Coherent excitation of the $n = 3$ states in hydrogen*

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This paper is a theoretical discussion of a "coherence effect" in the excitation of hydrogen atoms to the $n = 3$ state by electron bombardment. By coherence is meant that the density matrix describing the atom after the collision has off-diagonal matrix elements in the field-free basis. The differential cross section for producing Balmer-α photons at 90° to the electron beam is calculated as a function of an applied longitudinal electric field. The off-diagonal elements show up as a dependence of the observed light on the directions of the electric field. Theoretical results based on the Born approximation are compared with an experiment at 200 and 500 eV. It is pointed out that this method for measuring relative phases of scattering amplitudes can be generally applied and is not restricted to $n = 3$ excitation of hydrogen.

I. INTRODUCTION

The purpose of this paper is to discuss a coherent excitation effect in the inelastic scattering of electrons by hydrogen atoms. There is nothing fundamentally strange or unusual about this effect, but until recently not much attention appears to have been paid to ideas like this in atomic-collision physics. In general, observation of a coherent effect gives information on relative phases of scattering amplitudes, while measurements of cross sections of course give information only about the absolute squares of scattering amplitudes.

The experiment in mind is the excitation of the $n=3$ states in hydrogen by electron impact and observation of the subsequent Balmer-α radiation. The theoretical work to be described in this paper was motivated by such an experiment, which has been carried out by Mahan, Gallagher, and Smith[1] at the Joint Institute for Laboratory Astrophysics (JILA). The primary purpose of their experiment was to measure the cross-section ratios $\sigma_{3s}:\sigma_{3p}:\sigma_{3d}$. The coherent effects to be described here enter into a full understanding of their experiment but probably do not significantly affect the cross-section ratios.

A general plan of the experiment is shown in Fig. 1. An electron beam intersects a beam of hydrogen atoms traveling out of the plane of the paper. After excitation to various $n=3$ states, the atoms decay, emitting Balmer-α radiation detected by the photomultiplier. The excitation and radiation take place in an electric field directed parallel or antiparallel to the electron velocity. This field was not essential to the main point of the experiment (i.e., to a measurement of the $3s:3p:3d$ ratio), but does make coherent excitation effects observable.

The $n=3$ fine-structure states of atomic hydrogen are shown in Fig. 2. (Hyperfine structure is not shown in this figure. Various level parameters are listed in Table I.) The excitation process is unaffected by the field because it is weak compared to atomic fields. However, the field does affect the subsequent time evolution of the atomic state by mixing neighboring levels (such as a and b in Fig. 2). One consequence of the mixing is that Balmer emission is enhanced. This is because the dominant excitation is to the $3p$ state, which decays primarily by Lyman-β emission, while the field mixes in $3d$ states, which can decay only by Balmer emission. This enhancement would occur even if there were no coherent excitation.

However, a second consequence of the mixing is that the degree of enhancement depends on the direction of the applied field. This effect occurs only if the collision puts the atom into a linear superposition of states like a and b. In the time evolution of such a superposition, the probability that the atom will be in state a, for example, contains a cross term between the scattering amplitudes to the two states, and the magnitude of the cross term depends linearly on the field. A brief summary of the coherent excitation effects has been presented at a conference.[2]

The fundamental idea is that an atom, upon leaving a collision in a definite direction, will in general be in an internal state which is a linear superposition of its various (internal) energy eigenstates, the coefficients being scattered amplitudes evaluated as the scattering angle in question. (The scattering amplitudes are more precisely off-shell T-matrix elements, as will be discussed in Sec. II.) If this internal state is unstable and decays, emitting photons, there will be interference effects in the light, and in this paper we work out the details of the special case, $n=3$ excitation.

A general way to calculate such interference effects, given the initial state created in the collision, has been described by Fano and Macek in their review paper.[3] However, these authors do

not explicitly work out cases where an electric field is applied. The effect to be worked out in this paper is a change in light intensity when an electric field is reversed, so the formalism of Fano and Macek cannot be applied directly without further development.

An electric field effect similar to the one to be described here has been considered theoretically by Eck[4] and observed in beam-foil experiments by Sellin *et al.*[5] and Gaupp *et al.*[6] In these experiments, the time of excitation was well defined and a field-dependent beat signal was observed in light emission downstream from the foil. In the JILA experiment, the light was emitted from the intersection of two unmodulated (for our purposes) crossed beams, and oscillatory signals were averaged out. However, as will be shown, the initial coherence could still be observed as a change in light intensity when the field direction was reversed.

