Coherent Electron Impact Excitation of Different L States in the $n = 3$ Shell of Atomic Hydrogen

Stephen J. Smith

Mahan and his colleagues have recently shown that the Balmer $a$ flux emitted in a direction perpendicular to an electron beam incident on atomic hydrogen is dependent on the value of an applied axial electric field and that this dependence is asymmetric in the direction of the applied field. This result is interpreted in terms of excitation of coherent superpositions of different orbital angular momentum states of the $n = 3$ shell. The observed asymmetry is specifically related to superpositions of states of opposite parity which represent electronic charge distributions displaced with respect to the nuclear charge by the collision process. This work is related to results of beam foil spectroscopy in which observed beats are ascribed to coherent excitation at the foil. The interpretation of such observations of the effects of coherent excitation processes in terms of the dynamics of the collision processes greatly enhances our physical insight into such processes. The work of Mahan and his colleagues provides the first case of the extension of these ideas to binary collisions.

Observations of effects in the emission of radiation which can be attributed to coherent superpositions of states of the radiating atom are particularly intriguing because of the insight they may provide into the dynamics of excitation and radiation processes. The superposition of two nearly degenerate states, for example, of two states differing by a fine or hyperfine interaction energy, or of two different orbital angular momentum states in the same shell of atomic hydrogen, will in general represent a nonspherical charge

Stephen J. Smith • Joint Institute for Laboratory Astrophysics, National Bureau of Standards and University of Colorado, Boulder, Colorado 80302, U.S.A.
distribution which oscillates with a frequency $\Delta E/\hbar$. Thus the spontaneous radiation is anisotropic, and if the period of oscillation is comparable with or shorter than the radiative life of the atom, the observed emission (fluorescence) is modulated. The Hanle effect (Hanle, 1924; Hanle and Pepperl, 1971) is a familiar case in point. The precession of an aligned radiating atom is represented by a superposition of magnetic substrates separated by the Zeeman energy.

In 1965 Bashkin and his colleagues (Bashkin et al., 1965; Bickel and Bashkin, 1967) published an account of the first observations, carried out at the University of Arizona, of modulation effects in the radiation from hydrogen-like ions excited by passage through a thin carbon foil. Ions moving at velocities $\sim 4 \times 10^8 \text{ cm/sec}$ passed through the foil with interaction times of about $10^{-14} \text{ sec}$, very short compared to any periods associated with observable modulations in the radiation process. In the Arizona work, carried out with different ambient electric and magnetic field conditions, radiation in several spectral lines showed oscillations in intensity as a function of distance downstream from the foil, hence as a function of time $t$ of travel from the foil passage at $t = 0$, for an essentially monoenergetic beam.

Sellin and his colleagues from the University of Tennessee (Sellin et al., 1969a,b), working at Oak Ridge, carried out measurements a few years later which greatly clarified the role of external fields. Further clarification was provided in theoretical discussions by Macek (1969), in which he emphasized that oscillatory terms arise naturally in the absence of external fields. His calculation of light emission uses superpositions of states $u_{JM,j}$ excited at $t = 0$, i.e.,

$$\Psi(t) = \sum_{J,M,j} a_{JM,j} u_{JM,j} \exp \left[ -\left( \frac{\gamma_j}{2} + \frac{i E_j}{\hbar} \right) t \right]$$

Nonrandom initial phases may be implicit in the excitation amplitudes $a_{JM,j}$. The intensity of radiation to a lower state ($J = J_0$) is

$$\sum_{M_0} |\langle \Psi(t) | V_q | J_0 M_0 \rangle|^2$$

where $V_q$ is a component of the dipole operator. This includes cross terms

$$a_{JM,j} a_{J'M,j}^* \langle J_0 M_0 | V_q | J'M_j \rangle^* \langle J_0 M_0 | V_q | JM_j \rangle \exp \left[ i \left( \frac{E_j - E_{j'}}{\hbar} \right) t - \frac{(\gamma_j + \gamma_{j'})}{2} t \right]$$

This entire array of terms, averaged over the beam population, will be referred to here as the intensity matrix. The significant point is that each of the cross terms will average to zero unless $M_j = M_{j'}$, assuming axial
symmetry in the excitation process. Nonzero cross terms may occur in the intensity matrix, but only for superpositions of states that share the same axial component of angular moment, $M_J$, and only if the initial phases of those excited states are nonrandom. Such cross terms represent radiation from "coherent" superpositions of states.

