

Response to Electromagnetic Excitation in a Quantized-Field Formalism.

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Summary. — The statistical operator of a system in contact with a thermal bath, in the presence of one or more e.m. external excitations, is calculated in the quantized field formalism. This gives a great formal simplification with respect to usual treatments. The result is a set of simple prescriptions for calculating physical quantities which allow a clear insight in the physics without formal complications. The procedure is applied, as an illustration, to many-photon paramagnetic resonance and to double-resonance effects.

1. — Introduction.

In this paper we shall develop a technique for calculating the response of a quantum system in contact with a thermal bath to one or more monochromatic e.m. excitations. The treatment applies to a wide class of physical situations, namely every time the field strengths acting on each absorbing system (atom, molecule or spin) in a medium can be put equal to the external field strengths to a good approximation. Extension to problems for which this is not the case, although possible, have not been considered.

Our method allows a considerable formal simplification with respect to usual treatments. This is due to the adoption of a very elegant technical im-

provement which has first been introduced by SHIRLEY ⁽¹⁾, and then widely applied to problems of double light and r.f. irradiation in optical pumping ⁽²⁻⁴⁾. The main idea is that considering the external field as a quantized field, and extending the system to include the radiation, makes the Hamiltonian time independent. A time-independent Hamiltonian is much simpler and more familiar to handle than a time-dependent one. Of course using quantized fields is equivalent to the semi-classical treatment, due to the exceedingly high number of photons present in all practical situations.

The statistical operator of the system becomes in our treatment a « dressed » operator, depending on the field variables. Its time evolution is determined by the total Hamiltonian \mathcal{H} of the system+field. The determination of the steady-state solution of the equation of motion for the statistical operator is reduced to the diagonalization of \mathcal{H} . Time averages of the expectation values of physical quantities are traces of the corresponding operators times the dressed statistical operator of the system.

Some specific problems, which have been discussed in the literature by conventional methods, will here be rephrased in the new formalism as an illustration of the method. In many cases the great simplification will allow a deeper and clearer insight in the physics.

The plan of the work is the following:

In Sect. 2 we introduce the formalism. We write down the equation for the « dressed » statistical operator, and give the rules for calculating physical quantities.

In Sect. 3 we give a treatment of paramagnetic resonance.

In Sect. 4 we apply the method to double-resonance effects.

2. - Theory.

We want to study the behaviour of a system S , which is in contact with a thermal bath, and is subjected to one or more monochromatic e.m. excitations.

We shall consider the radiation R as a quantized field interacting with S . The Hamiltonian for the extended system $S+R$ is

$$(2.1) \quad \mathcal{H} = \mathcal{H}_S + \mathcal{H}_R + \mathcal{H}_I,$$

⁽¹⁾ J. H. SHIRLEY: *Phys. Rev.*, **138**, B 979 (1965).

⁽²⁾ N. POLONSKY and C. COHEN-TANNOUDJI: *Journ. de Phys.*, **26**, 409 (1965).

⁽³⁾ C. COHEN-TANNOUDJI and S. HAROCHE: *Compt. Rend.*, **262**, 37 (1966).

⁽⁴⁾ C. COHEN-TANNOUDJI and S. HAROCHE: *Compt. Rend.*, **262**, 268 (1966).

where \mathcal{H}_S is the Hamiltonian for S considered as isolated,

$$(2.2) \quad \mathcal{H}_R \equiv \sum_i \mathcal{H}_R^i = \sum_i \omega_i a_i^\dagger a_i \quad (h = 1)$$

is in the usual notation the Hamiltonian for the free radiation field, and

$$(2.3) \quad \mathcal{H}_I \equiv \sum_i \mathcal{H}_I^i = - \sum_i p_i F_i = - \sum_i \lambda_i p_i (a_i^\dagger + a_i)$$

describes the interaction between R and S . In eq. (2.3) $\lambda_i(a_i^\dagger + a_i)$ is the (electric or magnetic) field strength operator of the i -th mode of the radiation, p_i the component of the (electric or magnetic) dipole moment which is coupled to it, and $\lambda_i = \sqrt{2\pi\omega_i}$.

In eq. (2.3) the field strength acting on S is the field strength one would have in vacuum. In dense matter, where the refraction index is large, it has to be replaced by an « effective » field. Some self-consistent treatment or distorted-wave approximation would then be needed. We shall disregard this possibility. In our treatment relaxation is the only effect of the medium on S .

We shall also neglect modifications of the external field state due to the presence of matter. The external field acting on each system S will be described by a statistical operator ϱ_R corresponding to an approximately coherent state ⁽⁵⁾ $\alpha = (\alpha_1 \dots \alpha_m)$ of the m exciting modes,

$$(2.4) \quad \varrho_R = |\alpha\rangle \langle \alpha|.$$

If the interaction were absent the statistical operator for $R+S$ would be $\varrho_R \cdot \varrho_S$,

$$(2.5) \quad \varrho_S = \frac{\exp[-\beta \mathcal{H}_S]}{\text{Tr} \{ \exp[-\beta \mathcal{H}_S] \}}$$

being the thermal-equilibrium distribution for S . Switching on the interaction \mathcal{H}_I , leaves ϱ_R unchanged in our approximation, while ϱ_S evolves under the action of the total Hamiltonian \mathcal{H} . It becomes a « dressed » operator ϱ , depending on the field operators a_i and a_i^\dagger . The statistical operator for $R+S$ becomes

$$(2.6) \quad \varrho_{R+S} = \varrho_R \cdot \varrho.$$

The equation of motion for ϱ is

$$(2.7) \quad i \left(\frac{\partial}{\partial t} + \frac{1}{\tau} \right) \varrho = [\mathcal{H}, \varrho],$$

⁽⁵⁾ R. J. GLAUBER: *Phys. Rev.*, **131**, 2766 (1963).

where by $1/\tau$ we have symbolically indicated the effect of relaxation. In a steady-state condition ϱ is time independent, \mathcal{H} being time independent, so eq. (2.7) becomes

$$(2.8) \quad \frac{i}{\tau} \varrho = [\mathcal{H}, \varrho].$$

In the semi-classical treatment, the statistical operator for S is assumed to relax exponentially towards the instantaneous thermal equilibrium. In our formalism this is equivalent (*) to assuming that the dressed operator ϱ relaxes exponentially towards

$$(2.9) \quad \varrho_0 = \frac{\exp[-\beta(\mathcal{H}_s + \mathcal{H}_I)]}{\text{Tr}\{\varrho_R \exp[-\beta(\mathcal{H}_s + \mathcal{H}_I)]\}}.$$

