Theory of Elliptically Polarized Photons

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The unitary transformation from linearly to elliptically polarized states of photons is determined in a scheme of the second quantization (§1). It is given by $\mathbf{e}_l=\mathbf{e}_1\cos\varphi+i\mathbf{e}_2\sin\varphi$, $\mathbf{e}_r=i\mathbf{e}_1\sin\varphi+\mathbf{e}_2\cos\varphi$ where $\mathbf{e}_1$ and $\mathbf{e}_2$ are orthogonal unit vectors corresponding to linearly polarized states of photons and $\mathbf{e}_l$ and $\mathbf{e}_r$ are those corresponding to left and right elliptically polarized states of photons. A general formula for a probability of an emission of light from an atom is deduced on the basis of the Dirac electron theory so as to include up to both a magnetic dipole and an electric quadrupole term (§2). Its general form is improved as compared with the hitherto obtained one. The general theory is applied to electric dipole and quadrupole and magnetic dipole spectral lines (§3 and §4). Polarization states of the Zeeman components corresponding to all combinations of magnetic and orbital magnetic quantum numbers of an atom are completely determined for an arbitrary given direction of an observation on the basis of quantum mechanics.

INTRODUCTION

THE relation between various polarization states of photons has not yet been fully discussed, because scientists have been little interested in this line from the theoretical point of view. However, it becomes necessary to know this relation if one wishes to apply the theory to practical cases. For example, in order to discuss polarizations of spectral lines emitted from an atom on the basis of quantum mechanics of light it is necessary to know in what way elliptically polarized states of photons are represented in the scheme of the second quantization.

Kramers[1] discussed the quantization of free radiation, taking circularly polarized states as its bases. A detailed discussion on the circularly polarized states of photons was given later by the author.[2] It was shown that the spin angular momentum[3] of a system consisting of an assemblage of circularly polarized photons has a normal form and this assemblage is only a system having a normal form of its spin angular momentum.[4] It was also found that a left circularly polarized photon has a spin $+1$ in a direction of its momentum and a right circularly polarized photon has a -1.[5]

The general theory was applied to the longitudinal Zeeman effect of electric dipole spectral lines.[6] When Zeeman components of spectral lines are oblique to an applied magnetic field, their polarization states vary in a complex way as a direction of the observation changes.[7] Such a change for quadrupole lines was discussed by Rubinowicz.[8] However, his theory was based on the classical electrodynamics. A theory of this phenomenon based on the quantum mechanics of light has not yet been worked out.

The theory contained in the present paper is a generalization of the previous paper.[2,6] Its purpose is to work out a complete theory of polarizations of photons and spectral lines, to determine an elliptically polarized state of a photon in a scheme of the second quantization, and to apply the general theory thus obtained to the above-mentioned special phenomena.

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[1] H. A. Kramers, "Theorien des Aufbaues der Materie," *Hand-und Jahrbuch der chem. Phys.* (Eucken-Wolf, Leipzig, 1938), Vol. 1, p. 429.

[2] G. Araki, Prog. theor. Phys. **1**, 125 (1946). This paper will be referred to as I.

[3] The separation of angular momentum into orbital and spin was first carried out by Darwin, but in a form of special representation for a field of light as an assemblage of linearly polarized plane waves. The separation in a form which is independent of such a representation is also given in I. C. G. Darwin, Proc. Roy. Soc. London **A136**, 36 (1932). W. Pauli, *Handbuch der Physik* (Verlag-Julius Springer, Berlin, 1933), 24/1, p. 247.

[4] An unitary transformation between polarization states also discussed briefly from another standpoint by W. Pauli, reference 3, p. 252.

[5] It is cited, in W. Heitler, *Quantum Theory of Radiation* (Clarendon Press, Oxford, 1936), p. 63, that the angular momentum of light is discussed by N. Bohr, C. Mannebeck, G. Placzek, and L. Rosenfeld.

[6] G. Araki, Prog. theor. Phys. **2**, 1 (1947). This paper will be referred to as II.

[7] E. Segré, Zeits. f. Physik **66**, 827 (1930); E. Segré und C. J. Bakker, Zeits. f. Physik **72**, 724 (1931).

[8] A. Rubinowicz, Naturwiss. **18**, 227 (1930); Zeits. f. Physik **61**, 338 (1930); **65**, 662 (1930). A. Rubinowicz und J. Biaton, Ergeb. d. exakt. Naturwiss. **11**, 176 (1932).

It was shown in I[2] that a unitary transformation of polarization vectors of a photon has two parameters except for a trivial transformation, and the values of these parameters corresponding to linearly and circularly polarized states were determined. The values of these parameters which correspond to elliptically polarized states of a photon will be determined in the following.

To apply the general theory to a problem of polarizations of spectral lines, a general formula for a probability of an emission of light will next be deduced on the basis of the Dirac electron theory so as to include up to both a magnetic dipole and an electric quadrupole term. The expression of the formula will be improved in a general form compared with the one formerly obtained.

These general theories will finally be applied to electric dipole and quadrupole and magnetic dipole spectral lines. Polarization states of the Zeeman components corresponding to all combinations of magnetic or orbital magnetic quantum numbers will be completely determined for an arbitrary given direction of an observation.

