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Molecular orbital x-ray emission from primary exciting collisions

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The theory of molecular-orbital x-ray emission occurring during the primary vacancy-producing collision (the "one-collision spectrum") is developed. Calculations are presented for an illustrative excitation process (direct impact ionization in a symmetric collision system). It is shown that because of coherence of the excitation and radiative processes the resulting emission profile is very different from that expected if the events were incoherent (quasistatic model). In particular, the profile undergoes a strong red shift relative to the incoherent component and is relatively velocity independent in shape.

I. INTRODUCTION

Recently considerable interest has been shown in the emission of x rays of noncharacteristic wavelengths during heavy-ion bombardment of solid (or dense gas) targets.[1-9] Though weak compared to the characteristic atomic lines, such emission is easily observed since it is shifted to much shorter wavelengths. It can be attributed to a number of processes (including for example such direct sources as nucleus-nucleus bremsstrahlung), but even the nonrelativistic theoretical problem is very complicated; a variety of novel effects and interpretations has been discussed,[7,11-16] and as yet there is not complete agreement about the dominant processes responsible for the observed frequency distribution and intensity of the emission.

In particular, much discussion concerns *molecular-orbital x rays*. In the experiments, heavy-ion speeds are typically less than K-shell electron orbital speeds and under these conditions these electrons occupy molecular-orbital (MO) levels whose energies change with the slowly moving nuclei. If a K vacancy is present during a collision, an x-ray photon may be emitted at frequencies related to the transient MO energy-level separations rather than those of the isolated atoms. Using the Weisskopf theory[10] of collision broadening, Briggs[11] and Macek and Briggs[12] have discussed the molecular-orbital x rays emitted during *secondary* collisions of symmetric heavy-ion systems having a K vacancy produced in an earlier primary collision; this may be called the "two-collision MO x-ray spectrum."

In this paper we consider the "one-collision spectrum," i.e., molecular-orbital x-ray emission occurring during a primary vacancy-producing collision. A simple classical interpretation of this process along the lines of Briggs' treatment of the two-collision spectrum at first suggests that the frequency profile of the one-collision spectrum contains direct information about the K-vacancy production process, itself a topic of some debate at present. *However, we show here that such a simple interpretation is not correct and that there is no simple relation between the one-collision emission profile and the K-vacancy production probability.*[17] The emission is a second-order process and must be treated coherently. The complete second-order emission amplitude does contain a term having a simple relation to the vacancy-production amplitude, but in addition there is a second "transient" term arising from coherence of the vacancy production and radiative transition events, and leading to a general continuous emission not directly related to the final vacancy-production amplitude. This second term may be comparable to or even larger than the first term. In the terminology of formal scattering theory, the new effects result from large "off-shell" contributions to the second-order T matrix for the process.

In much of this paper, we make no specific assumptions regarding the K-vacancy production mechanism to be considered, since we wish to emphasize the very general nature of the effect under discussion, and since there remains some controversy about the effective K-vacancy production mechanisms. However, we present some illustrative computations for a particular model process, in this case direct impact ionization of an electron from the $1s\sigma_g$ molecular orbital of a symmetric heavy-ion system. These results are intended to illustrate the marked differences between the one-collision emission profile and that of the two-collision spectrum, and are not intended for direct comparison with experimental observations, as there is now some reason to think that this vacancy-production mechanism is not an important contributor to K-vacancy production. Nevertheless, certain qualitative general conclusions regarding one-collision profiles may be drawn from the results. In a subsequent paper we will present model calculations

on the one-collision spectrum for the probably more relevant case where a K vacancy of the higher-Z partner in an asymmetric collision system is produced by the "vacancy-sharing" mechanism.[18,19]

II. PROBLEM DESCRIPTION

A. Inner-shell vacancy creation in slow heavy-ion collisions

Consider the impact ejection of inner-shell electrons in collisions of heavy-ion systems, such as may occur in heavy-ion bombardment of a solid or dense gas target. According to the Massey adiabatic criterion, efficient impact excitation of a bound electron will occur when $(v_c/v_e) \approx 1$, where v_c is the relative heavy-particle speed and v_e the orbital speed of that electron; this condition corresponds to a c.m. collision energy $E \approx (M/m_e)\bar{\epsilon}_n$ where $\bar{\epsilon}_n$ is the mean electron binding energy, M the reduced heavy-ion mass, and m_e the electron mass. In the experiments of interest to this work, v_c/v_K is typically less than 1, with values ≈ 0.1, though some data is available for higher energies. This means that the inner-shell electrons occupy molecular orbitals which depend parametrically on the slowly changing nuclear positions, and the theory of excitation from such states is based upon the dynamical perturbations to an adiabatic zero-order description of the electron states.[20] Meanwhile, since the outer-shell electrons are much less tightly bound, such a "slow collision" description is certainly not applicable to them; the effective coupling is much stronger and a massive and very complicated disturbance of the outer shells occurs.

In this work we will make no effort to describe the behavior of the outer-shell system, except to note that since vacancy-production probabilities for the outer shells are very much larger than those we consider for inner shells, we can consider K-vacancy production mechanisms (based on multistep processes) in which a previously produced outer-shell vacancy is "demoted" to the inner shell upon collision. The importance of such multistep processes has been recognized widely.[1,21-23]

Since the mechanisms considered here all involve direct excitation of a single electron by the moving nuclei, we can use an independent-particle model and obtain effectively a one-electron description. In the specific calculations presented in Sec. IV, which involve direct impact ionization from the $1s\sigma_g$ level in a symmetric system ($Z_A = Z_B$) as the vacancy-production event, we use the wave functions, orbital energies, and matrix elements of the H_2^+ system for our model; a simple Z-scaling law can be applied to obtain the results for the arbitrary symmetric system of heavier ions and a single electron.[21]

Figure 1 depicts some relevant low-lying inner-shell MO levels in schematic fashion for a near-symmetric system ($Z_B \leq Z_A$, but $Z_B \gg Z_A/2$; under these conditions the atomic $1s_B$ level lies well below the $2s_A$-$2p_A$ levels, but at or above the $1s_A$ level). Orbitals are denoted by united-atom labels. We consider processes creating vacancies in the $1s\sigma$ and $2p\sigma$ MO's, especially the former, which corresponds to a K vacancy in the ion of higher Z (Z_A). These fall into several categories[19,21-27]:

(1) Demotion of a $2p\pi$ vacancy to a $2p\sigma$ vacancy via rotational coupling. This is the most efficient mechanism for transfer of an L-shell vacancy into the K-shell of the lower-Z partner, as it is a strong-coupling process mediated by the orbital degeneracy of the $2p\sigma$ and $2p\pi$ levels in the united-atom limit. The prototype problem (in the H_2^+ system) was studied by Bates and Williams[28] and by Knudson and Thorson[29]; its important role in creating inner-shell K vacancies has been discussed by Briggs and Macek[21] [see also the review articles, Refs. 1(a)–1(e)], and some extensive calculations on a specific system where it plays a role have been made by Briggs and Taulbjerg.[22,23]

(2) Creation of $2p\sigma$ vacancies by direct impact excitation or ionization. These processes are much less efficient than (1), since the excitation energies are substantial and no mediating degeneracy of the coupled states occurs during collision. A theoretical calculation of the ionization cross section has been made by Thorson and coworkers[25,26] for the H_2^+ prototype.

(3) Creation of a $1s\sigma$ vacancy by "vacancy-shar-

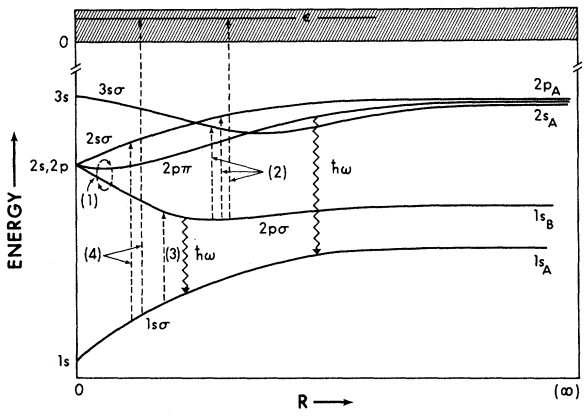

FIG. 1. Schematic energy-level diagram for inner-shell molecular orbitals (one-electron problem) of a near-symmetric heavy-ion system. Dashed lines indicate possible excitations creating vacancies; zigzag line indicates x-ray transitions.

ing" of a 2pσ vacancy. In an asymmetric system, coupling is possible between the $2p\sigma$ and $1s\sigma$ states, but will be weak if these levels are widely separated at all R. As charge asymmetry and the asymptotic $1s_A$-$1s_B$ splitting decrease, the Demkov-type coupling becomes stronger; finally, in the symmetric and degenerate case there is formally no coupling between the levels $1s\sigma_g$ and $2p\sigma_u$, but the $2p\sigma_u$ vacancy corresponds to a K vacancy in either partner and hence appears on a subsequent collision with probability $\frac{1}{2}$ as a $1s\sigma_g$ vacancy. The dominant importance of the vacancy-sharing process for K-vacancy production in the higher-Z partner has been emphasized by the work of Meyerhof[18,19]; more elaborate computations by Briggs and Taulbjerg[22] and Taulbjerg, Vaaben, and Fastrup[24] take vacancy sharing into account also.

