The Polarization of Atomic Line Radiation Excited by Electron Impact

I. C. Percival and M. J. Seaton

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THE POLARIZATION OF ATOMIC LINE RADIATION EXCITED BY ELECTRON IMPACT

By I. C. PERCIVAL and M. J. SEATON
Department of Physics, University College London

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The dipole radiation emitted by an atom excited by a unidirectional electron beam has a non-uniform angular distribution which is simply related to the percentage polarization P of the radiation emitted perpendicular to the beam. P was first calculated using the Oppenheimer–Penney (O.-P.) theory. In this theory the probability of excitation of an upper quantum state and the probability of subsequent emission of a polarized photon from such a state are considered independently.

P is finally expressed in terms of the cross-sections $Q_{|M_L|}$ for excitation of states of definite component of angular momentum along the direction of the electron beam. In general, P is dependent on detailed numerical calculations of $Q_{|M\ |}$, but the selection rule $\Delta M_L = 0$ removes this dependence at threshold.

In the O.-P. theory allowance may be made for fine structure and hyperfine structure, but the theory is ambiguous when the f.s. or h.f.s. separations are comparable with the line width. A theory is therefore developed which is based on the calculation of the probability of a polarized photon being emitted by the complete system of atom + electron. The ambiguity of the O.-P. theory is removed by integration over line profiles, but the expressions reduce to O.-P. expressions when the f.s. or h.f.s. separations are much smaller or much larger than the line width. The *Ly*α line of hydrogen is an intermediate case for which the line widths and the h.f.s. separations are comparable.

Assuming the validity of the Born approximation, a simple expression is obtained which allows the $Q_{|M_L|}$ to be calculated from the angular distribution of the scattered electrons.

Theoretical predictions are compared with experimental results. For the Na*D* lines the predicted polarization is small enough to escape experimental detection. Polarizations observed by Skinner & Appleyard in 1927 for various Hg lines rise to maxima with decreasing electron energy, and then tend to values close to zero at threshold. These experimental results at low energies appear to be inexplicable in terms of the reactions considered, but if the polarization curve above the maximum is extrapolated to threshold, the theory and experiment are found to be in reasonable agreement. Further experimental work is thought to be desirable.

1. INTRODUCTION

Atomic line radiation excited by an electron beam will, in general, be polarized and will have an anisotropic angular distribution. If the beam is in the Oz-direction the radiation may be considered to be due to an electric dipole in the Oz-direction and two electric dipoles of equal strength in the Ox and Oy-directions. Let $I(\theta)$ be the radiation intensity per unit solid angle in a direction making an angle θ with Oz and let $I^{\parallel}$ and $I^{\perp}$ be the intensities, in a direction perpendicular to Oz, with electric vectors respectively parallel and perpendicular to Oz. The percentage polarization is defined by

$$P = \frac{100(I^{\parallel} - I^{\perp})}{I^{\parallel} + I^{\perp}}. \tag{1·1}$$

Using the fact that the intensity of dipole radiation, in a direction making an angle χ with the dipole axis, is proportional to $\sin^2\chi$ one obtains

$$I(\theta) = \bar{I}\left[\frac{3(100 - P\cos^2\theta)}{300 - P}\right]. \tag{1·2}$$

The total intensity, integrated over all angles, is $4\pi\bar{I}$. The polarization P may therefore be determined either by measuring $I^{\parallel}$ and $I^{\perp}$ or by obtaining the photon angular distribution $I(\theta)$ (Smit 1935). In order to determine absolute cross-sections by optical methods the quantity $\bar{I}$ must be determined. To do this one may combine measurements of P with an absolute measurement of $I(\theta)$ for any one direction.

Experimental determinations of P for a number of cases were made about 30 years ago.† Since that time little experimental work of this type has been attempted but a recent

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† Kossel & Gerthsen (1925) (Na); Skinner (1926) (Hg); Ellett, Foote & Mohler (1926) (Hg and Na); Eldridge & Olson (1926) (Hg); Quarder (1927) (Hg); Skinner & Appleyard (1927) (Hg); Steiner (1928) (He and Ne); Hanle & Quarder (1929) (Ne); Smit (1935) (He).

revival of interest in the subject has resulted from the possibility of using polarization measurements in conjunction with microwave studies (Dehmelt 1956; Lamb 1957; Lamb & Maiman 1957).

The theory of polarization of impact radiation was first developed by Oppenheimer (1927*a*, *b*, 1928). The essential idea is to calculate the probabilities of exciting individual quantum states and the probabilities of emission of polarized photons in transitions from these states. The first attempt at detailed calculation was made by Penney (1932) who showed that it was necessary to allow not only for electron spin and fine structure (f.s.) but also for nuclear spin and hyperfine structure (h.f.s.). The theory developed by Oppenheimer and by Penney will be referred to as the O.-P. theory. (For previous discussion of this theory see Bethe (1933) and Lamb (1957).)

We distinguish three atomic energy levels: an *initial* level *a* (usually the ground level), an *upper* level *b* populated after collision and before photon emission, and the *final* level *c* reached after photon emission. We assume the experimental conditions to be such that there is a completely isotropic distribution of spin directions in the incident beam and in the initial states of the atom.

To simplify the discussion we also assume that the initial level of the atom has zero orbital angular momentum. The anisotropy of the problem is then introduced entirely through that of the motion of the incident electron. One calculates cross-sections for exciting quantum states of the upper level with definite orbital angular momentum component M_L, the quantization axis being in the direction of the incident beam. If the upper level has well defined f.s. and possibly h.f.s. the upper states must be described in a representation in which spin and orbital angular momenta are coupled. One must therefore develop the algebraic theory required to express cross-sections for excitation of vector-coupled states in terms of those for excitation of M_L states. The corresponding algebraic theory required for the radiative transition probabilities is well known (Condon & Shortley 1951); we shall find it convenient to use expressions in a form obtained by using tensor operator methods (Racah 1942, 1943).

The interaction producing the collisional transition is assumed to be such that total spin and total orbital angular momenta are separately conserved. Since the total component of orbital angular momentum is assumed to be zero the angular momentum of the scattered electron, after exciting the upper state M_L, must be equal to $-M_L\hbar$. This rule enables us to calculate the threshold polarization. At the excitation threshold the scattered electron has zero velocity and hence zero orbital angular momentum and therefore only states with $M_L = 0$ can be excited. (A formal proof may be obtained by the method of Wigner (1948).) Threshold polarizations can therefore be calculated without detailed calculation of cross-sections. At energies above the threshold comparison of theory and experiment should provide a sensitive test of the accuracy of calculated cross-sections. In the limit of high energies the relative cross-sections for excitation of various M_L states may be obtained using Born's approximation (in cases for which no change of atom spin occurs during the collision). The high-energy results are of less interest, however, since appreciable population of the upper level by cascade transitions makes comparison with experiment more difficult.

The polarization and angular distribution of emitted photons is related to the angular distribution of scattered electrons. Thus, if the angular distribution of the electrons is isotropic the polarization must be equal to its threshold value. Assuming the validity of Born's approximation a simple relation between polarization and electron angular distribution may be obtained (§ 6·1).

Since we assume that there are no preferred spin directions the complete system becomes more isotropic when additional spin variables are included. Thus, the calculated polarization for an isotope with nuclear spin is generally smaller than that for an isotope of the same chemical element without nuclear spin. It is shown, however, that uncertainty arises in the application of the O.-P. theory if there is doubt about the manner of specifying quantum states. Such uncertainties arise whenever the f.s. or h.f.s. splittings are of a magnitude comparable with the natural line widths, and in the limit of vanishingly small f.s. or h.f.s. separations the O.-P. theory fails to give unambiguous predictions (§ 3·7). A re-examination of the fundamental ideas of the theory appeared desirable, first, because the h.f.s. separations for excited states of hydrogen are less than the line widths, and, secondly, because certain experimental results for Hg are not consistent with theoretical predictions (§ 7·3). Our approach (first suggested to us by Mr L. Castillejo) (§ 4) is to consider the probabilities of photons of definite polarization being emitted by the entire system of atom and colliding electron. Allowing for radiation damping we obtain an expression involving integrals over the line profiles. The O.-P. expressions with h.f.s. are then obtained when there is negligible overlap between the profiles of the h.f.s. components and the O.-P. expressions calculated with neglect of nuclear spin are obtained when the h.f.s. profiles overlap completely. The polarization may also be calculated for intermediate cases.

Although some features of the observed results for Hg are shown to be in satisfactory agreement with theory (§ 7·3), we are unable to offer a theoretical explanation of the fact that the observed polarizations of a number of lines appear to go to zero at excitation thresholds. It is considered that the experiments should be repeated using modern techniques.

2. The Oppenheimer–Penney theory

2·1. *Radiative transition probabilities*

Let b represent either a simple energy level or a group of closely spaced energy levels and denote the quantum states of b by ψ_β; the number of such states is equal to the statistical weight ω_b of b. Let c represent a second level or group of levels with states ψ_γ. And let ξ stand for x, y or z. Photons having polarization and directional distribution characteristic of the emission by an electric dipole lying in the ξ-direction will be referred to as ξ-photons. The probability per unit time of an atom in state β undergoing the transition $\beta \rightarrow \gamma$ with emission of a ξ-photon is

$$A_\xi(\beta \rightarrow \gamma) = C(\nu_{bc}) \mid (\gamma \mid \xi \mid \beta) \mid^2, \tag{2·1}$$

where

$$C(\nu) = \frac{64\pi^4 e^2 \nu^3}{3hc^3} \tag{2·2}$$

and where $h\nu_{bc} = E_b - E_c$. We here neglect possible energy differences within b or c, assuming such differences to be much smaller than $h\nu_{bc}$. The total probability of emission of a ξ-photon of frequency ν_{bc} in transition from β is

$$A_\xi(\beta) = \sum_\gamma A_\xi(\beta \rightarrow \gamma). \tag{2·3}$$

The total probability of emission of a photon of frequency ν_{bc}, obtained on summing (3) over ξ, is the same for all quantum states β of b. We therefore put

$$A(b) = \sum_{\xi} A_{\xi}(\beta). \tag{2·4}$$

2·2. *The percentage polarization*

For light propagated in the Ox-direction let $I^{\perp}$ and $I^{\parallel}$ be the intensities with electric vector, respectively, perpendicular and parallel to Oz. Then

$$I^{\perp} = D \sum_{\beta} n(\beta)\, A_y(\beta) \tag{2·5}$$

and

$$I^{\parallel} = D \sum_{\beta} n(\beta)\, A_z(\beta), \tag{2·6}$$

where $n(\beta)$ is the number density of atoms in state β and D is a constant. The percentage polarization is

$$P = 100\frac{I^{\parallel}-I^{\perp}}{I^{\parallel}+I^{\perp}}. \tag{2·7}$$

Assuming symmetry about Oz we have $A_x = A_y = \frac{1}{2}(A-A_z)$ and $\bar{I} = I^{\parallel}+2I^{\perp}$, where

$$\bar{I} = Dn(b)\, A(b) \tag{2·8}$$

and

$$n(b) = \sum_{\beta} n(\beta). \tag{2·9}$$

The expression for the polarization may therefore be written

$$P = 100\frac{3I^{\parallel}-\bar{I}}{I^{\parallel}+\bar{I}}. \tag{2·10}$$

2·3. *Calculation of populations and of rate coefficients*

Suppose that a beam of electrons with electron number density $n(e)$ and velocity v_a is incident on atoms in level a and that the number density $n(\alpha)$ of atoms in quantum states α of a is the same for all α. Assume that the states β are excited only by collisional transitions from a and that they are depopulated only by radiative transitions to c. We denote the cross-sections for $\alpha \to \beta$ transitions by $Q(\alpha \to \beta)$ and put

$$Q(\beta) = \omega_a^{-1} \sum_{\alpha} Q(\alpha \to \beta). \tag{2·11}$$

The rate of transitions to β is then $n(e)\, n(a)\, K(\beta)$, where the *rate coefficient* $K(\beta)$ is

$$K(\beta) = v_a Q(\beta). \tag{2·12}$$

Equating the number entering β to the number leaving, which is $A(b)\, n(\beta)$, we obtain

$$n(\beta) = \frac{n(e)\, n(a)\, K(\beta)}{A(b)}. \tag{2·13}$$

The rate of emission of ξ-photons from β is

$$n(\beta)\, A_{\xi}(\beta) = n(e)\, n(a)\, K_{\xi}(\beta), \tag{2·14}$$

where the rate coefficient is

$$K_{\xi}(\beta) = \frac{A_{\xi}(\beta)}{A(b)} v_a Q(\beta). \tag{2·15}$$

The total rate coefficient for emission of ξ-photons is

$$K_\xi = \sum_\beta K_\xi(\beta) = \frac{v_a}{A} \sum_\beta A_\xi(\beta)\, Q(\beta) \tag{2·16}$$

and the total rate coefficient for emission of all photons is

$$K = \sum_\xi K_\xi = v_a Q, \tag{2·17}$$

where

$$Q = \sum_\beta Q(\beta). \tag{2·18}$$

The radiation intensity being proportional to the rate coefficient, we have in place of (2·10)

$$P = 100\,\frac{3K_z - K}{K_z + K}. \tag{2·19}$$

3. Expressions for the polarization

3·1. *Angular momentum conservation*

In order to apply the O.-P. theory we require cross-sections for excitation of the various quantum states of the upper level. We consider the LS coupling representations

$$\beta = \Delta S L M_S M_L \tag{3·1}$$

for the upper states, and

$$\alpha = \Delta' S' L' M'_S M'_L \tag{3·2}$$

for the initial states. We here use Δ and Δ' to denote all quantum numbers other than those specifying the angular momenta; for brevity the quantum numbers Δ and Δ' will be omitted in most of the following discussion.

