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A quantum theoretic treatment of double-resonance phenomena

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Abstract. We present a quantum mechanical method capable of providing exact non-perturbative solutions in problems involving the interaction of atoms and molecules with the electromagnetic field. To illustrate the method we consider two examples of double-resonance phenomena. In the first example we study the interaction of a near-resonance rf field with the Zeeman sublevels of atomic hydrogen. In the second we study the interaction of a three-level molecule with two applied electromagnetic fields. Both the molecular levels and the electromagnetic field are quantized. Our method eliminates the deficiencies of a semiclassical treatment, yet does not require the sophisticated computations of the resolvent formalism of Cohen-Tannoudji.

1. Introduction

We present a quantum mechanical method of general applicability in describing the interaction of atoms with the electromagnetic field. To illustrate the method we consider two examples of double-resonance phenomena. In our analysis both the atomic levels and the radiation field are quantized. The basic technique involves finding two constants of the motion which allows an exact solution of the Schrödinger equation to be found. This method was first used by Jaynes and Cummings (1963) for the problem of one atom interacting with one electromagnetic field mode and has since been applied with success to more general problems (see Tavis and Cummings 1967, 1968, Walls and Barakat 1970, Scharf 1970, Walls 1970) involving the interaction of radiation with matter.

The first example we shall study is the interaction of a near-resonance rf field with the Zeeman sublevels of atomic hydrogen. Audoin *et al.* (1968) have reported that a hyperfine line can be split into a multiplet when an rf field whose frequency corresponds to the energy difference between the Zeeman sublevels (Andresen 1968) is applied. Audoin *et al.* (1969) have shown that the measurement of the intensities of these lines provides a very good means of determining the populations of the different states. In particular they studied experimentally the triplet splitting of the $\Delta m = 0$ transition of a hydrogen maser used as an amplifier. The results were analysed using the theoretical calculations of Piéjus (1968) who used the resolvent method developed by Cohen-Tannoudji (1967). A very good agreement between the predicted and observed amplitudes of the different lines was obtained.

We believe that our analysis illustrates the underlying physics to a greater extent than the resolvent method. Further, our method does not require the mathematical sophistication of the resolvent method, nor does it resort to perturbative techniques. The solution of the nonlinear operator problem is reduced to the diagonalization of a 3×3 matrix. In this mathematical simplicity lies the potential of this technique for solving related problems involving the nonlinear interaction of light with atoms.

In the second example of a double-resonance experiment we consider a three-level molecule with allowed electric dipole transitions between levels $1 \leftrightarrow 2$ and levels

$2 \leftrightarrow 3$ but not between levels $1 \leftrightarrow 3$. In the presence of a pumping transition $1 \rightarrow 2$, the absorption of a signal between $2 \rightarrow 3$ increases. The first experiment of this nature was performed by Autler and Townes (1950) who observed a splitting of a microwave absorption line when in the presence of a field which induces transitions between the initial and final energy levels of the line and some other level of the molecule. More recently a similar double-resonance experiment has been used by Macke *et al.* (1969) to study two rotational transitions of an asymmetric top molecule with a common level. A semiclassical analysis of this type of double-resonance experiment has been given by Javan (1957) and Macke *et al.* (1969). A perturbative quantum treatment using the resolvent formalism has been given by Di Giacomo and Santucci (1969). In our fully quantum mechanical treatment an exact non-perturbative solution is derived in which spontaneous emission is included.

2. Interaction of an rf field with the Zeeman levels of hydrogen

We consider the effect of an rf field of frequency ω_x and amplitude H_x on the multiplicity $F = 1$ of the ground state of atomic hydrogen (see figure 1).

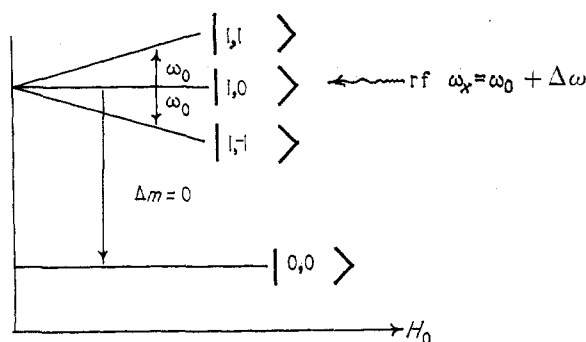


Figure 1. Energy levels of a hydrogen atom in the ground state as a function of the magnetic field H_0 .

In very low magnetic fields the three Zeeman sublevels $F = 1$ may be treated as the three levels of a spin 1 henceforth designated by S . The energy of the three Zeeman levels in a dc magnetic field H_{dc} is then given by the Hamiltonian

$$H_{\text{spin}} = \hbar\omega_0 S_z \tag{2.1}$$

where S_z is the z component of the spin S and $\omega_0 = \frac{1}{2}\gamma H_{dc}$ where γ is the electron gyromagnetic ratio.