1. ELLIPTICALLY POLARIZED STATES OF A PHOTON

A system of photons is described by a vector potential[9] (an operator) in a scheme of the second quantization. We shall denote this potential by **A**. If the photons are characterized by the energy $\hbar\omega$ and momentum $\hbar\mathbf{k}$ the vector potential is written in the following form:

$$\mathbf{A}=c(2\pi/V)^{\frac{1}{2}}\sum_{\mathbf{k}}\mathbf{A}(\mathbf{k}), \tag{1.1}$$

where

$$\mathbf{A}(\mathbf{k})=(\hbar/\omega)^{\frac{1}{2}}\{\mathbf{a}(\mathbf{k})\exp(i\mathbf{kx}) +\mathbf{a}^{\dagger}(\mathbf{k})\exp(-i\mathbf{kx})\} \tag{1.2}$$

is a monochromatic constituent and † means an adjoint (a Hermitian conjugate). In this representation the Hamiltonian and momentum of the whole system have normal forms [cf. (2.4) of I]. These expressions are independent of the way in which polarizations of photons are represented.

TABLE I.

	Direction of major axis	Eccentricity	
$\mathbf{b}_l$ $0<\varphi<\pi/4$	$\mathbf{e}_1$	$(1-\tan^2\varphi)^{\frac{1}{2}}$	(1.10a)
$\mathbf{b}_l$ $\pi/4<\varphi<\pi/2$	$\mathbf{e}_2$	$(1-\cot^2\varphi)^{\frac{1}{2}}$	
$\mathbf{b}_r$ $0<\varphi<\pi/4$	$\mathbf{e}_2$	$(1-\tan^2\varphi)^{\frac{1}{2}}$	(1.10b)
$\mathbf{b}_r$ $\pi/4<\varphi<\pi/2$	$\mathbf{e}_1$	$(1-\cot^2\varphi)^{\frac{1}{2}}$.	

[9] A longitudinal part of the vector potential and a scalar potential are omitted by a gauge transformation.

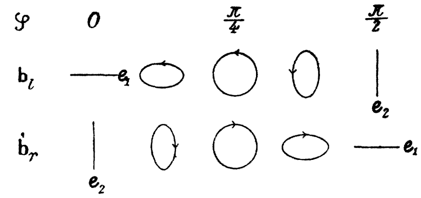

FIG. 1. Polarization ellipses.

We shall now introduce modes of polarizations. The operator $\mathbf{a}(\mathbf{k})$ is represented in two different ways as follows:

$$\mathbf{a}(\mathbf{k})=\mathbf{e}_1(\mathbf{k})a_1(\mathbf{k})+\mathbf{e}_2(\mathbf{k})a_2(\mathbf{k}) =\mathbf{e}_1'(\mathbf{k})a_1'(\mathbf{k})+\mathbf{e}_2'(\mathbf{k})a_2'(\mathbf{k}), \tag{1.3}$$

where $\mathbf{e}_1$ and $\mathbf{e}_2$ are real unit vectors which are perpendicular to each other and to **k**, and $\mathbf{e}_1'$ and $\mathbf{e}_2'$ are normalized complex vectors which are orthogonal to each other and to **k** in the sense of a unitary geometry. The transformation from $(\mathbf{e}_1, \mathbf{e}_2)$ to $(\mathbf{e}_1', \mathbf{e}_2')$ is then unitary, and a Hermitian unit form of components of **a** is its invariant. These normalized vectors will be referred to as polarization vectors of **k** photons. Hermitian operators $a_1^{\dagger}(\mathbf{k})a_1(\mathbf{k})$ and $a_2^{\dagger}(\mathbf{k})a_2(\mathbf{k})$ represent numbers of linearly polarized photons, and $a_1'^{\dagger}(\mathbf{k})a_1'(\mathbf{k})$ and $a_2'^{\dagger}(\mathbf{k})a_2'(\mathbf{k})$ are those characterized by the polarization vectors $\mathbf{e}_1'(\mathbf{k})$ and $\mathbf{e}_2'(\mathbf{k})$. $a_j(\mathbf{k})$ and $a_j'(\mathbf{k})$ $(j=1, 2)$ will be referred to as number amplitude operators.

The most general unitary $2\cdot 2$ matrix is given by

$$\begin{pmatrix}\cos\varphi\exp i\theta_1 & \sin\varphi\exp i(\theta_1+\theta)\\ -\sin\varphi\exp i(\theta_2-\theta) & \cos\varphi\exp i\theta_2\end{pmatrix} \tag{1.4}$$

[cf. (3.11) of I]. A transformation such as

$$\begin{pmatrix}\exp i\theta_1 & 0\\ 0 & \exp i\theta_2\end{pmatrix} \tag{1.5}$$

is trivial for polarization vectors. Consequently, we can omit this type. The most general unitary transformation of polarization vectors can thus be written as follows:

$$\begin{aligned}\mathbf{e}_1'&=\mathbf{e}_1\cos\varphi-\mathbf{e}_2\sin\varphi\exp(-i\delta),\\ \mathbf{e}_2'&=\mathbf{e}_1\sin\varphi\exp(i\delta)+\mathbf{e}_2\cos\varphi,\end{aligned} \tag{1.6}$$

where δ is equal to $\theta+\theta_1-\theta_2$ [cf. (3.1), (3.4), and (3.5) of I] and $\mathbf{k}$ is omitted for the sake of simplicity.

It was shown in I that $\mathbf{e}_1'$ and $\mathbf{e}_2'$ correspond to two linearly polarized states for $\delta=0$ and an arbitrary value of φ, and to left and right circularly polarized states of the photon for $\delta=\pi/2$ and $\varphi=\pi/4$. Elliptically polarized states must correspond to another set of values for δ and φ. We shall now determine values of these parameters which correspond to elliptically polarized states with given major axes and eccentricities.

