9), we assume a polarization-insensitive detection apparatus.

To zero order in ka , we may write

$$M_{1s}^{2s}((\vec{p} \cdot \vec{A})^2) = \frac{-m}{\hbar} (\hat{u}_1 \cdot \hat{u}_2) \sum_p \langle 2s | z | p \rangle \langle p | z | 1s \rangle \\ \times \Omega_{p,2s} \Omega_{p,1s} \left(\frac{1}{\Omega_{p,1s} - \omega_1} + \frac{1}{\Omega_{p,1s} - \omega_2} \right). \quad (10)$$

Note that

$$\lim M_{1s}^{2s}((\vec{p} \cdot \vec{A})^2) = 0 \text{ as } \omega_1 \rightarrow 0. \quad (11)$$

This may be easily established with the aid of an important theorem¹³:

$$\sum_p (\Omega_{ph} + \Omega_{pi}) \langle h | z | p \rangle \langle p | z | l \rangle = 0. \quad (12)$$

We proceed to an evaluation of Eq. (10) by establishing a relationship between the sum over bound states and the integration over the continuum. From Fig. 1 we observe that for all intermediate bound states $|p\rangle$, $\Omega_{p,2s}$ may be well approximated as constant and equal to the frequency of the L -absorption edge, Ω_L . Similarly, $\Omega_{p,1s}$ may be set equal to the K -absorption edge frequency Ω_K . All that we require about the bound states, then, is the sum

$$\sum_{\text{bound states}} \langle 2s | z | p \rangle \langle p | z | 1s \rangle. \quad (13)$$

This expression may be related through Eq. (12) to an integration over the continuum states. Our

problem thus reduces to finding a form for the dependence on energy of the matrix elements $\langle 2s | z | p \rangle$ and $\langle p | z | 1s \rangle$ when $|p\rangle$ is a state in the continuum.

Following Breit and Teller,^{5(a)} we write for continuum states:

$$\langle 2s | z | p \rangle \langle p | z | 1s \rangle \\ = + (|\langle 2s | z | p \rangle|^2 \cdot |\langle 1s | z | p \rangle|^2)^{1/2}. \quad (14)$$

The justification for Eq. (14) is discussed further in the Appendix. The right-hand side of Eq. (14) we obtain from the absorption cross section

$$\mu_J(\Omega_{p,J}) = 4\pi \alpha \Omega_{p,J} |\langle J | z | p \rangle|^2, \quad (15)$$

where $J=K$ or L for the $1s$ or $2s$ states. In Eqs. (10), (11), (14), and (15), the necessary density-of-states factors have been absorbed into the matrix elements. Although several-term expansions are available as a representation of the absorption spectrum,¹⁴ here we use only the simple result¹⁵

$$\mu_J(\Omega_{p,J}) = 4\pi r_0 c \Omega_J^2 g_J / \Omega_{p,J}^3, \quad (16)$$

where g_J is the *total* oscillator strength of the $J=K$ or L electron. We thus have

$$\langle | M_{1s}^{2s}((\vec{p} \cdot \vec{A})^2) |^2 \rangle_{\text{polarizations}} = \left[\frac{1}{2}(1 + \cos^2 \theta) \right] g_K g_L \\ \times [\phi_{12} + (\Omega_K \Omega_L / \omega_1 \omega_2) \ln \phi_{12}]^2, \quad (17)$$

where

$$\phi_{12} = \Omega_K \Omega_L / (\Omega_K - \omega_1)(\Omega_K - \omega_2). \quad (17')$$

Note that our final results, Eqs. (9) and (17), contain only parameters relevant to the process of *one-photon* emission and absorption, so that we have achieved a reduction of the problem in terms of quantities that may be presumed known.

