Theory of Quantum-Beat and Level-Crossing Experiments Utilizing Electronic Excitation*

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The coherent excitation of several atomic states by inelastic electron scattering and their subsequent radiative decay is considered. General expressions are derived for the photon counting rate in a quantum-beat experiment, and for the total number of photons counted in a level-crossing experiment. The general results are used to calculate the phase of the oscillatory part of the photon counting rate in the Hadeishi-Nierenberg quantum-beat experiment.

I. INTRODUCTION

INTERFERENCE effects associated with the decay of coherently excited nondegenerate atomic states have been observed and studied for some time.[1] Most of the interest in these effects has been concerned with the decay of radiatively excited states. However, several recent experiments have demonstrated the possibility of observing such effects in the decay of electronically excited states.[2–4,4a] In this paper we derive a general expression for the integrated photon counting rate in an experiment in which an arbitrary number of atomic states are coherently excited by electron impact and the resultant luminescence is detected by an arbitrary system of photon counters. The result is directly applicable to quantum-beat[3] and level-crossing[4] experiments. In Sec. II we consider the excitation process and derive the scattered wave function for the electron-atom system. The decay process is described in Sec. III, and the expression for the counting rate is obtained. In Sec. IV we apply our general results to a calculation of the phase of the oscillatory part of the photon counting rate in the Hadeishi-Nierenberg experiment.[3] The effect of exchange scattering is considered in the Appendix.

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[1] Some representative papers are: G. Breit, Rev. Mod. Phys. **5**, 91 (1933); J. Brossel and F. Bitter, Phys. Rev. **86**, 308 (1952); F. Colegrove, P. Franken, R. Lewis, and R. Sands, Phys. Rev. Letters **3**, 420 (1959); P. Franken, Phys. Rev. **121**, 508 (1961); J. Dodd and G. Series, Proc. Roy. Soc. (London) **A263**, 353 (1961); M. Podgoretskii and O. Khrustalev, Usp. Fiz. Nauk **81**, 217 (1963) [English transl.: Soviet Phys.—Usp. **6**, 682 (1964)]; J. Dodd, R. Kaul, and D. Warrington, Proc. Phys. Soc. (London) **84**, 176 (1964).

[2] E. Aleksandrov, Opt. i Spektroskopiya **16**, 377 (1964) [English transl.: Opt. Spectry. (USSR) **16**, 209 (1964)].

[3] T. Hadeishi and W. Nierenberg, Phys. Rev. Letters **14**, 891 (1965).

[4] T. Hadeishi has recently performed a level-crossing experiment using electronic excitation (T. Hadeishi, private communication). For an account of a level-crossing experiment using radiative excitation see, for example, F. Colegrove *et al.*, Ref. 1.

[4a] *Note added in proof.* Dr. G. W. Series has kindly brought to my attention a number of experiments utilizing electronic excitation which have been performed in France. Some representative papers are: O. Nedelec and J.-C. Pebay-Peyroula, Compt. Rend. **254**, 1951 (1962); A. Faure, O. Nedelec, and J.-C. Pebay-Peyroula, *ibid.* **256**, 5088 (1963); O. Nedelec, M.-N. Deschizeaux, and J.-C. Pebay-Peyroula, *ibid.* **257**, 3130 (1963); J.-P. Descoubes, *ibid.* **259**, 327 (1964).

II. THE EXCITATION PROCESS

The excitation and subsequent decay will be described in terms of a single incident electron and a single infinitely heavy atom[5] located at the origin. An actual experiment, of course, involves a beam of electrons incident on a many-atom target, and it may be that different scattering events are correlated. Our treatment is applicable only to situations in which individual scattering events are independent. It is perhaps worth noting that by choosing the atom to be initially at rest we are simply making a convenient choice of inertial frame and are not neglecting effects associated with finite atomic velocities. Recoil effects, on the other hand, are completely neglected.

The atomic Hamiltonian will be denoted by h, where h includes the interaction with an external magnetic field if one is present. The internal atomic variables will be denoted by ξ, and the eigenstates of h by $g_a(\xi)$:

$$hg_a(\xi)=W_a g_a(\xi). \tag{1}$$

For definiteness, we will assume that the atom has a nondegenerate ground state g_0 with energy W_0, and that it is initially in this state. In order to avoid cumbersome notation the incident electron will be treated as if it were distinguishable from the atomic electrons. The modifications which are necessary for inclusion of exchange effects are given in the Appendix. The incident electron's kinetic energy operator is T_e, and if a magnetic field is present the interaction energy operator is $-\mu\mathbf{B}\cdot\boldsymbol{\sigma}$. The interaction of the electron's orbital angular momentum with the field will change its trajectory from a straight line to a path which obeys the equation of motion $d\mathbf{v}/dt=(e/m)\mathbf{v}\times\mathbf{B}$. It will be assumed that the Larmor radius is large enough so that this effect may be neglected. It is convenient to choose the positive z direction in the direction of $\mathbf{B}$. Then the electron Hamiltonian is $T_e-\mu B\sigma_z$.

We will use the wave-packet formalism of Goldberger and Watson[6] to describe the excitation process. The

[5] We use the word "atom" for convenience. Our results apply equally well to atoms or molecules.

[6] M. Goldberger and K. Watson, *Collision Theory* (John Wiley & Sons, Inc., New York, 1964). See particularly pp. 95–101.

precollision wave packet for the electron-atom system is

$$X(t)=\int d^3p\, a(\mathbf{p}-\mathbf{q})e^{-iEt}\chi=e^{-iKt}g(\mathbf{r})\bar{\chi}, \quad (2a)$$

where

$$\chi=(2\pi)^{-3/2}e^{i\mathbf{p}\cdot\mathbf{r}}u_s g_0(\xi), \quad (2b)$$

$$\bar{\chi}=(2\pi)^{-3/2}e^{i\mathbf{q}\cdot\mathbf{r}}u_s g_0(\xi), \quad (2c)$$

$$E=p^2/2m-\mu Bs+W_0, \quad (2d)$$

$$K=T_e-\mu B\sigma_z+h, \quad (2e)$$

$$g(\mathbf{r})=\int d^3\rho\, a(\boldsymbol{\rho})e^{i\rho\cdot\mathbf{r}}. \quad (2f)$$