It is thus convenient to put (6)

$$(2.10) \quad \varrho = \varrho_0 + D.$$

The operator D , defined by eq. (2.10) is the part of ϱ which is affected by relaxation. By using this fact, and eq. (2.9), eq. (2.7) can be written

$$(2.11) \quad \frac{i}{\tau} D = [\mathcal{H}, D] + [\mathcal{H}_R, \varrho_0].$$

Use has been made of the relation $[\mathcal{H}, \varrho_0] = [\mathcal{H}_R, \varrho_0]$. Exponential decay means that the operator $1/\tau$ in the left-hand side of eq. (2.11) consists in multiplying by suitable time constants the matrix elements of D between the eigenstates of \mathcal{H}_s .

Since in all practical situations $\beta\mathcal{H}_I \ll 1$, ϱ_0 as defined in eq. (2.8) can be approximated by (6)

$$(2.12) \quad \varrho_0 \approx \varrho_s + \frac{\Delta P_s}{\Delta E_s} \mathcal{H}_I,$$

where $\Delta P_s/\Delta E_s = (\bar{Q}_s - \bar{Q}'_s)/(\bar{\mathcal{H}}_s - \bar{\mathcal{H}}'_s)$ is the operator (population difference)/(energy difference) between the state to the left and that to the right.

(*) In translating the classical equations in our formalism we simply have to replace classical fields by the corresponding quantum operators.

This because all physical quantities are of the form of eq. (2.17) below, and then the effect of the radiation density operator ϱ_R , which is a coherent state, is to replace each annihilation operator a by α (and each a^\dagger by α^*) which is just the classical field. All this will appear clear from what follows.

(6) R. KARPLUS and J. SCHWINGER: *Phys. Rev.*, **73**, 1020 (1948).

When ⁽⁶⁾ $\beta \mathcal{H}_s \ll 1$,

$$(2.13) \quad \frac{\Delta P_s}{\Delta E_s} = -\beta \varrho_s .$$

By using eq. (2.11), (2.12) can finally be written

$$(2.14) \quad \frac{i}{\tau} D = [\mathcal{H}, D] + \frac{\Delta P_s}{\Delta E_s} [\mathcal{H}_R, \mathcal{H}_I] .$$

We shall now discuss how physical quantities are to be calculated in terms of the dressed statistical operator. The solution of eq. (2.11) will have the form

$$(2.15) \quad D = \sum \bar{d}_{mn}^{(s)} a^{\dagger m} a^n .$$

For the sake of simplicity we assume that one external frequency is present. The argument is easily extended to the general case.

In eq. (2.15) $\bar{d}_{mn}^{(s)}$ are operators in the Hilbert space of \mathcal{S} . The expression for D has been put in a normal form (*i.e.* with creation operators on the left and annihilation operators on the right). We note that, since the average number \bar{n} of present photons is very large, any operator can be directly put in the normal form, neglecting the commutators between a and a^\dagger . The approximation involved is $\sim 1/\bar{n}$. Any observable operator O will be of the form

$$(2.16) \quad O = \sum O_{kl}^{(s)} a^{\dagger k} a^l .$$

According to eq. (2.6) the expectation value of O is

$$(2.17) \quad \langle O \rangle = \text{Tr} \{ \varrho_R O \} = \text{Tr} \{ \varrho_R \varrho_0 O \} + \text{Tr} \{ \varrho_R D O \} .$$

Both $\varrho_0 D$ and $D O$ can be put in the normal form simply changing the order of the operators and neglecting commutators. Multiplication by ϱ_R and trace over the degrees of freedom of the field consists in calculating the expectation value on the coherent state $|\alpha\rangle$. This is equivalent to replacing each operator a in eqs. (2.15) and (2.16) by α , each a^\dagger by α^* .

Equation (2.14), when averaged on the field state, is just the semi-classical equation for D .

Once the trace on the radiation has been computed the quantity $\langle O \rangle$ in eq. (2.17) is a power series in α and α^* . Now α and α^* depend on time according to the equations

$$(2.18) \quad \alpha(t) = \alpha(0) \exp[-i\omega t], \quad \alpha^*(t) = \alpha^*(0) \exp[+i\omega t] .$$

If one wants to calculate the time average $\langle \bar{O} \rangle$ of the expectation value $\langle O \rangle$, one has just to consider, in the trace on the left-hand side of eq. (2.17), the terms of ϱO having an equal number of creation and annihilation operators. Only that part of ϱ_n has then to be considered which is diagonal with respect to the number of photons.

This means

$$(2.19) \quad \langle \bar{O} \rangle = \text{Tr} \{ \mathcal{P} \varrho O \},$$

where $\mathcal{P} = \sum \mathcal{P}_n |n\rangle \langle n|$. \mathcal{P}_n is the weight of $|n\rangle$ in the state $|\alpha\rangle$. \mathcal{P}_n is peaked on the average number \bar{n} of photons with a negligible relative spread Δn . (In practice this is possible by allowing a negligible indetermination of α .)

This spread has to be small compared with \bar{n} , but it may contain an enormous number of states, \bar{n} being very large.

In eq. (2.19) each matrix element of a and a^\dagger can be put equal to

$$|\alpha| = \sqrt{\langle \bar{n} \rangle} = \frac{F}{\lambda}.$$

Phases disappear because there is an equal number of a and a^\dagger 's.

We shall solve eq. (2.14) in a representation in which \mathcal{H} , the total Hamiltonian of $R+S$, is diagonal. Since the state of the field is not appreciably modified by the presence of matter, the eigenstates of \mathcal{H} will differ from the eigenstates $|n\rangle$ of \mathcal{H}_R by an admixture of states $|n'\rangle$, with n' not much different from n . (The difference $n' - n$ depends on the order of perturbation since the coupling \mathcal{H}_I is linear with respect to a and a^\dagger .) Then apart from terms $\sim 1/\Delta n$, the unitary transformation which diagonalized \mathcal{H} commutes with \mathcal{P} . The distribution \mathcal{P}_n of the states $|n\rangle$ becomes the distribution of the corresponding eigenstates of \mathcal{H} . Eigenstates of \mathcal{H} can be labelled, among other quantum numbers, by the number n of photons of the corresponding unperturbed state $|n\rangle$ which one gets by switching-off the interactions.