III. TRANSITION RATES

The rate at which a K -shell vacancy is filled by an L -shell electron which emits ω_1 spontaneously into a solid angle $\Delta\Omega_1$ and ω_2 into $\Delta\Omega_2$ is⁸

$$W_{L,K}^{(0)} = \frac{16r_0^2 \omega_1 \omega_2 d\omega}{\pi c^2} \langle | \mathfrak{M}_K^L |^2 \rangle \frac{\Delta\Omega_1}{4\pi} \frac{\Delta\Omega_2}{4\pi}, \quad (18)$$

where $d\omega$ is the bandwidth of the emission and r_0 the classical electron radius. Here we write

$$\langle | \mathfrak{M}_K^L |^2 \rangle = \langle | M_{1s}^{2p} |^2 \rangle + \langle | M_{1s}^{2s} |^2 \rangle. \quad (19)$$

In the presence of an unpolarized field with intensity I_1 at ω_1 , we have for the process of singly stimulated emission:

$$W_{L,K}^{(1)} = 8\pi \alpha^2 (\hbar \omega_2 / mc^2) (I_1 / m \omega_1^2) \langle | \mathfrak{M}_K^L |^2 \rangle \Delta\Omega_2 / 4\pi. \quad (20)$$

In the presence of two unpolarized uncorrelated

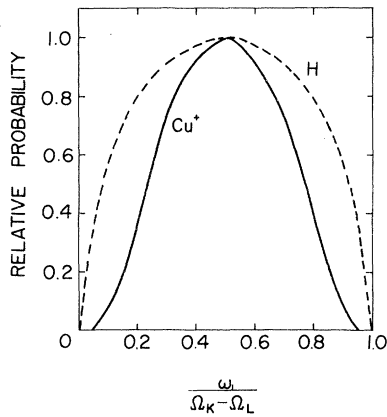


FIG. 2. Two-photon spectrum [Eq. (17)] of Cu (solid curve) and of H [Ref. 5(c)] (dashed curve). The H spectrum goes to zero linearly with ω_1 because of the $2s$ - $2p$ degeneracy. The Cu spectrum goes to zero as ω_1^3 . This latter behavior follows quite generally from Eqs. (6) and (18) and is not dependent upon the detailed assumptions of the calculation.

fields with intensities I_1 and I_2 , we have for doubly stimulated emission:

$$W_{L,K}^{(2)} = 8\pi^3 \alpha^2 (I_1/m\omega_1^2) (I_2/m\omega_2^2) [\sigma_{2p}(\omega_1 + \omega_2) \langle |M_{1s}^{2p}|^2 \rangle + \sigma_{2s}(\omega_1 + \omega_2) \langle |M_{1s}^{2s}|^2 \rangle]; \quad (21)$$

σ_{2p} is a normalized line-shape function for the $2p$ level, and σ_{2s} is the corresponding quantity for the $2s$ level.

If the fields are polarized, the factor $1 + \cos^2\theta$ in Eqs. (9) and (17) must undergo suitable replacement. When the fields at ω_1 and ω_2 are correlated, the product $I_1 I_2$ must be replaced by the appropriate correlation function.¹⁶ If the transition proceeds by absorption of ω_1 or ω_2 , the sign of the frequency being absorbed is to be changed.

At present only weak x-ray fields are available, so that the stimulated processes in Eqs. (20) and (21) are not amenable to observation. This is not the case for the spontaneous process in Eq. (18). With $\Delta\Omega_1 \sim \Delta\Omega_2 \sim 4\pi$, $d\omega \sim \omega \sim 10^{19}$ Hz, and $|3\pi|^2 \sim 10^{-2}$, we have $W_{L,K}^{(0)} \sim 3 \times 10^9 \text{ sec}^{-1}$. This is approximately 10^{-6} the one-photon transition rate and does not, in fact, differ greatly from that expected for a hydrogenic model^{5(a), 5(b)} ($W_{L,K}^{(0)} \sim 8Z^6 = 5 \times 10^9 \text{ sec}^{-1}$) for Cu. In Fig. 2 we compare the two-photon spectrum we compute here for Cu and that computed by Spitzer and Greenstein^{5(c)} for a hydrogenic system.

