Quantum Theory of Optical Pumping

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IN a previous paper,[1] a light shift experiment[2] performed on ^{199}Hg has been described. We will try here to show how optical excitation gives a finite lifetime and a self-energy to the ground state of an atom. This theoretical explanation is based on a quantum theory of optical pumping which has been recently developed.[3]

In view of the short time allowed, only a brief outline of these calculations will be given here. More details will be found in two articles to be published in the "Journal de physique et le radium."[4]

Let us first give our notations: μ, ω_f (and m, ω_e) are the sublevels and the Zeeman splittings in the ground (and in the excited) states; k_o, Γ, ΔE are the energy, the natural width, and the self-energy of the excited state. The exciting beam is described by an ensemble of N photons (N very large), with wave numbers $k_1, k_2 \ldots k_N$. All these photons have the same direction of propagation and the same polarization vector $e\lambda_o$. Their frequency distribution corresponds to the shape $u(k)$ of the exciting line. The width Δ of $u(k)$ is supposed large compared to ω_e, ω_f, Γ;

$$\Delta \gg \Gamma, \omega_e, \omega_f. \tag{1}$$

We choose three different kinds of basis vectors for the total system atom plus radiation field: states $|\mu>$ corresponding to the atom in the sublevel μ with the N photons present; states $|m; -k_i>$ corresponding to the absorption of the photon k_i; states $|\mu; -k_i; k; \lambda>$ corresponding to the fall back to the ground state with emission of the photon k, $e\lambda$.

The interaction between the atom and the radiation field is described by the Hamiltonian H_I (H_I' in interaction representa-

tion); the matrix elements of H_I are

$$<\mu k \lambda \mid H_I \mid m> = A_k e^{-ikR} <\mu \mid e\lambda D \mid m>; \tag{2}$$

A_k is related to the radial wave functions of the atom and varies with k as $1/(k)^{\frac{1}{2}}$, $\boldsymbol{R}$ is the geometric position of the atom, and $\boldsymbol{D}$ the electric dipole moment operator. If $\mid \phi >$ is the state vector of the system in interaction representation, the Schrödinger's equation is

$$i \frac{d}{dt} \mid \phi > = H_I' \mid \phi >. \tag{3}$$

By expanding (3), we obtain

$$\begin{cases} i\dot{b}_\mu = \sum_{m,\, i} <\mu k_i \lambda_o \mid H_I' \mid m> b_{m-k_i} & \text{(4-a)} \\ i\dot{b}_{m-k_i} = \sum_{\mu'} <m \mid H_I' \mid \mu' k_i \lambda_o > b_{\mu'} + \sum_{\mu'' k \lambda} <m \mid H_I' \mid \mu'' k \lambda > b_{\mu''-k_i k \lambda} & \text{(4-b)} \\ i\dot{b}_{\mu''-k_i k \lambda} = \sum_{m'} <\mu'' k \lambda \mid H_I' \mid m' > b_{m'-k_i}. & \text{(4-c)} \end{cases}$$

This set of equations describes the different steps of the "optical pumping cycle": (4-a) describes absorption of photons and excitation of the atom; (4-b), evolution of the excited state; (4-c), reemission of photons and fall back to the ground state.

Integrating (4-c) and carrying back the so obtained value of $b_{\mu''-k_i k \lambda}$ into (4-b) gives the same expressions which are encountered in the quantum theory of spontaneous emission.[5]

Thus, they are readily evaluated and (4-b) may be replaced by

$$i\dot{b}_{m-k_i} = \sum_{\mu'} <m \mid H_I' \mid \mu' k_i \lambda_o > b_{\mu'} - i[(\Gamma/2) + i\Delta E] b_{m-k_i} \tag{4-d}$$