States can be grouped into sets such that the states in a set have equal all quantum numbers but n . States which are in the same set are physically equivalent, since the matrix elements of a and a^\dagger are practically independent of n in the manifold projected by \mathcal{P} .

$$(2.20) \quad \left\{ \begin{array}{l} \text{Trace (2.19) can then be calculated as follows:} \\ \text{i) Construct a manifold } \mathcal{M} \text{ containing one state for each set of} \\ \text{equivalent states.} \\ \text{ii) Calculate the trace (2.19) of the operator } \varrho O \text{ inside } \mathcal{M}. \\ \text{iii) Put } n = \bar{n}. \end{array} \right.$$

The choice of the state inside a set is a matter of convenience.

Let us illustrate in detail this procedure, in the case that the term \mathcal{H}_I in the Hamiltonian eq. (2.1) can be treated as a perturbation.

The unperturbed Hamiltonian is $h = \mathcal{H}_S + \mathcal{H}_R$. Its eigenstates are $|\varepsilon_s\rangle|n\rangle$ with eigenvalues $\varepsilon_s + n\omega$. The matrix elements of \mathcal{H}_I between these states are small compared with ω and with the corresponding energy differences $\varepsilon_s - \varepsilon_{s'}$. The eigenstates of \mathcal{H} are equal to the approximation $\sim \mathcal{H}_I/h$ to the eigenstates of h unless, for some value of ω , some of them become degenerate. Such a degeneration is nothing but a resonance. It appears also from eq. (2.14) that the only relevant matrix elements of D will be those between nearly degenerate states, connected by the operator $[\mathcal{H}_R, \mathcal{H}_I]$.

Equation (2.14) has then to be solved inside degenerate manifolds of states. Other matrix elements will be neglected.

Let

$$\begin{aligned} &|\varepsilon_{s_1}\rangle|n_1\rangle, \\ &|\varepsilon_{s_1}\rangle|n_2\rangle, \\ &\dots \end{aligned}$$

be a degenerate manifold.

As explained before the states $|\varepsilon_{s_i}\rangle|n_i + K\rangle$ for any $K < \Delta n$ are physically equivalent. There will be an infinite number of equivalent degenerate manifolds whose corresponding states differ by an equal number of photons. A degenerate manifold is a convenient choice for the manifold \mathcal{M} . The effect of perturbation inside the degenerate manifold is equivalent to replacing the Hamiltonian by an effective Hamiltonian (7)

$$(2.21) \quad PhP + \mathcal{H}_I^{\text{eff}},$$

$$(2.22) \quad \mathcal{H}_I^{\text{eff}} = P\mathcal{H}_IP + P\mathcal{H}_IQ \frac{1}{E - h - Q\mathcal{H}_IQ} Q\mathcal{H}_IP$$

and the perturbation \mathcal{H}_I by $\mathcal{H}_I^{\text{eff}}$.

P is the projection operator on degenerate set, Q is the projection on the remainder of the Hilbert space. E is eigenvalue of h in \mathcal{M} . $\mathcal{H}_I^{\text{eff}}$ can be evaluated to the desired order of accuracy. The solution of eq. (2.14) is then reduced to an algebraic problem in a number of dimensions equal to the number of degenerate states of h . The physical quantities O which will have expectation values appreciably different from the equilibrium values, will be those having matrix elements inside a degenerate manifold. The time average of their expectation values $\langle \bar{O} \rangle$ will just be equal to the trace $\text{Tr}\{O_Q\}$ inside a degen-

(7) A. MESSIAH: *Mécanique quantique*, vol. 2 (Paris, 1964); C. COHEN TANNOUDJI: *Cargèse Lectures in Physics*, vol. 2 (New York, 1968), p. 347.

erate manifold. The average on field variables is obtained by putting $n = \bar{n}$ in all matrix elements.

Applications of this procedure will be given in Sect. 3 and 4.

When \mathcal{H}_I is greater than \mathcal{H}_s , \mathcal{H}_s has to be treated as a perturbation. The problem is then to diagonalize $\mathcal{H}_p + \mathcal{H}_I$. No general rule can be given in this case. An example is treated in Sect. 3.

In conclusion calculating the trace of ρO in a representation in which \mathcal{H} is diagonal and averaging over n with weights \mathcal{P}_n gives statistical average and time average. If one wants the k -th harmonic of the statistical average of a quantity O one just has to calculate

$$\overline{\langle O a^{1k} \rangle}$$

and then divide the result by $\alpha^{*k} = (F/\lambda) \exp [+ik\omega t]$.

The choice of the phases in $\alpha(0)$, $\alpha^*(0)$ is irrelevant, corresponding to a definition of time $t = 0$.

The expectation value of any quantity can then be obtained.

The usual semi-classical procedure^(8,9) is to use Floquet's theorem to write the stationary solution of the equation for ρ or the solution of the Schrödinger equation for the states as a sum of harmonics $\exp [in\omega t]$ of the external frequencies. Then, by equating the coefficients of the exponentials with the same time dependence an infinite set of linear equations is obtained which has to be solved some way. The formalism is complicated and it is difficult to evaluate what has been neglected in approximate solutions.

In our formalism:

1) Frequency shifts are directly calculated before solving the equations. Since by eq. (2.14) these quantities appear in the denominators of the matrix elements of D , our method is equivalent to a resolvent formalism technique⁽⁷⁾. The perturbation expansion of the denominator amounts to summing an infinite number of ordinary perturbation terms.

2) The problem is in general reduced to an algebraic problem in a finite number of dimensions, and time-independent perturbation theory immediately gives an estimate of what has been neglected.

In what follows, we shall be particularly interested in the absorption coefficient α_k of the k -th impinging wave. α_k is the time average of the mean rate of energy loss of the wave, divided by the incident energy flux.

⁽⁸⁾ S. H. AUTLER and C. H. TOWNES: *Phys. Rev.*, **100**, 703 (1955).

⁽⁹⁾ A. DI GIACOMO: *Nuovo Cimento*, **14**, 1083 (1959).