In the previous paper $\mathbf{A}(\mathbf{k})$ was represented by two linearly polarized orthogonal states or by left and right circularly polarized states as its base. Now we adopt, as the base, left and right elliptically polarized plane waves as follows:

$$\begin{aligned}\mathbf{b}_l(\mathbf{k})&=\mathbf{e}_1\cos\varphi\sin(\omega t-\mathbf{kx}+\epsilon_l)\\&\qquad-\mathbf{e}_2\sin\varphi\cos(\omega t-\mathbf{kx}+\epsilon_l),\\\mathbf{b}_r(\mathbf{k})&=-\mathbf{e}_1\sin\varphi\cos(\omega t-\mathbf{kx}+\epsilon_r)\\&\qquad+\mathbf{e}_2\cos\varphi\sin(\omega t-\mathbf{kx}+\epsilon_r),\end{aligned}\tag{1.7}$$

where

$$0\leqq\varphi\leqq\pi/2.\tag{1.8}$$

The monochromatic constituent of the vector potential is then given by

$$2^{-\frac{1}{2}}\mathbf{A}(\mathbf{k})=A_l(\mathbf{k})\mathbf{b}_l(\mathbf{k})+A_r(\mathbf{k})\mathbf{b}_r(\mathbf{k}).\tag{1.9}$$

If we assume for the sake of convenience that $\mathbf{e}_1$, $\mathbf{e}_2$, and $\mathbf{k}$ form a right-handed system, vector potentials given by $\mathbf{b}_l(\mathbf{k})$ and $\mathbf{b}_r(\mathbf{k})$, correspond, in general, to left and right elliptically polarized plane waves of monochromatic lights, respectively, because an electric field of light is given by $\dot{\mathbf{A}}-/c$. Particularly in the cases where $\varphi=0$ or $\varphi=\pi/2$ linearly polarized lights are given whose directions of oscillations are perpendicular to each other, and for $\varphi=\pi/4$ they correspond to left and right circularly polarized lights, respectively. When φ is not equal to 0, $\pi/4$, or $\pi/2$, ends of electric vectors derived from $\mathbf{b}_l(\mathbf{k})$ and $\mathbf{b}_r(\mathbf{k})$ describe ellipses. Directions of their major axes and their eccentricities are given in Table I. This is shown in Fig. 1 (against light). These ellipses will be referred to as polarization ellipses.

Now we put

$$\begin{aligned}\mathbf{q}_l(\mathbf{k})&=A_l\{\mathbf{e}_1\cos\varphi\sin(\omega t+\epsilon_l)\\&\qquad-\mathbf{e}_2\sin\varphi\cos(\omega t+\epsilon_l)\},\\\mathbf{q}_r(\mathbf{k})&=A_r\{-\mathbf{e}_1\sin\varphi\cos(\omega t+\epsilon_r)\\&\qquad+\mathbf{e}_2\cos\varphi\sin(\omega t+\epsilon_r)\},\\\mathbf{p}_l(\mathbf{k})&=\dot{\mathbf{q}}_l(\mathbf{k}),\quad\mathbf{p}_r(\mathbf{k})=\dot{\mathbf{q}}_r(\mathbf{k}).\end{aligned}\tag{1.11}$$

$$\mathbf{a}(\mathbf{k})=(\omega/2\hbar)^{\frac{1}{2}}\{\mathbf{q}(\mathbf{k})+i\mathbf{p}(\mathbf{k})/\omega\},\tag{1.12a}$$

$$\mathbf{a}_j(\mathbf{k})=(\omega/2\hbar)^{\frac{1}{2}}\{\mathbf{q}_j(\mathbf{k})+i\mathbf{p}_j(\mathbf{k})/\omega\}\quad(j=l,r),\tag{1.12b}$$

and substitute these expressions for the right-hand side of (1.9). Comparing the result with (1.2) and (1.12a) we find that $\mathbf{a}$, $\mathbf{q}$, and $\mathbf{p}$ are decomposed as follows:

$$\mathbf{a}(\mathbf{k})=\mathbf{a}_l(\mathbf{k})+\mathbf{a}_r(\mathbf{k}),\tag{1.13a}$$

$$\mathbf{q}(\mathbf{k})=\mathbf{q}_l(\mathbf{k})+\mathbf{q}_r(\mathbf{k}),\quad\mathbf{p}(\mathbf{k})=\mathbf{p}_l(\mathbf{k})+\mathbf{p}_r(\mathbf{k}).\tag{1.13b}$$

The operators with a suffix l correspond to a system of left elliptically polarized photons characterized by (1.10a), and the operators with a suffix r correspond to a system of right elliptically polarized photons characterized by (1.10b).

Further, if we introduce

$$\begin{aligned}q_l(\mathbf{k})&=A_l\sin(\omega t+\epsilon_l),\\q_r(\mathbf{k})&=A_r\sin(\omega t+\epsilon_r),\\p_l(\mathbf{k})&=\dot{q}_l(\mathbf{k}),\quad p_r(\mathbf{k})=\dot{q}_r(\mathbf{k}),\end{aligned}\tag{1.14}$$