(4) $1s\sigma$ vacancy creation by direct impact excitation or ionization. These processes are inefficient for the same reasons as for processes (2) above. Indeed, the greater binding energy of the $1s\sigma_g$ orbital in H_2^+ leads to a cross section for ionization more than two orders of magnitude less than that for the $2p\sigma_u$ orbital.[25-27]

Further, in-depth discussion of these processes is not appropriate here, since the detailed mechanisms of K-vacancy production remain a subject of dispute, especially as to relative magnitudes in asymmetric or near-symmetric systems; however, it is probably safe to say that processes (1) and (3) are the dominant source of $1s\sigma$ vacancy production in most near-symmetric systems when $v_c/v_K \ll 1$, and to this end the computations of Taulbjerg *et al.*[22-24] are probably most relevant.

B. Molecular-orbital x rays and the two-collision spectrum

A brief review of some aspects of Briggs' treatment[11,12] of the two-collision molecular-orbital x-ray emission is useful to our own problem. Briggs assumes a colliding system with a previously created K vacancy in one of the partners (he treats only the symmetric case), and considers the spontaneous emission of photons coming from all subsequent secondary collisions, using the Weisskopf formula[10] for collision broadening of an atomic line. For an incident projectile having a given collision path through the target, the number of photons emitted at frequency ω to $\omega+d\omega$ is

$$I(\omega)d\omega = (4e^2\omega/3\hbar c^3)\left|D_c^{2p\lambda}(\omega)\right|^2 d\omega, \tag{1}$$

where $D_c^{2p\lambda}(\omega)$ is given by a Fourier transform of the time-dependent dipole matrix element,

$$D_c^{2p\lambda}(\omega) = (2\pi)^{-1/2}\int_0^\infty dt\, D_{2p\lambda}[R(t)]e^{-\Gamma t/2} \times \exp\left(i\omega t - i\hbar^{-1}\int_0^t dt'\,(\epsilon_{2p\lambda}-\epsilon_{1s\sigma})\right); \tag{2}$$

the integral is evaluated over the entire secondary collision history. $D_{2p\lambda}[R]$ is the *dipole-velocity* matrix element for an electronic transition between the $2p\lambda$ ($\lambda=\pi$ or σ) and $1s\sigma$ molecular orbitals at internuclear separation R. The $1s\sigma$ vacancy amplitude is assumed to decay in secular fashion as $e^{-\Gamma t/2}$ where Γ is the cumulative decay rate due to all radiative and nonradiative processes; this factor guarantees the convergence of the integral in the neighborhood of the atomic K x-ray line ($\lambda=\pi$ only) and gives there the usual Lorentzian line shape. Briggs discusses the problem of relative intensity of the Lorentzian line and the remaining emission (in this connection see also Ref. 37), but the main objective is the computation of emission at frequencies far from the atomic line. Equation (2) contains contributions from each of the distinct collisions in the projectile path; assuming these are incoherent, Briggs shows that (except for simple multiplicative factors representing the target particle size and density, etc.) the number of photons emitted at ω to $\omega+d\omega$, per incident projectile with a $1s\sigma$ vacancy, is given by the average of expression (1) over all collision impact parameters, where expression (2) is now taken to be the integral over a single collision trajectory, of specified impact parameter, and the decaying amplitude factor is omitted.

Quasistatic approximation. A simple physical interpretation can be given if the Fourier transform (2) be evaluated by the stationary phase approximation; one then finds that contributions to emission at ω come entirely from points on the collision trajectory where $\Delta\epsilon = \epsilon_{2p\lambda} - \epsilon_{1s\sigma} = \hbar\omega$. Assuming further the incoherence of contributions from the distinct points on the trajectory where this condition holds, and assuming for simplicity that it holds at a single distance $R = R_0(\omega)$, Briggs obtains (after averaging over impact parameters)

$$I(\omega)\,d\omega = \frac{4e^2\omega}{3\hbar c^3}D_{2p\lambda}^2(R_0)\frac{4N_0\hbar\pi R_0^2}{\Gamma\{d\Delta\epsilon/dR\}_{R_0}} \times\left(1-\frac{U(R_0)}{E_0}\right)^{1/2} d\omega\,, \tag{3}$$

where N_0 is the target particle density, E_0 the collision energy, and $U(R)$ the potential determining the trajectory. In effect then the emission profile for the two-collision spectrum is a kind of mapping of the square of the static dipole moment matrix element, divided by the slope of $\Delta\epsilon$, via the connection $\hbar\omega = \Delta\epsilon(R_0)$. Macek and Briggs[12] did the accurate evaluation of the trajectory integrals (2), and found that the quasistatic approximation is a rather good one over most of the emission profile. Its main defects are (1) a sharp cut-off of emis-

sion at the united-atom limit $\hbar\omega_{UA} = \Delta\epsilon(0)$, where in fact a tail of emission to higher ω occurs, and (2) omission of certain oscillatory features associated with coherence of emission from R_0 during incoming/outgoing halves of the collision trajectory (similar to effects of rainbows in scattering cross sections); these are both effects of detail only and do not alter the qualitative picture of the two-collision spectrum given by the quasistatic approximation.

C. One-collision spectrum

Frequency-shifted molecular-orbital x rays can also be emitted during the primary collision which produces the $1s\sigma$ vacancy. For a particular collision the number of emitted photons is again given by Eq. (1), but now $D_c^{2p\lambda}(\omega)$ is given by

$$D_c^{2p\lambda}(\omega) = (2\pi)^{-1/2} \int_{-\infty}^{\infty} dt\, D_{2p\lambda}[R(t)] a^{\mu}_{1s\sigma}(t) \times \exp\left(i\omega t - i\hbar^{-1} \int_0^t dt' \, (\epsilon_{2p\lambda} - \epsilon_{1s\sigma}) \right), \quad (4)$$

where the integral is understood to be evaluated only over a single collision trajectory; contributions from all later collisions can be treated by the theory of Briggs and Macek. The time origin has been shifted so that $t = 0$ is the collision midpoint. $a^{\mu}_{1s\sigma}(t)$ is the (interaction picture) amplitude for the existence of a K vacancy produced during collision by some particular excitation process (designated by the label μ); $a^{\mu}_{1s\sigma}(-\infty) = 0$.

Evidently the process considered here is higher order than the simple first-order emission process considered in the two-collision spectrum. $a^{\mu}_{1s\sigma}(t)$ is calculated by solving a time-dependent coupling problem, starting from an initial state with no vacancy. If a first-order perturbation theory is employed, then the emission process is second-order, involving the vacancy-creating perturbation first and the radiative emission step second.

Naive quasistatic picture. If it be assumed that $a^{\mu}_{1s\sigma}(t)$ grows in essentially a secular fashion until it reaches the final vacancy-production amplitude $a^{\mu}_{1s\sigma}(\infty)$, then the stationary-phase approximation can be used to evaluate (4) and give a kind of quasistatic account of the emission. For example, suppose

$$a^{\mu}_{1s\sigma}(t) = \tfrac{1}{2}[a^{\mu}_{1s\sigma}(\infty) + f(t)],$$

where $f(-t) = -f(t)$ and $f(\infty) = a^{\mu}_{1s\sigma}(\infty)$, and suppose $f(t)$ grows in some smooth fashion; it might be reasonable to relate it in some direct way to the coupling matrix element producing the excitation.[6] We do not develop this argument in detail, since it is mistaken, but it will evidently lead to a result in which the emission at frequency ω to $\omega + d\omega$ for a collision of specified impact parameter is proportional as in quasistatic approximation to $D^2_{2p\lambda}[R_0(\omega)]/\{d\Delta\epsilon/dR\}_{R_0}$, but also to $P^{\mu}_{1s\sigma}(b)$, the probability of creating a $1s\sigma$ vacancy by excitation process μ in a collision of impact parameter b. Given such a formula, there is a certain amount of information about the shape of $P^{\mu}_{1s\sigma}(b)$ vs b folded into the overall emission profile, and emission attributed to a one-collision spectrum has in some instances been so analyzed.[36]

The most important conclusion of this work is that this simple quasistatic picture of the one-collision spectrum is incorrect. The error lies in the assumption that the amplitude $a^{\mu}_{1s\sigma}(t)$ changes in smooth and secular fashion. In reality, the vacancy-creating processes involve inefficient coupling, usually with significant electronic energy transfer from the heavy-particle motion, and in most cases can be treated almost perturbatively. The resulting amplitude $a^{\mu}_{1s\sigma}(t)$ then oscillates rapidly at the frequency of the electronic transition, that is, the response to the coupling is that of the nonresonant driven oscillator. As a consequence the quasistatic result no longer is obtained and with it the simple interpretation of the emission is lost.