Another difference between the beam-foil experiments and the one on $n=3$ excitation is that in the beam-foil experiments the initial state of excited atoms emerging from the foil cannot be calculated from first principles. In the $n=3$ experiment, the initial state *is* calculable from first principles (if electron-hydrogen scattering is considered to be calculable) and so experimental results can be compared with theory.

Eminyan *et al.*[7] have reported a coincidence experiment in which the direction of the excited atom's velocity was essentially fixed by observing a scattered electron. The coherent state excited was a linear combination of the three magnetic substates of the 3^1P_1 level in helium. By observing the angular distribution of the emitted photon the authors were able to measure the phase difference between two scattering amplitudes, one to an $m=0$ state, the other to an $m=1$ state. The JILA experiment differs in that the observed signal is an average over all scattering angles, and the coherence is between states of the same magnetic quantum number m but different orbital angular momentum l.

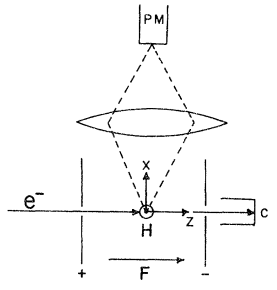

FIG. 1. Schematic diagram of the JILA experiment. H denotes a hydrogen atom beam coming out of the paper, e^- an electron beam, and F an electric field. PM, photomultiplier sensitive to Balmer-α only. C, Faraday cup.

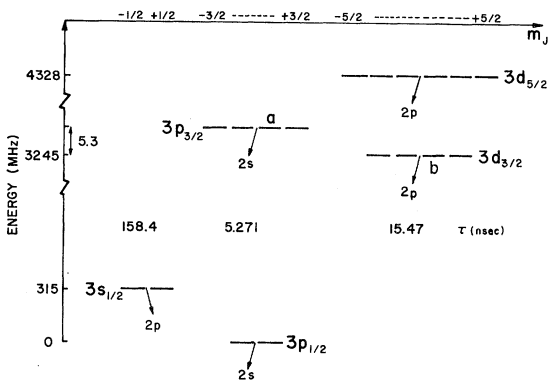

FIG. 2. Fine structure of the $n=3$ levels in hydrogen. For given l, the lifetime τ is independent of j and m_j. The letters a and b label states referred to in the text.

II. FORMULATION OF THE PROBLEM

It is intuitively appealing to view the scattering process as made up of two steps: First the electron prepares the atom in some excited state, and then the atom decays, emitting a photon. Although it may not be rigorously correct to adopt this two-step picture, it is surely a very good approximation.

The question then arises: What is the atomic state prepared by the electron? Speaking somewhat imprecisely, should the atom be thought of

TABLE I. Parameters of the $n=3$ states in hydrogen. Γ's are decay rates to all final states and γ's are partial decay rates for emission of Balmer-α. Energies are measured relative to the $3p_{1/2}$ state. ΔE is the hyperfine splitting.

State	Energy[a] (GHz)	Γ[b] (sec^{-1})	γ[b] (sec^{-1})	ΔE[c] (MHz)
$3s_{1/2}$	0.314 81	6.313(6)	6.313(6)	52.6
$3p_{1/2}$	0.	1.897(8)	2.245(7)	17.5
$3p_{3/2}$	3.249 93	1.897(8)	2.245(7)	7.0
$3d_{3/2}$	3.244 62	6.465(7)	6.465(7)	4.2
$3d_{5/2}$	4.327 89	6.465(7)	6.465(7)	2.7

[a] J. D. Garcia and J. E. Mack, J. Opt. Soc. Am. 55, 654 (1965).

[b] W. L. Wiese, M. W. Smith, and B. M. Glennon, *Atomic Transition Probabilities* (National Standard Reference Data Series-NBS 4, U. S. GPO, Washington, D. C.), Vol. 1.

[c] H. Bethe and E. E. Salpeter, *Quantum Mechanics of One and Two Electron Atoms* (Academic, New York, 1957) p. 110.

as an incoherent mixture of all the energy eigenstates allowed by energy conservation, each state being weighted by the appropriate cross section? Or, to go to another extreme, should the atom be thought of as in a "coherent" (linear) superposition of all the (allowed) energy eigenstates, the coefficient of each state being the scattering amplitude to that state? Or, thirdly, is the atom in some other state intermediate between these two extremes?

