

follows from the fact that when we look at the wave equation from the calculus of variations standpoint, we know that in the neighborhood of the correct "Eigenfunktion" ψ and the correct "Eigenwerte" E , $\delta E = 0$ for any $\delta\psi$. Incidentally, this also indicates why the Ritz method seems to be a particularly powerful one in calculating the approximate energy values of the wave equation.

¹ Van Vleck, J. H., *Proc. Nat. Acad. Sci.*, **12**, 662, 1926.

² An abstract of this paper has appeared in the Bulletins of *Amer. Phys. Soc.*, Chicago meeting, November, 1927.

³ Kellner, G. W., *Zeits. Physik*, **44**, 91, 1927.

⁴ Wills and Hector, *Physic. Rev.*, **23**, 209, 1926; Hector, *ibid.*, **24**, 418, 1926.

⁵ Soné, T., *Phil. Mag.*, **39**, 305, 1920.

⁶ Lehrer, E., *Ann. Physik*, **81**, 229, 1926.

ON THE QUANTUM THEORY OF THE POLARIZATION OF IMPACT RADIATION

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The general theory of the polarization of light excited by electronic impact has been given in a previous paper.¹ In particular, it is shown that the polarization computed on the quantum mechanics is independent of the axis chosen for describing the directional degeneracy of the atom. It is further shown that, if one neglects the spin of the impacting electron and if one assumes that the perturbing interaction energy is small, the polarization of the emitted light may be computed "as if" only those states were excited, for which the component of angular momentum in a certain direction is the same as in the normal state; and the direction is that of the vector difference of the velocities of the incident and scattered electron. If this result is applied to electrons with just the necessary energy to excite the atom, it yields the momentum rule formulated by Skinner; the excitation does not change the component of angular momentum in the direction of the electron beam. Experimentally² one finds that these rules fail in two ways: (1) They do not apply to intercombination lines; in particular, they fail conspicuously for radiation from the 3S_1 and 3P_1 states of mercury; and (2) the observed polarization tends, as the energy of the exciting electron is diminished, first, towards a maximum, which in the case of normal lines is proportional to and of the same sign as that given by the rule, and, as the energy is further decreased, tends to zero. In this paper we shall show that the first of these discrepancies

may be explained when one takes into account the spin of the impacting electron and the Heisenberg resonance principle,³ and that the second follows when one discards the assumption that the perturbing energy is small. The theory may thus be made to give a complete account of the experimental results.

We shall first show that, as the velocity of the exciting electron approaches that of the resonance potential in question, the polarization of the excited line tends to zero. If $\psi_n(X)$ be the wave functions of the atom, we may write⁴ the wave function for the system atom + electron:

$$\Psi(X; r, \vartheta, \varphi) = \sum_{n=0} \psi_n(X) \chi_n(r, \vartheta, \varphi) = \sum_{n=0} \sum_{p=0} \sum_{s=-p}^{s=+p} \psi_n(X) Y_{ps}(\vartheta, \varphi) y_{nps}(r) \quad (1)$$

where $r^{-2}(r^2 y'_{nps})' + [\lambda_n^2 - p(p+1)r^{-2}]y_{nps} + \alpha_{nps}(r) = 0 \quad (2)$

$$\alpha_{nps}(r) = \int_0^{2\pi} d\varphi \int_0^\pi \sin \vartheta d\vartheta Y_{ps}^*(\vartheta, \varphi) \sum_{n'=0} V_{nn'} \chi_{n'}. \quad (3)$$

Here $\frac{h^2 \lambda_n^2}{8\pi^2 m}$ is the excess of the energy of the exciting electron over the resonance energy; r, ϑ, φ , are the polar coördinates of the electron with the polar axis chosen in the same arbitrary direction as for the atom; Y_{ps} are the normalized spherical harmonics; and V is the interaction energy of atom and electron. Whenever λ_n^2 is positive, y_{nps} will be the amplitude of the probability of the excitation of the state n , which is associated with that electronic wave which behaves asymptotically like

$$\frac{e^{-i\lambda_n r}}{r} Y_{ps}(\vartheta, \varphi). \quad (4)$$

Thus y_{n00} is the amplitude for the excitation which is independent of the initial direction of the electron; if $y_{nps} = 0$ for $p \neq 0$, the light emitted from the state n would be unpolarized. We have thus to show that

$$\lim_{\lambda_n \rightarrow 0} y_{nps}/y_{n00} \rightarrow 0 \quad \text{For } p \neq 0, n \neq 0. \quad (5)$$

Now, uniformly in $\lambda_n \rightarrow 0$, for $n \neq 0$,

$$\alpha_{nps} \leq A/r^{\alpha+\epsilon} \text{ for } r \geq r_0; \quad \alpha_{nps} \leq A/r \text{ for } r \leq r_0; \quad \epsilon > 0. \quad (6)$$

For the non-diagonal terms this is shown in l. c. 2. For the diagonal term $V_{nn}\chi_n$ it follows from the fact that the dipole moment of the atom has no diagonal elements; and this excludes only the case of atomic hydrogen, which has a first order Stark effect.