Thus

$$(2.23) \quad \alpha_k = \frac{8\pi}{cF_k^2} \langle i [\overline{\mathcal{H}_R^{(k)}}, \overline{\mathcal{H}}] \rangle = \frac{8\pi}{cF_k^2} i \text{Tr} \{ \mathcal{P} D[\mathcal{H}_R^{(k)}, \mathcal{H}_I] \} .$$

The trace in the last expression can be evaluated by the rules (2.20).

3. - Paramagnetic resonance.

As a first application of our method we shall treat paramagnetic resonance. The system S is a spin \mathbf{J} , with gyromagnetic ratio γ , in a static field \mathbf{H}_0 , whose direction we shall assume as z -axis. The spin is also subjected to an oscillating linear field \mathbf{H}_1 , whose direction \mathbf{n} forms an angle θ with \mathbf{H}_0 . We can assume it to lie in the (x, z) -plane so that $\mathbf{n} = (\sin\theta, 0, \cos\theta)$. The Hamiltonian \mathcal{H} is given by $\mathcal{H} = \mathcal{H}_s + \mathcal{H}_R + \mathcal{H}_I$, where

$$(3.1) \quad \begin{cases} \mathcal{H}_s = \omega_0 J_z & (\omega_0 = -\gamma H_0), \\ \mathcal{H}_R = \omega a^\dagger a, \\ \mathcal{H}_I = -\lambda \gamma J_n (a^\dagger + a), & J_n = \sin\theta J_x + \cos\theta J_z. \end{cases}$$

We shall discuss separately the two situations

$$A) H_1 \ll H_0, \quad B) H_1 \gg H_0 .$$

In order to calculate D by eq. (2.14) we have to find the eigenvalues of \mathcal{H} and the matrix elements between the corresponding eigenstates of the operator $[\mathcal{H}_R, \mathcal{H}_I]$. The absorption coefficient will then be calculated by using eq. (2.23).

A) $H_1 \ll H_0$. In this case \mathcal{H}_I can be treated as a perturbation. The eigenstates of the unperturbed Hamiltonian

$$(3.2) \quad h = \mathcal{H}_s + \mathcal{H}_R$$

are $|M\rangle |n\rangle$ with eigenvalues $M\omega_0 + n\omega$. The label M is the eigenvalue of J_z , the label n is the number of r.f. photons.

When $\omega_0 \sim p\omega$ (p -photon resonance) the manifold \mathcal{M}_n

$$(3.3) \quad \left\{ \begin{array}{l} |J\rangle |n\rangle, \\ |J-1\rangle |n+p\rangle, \\ \dots\dots\dots, \\ \dots\dots\dots, \\ |-J\rangle |n+2Jp\rangle, \end{array} \right.$$

is nearly degenerate. There is one such manifold \mathcal{M}_n for each value of n , and each state belongs to one \mathcal{M}_n . The unperturbed Hamiltonian inside the manifold (3.3) is represented by

$$(3.4) \quad h = \delta_p J_z \quad (\delta_p = \omega_0 - p\omega)$$

apart from an unimportant additive constant.

The energy difference between $\mathcal{M}_n, \mathcal{M}_{n'}$ is $(n - n')\omega$. From eq. (2.14) it appears that D can have resonant matrix elements only between states of a degenerate manifold, which are connected by the perturbation.

$[\mathcal{H}_R, \mathcal{H}_I]$ has no matrix elements between the unperturbed states (3.3), unless $p = 1$. For $p > 1$ the admixture of other states by the perturbation has to be considered. Due to the selection rules $\Delta n = \pm 1$ for \mathcal{H}_I the effective interaction can have only diagonal matrix elements up to order $p - 1$. The second-order contribution to the diagonal part is in any case the lowest-order contribution to it. Direct calculation gives

$$(3.5) \quad P\mathcal{H}_I Q \frac{1}{E - k} Q\mathcal{H}_I P = J_z \frac{2\omega_1^2}{\omega} \sin^2 \theta \left\{ \frac{1}{p+1} + \frac{1}{p-1} \right\} = J_z s_p$$

($\omega_1 = -\gamma H_1$).

The second term in the curly bracket is to be put equal to zero when $p = 1$. This frequency displacement is known as Bloch-Siegert⁽¹⁰⁾ shift. The lowest-order off-diagonal matrix elements of \mathcal{H}^{eff} defined by eq. (2.22) are of order p , and are of the form

$$(3.6) \quad \langle M | \overbrace{\langle n | \mathcal{H}_I Q \frac{1}{E - \hbar} Q \mathcal{H}_I Q \frac{1}{E - \hbar} \dots Q \mathcal{H}_I}^{p \text{ times}} | M - 1 \rangle} | n + p \rangle,$$

$$(3.7) \quad \langle M | \langle n | \mathcal{H}_I Q \frac{1}{E - \hbar} Q \mathcal{H}_I Q \frac{1}{E - \hbar} \dots Q \mathcal{H}_I | M + 1 \rangle | n - p \rangle.$$

The matrix elements of $[\mathcal{H}_R, \mathcal{H}_I] = [\mathcal{H}_R, \mathcal{H} - \hbar]$ are simply obtained multiplying by $-p\omega$ the raising matrix elements of \mathcal{H}^{eff} and by $+p\omega$ the lowering ones. Our problem is then reduced to finding the matrix elements (3.6), (3.7). Each matrix element is the complex conjugate of one of the type (3.6).

It can be proved that the effective, p -th-order perturbation behaves like a vector orthogonal to \mathbf{H}_0 .

By the usual choice of the phases (CONDON and SHORTLEY)⁽¹¹⁾ the matrix

⁽¹⁰⁾ F. BLOCH and A. SIEGERT: *Phys. Rev.*, **57**, 522 (1940).