To calculate the cross-section $Q(SLM_SM_L)$ we average over spins m'_s of the incident electron and sum over spins m_s of the scattered electron. We then have

$$Q(SLM_SM_L) = \frac{v_b}{v_a}\,\frac{1}{2(2S'+1)\,(2L'+1)} \sum_{M'_S M'_L m_s m'_s} \int |\, f_{SLM_SM_Lm_s}(S'L'M'_SM'_Lm'_s\mathbf{k}_a \,|\, \hat{\mathbf{k}}_b)|^2\, \mathrm{d}\omega(\hat{\mathbf{k}}_b), \tag{3·3}$$

where $f_{\beta m_s}$ is the *scattering amplitude* (which is defined in terms of the asymptotic form of the wave function in § 4·2) and where the integration is over all directions $\hat{\mathbf{k}}_b$ of the scattered electrons. The incident electron is in the direction of the vector $\hat{\mathbf{k}}_a$.

We now make two simplifying assumptions: (i) The interaction potential producing the transition is assumed not to involve spin co-ordinates and (ii) the initial state α is assumed to have zero orbital angular momentum (i.e. we put $L' = 0$). The first of these gives us the spin conservation condition

$$M_S + m_s = M'_S + m'_s.$$

Since orbital and spin angular momenta are separately conserved and since there is no preferred spin direction, $Q(SLM_SM_L)$ is independent of M_S. Furthermore, owing to symmetry about Oz, $Q(SLM_SM_L)$ does not depend on the sign of M_L. We may therefore put

$$Q(SLM_SM_L) = (2S+1)^{-1}\, Q_{|M_L|}, \tag{3·4}$$

giving

$$Q(SL) = \sum_{M_L} Q_{|M_L|}. \tag{3·5}$$

To obtain the conservation condition for orbital angular momentum we use the expansion

$$f_{\beta m_s}(\alpha m_s' \mathbf{k}_a \,|\, \hat{\mathbf{k}}_b) = \sum_{l m_l} Y_{lm}(\hat{\mathbf{k}}_b)\, f(\beta l m_s m_l, \alpha m_s' \mathbf{k}_a), \tag{3·6}$$

where Y_{lm_l} is a normalized spherical harmonic. Taking $\mathbf{k}_a$ to be in the direction of the quantization axis Oz the initial total orbital angular momentum in the Oz-direction is zero and the conservation condition is therefore

$$M_L + m_l = 0. \tag{3·7}$$

The two conservation conditions give us the relation

$$\frac{v_b}{v_a}\frac{1}{2(2S'+1)} \sum_{\alpha m_s m_s'} \int f^*_{\beta m_s}(\alpha m_s' \mathbf{k}_a \,|\, \hat{\mathbf{k}}_b)\, f_{\beta^0 m_s}(\alpha m_s' \mathbf{k}_a \,|\, \hat{\mathbf{k}}_b)\, \mathrm{d}\omega(\hat{\mathbf{k}}_b) = \delta(\beta, \beta^0)\, Q(\beta), \tag{3·8}$$

where $\beta = SLM_SM_L$ and $\beta^0 = SLM_S^0M_L^0$.

3·2. *Cross-sections for fine-structure levels*

With a weak spin-orbit interaction we use, in place of (3·1), the representation

$$\beta = SLJM_J. \tag{3·9}$$

The transformation relation for the scattering amplitude is

$$f_{SLJM_Jm_s} = \sum_{M_SM_L} C^{S\ L\ J}_{M_S M_L M_J}\, f_{SLM_SM_Lm_s}, \tag{3·10}$$

where C is a vector coupling or Clebsch–Gordan coefficient. Using (3·8) we obtain the cross-section transformation relation

$$Q(SLJM_J) = \sum_{M_SM_L} (C^{S\ L\ J}_{M_S M_L M_J})^2\, Q(SLM_SM_L). \tag{3·11}$$

It should be emphasized that this relation is valid only so long as LS coupling may be assumed and so long as the initial state of the atom has zero orbital angular momentum.

The cross-section for excitation of the level SLJ is obtained in summing (3·11) over M_J. Using (3·4) and the relation

$$\sum_{m_1 m} C^{j_1\ j_2\ j}_{m_1 m_2 m}\, C^{j_1\ j_2'\ j}_{m_1 m_2' m} = \frac{2j+1}{2j_2+1}\,\delta_{j_2 j_2'}\delta_{m_2 m_2'} \tag{3·12}$$

(Racah 1942), we obtain

$$Q(SLJ) = \frac{2J+1}{(2S+1)(2L+1)}\, Q(SL). \tag{3·13}$$

It is seen that the cross-sections for excitation of the levels SLJ are proportional to the statistical weights $(2J+1)$.

3·3. *Cross-sections for hyperfine-structure levels*

The representation for h.f.s. states is

$$\beta = SLJIFM_F, \tag{3·14}$$

where I is the nuclear spin and F the resultant of J and I. For the cross-sections we could use the transformation

$$Q(SLJIFM_F) = (2I+1)^{-1} \sum_{M_JM_I} (C^{J\ I\ F}_{M_J M_I M_F})^2\, Q(SLJM_J). \tag{3·15}$$

It is convenient to consider the representation

$$\beta = SITLM_T M_J, \tag{3·16}$$

in which S and I are coupled to give a total atomic spin angular momentum T. In this representation we have

$$Q(SITLM_T M_L) = \frac{1}{(2S+1)(2I+1)} Q_{|M_L|}. \tag{3·17}$$

The representations (3·14), (3·16) are related by the transformation

$$(SITLM_T M_L \,|\, SLJIFM_F) = C^{T\;L\;F}_{M_T M_L M_F}(SI(T)\,LF \,|\, SL(J)\,IF), \tag{3·18}$$

where $$(SI(T)\,LF \,|\, SL(J)\,IF) = [(2T+1)(2J+1)]^{\frac{1}{2}}(-1)^{F+S-T-J}\,W(SLIF;\,JT) \tag{3·19}$$

(Racah 1943, equation (5)), W being a Racah coefficient.† We then have

$$Q(SLJIFM_F) = \frac{2J+1}{(2S+1)(2I+1)} \sum_{TM_T M_L} (2T+1)\,[W(SLIF;\,JT)\,C^{T\;L\;F}_{M_T M_L M_F}]^2\, Q_{|M_L|}. \tag{3·20}$$

3·4. *Transition probability transformation relations*

The transformation relations are obtained in the most convenient form on expressing the transition probabilities in terms of matrix elements of the tensor operator $\mathbf{T}_1$ with components‡

$$T_{1\mu} = \sum_i r_i C_{1\mu}(\hat{\mathbf{r}}_i), \tag{3·21}$$

where the sum is over all atomic electrons and where

$$C_{\lambda\mu}(\hat{\mathbf{r}}) = \left(\frac{4\pi}{2\lambda+1}\right)^{\frac{1}{2}} Y_{\lambda\mu}(\hat{\mathbf{r}}), \tag{3·22}$$

$Y_{\lambda\mu}$ being a normalized spherical harmonic. Putting

$$A^{(\mu)}(\beta\to\gamma) = C(\nu_{bc})\,|\,(\gamma\,|\,T_{1\mu}\,|\,\beta)\,|^2, \tag{3·23}$$

we have for electric dipole transitions

$$A_z(\beta\to\gamma) = A^{(0)}(\beta\to\gamma) \tag{3·24}$$

and $$A(\beta\to\gamma) = \sum_\mu A^{(\mu)}(\beta\to\gamma). \tag{3·25}$$

Since $\mathbf{T}_1$ does not operate on spin variables we have

$$A_z(SLM_S M_L \to S''L'') = \delta(S, S'')\,\delta(M_L, O)\,A(SL\to SL''). \tag{3·26}$$

For transitions between two states JM_J, $J''M''_J$ we have, using the theory of tensor operators (Racah 1942, equation (29))

$$A^{(\mu)}(JM_J\to J''M''_J) = (C^{J''\;1\;\;J}_{M''_J\,-\mu\,M_J})^2\,A(J\to J''), \tag{3·27}$$

where $$A(J\to J'') = \sum_{M''_J\mu} A^{(\mu)}(JM_J\to J''M''_J). \tag{3·28}$$

It should be emphasized that the quantum numbers SL, $S''L''$ do not occur in these expressions. Equations (3·27), (3·28) may therefore be used for intercombination electric dipole transitions which can occur only if there are departures from LS coupling.

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† Tables of these coefficients are available (Simon, Vander Sluis & Biedenharn 1954; Obi *et al.* 1953).

‡ We consider, in effect, the matrix elements of $(x\pm iy)/\sqrt{2}$ and of z instead of those of x, y and z.

In order to calculate the polarization of the total light in an optically allowed multiplet $SL \rightarrow SL''$, assuming the lines of the multiplet to be unresolved, it is necessary to know the relative values of the transition probabilities $A(SLJ \rightarrow SL''J'')$. Using tensor operator methods (Racah 1942, § 5) the required relation is obtained in the form

$$A(SLJ \rightarrow SL''J'') = (2L+1)\,(2J''+1)\,W^2(LJL''J'';\,S1)\,A(SL \rightarrow SL''), \tag{3·29}$$

where W is a Racah coefficient.