Using a perturbative theory of the $1s\sigma$ vacancy-creation process, we derive in the next section the correct formula for the one-collision emission spectrum. The main derivation will be given in the time-dependent approach already suggested here, but we will also sketch the result of a more formal stationary-state treatment.

III. THEORY OF THE ONE-COLLISION SPECTRUM

A. Time-dependent formulation

1. General expressions

Consider collisions with no initial $1s\sigma$ vacancy; a vacancy is created by one of several processes: *(a) Given a vacancy in a higher level, n, the electron is promoted to n.* Two subcases should be distinguished. (i) Vacancy sharing, $n = 2p\sigma$. Depending on the charge asymmetry and collision energy, coupling may be weak, or so strong that a perturbation treatment of the excitation is inappropriate. We present calculations for this case in a subsequent paper. (ii) n is a level above $2p\sigma$; in this case the coupling is weak and perturbation theory is applicable. *(b) Direct impact ionization of a $1s\sigma$ electron into a continuum state of energy ϵ.* Coupling is weak, and first-order perturbation theory is used to calculate vacancy amplitudes by the theory of Refs. 25–27. Calculations presented in this paper (Sec. IV) treat this process for the

symmetric heavy-ion case, using H_2^+ as prototype system.[30]

Let $a_K(\mu;t)$ be the time-dependent amplitude for vacancy production by excitation to level μ; K denotes $1s\sigma$, for brevity. A photon may be emitted by the radiative transition $2p\lambda \to 1s\sigma$ (see Fig. 1). Per primary collision of impact parameter b and energy E, the number of photons emitted at frequency ω to $\omega+d\omega$ in this two-step process is

$$I^\lambda(\omega;\mu,b,E)d\omega = (4e^2\omega/3\hbar c^3)\,|D_c^\lambda(\omega;\mu,b,E)|^2 d\omega, \tag{5}$$

where [Eq. (4)]

$$D_c^\lambda(\omega;\mu,b,E) = (2\pi)^{-1/2}\int_{-\infty}^{\infty} dt\, D_{2p\lambda}[R(t)]a_K(\mu;t) \times \exp\left(i\omega t - i\hbar^{-1}\int_0^t dt'\,(\epsilon_{2p\lambda}-\epsilon_{1s\sigma})\right) \tag{6}$$

with $a_K(\mu;-\infty)=0$. The total photon emission is the sum of (incoherent) contributions from all such processes,

$$I_T(\omega;b,E) = \sum_\lambda \sum_\mu I^\lambda(\omega;\mu,b,E); \tag{7}$$

in the case of ionization the sum over μ is an integral over continuum energy ϵ. Finally we integrate over primary impact parameters b and divide by the relevant K-vacancy production cross section to obtain the photon emission per K vacancy produced:

$$\bar{I}_T(\omega;E) = \int_0^\infty 2\pi b\, db\, I_T(\omega;b,E)/\sigma_K(E). \tag{8}$$

2. *Relative intensities of one-collision and two-collision emission*

In principle, the above expressions include the two-collision emission discussed by Macek and Briggs,[11,12] as well as the characteristic atomic x-ray line, since the integral in (6) extends over both the primary and all secondary collision history. The one-collision emission is separated from the rest if we divide the integral into the primary collision part, from $-\infty$ to t_1^∞, and the secondary collision part, from t_1^∞ to ∞, and assume that the two contribute incoherently when all averages are performed. We define then the primary and secondary emission intensities

$$I_j^\lambda(\omega;\mu,b,E) = (4e^2\omega/3\hbar c^3)\,|D_{cj}^\lambda(\omega;\mu,b,E)|^2 \tag{5'}$$

for $j=1$ or 2, with the primary term

$$D_{c1}^\lambda(\omega_i\mu,b,E) = (2\pi)^{-1/2}\int_{-\infty}^{t_1^\infty} dt\, D_{2p\lambda}[R(t)]a_K(\mu;t)\exp\left(i\omega t - i\hbar^{-1}\int_0^t (\epsilon_{2p\lambda}-\epsilon_{1s\sigma})\,dt'\right), \tag{9a}$$

and secondary term

$$D_{c2}^\lambda(\omega;\mu,b,E) = (2\pi)^{-1/2} c_{K\mu}^0(b,E)\int_{t_1^\infty}^\infty dt\, D_{2p\lambda}[R(t)]\,\exp[-\Gamma(t-t_1^\infty)/2]\exp\left(i\omega t - i\hbar^{-1}\int_0^t (\epsilon_{2p\lambda}-\epsilon_{1s\sigma})\,dt'\right)^{t_1^\infty}. \tag{9b}$$

In Eq. (9b) we have written

$$a_K(\mu;t) = c_{K\mu}^0(b,E)\,\exp[-\Gamma(t-t_1^\infty)/2], \tag{10}$$

where $c_{K\mu}^0(b,E) = a_K(\mu;t_1^\infty)$, i.e., $|c_{K\mu}^0|^2$ is the probability of excitation $1s\sigma \to \mu$ in a primary collision at b, E, and we assume as in the two-collision theory a subsequent secular decay of the vacancy amplitude. Now, except for $c_{K\mu}^0$ and an irrelevant phase, the expression (9b) is exactly the same as that for the two-collision theory, Eq. (2), and if we assume that the secondary collision history is random with respect to primary collision impact parameters, then the integral over them just gives the (μ-excitation) vacancy-production cross section

$$\sigma_{K\mu}(E) = \int_0^\infty 2\pi b\, db\,|c_{K\mu}^0(b,E)|^2 \tag{11}$$

as a factor multiplying the two-collision spectrum. Then we can calculate the contributions of all secondary collisions in a manner similar to that used by Macek and Briggs; for brevity, we omit the details, and give the final result for molecular orbital x-ray emission in photons per separated atom K vacancy produced, per unit frequency, at frequency ω:

$$\bar{I}_T(\omega,E) = \frac{1}{\sigma_K(E)}\int_0^\infty 2\pi b\, db\,\frac{4e^2\omega}{3\hbar c^3}\sum_\mu |D_{c1}^\lambda(\omega;\mu,b,E)|^2 + \frac{N_0 v}{\Gamma}\int_0^\infty 2\pi b'\,db'\,\frac{4e^2\omega}{3\hbar c^3}|D_c^{2p\lambda}(\omega;b',E)|^2. \tag{12}$$

Here $\sigma_K(E)$ is the summed K-vacancy production cross section

$$\sigma_K(E) = \sum_\mu \sigma_{K\mu}(E), \tag{11'}$$

N_0 is the target particle density, and v the average collision velocity; Macek and Briggs have shown how the factor $N_0 v/\Gamma$ emerges from an incoherent sum over the distinct secondary collisions and ef-

fectively counts the number of them involved. When the normalized intensity in (12) is multiplied by the actual yield of K-vacancies in a target, then the second term will show the expected quadratic dependence of the two-collision emission on target particle density and the effect of the number of secondary collisions in lifetime Γ^{-1}. In the rest of this work we consider only the fundamental emission *profiles* of one-collision and two-collision spectra; Eq. (12) would give their qualitative relative intensities.

Contributions of the characteristic atomic line have been omitted from (12). They can be explicitly included using the method of Macek and Briggs to extract the Lorentzian line shape (width Γ), although it has been shown recently by Anholt[37] that the contribution is far from Lorentzian away from the line center. In symmetric systems the characteristic line appears only for the $2p\pi$ transition, since $D_{2p\sigma}(R)$ tends to zero as $R \to \infty$. As ω approaches the atomic line frequency ω_0, the single collision integrals (9a) and (2) both diverge unless the decay factor $\exp[-\Gamma t/2]$ is included for $t>0$. Evaluation of such modified integrals can be done, but we have chosen to ignore the problem and compute only the molecular-orbital x-ray emission for frequencies not too close to ω_0.

3. *Nonadiabatic excitations*

To compute the one-collision profile we must now evaluate the Fourier transform $D^{\lambda}_{c1}(\omega;\mu,b,E)$; the upper limit t_1^{∞} can be extended to ∞, provided it be understood to cover only one collision, and ω is not too close to $\omega_0=[\epsilon_{2p\pi}(\infty)-\epsilon_{1s\sigma}(\infty)]/\hbar$. We require a method for computing the vacancy amplitudes $a_K(\mu;t)$, created by nonadiabatic excitation.