The right answer is the third alternative; the atom is to be described by neither of the two extreme cases. The scattered electron *could* be observed (though it many experiments it is not), and the probability of detecting a photon involves a sum over electron final states. This tends to randomize residual atomic states and introduce incoherence, but it is not true that the final atomic states are all totally incoherent with each other.

To consider the matter more precisely, assume that the two-step picture may be formulated as follows: in the center of mass frame, let $T(\vec{k}, \vec{p}', \vec{P}; \vec{p})$ be the scattering amplitude from the initial state of an electron of momentum $\vec{p}$ plus an atom (in its ground state) of momentum $-\vec{p}$ to the final state of a scattered electron of momentum $\vec{p}'$ plus an atom (in its ground state) of momentum $\vec{P}$ plus a photon of momentum $\hbar\vec{k}$. Assume for now that the ground state is nondegenerate. (This assumption will be relaxed at the end of this section.) Momentum indices $\vec{p}, \vec{k}, \vec{p}'$ include a specification of electron spin and photon polarization. The two-step assumption is that T may be written as a sum over intermediate states, each term in the sum being a product of two factors. One factor is the scattering amplitude from the state of a free electron of momentum $\vec{p}$ plus a ground-state hydrogen atom to the state of a free electron of momentum $\vec{p}'$ plus a hydrogen atom in an excited state n. The second factor is the probability amplitude that the excited state n will, in its decay, emit a photon of momentum $\hbar\vec{k}$. In computing the scattering amplitude, coupling to the radiation field is neglected, while in computing the photon emission amplitude, coupling to the beam electron is neglected. In symbols, with obvious notation,

$$T(\vec{k}, \vec{p}', \vec{P}; \vec{p}) = \sum_n A_n(\vec{k}, \vec{P}) f_n(\vec{p}', \vec{p}) . \tag{1}$$

A_n depends (weakly) on $\vec{P}$ because of the Doppler shift in the frequency of a photon emitted from a moving atom.

The momenta $\hbar k$, p', P, and p are related by conservation of energy and momentum

$$\hbar\vec{k} + \vec{P} + \vec{p}' = 0 \tag{2}$$

and

$$\hbar ck + \tfrac{1}{2}P^2/M + \tfrac{1}{2}p'^2/m = \tfrac{1}{2}p^2/\mu , \tag{3}$$

where c is the velocity of light, μ is the reduced mass of the electron-hydrogen system, m is the mass of an electron, and M is the mass of a hydrogen atom in its ground state. In the intermediate state, the scattered electron is taken to have the same momentum ($\vec{p}'$) as the scattered electron in the final state because the photon is thought of as being emitted by the excited atom, and its emission does not affect the scattered electron. For similar reasons the excited atom is taken to have linear momentum $\hbar k + \vec{P}$.

$\vec{p}'$ and $\vec{p}$ will not, in general, satisfy energy conservation for the electron-atom scattering amplitude $f_n(\vec{p}', \vec{p})$. The f_n are off-shell matrix elements. However, since recoil effects are small and spectral lines sharp, the f_n are close to being on shell. We assume that negligible error is made in (1) by replacing $\vec{p}'$ in each $f_n(\vec{p}', \vec{p})$ by $\vec{p}_n'$ as given by energy conservation for electron-atom scattering with radiative effects ignored.

For given incident momentum $\vec{p}$, to compute the counting rate in a photon detector sensitive only to photon $\vec{k}$, the sum on the right-hand side of (1) must first be calculated for this value of $\vec{k}$ and for some values of the other parameters; then the result must be squared and summed over all the other parameters.

The prescription of the last paragraph may be rephrased as follows: Fixing the initial electron momentum $\vec{p}$, consider those atoms "left behind" by electrons scattering into direction (θ', ϕ'). These atoms may be thought of as forming a beam, each atom in the beam being in a "totally coherent" state

$$\psi(\theta', \phi') = \sum_n f_n(\vec{p}_n', \vec{p}) u_n , \tag{4}$$

where the u_n are a complete set of atomic states. For fixed θ', ϕ', the f_n in (4) are just a set of complex numbers and the amplitude for $\psi(\theta', \phi')$ to emit a photon $\vec{k}$ is then just as given by the right-hand side of (1).