In Eqs. (2), $\mathbf{q}$ is the mean incident momentum and u_s is the initial electron-spin wave function with $\sigma_z u_s=su_s$, where s is either $+1$ or -1. $g(\mathbf{r})$ is the spatial packeting factor, centered at $\mathbf{r}=0$. Thus $X(t)$ is centered at $\mathbf{r}=0$ when $t=0$, i.e., the electron-atom collision occurs at $t=0$. The complete time-dependent solution of the Schrödinger equation corresponding to the precollision wave packet $X(t)$ is

$$\Psi(t)=\int d^3p\, a(\mathbf{p}-\mathbf{q})e^{-iEt}\psi^+, \quad (3a)$$

where

$$\psi^+=\chi+(2\pi)^{-3/2}\sum_{g_a}\sum_{s_a} g_a(\xi)u_{s_a}\times\int d^3p_a\frac{e^{i\mathbf{p}_a\cdot\mathbf{r}}T_a(\mathbf{p}_a,\mathbf{p})}{\Delta_a+i\eta-p_a^2/2m}, \quad (3b)$$

$$\Delta_a=E-(-\mu Bs_a+W_a). \quad (3c)$$

In (3b) ψ^+ has been expanded in the complete set of eigenstates of K,

$$K\chi_a=E_a\chi_a, \quad (4a)$$

$$\chi_a=(2\pi)^{-3/2}e^{i\mathbf{p}_a\cdot\mathbf{r}}u_{s_a}g_a(\xi), \quad (4b)$$

$$E_a=p_a^2/2m-\mu Bs_a+W_a, \quad (4c)$$

and $T_a(\mathbf{p}_a,\mathbf{p})$ is the matrix element of the scattering matrix for scattering from χ to χ_a. The asymptotic value of the integral in (3b) is,

$$\lim_{r\to\infty}\int d^3p_a\frac{e^{i\mathbf{p}_a\cdot\mathbf{r}}T_a(\mathbf{p}_a,\mathbf{p})}{\Delta_a+i\eta-p_a^2/2m}=-\frac{(2\pi)^2m}{r}e^{ip_a'r}T_a(p_a'\hat{r},\mathbf{p}), \quad \Delta_a>0;$$

$$=O\left(\frac{m}{r}e^{-r/d_a}T_a\right), \quad \Delta_a<0, \quad (5a)$$

where

$$p_a'=(2m\Delta_a)^{1/2}, \quad (5b)$$

$$d_a=(-2m\Delta_a)^{1/2}, \quad (5c)$$

and $\hat{r}$ is a unit vector in the direction of $\mathbf{r}$. Hereafter we will drop the prime on p_a' and denote it simply as p_a. Dropping terms with $\Delta_a<0$ and defining the scattering amplitude,

$$f_a(\hat{r},\mathbf{p})=-(2\pi)^2mT_a(p_a\hat{r},\mathbf{p}), \quad (6)$$

the asymptotic expression for ψ^+ becomes

$$\psi^+=\chi+\sum_{g_a}'\sum_{s_a}' f_a(\hat{r},\mathbf{p})\frac{e^{ip_ar}}{(2\pi)^{3/2}r}u_{s_a}g_a(\xi), \quad (7)$$

where the sum $\sum_{g_a}'\sum_{s_a}'$ includes only those $u_{s_a}g_a$ for which $\Delta_a>0$.

The scattered wave packet at large distances is obtained by inserting (7) into (3a). In doing this we will assume that the entire incident wave packet lies far enough from any excitation threshold so that $f_a(\hat{r},\mathbf{p})$ is slowly varying over the packet and may be removed from the integral and replaced by $f_a(\hat{r},\mathbf{q})$. It will also be assumed that the distance from threshold is much greater than μB so that $\sum_{s_a}'$ may be replaced by $\sum_{s_a}$ and $\sum_{g_a}'$ may be interpreted as a sum over those atomic states for which $W_a<q^2/2m+W_0$. We will take $q^2/2m$ to be less than the ionization energy so that $\sum_{g_a}'$ includes only discrete states. Finally, we will neglect spreading of the scattered wave packet, i.e., we will neglect terms of order $|\mathbf{p}-\mathbf{q}|^2$ in p_ar-Et.

$$p_ar-Et=p_ar-(p_a^2/2m-\mu Bs_a+W_a)t=p_{\bar{a}}r-(\epsilon_{\bar{a}}-\mu Bs_a+W_a)t+[\mathbf{q}\cdot(\mathbf{p}-\mathbf{q})/p_{\bar{a}}]\times(r-[p_{\bar{a}}/m]t)+O(|\mathbf{p}-\mathbf{q}|^2), \quad (8a)$$

where

$$\epsilon_{\bar{a}}=p_{\bar{a}}^2/2m=(q^2/2m-\mu Bs+W_0)-(-\mu Bs_a+W_a). \quad (8b)$$

The resulting expression for the scattered wave function of the electron-atom system is

$$\Psi_{sc}(t)\equiv\Psi(t)-X(t)=\sum_{g_a}'\phi_a(\mathbf{r},t)e^{-iht}g_a(\xi), \quad (9a)$$

where

$$\phi_a(\mathbf{r},t)=\sum_{s_a} f_a(\hat{r},\mathbf{q})\frac{\exp[i(p_{\bar{a}}r-\epsilon_{\bar{a}}t)]}{(2\pi)^{3/2}r}\times e^{i\mu Bs_at}u_{s_a}g\left(\frac{\mathbf{q}}{p_{\bar{a}}}\left(r-\frac{p_{\bar{a}}}{m}t\right)\right). \quad (9b)$$

The modifications of Eqs. (9) which are necessary in order to include exchange scattering are discussed in the Appendix. It is shown there that one need only redefine f_a to be

$$f_a(\hat{r},\mathbf{q})=-(2\pi)^2m\{T_a(p_{\bar{a}}\hat{r},\mathbf{q})-ZT_a^{ex}(p_{\bar{a}}\hat{r},\mathbf{q})\}, \quad (10)$$

where Z is the number of electrons in the atom and

T_a^{ex} is an exchange scattering matrix defined in the Appendix. Hereafter f_a will be defined by Eq. (10) rather than Eq. (6).

III. THE DECAY PROCESS

In order to describe the decay process we will replace h by $H_r=h+K_r+V_r$ in (9a). K_r is the Hamiltonian for the free electromagnetic field, and V_r is the interaction between the electromagnetic field and the atom. The physical reasoning behind this prescription is as follows. The excitation process takes place over a time of order $(m/q)(\Delta r)\approx(m/q)(\Delta q)^{-1}\equiv\Delta t$ where Δr is the spatial extent of $g(\mathbf{r})$ and Δq is the width of $a(\varrho)$. The uncertainty in the energy of the incident wave packet is $q\Delta q/m=(\Delta t)^{-1}$. The lifetime of an excited atomic state is Γ^{-1} (say) and its linewidth is Γ. We will require that $\Delta t\ll\Gamma^{-1}$. This condition may be interpreted either as requiring an experimental situation in which a well-resolved temporal behavior of the decay luminescence may be observed ($\Delta t\ll\Gamma^{-1}$), or as requiring a situation in which the uncertainty in the incident electron energy is much greater than the linewidth ($q\Delta q/m\gg\Gamma$). During the excitation V_r has little effect and may be neglected in comparison with the electron-atom interaction, but after the atom is excited and the electron has moved away V_r becomes the dominant interaction and causes the atom to decay. Since the excitation is very fast compared to the decay we may describe the decay process by treating the excitation as an impulse at $t=0$, and this is just what our prescription of replacing h by H_r does. The error associated with this approximation is an error of order Δt in t, e.g., if we obtain a decay law of the form $e^{-\Gamma t}$ it is in error by an amount $e^{-\Gamma(t\pm\Delta t)}-e^{-\Gamma t}\approx\pm\Gamma(\Delta t)e^{-\Gamma t}$. In order to describe the decay we must include the initial state of the radiation field in (9a); we will neglect background radiation and take this initial state to be the vacuum state. Thus the wave function describing the decay of the excited atom is