Throughout this paper we assume that Russell–Saunders coupling holds. Then a further condition on nonzero cross terms in the intensity matrix is the radiation selection rule $\Delta L = \pm 1$, if we limit discussion to dipole-allowed transitions. Therefore, in a zero-field configuration, the only nonzero cross terms will be those involving two states of the same parity (orbital angular moment $L - L' = 0$, $\pm 2$) decaying to the same lower state. Such a superposition of states of the same parity is symmetric about a plane perpendicular to the beam direction at the nucleus. A nonspherical atom with this kind of symmetry is aligned along the beam axis. This represents one aspect of distortion of the atom by the beam foil interaction, but we see that collision dynamics having to do with relative displacement of electron cloud and nuclear charge centers is not represented in the information obtainable in a field-free experiment.

In order to emphasize a further distinction between types of coherent excitation it is useful to note that in view of the $10^{-14}$ sec time scale of the foil interaction, an uncoupled representation $(L, S, M_L, M_S)$ is appropriate for describing the excitation process. The amplitudes $a_{JM_J}$ are obtained by first calculating corresponding amplitudes $a_{LM_L,M_S}$ and transforming with appropriate Clebsch–Gordan coefficients. A matrix of the $a^*_{LM_L,M_S}, a_{LM_L,M_S}$ contains cross terms analogous to those of the intensity matrix, which also vanish with integration over the beam population unless $M_L = M_L'$ and $M_S = M_S'$. It can be seen at once that if $L = L'$ (and taking $S = S' = \frac{1}{2}$), the conditions $M_L = M_L'$ and $M_S = M_S'$ define a pure initial state and the result is trivial. Coherent excitation of a superposition of states does not occur. However, nonzero cross terms arise in the $J, M_J$ representation representing the evolution, from initial $M_L,M_S$ states, of spin–orbit coupled states for which $J \neq J'$ but for which $M_J = M_J'$. With averaging over the entire beam population, such cross terms are nonzero only if the excitation cross sections $\sigma_{M_L = \pm 1} \neq \sigma_{M_L = 0}$. The radiation must be anisotropic for the modulation to be observable. Thus, the zero-field beats observed by Andrä (1970) corresponded to fine-structure separation of states of the same orbital angular momentum and provided a demonstration of the alignment of excited states by the foil interaction. On the other hand, the first convincing demonstration of alignment involving coherent excitation at $t = 0$ of a superposition of distinct states in the $LS, LM_S$ representation was the observation of beats corresponding to energy intervals between pairs of $J, M_J$ states, $S_{1/2,1/2} - D_{3/2,1/2}$ and $S_{1/2,1/2} - D_{5/2,1/2}$, by Burns and Hancock (1971).
It remained to demonstrate observational effects of coherent excitation of superpositions representing charge polarization resulting from the collision process. The work I will describe here was carried out by H. Mahan as a part of his doctoral thesis project (Mahan, 1974; also Mahan et al., 1973), in collaboration with A. C. Gallagher and myself. R. V. Krotkov also made important contributions to the interpretation of the results.

This work was carried out in an apparatus (Figure 1) set up for the study of Balmer α excitation by electron impact on a thermal beam of atomic hydrogen. The immediate objective of this work was the separate determination, using time resolution, of the $S$, $P$, and $D$ excitation cross sections.

![Figure 1](image-url)  

**Figure 1.** The experimental configuration represented schematically. A thermally dissociated hydrogen beam intersects an electron beam in the field of view of an f1.2 optical system with photomultiplier detection (RCA C31034 cooled to dry ice temperature). Atom densities are about $6 \times 10^8$ atoms/cm³. Electron gun currents range from 10 to 50 μA in a beam 1–2 mm in diameter interacting with the atom beam over a path length of 4 mm. Signal count ranges from 40 to 400 counts/sec against a background $\sim 100$ counts/sec due to light from the hydrogen atom source, which operates at 2500°K to dissociate molecular hydrogen.
The ratios of these cross sections proved to be quite sensitive to electric field mixing, and a careful study of mixing effects was necessary as a basis for obtaining cross sections valid at zero field. Electrodes were installed to permit application of static electric fields in the interaction region along the electron beam axis and in two directions perpendicular to the beam axis. Balmer $\alpha$ intensity was measured along an axis perpendicular to the electron beam by a photomultiplier looking through a Balmer $\alpha$ interference filter.