⁽¹¹⁾ E. V. CONDON and G. H. SHORTLEY: *The Theory of Atomic Spectra* (Cambridge, 1953).

elements are real. So, if we introduce a fictitious spin $\tilde{\mathbf{J}}$ (*) the degenerate manifold

$$(3.8) \quad \begin{cases} \mathcal{H}_I^{\text{eff}} = \omega_1^{(p)} \tilde{\mathbf{J}}_x, \\ \mathcal{H} = (\delta_p + s_p) \tilde{\mathbf{J}}_z + \omega_1^{(p)} \tilde{\mathbf{J}}_x \end{cases}$$

and

$$[\mathcal{H}_R, \mathcal{H}_I] = i\omega\omega_1^{(p)} \tilde{\mathbf{J}}_y.$$

The solution for D is of the form $D = \mathbf{d} \cdot \tilde{\mathbf{J}}$. Equation (2.14) gives

$$\frac{1}{\tau} \mathbf{d} = [(\delta_p + s_p) \mathbf{k} + \omega_1^{(p)} \mathbf{i}] \wedge \mathbf{d} + \frac{\omega\beta}{(2J+1)} \omega_1^{(p)} \mathbf{j}.$$

d_z relaxes with T_1 , d_x and d_y with T_2 . The result for $\alpha^{(p)}$ is

$$(3.9) \quad \alpha^{(p)} = \frac{4\pi}{c} \beta \frac{J(J+1)}{3} \frac{\omega_1^{(p)3}}{\omega_1^2} \frac{T_2}{1 + (\delta_p + s_p)^2 T_2^2 + T_1 T_2 \omega_1^{(p)2}}.$$

$\mathcal{H}_I^{\text{eff}}$ is thus obtained calculating by reduction the vector part of the operator

$$\overbrace{P \mathcal{H}_I Q \frac{1}{E - \hbar} Q \mathcal{H}_I Q \frac{1}{E - \hbar} \dots \mathcal{H}_I P}^{p \text{ times}}.$$

This is achieved by using the algebra of the rotation group, *i.e.* the commutation relations of angular momentum and the result is independent of the value of J . One can then evaluate the matrix element (3.6) in the simplest case, *i.e.* that of spin $\frac{1}{2}$. The result is equal to $\omega_1^{(p)}/2$. The result already exists in the literature for transverse oscillating field ⁽¹²⁾.

We shall give a simple procedure for calculating it in the more general case of an oscillating linear field at any angle θ with respect to the static field. We shall write \mathcal{H}_I in the form

$$\mathcal{H}_I = -\frac{\lambda\gamma}{2} (a + a^\dagger) [\sigma_z \cos \theta + (\sigma_+ + \sigma_-) \sin \theta],$$

where

$$\sigma_z \cos \theta + (\sigma_+ + \sigma_-) \sin \theta = \sigma_n.$$

(*) By a fictitious spin we mean, as usual, a set of three operators which are represented by the usual angular-momentum matrices in our discussion representation.

⁽¹²⁾ J. WINTER: *Ann. de Phys.*, **4**, 745 (1959).

The matrix element (3.6) is then

$$(3.10) \quad \left(\frac{\lambda\gamma}{2}\right)^p \langle n|a^p|n+p\rangle \overbrace{\langle +|\sigma_n \frac{1}{E-\hbar} \sigma_n \frac{1}{E-\hbar} \dots \sigma_n|-\rangle}^{p \text{ times}} = \\ = \left(\frac{\omega_1}{4}\right)^p \frac{1}{\omega^{p-1}} \langle +|\sigma_n \frac{1}{E-\hbar} \sigma_n \dots \sigma_n|-\rangle$$

if the energy differences are measured in units $\omega = 1$. Then

$$\omega_1^{(p)} = \frac{\omega_1}{2} \left(\frac{\omega_1}{4\omega}\right)^{p-1} \langle +|\sigma_n \frac{1}{E-\hbar} \sigma_n \dots \sigma_n|-\rangle.$$

We have now to calculate the matrix element in eq. (3.10). The energy differences between the states involved in the matrix elements of the perturbation are

matrix elements	energy jump $(E_\alpha - E_\beta)/\omega$
$\langle \alpha a\sigma_z \beta\rangle$	- 1 ,
$\langle \alpha a\sigma_+ \beta\rangle$	- (1 + p) ,
$\langle \alpha a\sigma_- \beta\rangle$	- (1 - p) .

(3.11)

The rules for getting the matrix element in eq. (3.10) are now easily found.

For a given choice of intermediate states, we shall associate to each energy denominator a + sign or a - sign according to whether the corresponding intermediate state has $\sigma_z = \pm 1$. So all possible choices of intermediate states are in a one-to-one correspondence with sequences of $(p-1)$ + or - signs.

For calculating the matrix element in eq. (3.10):

- 1) Consider all possible sets of $(p-1)$ + or - signs:

$$+ - + + \dots - .$$

- 2) The n -th sign corresponds to a denominator

$$\frac{1}{-n} \text{ if it is } - , \\ \frac{1}{-(n-p)} \text{ if it is } + .$$

- 3) Each jump between subsequent signs gives a factor $\sin\theta$, each permanence gives a factor $\cos\theta$.

There is in addition an initial jump or permanence according to whether the first sign is + or -- and a final jump or permanence according to whether the last sign is -- or +.

- 4) Multiply by a factor -1 for each permanence of - signs.
- 5) Add the contribution of all sets.

Examples.

$p = 1$. No denominator, one jump

$$\omega_1^{(1)} = \frac{\omega_1}{2} \sin \theta .$$

$p = 2$. One denominator

possible sets i) +, ii) - .

Set i) has an initial jump and a final permanence; set ii) has an initial permanence and a final jump.

Since the permanence is in a - sign, by rule 4) ii) has an additional factor (-1).

The denominator i) is 1; the denominator ii) is -1. The result is

$$\omega_1^{(2)} = \frac{\omega_1^2}{4\omega} \sin \theta \cos \theta .$$

$p = 3$

$$\omega_1^{(3)} = \frac{\omega_1}{2} \left(\frac{\omega_1}{4\omega} \right)^2 \left\{ 2 \sin \theta \cos \theta - \frac{1}{4} \sin^3 \theta \right\} .$$

For higher values of p the rules are to be intended as a programme for the computer since the number of possible sets becomes very high. We were not able to find a compact expression for the sums.

The result becomes simple when the field is transverse ($\theta = \pi/2$). Then no permanence is allowed and the only diagram which contributes is

$$+ - + - + - \dots - .$$

The diagram must begin with a + and end with a -, so $p-1$ is even and p is odd, as expected by angular-momentum considerations. The diagram is simple to evaluate:

$$\omega_1^{2k+1} = -\frac{\omega_1}{2} \left(\frac{\omega_1}{4\omega} \right)^{2k} .$$

B) $H_1 \gg H_0$. In this case we shall assume

$$(3.12) \quad h = \mathcal{H}_x + \mathcal{H}_y = \omega a^\dagger a - \lambda \gamma J_z (a + a^\dagger)$$

as unperturbed Hamiltonian and \mathcal{H}_s as a perturbation. The direction of the r.f. field has been taken as z axis. Then $\mathcal{H}_s = \omega_0 (J_z \cos \theta + J_x \sin \theta)$, θ being the angle between H_0 and H_1 . The procedure for diagonalizing h of eq. (3.12) is well known. h can be put in the form

$$h = \omega \alpha^\dagger \alpha - \frac{\lambda \gamma}{2} J_z^2,$$

where

$$\alpha = a - \frac{\lambda \gamma}{2\omega} \bar{J}_z.$$

The commutation rules for α and α^\dagger are of course the same as for a and a^\dagger .