Consider the case where the coupling producing the excitation $1s\sigma \to \mu$ is weak and can be treated by first-order perturbation theory (the vacancy-sharing process is the only one for which this might not be valid). For discrete transitions it can be shown that[25]

$$\frac{da_K(\mu;t)}{dt}=a_0\mathcal{T}_{\mu 0}\exp\left(\frac{i}{\hbar}\int_0^t(\epsilon_\mu-\epsilon_{1s\sigma})\,dt'\right), \quad (13)$$

where a_0 is the initial state amplitude (assumed approximately equal to unity), and the coupling $\mathcal{T}_{\mu 0}(t)$ can be expressed in terms of radial and angular velocity couplings of the forms

$$\mathcal{T}^R_{\mu 0}=\dot{R}T^R_{\mu 0}(R), \quad \mathcal{T}^{\theta}_{\mu 0}=\dot{\theta}T^{\theta}_{\mu 0}(R), \quad (14)$$

where $\dot{R},\dot{\theta}$ are the classical radial and angular heavy-particle velocities and $T^R_{\mu 0}, T^{\theta}_{\mu 0}$ are electronic matrix elements of suitably defined nonadiabatic coupling operators between $1s\sigma$ and μ electronic orbitals (cf. Refs. 25 and 26). (For symmetric or near-symmetric systems, the radial couplings are likely to be dominant in $1s\sigma$ excitations, because the $1s\sigma$ orbital is so nearly spherical in shape in the interaction region.) Integration of (13) gives

$$a_K(\mu;t)=\int_{-\infty}^{t}dt'\,\mathcal{T}_{\mu 0}(t')\times\exp\left(\frac{i}{\hbar}\int_0^{t'}(\epsilon_\mu-\epsilon_{1s\sigma})\,dt''\right). \quad (13')$$

In the case of impact ionization, it was shown by Thorson and Levy[25] that Eq. (13′) is also valid, except that the accompanying description of the *ionized particle* is accurate only in the asymptotic limit $t\to\infty$. Since recapture is improbable, and we are interested only in the hole, we can use (13′) to calculate the transient vacancy-production amplitude for ionization also.

We can derive certain symmetry relations between $a_K(\mu;t)$ and $a_K(\mu;-t)$ ($t=0$ is the collision midpoint). Note that

$$\mathcal{T}^R_{\mu 0}(-t)=-\mathcal{T}^R_{\mu 0}(t), \quad \mathcal{T}^{\theta}_{\mu 0}(-t)=\mathcal{T}^{\theta}_{\mu 0}(t), \quad (15)$$

since $T_{\mu 0}(R)$ are symmetric; $(\epsilon_\mu-\epsilon_{1s\sigma})$ is also symmetric. We can write

$$a_K(\mu;t)=c^0_{K\mu}-\int_t^{\infty}dt'\,\mathcal{T}_{\mu 0}(t')\times\exp\left(i\hbar^{-1}\int_0^{t'}(\epsilon_\mu-\epsilon_{1s\sigma})\,dt''\right)$$

and obtain, on substitution $t'\to-\bar{t}\,'$ in the second term,

$$a_K(\mu;t)=c^0_{K\mu}-(-1)^{\gamma}a^*_K(\mu;-t) \quad (16)$$

with the special result

$$c^0_{K\mu}=a_K(\mu;0)+(-1)^{\gamma}a^*_K(\mu;0), \quad (17)$$

where the parity index γ is 1 for radial, and 0 for angular, couplings.

4. *Behavior of amplitude*

The behavior of the vacancy amplitude $a_K(\mu;t)$ is crucial to the theory. As noted in Sec. IIC, it is obvious that the method of stationary phase can be used to do the integral (9a), if $a_K(\mu;t)$ grows in a smooth secular fashion from its zero initial value to the final value $c^0_{K\mu}(b,E)$, *but this is not the case*. In the situations of interest, the K-vacancy production cross section is not large; the coupling is weak, and substantial excitation energy is transferred to the electron from the heavy particles. Under these conditions the response of the system is like that of a nonresonant driven oscillator; that is, for $t<0$ we have

$$a_K(\mu;t)=\phi_{K\mu}(t)\exp\left(i\hbar^{-1}\int_0^t(\epsilon_\mu-\epsilon_{1s\sigma})\,dt'\right), \quad (18)$$

where we expect $\phi_{K\mu}(t)$, rather than $a_K(\mu;t)$, to be a smooth, secular function. The equation for $\phi_{K\mu}$ can be obtained from Eqs. (13) and it can be shown that $\phi_{K\mu}(t)$ is indeed a slowly varying, nonoscillatory function which grows in a manner related to $\Gamma_{\mu 0}(t)$ and $\Delta\epsilon = \epsilon_\mu - \epsilon_{1s\sigma}$. In fact, rapid and accurate computation of $\phi_{K\mu}$ can be done using such equations[31,32] if the coupling is at least asymptotically weak.

5. *Expression for $D^\lambda_{c1}(\omega)$*

Substitution of (18) and (16) into Eq. (9a) gives, after some manipulation,

$$D^\lambda_{c1}(\omega;\mu,b,E) = c^0_{K\mu}(b,E)D^\lambda_{c\,\mathrm{sec}}(\omega;b,E) + D^\lambda_{c\,\mathrm{trans}}(\omega;\mu,b,E), \quad (19)$$

where the *secular* term $D^\lambda_{c\,\mathrm{sec}}$ is given by

$$D^\lambda_{c\,\mathrm{sec}}(\omega;b,E) = (2\pi)^{-1/2}\int_0^\infty dt\, D_{2p\lambda}[R(t)] \times \exp\left(i\omega t - i\hbar^{-1}\int_0^t (\epsilon_{2p\lambda} - \epsilon_{1s\sigma})\,dt'\right) \quad (20)$$

and the *transient* term $D^\lambda_{c\,\mathrm{trans}}$ by

$$D^\lambda_{c\,\mathrm{trans}}(\omega;\mu,b,E) = \{\mathfrak{D}^\lambda_{\mathrm{trans}}(\omega;\mu,b,E) - (-1)^\gamma[\mathfrak{D}^\lambda_{\mathrm{trans}}(\omega;\mu,b,E)]^*\} \quad (21a)$$

with

$$\mathfrak{D}^\lambda_{\mathrm{trans}}(\omega;\mu,b,E) = (2\pi)^{-1/2}\int_{-\infty}^0 dt\, D_{2p\lambda}[R(t)]\phi_{K\mu}(t) \times \exp\left(i\omega t + i\hbar^{-1}\int_0^t (\epsilon_\mu - \epsilon_{2p\lambda})dt'\right). \quad (21b)$$

If the transient term in (19) were negligible, the remaining secular term would have a simple emission profile. Comparing Eqs. (20) and (2), we find that the two-collision spectral amplitude $D^{2p\lambda}_c$ is related to $D^\lambda_{c\,\mathrm{sec}}$:

$$D^{2p\lambda}_c(\omega;b,E) = 2\ \mathrm{Re}[D^\lambda_{c\,\mathrm{sec}}(\omega;b,E)],$$

and we can also use the stationary phase method to evaluate the integral. After averaging the emission over all primary impact parameters, we obtain the *quasistatic approximation* to the secular term of the one-collision spectrum [cf. Eqs. (2) and (3) of Ref. 6]:

$$I^\lambda_{\mathrm{sec}}(\omega;\mu,E) = \{(4e^2\omega/3\hbar c^3)D^2_{2p\lambda}(R_0)\} \times [\hbar(d\Delta\epsilon/dR)^{-1}_{R_0}]\, f_{K\mu}(R_0;E), \quad (22a)$$

where

$$f_{K\mu}(R_0;E) = [\sigma_{K\mu}(E)]^{-1}\int_0^{b_0(R_0)} 2\pi b\, db\, P_{K\mu}(b,E) \times \left(1 - \frac{U(R_0)}{E} - \frac{b^2}{R_0^2}\right)^{-1/2}. \quad (22b)$$

In these equations, $R_0(\omega)$ is the internuclear distance (here assumed unique for simplicity) such that

$$\Delta\epsilon(R_0) = \epsilon_{2p\lambda}(R_0) - \epsilon_{1s\sigma}(R_0) = \hbar\omega,$$

b_0 is that value of b for which R_0 is the closest distance of approach on the trajectory determined by the potential $U(R)$, and $P_{K\mu}(b,E) = |c^0_{K\mu}(b,E)|^2$ is the probability of excitation $1s\sigma \to \mu$ per collision at b,E. It is evident that in this case the one-collision emission profile contains information about $P_{K\mu}(b;E)$ in the function $f_{K\mu}(R_0(\omega);E)$ [the vacancy-production cross section $\sigma_{K\mu}(E)$ is given by Eq. (11)].