Since more than 10^{11} K -shell vacancies/sec can easily be produced in the laboratory, 10^5 photon pairs/sec are available for detection. This exceeds the rates available in the experiments of Marrus and Schmieder.^{6(a)} The present experiment, however, is plagued by the presence of a

very large one-photon background. Nonetheless, elimination of this background by suitable energy discrimination and fast-coincidence techniques seems possible. It thus appears that it is presently feasible to measure the two-photon spectra described here.

ACKNOWLEDGMENTS

I am pleased to acknowledge useful discussions with Professor M. Luban and Professor A. J. Greenfield.

APPENDIX

We discuss here the justification of using Eq. (14) for the continuum states. A necessary condition for its use is that the matrix elements be real single-valued functions of the energy of the states $|p\rangle$. Since the angular momentum selection rules effectively eliminate the orbital degeneracies, we need only demonstrate that the radial part R of the continuum functions can be taken as real and non-degenerate. Writing

$$\chi = rR = Me^{i\phi}, \quad (A1)$$

χ satisfies

$$\chi'' + f\chi = 0, \quad (A2)$$

where f is some real function assumed analytic everywhere except at the origin. Then

$$M\phi'' + 2\phi'M' = 0, \quad (A3)$$

so that for all $r \neq 0$,

$$M^2\phi' = C, \quad (A4)$$

where C is a constant.

If at some point $r = \rho \neq 0$, $M(\rho) = 0$, then $C = 0$ and ϕ' is everywhere zero. Therefore, either ϕ is a constant and R is pure real, or M is nowhere zero. Since the former assertion already satisfies our requirements, we concern ourselves with the implications of the latter. Forming the set of degenerate real functions

$$\chi_+ = \chi + \chi^* \quad (A5a)$$

$$\chi_- = i(\chi - \chi^*), \quad (A5b)$$

we observe that if $\chi_+(r) = 0$, $\chi_-(r) \neq 0$, and vice versa, for all $r \neq 0$. If we enclose the system in an impenetrable spherical container, then if χ_+ satisfies the resulting boundary conditions, χ_- cannot, and vice versa, so that only one of these functions need be retained.

An additional requirement for our use of Eq. (14) is that the energy dependence of the sign of the product of the matrix elements be known. It is easily seen that this sign is independent of energy, since a change of sign implies, by continuity, that the matrix element, and hence, the photoionization cross section, vanish at the crossover point. This, however, is contrary to experience.

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Auger Spectra of Carbon and Argon Following Ionization by Equal-Velocity α Particles and Deuterons*

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(Received 26 December 1972)

The spectra of carbon *K*- and argon *L*-shell Auger electrons resulting from ionization produced by 0.15–0.50-MeV/amu α particles and deuterons incident on a thin gas cell have been measured. Absolute ionization cross sections were obtained from the Auger-electron yields and, in addition, the yields obtained with equal-velocity projectiles were used to test the projectile *z* dependence of the ionization process. Intense satellite structure was observed in the Auger spectra and these features were attributed to Auger transitions from multiple vacancy states formed during the collision.

I. INTRODUCTION

Several measurements have been reported^{1,2} in which comparisons of x-ray yields resulting from equal-velocity α -particle and deuteron or proton bombardments have been used to test the theoretical prediction^{3,4} that *K*-shell ionization cross sections are directly proportional to the square of the projectile charge. Significant deviations from the expected dependence have been deduced on the assumption that the fluorescence yields (which relate x-ray production cross sections to ionization cross sections) are the same for a given target element,

regardless of the type of projectile being used to produce the ionization. It has recently been discovered, however, that even in collisions involving relatively light ions, such as α particles and protons, appreciable *L*-shell ionization frequently accompanies the production of a *K*-shell vacancy.^{5–7} Since the fluorescence yields for multiply ionized states are expected to differ from those for singly ionized states, the assumption that the fluorescence yield is independent of the exciting particle could lead to erroneous results, especially for light elements where the effects of multiple ionization may result in a relatively large change in