For transitions between h.f.s. states we obtain in a similar way

$$\left.\begin{aligned} A^{(\mu)}(JIFM_F \rightarrow J''IF''M''_F) &= (C^{F''\,1\,F}_{M''_F\,-\mu\,M_F})^2\,A(JIF \rightarrow J''IF''),\\ A(JIF \rightarrow J''IF'') &= (2J+1)\,(2F''+1)\,W^2(JFJ''F'';\,I1)\,A(J \rightarrow J'').\end{aligned}\right\} \tag{3·30}$$

3·5. *Expressions for the polarization without h.f.s.*

We continue to assume an initial state with $L' = 0$. With an upper state SLJ and a final state J'' we have

$$K_z(SLJ \rightarrow J'') = \frac{v_a A(SLJ \rightarrow J'')}{(2S+1)\,A(SLJ)} \sum_{M_S M_L M_J} [C^{S\,L\,J}_{M_S M_L M_J}\,C^{J''\,1\,J}_{M''_J\,0\,M_J}]^2\,Q_{|M_L|}, \tag{3·31}$$

$$K(SLJ \rightarrow J'') = \frac{v_a A(SLJ \rightarrow J'')}{(2S+1)\,A(SLJ)}\,\frac{2J+1}{2L+1} \sum_{M_L} Q_{|M_L|}. \tag{3·32}$$

For the total light in the multiplet $SL \rightarrow SL''$ we have

$$K_z(SL \rightarrow SL'') = \frac{v_a A(SL \rightarrow SL'')}{(2S+1)\,A(SL)}\,(2L+1) \sum_{JJ''M_S M_L M_J} (2J''+1)\,[C^{S\,L\,J}_{M_S M_L M_J}\,C^{J''\,1\,J}_{M''_J\,0\,M_J}\,W(LJL''J'';\,S1)]^2\,Q_{|M_L|}, \tag{3·33}$$

$$K(SL \rightarrow SL'') = \frac{v_a A(SL \rightarrow SL'')}{(2S+1)\,A(SL)} \sum_{M} Q_{|M\ |}. \tag{3·34}$$

These formulae are of interest for He, which has zero nuclear spin, and for Hg isotopes having zero nuclear spin. We therefore consider the atomic spin S to be 0 or 1. With upper states for which $L = 0$ the polarization is always zero in LS coupling. For upper P states ($L = 1$) the polarization formula may be written

$$P = 100\,\frac{G(Q_0 - Q_1)}{h_0 Q_0 + h_1 Q_1} \tag{3·35}$$

and for upper D states ($L = 2$)

$$P = 100\,\frac{G(Q_0 + Q_1 - 2Q_2)}{h_0 Q_0 + h_1 Q_1 + h_2 Q_2}. \tag{3·36}$$

The coefficients G, h_0, h_1 and h_2 are given in tables 1 and 2.

3·6. *Expressions for the polarization of* ${}^2\mathrm{P} \rightarrow {}^2\mathrm{S}$ *transitions with h.f.s.*

Particular interest attaches to the *Lyα* line of hydrogen and to the resonance lines of the alkali metals. We therefore consider the case of an initial ^{2}S state, an upper ^{2}P state and a final ^{2}S state.

From the unitary character of the transformation (3·18) we have

$$\sum_{TM_T M_L} (2T+1)\,(2J+1)\,W^2(SLIF;\,JT)\,(C^{T\,L\,F}_{M_T M_L M_F})^2 = 1. \tag{3·37}$$

With $L = 1$, $S = \frac{1}{2}$ the cross-section expression (3·20) may therefore be written

$$Q(^2\mathrm{P}, JIFM_F) = \frac{1}{2(2I+1)}\{\tau(\tfrac{1}{2}1JIFM_F)\,Q_0 + [1-\tau(\tfrac{1}{2}1JIFM_F)]\,Q_1\}, \tag{3·38}$$

with

$$\tau(\tfrac{1}{2}1JIFM_F) = \sum_T (2T+1)\,(2J+1)\,[W(\tfrac{1}{2}1IF;\,JT)\,C^{T\,I\,F}_{M_F 0 M_F}]^2. \tag{3·39}$$

TABLE 1. POLARIZATION FORMULAE FOR He LINES $SLJ \rightarrow J'$

$$P(S0J\rightarrow J') = 0, \quad P(S1J\rightarrow J') = 100\,\frac{G(Q_0-Q_1)}{h_0Q_0+h_1Q_1}, \quad P(S2J\rightarrow J') = 100\,\frac{G(Q_0+Q_1-2Q_2)}{h_0Q_0+h_1Q_1+h_2Q_2}$$

SLJ	J'	G	h_0	h_1	h_2
011	0	1	1	1	—
	1	−1	1	3	—
	2	1	7	13	—
022	1	3	5	9	6
	2	−3	3	7	10
	3	3	15	29	26
110	1	0	—	—	—
111	0	−1	1	3	—
	1	1	3	5	—
	2	−1	13	27	—
112	1	21	47	73	—
	2	−7	11	29	—
	3	1	7	13	—
121	0	3	5	9	6
	1	−3	7	15	18
	2	3	41	81	78
122	1	3	9	17	14
	2	−3	7	15	18
	3	3	29	57	54
123	2	18	41	76	58
	3	−9	11	25	34
	4	3	15	29	26

TABLE 2. POLARIZATION FORMULAE FOR He MULTIPLETS $SL \rightarrow SL'$

$$P(S0\rightarrow S1) = 0, \quad P(S1\rightarrow SL') = 100\,\frac{G(Q_0-Q_1)}{h_0Q_0+h_1Q_1}, \quad P(S2\rightarrow SL') = 100G(Q_0+Q_1-2Q_2)$$

SL	L'	G	h_0	h_1	h_2
01	0	1	1	1	—
	2	1	7	13	—
02	1	3	5	9	6
	3	3	15	29	26
11	0	15	41	67	—
	2	3	73	143	—
12	1	213	671	1271	1058
	3	213	2171	4271	4058

The transition probabilities are given by†

$$A_z(^2\mathrm{P}, JIFM_F \rightarrow {}^2\mathrm{S}) = \tau(\tfrac{1}{2}1JIFM_F)\,A, \tag{3·40}$$

where $A = A(^2\mathrm{P}\rightarrow{}^2\mathrm{S})$. We therefore have

$$K_z(^2\mathrm{P}_J \rightarrow {}^2\mathrm{S}) = \frac{v_a}{2(2I+1)} \sum_{FM_F} \tau(\tfrac{1}{2}1JIFM_F)\,\{Q_1 + \tau(\tfrac{1}{2}1JIFM_F)\,(Q_0-Q_1)\}. \tag{3·41}$$

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† This may be obtained on putting $L'' = 0$, $S = \frac{1}{2}$ in (3·29) and (3·30), or may be obtained directly using the transformation (3·18).

Using (3·12) and the unitary relation for the transformation (3·19) we have

$$\sum_{FM_F} \tau(\tfrac{1}{2}1JIFM_F) = (2J+1)\,(2I+1) \tag{3·42}$$

and therefore

$$K_z(^2\mathrm{P}_J\rightarrow {}^2\mathrm{S}) = \frac{v_a}{2(2I+1)}\{(2J+1)\,(2I+1)\,Q_1+\mu(\tfrac{1}{2}1JI)\,(Q_0-Q_1)\}, \tag{3·43}$$

with
$$\mu(\tfrac{1}{2}1JI) = \sum_{FM_F}[\tau(\tfrac{1}{2}1JIFM_F)]^2. \tag{3·44}$$

Using
$$K(^2\mathrm{P}_J\rightarrow {}^2\mathrm{S}) = \frac{2J+1}{6}\{2Q_1+Q_0\}, \tag{3·45}$$

the polarization formula is found to be

$$P(^2\mathrm{P}_J\rightarrow {}^2\mathrm{S}) = \frac{100[9\mu(\tfrac{1}{2}1JI)-(2I+1)\,(2J+1)]\,(Q_0-Q_1)}{[3\mu(\tfrac{1}{2}1JI)+(2I+1)\,(2J+1)]\,Q_0+3[(2I+1)\,(2J+1)-\mu(\tfrac{1}{2}1JI)]\,Q_1}. \tag{3·46}$$

Table 3. Polarization formulae for $^2\mathrm{P}_J\rightarrow {}^2\mathrm{S}$ transitions

$$P(^2\mathrm{P}_{\frac{1}{2}}\rightarrow {}^2\mathrm{S}) = 0, \quad P(^2\mathrm{P}_{\frac{3}{2}}\rightarrow {}^2\mathrm{S}) = 100\,\frac{G(Q_0-Q_1)}{h_0Q_0+h_1Q_1}$$

I	G	h_0	h_1	$P_0(^2\mathrm{P}_{\frac{3}{2}}\rightarrow {}^2\mathrm{S})$	$P_\infty(^2\mathrm{P}_{\frac{3}{2}}\rightarrow {}^2\mathrm{S})$
0	3	5	7	60·0	−42·9
$\frac{1}{2}$	15	37	59	40·5	−25·4
1	33	161	289	20·5	−11·4
$\frac{3}{2}$	81	427	773	19·0	−10·5

Table 4. Polarization formulae for $^2\mathrm{P}\rightarrow {}^2\mathrm{S}$ multiplets

$$P(^2\mathrm{P}\rightarrow {}^2\mathrm{S}) = 100\,\frac{G(Q_0-Q_1)}{h_0Q_0+h_1Q_1}$$

I	G	h_0	h_1	$P_0(^2\mathrm{P}\rightarrow {}^2\mathrm{S})$	$P_\infty(^2\mathrm{P}\rightarrow {}^2\mathrm{S})$
0	3	7	11	42·9	−27·3
$\frac{1}{2}$	15	53	91	28·3	−16·5
1	33	236	439	14·0	− 7·5
$\frac{3}{2}$	27	209	391	12·9	− 6·9

To obtain the polarization for the total light from the $^2\mathrm{P}\rightarrow {}^2\mathrm{S}$ multiplet we sum (3·43) and (3·45) over J. We obtain

$$P(^2\mathrm{P}\rightarrow {}^2\mathrm{S}) = \frac{100[9\mu(\tfrac{1}{2}1I)-6(2I+1)]\,(Q_0-Q_1)}{[3\mu(\tfrac{1}{2}1I)+6(2I+1)]\,Q_0+3[6(2I+1)-\mu(\tfrac{1}{2}1I)]\,Q_1} \tag{3·47}$$

with
$$\mu(\tfrac{1}{2}1I) = \sum_J \mu(\tfrac{1}{2}1JI). \tag{3·48}$$

For purposes of tabulation the polarization formulae are conveniently written as in equation (3·35).

The coefficients have been evaluated for $I = 0, \frac{1}{2}, 1$ and $\frac{3}{2}$. For all cases it is found that $P(^2\mathrm{P}_{\frac{1}{2}}\rightarrow {}^2\mathrm{S})$ is zero. The coefficients G, h_0 and h_1 for $P(^2\mathrm{P}_{\frac{3}{2}}\rightarrow {}^2\mathrm{S})$ are given in table 3 and those for $P(^2\mathrm{P}\rightarrow {}^2\mathrm{S})$ are given in table 4. We include values of P_0, the threshold polarization $((Q_1/Q_0) = 0)$, and of P_∞, the polarization in the limit of high energy, neglecting cascade $((Q_1/Q_0)\rightarrow\infty)$.

3·7. *The O.-P. theory and the principle of spectroscopic stability*

The requirement of the principle of spectroscopic stability is that quantum mechanical expressions for observable quantities should be independent of the choice of representation. Thus, in the expression for the polarization the same results should be obtained using either one of two different representations so long as both diagonalize the energy matrix for the atom. It will be shown that the O.-P. theory does not always satisfy this requirement.

Consider first the case of $^2\mathrm{P}\rightarrow{}^2\mathrm{S}$ transitions with $I = 0$. If the spin-orbit and relativistic energy is sufficiently large to give two completely separate f.s. levels we may use the representation†

$$\beta = {}^2\mathrm{P}, JM_J. \tag{3·49}$$

We then have

$$K_z = \frac{v_a}{2}\sum_{M_S M_L J M_J}[C^{\frac{1}{2}\ 1\ J}_{M_S M_L M_J}\, C^{\frac{1}{2}\ 1\ J}_{M_J\ 0\ M_J}]^2\, Q_{|M_L|}, \tag{3·50}$$

which gives

$$P(^2\mathrm{P}\rightarrow{}^2\mathrm{S}) = \frac{300(Q_0-Q_1)}{7Q_0+11Q_1}. \tag{3·51}$$

But the magnitude of the f.s. energy does not appear in the O.-P. theory. In the limit of vanishingly small f.s. energy one should be able to use either the representation (3·49) or the representation

$$\beta = {}^2\mathrm{P}, M_S M_L. \tag{3·52}$$

The second of these gives, in consequence of (3·4) and (3·26)

$$K_z(^2\mathrm{P}\rightarrow{}^2\mathrm{S}) = v_a Q_0 \tag{3·53}$$

and

$$P(^2\mathrm{P}\rightarrow{}^2\mathrm{S}) = 100\,\frac{Q_0-Q_1}{Q_0+Q_1}. \tag{3·54}$$

The O.-P. theory therefore fails to give unambiguous results in the limit of small f.s. energy. With $I \neq 0$ a similar failure occurs in the limit of small h.f.s. energy.