In general, however, the transient contribution to (19) is not negligible, and it does not possess a simple interpretation in terms of the final vacancy-production amplitude $c^0_{K\mu}$. Since in every case except that of vacancy sharing the energy difference $(\epsilon_\mu - \epsilon_{2p\lambda})$ is positive, the integral (21b) has no points of stationary phase. The magnitude of the integral is related to the transient amplitude function $\phi_{K\mu}(t)$, and can have a significant size because it happens that $|\phi_{K\mu}(t)|$ has maximum transient values which may be much larger than the final value $|a_K(\mu;0)|$ which determines the secular amplitude $c^0_{K\mu}$. It may also be important to keep track of the coherence of the secular and transient terms in (19), as our computations in Sec. IV demonstrate.

B. Equivalent stationary-state formulation

Additional insight into the problem is provided if we formulate the theory of one-collision emission from first principles using stationary-state perturbation theory of the second-order process involved. We will quote only the main results for the sake of brevity.

Formally, the rate of transitions (photon emissions) is given by

$$\tau^{-1} = \frac{2\pi}{\hbar}\sum_f \left|\sum_m \frac{\langle f|\mathcal{H}_1|m\rangle\langle m|\mathcal{H}_1|i\rangle}{E_i - E_m + i\eta}\right|^2 \delta(E_i - E_f) \quad (23)$$

($\lim \eta \to 0^+$). Here $\mathcal{H}_1$ is the perturbation or perturbations causing transitions among the eigenstates $|j\rangle$ of a zero-order Hamiltonian $\mathcal{H}_0$. The denominator $(E_i - E_m + i\eta)^{-1}$ has the usual operative meaning $\{\mathcal{P}[(E_i - E_m)^{-1}] - i\pi\delta(E_i - E_m)\}$ in the sum over intermediate states $|m\rangle$, $\mathcal{P}$ being the principal value of any integral or sum encountered. The relevant point is that the virtual intermediate states $|m\rangle$ need not conserve energy $(E_m \neq E_i)$ and

the principal value represents the contribution of such states. These "off-shell" contributions to the overall transition amplitude can be large in this problem and are the rough counterpart in this formulation to the transient terms found in the time-dependent theory.

The process considered here involves two perturbations, first, the nonadiabatic coupling linking initial state $|i\rangle$ (no $1s\sigma$ vacancy, μ vacancy, no photon) to intermediate state $|m\rangle$ ($1s\sigma$ vacancy, electron in μ, no photon) and second, the radiative emission coupling linking $|m\rangle$ to final state $|f\rangle$ ($2p\lambda$ vacancy, no $1s\sigma$ vacancy, photon of energy $\hbar\omega$). Only this sequence can lead to nonzero amplitudes of interest to us. The energies E_i and E_f (E) are equal but E_m (E') may be different, and the translational kinetic energy of the heavy particle scattering states is determined accordingly.

A quantum-mechanical formulation of the nonadiabatic excitation is employed,[33] as well as for the radiative process. However, the resulting configurational integrals over heavy-particle wave functions are evaluated by a well-known semiclassical scheme (already used by Weisskopf[10] in the theory of collision broadening): the wave functions are approximated by JWKB forms and the configuration space integrals converted to trajectory integrals of the sort already seen in Sec. III A above.

Results obtained are as follows: per collision of impact parameter b and energy E, the number of photons emitted in the primary collision at frequency ω is again the sum over excitation levels μ and radiative components $\lambda(\sigma,\pi)$ of $I_1^\lambda(\omega;\mu,b,E)$ given in Eq. (5′), but now the one-collision spectral amplitude is given by

$$D_{c1}^{\lambda}(\omega;\mu,b,E)=\tfrac{1}{2}c_{K\mu}^{0}(b,E)D_c^{2p\lambda}(\omega;b,E)+\frac{i}{2\pi}\int d(\Delta E)\,\mathcal{P}(1/\Delta E)F_{K\mu}(\Delta E;b,E)D_c^{2p\lambda}(\omega-\Delta E/\hbar;b,E). \tag{24}$$

$D_c^{2p\lambda}(x;b,E)$ is just the two-collision spectral amplitude function at frequency x,

$$D_c^{2p\lambda}(x;b,E)=(2\pi)^{-1/2}\int_{-\infty}^{\infty}dt\,D_{2p\lambda}[R(t)]\times\exp\left(ixt-i\hbar^{-1}\int_0^t(\epsilon_{2p\lambda}-\epsilon_{1s\sigma})dt'\right), \tag{25}$$

and the quantity $F_{K\mu}(\Delta E;b,E)$ is defined

$$F_{K\mu}(\Delta E;b,E)=\int_{-\infty}^{\infty}dt\,\mathcal{T}_{\mu 0}(t)\times\exp\left[\frac{i}{\hbar}\left(\Delta Et+\int_0^t(\epsilon_\mu-\epsilon_{1s\sigma})\,dt'\right)\right]; \tag{26}$$

note that $F_{K\mu}(0;b,E)=c_{K\mu}^{0}(b,E)$.

The first term in (24) is the "on-shell" contribution (energy of virtual intermediate state in resonance with initial state), while the second term is the "off-shell" part. Comparison of (24) and the time-dependent expression (19) shows that the "secular" and "transient" terms are not perfectly in correspondence with the "on-shell" and "off-shell" terms, respectively, but it is true that the "transient" is entirely contained in the "off-shell" part (it also contains the imaginary part of the "secular" term).

A proof of the rigorous formal equivalence of the two expressions (19) and (24) can readily be given by the usual techniques of Fourier-transform theory. If we define the Fourier transform of $a_K(\mu;t)$,

$$A_{K\mu}(x)=(2\pi)^{-1/2}\int_{-\infty}^{\infty}e^{ixt}a_K(\mu;t)\,dt$$

and use integration by parts and Eqs. (13), we can obtain

$$A_{K\mu}(\Delta E/\hbar)=\pi c_{K\mu}^{0}(b,E)\hbar\delta(\Delta E)+\mathcal{P}(i\hbar/\Delta E)F_{K\mu}(\Delta E;b,\mu). \tag{27}$$

Then, using the inverse transform (properly defined!)

$$a_K(\mu;t)=(2\pi)^{-1/2}\int_{-\infty}^{\infty}e^{-ixt}A_{K\mu}(x)\,dx$$

for $a_K(\mu;t)$ in the expression (9a) for D_{c1}^{λ}, we obtain Eq. (24).

Some further physical insight into the importance of the "off-shell" or "transient" terms is provided in this formulation. Since the virtual intermediate states need not conserve energy, we may ask, why this might be advantageous? The reason is that the energy-conserving transfer of heavy-particle energy to electron excitation in the first step is rather inefficient, as is evidenced in the rapidly oscillatory factor $\exp[(i/\hbar)\int_0^t(\epsilon_\mu-\epsilon_{1s\sigma})dt']$, which appears in the computation of $c_{K\mu}^{0}$. If in the first step we need not conserve energy, the obvious thing to do is to excite the electron but keep the heavy-particle energy the same; this corresponds to off-shell contributions in the region $\Delta E \approx -\hbar^{-1}(\epsilon_\mu-\epsilon_{1s\sigma})_{\text{ave}}$ which clearly give quite large values to $F_{K\mu}(\Delta E;b,E)$ there. Then, in the second step, when we must return to energy conservation, we can economize by "cheating" the photon and giving it an energy $\hbar\omega$ less than it would have in the secular emission. We may therefore expect to see the off-shell or transient part contributing substantially to emission which is red-shifted in

comparison to the MO x-ray spectrum produced by the secular term alone, and as our illustrative calculations in Sec. IV show, this is indeed the case.

The time-dependent expressions (19)–(21) are the most convenient for computations.

IV. ILLUSTRATIVE COMPUTATION

To illustrate the above theory we compute one-collision emission profiles for the case where the K-vacancy is produced by direct impact ionization of a $1s\sigma$ electron, in the symmetric case $Z_A = Z_B$. The orbitals from which radiative transitions occur ($2p\sigma_u$, $2p\pi_u$) are assumed to have no vacancies. A simple model of this ionization process based on the H_2^+ system is used, the main features of which are described in Ref. 27. We neglect complications and mixing effects due to the nonspherical molecular symmetry, and consider ionization due to radial couplings to s-wave electronic continuum states only (however, note that Anholt[35] has found that partial wave contributions for $L = 2, 4$ are larger than those for $L = 0$.) The s-wave radial electronic coupling matrix element $T^R_{\epsilon 0}(R)$ (to an electronic continuum state of energy ϵ) is taken to be

$$T^R_{\epsilon 0}(R) = A_0(\epsilon) R \exp[-\alpha_0(\epsilon) R], \tag{28}$$

where $A_0(\epsilon) = \text{const.} = 0.5$, and $\alpha_0(\epsilon) = 2.890 - 2.222/(\epsilon + 1.50)$ as in Ref. 27. The collision trajectories are taken to be Coulomb trajectories for the bare nuclei. However, unlike the computations of Ref. 27, we do *not* assume the energy gap $[\epsilon - \epsilon_{1s\sigma_g}]$ constant and we evaluate the trajectory integrals exactly (the resulting vacancy-production probabilities are markedly different from those reported in Ref. 27 using constant energy gap and certain approximations to the integrals).