If we now use, as in l. c. 2, for the solution of (2),

$$y_{nps} = c_+ \xi^{-1/2} J_{+p+1/2}(\xi) + c_- \xi^{-1/2} J_{-p-1/2}(\xi) + I(\xi); \quad \xi = \lambda_n r; \quad (7)$$

with
$$I(\xi) = \int_{+\infty}^{\xi} dx G(x, \xi) \alpha_{nps}(x/\lambda_n); \quad (8)$$

$$G(x, \xi) = \frac{J_{+p+1/2}(x) J_{-p-1/2}(\xi) - J_{-p-1/2}(x) J_{+p+1/2}(\xi)}{J_{+p+1/2}(x) J'_{-p-1/2}(x) - J'_{+p+1/2}(x) J_{-p-1/2}(x)} \quad (9)$$

we find, for the asymptotic outgoing wave associated with that solution (F) which is everywhere finite, and which corresponds to no incident wave—since there are initially no atoms in the excited state n —

$$2c_{nps}/\xi \cdot e^{-i(\xi+p/2\pi)} \quad (10)$$

where
$$c_{nps} = \lim_{\xi \rightarrow 0} \int_{+\infty}^{\xi} dx F(x, \xi) \alpha_{nps}(x/\lambda_n) \quad (11)$$

$$F(x, \xi) = \frac{-G(x, \xi) \cdot \xi^{1/2}}{J_{-p-1/2}(\xi)}. \quad (12)$$

With
$$\lim_{\xi \rightarrow 0} F(x, \xi) \leq Ax^{\alpha+p} \quad \text{for } x \leq x_0; \quad (13a)$$

$$\lim_{\xi \rightarrow 0} F(x, \xi) \leq Ax \quad \text{for } x \geq x_0; \quad (13b)$$

this gives

$$\lim_{\lambda_n \rightarrow 0} c_{nps}/c_{n00} \sim \lambda^p \rightarrow 0 \quad \text{for } p \neq 0. \quad (14)$$

This establishes our first point.

As was explained in l. c. 1,⁵ the spin of the exciting electron is important only because of Heisenberg's resonance: there is a chance that the colliding electron will change places with one of the valence electrons of the atom. For normal lines this effect is not important, since in the excitation of these lines the magnitude of the total spin vector of the system will not change; the probability of interchange of electrons will thus be of the order of the interaction energy of the spins compared with that of the atomic spin and atomic orbit, and this will be negligible. It is thus permissible, for these cases, to couple the atomic spin and atomic orbital angular momentum before applying the perturbation; and this leads at once to Skinner's rules for the *total* angular momentum of the atom. For intercombination excitations the situation is different: the total spin vector can only be conserved if the spin of the impacting electron changes during the excitation. This form of excitation (A) will be more probable than that (B) in which the atomic coupling remains undisturbed, in the same way in which normal transitions are more probable the intercombination transitions in an atom. We may thus expect that when a state can be excited by (A), the momentum rules will fail, and that the correct

polarization must be computed by coupling spin and angular momentum *after* considering the perturbation; when (A) is impossible, the lines should be considerably weaker, and should be polarized in the same way, but not so completely, as predicted by the momentum rules.⁶

We shall now show how to compute the polarization of lines excited by scheme (A). If we treat the collision problem with neglect of all spins, we find⁷ that the component of atomic orbital angular momentum parallel to the vector difference of velocities of incident and scattered electron remains unchanged by the excitation. We thus know k, s and the component in this direction, k_z , of k ; what we want to know is the probability amplitude of $j, k, s, j_z = m$. For from these amplitudes, for given j and all m , we can calculate, by the methods of l. c. 1, the polarization of the spontaneous radiation from the state j, k, s . Thus we need only the transformation functions from the quantities $k, s, k_z, s_z = m - k_z$, to j, k, s, m . This problem can be solved by the canonical methods of the quantum mechanics. For if we can write j as a function of the quantities k, s, k_z, s_z , and other quantities whose laws of commutation with these are known, then the required amplitude will be given by

$$\{j(k', s', k'_z, m' \dots) - j'\}(j', k', s', m'/k', s', k'_z, m') = 0. \quad (15)$$

Now

$$j(j + 1) = k(k + 1) + s(s + 1) - 2(k \cdot s); \quad (k \cdot s) = k_x s_x + k_y s_y + k_z s_z; \quad (16)$$

so that

$$j(j + 1) = k(k + 1) + s(s + 1) - 2[k_x s_x + k_y s_y + k_z s_z]. \quad (17)$$

Instead of solving (15) directly as a matrix equation, we may, by repeated applications of the formula

$$(x'/z') = \int (x'/y') dy'(y'/z') \quad (18)$$

obtain $\gamma(j', k'_z, m') = (j', k', s', m'/k', s', k'_z, m') =$

$$\sum_{k'_x, k'_y, s'_x, s'_y, q'_x, q'_y} (s'_x/s'_z)(s'_y/s'_z)(k'_x/k'_z)(k'_y/k'_z) \delta_{m'-k'_z}^{s'_z} \delta_{s'_x k'_x}^{q'_x} \delta_{s'_y k'_y}^{q'_y} \dots \delta_{2q'_x + 2q'_y + 2k'_z}^{j'(j'+1) - s'(s'+1) - k'(k'+1)}. \quad (19)$$