![Diagram of relative Balmer-$\alpha$ intensity](image)

**Figure 2.** The effects on observed Balmer $\alpha$ emission due to mixing by an axial electric field are represented on the basis of two-state mixing equations and Born excitation cross sections, assuming noncoherent excitation. Hyperfine structure is neglected. In addition to the total, the combined contributions of pairs which are strongly mixed are shown separately. Radiation from the 3D$\frac{5}{2}$ state is shown constant in this approximation.
Figure 2 shows the result of a simple calculation of the Balmer $\alpha$ intensity as a function of electric field along the electron beam, based on two-state mixing equations and Born approximation excitation cross sections, and neglecting the possibility of coherent excitations. Because only $1/9$ of the $3P$ population radiates to the $n = 2$ level as indicated in Figure 3, the remainder going to the ground state, Stark-induced mixing of $P$ level populations into $D$ levels will increase the Balmer $\alpha$ radiation. Since the cross section for $P$ excitation is larger than that for $S$ and $D$ levels, and since $P-D$ mixing is relatively efficient, as indicated below, this effect determines the character of the predicted response.

The result of a measurement of the Balmer $\alpha$ intensity, as a function of applied electric field, is shown in Figure 4. Here the electron beam energy is 500 eV. (This is the average collision energy and has been corrected for the gain or loss of energy in the applied axial field.) Atomic deuterium was used to minimize hyperfine structure effects.

The interesting characteristic of this result is the pronounced asymmetry in the Balmer $\alpha$ response with respect to the direction of the applied electric field. This requires of the intensity matrix, rewritten with appropriate regard for Stark mixing, that it include terms linear in the electric field. These will necessarily be off-diagonal terms (the diagonal terms must be quadratic) and must involve pairs of states excited in nonrandom relative phase.

A glance at the level structure within the $n = 3$ shell, shown in Figure 5, gives a clear indication of what levels will dominate in the mixing process, and why the two-state mixing formulation is reasonable. The mixing

![Diagram](attachment:image.png)

Figure 3. The effects of mixing between the $S$, $P$, and $D$ levels of the $n = 3$ shell, as observed in the total Balmer $\alpha$ intensity, are due to net depopulation, by Stark mixing, of the $3P$ levels, which decay predominantly in Lyman $\beta$ lines (Bethe and Salpeter, 1957).
Figure 4. The intensity of Balmer $\alpha$ radiation, observed as indicated schematically in Figure 1, is plotted against applied electric field, normalized to the zero field intensity. The energy of the electron beam is compensated for the effect of the field applied in the interaction region. The results plotted are for deuterium. Similar results obtained using atomic hydrogen show a less pronounced asymmetry due to the more complex hyperfine structure.

Figure 5. The energy intervals (Garcia and Mack, 1965) within the $n = 3$ shell are represented, with the $P_{3/2}-D_{3/2}$ spacing necessarily exaggerated. Only mixing of the $P_{3/2,3/2}-D_{3/2,3/2}$, $P_{3/2,1/2}-D_{3/2,1/2}$, and $S_{1/2,1/2}-P_{1/2,1/2}$ pairs were considered in calculations of mixing effects.
coefficients have an inverse dependence on the separation of any given pair of states, so the very nearly degenerate pairs, notably the $P_{3/2} - D_{3/2}$ pair, should dominate. Furthermore, only states with the same axial projection of orbital angular momentum ($M_L$) and with opposite parity will have nonzero mixing coefficients.

It follows that the asymmetry observed in the Balmer $\alpha$ emission excited by electron impact is the result of coherent excitation of states of opposite parity, predominantly the $P_{3/2} - D_{3/2}, P_{3/2} - D_{3/2}, S_{1/2} - P_{1/2}$ pairs. As pointed out by Eck (1973), a coherent superposition of states of opposite parity implies a nonzero dipole moment. A calculation of the charge density

$$|\psi_{\text{even}} + \psi_{\text{odd}}|^2$$

yields cross terms that change sign across the plane transverse to the electron beam at the nucleus. The classical picture is of a collision-induced displacement of the electronic charge cloud along the axis of the electron beam. The cross terms oscillate with a frequency corresponding to the energy interval for a pair of states. In this classical context the role of the static external field is to superpose an additional displacement of the charge cloud, which increases or decreases the charge polarization of the upper state during the radiation period. This picture is particularly appropriate for nearly degenerate states such as the $P_{3/2} - D_{3/2}$ pair, for which the period corresponding to the energy difference (5 MHz) is long compared to the radiative lifetime.