(1.11) has the following form:

$$\begin{aligned}\mathbf{q}_l&=\mathbf{e}_1q_l\cos\varphi-\mathbf{e}_2(p_l/\omega)\sin\varphi,\\\mathbf{p}_l&=\mathbf{e}_1p_l\cos\varphi+\mathbf{e}_2\omega q_l\sin\varphi,\end{aligned}\tag{1.15a}$$

$$\begin{aligned}\mathbf{q}_r&=-\mathbf{e}_1(p_r/\omega)\sin\varphi+\mathbf{e}_2q_r\cos\varphi,\\\mathbf{p}_r&=\mathbf{e}_1\omega q_r\sin\varphi+\mathbf{e}_2p_r\cos\varphi,\end{aligned}\tag{1.15b}$$

where $\mathbf{k}$ is omitted for the sake of simplicity. In this transformation operators with a suffix l or r are substituted, respectively, by those with the same suffix and do not mix with those with different suffices. Consequently, the operators with a suffix l or r still correspond to left or right elliptically polarized photons, respectively. The relation between (a_1, a_2) and (q_1, p_1, q_2, p_2) is given by an isomorphic equation of (1.12):

$$a_j(\mathbf{k})=(\omega/2\hbar)^{\frac{1}{2}}\{q_j(\mathbf{k})+ip_j(\mathbf{k})/\omega\}\quad(j=1,2),\tag{1.16}$$

where (q_1, p_1) and (q_2, p_2) are canonically conjugate Hermitian operators of linearly polarized photons which are, respectively, characterized by $\mathbf{e}_1(\mathbf{k})$ and $\mathbf{e}_2(\mathbf{k})$.

By (1.3), (1.12b), (1.13a), (1.15), and (1.16) the transformation from (q_1, p_1, q_2, p_2) to (q_l, p_l, q_r, p_r) can be obtained as follows:

$$\begin{aligned}q_l&=q_1\cos\varphi+(p_2/\omega)\sin\varphi,\\p_l&=p_1\cos\varphi-\omega q_2\sin\varphi,\\q_r&=q_2\cos\varphi+(p_1/\omega)\sin\varphi,\\p_r&=p_2\cos\varphi-\omega q_1\sin\varphi.\end{aligned}\tag{1.17}$$

A commutation relation between q_1, p_1, q_2, and p_2 is that

$$q_1p_1-p_1q_1=q_2p_2-p_2q_2=i\hbar \tag{1.18}$$

and other pairs are commutative. This relation is invariant for the transformation (1.17):

$$q_lp_l-p_lq_l=q_rp_r-p_rq_r=i\hbar, \tag{1.19}$$

other pairs being commutative. Moreover, it is also invariant for the transformation (1.15):

$$\mathbf{q}_l\mathbf{p}_l-\mathbf{p}_l\mathbf{q}_l=\mathbf{q}_r\mathbf{p}_r-\mathbf{p}_r\mathbf{q}_r=i\hbar, \tag{1.20}$$

other pairs being commutative. By (1.15) and (1.19), $\mathbf{q}_l$, $\mathbf{p}_l$, $\mathbf{q}_r$, and $\mathbf{p}_r$ satisfy

$$\mathbf{p}_l\mathbf{p}_r+\omega^2\mathbf{q}_l\mathbf{q}_r=0. \tag{1.21}$$

Therefore, the Hamiltonian and the momentum of a system of photons take normal forms for the representation given by (1.13b):

$$\mathbf{p}^2(\mathbf{k})+\omega^2\mathbf{q}^2(\mathbf{k})=\mathbf{p}_l^2(\mathbf{k})+\omega^2\mathbf{q}_l^2(\mathbf{k}) +\mathbf{p}_r^2(\mathbf{k})+\omega^2\mathbf{q}_r^2(\mathbf{k}), \tag{1.22}$$

[cf. (1.15) of I].[10] This normal form is invariant for both the transformations (1.15) and (1.17):

$$\begin{aligned}\mathbf{p}_l^2+\omega^2\mathbf{q}_l^2&=p_l^2+\omega^2q_l^2,\\ \mathbf{p}_r^2+\omega^2\mathbf{q}_r^2&=p_r^2+\omega^2q_r^2.\end{aligned} \tag{1.23a}$$

$$p_l^2+\omega^2q_l^2+p_r^2+\omega^2q_r^2 =p_1^2+\omega^2q_1^2+p_2^2+\omega^2q_2^2. \tag{1.23b}$$

Consequently, the real transformations (1.15) and (1.17) are canonical. Two pairs (q_l, p_l) and (q_r, p_r) are canonically conjugate Hermitian operators of left and right elliptically polarized photons, respectively, because of the invariant relation given by (1.23a). A transformation from canonically conjugate coordinates and momenta to number amplitude operators is therefore given by (1.12) and

$$\begin{aligned}a_l&=(\omega/2\hbar)^{\frac{1}{2}}(q_l+ip_l/\omega),\\ a_r&=(\omega/2\hbar)^{\frac{1}{2}}(q_r+ip_r/\omega),\end{aligned} \tag{1.24}$$

[cf. §§2 and 3 of I]. The Hermitian operators $\mathbf{a}_l\dagger\mathbf{a}_l$ and $a_l\dagger a_l$ represent the number of left elliptically polarized photons characterized by a polarization ellipse specified by (1.10) (a), and $\mathbf{a}_r\dagger\mathbf{a}_r$ and $a_r\dagger a_r$ represent that of right elliptically polarized photons characterized by (1.10) (b).