The same method may be used again for eliminating b_{m-k_i} between (4-a) and (4-d). Similar calculations lead to the following result: By means of optical excitation, the sublevel μ gets a

finite lifetime $T_p/A_{\mu\mu}$ and a self-energy $A_{\mu\mu}\Delta E'$, where $A_{\mu\mu}$, T_p, and $\Delta E'$ are defined by

$$A_{\mu\mu'} = \sum_m \langle \mu | \mathbf{e}\lambda_o \mathbf{D} | m \rangle \langle m | \mathbf{e}\lambda_o \mathbf{D} | \mu' \rangle \qquad (5\text{-a})$$

$$\frac{1}{2T_p} = \int_{-\infty}^{+\infty} u(k) | A_k |^2 \frac{\Gamma/2}{(k-k_o)^2 + \Gamma^2/4} dk \qquad (5\text{-b})$$

$$\Delta E' = \int_{-\infty}^{+\infty} u(k) | A_k |^2 \frac{k-k_o}{(k-k_o)^2 + \Gamma^2/4} dk. \qquad (5\text{-c})$$

The $1/2T_p$ may also be written as $\Gamma u(k_o) | A_{k_o} |^2$. Thus the lifetime of the ground state is inversely proportional to the intensity of the exciting light at the absorption frequency of the atom, as one could expect.

The $\Delta E'$ is the integral of the product of $u(k) | A_k |^2$ by a dispersion curve centered at k_o. The $\Delta E'$ is equal to zero if the center k_1 of $u(k)$ coincides with k_o. It increases with $k_1 - k_o$ until a maximum value which is reached for $k_1 - k_o$ of the order of Δ. The order of magnitude of this maximum is $(1/2T_p)_o$, where $(1/2T_p)_o$ is the value of $(1/2T_p)$ for $k_1 = k_o$. For $\Delta \ll k_1 - k_o$, $\Delta E'$ decreases with $k_1 - k_o$ and varies as $(1/2T_p)_o \, \Delta/k_1 - k_o$.

The physical interpretation of $\Delta E'$ is the following: When the exciting beam contains frequencies k_1 which differ from k_o, the atom cannot undergo real transitions, for energy would not be conserved; but it may undergo "*virtual*" ones, provided that they last a time smaller than $1/k_1 - k_o$ because of the fourth uncertainty relation. The effect of these virtual transitions is to bring back in the ground state a small part of the energy of the excited state, and so, to displace it.

This displacement may differ from one sublevel to another if the $A_{\mu\mu}$'s, which are the transition probabilities, differ too. Magnetic resonance lines in the ground state will then be shifted.

Let us now turn back to the light shift experiment on ^{199}Hg and analyze the effect of the second beam[1],[2] when it is circularly right polarized. The wave number k of this second beam falls between the wave numbers k_{01} and k_{02} of the hyperfine components of ^{199}Hg (see Fig. 1). In fact it is about one Doppler width higher than k_{01}. The numbers written on the figure are the $A_{\mu\mu}$.

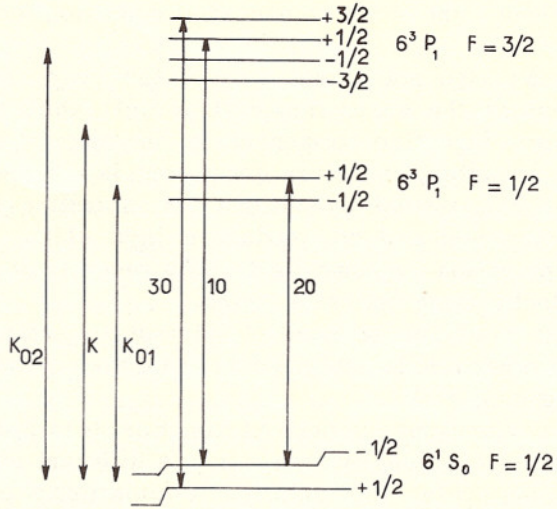

Fig. 1. Hyperfine components of ^{199}Hg

Virtual transitions to the 6^3P_1 $F = \frac{1}{2}$ level are characterized by $k - k_{01} > 0$ so $\Delta E'$ is positive. Owing to the polarization of light, $A_{\frac{1}{2}\frac{1}{2}} = 0$ and only the sublevel $-\frac{1}{2}$ is shifted, and *shifted upwards*. This displacement is shown on the right part of the figure.