The energy eigenstates are then $|M, \bar{n}\rangle$, where M is the eigenvalue of J_z and \bar{n} the eigenvalue of $\alpha^\dagger \alpha$.

The corresponding energy values are $\bar{n}\omega$.

The matrix elements of J_\pm are (²)

$$(3.13) \quad \langle \bar{n}M | J_\pm | \bar{n}'M' \rangle = J_{\bar{n}-\bar{n}'} \left(\pm \frac{\omega_1}{\omega} \right) \cdot \langle M | J_\pm | M' \rangle.$$

$J_k(z)$ is the Bessel function of order k .

The total Hamiltonian \mathcal{H} inside a degenerate manifold is, apart from a constant,

$$(3.14) \quad \mathcal{H} = \omega_0 \cos \theta \tilde{J}_z + \omega_0 \sin \theta \tilde{J}_x J_0 \left(\frac{\omega_1}{\omega} \right).$$

The matrix elements of the perturbation \mathcal{H}_s between different manifolds \bar{n}, \bar{n}' are

$$(3.15) \quad \langle M\bar{n} | \mathcal{H}_s | M'\bar{n}' \rangle = \omega_0 \sin \theta J_{\bar{n}-\bar{n}'} \left([M - M'] \frac{\omega_1}{\omega} \right) \langle M | J_x | M' \rangle,$$

which are to be compared with the energy difference $(n - n')\omega$ in order to test the validity of the perturbation expansion. If $\omega_1 \gg \omega$ the equality

$$(3.16) \quad J_0^2 + 2 \sum_1^\infty J_n^2 = 1$$

gives

$$(3.17) \quad \sum J_n^2 \left(\frac{\omega_1}{\omega} \right) \simeq \frac{1}{2}.$$

The parameter which has to be small is $|(\omega_0/n\omega)J_n(\omega_1/\omega)| = \varepsilon$. We have

$$(3.18) \quad \left(\frac{\omega_0 J_n}{n\omega} \right)^2 < \frac{\omega_0^2}{\omega^2} \sum_1^{\infty} \frac{J_n^2}{n^2}.$$

Now $\sum_1^{\infty} J_n^2/n^2$ is some kind average of $1/n^2$ with weight J_n^2 normalized according to eq. (3.17). The maximum weight is that of the J_n^2 such that the argument is of the order of the index. So $\sum (J_n^2/n^2) \sim \frac{1}{2}(\omega/\omega_1)^2$. The inequality (3.18) reads now

$$\varepsilon^2 < \frac{\omega_0^2}{2\omega_1^2} \ll 1.$$

If on the other hand $\omega_1 \ll \omega$ from the inequality

$$|J_n| \leq \frac{1}{\sqrt{2}},$$

which is a direct consequence of eq. (3.16)

$$\varepsilon \ll \frac{\omega_0}{n\omega} \sim \frac{\omega_0}{n\omega_1} \ll 1.$$

So if $\omega_1 \gg \omega_0$ perturbation expansion is always possible. The second-order correction to the energy levels $\mathcal{H}^{(2)}$ is readily calculated by using the matrix elements in eq. (3.15). The result is

$$\mathcal{H}^{(2)} = \frac{4\omega_0^3}{\omega} \sin^2 \theta \sum_{\substack{+\infty \\ n \neq 0}} \frac{1}{n} J_n^2 \left(\frac{\omega_1}{\omega} \right) \tilde{J}_z = 0.$$

Neglecting third-order effects

$$(3.19) \quad \mathcal{H}^{\text{eff}} = \omega_0 \cos \theta \tilde{J}_z + \omega_0 \sin \theta \tilde{J}_x J_0 \left(\frac{\omega_1}{\omega} \right).$$

The operator

$$[\mathcal{H}_R, \mathcal{H}_I] = \lambda\gamma(\alpha^\dagger - \alpha) J_z$$

has matrix elements between contiguous manifolds

$$\langle \bar{n}M | [\mathcal{H}_R, \mathcal{H}_I] | \bar{n} \pm 1, M' \rangle = \mp \omega_1 \omega \langle M | J_z | M' \rangle.$$

The operator \mathcal{H}^{eff} in eq. (3.16) is easily diagonalized by a rotation

$$R = \exp[-i\varphi\tilde{J}_y]$$

with

$$\cos \varphi = \frac{\omega_0 \cos \theta}{\Omega}, \quad \sin \varphi = \frac{\omega_0 \sin \theta}{\Omega} J_0 \left(\frac{\omega_1}{\omega} \right),$$

$$\Omega = \omega_0 \sqrt{\cos^2 \theta + \sin^2 \theta J_0^2 \left(\frac{\omega_1}{\omega} \right)}.$$

The result is

$$\mathcal{H}^{\text{eff}} = \Omega \tilde{J}_z.$$

So eq. (2.14) gives

$$\frac{i}{\tau} D_{M, \bar{n}; M', \bar{n} \pm 1} = [\mp \omega + \Omega(M - M')] D_{M, \bar{n}; M', \bar{n} \pm 1} + \frac{\beta \omega_0}{2J + 1} \langle M | R J_z R^\dagger | M' \rangle$$

and by eq. (2.23)

$$\alpha = \frac{4\pi\beta}{e} \frac{J(J+1)}{3} \gamma^2 \omega^2 \cdot \left\{ \frac{\omega_0^2 \cos^2 \theta}{\Omega^2} \frac{1/T}{1/T^2 + \omega^2} + \frac{\omega_0^2 \sin^2 \theta J_0^2(\omega_1/\omega)}{\Omega^2} \frac{1}{T} \left[\frac{1}{1/T^2 + (\omega - \Omega)^2} + \frac{1}{1/T^2 + (\omega + \Omega)^2} \right] \right\}.$$

As $\omega_0 \rightarrow 0$

$$\alpha = \frac{4\pi\beta}{e} \gamma^2 J(J+1) \omega^2 \frac{1/T}{1/T^2 + \omega^2}.$$

This is Debye absorption.