$$\Psi_{dc}(t)=\sum_{g_a}{}'\,\phi_a(\mathbf{r},t)e^{-iH_rt}g_a(\xi)\,|\,\mathrm{vac}\rangle. \tag{11}$$

The decay channel which will be considered here is a single-photon emission which leaves the atom in its ground state; it will be assumed that only this decay channel contributes appreciably to the observed decay luminescence. The emitted photons are to be observed by a photon counting apparatus which operates continuously from some negative time onwards. The integrated photon counting rate, i.e., the probability that a photon has been observed prior to time t ($t>0$) is the expectation value of the operator,

$$P=\sum_{\mathbf{k},\hat{e}}^{P}|\,\mathbf{k},\hat{e}\rangle\langle\mathbf{k},\hat{e}\,| \tag{12}$$

taken with respect to $\Psi_{dc}(t)$. In (12), $|\,\mathbf{k},\hat{e}\rangle$ is a one-photon eigenstate of K_r with wave vector $\mathbf{k}$ and polarization $\hat{e}$. The photon field will be quantized in a box of volume V_0 so that K_r has discrete eigenstates. The sum $\sum^{P}_{\mathbf{k},\hat{e}}$ includes all photons admitted by the counting apparatus, e.g., the range of k in $\sum^{P}_{\mathbf{k},\hat{e}}$ may be determined by an optical filter, the directional range of $\hat{k}$ by the size and location of a photon counter, and the choice of $\hat{e}$ by a polarizer. In using (12) we have assumed for the sake of simplicity that the counting apparatus detects all photons in its range of admittance with equal sensitivity; if this were not an adequate approximation we could replace P by $\sum^{P}_{\mathbf{k},\hat{e}}s(\mathbf{k},\hat{e})\,|\,\mathbf{k},\hat{e}\rangle\langle\mathbf{k},\hat{e}\,|$, where $s(\mathbf{k},\hat{e})$ is a sensitivity function, e.g., the dependence of s on k might be determined by the shape of the pass band of an optical filter. The integrated photon counting rate is

$$\begin{aligned}\langle P(t)\rangle&=\langle\Psi_{dc}(t)\,|\,P\,|\,\Psi_{dc}(t)\rangle\\&=\sum_{\mathbf{k},\hat{e}}^{P}\sum_{g_a}|\,\langle g_a,\mathbf{k},\hat{e}\,|\,\Psi_{dc}(t)\rangle\,|^2,\end{aligned} \tag{13}$$

where we have multiplied by unity in the form $\sum_{g_a}g_ag_a^{\dagger}$ and used the notation $g_a|\,\mathbf{k},\hat{e}\rangle=|\,g_a,\mathbf{k},\hat{e}\rangle$. By assumption a photon $|\,\mathbf{k},\hat{e}\rangle$ that is included in $\sum^{P}_{\mathbf{k},\hat{e}}$ can be emitted with appreciable probability only by decay of $\Psi_{dc}(t)$ to the ground state, so the only appreciable term in the sum $\sum_{g_a}$ in (13) is the g_0 term. Thus,

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$$\begin{aligned}\langle P(t)\rangle&=\sum_{\mathbf{k},\hat{e}}^{P}|\,\langle g_0,\mathbf{k},\hat{e}\,|\,\Psi_{dc}(t)\rangle\,|^2\\&=\sum_{\mathbf{k},\hat{e}}^{P}\{\sum_{g_a}{}'\langle\phi_a(t)\,|\,\phi_a(t)\rangle\,|\,\langle g_0,\mathbf{k},\hat{e}\,|\,e^{-iH_rt}\,|\,g_a,\mathrm{vac}\rangle\,|^2\\&\qquad+2\,\mathrm{Re}\sum_{\substack{g_b,\,g_a\\ b>a}}{}'\langle\phi_b(t)\,|\,\phi_a(t)\rangle\langle g_0,\mathbf{k},\hat{e}\,|\,e^{-iH_rt}\,|\,g_b,\mathrm{vac}\rangle^*\langle g_0,\mathbf{k},\hat{e}\,|\,e^{-iH_rt}\,|\,g_a,\mathrm{vac}\rangle\}.\end{aligned} \tag{14}$$

In (14) the sum $\sum_{g_a}{}'$ may be restricted to those atomic states which can actually emit a detectable photon, i.e., those states for which $\langle g_0,\mathbf{k},\hat{e}\,|\,e^{-iH_rt}\,|\,g_a,\mathrm{vac}\rangle$ is appreciable when $|\,\mathbf{k},\hat{e}\rangle$ is included in $\sum^{P}_{\mathbf{k},\hat{e}}$. Hereafter we will consider the sum to be so restricted.

We will begin our evaluation of $\langle P(t)\rangle$ by evaluating the scalar products $\langle\phi_a(t)\,|\,\phi_a(t)\rangle$ and $\langle\phi_b(t)\,|\,\phi_a(t)\rangle$. The first of these is time-independent but we will choose t to be much larger than $(m/p_{\bar{a}})p_{\bar{a}}^{-1}$ so that we may use (9b). This

gives

$$\langle\phi_a|\phi_a\rangle=F\sigma_a(\mathbf{q}), \tag{15a}$$

where

$$\sigma_a(\mathbf{q})=\sum_{s_a}\frac{p_{\bar{a}}}{q}\int d\Omega_r|f_a(\hat{r},\mathbf{q})|^2 \tag{15b}$$

is the total cross section for excitation of state g_a, and

$$F=(2\pi)^{-3}\int_{-\infty}^{\infty}dr|g(\hat{q}r)|^2=(2\pi)^{-3}\int_0^{\infty}dr'\left|g\left(\hat{q}\left(r'-\frac{p_{\bar{a}}}{m}t\right)\right)\right|^2 \tag{15c}$$

is the net incident electron flux (electrons per unit area) in the direction $\hat{q}$. The first integral in (15c) is defined to be the flux; the second integral is the one that actually occurs in the evaluation of $\langle\phi_a(t)|\phi_a(t)\rangle$. The equality of these two integrals follows from the largeness of t.