The moduli of the functions

$$(s'_x/s'_z) \dots \dots \dots (k'_y/k'_z)$$

are known, but their phases are indeterminate, and one must average over them in the final result. The phases of

$$(s'_x/s'_z) \quad \text{and} \quad (k'_x/k'_z)$$

are independent of each other, but those of

$$(s'_x/s'_x), (s'_y/s'_y) \text{ and of } (k'_x/k'_x), (k'_y/k'_y)$$

are not. One has thus to average only over the independent phases of (s'_x/s'_x) and (k'_x/k'_x) .

We may apply these results to the case of mercury, which has been studied in detail by Skinner.² Let us take first the simple case of the 3S_1 states. Here

$$k' = 0, \quad j' = s' = 1; \quad m' = \pm 1, 0;$$

and one readily finds

$$|\gamma(1, 0, 0)|^2 = |\gamma(1, 0, \pm 1)|^2 = 1. \quad (20)$$

The radiation from this state is thus unpolarized on scheme (A). If it were excited by (B), it would be completely polarized. Actually Skinner finds that the polarization is either absent or extremely weak.

Another case of interest is that of 3P_1 , which gives the resonance line. Here $j' = k' = s' = 1; m' = 0, \pm 1;$

$$(0/0) = \int_0^{2\pi} d\varphi \int_0^\pi \sin \vartheta d\vartheta \sin \vartheta \cos(\varphi + \beta) \cos \vartheta = 0 \quad (21)$$

so that $\gamma(1, 0, 0) = 0$. Further, (19) gives

$$|\gamma(1, 0, \pm 1)|^2 = 1/2. \quad (22)$$

The polarization of the resonance line is thus of opposite sign and similar magnitude to that given by the momentum rules. That is what is found.² By the same methods one finds for the 3P_2 terms:

$$\left. \begin{aligned} \gamma(2, 0, 0) &= \gamma(2, 0, \pm 2) = 0, \\ |\gamma(2, 0, \pm 1)|^2 &= 1/2. \end{aligned} \right\} \quad (23)$$

For the 3D_1 and 3D_2 states the excitation (A) is impossible. Lines from these states should, therefore, be weaker than the others, and their polarization should fall rather below that of the momentum rules. For 3D_1 this has been reported by Skinner.² For the 3D_2 the excitation (A) is possible; the states $m = 0, \pm 1$ are all excited, but the polarization is only slightly less than that of the momentum rules. This is also confirmed.

It may be mentioned that the transformation function $\gamma(j', k'_x, m')$ enables one to answer the question: Given that an atom has a certain energy in a weak magnetic field; what is the probability that it will have a given energy (Paschen-Back level) in a strong field?

In conclusion we may summarize the theoretical predictions on the polarization of impact radiation: For very high electronic velocities the line has,¹ insofar as the excitation is direct (in principle this can be sepa-

rated from cascade effects), a polarization $-p$. As the velocity of the exciting electron is diminished, this polarization also diminishes, and changes sign at a voltage of the order of 200. The polarization then increases with diminishing velocity, and the curve, if extrapolated to the resonance velocity, gives a polarization $+p$. When the velocity of the electron approaches that of the resonance potential, the polarization grows more slowly, and has a maximum within a volt or so of the resonance potential; thereafter it approaches zero. The polarization p may, for normal lines, and for intercombination lines for which the excitation (A) is impossible, be computed by the momentum rule; for other intercombination lines it is more nearly given by the method (19) outlined above.

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¹ Oppenheimer, J. R., *Z. Physik*, **43**, 27, 1927. Referred to as l. c., 1.

² For the former discrepancy see Skinner, H. W. B., *Roy. Soc. Proc.*, **A112**, 642, 1926. I am much indebted to Dr. Skinner for informing me of his recent results by letter.

³ L. c., 1, p. 46.

⁴ See a paper on the Ramsauer effect, referred to as l. c., 2, to appear shortly in the *Z. Physik*.

⁵ P. 45.

⁶ The polarization should be less marked in part because of the relative importance of cascade excitation.

⁷ L. c., 1, p. 38.

THE RESIDUAL SET OF A COMPLEX ON A MANIFOLD AND RELATED QUESTIONS (SECOND NOTE)

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1. In a recent Note under the same title¹ I communicated two very general formulas concerning certain topological simultaneous invariants of a C_k on an M_n , true subset of the manifold (formulas (3), (4) of the Note). The proofs were given explicitly and completely for a polyhedral C_k , i.e., a subcomplex of a subdivision of the C_n defining M_n . Regarding the general C_k it was stated on the strength of a certain theorem that the derivation of the formulas could proceed without change, and likewise for the most general closed subset G of M_n . On more searching examination it turned out to be decidedly otherwise, partly due to a necessary change in the theorem, and that the proofs for the polyhedral C_k would have to undergo profound change before they could carry over to the more general