For computation it is convenient to introduce the trajectory variable $x = [(R - \eta b)^2 - c^2]^{1/2}$ in place of t, where ηb is the Coulomb parameter $Z_A Z_B / 2E$ and $c^2 = b^2(1 + \eta^2)$, with b the impact parameter, $E = \frac{1}{2} M v^2$ the collision energy; $x = 0$ at the turning point $t = 0$, and the branch cuts of the square root are chosen so that x has the sign of t. The function $\phi_{K\epsilon}$ defined by Eq. (18) then obeys the equation

$$d\phi_{K\epsilon}/dx + i\Omega_{K\epsilon}(x)\phi_{K\epsilon}(x) = P_{K\epsilon}(x), \tag{29}$$

where

$$\Omega_{K\epsilon}(x) = (\hbar v)^{-1}\{\epsilon - \epsilon_{1s\sigma_g}[R(x)]\}[1 + \eta b/(x^2 + c^2)^{1/2}] \tag{30a}$$

is essentially the energy gap, and

$$P_{K\epsilon}(x) = A_0(\epsilon) x \exp\{-\alpha_0(\epsilon)[(x^2 + c^2)^{1/2} + \eta b]\} \times [1 + \eta b/(x^2 + c^2)^{1/2}] \tag{30b}$$

is essentially the perturbative coupling $T^R_{\epsilon 0}$. The initial condition is $\phi_{K\epsilon}(-\infty) = 0$; $\phi_{K\epsilon}(x)$ is computed by (i) calculation of an asymptotic initial value $\phi_{K\epsilon}(x_0)$ at some finite but suitably large negative x_0, via the iteration process described in Refs. 31 and 32, and (ii) numerical integration of (29) from x_0 to the origin $x = 0$. Relative accuracy of results reported is better than 1×10^{-4} over the range of significant values. As expected, $\phi_{K\epsilon}(x)$ is found to be a smooth, nonoscillatory function. Figure 2 depicts the typical behavior of the real and imaginary parts of $\phi_{K\epsilon}(x)$ and the functions $\Omega_{K\epsilon}(x)$ and $P_{K\epsilon}(x)$. Note especially that transient magnitudes of $\mathrm{Im}[\phi_{K\epsilon}(x)]$ are typically much larger than the final value $\mathrm{Im}[\phi_{K\epsilon}(0)]$, which determines the ionization amplitude $c^0_{K\epsilon}$ [Eq. (17)]; in some cases the maximum transient may be several orders of magnitude larger than the final value, and it depends differently on the collision velocity and

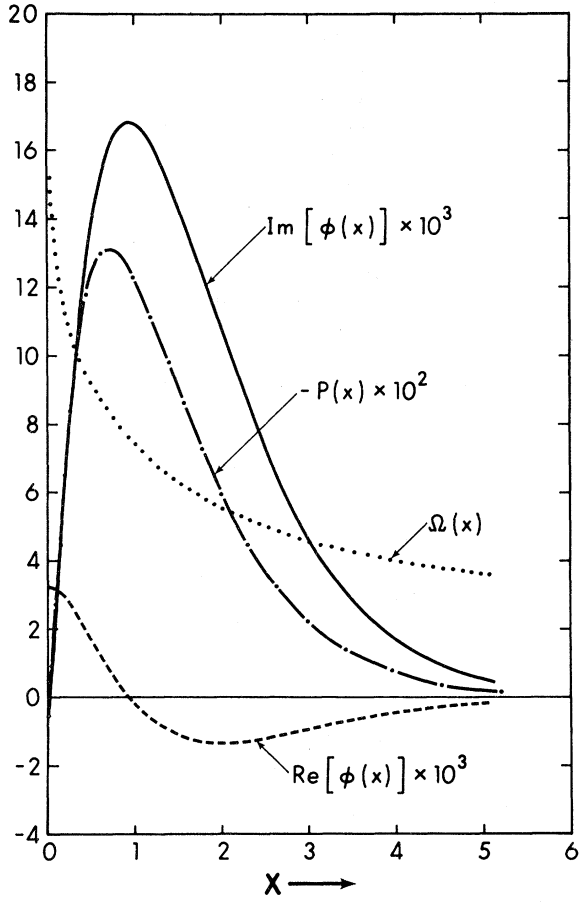

FIG. 2. Behavior of coupling function $P(x)$, excitation energy gap $\Omega(x)$, and excitation response function $\phi(x)$, as functions of trajectory variable x. Note the very large maximum transients in ϕ relative to the final value $\phi(0)$ determining the excitation probability. Data for $E = 500$ eV, $b = 0.0$, $\epsilon = 0.0$.

impact parameter. This is important for the appearance of large "transient" contributions to the emission.

Figure 3 shows the typical dependence of $\phi_{K\epsilon}(0)$ on ionized electron energy ϵ, which is smooth and unexceptional, as it is for most other quantities of interest. As shown in Fig. 4, the typical impact-parameter dependence is more interesting and is responsible for some complicated features. Note that the imaginary part is about an order of magnitude smaller than the real part, damps off rapidly for $b \gtrsim 0.5$, and changes sign at $b \simeq 0.05$. These characteristics persist at different collision energies but shift to other b values as the velocity decreases. Figure 5 shows the ionization probability $P_g(E,b)$

$$P_g(E,b) = \int_0^\infty d\epsilon \, |c^0_{K\epsilon}|^2 \tag{31}$$

vs impact parameter, for relative collision energies $E = 200$ eV and 500 eV (proton masses). Anholt[35] has obtained a similar curve for $E = 500$ eV (lab energy 1000 eV). The pronounced dips at small b are related to the node in $\mathrm{Im}[\phi_{K\epsilon}(0)]$. Note the strong velocity dependence, a feature of P_g predicted in Ref. 27 (on the other hand, note also that the absolute magnitudes of $P_g(E,b)$ from these accurate evaluations of trajectory integrals are much smaller[35] than those obtained in the approximate analytical evaluations of Ref. 27, a result which is somewhat surprising but is partly explained by the fact that the effective energy gap

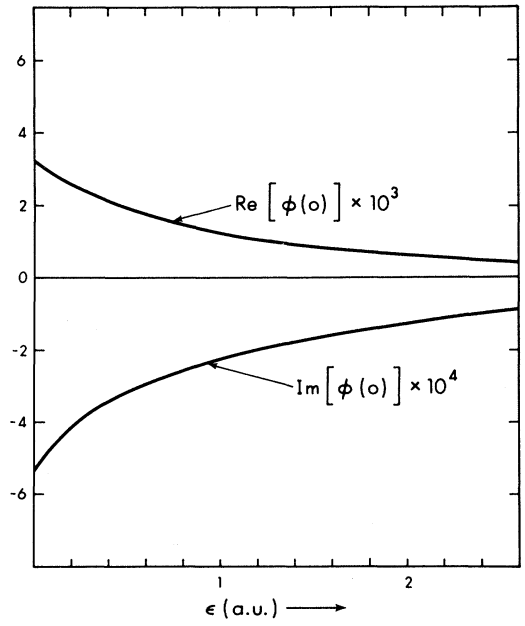

FIG. 3. Typical dependence of $\phi(0)$ upon ionization energy ϵ. Data for $E = 500$ eV, $b = 0.0$.

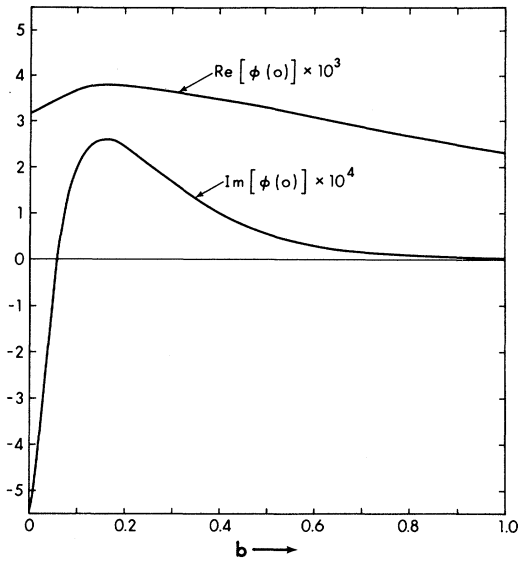

FIG. 4. Typical dependence of $\phi(0)$ upon impact parameter b. Data for $E = 500$ eV, $\epsilon = 0.0$.