In the next section it will be shown that these ambiguities arise from assuming that one may calculate separately the probabilities of exciting individual quantum states and the probabilities of emission of polarized photons in transitions from these states.

4. EMISSION OF RADIATION BY THE COMPLETE SYSTEM

In order to obtain an improved theory we consider the probability of polarized photons being emitted by the complete system of atom plus colliding electron. We proceed by generalizing the usual Bremsstrahlung formula.

4·1. *Bremsstrahlung emission by an electron in a central field*

Consider that an electron with energy $E = \frac{1}{2}mv^2$ is incident in the direction $\hat{\mathbf{k}}$ on a scattering centre at the origin of the co-ordinate system. The initial wave function has asymptotic form

$$\psi(\mathbf{k}\,|\,\mathbf{r}) \sim \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} + f(\mathbf{k}\,|\,\hat{\mathbf{r}})\,\frac{\mathrm{e}^{ikr}}{r}, \tag{4·1}$$

where $k = mv/\hbar$ and where $\hat{\mathbf{r}}$ is the unit radial vector $\mathbf{r}/r$. Let a ξ-photon be emitted with energy $h\nu = (E-E')$ in the range $\mathrm{d}(h\nu)$, the electron being scattered with energy

$$E' = \hbar^2k'^2/2m$$

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† It is assumed at the same time that the f.s. energy is not large enough to cause significant departures from LS coupling.

in a direction $\hat{\mathbf{k}}'$ lying within a solid angle $d\omega(\hat{\mathbf{k}}')$. The rate coefficient for this process is

$$K_\xi \, d\omega(\hat{\mathbf{k}}') \, d(h\nu) = \frac{C(\nu)\, k' m}{(2\pi)^3 \hbar^2} \, |(\mathbf{k}' \,|\, \xi \,|\, \mathbf{k})|^2 \, d\omega(\hat{\mathbf{k}}') \, d(h\nu), \tag{4·2}$$

(see Heitler 1954) where $C(\nu)$ is given by (2·2), where

$$(\mathbf{k}' \,|\, \xi \,|\, \mathbf{k}) = \int \psi^+(\mathbf{k}' \,|\, \mathbf{r}) \, \xi \psi(\mathbf{k} \,|\, \mathbf{r}) \, d\tau \tag{4·3}$$

and where the conjugate function for the final state has asymptotic form

$$\psi^+(\mathbf{k}' \,|\, \mathbf{r}) \sim e^{-i\mathbf{k}'\cdot\mathbf{r}} + f^+(\mathbf{k}' \,|\, \hat{\mathbf{r}}) \, e^{ik'r}/r \tag{4·4}$$

(the reason for the choice of (4·4) is discussed by Mott & Massey (1949, chap. XIV)).

4·2. *Wave functions for collisions between an electron and a one-electron atom*

Spin variables and symmetry requirements are for the moment neglected. Let E be the total energy of the whole system and E_p the energy of state p of the atom. When the atom is in state p the colliding electron will have wave number $k_p/2\pi$ where

$$k_p = \left[\frac{2m}{\hbar^2}(E - E_p)\right]^{\frac{1}{2}}. \tag{4·5}$$

For a different total energy E' we put

$$k_p' = \left[\frac{2m}{\hbar^2}(E' - E_p)\right]^{\frac{1}{2}}. \tag{4·6}$$

Any wave function for the whole system may be represented by an expansion of the type

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_p \psi_p(\mathbf{r}_1) \, \chi_p(\mathbf{r}_2), \tag{4·7}$$

the ψ_p being atom wave functions. We denote by $\Psi(\alpha\mathbf{k}_a \,|\, \mathbf{r}_1, \mathbf{r}_2)$ the wave function representing a state of the system for which an electron collides with an atom in state α, the total energy being E. Then

$$\Psi(\alpha\mathbf{k}_a \,|\, \mathbf{r}_1, \mathbf{r}_2) = \sum_p \psi_p(\mathbf{r}_1) \, \chi_p(\alpha\mathbf{k}_a \,|\, \mathbf{r}_2), \tag{4·8}$$

where

$$\chi_p(\alpha\mathbf{k}_a \,|\, \mathbf{r}) \sim \delta(p, \alpha) \, e^{i\mathbf{k}_a\cdot\mathbf{r}} + f_p(\alpha\mathbf{k}_a \,|\, \hat{\mathbf{r}}) \, e^{ik_p r}/r. \tag{4·9}$$

The total cross-section for excitation of state β is

$$Q(\alpha\mathbf{k}_a \rightarrow \beta) = \frac{k_b}{\omega_a k_a} \sum_\alpha \int |f_\beta(\alpha\mathbf{k}_a \,|\, \hat{\mathbf{r}})|^2 \, d\omega(\hat{\mathbf{r}}), \tag{4·10}$$

assuming equal probabilities for the atom being initially in any one of the quantum states α of level a.

We shall also require the conjugate of the wave function representing the final state of the entire system for which the electron leaves the atom in state s, the final total energy being E'. This conjugate function is

$$\Psi^+(s\mathbf{k}_s' \,|\, \mathbf{r}_1, \mathbf{r}_2) = \sum_q \psi_q^*(\mathbf{r}_1) \, \chi_q^+(s\mathbf{k}_s' \,|\, \mathbf{r}_2), \tag{4·11}$$

where

$$\chi_q^+(s\mathbf{k}_s' \,|\, \mathbf{r}) \sim \delta(q, s) \, e^{-i\mathbf{k}_s'\cdot\mathbf{r}} + f_q^+(s\mathbf{k}_s' \,|\, \hat{\mathbf{r}}) \, e^{ik_q' r}/r. \tag{4·12}$$

It may be noted that $\Psi^+(s\mathbf{k}_s')$ is the complex conjugate of a function in which outgoing waves are associated only with state s of the atom and with the direction $\hat{\mathbf{k}}_s'$.

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4·3. *Radiative dipole transitions in the electron-atom system*

With initial states $\Psi(\alpha\mathbf{k}_a)$ we obtain, by an obvious generalization of the Bremsstrahlung formula (4·2), the rate coefficient for emission of ξ-photons with energy $h\nu = (E-E')$ in the range $\mathrm{d}(h\nu)$:

$$K_\xi(\nu)\,\mathrm{d}(h\nu) = \frac{C(\nu)\,m\mathrm{d}(h\nu)}{(2\pi)^3\hbar^2\omega_a}\sum_\alpha\sum_s k'_s\int|(s\mathbf{k}'_s\,|\,\xi_1+\xi_2\,|\,\alpha\mathbf{k}_a)|^2\,\mathrm{d}\omega(\hat{\mathbf{k}}'_s). \tag{4·13}$$

Taking the ψ_p to form an orthonormal set the matrix element may be written

$$(s\mathbf{k}'_s\,|\,\xi_1+\xi_2\,|\,\alpha\mathbf{k}_a) = \sum_{pq}(q\,|\,\xi_1\,|\,p)\int\chi_q^+(s\mathbf{k}'_s\,|\,\mathbf{r}_2)\,\chi_p(\alpha\mathbf{k}_a\,|\,\mathbf{r}_2)\,\mathrm{d}\tau_2$$
$$+\sum_q\int\chi_p^+(s\mathbf{k}'_s\,|\,\mathbf{r}_2)\,\xi_2\chi_p(\alpha\mathbf{k}_a\,|\,\mathbf{r}_2)\,\mathrm{d}\tau_2. \tag{4·14}$$

The second sum represents continuous Bremsstrahlung emission and need not be considered further. The integral

$$\int\chi_q^+(s\mathbf{k}'_s\,|\,\mathbf{r})\,\chi_p(\alpha\mathbf{k}_a\,|\,\mathbf{r})\,\mathrm{d}\tau \tag{4·15}$$

is generally very small owing to interference between functions χ_q^+ and χ_p of different wave number but it will be shown to increase without limit when $q=s$ and when $(k_p-k'_s)\to 0$, which occurs when $h\nu=(E-E')$ tends to $h\nu_{ps}=(E_p-E_s)$. Due to the factor $(q\,|\,\xi_1\,|\,p)$ in the first sum of (4·14) such contributions need be considered only when the transition $p\to s$ is optically allowed. We are thus able to identify in (4·14) the contribution due to line radiation.

4·4. *Reduction of integrals*

Since the main contributions to (4·15) come from large values of r the functions χ_p, χ_q^+ may be replaced by their asymptotic forms. The plane waves are conveniently expressed in terms of spherical waves using the relation

$$\mathrm{e}^{\mathrm{i}\mathbf{k}.\mathbf{r}}\sim\frac{2\pi}{\mathrm{i}kr}[\delta(\hat{\mathbf{k}}-\hat{\mathbf{r}})\,\mathrm{e}^{\mathrm{i}kr}-\delta(\hat{\mathbf{k}}+\hat{\mathbf{r}})\,\mathrm{e}^{-\mathrm{i}kr}]. \tag{4·16}$$

This may be proved as follows. The usual plane wave expansion is

$$\mathrm{e}^{\mathrm{i}\mathbf{k}.\mathbf{r}} = \sum_l(2l+1)\,P_l(\hat{\mathbf{k}}\,.\hat{\mathbf{r}})\,\mathrm{i}^l f_l(kr) \tag{4·17}$$

(Mott & Massey 1949, p. 22), where

$$f_l(x) = (\pi/2x)^{\frac{1}{2}}J_{l+\frac{1}{2}}(x) \tag{4·18}$$

has asymptotic form $f_l(x)\sim x^{-1}\sin(x-\frac{1}{2}l\pi)$. Therefore

$$\mathrm{e}^{\mathrm{i}\mathbf{k}.\mathbf{r}}\sim\frac{1}{2\mathrm{i}kr}\sum_l(2l+1)\,P_l(\hat{\mathbf{k}}\,.\hat{\mathbf{r}})\,[\mathrm{e}^{\mathrm{i}kr}-(-1)^l\,\mathrm{e}^{-\mathrm{i}kr}]. \tag{4·19}$$

We use the spherical harmonic addition theorem

$$P_l(\hat{\mathbf{k}}\,.\hat{\mathbf{r}}) = \frac{4\pi}{2l+1}\sum_m Y^*_{lm}(\hat{\mathbf{k}})\,Y_{lm}(\hat{\mathbf{r}}) \tag{4·20}$$

(Condon & Shortley 1951, p. 53), where the Y_{lm} are normalized spherical harmonics. Since the Y_{lm} form a complete orthonormal set,

$$\sum_{lm}Y^*_{lm}(\hat{\mathbf{k}})\,Y_{lm}(\hat{\mathbf{r}}) = \delta(\hat{\mathbf{k}}-\hat{\mathbf{r}}), \tag{4·21}$$

where the δ-function is defined on the unit sphere. We also require

$$(-1)^l Y_{lm}(\hat{\mathbf{r}}) = Y_{lm}(-\hat{\mathbf{r}}) \tag{4·22}$$

(Condon & Shortley 1951, p. 186). Equation (4·16) is readily obtained from (4·19), (4·20), (4·21) and (4·22).