According to Eq. (4), an atom may be coherently excited to two (or more) states differing in their energies by more than their widths. If two such states were then to emit light in the absence of any external fields, interference effects associated with the coherent excitation would be lost—or, more precisely, be reduced by a factor of order (line width)/(line separation). For such experiments, two states differing in energy by more than their line width might as well be thought of as excited incoherently. However, if the two

states can be mixed by an external field (as will be the case for $n=3$ excitation), then one can "feed" the other and the light emitted by each will contain information about the relative phases of the initial scattering amplitudes.

Returning to Eq. (4), how about atoms going off into some other direction (θ', ϕ')? These are to be regarded as incoherent with those just discussed; their light is to be added by just adding intensities. All the excited atoms are then to be regarded as a set of beams, the atoms in one beam each being in the same state (4), but beams going in different directions being independent of each other.

It is convenient to describe the situation by an atomic density matrix. Atoms in the beam corresponding to scattered electrons θ', ϕ' have a density matrix $\rho(\theta', \phi')$ with elements, in the basis u_n, given by

$$\rho_{nn'}(\theta', \phi') = f_n(\theta', \phi') f_{n'}^*(\theta', \phi'), \tag{5}$$

where the variable $\vec{p}$ has been suppressed. This density matrix has many nondiagonal elements and is in fact a multiple of the projection operator onto the state (4). The fact that atoms made by electrons going off in different directions are incoherent with each other is expressed by saying that the density matrix ρ describing all the atoms is to be obtained by integrating (5) over θ', ϕ'

$$\rho_{nn'} = \sum_{m_s} (p_n'/p) \int d\Omega' f_n(\theta', \phi') f_{n'}^*(\theta', \phi'), \tag{6}$$

where a summation over spin directions of the scattered electron has been included. Though for simplicity this internal degree of freedom was not addressed in the discussion above, it is clear from the discussion that atoms made by electrons of different final spin directions are incoherent with each other; their density matrices are to be added. [If the exciting particle were not an electron but another atom, the sum in (6) would be over all internal states of the scattered, unobserved, atom.] The factor p_n'/p has been introduced so that diagonal elements of ρ are cross sections.

In the above discussion it has been implicitly assumed that the initial state of electron-plus-atom had been completely specified, including all spin components. If this were not so, density matrices (6) must of course be averaged over all initial states.

It has also been assumed that the scattered electron was not observed. If it were, and photons from the excited atoms were counted in coincidence with electrons scattered in a certain direction, then clearly the integration in (6) should be carried out over a restricted solid angle defined by the electron detector.

III. EMISSION OF LIGHT

We turn now to the question of how the off-diagonal elements of (6) may be measured. In the experiment of Ref. 7 these elements could be extracted from the angular distribution of the emitted photons. We discuss a different method which is particularly suitable for excitation of the $n=3$ states of hydrogen. In this method an electric field is applied either parallel or antiparallel to the electron beam direction, and Balmer-α photons observed at right angles. The difference in count rate when the field is reversed is proportional to the off-diagonal elements and may be used to measure them.

In the JILA experiment, a photomultiplier viewed the interaction of two crossed beams at right angles to both, as shown in Fig. 1. The optical system was not sensitive to polarization. Both the H beam and the electron beam were, for present purposes, constant in time. If, at $t=0$, the atom were in some state $\psi(0)$, a linear combination of $n=3$ states, then the observed light signal would be proportional to the integral B defined by

$$B = \sum_f \int_0^\infty dt \left[|\langle u_f | y | \psi(t) \rangle|^2 + |\langle u_f | z | \psi(t) \rangle|^2 \right], \tag{7}$$

where the sum on f is over all $2s$ and $2p$ states, the z axis is taken along the electron beam, while the y axis points along the H atom beam. $\psi(t)$ is the state that $\psi(0)$ evolves into under the action of the usual phenomenological Hamiltonian. (That is, the sum of a field-free part, plus the usual terms for any applied electric or magnetic fields, plus a purely imaginary part describing the decay. The imaginary part is diagonal in the field-free basis.)

The final state u_f in (7) is regarded as time independent, though as a matter of fact the $2p$ state does of course have a finite lifetime. This lifetime would be important if we wished to calculate the (natural) width of the Balmer-α spectrum, but it may be shown that it may be ignored if we are interested only in the probability of some Balmer-α photon being emitted, regardless of frequency.