The eigenstates of the spin Hamiltonian are the states $|S, S_z\rangle$, explicitly $|1, 1\rangle$, $|1, 0\rangle$ and $|1, -1\rangle$ with energies $\hbar\omega_0$, 0 , $-\hbar\omega_0$ respectively.

The Hamiltonian for the perturbing rf field of frequency ω_x is

$$H_{\text{rf}} = \hbar\omega_x a^\dagger a \tag{2.2}$$

where a , a^\dagger obey the usual boson commutation relations. The total Hamiltonian for the system is

$$H = H_0 + H_1 \tag{2.3}$$

where H_0 the free Hamiltonian is given by

$$H_0 = \hbar\omega_x a^\dagger a + \hbar\omega_0 S_z \tag{2.4}$$

where we have allowed the rf field to be off-resonance by an amount $\Delta\omega$.

$$\omega_x = \omega_0 + \Delta\omega. \quad (2.5)$$

The interaction Hamiltonian H_1 may be written as

$$H_1 = \hbar\kappa(a + a^\dagger)S_x. \quad (2.6)$$

On neglecting highly non-resonant terms, that is, making the rotating-wave approximation, this becomes

$$H_1 = \hbar\kappa(aS_+ + a^\dagger S_-) \quad (2.7)$$

where

$$S_+ = \frac{1}{\sqrt{2}}(S_x + iS_y)$$

$$S_- = \frac{1}{\sqrt{2}}(S_x - iS_y) \quad (2.8)$$

are the raising and lowering operators for the three-level system. The coupling constant $\kappa = \gamma H_x$.

The Heisenberg equations of motion following from the above Hamiltonian are nonlinear operator equations. To circumvent this intractable problem we look for a solution of the Schrödinger equation by constructing two constants of the motion. We proceed by constructing the following two operators

$$I_0 = \hbar\omega_0 a^\dagger a + \hbar\omega_0 S_z + K \quad (2.9)$$

$$I_1 = H_1 + \hbar\Delta\omega a^\dagger a - K \quad (2.10)$$

such that

$$H = I_0 + I_1 \quad (2.11)$$

and K is an arbitrary constant.

It is easy to verify the following commutation relations

$$[I_0, I_1] = [I_0, H] = [I_1, H] = 0. \quad (2.12)$$

Thus I_0 and I_1 are constants of the motion. Since they commute with each other a representation exists in which the total Hamiltonian is diagonal. We consider the following set of basis states with notation $|S_z, n\rangle$ which are all eigenstates of I_0 :

$$\psi^\dagger = (|1, n-1\rangle, |0, n\rangle, |-1, n+1\rangle). \quad (2.13)$$

Since we are considering a three-level system this set of states is closed and forms a complete set of basis states for the system. We shall attempt to express the eigenstates of I_1 as a linear combination of these basis states. The Schrödinger equation takes the following form

$$I_1\psi = \hbar A\psi \quad (2.14)$$

where A is the 3×3 matrix

$$A = \begin{pmatrix} -\Delta\omega & \kappa\sqrt{n} & 0 \\ \kappa\sqrt{n} & 0 & \kappa(n+1)^{1/2} \\ 0 & \kappa(n+1)^{1/2} & \Delta\omega \end{pmatrix} \quad (2.15)$$

where the arbitrary constant K has been chosen $K = \hbar m\Delta\omega$. The eigenstates and eigenvalues of the system are found by diagonalizing this matrix. The eigenvalues

are roots of the cubic equation

$$\lambda^3 - \lambda\{\Delta\omega^2 + (2n+1)\kappa^2\} - \kappa^2\Delta\omega = 0. \tag{2.16}$$

This equation has no simple roots hence in equation (2.15) we make the approximation $(n+1)^{1/2} \simeq n^{1/2}$. This is the only approximation made in the analysis of the nonlinear Hamiltonian equations (2.3), (2.4), (2.7). This approximation is valid for large n and thus is expected to be a good approximation for rf fields. The eigenvalues are now found to be $0, \pm G$ where

$$G = (\Delta\omega^2 + g^2)^{1/2} \tag{2.17}$$

and

$$g^2 = 2n\kappa^2.$$

The corresponding eigenstates of the system are

$$\Phi = U\psi \tag{2.18}$$

where U is the 3×3 matrix

$$U = \begin{pmatrix} \frac{1-u}{2} & \left(\frac{1-u^2}{2}\right)^{1/2} & \frac{1+u}{2} \\ \left(\frac{1-u^2}{2}\right)^{1/2} & u & -\left(\frac{1-u^2}{2}\right)^{1/2} \\ \frac{1+u}{2} & -\left(\frac{1-u^2}{2}\right)^{1/2} & \frac{1-u}{2} \end{pmatrix} \tag{2.19}$$

with $u = \Delta\omega/G$ and

$$\Phi^\dagger = (\phi_+, \phi_0, \phi_-) \tag{2.20}$$

ψ is defined by equation (2.13).

These results are identical to those obtained by Audoin *et al.* (16) (taking into account the different normalization of the coupling constant) calculated using the resolvent method. However our method does not involve the computational complexity of the resolvent method nor does it resort to perturbative calculations. The coincidence of our results with those of Audoin *et al.* (1969) is due to our introduction of the approximation $(n+1)^{1/2} = n^{1/2}$ made in order to present the solutions in closed form.