In the integral (4·15) we replace χ_q^+ by

$$\frac{2\pi\delta(q,s)}{\mathrm{i}kr}\,[\delta(-\hat{\mathbf{k}}'_s-\hat{\mathbf{r}})\,\mathrm{e}^{\mathrm{i}k'_s r}-\delta(-\hat{\mathbf{k}}'_s+\hat{\mathbf{r}})\,\mathrm{e}^{-\mathrm{i}k'_s r}]+f_q^+(s\mathbf{k}'_s\,|\,\hat{\mathbf{r}})\,\frac{\mathrm{e}^{\mathrm{i}k'_q r}}{r} \tag{4·23}$$

and, for $p \neq \alpha$, we replace χ_p by

$$f_p(\alpha\hat{\mathbf{k}}_a\,|\,\hat{\mathbf{r}})\,\mathrm{e}^{\mathrm{i}k_p r}/r. \tag{4·24}$$

We then obtain integrals of the type†

$$\int_0^\infty \mathrm{e}^{\mathrm{i}(k_p+k'_q)r}\,\mathrm{d}r \quad \text{and} \quad \delta(q,s)\int_0^\infty \mathrm{e}^{\mathrm{i}(k_p-k'_s)r}\,\mathrm{d}r. \tag{4·25}$$

The second of these integrals will be large when $(k_p-k'_s)$ is small. It is readily shown that such large integrals do not occur when $p=\alpha$ if α is a ground state. Retaining only those integrals which may become large we have

$$\int \chi_q^+(s\mathbf{k}'_s\,|\,\mathbf{r})\,\chi_p(\alpha\mathbf{k}_a\,|\,\mathbf{r})\,\mathrm{d}\tau = \delta(q,s)\,2\pi\mathrm{i}k_s'^{-1}f_p(\alpha\mathbf{k}_a\,|\,\hat{\mathbf{k}}'_s)\int_0^\infty \mathrm{e}^{\mathrm{i}(k_p-k'_s)r}\,\mathrm{d}r \tag{4·26}$$

and substitution in (4·13) gives

$$K_\xi(\nu)\,\mathrm{d}(h\nu) = \frac{C(\nu)\,m\mathrm{d}(h\nu)}{2\pi\hbar^2\omega_a}\sum_{\alpha s} k_s'^{-1}\int\left|\sum_p (s\,|\,\xi\,|\,p)\,f_p(\alpha\mathbf{k}_a\,|\,\hat{\mathbf{k}})\int_0^\infty \mathrm{e}^{\mathrm{i}(k_p-k_s)r}\,\mathrm{d}r\right|^2\mathrm{d}\omega(\hat{\mathbf{k}}). \tag{4·27}$$

The sum over s occurs outside the modulus. We may therefore consider only those final states $s=\gamma$ belonging to an energy level c. Furthermore, we need consider only those photons with energy close to $h\nu_{bc}=(E_b-E_c)$; in the sum over p the only large terms will be those for which $p=\beta$, where β is a state belonging to level b. We then have

$$K_\xi(\nu)\,\mathrm{d}(h\nu) = \frac{C(\nu)\,m\mathrm{d}(h\nu)}{2\pi\hbar^2\omega_a}\sum_{\alpha\gamma} k_\gamma'^{-1}\int\left|\sum_\beta (\gamma\,|\,\xi\,|\,\beta)\,f_\beta(\alpha\mathbf{k}_a\,|\,\hat{\mathbf{k}})\int_0^\infty \mathrm{e}^{\mathrm{i}(k_\beta-k'_\gamma)r}\,\mathrm{d}r\right|^2\mathrm{d}\omega(\hat{\mathbf{k}}). \tag{4·28}$$

This is incomplete in that it gives an incorrect expression for the line profile: one obtains an infinite intensity for the centre of the line $(k_\beta = k'_\gamma)$ and a divergent integral for the total number of quanta emitted in the line. This divergence is a consequence of neglect of radiation damping.

4·5. *Corrections for radiation damping*

In a more exact treatment one would consider the collision problem using a Hamiltonian including radiative terms. One would then obtain coupling between the system of (electron + atom of energy E) and the system of (electron + atom of energy E' + photon). The formulae considered so far are obtained using first-order perturbation theory to calculate the pro-

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† Such integrals may be evaluated by introducing a factor $\mathrm{e}^{-\epsilon r}$ and letting $\epsilon \to 0$ after integration.

bability of a transition between these two systems. A more exact treatment of the coupling terms shows that the radial factors $r^{-1}\exp[\mathrm{i}k_\beta r]$ should be replaced by

$$r^{-1}\exp[(\mathrm{i}k_\beta-\Gamma/2v_\beta)\,r],$$

where Γ is the total downward transition probability from β. We consider the simplest case for which $\beta\to c$ transitions are the only optically allowed transitions from β: then $\Gamma=A(b)$ as defined in § 2·1.

The decaying exponential factor can be obtained by the following physical argument. We suppose the atom to be excited by a wave packet at time $t=0$ and consider the wave packet to be so long that it is essentially monochromatic so far as atomic excitation processes are concerned yet so short that it can be considered to have left the atom completely at time t_1, where t_1 is small compared with the radiative lifetime $1/A$ of the excited state. If state β has been excited the probability of the atom still being in state β at time $t>t_1$ varies as $\exp[-At]$. The corresponding wave function should therefore be multiplied by a factor $\exp[-\frac{1}{2}At]$. But since the wave packet moves with a velocity v_β the wave function vanishes unless $t\simeq r/v_\beta$. Therefore the factor $\exp[-\frac{1}{2}At]$ may be replaced by $\exp[-Ar/2v_\beta]$. Since the latter factor does not contain the time explicitly it will also occur in a time-independent wave function, which may be considered to result from the superposition of wave packets arriving at different epochs.

If we suppose that no further radiative transitions occur when the atom is in the state γ it follows that the integral over r in (4·28) should be replaced by

$$\int_0^\infty \exp\{\mathrm{i}[(k_\beta-k'_\gamma)-A/2v_\beta]\,r\}\,\mathrm{d}r=\frac{v_\beta}{\mathrm{i}v_\beta(k_\beta-k'_\gamma)-\frac{1}{2}A}. \tag{4·29}$$

It will be recalled (§ 2·1) that we consider b and c to be either single energy levels with energies E_b, E_c or groups of very closely spaced energy levels with mean energies E_b, E_c. Since the expression (4·29) will be large only when $(k_\beta-k'_\gamma)$ is small we are interested only in values of k'_γ nearly equal to k_β. Except when the difference $(k_\beta-k'_\gamma)$ occurs explicitly we may put $k_\beta=k_b$, $k'_\gamma=k'_c$ and $k_b=k'_c$. Since

$$\left.\begin{aligned}E=E_b+\frac{\hbar^2k_b^2}{2m},\quad E'=E_c+\frac{\hbar^2k_c'^2}{2m},\\ E-E'=h\nu,\quad E_\beta-E_\gamma=h\nu_{\beta\gamma},\end{aligned}\right\} \tag{4·30}$$

we obtain

$$v_\beta(k_\beta-k'_\gamma)=2\pi(\nu-\nu_{\beta\gamma}). \tag{4·31}$$

The expression for the rate coefficient then becomes

$$K_\xi(\nu)\,\mathrm{d}(h\nu)=\frac{v_bC(\nu_{bc})\,\mathrm{d}\nu}{\omega_a}\sum_{\alpha\gamma}\int\left|\sum_\beta\frac{(\gamma\,|\,\xi\,|\,\beta)\,f_\beta(\alpha\mathbf{k}_a\,|\,\hat{\mathbf{k}})}{2\pi\mathrm{i}(\nu-\nu_{\beta\gamma})-\frac{1}{2}A}\right|^2\mathrm{d}\omega(\hat{\mathbf{k}}). \tag{4·32}$$

The same formula would have been obtained had we included spin variables and used properly symmetrized wave functions.†

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† In the same general case the quantum numbers α, β, γ could be taken to include a specification of spin quantum numbers for the colliding electron. The statistical weight ω_a should then include a factor of 2 for the statistical weight of the incident electron.

4·6. *Final results for the rate coefficients*

An important feature of (4·32) is that the sum over β occurs inside the modulus; had this sum occurred outside the modulus we would have been able to integrate (4·32) over the line profile to obtain equation (2·16) of the O.-P. theory.

The rate coefficient for all polarizations

$$K(\nu) = \sum_{\xi} K_{\xi}(\nu), \tag{4·33}$$

may be simplified using the relation

$$C(\nu_{bc}) \sum_{\gamma\xi} (\gamma \,|\, \xi \,|\, \beta)^* \, (\gamma \,|\, \xi \,|\, \beta^0) = \delta(\beta, \beta^0)\, A(b); \tag{4·34}$$

this may be proved by the methods of Condon & Shortley (1951, pp. 20 and 71) or by the methods of Racah (1942). Using the expression (4·1) for the cross-section and assuming b and c to be single energy levels we obtain

$$K(\nu)\, \mathrm{d}(h\nu) = \frac{v_a Q(b)\, A(b)\, \mathrm{d}\nu}{[2\pi(\nu-\nu_{bc})]^2 - [\frac{1}{2}A(b)]^2}, \tag{4·35}$$

which is the correct expression for the line profile. It follows from (4·35) that the *width* of the line, defined as the frequency separation of the positions of the profile for which the intensity is half maximum intensity, is $(A/2\pi)$.

Integration of (4·32) over the line profiles may be carried out using the integral (for the sake of simplicity it is assumed that all states α have identical energies):

$$\int_{-\infty}^{\infty} \frac{\mathrm{d}\nu}{[2\pi\mathrm{i}(\nu-\nu_{\beta^0\gamma}) - \frac{1}{2}A]^* \, [2\pi\mathrm{i}(\nu-\nu_{\beta\gamma}) - \frac{1}{2}A]} = \frac{1}{2\pi\mathrm{i}\nu_{\beta\beta^0} + A}, \tag{4·36}$$

where

$$h\nu_{\beta\beta^0} = h(\nu_{\beta\gamma} - \nu_{\beta^0\gamma}) = E_{\beta} - E_{\beta^0} \tag{4·37}$$

and β and β^0 are two states of b. A convenient expression is obtained on introducing unit complex vectors $\mathbf{F}(\beta)$ satisfying

$$\mathbf{F}^*(\beta^0) \,.\, \mathbf{F}(\beta) = \frac{A}{2\pi\mathrm{i}\nu_{\beta\beta^0} + A}. \tag{4·38}$$

The rate coefficient for emission of ξ-photons in $b \to c$ transitions is then

$$K_{\xi}(b \to c) = \frac{v_b C(\nu_{bc})}{A\omega_a} \sum_{\alpha\gamma} \int \Big| \sum_{\beta} (\gamma \,|\, \xi \,|\, \beta)\, \mathbf{F}(\beta)\, f_{\beta}(\alpha \mathbf{k}_a \,|\, \hat{\mathbf{k}}) \Big|^2 \mathrm{d}\omega(\hat{\mathbf{k}}). \tag{4·39}$$

The rate coefficient for all polarizations is obtained on summing (4·39) over ξ. Using (4·10) and (4·34) we obtain $K(b \to c) = v_a Q(b)$ in agreement with the O.-P. theory. Further discussion of (4·39) may therefore be restricted to the case $\xi = z$.

5. Reconsideration of ^{2}P → ^{2}S transitions

In § 3·7 we showed, taking ^{2}P → ^{2}S transitions as an example, that the O.-P. theory did not always satisfy the principle of spectroscopic stability. The case of ^{2}P → ^{2}S transitions will be reconsidered in the present section using the expression (4·39).