Actually, the state of the atom just after the collision is not a pure state $\psi(0)$, but is to be described by a density matrix $\rho(0)$ [Eq. (6)]. Upon rewriting (7) in terms of $\rho(0)$, it may be shown that the differential cross section $d\sigma(\theta, \phi)/d\Omega$ for emission of Balmer-α photons into a unit solid angle about direction θ, ϕ with the electron beam is given by

$$\frac{d\sigma}{d\Omega}(\theta, \phi) = \mathrm{Tr}\left(\int_0^\infty dt M(\theta, \phi) \rho(t) \right), \tag{8}$$

where $\rho(t)$ evolves from $\rho(0)$ by action of the effective Hamiltonian described above, that is, if H is this Hamiltonian, then $\rho(t)$ is given by

$$\rho(t)=\exp(-iHt/\hbar)\rho(0)\exp(iH^{\dagger}t/\hbar)\,. \tag{9}$$

The matrix M is constructed from dipole matrix elements linking the upper, $n=3$ states to the lower, $n=2$ states. More precisely, in Gaussian units,

$$M_{ij}(\theta,\phi)=\left(\frac{e^2\omega^3}{2\pi\hbar c^3}\right)\sum_{f,m}\langle u_i|\xi_m^{\dagger}|u_f\rangle\langle u_f|\xi_m|u_j\rangle\,, \tag{10}$$

where i and j label two states with $n=3$, the sum on f is over all $n=2$ states, and the ξ_m are dipole operators: $\xi_{-1}=(x'+iy')/\sqrt{2}$, $\xi_0=z'$, and $\xi_1=(-x'+iy')/\sqrt{2}$ if x', y', and z' are coordinates relative to a frame in which the z' axis points to the detector. The (θ,ϕ) dependence of M appears when primed coordinates are related to unprimed. For the geometry of the JILA experiment, $\theta=90°$, $\phi=0°$ and the sum on m in (10) is over $m=-1$ and $+1$.

A diagonal element $M_{ii}(\theta,\phi)$ in (10) is the decay rate at which state i emits Balmer photons into the unit solid angle around (θ,ϕ) and has dimensions photons per second per steradian. Off-diagonal elements have the same units but represent interference effects arising if the atom is in a linear superposition state, i.e., if $\int_0^{\infty}\rho(t)$ in (8) has off-diagonal elements. However, for excitation of $n=3$ states in hydrogen, off-diagonal elements of M may be neglected. With reference to Fig. 2, off-diagonal elements of M linking states differing in energy by many line widths [e.g., $3s_{1/2}$ $(m_j=+\frac{1}{2})$ and $3p_{3/2}$ $(m_j=\frac{1}{2})$] may formally appear on the right-hand side of Eq. (8), but will contribute little because the integration over time will introduce factors of order (line widths)/separation. In addition, even the small contribution such a term does make will be field-independent because such states are too far apart to be appreciably mixed by the fields used in the JILA experiment.

On the other hand, levels separated by a line width or less [e.g., $3p_{3/2}$ $(m_j=\frac{1}{2})$ and $3d_{3/2}$ $(m_j=\frac{1}{2})$] differ in parity and so are not connected by matrix elements of M anyway.

Neglecting off-diagonal elements of M is equivalent to thinking of each level in Fig. 2 as independent of all the others, as far as the radiation process itself goes. The light emitted by each level depends only on the probability that the atom be in that level, i.e., on the corresponding diagonal element of the density matrix. Coherent excitation [off-diagonal elements of $\rho(0)$] shows up in the emitted light only because the integral $\int\rho_{aa}(t)dt$ of a diagonal element depends on off-diagonal elements created at the collision.

IV. RESULTS

For computational purposes, (8) was written in the form

$$\frac{d\sigma}{d\Omega}(\theta,\phi)=\mathrm{Tr}[\eta_F(\theta,\phi)\rho(0)]\,, \tag{11}$$

where the matrix η_F is defined by

$$\eta_F(\theta,\phi)=\int_0^{\infty}dt\exp(iH^{\dagger}t/\hbar)M(\theta,\phi)\exp(-iHt/\hbar)\,. \tag{12}$$

F is the component of the electric field along the electron velocity, and in the right-hand side of 12 appears implicitly in the Hamiltonian H.