Evaluating $\langle\phi_b(t)|\phi_a(t)\rangle$ similarly one obtains

$$\langle\phi_b(t)|\phi_a(t)\rangle=\sum_{s_bs_a}F_{ba}(t)\sigma_{ba}'\delta_{s_bs_a}, \tag{16a}$$

where

$$\sigma_{ba}'=\frac{(p_{\bar{b}}p_{\bar{a}})^{1/2}}{q}\int d\Omega_r\, f_b^*(\hat{r},\mathbf{q})f_a(\hat{r},\mathbf{q}), \tag{16b}$$

$$F_{ba}(t)=\frac{q}{(p_{\bar{b}}p_{\bar{a}})^{1/2}}\int_{-\infty}^{\infty}\frac{dr}{(2\pi)^3}\exp\{i[(p_{\bar{a}}-p_{\bar{b}})r-(\epsilon_{\bar{a}}-\epsilon_{\bar{b}})t]\}g^*\left(\frac{\mathbf{q}}{p_{\bar{b}}}\left(r-\frac{p_{\bar{b}}}{m}t\right)\right)g\left(\frac{\mathbf{q}}{p_{\bar{a}}}\left(\mathrm{r}-\frac{p_{\bar{a}}}{m}t\right)\right). \tag{16c}$$

σ_{ba}' may be interpreted roughly as a total cross section for coherent excitation of states g_b and g_a. (Note, however, that σ_{ba}' is in general complex.) $F_{ba}(t)$ has the dimensions of flux, and as $\epsilon_{\bar{a}}-\epsilon_{\bar{b}}$ approaches zero $F_{ba}(t)$ approaches F. In order to see what is involved in this limit we will put $F_{ba}(t)$ in a different form.[7] Inserting (2f) into (16c) and carrying out the integral over r, one obtains

$$F_{ba}(t)=\frac{(2\pi)^{-2}q}{(p_{\bar{b}}p_{\bar{a}})^{1/2}}\int d^3\rho'd^3\rho\, a^*(\boldsymbol{\varrho}')a(\boldsymbol{\varrho})\exp\left\{i\left[\epsilon_{\bar{b}}-\epsilon_{\bar{a}}+\frac{\mathbf{q}\cdot(\boldsymbol{\varrho}'-\boldsymbol{\varrho})}{m}\right]t\right\}\delta\left(p_{\bar{b}}-p_{\bar{a}}-\frac{\boldsymbol{\varrho}'\cdot\mathbf{q}}{p_{\bar{b}}}+\frac{\boldsymbol{\varrho}\cdot\mathbf{q}}{p_{\bar{a}}}\right). \tag{17}$$

The δ function may be removed by integrating over the component of $\boldsymbol{\varrho}'$ which is parallel to $\mathbf{q}$. This gives

$$F_{ba}(t)=(2\pi)^{-2}\left(\frac{p_{\bar{b}}}{p_{\bar{a}}}\right)^{1/2}\int d^2\rho_\perp'\,d^3\rho\, a^*(\boldsymbol{\varrho}_\perp'+\boldsymbol{\varrho}_{\|}')a(\boldsymbol{\varrho})\exp\left\{i\left[\epsilon_{\bar{b}}-\epsilon_{\bar{a}}-\frac{\boldsymbol{\varrho}\cdot\mathbf{q}}{m}+\frac{\rho_{\|}'q}{m}\right]t\right\}, \tag{18a}$$

where $\boldsymbol{\varrho}_\perp'$ is perpendicular to $\hat{q}$ and

$$\boldsymbol{\varrho}_{\|}'=\hat{q}\frac{p_{\bar{b}}}{q}\left(p_{\bar{a}}-p_{\bar{b}}+\frac{\boldsymbol{\varrho}\cdot\mathbf{q}}{p_{\bar{a}}}\right). \tag{18b}$$

In order to investigate the limit $\epsilon_{\bar{a}}-\epsilon_{\bar{b}}\to 0$, we introduce the variables

$$\omega=\epsilon_{\bar{a}}-\epsilon_{\bar{b}}, \tag{19a}$$

$$W=\tfrac{1}{2}(\epsilon_{\bar{a}}+\epsilon_{\bar{b}}). \tag{19b}$$

Expanding (18a) in powers of ω/W, one obtains

$$F_{ba}(t)=(2\pi)^{-2}[1+O(\omega/W)]\int d^2\rho_\perp d^3\rho a(\boldsymbol{\varrho})a^*(\boldsymbol{\varrho}_\perp'+\boldsymbol{\varrho}_{\|}-\omega\hat{q}[(\rho_{\|}/2W)-(m/q)][1+O(\omega/W)])$$
$$\times\exp\left\{-i\left(\omega+\frac{\omega q}{m}[(\rho_{\|}/2W)-(m/q)][1+O(\omega/W)]\right)t\right\}, \tag{20}$$

where $\boldsymbol{\varrho}_{\|}=(\boldsymbol{\varrho}\cdot\hat{q})\hat{q}$.

[7] The results we are about to derive can, of course, be derived directly from (16c). However, they emerge much more cleanly from (20).

We are now able to investigate the conditions under which it is a good approximation to set $\omega=0$ in $F_{ba}(t)$. First of all, we must have

$$\omega/W\ll 1 \tag{21}$$

for our expansion to be sensible. In order to neglect the first-order terms in the argument of a^*, we must have

$$\omega\Delta q/W\ll\Delta q, \tag{22}$$

$$\omega m/q\ll\Delta q. \tag{23a}$$

In order to set the exponential factor in (20) equal to unity, we must have

$$(\omega q\Delta q/mW)t\ll 1, \tag{24a}$$

$$(\omega^2/W)t\ll 1. \tag{25}$$

Inequality (22) is the same as (21), and (23a) and (24a) taken together imply (25), so we are left with three independent criteria [(21), (23a), and (24a)] for the smallness of ω. Inequality (23a) may be written as

$$q\Delta q/m\gg\omega, \tag{23b}$$

or

$$\Delta t\ll\omega^{-1}. \tag{23c}$$

This inequality has a simple physical interpretation. The inequality $q\Delta q/m\gtrsim\omega$ must be satisfied in order for interference effects between states g_a and g_b to be observable at all, i.e., in order to have $\langle\phi_b(t)|\phi_a(t)\rangle\neq 0$. The stronger inequality (23b) must be satisfied if the interference effects are not to be dependent on the detailed structure of the incident-electron wave packet. This is shown most clearly by (23c) which is an obvious criterion for the observability of well resolved beats in a quantum-beat experiment. Let us agree to restrict our observations to the first few beats, so that