5·1. *Zero nuclear spin*

We consider initial states $\alpha = \Delta'\,{}^2\mathrm{S}, M'_J$, upper states $\beta = \Delta\,{}^2\mathrm{P}, JM_J$ and final states $\gamma = \Delta''\,{}^2\mathrm{S}, M''_J$. The f.s. energy separation of the upper states will be $h\delta\nu = E({}^2\mathrm{P}_{\frac{3}{2}}) - E({}^2\mathrm{P}_{\frac{1}{2}})$. The polarization depends on the ratio

$$\epsilon = 2\pi\delta\nu/A \tag{5·1}$$

of f.s. separation to line width. From (4·39) we have

$$K_z^{(\epsilon)}({}^2\mathrm{P}\rightarrow{}^2\mathrm{S}) = \frac{v_b\, C(\nu_{bc})}{4A}$$

$$\times \sum_{M_J M''_J m'_s m_s} \int \Big| \sum_{JM_J} ({}^2\mathrm{S}, M''_J \,|\, z \,|\, {}^2\mathrm{P}, JM_J)\, \mathbf{F}(J)\, f_{{}^2\mathrm{P},JM_Jm_s}({}^2\mathrm{S}, M'_J m'_s \mathbf{k}_a \,|\, \hat{\mathbf{k}}) \Big|^2 \mathrm{d}\omega(\hat{\mathbf{k}}) \tag{5·2}$$

with

$$\mathbf{F}^*(J)\,.\,\mathbf{F}(J) = 1 \tag{5·3}$$

and

$$\mathbf{F}^*(\tfrac{1}{2})\,.\,\mathbf{F}(\tfrac{3}{2}) = [\mathbf{F}^*(\tfrac{3}{2})\,.\,\mathbf{F}(\tfrac{1}{2})]^* = \frac{1}{1+\mathrm{i}\epsilon}. \tag{5·4}$$

We now use the relations

$$({}^2\mathrm{S}, M''_J \,|\, z \,|\, {}^2\mathrm{P}, JM_J) = C^{\frac{1}{2}\,1\,J}_{M_J\,0\,M_J}\, \delta(M''_J, M_J)\, ({}^2\mathrm{S}, M_S \,|\, z \,|\, {}^2\mathrm{P}, M_S M_L = 0), \tag{5·5}$$

$$A = C(\nu_{bc})\, |\, ({}^2\mathrm{S}, M_S \,|\, z \,|\, {}^2\mathrm{P}, M_S M_L = 0)\, |^2, \tag{5·6}$$

$$f_{{}^2\mathrm{P},JM_Jm_s} = \sum_{M_S M_L} C^{\frac{1}{2}\,1\,J}_{M_S\,M_L\,M_J}\, f_{{}^2\mathrm{P},M_SM_Lm_s} \tag{5·7}$$

and

$$\delta(M_S M_L, M_S^0 M_L^0)\, \tfrac{1}{2} Q_{|M_L|} = \frac{v_b}{4v_a} \sum_{M'_J m_s m'_s} \int f^*_{M_SM_Lm_s}(M'_J m'_s \mathbf{k}_a \,|\, \hat{\mathbf{k}})\, f_{M_S^0M_L^0m_s}(M'_J m'_s \mathbf{k}_a \,|\, \hat{\mathbf{k}})\, \mathrm{d}\omega(\hat{\mathbf{k}}), \tag{5·8}$$

equation (5·8) following from (3·4) and (3·8). Substitution in (5·2) gives

$$K_z^{(\epsilon)} = \frac{v_a}{2} \sum_{M_S M_L M_J} \Big| \sum_J C^{\frac{1}{2}\,1\,J}_{M_S\,M_L\,M_J}\, C^{\frac{1}{2}\,1\,J}_{M_J\,0\,M_J}\, \mathbf{F}(J) \Big|^2 Q_{|M_L|}. \tag{5·9}$$

We consider the two limiting cases of $\epsilon = 0$ and of $\epsilon \rightarrow \infty$. For $\epsilon \ll 1$ the line profiles overlap completely and all vectors $\mathbf{F}(J)$, $\mathbf{F}^*(J^0)$ are parallel. We have therefore

$$K_z^{(0)} = \frac{v_a}{2} \sum_{M_S M_L M_J} \Big| \sum_J C^{\frac{1}{2}\,1\,J}_{M_S\,M_L\,M_J}\, C^{\frac{1}{2}\,1\,J}_{M_J\,0\,M_J} \Big|^2 Q_{|M_L|}. \tag{5·10}$$

From the orthonormality relations for the C-coefficients the sum over J is equal to $\delta(M_S, M_J)\,\delta(M_L, 0)$. Therefore

$$K_z^{(0)} = v_a Q_0, \tag{5·11}$$

which agrees with the result obtained in the O.-P. theory if we use the representation $\beta = {}^2\mathrm{P}, M_S M_L$. For $\epsilon \gg 1$, on the other hand, there is negligible overlap between the line profiles, and the vectors $\mathbf{F}^*(\frac{1}{2})$, $\mathbf{F}(\frac{3}{2})$ are orthogonal. We have therefore

$$K_z^{(\infty)} = \frac{v_a}{2} \sum_{M_S M_L J M_J} [C^{\frac{1}{2}\,1\,J}_{M_S\,M_L\,M_J}\, C^{\frac{1}{2}\,1\,J}_{M_J\,0\,M_J}]^2\, Q_{|M_L|}, \tag{5·12}$$

which agrees with the result obtained in the O.-P. theory using the representation $\beta = {}^2\mathrm{P}, JM_J$.

On expanding (5·9) we readily obtain, for any ϵ,

$$K_z^{(\epsilon)} = \frac{K_z^{(0)} + \epsilon^2 K_z^{(\infty)}}{1+\epsilon^2}. \tag{5·13}$$

5·2. *Nuclear spin and hyperfine structure*

We assume the f.s. separation to be large compared with the line width. We then obtain the O.-P. theory expression for $\beta = {}^2\mathrm{P}, JIFM_F$ if the h.f.s. separations are also much greater than the line width and the O.-P. expression for $\beta = {}^2\mathrm{P}, JM_J$ if the h.f.s. separations are much smaller than the line width.

For $I = \frac{1}{2}$ each f.s. level is split into two h.f.s. levels with separation $\delta\nu_J$. For each value of J we obtain as in the previous section

$$K_z^{(\epsilon_J)}(J) = \frac{K_z^{(0)}(J) + \epsilon_J^2 K_z^{(\infty)}(J)}{1+\epsilon_J^2}, \tag{5·14}$$

where $\epsilon_J^2 = (2\pi\delta\nu_J/A)^2$.

5·3. *Numerical results for hydrogen*

The value of A for $2p \rightarrow 1s$ transitions is $6{\cdot}25 \times 10^8\,\mathrm{sec}^{-1}$ giving a line width

$$(A/2\pi c) = 3{\cdot}3 \times 10^{-3}\,\mathrm{cm}^{-1}.$$

The $2p$ f.s. separation is $0{\cdot}36\,\mathrm{cm}^{-1}$.

The h.f.s. separations are $(\delta\nu_{\frac{1}{2}}/c) = 1{\cdot}97 \times 10^{-3}\,\mathrm{cm}^{-1}$ and $(\delta\nu_{\frac{3}{2}}/c) = 0{\cdot}79 \times 10^{-3}\,\mathrm{cm}^{-1}$. The h.f.s. separations are therefore smaller than the line width but of comparable order of magnitude. We must therefore use (5·13) in order to make an exact calculation of the polarization. The values of ϵ_J^2 are $\epsilon_{\frac{1}{2}}^2 = 0{\cdot}356$ and $\epsilon_{\frac{3}{2}}^2 = 0{\cdot}057$. For transitions from $2p_{\frac{1}{2}}$ the polarization is always zero. For $2p_{\frac{3}{2}}$ we obtain

$$P(2p_{\frac{3}{2}}) = 100(Q_0 - Q_1)/(1{\cdot}694Q_0 + 2{\cdot}388Q_1), \tag{5·15}$$

compared with $P(2p_{\frac{3}{2}}) = 100(Q_0 - Q_1)/(1{\cdot}667Q_0 + 2{\cdot}333Q_1)$

in the O.-P. theory neglecting h.f.s. and

$$P(2p_{\frac{3}{2}}) = 100(Q_0 - Q_1)/(2{\cdot}467Q_0 + 3{\cdot}933Q_1)$$

in the O.-P. theory including h.f.s. For the total radiation from the $2p$ level we obtain

$$P(2p) = 100(Q_0 - Q_1)/(2{\cdot}375Q_0 + 3{\cdot}749Q_1), \tag{5·16}$$

compared with $100(Q_0 - Q_1)/(2{\cdot}333Q_0 + 3{\cdot}667Q_1)$ in the O.-P. theory without h.f.s. and $100(Q_0 - Q_1)/(3{\cdot}533Q_0 + 6{\cdot}067Q_1)$ in the O.-P. theory with h.f.s.

It is seen that the exact expressions (5·15), (5·16) differ little from those obtained neglecting h.f.s. This result has been used by Khashaba & Massey (1958) who give the polarization as a function of energy, the cross-sections being calculated using a distorted wave approximation.

For atoms other than hydrogen the h.f.s. separations will generally be large and the theory with inclusion of h.f.s. should be used for all but highly excited states.

For hydrogen we may check that the collision time is small compared with the radiative lifetime; putting $R = v_{2p}/A(2p)$ the condition is that R should be much larger than the Bohr radius a_0. We obtain $R = 1{\cdot}8 \times 10^7 \mathscr{E}^{\frac{1}{2}} a_0$ where $\mathscr{E}$ is the energy of the scattered electron measured in electron volts. The required condition is therefore satisfied for all cases of practical importance.

6. The Born approximation

We consider the use of the Born approximation for the calculation of cross-sections for excitation of M_L states. We start by considering transitions in hydrogen.

6·1. *The Born approximation for hydrogen*

For transitions $1s \rightarrow nlm$ the Born differential cross-section per unit solid angle is

$$I_{nlm}(K) = \frac{4k_n}{K^4 k_1} \,|\,(nlm \,|\, \mathrm{e}^{\mathrm{i}\mathbf{K}.\mathbf{r}} \,|\, 1s)\,|^2, \tag{6·1}$$

where

$$\mathbf{K} = \mathbf{k}_n - \mathbf{k}_1 \tag{6·2}$$

is the change of momentum vector. It is supposed that $\mathbf{k}_1$ is in the direction of the quantization axis; I_{nlm} then depends only on the energy and on the angle between $\mathbf{k}_1$ and $\mathbf{k}_n$.

The total cross-section is

$$Q(nlm) = \frac{2\pi}{k_1 k_n} \int_{K_1}^{K_2} I_{nlm}(K)\, K \,\mathrm{d}K, \tag{6·3}$$

where $K_1 = (k_1 - k_n)$ and $K_2 = (k_1 + k_n)$ (Mott & Massey 1949, p. 226). Using (4·17) and (4·20) we obtain

$$(nlm \,|\, \mathrm{e}^{\mathrm{i}\mathbf{K}.\mathbf{r}} \,|\, 1s) = 4\pi \sum_{\lambda\mu} Y^*_{\lambda\mu}(\hat{\mathbf{K}})\, \mathrm{i}^{\lambda} (nlm \,|\, Y_{\lambda\mu}(\hat{\mathbf{r}})\, f_\lambda(Kr) \,|\, 1s) \tag{6·4}$$

and, on carrying out the angular integrations,

$$(nlm \,|\, \mathrm{e}^{\mathrm{i}\mathbf{K}.\mathbf{r}} \,|\, 1s) = (2l+1)^{\frac{1}{2}}\, C^*_{lm}(\hat{\mathbf{K}})\, \mathrm{i}^{l} (nl \,|\, f_l(Kr) \,|\, 1s), \tag{6·5}$$

where C_{lm} is the spherical harmonic operator defined by (3·22) and where

$$(nl \,|\, f_l(Kr) \,|\, 1s) = \int_0^\infty P_{nl}(r)\, f_l(Kr)\, P_{1s}(r)\, \mathrm{d}r. \tag{6·6}$$

Hence

$$I_{nlm} = \frac{4k_n}{K^4 k_1} (2l+1) \,|\, C_{lm}(\hat{\mathbf{K}}) \,|^2 \,|\, (nl \,|\, f_l(Kr) \,|\, 1s) \,|^2. \tag{6·7}$$

The differential cross-section I_{nl} is obtained on summing I_{nlm} over m. Since $P_l(1) = 1$ we obtain from (3·22) and (4·20)

$$\sum_m |\, C_{lm}(\hat{\mathbf{K}}) \,|^2 = 1 \tag{6·8}$$

and therefore

$$I_{nl}(K) = \frac{4k_n}{K^4 k_1} (2l+1) \,|\, (nl \,|\, f_l \,|\, 1s) \,|^2. \tag{6·9}$$

Hence

$$I_{nlm}(K) = |\, C_{lm}(\hat{\mathbf{K}}) \,|^2\, I_{nl}(K) \tag{6·10}$$

and

$$Q(nlm) = \frac{2\pi}{k_1 k_n} \int_{K_1}^{K_2} |\, C_{lm}(\hat{\mathbf{K}}) \,|^2\, I_{nl}(K)\, K \,\mathrm{d}K. \tag{6·11}$$

We may put

$$|\, C_{lm}(\hat{\mathbf{K}}) \,| = \left(\frac{2}{2l+1}\right)^{\frac{1}{2}} |\, \mathscr{P}_l^{|m|}(\cos\omega) \,|, \tag{6·12}$$

where $\mathscr{P}_l^{|m|}$ is a normalized associated Legendre polynomial, and where ω is the angle between $\mathbf{K}$ and $\mathbf{k}_1$. Using (6·2) we have $\cos\omega = (\hat{\mathbf{K}}\,.\,\hat{\mathbf{k}}_1) = (K^2 + k_1^2 - k_n^2)/2Kk_1$. We thus obtain

$$Q(nlm) = \frac{4\pi}{(2l+1)\, k_1 k_n} \int_{K_1}^{K_2} \left|\, \mathscr{P}_l^{|m|} \left(\frac{K^2 + 2E_{n1}}{2Kk_1}\right) \right|^2 I_{nl}(K)\, K \,\mathrm{d}K, \tag{6·13}$$

where $E_{n1} = \frac{1}{2}(k_1^2 - k_n^2)$. This relation between $Q(nlm)$ and I_{nl} may be applied to systems other than hydrogen. It may be noted that, assuming the validity of the Born approximation, (6·13) may be used to determine $Q(nlm)$ from measured angular distributions.