The relations (1.12) (b), (1.13) (a), (1.15) and (1.24) give the following transformations of polarization vectors and number amplitude operators:

$$\begin{aligned}\mathbf{e}_l&=\mathbf{e}_1\cos\varphi+i\mathbf{e}_2\sin\varphi,\\ \mathbf{e}_r&=i\mathbf{e}_1\sin\varphi+\mathbf{e}_2\cos\varphi,\end{aligned} \tag{1.25}$$

$$\mathbf{a}_l=\mathbf{e}_la_l,\quad \mathbf{a}_r=\mathbf{e}_ra_r. \tag{1.26}$$

The transformation of number amplitude operators is contragredient to that of polarization vectors [see (1.3)]. Therefore, we have

$$\begin{aligned}a_l&=a_1\cos\varphi-ia_2\sin\varphi,\\ a_r&=-ia_1\sin\varphi+a_2\cos\varphi.\end{aligned} \tag{1.27}$$

The Hermitian unit form of number amplitude operators is invariant for the transformations (1.26) and (1.27).

Comparing (1.25) with (1.6) we see that elliptically polarized states correspond to $\delta=\pi/2$ and an arbitrary value of φ, where directions of major axes and eccentricities of polarization ellipses are characterized by φ according to (1.10). The other values of δ correspond to the other complex basic states of polarizations, in which we are interested not from a practical but only from a theoretical standpoint. The expression (1.25) of polarization vectors includes thus all practical cases of polarizations: linearly, circularly, and elliptically polarized states. The result discussed in I is naturally involved in the present case: $\mathbf{e}_l=\mathbf{e}^+$ and $\mathbf{e}_r=i\mathbf{e}^-$ for $\varphi=\pi/4$; the transformations (1.15) and (1.17) reduce to (4.8) and (3.23) of I, respectively, by putting $\varphi=\pi/4$, where p_r/ω and $-\omega q_r$ in I are to be replaced, respectively, by q_r and p_r in the present paper.

2. PROBABILITY FOR EMISSION OF PHOTON

A semirelativistic formula for an intensity of light emitted from an atom was discussed in §7 of II.[6] A probability per second per unit solid

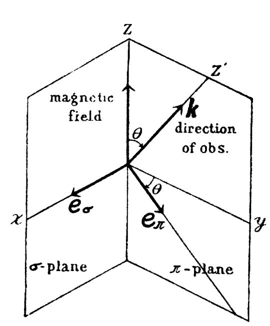

FIG. 2.

[10] The spin of the system does not take a normal form unless φ is equal to $\pi/4$. This was shown in §§3 and 4 of I.

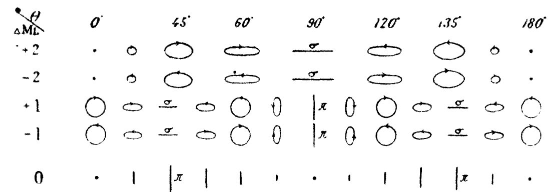

FIG. 3. Polarization states of quadrupole lines.

angle for an emission of a photon from the atom is given by

$$W=(2\pi)^2(\nu/c)^3|(\psi_b, O\psi_a)|^2, \qquad (2.1)$$

where

$$O=1/(2\pi\nu)\sum_{j=1}^{N}\exp(-i\mathbf{kx}_j)\{\mathbf{e}\nabla^{(j)}+\mathbf{S}^{(j)}[\mathbf{ke}]\} \quad (2.2)$$

and $2\pi\nu$, $\mathbf{k}$, and $\mathbf{e}$ are, respectively, an energy, a momentum, and a complex conjugate of a polarization vector of the emitted photon. ($\mathbf{e}$ is not a polarization vector itself but its complex conjugate!) The Hartree atomic unit is used throughout this and the following sections ($\hbar=e=m=1$). ψ_a and ψ_b are normalized eigenfunctions of the atom in its initial and final states, respectively. N is the number of electrons contained in the atom.

It is well known that electric dipole and quadrupole parts are included in the above formula.[11] A magnetic dipole part has, however, not been separated in the form corresponding just to the fact that an electron has a magnetic moment of unit Bohr's magneton, although it was imagined from a correspondence to the classical electrodynamics.[12] The separation of these parts can be carried out as follows.

We expand O in a power series in $|\mathbf{k}|$. We have then

$$O=1/(2\pi\nu)\sum_{j=1}^{N}\{\mathbf{e}\nabla^{(j)}+\mathbf{S}^{(j)}[\mathbf{ke}] -i(\mathbf{kx}_j)(\mathbf{e}\nabla^{(j)})+\cdots\}. \quad (2.3)$$

As was mentioned in §7 of II, if we assume that eigenfunctions of the atom satisfy the Schrödinger equation

$$-(1/2)\sum_{j=1}^{N}\Delta_j\psi_a+U\psi_a=E_a\psi_a, \qquad (2.4)$$

where U is a point function, it can be shown that

$$1/(2\pi\nu)\sum_{j=1}^{N}(\psi_b, \nabla^{(j)}\psi_a)=-(\psi_b, \mathbf{P}\psi_a), \qquad (2.5)$$

where E_a-E_b is replaced by $2\pi\nu$, and $\mathbf{P}=-\sum_{j=1}^{N}\mathbf{x}_j$ is an electric dipole moment of the atom. Using an identity

$$2(\mathbf{kx})(\mathbf{e}\nabla)=[\mathbf{ke}]\cdot[\mathbf{x}\nabla]+(\mathbf{ex})(\mathbf{k}\nabla)+(\mathbf{kx})(\mathbf{e}\nabla), \qquad (2.6)$$

the second and third terms of (2.3) can be transformed into the following form:

$$1/(2\pi\nu)\sum_{j=1}^{N}\{\mathbf{S}^{(j)}[\mathbf{ke}]-i(\mathbf{kx}_j)(\mathbf{e}\nabla^{(j)})\} =-[\mathbf{ke}/|\mathbf{k}|]\mathbf{M}-i/(4\pi\nu) \times\sum_{j=1}^{N}\{(\mathbf{ex}_j)(\mathbf{k}\nabla^{(j)})+(\mathbf{kx}_j)(\mathbf{e}\nabla^{(j)})\}, \qquad (2.7)$$

where a pseudovector

$$\mathbf{M}=-(\mathbf{L}+2\mathbf{S})\alpha/2 \qquad (2.8)$$

is a magnetic dipole moment of the atom, α is the Sommerfeld fine structure constant, and pseudovectors

$$\mathbf{L}=-\sum_{j=1}^{N}i[\mathbf{x}_j\nabla^{(j)}], \quad \mathbf{S}=\sum_{j=1}^{N}\mathbf{S}^{(j)} \qquad (2.9)$$

are, respectively, orbital and spin angular momenta of the atom.