$$\omega t\lesssim O(1). \tag{26}$$

Then (24a) reduces to

$$q\Delta q/m\ll W, \tag{24b}$$

but this is equivalent to our previous assumption that the entire wave packet is far from the threshold. Finally we note that (23b) and (24b) taken together imply (21). Thus (23) and (26) are the only new conditions which must be satisfied in order to set $F_{ba}(t)$ equal to F. Note that a sufficient condition for the validity of (26) is,

$$\omega/\Gamma\lesssim O(1), \tag{27}$$

since observations cannot be performed after the decay is completed. Assuming (23) and (26) are satisfied for all pairs of states in the (restricted) sum $\sum_{g_a}'$, we may now put

$$\langle\phi_b(t)|\phi_a(t)\rangle=F\sigma_{ba}, \tag{28a}$$

where

$$\sigma_{ba}=\sum_{s_b s_a}\sigma_{ba}'\delta_{s_b s_a}. \tag{28b}$$

It remains to calculate the matrix elements of $e^{-iH_r t}$ which occur in $\langle P(t)\rangle$. This is done in Goldberger and Watson,[8] and only the results will be presented here. We will consider only the case in which each state in the (restricted) sum $\sum_{g_a}'$ decays to the ground state through an allowed dipole transition and the dominant contributions to the linewidths arise from dipole transitions. In this case,

$$\langle g_0,\mathbf{k},\hat{e}|e^{-iH_r t}|g_a,\text{vac}\rangle=-\left(\frac{2\pi e^2}{V_0 k}\right)^{1/2}\langle g_0|\frac{\hat{e}\cdot\mathbf{P}}{m}|g_a\rangle e^{-i(W_0+k)t}\frac{1-\exp\{i[k-(W_a-W_0)+i\Gamma_a/2]t\}}{k-(W_a-W_0)+i\Gamma_a/2}, \tag{29a}$$

where

$$\mathbf{P}=\sum_{j=1}^{Z}\mathbf{p}_j \tag{29b}$$

is the total momentum operator for all the electrons in the atom, and

$$\Gamma_a=\sum_{\substack{g_b\\ W_b<W_a}}\frac{e^2(W_a-W_b)}{2\pi}\int d\Omega_k\sum_{\hat{e}}\left|\langle g_b|\frac{\hat{e}\cdot\mathbf{P}}{m}|g_a\rangle\right|^2 \tag{29c}$$

is the natural linewidth. Using (15a) and (29a) and changing the sum $\sum^{P}_{\mathbf{k},\hat{e}}$ in (14) to an integral, the noninterferential part of $\langle P(t)\rangle$ becomes

$$\langle P(t)\rangle_n=F\sum_{g_a}'\sigma_a(\mathbf{q})\int_P d\Omega_k\sum_{\hat{e}}^{P}\frac{e^2}{(2\pi)^2}\left|\langle g_0|\frac{\hat{e}\cdot\mathbf{P}}{m}|g_a\rangle\right|^2\int_P dk\,k\left|\frac{1-\exp\{i[k-(W_a-W_0)+i\Gamma_a/2]t\}}{k-(W_a-W_0)+i\Gamma_a/2}\right|^2. \tag{30}$$

We will assume that the filter used in the experiment passes all radiation with a frequency in the vicinity of W_a-W_0 (for all g_a included in $\sum_{g_a}'$). By "vicinity" we mean a frequency range much wider than Γ_a. This allows us to re-

[8] Reference 6, Chap. 8. Our Eq. (29a) is a special case of Goldberger and Watson's Eq. (8.119b), p. 451. See also the discussion of radiative decay on pp. 460–469.

place $\int_P dk\, k$ by $(W_a-W_0)\int_{-\infty}^{\infty} dk$ in (30). The result of this replacement is

$$\langle P(t)\rangle_n = F\sum_{g_a}{}' \sigma_a(\mathbf{q})\frac{\Gamma^P{}_a}{\Gamma_a}(1-e^{-\Gamma_a t}), \tag{31a}$$

where

$$\Gamma^P{}_a = \frac{e^2(W_a-W_0)}{2\pi}\int_P d\Omega_k \sum_{\hat{e}}^{P}\left|\langle g_0|\frac{\hat{e}\cdot\mathbf{P}}{m}|g_a\rangle\right|^2. \tag{31b}$$

Using (28a) and (29a) the interferential part of $\langle P(t)\rangle$ becomes

$$\langle P(t)\rangle_i = 2F\,\mathrm{Re}\sum_{\substack{g_b,\,g_a\\ b>a}}{}' \sigma_{ba}(\mathbf{q})\int_P d\Omega_k \sum_{\hat{e}}^{P}\frac{e^2}{(2\pi)^2}\langle g_0|\frac{\hat{e}\cdot\mathbf{P}}{m}|g_b\rangle^*\langle g_0|\frac{\hat{e}\cdot\mathbf{P}}{m}|g_a\rangle$$
$$\times\int_P dk\, k\left(\frac{1-\exp\{i[k-(W_b-W_0)+i\Gamma_b/2]t\}}{k-(W_b-W_0)+i\Gamma_b/2}\right)^*\left(\frac{1-\exp\{i[k-(W_a-W_0)+i\Gamma_a/2]t\}}{k-(W_a-W_0)+i\Gamma_a/2}\right). \tag{32}$$

The integral over k in (32) may be put in the form

$$[W_b-W_a+i(\Gamma_b+\Gamma_a)/2]^{-1}\int_P dk\, k([k-(W_b-W_0)-i\Gamma_b/2]^{-1}-[k-(W_a-W_0)+i\Gamma_a/2]^{-1})$$
$$\times(1-\exp\{i[k-(W_b-W_0)+i\Gamma_b/2]t\})^*(1-\exp\{i[k-(W_a-W_0)+i\Gamma_a/2]t\}). \tag{33}$$

The over-all multiplicative factor of k in (33) will be replaced by W_b-W_0 when it multiplies $[k-(W_b-W_0)-i\Gamma_b/2]^{-1}$ and by W_a-W_0 when it multiplies $[k-(W_a-W_0)+i\Gamma_a/2]^{-1}$. With these replacements (32) becomes

$$\langle P(t)\rangle_i = 2F\,\mathrm{Re}\sum_{\substack{g_b,\,g_a\\ b>a}}{}' \frac{i\sigma_{ba}(\mathbf{q})\Gamma^P{}_{ba}}{W_b-W_a+i(\Gamma_b+\Gamma_a)/2}(1-e^{i(W_b-W_a)t}e^{-\frac{1}{2}(\Gamma_b+\Gamma_a)t}), \tag{34a}$$

where

$$\Gamma^P{}_{ba} = \frac{e^2[\frac{1}{2}(W_b+W_a)-W_0]}{2\pi}\int_P d\Omega_k \sum_{\hat{e}}^{P}\langle g_0|\frac{\hat{e}\cdot\mathbf{P}}{m}|g_b\rangle^*\langle g_0|\frac{\hat{e}\cdot\mathbf{P}}{m}|g_a\rangle. \tag{34b}$$