6·2. *The high-energy limit*

For any finite value of K we obtain $[(K^2+2E_{n1})/2Kk_1] \to 0$ as $k_1 \to \infty$. Since

$$Q(nl) = \frac{2\pi}{k_1 k_n} \int_{K_1}^{K_2} I_{nl}(K)\, K\, \mathrm{d}K, \tag{6·14}$$

we obtain from (6·13)

$$\lim_{k_1 \to \infty} \left[\frac{Q(nlm)}{Q(nl)}\right] = \left(\frac{2}{2l+1}\right) |\mathscr{P}_l^{|m|}(0)|^2. \tag{6·15}$$

Numerical values of this limit are given in table 5.

TABLE 5

L	$\lvert M_L \rvert$	$\left(\frac{2}{2L+1}\right) \lvert\mathscr{P}_L^{\lvert M_L\rvert}(0)\rvert^2$	L	$\lvert M_L \rvert$	$\left(\frac{2}{2L+1}\right) \lvert\mathscr{P}_L^{\lvert M_L\rvert}(0)\rvert^2$
1	1	$\frac{1}{2}$	3	3	$\frac{5}{16}$
	0	0		2	0
2	2	$\frac{3}{8}$		1	$\frac{3}{16}$
	1	0		0	0
	0	$\frac{1}{4}$			

The physical significance of this result is that at high energies most of the scattering occurs at small angles between $\mathbf{k}_n$ and $\mathbf{k}_1$; as $k_1 \to \infty$ the change-of-momentum vector $\mathbf{K}$ is therefore at right angles to $\mathbf{k}_1$. The polarization observed at high energies will generally be less than that predicted, due to the upper state being populated by cascade. For the alkali metals, however, the cross-sections for excitation of resonance lines will be much larger than all other inelastic cross-sections and the observed polarization at high energies may not be far different from that calculated neglecting cascade.

6·3. *Born calculations for* $3\,{}^1\mathrm{D} \to {}^1\mathrm{P}$ *transitions in* He

With separable He functions

$$\left.\begin{aligned} \psi(1s^2) &= \psi_{1s}(\mathbf{r}_1)\,\psi_{1s}(\mathbf{r}_2), \quad \psi_{1s}(\mathbf{r}) = (4\pi)^{-\frac{1}{2}}\,r^{-1}P_{1s}(r), \\ \psi(1snl\,{}^1L) &= 2^{-\frac{1}{2}}[\psi_{1s'}(\mathbf{r}_1)\,\psi_{nlm}(\mathbf{r}_2) + \psi_{1s'}(\mathbf{r}_2)\,\psi_{nlm}(\mathbf{r}_1)], \\ \psi_{1s'}(\mathbf{r}) &= (4\pi)^{-\frac{1}{2}}\,r^{-1}P_{1s'}(r), \quad \psi_{nlm}(\mathbf{r}) = Y_{lm}(\hat{\mathbf{r}})\,r^{-1}P_{nl}(r), \end{aligned}\right\} \tag{6·16}$$

we obtain

$$I_{nl} = \frac{8k_n(2l+1)}{K^4 k_1}\, |(1s' \mid 1s)|^2\, |(nl \mid f_l \mid 1s)|^2. \tag{6·17}$$

We use the ground-state function

$$P_{1s} = 2Z^{\frac{3}{2}} r\,\mathrm{e}^{-Zr} \quad (Z = 27/16),$$

a He$^+$ function for $P_{1s'}$ and a hydrogen $3d$ radial function to obtain

$$(3d \mid f_2 \mid 1s) = \frac{128 Z^{\frac{3}{2}} K^2 \alpha}{27(30)^{\frac{1}{2}}(\alpha^2+K^2)^4} \quad (\alpha = Z + \tfrac{1}{3}) \tag{6·18}$$

and

$$|(1s' \mid 1s)| = \frac{64(2Z)^3}{(2+Z)^6} = 0·9785. \tag{6·19}$$

The total cross-section is shown in figure 1. Our results are in agreement with those of Massey & Mohr (1931). The shape of the curve is very similar to that of the experimental curves for 4 ^{1}D and 5 ^{1}D (see Bates, Fundaminsky, Leech & Massey 1950) but at 100 eV the calculated 3 ^{1}D cross-section is $0\cdot5\times10^{-3}\pi a_0^2$ compared with the much larger value of $2\cdot5\times10^{-3}\pi a_0^2$ measured by Dr D. W. O. Heddle (private communication). The discrepancy may be due to the approximate nature of the wave functions used rather than to the Born approximation being unreliable. The ratios of the cross-sections $Q_{|M_L|}$ may be more accurate than the absolute value of the total cross-section. The integrals in (6·13) have been evaluated numerically; the ratios Q_0/Q, $2Q_1/Q$ and $2Q_2/Q$ are shown in figure 2. For the polarization we obtain by the method of §§ 2 and 3,

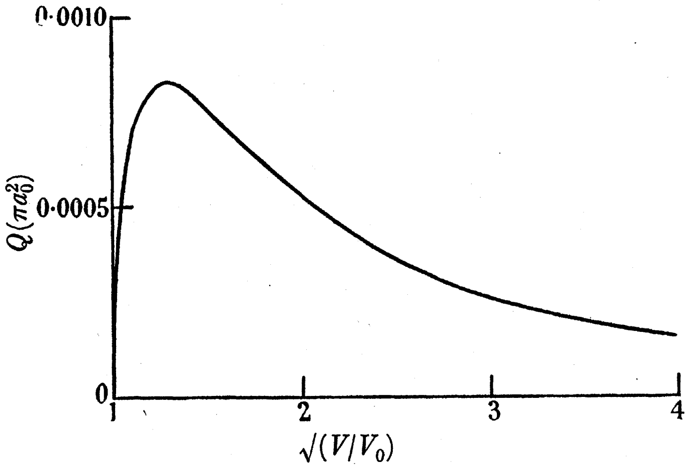

FIGURE 1. Cross-section Q for excitation of He 3 ^{1}D as a function of $\surd(V/V_0)$ (V = energy of incident electron, V_0 = threshold energy). Born approximation.

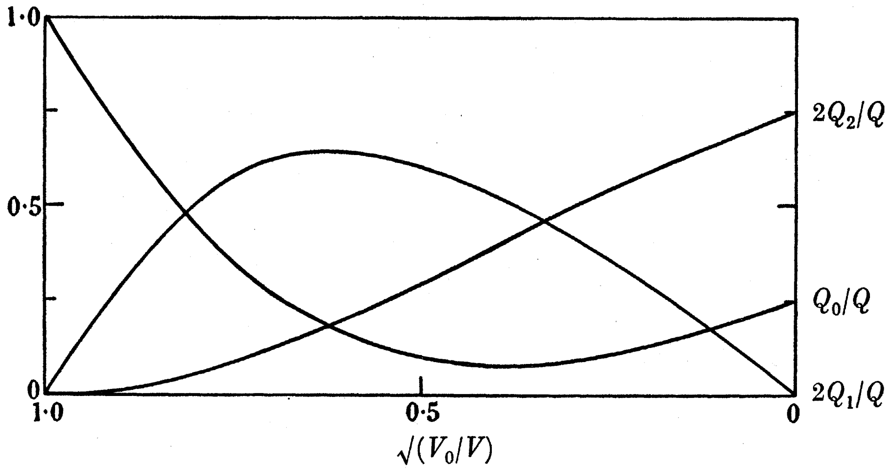

FIGURE 2. Cross-sections $Q_{|M_L|}$ for excitation of He 3 ^{1}D, M_L as functions of $\surd(V_0/V)$ (V_0 = threshold energy, V = energy of incident electron). Curves give Q_0/Q, $2Q_1/Q$ and $2Q_2/Q$, where $Q = Q_0+2Q_1+2Q_2$. Born approximation.

$$P(^1\mathrm{D}\to{}^1\mathrm{P}) = \frac{300(Q_0+Q_1-2Q_2)}{5Q_0+9Q_1+6Q_2}, \tag{6·20}$$

the nuclear spin being zero for He. The calculated polarization curve is shown in figure 3.

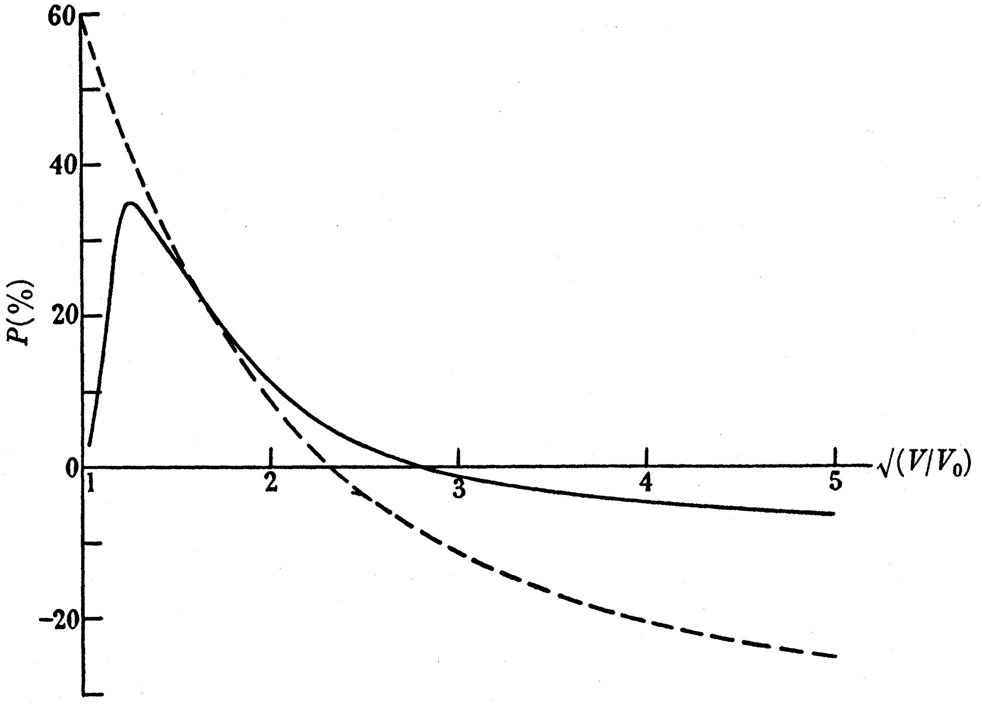

FIGURE 3. Percentage polarization for ${}^1\mathrm{D}\rightarrow{}^1\mathrm{P}$ transitions as functions of $\sqrt{(V/V_0)}$. Dashed curve gives calculated result for He $3\,{}^1\mathrm{D}\rightarrow{}^1\mathrm{P}$ (Born approximation). Full line curve gives experimental result for Hg $7\,{}^1\mathrm{D}\rightarrow 6\,{}^1\mathrm{P}$ (Skinner & Appleyard 1927).