4. - Double-resonance effects ^(5,9,13).

Typical double-resonance effects are schematically illustrated in Fig. 1.

A three-level system is subjected to two waves, both close to the resonance between a couple of them. The response to the wave with frequency ω_0 is observed in the presence of the wave with frequency ω_s , which is strong enough to produce saturation. For simplicity we shall put all relaxation times equal. We shall assume that the interaction with the external fields is small compared

⁽¹³⁾ A. JAVAN: *Phys. Rev.*, **107**, 1579 (1957).

with the spacing of the levels. Then we can treat

$$h = \mathcal{H}_s + \mathcal{H}_R = \mathcal{H}_s + \omega_s a_s^\dagger a_s + \omega_0 a_0^\dagger a_0$$

as unperturbed Hamiltonian and \mathcal{H}_I as a perturbation. We shall study in detail the situation of Fig. 1a). The extension to the others is straightforward.

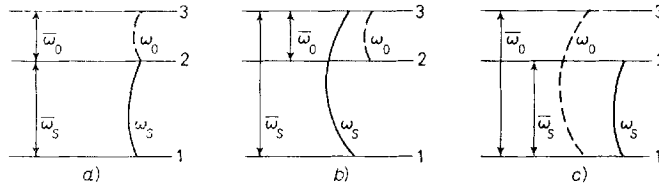


Fig. 1.

Near the resonances the unperturbed eigenstates can be grouped in sets of three nearly degenerate states.

$$\begin{cases} |\alpha\rangle = |3\rangle |n_s, n_0 - 1\rangle \\ |\beta\rangle = |2\rangle |n_s, n_0\rangle \\ |\gamma\rangle = |1\rangle |n_s + 1, n_0\rangle \end{cases} \text{ with eigenvalues (apart from a constant) } \begin{cases} \delta_0 = \bar{\omega}_0 - \omega_0 \\ 0 \\ -\delta_s = -(\bar{\omega}_s - \bar{\omega}_s) \end{cases}$$

Within an approximation $\sim \mathcal{H}_I | \mathcal{H}_s, \mathcal{H}^{\text{eff}}$ of eq. (2.22) is equal to \mathcal{H}_I . In the representation where $|\alpha\rangle, |\beta\rangle$ and $|\gamma\rangle$ are a basis, \mathcal{H}_I is represented by the matrix

$$\mathcal{H}_I = -\frac{1}{2} \begin{pmatrix} 0 & E_0 p_0 & 0 \\ E_0 p_0 & 0 & E_s p_s \\ 0 & E_s p_s & 0 \end{pmatrix},$$

$[\mathcal{H}_R, \mathcal{H}_I]$ by the matrix

$$[\mathcal{H}_R, \mathcal{H}_I] = \frac{1}{2} \begin{pmatrix} 0 & \omega_0 E_0 p_0 & 0 \\ -\omega_0 E_0 p_0 & 0 & \omega_s E_s p_s \\ 0 & -\omega_s E_s p_s & 0 \end{pmatrix}.$$

Equation (2.14) could be directly solved in this representation. The approximation of the result is $\sim \mathcal{H}_I | \mathcal{H}_s$, and one has merely to invert a 3×3 matrix.

This inversion is equivalent to diagonalizing the Hamiltonian

$$\mathcal{H} = \begin{pmatrix} \delta_0 & -\frac{E_0 p_0}{2} & 0 \\ -\frac{E_0 p_0}{2} & 0 & -\frac{E_s p_s}{2} \\ 0 & -\frac{E_s p_s}{2} & -\delta_s \end{pmatrix}.$$

The general result is yet rather complicated. However we shall see that the essential features can be studied by an approximate diagonalization giving a simple result. Since we put no limitation to the power of the field s , we shall begin by diagonalizing the 2×2 subspace involving the saturating wave s , in order to treat it exactly. This is accomplished by a rotation

$$R = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \exp\left[-i\frac{\theta}{2}\sigma_2\right] & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

with

$$(4.1) \quad \cos \theta = \frac{\delta_s}{\Delta_s}, \quad \sin \theta = \frac{E_s p_s}{\Delta_s}, \quad \Delta_s = \text{sign } \delta_s \cdot \sqrt{\delta_s^2 + p_s^2 E_s^2}.$$

In the new representation

$$(4.2) \quad \mathcal{H} = \begin{pmatrix} \delta_0 & -\frac{E_0 p_0}{2} \cos \frac{\theta}{2} & \frac{E_0 p_0}{2} \sin \frac{\theta}{2} \\ -\frac{E_0 p_0}{2} \cos \frac{\theta}{2} & -\frac{\delta_s}{2} + \frac{\Delta_s}{2} & 0 \\ \frac{E_0 p_0}{2} \sin \frac{\theta}{2} & 0 & -\frac{\delta_s}{2} - \frac{\Delta_s}{2} \end{pmatrix}.$$

We shall confine ourselves to the frequency intervals where two diagonal elements connected by nondiagonal ones are nearly degenerate compared to $E_0 p_0$ but not the other, *i.e.*

$$(4.3) \quad \left. \begin{array}{l} \text{i) } |\delta| \equiv |\delta_0 + \frac{1}{2}(\delta_s - \Delta_s)| \ll E_0 p_0 \\ \text{ii) } |\Delta| \equiv |\delta_0 + \delta_s - \frac{1}{2}(\delta_s - \Delta_s)| \ll E_0 p_0 \end{array} \right\} \text{ and } |\Delta_s| \gg E_0 p_0.$$

The condition $|\Delta_s| \gg E_0 p_0$ which means that only two levels must be degenerate is always satisfied when $E_s p_s \gg E_0 p_0$, otherwise it must be that $|\delta_s| \gg E_0 p_0$.

Conditions i) and ii) correspond to two resonances. $|\Delta_s| \gg E_0 p_0$ means that they are well separated with respect to $E_0 p_0$.

If condition i) is satisfied, the matrix elements (1.3) (3.1) of \mathcal{H} eq. (4.2) can be neglected. If condition ii) is satisfied, the matrix elements (1.2) (2.1) can be neglected.