$[\epsilon - \epsilon_{1s\sigma_g}(R)]$ at $R \lesssim 0.5$, where most excitation occurs, is much larger than the empirically adjusted constant value we used in Ref. 27). The resulting vacancy-production cross sections $\sigma_K(E)$ (for di-

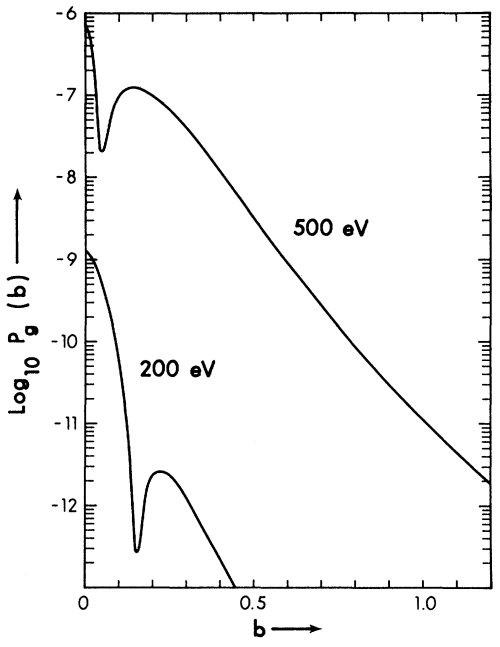

FIG. 5. Ionization probability $P_g(E,b)$ vs impact parameter, for $E = 500$ and 200 eV. The dips at small b are produced by the node in $\mathrm{Im}[\phi(0)]$ (see Fig. 4). Note strong velocity-dependence of both magnitude and profile.

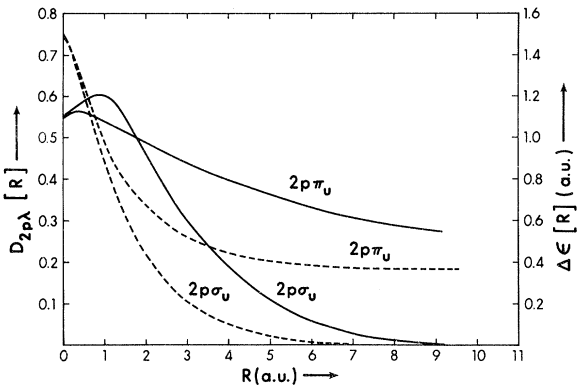

FIG. 6. Dipole velocity matrix elements (solid curves) and energy-level differences ($\epsilon_{2p\lambda u} - \epsilon_{1s\sigma_g}$) (dashed curves), vs R, for $\lambda = 0$ (σ_u) and $\lambda = 1$ (π_u).

rect ionization) are $3.22 \times 10^{-8} a_0^2$ at 500 eV and $1.35 \times 10^{-11} a_0^2$ at 200 eV.

Figure 6 shows the velocity dipole matrix elements $D_{2p\pi_u}(R)$ and $D_{2p\sigma_u}(R)$, and the corresponding energy gaps ($\epsilon_{2p\pi_u} - \epsilon_{1s\sigma_g}$) and ($\epsilon_{2p\sigma_u} - \epsilon_{1s\sigma_g}$) for the relevant radiative transitions.[34] The required integrals [cf. Eqs. (20) and (21)] were done by the same computational methods as were used to calculate the vacancy-production amplitudes. Figure 7 shows the typical frequency dependence of the results for $D^{\lambda}_{c\,\mathrm{trans}}$ [Eq. (21)] and $c^0_{K\epsilon} D^{\lambda}_{c\,\mathrm{sec}}$ [Eqs. (19) and (20)] (for $\lambda = 2p\sigma_u$, $b = 0.0$ and $\epsilon = 0.0$ a.u.). Note that the transient contribution is a monotonic function of ω which increases to the red; secondly note that the transient part and the real part of the secular term are nearly equal in magnitude and opposite in sign at higher frequencies, while they add at lower frequencies. This shows that coherence of the secular and transient contributions is important and must be retained. The resulting red shift of the overall emission profile is consistent with the physical interpretation we gave to the effects of off-shell contributions at the end of Sec. III.

Finally, Figs. 8 and 9 depict one-collision emission profiles (summed over both radiative transitions and integrated over all ϵ and b), for the secular term alone (dashed curves) and for the total

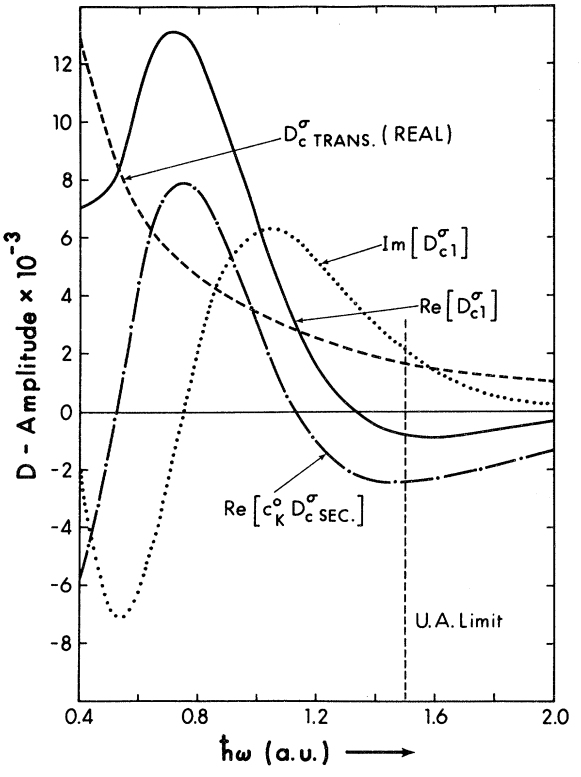

FIG. 7. Secular and transient coherent contributions to the emission amplitude $D^{\lambda}_{c1}(\omega;\epsilon,b,E)$ [Eq. (19)] vs frequency ω, for $E = 500$ eV, $\epsilon = 0.0$, $b = 0.0$, $\lambda = \sigma_u$. Dotted curve (• • •), imaginary part of D_{c1} arises entirely from secular term, Eq. (20); dashed curve (---), $D^{\sigma}_{c\,\mathrm{trans}}$ [Eq. (21)], transient part (real); dot-dash (-•-•-), real part of secular term; solid curve, real part of D^{σ}_{c1} (sum of the last two). United-atom limit on energy spacing is shown.

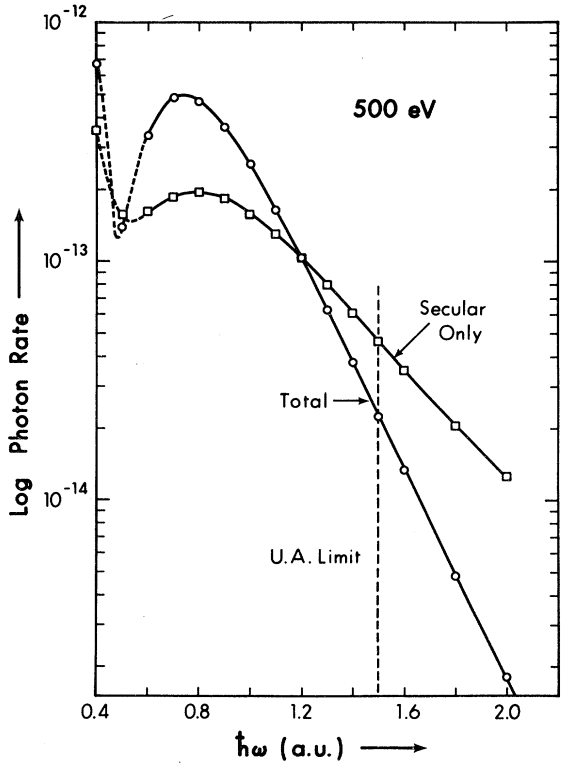

FIG. 8. One-collision emission profiles vs ω at 500 eV. Quantity shown is the one-collision part of $\bar{I}_T$ [Eq. (8)], multiplied by $\sigma_K(E) = 3.22 \times 10^{-8} a_0^2$. Divide by $\sigma_k(E)$ to get photons per SA K-vacancy per unit frequency. Frequency in scaled atomic units (Z^2 a.u., $Z = 1$ for H_2^+). ⊙, total intensity; ⊡, secular term only.