7. COMPARISON WITH EXPERIMENT

7·1. *The sodium D lines*

Polarization of the *D* lines excited by electron impact has not been detected (Kossel & Gerthsen 1925; Ellett, Foote & Mohler 1926); in the energy range studied the polarization may be less than 2 %. It was first suggested by Penney (1932) that the small polarization is due to h.f.s. but detailed calculations could not be made at that time since the value of *I* for sodium was unknown. It is now known that for sodium $I=\frac{3}{2}$. We see from table 4 that the predicted polarization is +13 % at threshold and −7 % at high energies (neglecting cascade).

Just beyond the threshold the polarization may decrease rapidly, since even at low energies many partial waves are important for the calculation of the cross-section (Seaton 1955). The chances of detecting polarization should be better if the $3p_{\frac{3}{2}}\rightarrow 3s$ line were isolated, since for this the values are +19 % at threshold and −10·5 % at high energies. Further experimental work would be worthwhile.

7·2. *Transitions in* He

The only published results giving the polarization as a function of electron energy are those of Lamb & Maiman (1957) for $3\,{}^3\mathrm{P}\rightarrow 2\,{}^3\mathrm{S}$. These are shown in figure 4. The calculated threshold polarization is 36·6 %. Lamb (1957) has calculated the threshold polarization as a function of the strength of an applied magnetic field. In the limit of zero field strength his results agree with ours. Further measurements at lower energies are required in order to check whether the polarization tends to the calculated threshold value.

7·3. *Transitions in* Hg

Mercury consists of a mixture of isotopes with normal abundances of 70 % for $I = 0$, 17 % for $I = \frac{1}{2}$ and 13 % for $I = \frac{3}{2}$. For a first approximation we may neglect the isotopes with $I \neq 0$ and neglect departures from *LS* coupling in calculating collision cross-sections; this is the approximation of table 1. An idea of the error introduced by this approximation is given by the work of Penney (1932) for the transitions $6s\,6p\,{}^3P_1 \rightarrow 6s^2\,{}^1S_0$. From table 2 we obtain a threshold† polarization $P = -100\,\%$ while with allowance for departures from *LS* coupling Penney obtains $P = -92\,\%$ for $I = 0$, $-53\,\%$ for $I = \frac{1}{2}$ and $-48\,\%$ for $I = \frac{3}{2}$; with the normal isotope mixture Penney's calculations give $P = -80\,\%$.

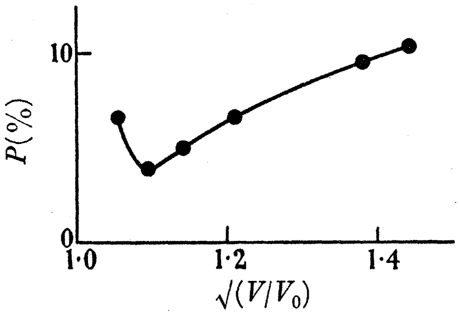

FIGURE 4. Polarization curve for He $3\,{}^3P - 2\,{}^3S$ as measured by Lamb & Maiman (1957).

Typical observed polarizations, taken from the work of Skinner & Appleyard (1927), are plotted as functions of $\surd(V/V_0)$ in figure 5, V being the energy of the incident electrons, V_0 the threshold energy. Very similar polarizations are observed for lines belonging to the same spectral series. It might be expected that the polarization curves for Hg, with ground configuration $6s^2$, would resemble those of similar lines in He, which has a ground $1s^2$ configuration. In figure 3 we have therefore plotted the observed polarization for Hg $7\,{}^1D_2 \rightarrow 6\,{}^1P_1$ and the Born approximation for the polarization of He $3\,{}^1D_2 \rightarrow {}^1P_1$, both being given as functions of $\surd(V/V_0)$.

The most puzzling feature of the experimental results is that with decreasing energy the observed polarization rises to a maximum and then decreases, tending to values close to zero at threshold. There is no evident theoretical explanation for this anomalous behaviour at energies less than those at which maximum polarization occurs (an explanation advanced by Oppenheimer (1927*b*) has been shown by Lamb (1957) to be fallacious). If we consider the observed results only for energies greater than those of maximum polarization one may make plausible extrapolations (dashed curves of figure 5) which are in reasonable agreement with the calculated threshold polarizations of table 1 (marked with crosses in figure 5). Referring to figure 3 we see that, apart from the anomalous low-energy experimental results, the agreement between the two curves is quite good, the discrepancy at high energies being very probably due mainly to cascade. A further prediction of the theory is that the polarization should be zero for upper S states. The observations for Hg give zero polarization for upper ${}^1S$ states and zero for ${}^3S_1 \rightarrow {}^3P_2$ transitions. For ${}^3S_1 \rightarrow {}^3P_1$ and ${}^3S_1 \rightarrow {}^3P_0$

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† We do not discuss further the numerical results of Penney for energies above threshold, since the Born–Oppenheimer approximation used has since been shown to be unreliable in this type of calculation (Bates *et al.* 1950).

the observed polarization is zero at moderate and high energies but rises to maxima at low energies of $-12\,\%$ for $7\,^3S_1 \to 6\,^3P_1$ and of $+8\,\%$ for $7\,^3S_1 \to 6\,^3P_0$. These small non-zero values for upper S states may be due to departures from *LS* coupling.

We may conclude that, apart from the anomalous low-energy results, theory and experiment for Hg are in reasonable accord. At energies less than those at which maximum polarization occurs the total light intensity will be small (see figures 1 and 3) and any background unpolarized light will become increasingly important. The problem of collimating the electron beam also becomes more difficult at low energies. Since there still appears to be no explanation of the disagreement with theory at low energies in terms of the reaction $\mathrm{Hg}+e \to \mathrm{Hg}+e+h\nu$ alone, more complicated pressure-dependent reactions may be involved, and further experimental work using modern techniques would be desirable.

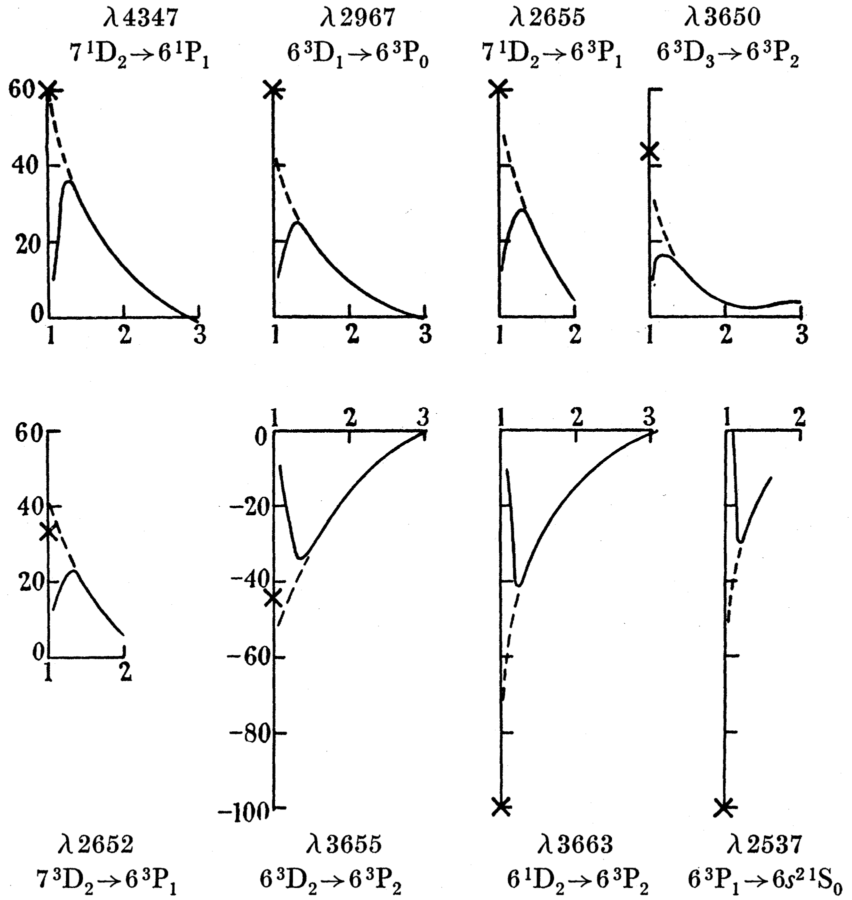

FIGURE 5. Polarization of Hg lines as functions of $\sqrt{(V/V_0)}$. Full line curves give experimental results of Skinner & Appleyard (1927). Crosses give calculated threshold polarizations (for isotopes with $I=0$ and assuming *LS* coupling for the collision process). Dashed curves are extrapolations of full line curves neglecting experimental results for energies less than those at which maximum polarization was measured.

Note added in proof, 20 August 1958: Baranger & Gerjuoy (1958) have discussed the polarization of impact radiation from the standpoint of a compound ion model. Fite & Brackmann (1958) have measured the polarization of *Lyα* radiation excited by electron impact.

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References

Baranger, E. & Gerjuoy, E. 1958 *Proc. Phys. Soc.* **72**, 326.
Bates, D. R., Fundaminsky, A., Leech, J. W. & Massey, H. S. W. 1950 *Phil. Trans.* A, **243**, 93.
Bethe, H. A. 1933 *Hand. Physik.* **24**, part I, pp. 508–515, 2nd ed. Berlin: Springer.
Condon, E. U. & Shortley, G. H. 1951 *The theory of atomic spectra.* (Reprint of 1st ed. 1935.) Cambridge University Press.
Dehmelt, H. G. 1956 *Phys. Rev.* **103**, 1125.
Eldridge, J. A. & Olson, H. F. 1926 *Phys. Rev.* **28**, 1151.
Ellett, A., Foote, P. D. & Mohler, F. L. 1926 *Phys. Rev.* **27**, 31.
Fite, W. L. & Brackmann, R. T. 1958 *Phys. Rev.* (in course of publication).
Hanle, W. & Quarder, B. 1929 *Z. Phys.* **54**, 819.
Heitler, W. 1954 *The quantum theory of radiation* (3rd ed., chap. 5). Oxford University Press.
Khashaba, S. & Massey, H. S. W. 1958 *Proc. Phys. Soc.* **71**, 574.
Kossel, W. & Gerthsen, C. 1925 *Ann. Phys., Lpz.*, **77**, 273.
Lamb, W. E. 1957 *Phys. Rev.* **105**, 559.
Lamb, W. E. & Maiman, T. H. 1957 *Phys. Rev.* **105**, 573.
Massey, H. S. W. & Mohr, C. B. O. 1931 *Proc. Roy. Soc.* A, **132**, 605.
Mott, N. F. & Massey, H. S. W. 1949 *Theory of atomic collisions*, 2nd ed. Oxford: Clarendon Press.
Obi, S., Ishidzu, T., Horie, H., Yanagawa, S., Tanabe, Y. & Sato, M. 1953 *Ann. Obs. astr. Tokyo*, **3**, no. 3 and succeeding issues.
Oppenheimer, J. R. 1927*a* *Z. Phys.* **43**, 27.
Oppenheimer, J. R. 1927*b* *Proc. Nat. Acad. Sci.* **13**, 800.
Oppenheimer, J. R. 1928 *Phys. Rev.* **32**, 361.
Penney, W. G. 1932 *Proc. Nat. Acad. Sci.* **18**, 231.
Quarder, B. 1927 *Z. Phys.* **41**, 674.
Racah, G. 1942 *Phys. Rev.* **62**, 438.
Racah, G. 1943 *Phys. Rev.* **63**, 367.
Seaton, M. J. 1955 *Proc. Phys. Soc.* A, **67**, 457.
Simon, A., Vander Sluis, J. H. & Biedenharn, L. C. 1954 *U.S. Atomic Energy Commission Report* ORNL-1679 (Oak Ridge, Tenn.).
Skinner, H. W. B. 1926 *Proc. Roy. Soc.* A, **112**, 642.
Skinner, H. W. B. & Appleyard, E. T. S. 1927 *Proc. Roy. Soc.* A, **117**, 224.
Smit, J. A. 1935 *Physica*, **2**, 104.
Steiner, K. 1928 *Z. Phys.* **52**, 516.
Wigner, E. P. 1948 *Phys. Rev.* **73**, 1002.