In order to provide some verification for this interpretation of our observed asymmetry in Balmer $\alpha$ emission, Mahan (1974; Mahan et al., 1973) has carried out calculations of the emission as a function of applied electric field, following from the formulation of Percival and Seaton (1958), using Born excitation cross sections, by inserting terms to represent Stark mixing between excitation and spontaneous emission.

In this formulation the total intensity may be represented by

$$I_{\text{total}} = \int_0^\infty I(t) \, dt \sim \frac{1}{k_i^2} \int \sum_{\alpha, \tilde{\alpha}} \sum_{\gamma, \tilde{\gamma}} \int_0^\infty F_{\beta \gamma}(\alpha, \tilde{\alpha}, \tilde{\beta}, \tilde{\gamma}) A_{\beta \delta, \beta' \delta'}(E, t) G_{\gamma \delta}(\hat{\epsilon}) \, dt \, K \, dK \, d\phi$$

where $f_\beta(\alpha, \tilde{\alpha})$ is the scattering amplitude for excitation of an atom from an initial state $\alpha$ to an excited state $\beta$ by electron impact with a momentum change vector in the direction $\tilde{\alpha}$; $g_{\gamma \delta}(\hat{\epsilon})$ is the radiation matrix element giving the transition probability in sec$^{-1}$ for emission of an $\hat{\epsilon}$ photon by an atom in an excited state $\beta$ radiating into the final state $\gamma$; $F_{\beta \gamma}(\alpha, \tilde{\alpha}, \tilde{\beta}, \tilde{\gamma}) \sim f_\beta(\alpha, \tilde{\alpha}) f_\beta^*(\alpha, \tilde{\alpha})$, where these $JM_J$ scattering amplitudes have been calculated from the appropriate vector-coupled Born $LM_L$ excitation amplitudes where relative phases of excitation are carefully preserved: $A_{\beta \delta, \beta' \delta'}(E, t) \sim$
$a_{\rho \delta}(E, t) a_{\rho' \delta'}^*(E, t)$, where the appropriate $a_{\rho \gamma}(E, t) \sim a(t)$ are the amplitudes of states coupled by an external electric field; and $G_{\rho \gamma}(\theta) \sim g_{\rho \gamma}(\theta) g_{\rho' \gamma}^*(\theta)$ are the radiation matrix elements connecting these Stark-mixed $\delta$ levels and the final $n = 2$ levels resulting in $H\alpha$ radiation.

We considered only the three pairs of states with smallest $\Delta E$ mentioned above. This simple calculation, in which the quantum-mechanical phases are carefully followed through the mixing process, predicts an asymmetry and provides some insight into the details of the process. It fails at quantitative prediction of the asymmetry observed, and this may be attributed to the inadequacy of the Born approximation, which does not take into account the substantial charge polarization effect that evidently occurs. Krotkov (1975) has carried out a similar calculation with equivalent results.

Our observations relate to the dynamics of excitation to the $n = 3$ shell of hydrogen by electron impact. Some additional beam foil measurements have been carried out following the appearance of Eck's paper. These measurements demonstrate the longitudinal asymmetry of the atom excited by interaction with a foil. Sellin et al. (1973) applied an electric field parallel and antiparallel to a beam of foil-excited hydrogen atoms and observed the effects of the oscillating charge distribution in the Lyman $\alpha$ signal difference as a function of displacement from the foil. Gaupp et al. (1974) carried out similar measurements, and from the analysis of their data determined the density matrix for foil-excited hydrogen for several energies.

Finally, in a very recent paper, Berry et al. (1974) have shown from analysis of 5016 Å radiation that the surface direction of a foil has a large effect in beam foil excitation of helium atoms. In the plane determined by the surface normal $\hat{n}$ and the beam direction $\hat{z}$, the $3p$-excited electron has a preferential direction of rotation so that the orbital angular momentum is preferentially oriented in the direction $\hat{n} \times \hat{z}$.

From experiments such as these a body of information directly interpretable in terms of coherent excitation and the dynamics of the collision process is being developed which will greatly enhance our physical insight into such processes. The present experiment of Mahan et al. (1973) demonstrates that coherent excitation processes and corresponding dynamical concepts are important for the case of binary collisional excitation by electrons, as well as for the collective effects that occur in excitation by a beam foil.

Acknowledgment

This work was supported by the National Science Foundation through Grant No. GP-39308X.
References