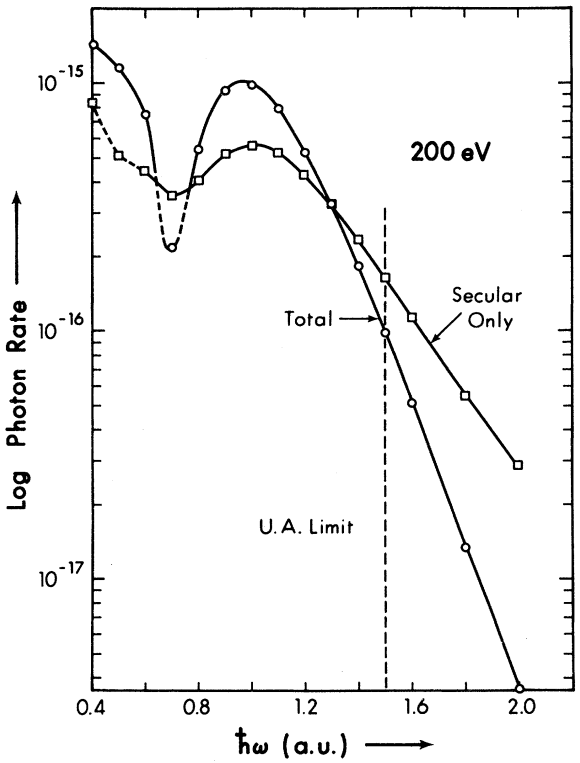

FIG. 9. One-collision emission profiles vs ω at 200 eV. Legend same as for Fig. 8, except that $\sigma_k(E) = 1.35 \times 10^{-11} a_0^2$.

result including coherent transient contributions, for collision energies $E = 500$ and 200 eV. Specifically, the quantities shown are the (secular or total) one-collision part of the quantity I_T defined in Eq. (8), except for the normalizing factor $\sigma_K(E)$. Dividing by the $\sigma_K(E)$ values cited above gives the photons per unit frequency per separated-atom K vacancy. Note that although the absolute intensity of the one-collision emission decreases markedly with lower velocity, the profile *shape* is almost the same. If the overall profile were to be interpreted assuming a quasistatic, secular term expression, in an attempt to deduce a hypothetical ionization probability envelope $\tilde{P}_g(E,b)$, this would be quite different from the true probability [Eq. (31)]; it would have a much greater relative probability at large b values, and its shape would be relatively independent of collision velocity. The emission profiles shown in Figs. 8 and 9 specifically do not include any contribution from the characteristic atomic line centered at $\hbar\omega = 0.375$ and it is likely that the growing wings of this line would obscure the emission shown here for $\hbar\omega \lesssim 0.7$–0.8 a.u. See, however, recent work by Anholt[37] regarding wings of the central line.

Although the results shown here refer to a process which may not actually be very important in K-vacancy production, the general features in fact are not very sensitive to the matrix elements or the type of excitation process considered. Results for an entirely different excitation mechanism (vacancy sharing in asymmetric systems) will be presented in a subsequent paper, and we can expect that the same general effect of an overall red shift of the spectrum relative to the secular part will again result.

ACKNOWLEDGMENTS

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[1]More complete bibliographies and background on this problem may be found in several recent reviews: (a) Q. C. Kessel and B. Fastrup, Case Stud. At. Phys. 3, 137 (1973); (b) J. D. Garcia, R. J. Fortner, and T. M. Kavanagh, Rev. Mod. Phys. 45, 111 (1973); (c) D. H. Madison and E. Merzbacher, At. Inner-Shell Processes 1, 1 (1975); (d) J. S. Briggs, Rep. Prog. Phys. 39, 217 (1976); (e) W. E. Meyerhof and K. S. Taulbjerg, Ann. Rev. Nucl. Sci. (to be published).

[2](a) F. W. Saris, W. F. van der Weg, H. Tawara, and R. Laubert, Phys. Rev. Lett. 28, 717 (1972); (b) F. W. Saris, I. V. Mitchell, D. C. Santry, J. A. Davies, and R. Laubert, in *Proceedings of the International Conference on Inner Shell Ionization Phenomena, and Future Applications, Atlanta, 1972* (Natl. Tech. Inform. Serv., Springfield, Va., 1972); (c) Th. P. Hoogkamer, P. Woerlee, C. Foster, and F. Saris, *Abstracts of the Ninth International Conference on the Physics of Electronic and Atomic Collisions*, edited by J. S. Risley and R. Geballe (Univ. of Washington, Seattle, 1975), p. 300.

[3]J. R. MacDonald, M. D. Brown, and T. Chiao, Phys. Rev. Lett. 30, 471 (1973).

[4]P. D. Mokler, H. J. Stein, and P. Armbruster, Phys. Rev. Lett. 29, 827 (1972).

[5]W. E. Meyerhof, T. K. Saylor, S. M. Lazarus, W. A. Little, B. B. Triplett, and L. F. Chase, Jr., Phys. Rev. Lett. 30, 1279 (1973).

[6]W. E. Meyerhof, T. K. Saylor, S. M. Lazarus, W. A. Little, B. B. Triplett, L. F. Chase, Jr., and R. Anholt, Phys. Rev. Lett. 32, 1279 (1974).

[7]W. E. Meyerhof, R. Anholt, T. K. Saylor, and P. D. Bond, Phys. Rev. A 11, 1083 (1975); R. Anholt and T. K. Saylor (unpublished); W. E. Meyerhof, T. K. Saylor, and R. Anholt, in Ref. 2(c), p. 308.
[8]D. Burch, W. B. Ingalls, H. Wieman, and R. Vandenbosch, Phys. Rev. A 10, 1245 (1974); D. Burch, W. B. Ingalls, H. Wieman, and R. Vandenbosch, in Ref. 2(c), p. 306.
[9]H. O. Lutz, W. R. MacMurray, R. Pretorius, I. J. van der Heerden, R. J. van Reener, and B. Fricke, J. Phys. B 9, L157 (1976).
[10]V. Weisskopf, Phys. Z. 34, 1 (1933).
[11]J. S. Briggs, J. Phys. B 7, 47 (1974).
[12]J. H. Macek and J. S. Briggs, J. Phys. B 7, 1312 (1974).
[13]J. S. Greenberg, C. K. Davis, and P. Vincent, Phys. Rev. Lett. 33, 473 (1974); R. K. Smith, B. Muller, W. Greiner, J. S. Greenberg, and C. K. Davis, Phys. Rev. Lett. 34, 117 (1975).
[14]M. Kleber and D. H. Jakubassa, Z. Phys. A 273, 29 (1975).
[15]B. Muller and W. Greiner, Phys. Rev. Lett. 33, 469 (1974).
[16]K. Smith, B. Muller, and W. Greiner, J. Phys. B 8, 75 (1975).
[17]W. R. Thorson and J. H. Choi, in Ref. 2(c), p. 298.
[18]W. E. Meyerhof, Phys. Rev. Lett. 31, 1341 (1973).
[19]W. E. Meyerhof, Phys. Rev. A 10, 1005 (1974).
[20]For the one-electron, two nucleus problem, the *adiabatic* levels exhibit the crossings characteristic of the Barat-Lichten "diabatic" states of a many-electron system.
[21]J. S. Briggs and J. H. Macek, J. Phys. B 5, 579 (1972); J. Phys. B 6, 982 (1973).
[22]J. S. Briggs and K. Taulbjerg, J. Phys. B 9, 1641 (1976).
[23]K. Taulbjerg, J. S. Briggs, and J. Vaaben, J. Phys. B 9, 1351 (1976).
[24]K. Taulbjerg, J. Vaaben, and B. Fastrup, Phys. Rev. A 12, 2325 (1975).
[25]W. R. Thorson and H. Levy II, Phys. Rev. 181, 230 (1969).
[26]V. SethuRaman, W. R. Thorson, and C. F. Lebeda, Phys. Rev. A 8, 1316 (1973). However, there is some evidence that significant computational errors were made in the evaluation of the trajectory integrals and the calculations are currently being repeated by more accurate methods.
[27]W. R. Thorson, Phys. Rev. A 12, 1365 (1975).
[28]D. R. Bates and D. A. Williams, Proc. Phys. Soc. London 83, 425 (1964).
[29]S. K. Knudson and W. R. Thorson, Can. J. Phys. 48, 313 (1970).
[30]Since outer-shell electrons in these collisions are massively disturbed, and since continuum levels of the bare nuclei probably don't much resemble those of the screened heavy-ion cores, the distinction between the weak-coupling direct impact processes (*a*(ii)) and (b) is somewhat artificial, but both should be distinguished from the vacancy-sharing process, which can exhibit degeneracy-mediated strong coupling in near-symmetric systems.
[31]C. F. Lebeda and W. R. Thorson, Can. J. Phys. 48, 2937 (1970).
[32]W. I. Newman and W. R. Thorson, Can. J. Phys. 50, 2997 (1972).
[33]See, for example, R. Loudon, *The Quantum Theory of Light* (Oxford U.P., Oxford, 1973), Chap. 11.
[34]We thank R. Anholt for providing the velocity dipole matrix elements in tabular form.
[35]This was first pointed out by R. Anholt, Ph.D. thesis (University of California, Berkeley, 1975) (unpublished); cf. Lawrence Berkeley Lab. Rep. No. LBL-4312 (unpublished).
[36]See for example, R. Anholt and W. E. Meyerhof, Abstracts of the Fifth International Conference on Atomic Physics, Berkeley, California, July, 1976.
[37]R. Anholt, J. Phys. B 9, L249 (1976).