The 18×18 matrix $\eta_F(\frac{1}{2}\pi,0)$ was computed numerically for electric fields in the range -50–$+50$

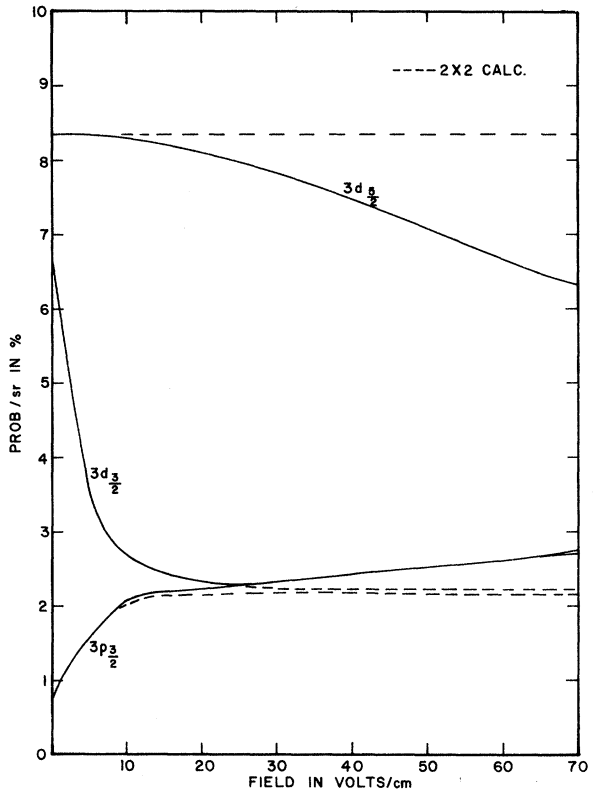

FIG. 3. Ordinate for the upper curve is the probability per steradian that an atom initially excited to the $3d_{5/2}$ state $(m_j=\frac{3}{2})$ emits a Balmer-α photon in a direction perpendicular to the velocity of the exciting electron. The other curves correspond to the $3d_{3/2}$ $(m_j=\frac{3}{2})$ and $3p_{3/2}$ $(m_j=\frac{3}{2})$ states. At a given field the three probabilities are diagonal elements of the matrix $\eta_F(\frac{1}{2}\pi,0)$ defined in Eq. (12).

V/cm. M in Eq. (12) was taken to be diagonal with components as listed in Table I. The matrix $\exp(-iHt/\hbar)$ was computed from the eigenvalues and eigenvectors of H. Though formally an 18×18 matrix was diagonalized, actually this matrix may be written in blocks down the main diagonal, with the largest block being 5×5. This block corresponds to the $m_j=\frac{1}{2}$ substates of the levels $s_{1/2}$, $p_{1/2}$, $p_{3/2}$, $d_{3/2}$, and $d_{5/2}$ (see Fig. 2). The electric field coupled all these states, though at the fields considered the coupling between the pairs $s_{1/2}, p_{1/2}$ and $p_{3/2}, d_{3/2}$ was the most important, since states in these pairs lie close together.

The nth diagonal element of $\eta_F(\frac{1}{2}\pi, 0)$ is the probability per unit solid angle that an atom excited to state n emits a Balmer-α photon in a direction perpendicular to the electron beam. For the three states with $m_j=+\frac{3}{2}$ these probabilities are shown in Fig. 3 as a function of electric field F. Only positive values of F are displayed; the probabilities depend only on the magnitude of F. For an atom excited to the $3p_{3/2}$ ($m_j=\frac{3}{2}$) state, the probability of emitting a Balmer-α photon increases with increasing field because the field mixes in d states which can decay only by Balmer emission.

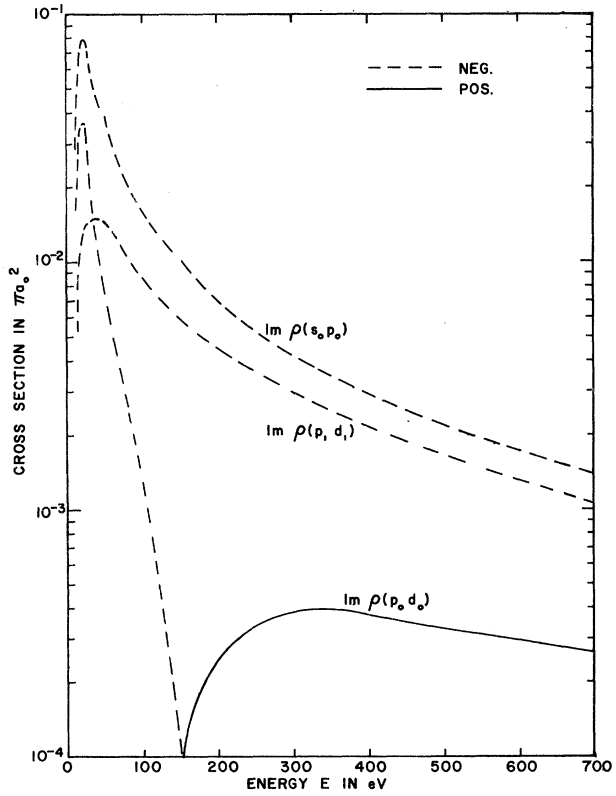

FIG. 4. Energy dependence of mixed cross sections defined as in Eq. (13) and calculated using the first Born approximation.