Virtual transitions to the 6^3P_1 $F = \frac{3}{2}$ level give a negative and much smaller self-energy (for $k - k_{02}$ is negative and much greater). The corresponding displacement, as shown on the left part of the figure is downwards and three times greater for sublevel $+\frac{1}{2}$ than for sublevel $-\frac{1}{2}$ (ratio between the transition probabilities).

The two effects lead together to an *increase* of the energy separation between the two sublevels. Conclusions are reversed for a σ^- excitation. This agrees with the experimental facts (see Fig. 1 of Reference 1).

In this experiment, polarization of light is used to produce different displacements for the two Zeeman sublevels of a same hyperfine level, separated by a distance much smaller than the Doppler breadth of the optical line. If this is not the case, as, for example, for the two hyperfine levels in the ground state of an alkali metal, $\Delta E'$ itself varies from one level to the other and

use of polarized light is not an essential condition for observing a shift.

It should be also noted that even if the lamp contains the same element as the absorption cell, a light shift may occur. Indeed, if some hyperfine components of the element differ by a few Doppler breadths, one given component in the lamp may induce in the cell virtual transitions corresponding to another hyperfine component and so, produce a light shift. This is a possible explanation for some light shifts recently discovered[6] in atomic clocks using optical pumping.

Finally, it would be perhaps of interest to summarize here some of the other results obtained in the above quantum theory of optical pumping.[3],[4]

Differential equations are derived from Eqs. (4) which describe the evolution of the density matrix at the different steps of the optical pumping cycle. Particularly, "circulation of coherence" as it was defined in Brossel's talk,[1] is quantitatively studied. It is shown that a partial conservation of coherence may occur during the resonance process. Other kinds of light shifts, due *to real transitions*, are associated with this effect. Its physical meaning lies in the coupling of the Zeeman effect of the ground state to the Zeeman effect of the excited state.

The final conclusion one arrives at is the following: The effect of optical pumping on the ground state appears as a relaxation process. Several longitudinal and transversal relaxation times associated with it may be so defined and evaluated.

Finally, optically detected signals, as, for example, the quantity of light absorbed or emitted per unit time in a given direction and with a given state of polarization, are expressed as a function of the elements of the density matrix in the ground state.

References

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Discussion

M. ARDITI: Light-intensity shifts of the hyperfine levels in the ground state of optically pumped alkali atoms have been previously reported.* The results of recent experiments are reported here in support of the suggestion by C. Cohen-Tannoudji that such shifts could be produced by virtual transitions induced in the absorption cell by the hyperfine components of the exciting resonance light. In particular, a positive or negative light-intensity frequency shift has been obtained by shifting slightly the hyperfine components of the exciting light compared to the hyperfine components of the resonance cell itself. In one experiment with rubidium 87 (using the natural isotopic mixture of Rb^{87} and Rb^{85}) this was done by placing the light source in a magnetic field: by varying the magnetic field intensity the light shift could be reduced, annulled, or reversed slightly. In another experiment, a filter cell was used between the light source and the resonance cell. In this case a positive frequency shift of $+7.5 \times 10^{-9}$ corresponding to a 2 to 1 change in light intensity, was changed to a negative shift of -6.5×10^{-9} where a magnetic field of about 500 gauss was applied to the filter cell. This intensity of the magnetic field corresponds to a shift of the hyperfine components of a few hundred megacycles and is of the order of the Doppler broadening. Although these experiments are in qualitative agreement with the theory, a quantitative treatment in this case is very complex due to the large number of hyperfine components and their mutual interaction.

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*M. Arditi and T. R. Carver, Bull. Am. Phys. Soc. *6*, 74 (1961).

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