In both cases the problem is reduced to the diagonalization of a 2×2 matrix.

This is simple algebra. We shall directly give the result for the absorption coefficient α_0 of the observed wave, in the two frequency ranges i) and ii)

$$\begin{aligned}
 \text{i) } \alpha_0 &= \frac{4\pi}{c} \frac{\Delta P_0}{\Delta E_0} \omega^2 p_0^2 \frac{1}{\tau} \cdot \left\{ \frac{\cos^2 \theta/2}{1/\tau^2 + \Delta'^2} + \frac{\sin^2 \theta/2}{1/\tau^2 + \Delta_s^2} + \frac{E_s p_s \omega_s}{2\omega_0} \frac{\Delta_s \sin \theta/2}{[1/\tau^2 + (\Delta'/2 + \Delta_s)^2][1/\tau^2 + (\Delta'/2 - \Delta_s)^2]} \right\}, \\
 \text{ii) } \alpha_0 &= \frac{4\pi}{c} \frac{\Delta P_0}{\Delta E_0} \omega^2 p_0^2 \frac{1}{\tau} \cdot \left\{ \frac{\sin^2 \theta/2}{1/\tau^2 + \Delta''^2} + \frac{\cos^2 \theta/2}{1/\tau^2 + \Delta_s^2} - \frac{E_s p_s \omega_s}{2\omega_0} \frac{\Delta_s \sin \theta/2}{[1/\tau^2 + (\Delta''/2 + \Delta_s)^2][1/\tau^2 + (\Delta''/2 - \Delta_s)^2]} \right\}.
 \end{aligned}$$

Here the only new quantities are

$$\Delta' = \text{sign } \delta \cdot \sqrt{\delta^2 + E_0^2 p_0^2 \cos^2 \theta/2}$$

and

$$\Delta'' = \text{sign } \Delta \cdot \sqrt{\Delta^2 + E_0^2 p_0^2 \sin^2 \theta/2}.$$

δ and Δ are defined by eq. (4.3), θ by eq. (4.1). We shall now briefly discuss the result.

If $|\delta_s| \gg E_s p_s$, *i.e.* if the saturating frequency is far off the saturation line width, then

$$\begin{aligned}
 \Delta_s &\simeq \delta_s + \frac{E_s^2 p_s^2}{2\delta_s}, & \cos \theta &\sim 1, & \sin \theta &\simeq \frac{E_s p_s}{\delta_s}, \\
 \delta &\sim \delta_0 - \frac{E_s^2 p_s^2}{4\delta_s}, & \Delta &\sim \delta_0 + \delta_s + \frac{E_s^2 p_s^2}{4\delta_s}, \\
 \Delta'^2 &\sim \left(\delta_0 - \frac{E_s^2 p_s^2}{4\delta_s} \right)^2 + E_0^2 p_0^2, \\
 \Delta''^2 &\sim \left(\delta_0 + \delta_s + \frac{E_s^2 p_s^2}{4\delta_s} \right)^2 + E_0^2 p_0^2 \frac{E_s^2 p_s^2}{4\delta_s^2}.
 \end{aligned}$$

Provided ω_s is not much greater than ω_0 , which means that the three levels are almost equally populated,

$$\begin{aligned} \text{i) } \alpha_0 &\sim \frac{4\pi}{c} \frac{\Delta P_0}{\Delta E_0} \omega^2 p_0^2 \frac{1}{\tau} \frac{1}{(\delta_0 - E_s^2 p_s^2 / 4\delta_s)^2 + 1/\tau^2 + E_0^2 p_0^2}, \\ \text{ii) } \alpha_0 &\sim \frac{4\pi}{c} \frac{\Delta P_0}{\Delta E_0} \omega^2 p_0^2 \frac{1}{\tau} \frac{1}{(\delta_0 + \delta_s + E_s^2 p_s^2 / 4\delta_s)^2 + 1/\tau^2 + E_0^2 p_0^2 (E_s^2 p_s^2 / 4\delta_s^2)}. \end{aligned}$$

The line presents two peaks shifted in an opposite direction by an equal amount $E_s^2 p_s^2 / 4\delta_s$ from $\bar{\omega}_0 - \omega_0 \simeq 0$ and $\bar{\omega}_s + \bar{\omega}_0 - \omega_s - \omega_0 = 0$. The first one suffers saturation by the observed wave, while the second one does not if ω_s is sufficiently far from resonance. This is a new result, which could not be given in previous treatments of the problem.

When $\delta_s \simeq 0$ and $E_s p_s \gg E_0 p_0$ then

$$\begin{aligned} \sin^2 \frac{\theta}{2} &= \frac{1}{2}, & \cos^2 \frac{\theta}{2} &= \frac{1}{2}, & \delta &= \delta_0 - \frac{E_s p_s}{2}, \\ \Delta &= \delta_0 + \frac{E_s p_s}{2}, \\ \Delta'^2 &= \delta^2 + \frac{E_0^2 p_0^2}{2}, & \Delta''^2 &= \Delta^2 + \frac{E_0^2 p_0^2}{2}. \end{aligned}$$

The line becomes a doublet with equal peaks at the frequencies $\pm E_s p_s / 2$.

* * *

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RIASSUNTO

Si studia l'operatore statistico di un sistema in contatto con un termostato, in presenza di una o più eccitazioni e.m. esterne, nel formalismo del campo quantizzato. Rispetto alle trattazioni usuali si ottiene una grande semplificazione formale. Il risultato

è un insieme di regole semplici per calcolare quantità fisiche, che permettono di capire le approssimazioni e gli aspetti fisici senza complicazioni formali. Il procedimento viene applicato come illustrazione alle risonanze paramagnetiche a più fotoni e ai fenomeni di doppia risonanza.

Реакция на электромагнитное возбуждение в формализме квантованного поля.

Резюме (*). — В формализме квантованного поля вычисляется статистический оператор системы, находящейся в контакте с термостатом, при наличии одного или более электромагнитных внешних возбуждений. Это приводит к существенным формальным упрощениям относительно обычных рассмотрений. Результат представляет систему простых рецептов для вычисления физических величин, которые допускают ясное физическое представление без формальных усложнений. В качестве иллюстрации эта процедура применяется к много-фотонному парамагнитному резонансу и к двойным резонансным эффектам.

(*) *Переведено редакцией.*