The probability of Balmer emission by an atom excited initially to the $3d_{3/2}$ or $3d_{5/2}$ state decreases with increasing field because the field mixes in p states which can decay not only by Balmer-α but also by Lyman-β emission.

The characteristic field F_0 required to mix the $p_{3/2}$ and $d_{3/2}$ states is given approximately by $eF_0a_0=\Delta E$, where ΔE is the zero-field separation between the two states; $\Delta E=5.31$ MHz, $F_0=4.2$ V/cm. In Fig. 3 it is evident that for fields greater than about 10 V/cm the $p_{3/2}$ and $d_{3/2}$ states behave as one state, while the distant $d_{5/2}$ state is affected much less. The dashed lines are the results of a calculation in which the coupling between the $p_{3/2}$ and $d_{5/2}$ states is neglected, so that the three-state problem reduces to a one-state problem and a two-state problem.

The results for the five states with $m_j=+\frac{1}{2}$ are qualitatively similar but more complicated in detail. They are not shown here.

The discussion above has concerned the diagonal elements of the matrix η_F. From Eq. (11), the off-diagonal ones play a role only if there is coherent excitation, i.e., if $\rho(0)$ has off-diagonal elements. They could be described by simply listing their numerical values, which have been computed, but since by themselves these are not meaningful to one's intuition they are not presented here. It may be shown that considered as a function of electric field, any matrix element of η_F between states which are coupled by the electric field is an odd function of the field, and others are even functions of the field. The asymmetry between positive and negative fields shown in Figs. 5 and 6 is an observable consequence of the odd matrix elements in η_F.

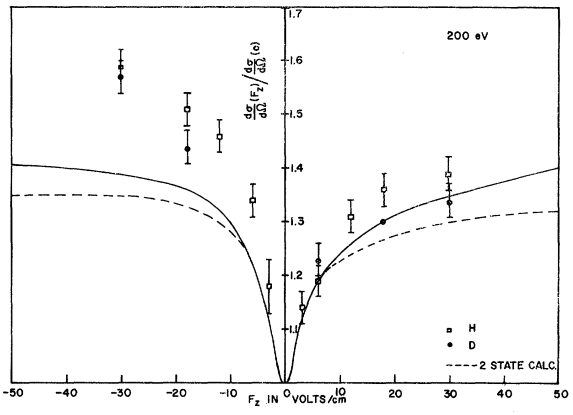

FIG. 5. Observed and predicted Balmer-α light signals as a function of applied field. All cross sections are evaluated at 90° to the electron beam and calculated for an electron energy of 200 eV.

The theoretically predicted Balmer-α signal is given by Eq. (11). At the experimental energies of 200 and 500 eV, it seems reasonable to use the Born approximation (without exchange) to calculate the density matrix ρ. Although cross sections calculated using the Born approximation have been published,[8] the off-diagonal elements which give rise to the field asymmetry of interest have not appeared. There are three nonzero "mixed" cross sections

$$\rho(s_0 p_0) \equiv \frac{k_f}{k_i} \int_{4\pi} d\Omega\, f_{3s}(\theta, \phi) f^*_{3p_0}(\theta, \phi)\,,$$

$$\rho(p_0 d_0) \equiv \frac{k_f}{k_i} \int d\Omega\, f_{3p_0}(\theta, \phi) f^*_{3d_0}(\theta, \phi)\,, \tag{13}$$

$$\rho(p_1 d_1) \equiv \frac{k_f}{k_i} \int d\Omega\, f_{3p_1}(\theta, \phi) f^*_{3d_1}(\theta, \phi)\,.$$

In the first Born approximation these are all purely imaginary. Their imaginary parts are plotted in Fig. 4 as a function of electron energy.

Combining the Born cross sections of Ref. 8 and Eq. (13) with the appropriate vector coupling coefficients, the trace of Eq. (11) was calculated. The results are shown in Figs. 5 and 6, which also display the experimental data of Ref. 1.