From the Schrödinger equation (2.4), it follows on account of a Hermitian property of a Laplacian operator that

$$\begin{aligned}2\pi\nu(\psi_b, (\mathbf{ex}_k)(\mathbf{kx}_k)\psi_a) &=(1/2)\sum_{j=1}^{N}\{(\psi_b, \Delta_j(\mathbf{ex}_k)(\mathbf{kx}_k)\psi_a) -(\psi_b, (\mathbf{ex}_k)(\mathbf{kx}_k)\Delta_j\psi_a)\}\\ &=(\psi_b, \{(\mathbf{ex}_k)(\mathbf{k}\nabla^{(k)})+(\mathbf{kx}_k)(\mathbf{e}\nabla^{(k)})\}\psi_a). \qquad (2.10)\end{aligned}$$

This equation enables us to write the second term of (2.7) as follows:

$$-i/(4\pi\nu)\sum_{j=1}^{N}(\psi_b, \{(\mathbf{ex}_j)(\mathbf{k}\nabla^{(j)}) +(\mathbf{kx}_j)(\mathbf{e}\nabla^{(j)})\}\psi_a)=(i/2)(\psi_b, \mathbf{e}Q\mathbf{k}\psi_a), \qquad (2.11)$$

where a tensor Q of the second rank with its

[11] H. Bethe, *Handbuch der Physik* (Geiger-Scheel, 1933), 24/1 pp. 429, 473; G. Wentzel, *ibid.*, pp. 779, 783.

[12] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (University Press, Cambridge, 1935), p. 90; O. Klein, Zeits. f. Physik **41**, 407 (1927).

components

$$Q_{xx} = -\sum_{j=1}^{N} x_j^2, \quad Q_{xy} = -\sum_{j=1}^{N} x_j y_j, \cdots \qquad (2.12)$$

is an electric quadrupole moment of the atom.

From (2.1), (2.3), (2.5), and (2.11) we have

$$W = (2\pi)^2(\nu/c)^3 |(\psi_b, O'\psi_a)|^2, \qquad (2.13a)$$

$$O' = \mathbf{eP} + [\mathbf{ke}/|\mathbf{k}|]\mathbf{M} + (1/2i)\mathbf{e}Q\mathbf{k} + \cdots. \qquad (2.13b)$$

This agrees, except for the second term, with an expression derived by Bethe,[13] but his expression is referred to special axes. The magnetic moment included in the second term is given by (2.8). This involves a spin term which is missing in Bethe's. This term is due to the second term in the brace of (2.2), and the latter follows from a semirelativistic term[14] in an approximation of the Dirac interaction between an atom and photons (cf. §6 of II)) and it is omitted from the usual expressions. The third term in (2.13b) is more general than Wentzel's expression.[15] Energy radiated per second per solid angle from the atom is given by $2\pi\nu W$. This intensity formula has a complete analogy with a classical one. According to the classical electrodynamics, a time average of an energy of a monochromatic light radiated from a point source with oscillating electric dipole and quadrupole and magnetic dipole moments per unit solid angle per second is given by[16]

$$I_{Cl} = (1/4)(2\pi/c)^3\nu^4\{\mathbf{e}_0\mathbf{P}_0 + [\mathbf{ke}_0/|\mathbf{k}|]\mathbf{M}_0 + (1/2)\mathbf{e}_0 Q_0 \mathbf{k}\}^2, \qquad (2.14)$$

where $\mathbf{e}_0$ is an unit real vector parallel to an electric field of the emitted light, and $\mathbf{P}_0$, $\mathbf{M}_0$, and Q_0 are amplitudes of electric dipole, magnetic dipole, and electric quadrupole moments of the source.

3. POLARIZATION STATES OF QUADRUPOLE LINES

We shall consider polarization states of electric quadrupole spectral lines emitted from an atom placed in a magnetic field. Let a direction of the magnetic field be z axis, a direction of an observation be z' axis, an angle between z and z' axes be $\theta(0 \leqq \theta \leqq \pi)$, a plane determined by z and z' axes be π-plane, and y axis be in π-plane. The xz plane will be referred to as σ-plane. If we assume $\mathbf{e}_1$ to be parallel to x axis, $\mathbf{e}_2$ must then be in π-plane and it makes an angle θ with y axis. We shall write $\mathbf{e}_\sigma$ and $\mathbf{e}_\pi$, respectively, instead of $\mathbf{e}_1$ and $\mathbf{e}_2$. Lines parallel to these vectors will be referred to as σ-axis and π-axis, respectively (see Fig. 2).

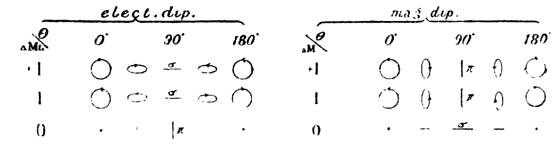

FIG. 4. Polarization states of dipole lines.