Adding (31a) and (34a), one obtains the follwing expression for the total integrated photon counting rate:

$$\langle P(t)\rangle = F\left\{\sum_{g_a}{}' \sigma_a(\mathbf{q})\frac{\Gamma^P{}_a}{\Gamma_a}(1-e^{-\Gamma_a t})-2\,\mathrm{Im}\sum_{\substack{g_b,\,g_a\\ b>a}}{}' \frac{\sigma_{ba}(\mathbf{q})\Gamma^P{}_{ba}}{W_b-W_a+i(\Gamma_b+\Gamma_a)/2}(1-e^{i(W_b-W_a)t}e^{-\frac{1}{2}(\Gamma_b+\Gamma_a)t})\right\}. \tag{35}$$

The differential counting rate observed in a quantum-beat experiment is

$$\frac{d\langle P(t)\rangle}{dt} = F\{\sum_{g_a}{}' \sigma_a(\mathbf{q})\Gamma^P{}_a e^{-\Gamma_a t}+2\,\mathrm{Re}\sum_{\substack{g_b,\,g_a\\ b>a}}{}' \sigma_{ba}(\mathbf{q})\Gamma^P{}_{ba}e^{i(W_b-W_a)t}e^{-\frac{1}{2}(\Gamma_b+\Gamma_a)t}\}. \tag{36}$$

The total number of photons counted in a level-crossing experiment is

$$\langle P(\infty)\rangle = F\left\{\sum_{g_a}{}' \frac{\sigma_a(\mathbf{q})\Gamma^P{}_a}{\Gamma_a}-2\,\mathrm{Im}\sum_{\substack{g_b,\,g_a\\ b>a}}{}' \frac{\sigma_{ba}(\mathbf{q})\Gamma^P{}_{ba}}{W_b-W_a+i(\Gamma_b+\Gamma_a)/2}\right\}. \tag{37}$$

In order that (26) will not be violated when we put $t=\infty$ in (37) we must assume that (27) is satisfied.

The expression for the counting rate must be modified if there are several possible initial and final states. The cross sections defined by (15b) and (28b) depend on the initial electron spin orientation. For an unpolarized incident electron beam these should be replaced by their averages over initial spin orientations,

$$\bar{\sigma}_a = \tfrac{1}{2}\textstyle\sum_s \sigma_a;\quad \bar{\sigma}_{ba} = \tfrac{1}{2}\textstyle\sum_s \sigma_{ba}. \tag{38}$$

There may be more than one possible initial atomic state. We will denote the initial states by a Greek subscript,

and let p_α be the probability that g_α is the initial state. Finally, there may be several possible final states which we will denote by a primed Greek subscript. The statement that $g_{\alpha'}$ is a possible final state means that when $\sum_{g_a} g_a g_a^\dagger$ is inserted into $\langle P(t)\rangle$ [as in (13)] the term $g_{\alpha'} g_{\alpha'}^\dagger$ gives an appreciable contribution. The generalized form of (35) for this situation is

$$\langle P(t)\rangle = F \sum_{g_\alpha} p_\alpha \sum_{g_{\alpha'}} \left\{ \sum_{g_a}{}' \bar{\sigma}_{a\alpha}(\mathbf{q}) \frac{\Gamma^P{}_{\alpha' a}}{\Gamma_a}(1-e^{-\Gamma_a t}) - 2\,\mathrm{Im} \sum_{\substack{g_b,\, g_a \\ b>a}}{}' \frac{\bar{\sigma}_{ba\alpha}(\mathbf{q})\Gamma^P{}_{\alpha' ba}}{W_b - W_a + i(\Gamma_b+\Gamma_a)/2}(1-e^{i(W_b-W_a)t}e^{-\frac{1}{2}(\Gamma_b+\Gamma_a)t}) \right\}. \quad (39)$$

$\bar{\sigma}_{a\alpha}$ and $\bar{\sigma}_{ba\alpha}$ are the same as $\bar{\sigma}_a$ and $\bar{\sigma}_{ba}$, respectively, except that the initial atomic state is g_α rather than g_0, and $\Gamma^P{}_{\alpha' a}$ and $\Gamma^P{}_{\alpha' ab}$ are the same as $\Gamma^P{}_a$ and $\Gamma^P{}_{ab}$, respectively, except that the final atomic state is $g_{\alpha'}$ rather than g_0.

In any given experiment there will be corrections to (35) [or (39)] arising from the finite extent of the target and the finite velocity of the atoms. The operator P, as given by (12), is not a strictly correct description of a photon counter, e.g., a counter measures the position of a photon, but does not measure the direction in which it is traveling. However, if it is known that the photon was emitted at the origin, then when the photon is counted it is also known that the portion of the photon wave packet intercepted by the counter consisted of plane waves whose wave vectors lay within the solid angle subtended by the counter at the origin. So P is an effective measurement operator valid for a particular atomic position and velocity. By performing a spatial translation and a velocity translation one can construct an operator $P_{\mathbf{R},\mathbf{V}}$ valid for an atom at position $\mathbf{R}$ and moving with velocity $\mathbf{V}$. The counting rate is then

$$\langle P(t)\rangle_{\mathrm{av}} = \int d^3R\, d^3V\, \rho(\mathbf{R}) F(\mathbf{V}) \langle P_{\mathbf{R},\mathbf{V}}(t)\rangle, \quad (40)$$

where $\rho(\mathbf{R})$ is the density of atoms in the part of the target intercepted by the beam and $F(\mathbf{V})$ is the atomic velocity distribution, both normalized to one. With respect to such corrections we only wish to note that the Doppler effect will be unimportant if the range of k in $\sum^P{}_{\mathbf{k},\hat{\epsilon}}$ is sufficiently greater than the Doppler widths of the lines involved in the experiment.

F is to be interpreted experimentally as the net beam flux, and $\langle P(t)\rangle$ as the integrated counting rate per atom in the part of the target intercepted by the beam. In a level-crossing experiment the total duration of the beam may be much greater than the value of Δt for individual electrons. The total number of counts is still given by (37) [or the modified version of (37) obtained from (39)] in this case since the increase in the number of counts with increasing beam duration is accounted for by the increase in F with increasing beam duration.

IV. THE HADEISHI-NIERENBERG EXPERIMENT

As a simple application of our general considerations we will calculate the phase of the interferential part of the photon counting rate in the Hadeishi-Nierenberg quantum-beat experiment.[3,9] We will not consider corrections arising from finite target volume or finite atomic velocities. Equation (36) will be used as it stands except that σ_a and σ_{ba} will be replaced by $\bar{\sigma}_a$ and $\bar{\sigma}_{ba}$, respectively.