V. DISCUSSION

The theoretical (solid) curves in Figs. 5 and 6 do show a field asymmetry, but the asymmetry is not as great as that observed in the experiments. The predicted sign is correct in the sense that at fields around 30 V/cm, more light is emitted for negative fields than for positive. (A negative field is directed so as to increase the kinetic energy of an electron.)

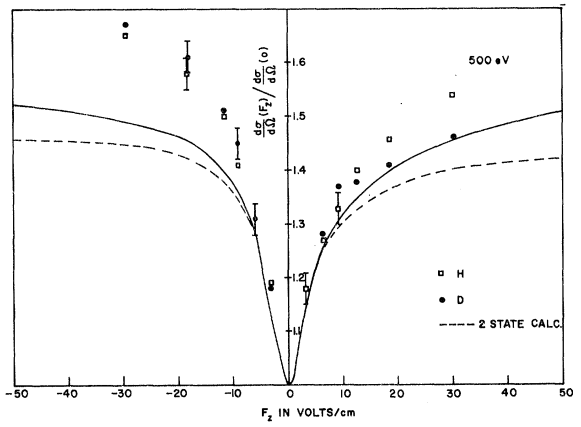

FIG. 6. Same caption as for Fig. 5 but for an electron energy of 500 eV.

What might be the cause of this discrepancy? One approximation that has been made in the theory is that hyperfine structure has been neglected. The fundamental justification for this approximation is that hyperfine splittings are small. More precisely, from Table I, the splittings in all levels except $3s_{1/2}$ are smaller than or comparable to the widths of the levels involved. In the $3s_{1/2}$ state the splitting (52.6 MHz) is small compared to the Lamb shift between the $3s_{1/2}$ and $3p_{1/2}$ states (315 MHz). Numerical experiments in which the $3s_{1/2}$ levels are arbitrarily shifted in energy by 50 MHz lead to changes in the theoretical curves shown in Figs. 5 and 6, which are small compared to the discrepancy between theory and experiment. A more detailed calculation in which hyperfine structure is taken into account could certainly be carried out, but it is most unlikely that the more elaborate calculation would fit the experiments significantly better.

A second approximation which has been made in the theory is that each (field-free) state in Fig. 2 has been considered to radiate independently, i.e., off-diagonal elements of M (Sec. III) have been neglected. This seems to be an excellent approximation for the reasons given in Sec. III and again is unlikely to be the cause of the discrepancy in Figs. 5 and 6.

A third approximation is the use of Born amplitudes. These are expected to be quite reliable, at least for total cross sections, at 200 and 500 eV. This is confirmed by the cross section ratios measured in Ref. 1. Although the Born approximation has not been previously tested for "mixed" integrals such as those in Eq. (13), it would be rather surprising if the mixed cross sections were badly approximated while total cross sections were well approximated.

It may be asked: How much must the Born amplitudes be modified in order to obtain agreement between theory and experiment in Figs. 5 and 6? In numerical experiments, good agreement can be obtained if the total $3p$ cross section is increased by 20%, while the mixed cross sections of (13) are arbitrarily multiplied by $\sqrt{-1}$. (An exhaustive search was not undertaken. Other modifications of the Born amplitudes will probably give good agreement with experiment.)

Another alternative explanation of the discrepancy, of course, is that the experimental results need to be corrected. I cannot comment on that.

This paper has been concerned with a special case: Balmer radiation produced in the impact of electrons on hydrogen. If the analysis has been essentially correct, then further work will remove the present discrepancy between theory and experiment. However, the underlying idea should be ap-

plicable to a wide variety of collisions. In general, coherent excitation effects should be present in any collision. For example, a field asymmetry should be present in Balmer-β, -γ, Paschen-α, -β, -γ, etc. light emitted in electron-hydrogen collisions. Similar comments apply to proton-hydrogen, electron-helium, and proton-helium collisions; in atom-atom collisions, both partners will in general also exhibit such effects.

The electric field in the present paper was constant in time. Resonance experiments could also be considered, in which an atom or molecule is excited by (say) electron bombardment, and light observed as a function of an externally applied high-frequency field. The line shape (light intensity versus applied frequency) is typically a Lorentzian. Coherent excitation effects would affect this line shape, as has already been recognized by Wilcox and Lamb.[9]

Coherent excitation effects will also appear in the frequency spectrum of emitted light (because of the off-diagonal terms in M which have been neglected here). In general, although one example has been analyzed here, many more can very likely be found.

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