Complex conjugates of the polarization vectors given by (1.25) are then

$$\mathbf{e}_l^* = \mathbf{e}_\sigma \cos\varphi - i\mathbf{e}_\pi \sin\varphi,$$
$$\mathbf{e}_r^* = -i\mathbf{e}_\sigma \sin\varphi + \mathbf{e}_\pi \cos\varphi. \qquad (3.1)$$

The electric quadrupole part of the operator O' takes then its explicit form as follows:

$$\begin{aligned} 1/(2i)\mathbf{e}_l^* Q\mathbf{k} &= (|\mathbf{k}|/8)\{Q^{++}\sin\theta(\cos\theta\sin\varphi - \cos\varphi) \\ &+ Q^{--}\sin\theta(\cos\theta\sin\varphi + \cos\varphi) \\ &+ 2iQ^{z+}[(2\cos^2\theta - 1)\sin\varphi - \cos\theta\cos\varphi] \\ &- 2iQ^{z-}[(2\cos^2\theta - 1)\sin\varphi + \cos\theta\cos\varphi] \\ &+ Q^0 \sin 2\theta \sin\varphi\}, \end{aligned} \qquad (3.2a)$$

$$\begin{aligned} 1/(2i)\mathbf{e}_r^* Q\mathbf{k} &= (|\mathbf{k}|/8)\{iQ^{++}\sin\theta(\cos\theta\cos\varphi + \sin\varphi) \\ &+ iQ^{--}\sin\theta(\cos\theta\cos\varphi - \sin\varphi) \\ &- 2Q^{z+}[(2\cos^2\theta - 1)\cos\varphi + \cos\theta\sin\varphi] \\ &+ 2Q^{z-}[(2\cos^2\theta - 1)\cos\varphi - \cos\theta\sin\varphi] \\ &+ iQ^0 \sin 2\theta \cos\varphi\}, \end{aligned} \qquad (3.2b)$$

where

$$Q^{++} = -\sum_{j=1}^{N}(x_j^+)^2, \qquad Q^{--} = -\sum_{j=1}^{N}(x_j^-)^2,$$

$$Q^{z+} = -\sum_{j=1}^{N} z_j x_j^+, \qquad Q^{z-} = -\sum_{j=1}^{N} z_j x_j^-, \qquad (3.3a)$$

$$Q^0 = -\sum_{j=1}^{N}(2z_j^2 - x_j^+ x_j^-),$$

$$x_j^+ = x_j + iy_j, \qquad x_j^- = x_j - iy_j. \qquad (3.3b)$$

From these expressions we shall now be able to determine a polarization state of the emitted

[13] H. Bethe, see reference 11, p. 473.

[14] This also follows from a correspondence to the classical electrodynamics. See reference 1, p. 460.

[15] G. Wentzel, reference 11, p. 783.

[16] A. Rubinowicz and J. Blaton, Ergeb. d. exakt. Naturwiss. 11, 176 (1932).

light. For example, a probability for an emission of the quadrupole Zeeman component corresponding to $\Delta M_L=+1$ is given by (2.13a) in which 0′ is replaced by the third term of (3.2a) or (3.2b), according to whether the emitted light is left elliptically or right elliptically polarized. Matrix elements of other terms vanish because selection rules for inner and azimuthal quantum numbers of a matrix of Q^{z+} are different from dipole terms and that for an orbital magnetic quantum number is also different from other quadrupole terms. If the coefficient of Q^{z+} in (3.2a) vanishes for a value of θ and that in (3.2b) does not for the same value of θ, there is no probability for an emission of a left elliptically polarized light, and the emitted light in this direction must be right elliptically polarized. The other cases can be examined in the same way.

Non-vanishing matrix elements of Q^{++}, Q^{--}, Q^{z+}, Q^{z-}, and Q^0 are given,[17] respectively, by $\Delta M_L=+2,\ -2,\ +1,\ -1$, and 0, where ΔM_L is an increment (not a difference!) of an orbital magnetic quantum number of the atom. Changes of polarization states, with θ, of the Zeeman components of electric quadrupole lines corresponding to these ΔM_L can conveniently be determined according to the following procedure. For this purpose we use the following two conditions for a coefficient of Q^{++}, Q^{--}, Q^{z+}, Q^{z-}, or Q^0 in (3.2): condition L—the coefficient in (3.2b) vanishes and that in (3.2a) does not; condition R—the coefficient in (3.2a) vanishes and that in (3.2b) does not.

Using these conditions we can proceed as follows:

1⁰. For $\varphi=0$ condition L gives directions in which σ-component is emitted, and condition R gives directions in which π-component is emitted.

2⁰. For $\varphi=\pi/4$ condition L gives directions in which a left circularly polarized component is emitted, and condition R gives directions in which a right circularly polarized component is emitted.

3⁰. For $0<\varphi<\pi/4$ or $\pi/4<\varphi<\pi/2$ condition L gives directions in which a left elliptically polarized component is emitted, and condition R gives directions in which a right elliptically polarized component is emitted. Eccentricities of polarization ellipses of these components are $(1-\tan^2\varphi)^{\frac{1}{2}}$ for $0<\varphi<\pi/4$ and $(1-\cot^2\varphi)^{\frac{1}{2}}$ for $\pi/4<\varphi<\pi/2$. The major axis in the left elliptically polarized case is σ-axis for $0<\varphi<\pi/4$ and π-axis for $\pi/4<\varphi<\pi/2$. In the right elliptically polarized case it is π-axis for $0<\varphi<\pi/4$ and σ-axis for $\pi/4<\varphi<\pi/2$.