In the Hadeishi-Nierenberg experiment g_0 is the 7^1S_0 ground state of Cd. The atom is in a weak magnetic field (0.88 G) and beats are observed between the 7^3P_1, $m_J=\pm 1$ excited states. The experimental configuration is shown in Fig. 1(a). The incident electron beam is perpendicular to $\mathbf{B}$, and the emitted photons are intercepted by a counter which subtends a small solid angle about the z axis. Denote the $m_J=+1(-1)$ excited states by $g_+(g_-)$. Let W_+ and W_- be the energies of g_+ and g_- when $\mathbf{B}$ is in the positive z direction as in Fig. 1(a). Then the interferential part of the differential counting rate is

$$d\langle P(t)\rangle_i/dt = 2F\,\mathrm{Re}\bar{\sigma}_{-+}(\mathbf{q})\Gamma^P{}_{-+} e^{i(W_- - W_+)t} e^{-\Gamma t}, \quad (41)$$

where we have put $\Gamma_+=\Gamma_-=\Gamma$. In Fig. 1(b) another experimental configuration is shown; it is obtained from Fig. 1(a) by a 180° rotation about the x axis. Clearly the counting rate for the situation pictured in Fig. 1(b) is the same as that for Fig. 1(a). Let us calculate the counting rate for Fig. 1(b) using (36). For a sufficiently weak field g_+, g_-, $\bar{\sigma}_{-+}(\mathbf{q})$, and $\Gamma^P{}_{-+}$ are essentially field-independent. Further, $\Gamma^P{}_{-+}$ is the same for both situations pictured in Fig. 1 since it is invariant under replacement of $\hat{k}$ by $-\hat{k}$. The energies of g_+ and g_- depend linearly on the field, and the effect of reversing the field is to replace $W_- - W_+$ by $W_+ - W_-$. Thus the counting rate calculated from Fig. 1(b) is

$$d\langle P(t)\rangle_i/dt = 2F\,\mathrm{Re}\bar{\sigma}_{-+}(\mathbf{q})\Gamma^P{}_{-+} e^{i(W_+ - W_-)t} e^{-\Gamma t}. \quad (42)$$

Comparison of (41) and (42) shows that

$$\mathrm{Im}\bar{\sigma}_{-+}(\mathbf{q})\Gamma^P{}_{-+} = 0, \quad (43)$$

and

$$d\langle P(t)\rangle_i/dt = 2F\bar{\sigma}_{-+}(\mathbf{q})\Gamma^P{}_{-+} e^{-\Gamma t}\cos(W_+ - W_-)t. \quad (44)$$

According to (44) the oscillations should start out at either a maximum or a minimum. Extrapolation of the data in Hadeishi and Nierenberg's Fig. 2 to $t=0$ shows

[9] Hadeishi and Nierenberg state that in their experiment the incident-electron energy was close to threshold while we have required that the incident-electron wave packet lies far from threshold. However, their criterion for an energy close to threshold was $\epsilon_a \ll W_a$, which clearly does not conflict with our criterion (24b). In fact, (24b) was well satisfied in the Hadeishi-Nierenberg experiment (T. Hadeishi, private communication).

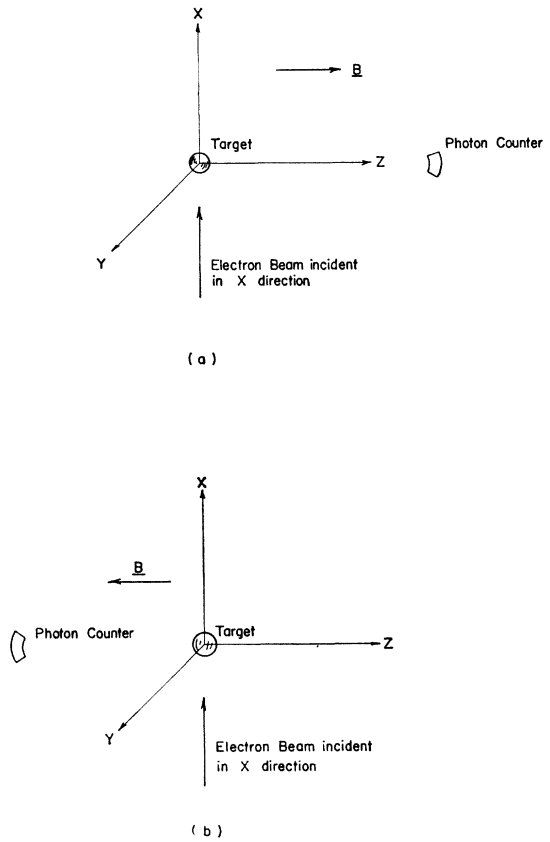

FIG. 1. (a) Experimental configuration of the Hadeishi-Nierenberg experiment. (b) Experimental configuration obtained from the Hadeishi-Nierenberg configuration by a 180° rotation about the x axis.

that the oscillations start at a maximum which indicates that $\bar{\sigma}_{-+}(\mathbf{q})\Gamma^{P}_{-+}$ is positive.

Note added in proof. It is incorrect to neglect wave-packet spreading, i.e., to use the approximation (8a). If ϕ_a [Eq. (9b)] and $\langle\phi_b|\phi_a\rangle$ [Eq. (16a)] are evaluated without the use of (8a) the same results are obtained except that t no longer need satisfy inequalities (24a) and (25). Inequalities (26) and (27) are also removed, but (24b) is retained.

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APPENDIX: EFFECTS OF EXCHANGE SCATTERING

In this Appendix we will justify the use of Eq. (10). This will be done in a rather brief manner since much of what is said here is also contained in Goldberger and Watson.[10] We first replace the initial unsymmetrized wave packet $X(t)$ by an antisymmetrized wave packet $X_s(t)$. Since the atomic wave functions $g_a(\xi)$ are already antisymmetrized we need only antisymmetrize with respect to interchange of the incident electron and each of the atomic electrons:

$$X_s(t)=(Z+1)^{1/2}\mathcal{S}X(t), \tag{A1a}$$

where $\mathcal{S}$ is the projection operator onto antisymmetrized states,

$$\mathcal{S}=(Z+1)^{-1}\sum_{j=0}^{Z}\delta_j Q_j. \tag{A1b}$$

Here Z is the number of electrons in the atom, $\delta_0=1$, $\delta_{j\neq 0}=-1$, $Q_0=1$, and $Q_{j\neq 0}$ interchanges the incident electron's variables and the jth atomic electron's variables. Q_j is Hermitian and unitary so adjoints and inverses will not be indicated explicitly. Let t_c be a large negative time at which the electron wave packet does not overlap the atom. Let $H=K+V$ where V is the electron-atom interaction. Then since all permutations commute[11] with H the symmetrized solution of the Schrödinger equation is

$$\Psi_s(t)=e^{-iH(t-t_c)}X_s(t_c)=(Z+1)^{1/2}\mathcal{S}e^{-iH(t-t_c)}X(t_c)$$

$$=X_s(t)+\int d^3p\, a(\mathbf{p}-\mathbf{q})e^{-iEt}\psi^{+}{}_{s(\mathrm{sc})}, \tag{A2a}$$

where

$$\psi^{+}{}_{s(\mathrm{sc})}=(Z+1)^{1/2}\mathcal{S}(\psi^{+}-\chi)$$

$$=(Z+1)^{-1/2}\sum_{j=0}^{Z}\delta_j Q_j\frac{1}{E+i\eta-K}T\chi. \tag{A2b}$$

We will expand $\Psi_{s(\mathrm{sc})}(t)\equiv\Psi_s(t)-X_s(t)$ in antisymmetrized eigenstates of K:

$$\chi_{s(a)}=(Z+1)^{1/2}\mathcal{S}\chi_a. \tag{A3}$$

In general the states $\chi_{s(a)}$ do not give rise to a simple expansion of the identity, but it is readily verified that

$$\textstyle\sum_a \chi_{s(a)}\langle\chi_{s(a)}|f_s\rangle=\sum_a \chi_{s(a)}\langle\chi_a|f\rangle=f_s, \tag{A4a}$$

whenever f_s is of the form

$$f_s=(Z+1)^{1/2}\mathcal{S}f, \tag{A4b}$$

where f is an unsymmetrized wave function in which the incident electron is localized far from the origin and the atomic electrons are localized near the origin. The nature of the sum $\sum_a$ in (A4a) is defined by $\sum_a \chi_a\chi_a{}^{\dagger}=1$; it is displayed explicitly in (3b). For sufficiently large positive times $\Psi_{s(\mathrm{sc})}(t)$ is of the form (A4b) (we assume the excited atom is not ionized) and admits the expansion

[10] Reference 6, Chap. 4.

[11] This is not strictly true since K does not include the interaction of the incident-electron's orbital angular momentum with **B**. It is assumed that this is of no physical significance.

(A4a). Before carrying out the expansion we will put $\psi^{+}{}_{s(sc)}$ in a more convenient form by using the operator identity

$$Q_j[E+i\eta-K]^{-1}T=[E+i\eta-K_{j'}]^{-1}T_{j'j}Q_j, \quad \text{(A5a)}$$

where j' is arbitrary, and

$$T_{j'j}=V_j+V_{j'}[E+i\eta-H]^{-1}V_j, \quad \text{(A5b)}$$

$$V_j=Q_jVQ_j, \quad \text{(A5c)}$$

$$K_j=H-V_j. \quad \text{(A5d)}$$

This leads to the expression

$$\langle\chi_{s(a)}|\psi^{+}{}_{s(sc)}\rangle=\frac{(Z+1)^{-1}}{E+i\eta-E_a}\sum_{kj}\delta_k\delta_j\langle Q_k\chi_a|T_{kj}|Q_j\chi\rangle$$
$$=[E+i\eta-E_a]^{-1}$$
$$\times\{T_a(\mathbf{p}_a,\mathbf{p})-ZT_a{}^{\mathrm{ex}}(\mathbf{p}_a,\mathbf{p})\}, \quad \text{(A6a)}$$

where

$$T_a(\mathbf{p}_a,\mathbf{p})=\langle\chi_a|T|\chi\rangle, \quad \text{(A6b)}$$

$$T_a{}^{\mathrm{ex}}(\mathbf{p}_a,\mathbf{p})=\langle\chi_a|T_{0k}|\chi\rangle, \quad \text{(A6c)}$$

with $k\neq 0$. $\Psi_{s(sc)}(t)$ is thus

$$\Psi_{s(sc)}(t)=(Z+1)^{1/2}$$
$$\times\mathcal{S}\sum_a\frac{\chi_a}{E+i\eta-E_a}\{T_a(\mathbf{p}_a,\mathbf{p})-ZT_a{}^{\mathrm{ex}}(\mathbf{p}_a,\mathbf{p})\}. \quad \text{(A7)}$$

Following the same line of development as in Sec. II, this may be put in the form

$$\Psi_{s(sc)}(t)=(Z+1)^{1/2}\mathcal{S}\Psi_{sc}(t), \quad \text{(A8)}$$

where $\Psi_{sc}(t)$ is given by Eq. (9) with f_a defined by (10).

The decay process is now described by

$$\Psi_{s(dc)}(t)=(Z+1)^{1/2}\mathcal{S}\Psi_{dc}(t) \quad \text{(A9)}$$

which is obtained from (A8) by replacing h with H_r and including the initial state of the radiation field. In the same way that one verifies (A4a), it is readily verified that

$$\langle P(t)\rangle\equiv\langle\Psi_{s(dc)}(t)|P|\Psi_{s(dc)}(t)\rangle$$
$$=\langle\Psi_{dc}(t)|P|\Psi_{dc}(t)\rangle. \quad \text{(A10)}$$

Thus the symmetrization in (A9) may be ignored for the purpose of calculating the photon counting rate.

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Superconducting Transitions of Amorphous Bismuth Alloys*†

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Measurements have been made of the critical temperatures T_c of binary-alloy films composed of amorphous bismuth with lead, thallium, or antimony in concentrations up to 13 at.%. The curves showing T_c as a function of impurity concentration are nearly linear, as expected for a superconductor with no crystalline anisotropy. The slopes of the curves are not simply related to the valence or free-atom size of the impurity atoms. It is suggested that this may be explainable by extending Faber and Ziman's theory of the breakdown of Linde's rule for liquid alloys. The transitions of the films into the superconducting state are extremely sharp (~5 mdeg wide). This indicates strongly that the electromagnetic coherence length does not limit the sharpness of the transition.

I. INTRODUCTION

THE superconducting critical temperatures of many different alloys have been measured in the last 50 years. However, only in the last few years have we had the theoretical knowledge required to examine the fundamental significance of the data. All of our present theoretical understanding of critical temperatures has, of course, arisen from the BCS theory,[1] and from elaborations on it. Two years after this theory was presented, Anderson made a major advance by suggesting two mechanisms which usually dominate the shift in the critical temperature T_c of a metal as impurities are added.[2] He suggested that nonmagnetic impurities depress T_c because of a decrease in the effect of crystal anisotropy on the electrons. This is called the anisotropy effect. He also showed that magnetic impurities are expected to cause an additional depression of T_c, because of their tendency to break down the electron pair-

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