For example, conditions L and R for $\Delta M_L=+1$ are as follows.

Condition L:

$$\left.\begin{aligned}(2\cos^2\theta-1)\cos\varphi+\cos\theta\sin\varphi=0\\(2\cos^2\theta-1)\sin\varphi-\cos\theta\cos\varphi\neq 0\end{aligned}\right\},\tag{3.4a}$$

Condition R:

$$\left.\begin{aligned}(2\cos^2\theta-1)\sin\varphi-\cos\theta\cos\varphi=0\\(2\cos^2\theta-1)\cos\varphi+\cos\theta\sin\varphi\neq 0\end{aligned}\right\}.\tag{3.4b}$$

For $\varphi=0$ they give

$$\text{Condition } L:\quad \theta=\pi/4,\ 3\pi/4;\tag{3.5a}$$

$$\text{Condition } R:\quad \theta=\pi/2.\tag{3.5b}$$

The quadrupole Zeeman component corresponding to $\Delta M_L=+1$ is, therefore, σ-component for $\theta=\pi/4$, $3\pi/4$, and π-component for $\theta=\pi/2$. In the other directions of an observation the emitted light is not linearly polarized.

For $\varphi=\pi/4$ the conditions (3.4) give

$$\text{Condition } L:\quad \theta=\pi/3,\ \pi;\tag{3.6a}$$

$$\text{Condition } R:\quad \theta=0,\ 2\pi/3.\tag{3.6b}$$

The emitted light is therefore left circularly polarized for $\theta=\pi/3$, π, and right circularly polarized for $\theta=0$, $2\pi/3$. Thus when θ is not equal to 0, $\pi/4$, $\pi/3$, $\pi/2$, $2\pi/3$, $3\pi/4$, and π, the emitted light is elliptically polarized. It is not in agreement with the result by Rubinowicz and Blaton[18] that the emitted light is circularly polarized for $\theta=\pi/3$, $2\pi/3$.

For $0<\varphi<\pi/4$ the conditions (3.4) give

Condition L:

$$\pi/4<\theta<\pi/3 \quad\text{and}\quad 3\pi/4<\theta<\pi;\tag{3.7a}$$

Condition R:

$$\pi/2<\theta<2\pi/3.\tag{3.7b}$$

[17] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (University Press, Cambridge, 1935), p. 59.

[18] A. Rubinowicz und J. Blaton, Ergeb. d. exakt. Naturwiss. 11, 176 (1932), Tables I and III.

For $\pi/4<\varphi<\pi/2$ they give

Condition L:

$$\pi/3<\theta<\pi/2; \qquad (3.8a)$$

Condition R:

$$0<\theta<\pi/4 \quad \text{and} \quad 2\pi/3<\theta<3\pi/4. \qquad (3.8b)$$

The emitted light is left elliptically polarized in the range given by (3.7a) and (3.8a), and right elliptically polarized in the range given by (3.7b) and (3.8b). Their polarization ellipses are characterized by the values of φ which are determined as functions of θ by Eq. (3.4).

Polarization states of the other components, corresponding to the other selection rules, can be determined in the same way. The result is represented in Fig. 3 (against light). In this figure a point means that the intensity vanishes.

4. ELECTRIC AND MAGNETIC DIPOLE LINES

Polarization states of the Zeeman components of electric and magnetic dipole lines can also be determined in the same way. The result is represented in Fig. 4 (against light). In the case of the magnetic dipole lines figures are arranged according to selection rules of a magnetic quantum number M of the atom, instead of an orbital magnetic quantum number M_L.

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Measurements of Thomson Coefficients for Metals at High Temperatures and of Peltier Coefficients for Solid-Liquid Interfaces of Metals

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Apparatus has been devised for measuring and measurements made of Thomson coefficients of metals at high temperatures. It is found that in the range from 400°C to the melting point the approximation $\sigma=\beta T$ is adequate for platinum, palladium, copper, and silver but not for gold, molybdenum, and tungsten.

Experimental results for the Peltier coefficients for solid-liquid interfaces of gold, silver, and copper are also reported. An experimental sensitivity of 0.1 millivolt revealed no effect in gold and silver, but +10.2 millivolts were obtained for copper.

I. INTRODUCTION

ALTHOUGH the thermoelectric Peltier and Thomson effects are usually of secondary importance in practical electrothermal phenomena they may become of immediate importance when thermal or electrical symmetry is a primary consideration. Thus such effects may play significant parts in contact phenomena; for example, in contact erosion and in the low frequency behavior of a circuit containing metal-semiconductor junctions. These thermoelectric effects are also of theoretical interest since they provide important clues to the electronic structure of conductors.

This article describes apparatus devised for measuring and measurements made of: (a) the liquid-solid Peltier coefficients of Au, Ag, and Cu; and (b) the Thomson coefficients for solid Pt, Pd, Ag, Au, Cu, W, and Mo at high temperatures.

II. THE LIQUID-SOLID PELTIER EFFECT OF Au, Ag, AND Cu

A. Theory

An electric current flowing through the boundary between two materials not having the same composition or structure produces heat in proportion to the current flowing. The Peltier coefficient between materials A and B at temperature T may be defined by

$${}_AP_B(T)=\Delta Q/i\times t,$$

where ΔQ is the heat evolved at the junction when current i flows for time t across the junction. Here a positive sign is taken to mean that heat is absorbed by the junction when electrons flow from B to A. This is the usual convention.