3. Probability amplitudes for the triplet transitions

We consider the case where the pumping process has created a population difference denoted by p_+, p_0, p_{-1} between the unperturbed states. We consider the case of sudden passage, that is when the time τ taken to apply the Zeeman perturbation is much less than $1/\omega_x$. The populations P_+, P_0 and P_- of the states ϕ_+, ϕ_0 and ϕ_- may then be read directly from equation (2.18).

$$\begin{aligned} P_+ &= p_+ \left(\frac{1-u}{2}\right)^2 + p_0 \left(\frac{1-u^2}{2}\right) + p_{-1} \left(\frac{1+u}{2}\right)^2 \\ P_0 &= p_+ \left(\frac{1-u^2}{2}\right) + p_0 u^2 + p_{-1} \left(\frac{1-u^2}{2}\right) \\ P_- &= p_+ \left(\frac{1+u}{2}\right)^2 + p_0 \left(\frac{1-u^2}{2}\right) + p_{-1} \left(\frac{1-u}{2}\right)^2 \end{aligned} \tag{3.1}$$

From the known eigenstates and eigenvalues (equations (2.17) and (2.18)) we may calculate exactly the probability amplitudes $a_1(t)$, $a_0(t)$ and $a_{-1}(t)$ of the atoms being in the states $|1\rangle$, $|0\rangle$ and $|-1\rangle$ at time t . The result is the following:

$$\begin{aligned} \begin{pmatrix} a_1(t) \\ a_0(t) \\ a_{-1}(t) \end{pmatrix} &= U^\dagger \begin{pmatrix} 1 & 0 & 0 \\ 0 & e^{iGt} & 0 \\ 0 & 0 & e^{-iGt} \end{pmatrix} U \begin{pmatrix} a_1 \\ a_0 \\ a_{-1} \end{pmatrix} \\ &= e^{-iAt} \begin{pmatrix} a_1 \\ a_0 \\ a_{-1} \end{pmatrix} \end{aligned} \quad (3.2)$$

where a_1 , a_0 , and a_{-1} are the probability amplitudes of the atoms initially being in the states $|1\rangle$, $|0\rangle$ and $|-1\rangle$. From the above general expression we may write down the probability amplitude of the level $|0\rangle$ being occupied at time t .

$$\begin{aligned} a_0(t) &= \left(\frac{1-u^2}{2}\right)^{1/2} \left\{ u - \left(\frac{1-u}{2}\right) e^{iGt} - \left(\frac{1+u}{2}\right) e^{-iGt} \right\} a_1 \\ &\quad + \left\{ u^2 + (1-u^2) \left(\frac{e^{iGt} + e^{-iGt}}{2}\right) \right\} a_0 \\ &\quad + \left(\frac{1-u^2}{2}\right)^{1/2} \left\{ -u + \left(\frac{1+u}{2}\right) e^{iGt} - \left(\frac{1-u}{2}\right) e^{-iGt} \right\} a_{-1}. \end{aligned} \quad (3.3)$$

Similar expressions for $a_1(t)$ and $a_{-1}(t)$ may be written down from equation (3.2).

The level $|0\rangle$ gives rise to the $\Delta m = 0$ transition. From equation (3.3) we see that there are three components with frequencies ω , $\omega \pm G$. The ratio of the intensities of the three lines $\omega + G$: ω : $\omega - G$ is seen from equation (3.3) to be

$$\left(\frac{1-u^2}{2}\right) P_+ : u^2 P_0 : \left(\frac{1-u^2}{2}\right) P_{-1}.$$

The intensities of the triplets in the $\Delta m = \pm 1$ transitions may be calculated in a similar fashion.

The above technique provides a very precise determination of the resonance frequency $\omega_x = \omega_0$, since we see that on resonance the intensity of the central line becomes zero ($\Delta\omega = u = 0$).

4. Interaction of two electromagnetic field modes with a three-level system

We shall now consider a more general double-resonance experiment than described in § 2 and § 3. We consider the system of a three-level molecule interacting with two electromagnetic field modes as shown in figure 2. It is seen that the system studied in § 2 is a special case of the system shown in figure 2 with $\omega_a = \omega_b$, $E_3 - E_2 = E_2 - E_1$ and $\mu_{12} = \mu_{23}$. The system shown in figure 2 may be described by the following Hamiltonian

$$H = H_0 + H_1 \quad (4.1)$$

$$H_0 = \hbar\omega_1 c_1^\dagger c_1 + \hbar\omega_2 c_2^\dagger c_2 + \hbar\omega_3 c_3^\dagger c_3 + \hbar\omega_a a^\dagger a + \hbar\omega_b b^\dagger b \quad (4.2)$$

$$H_1 = \hbar\kappa_a (c_1 a c_2^\dagger + c_1^\dagger a^\dagger c_2) + \hbar\kappa_b (c_2 b c_3^\dagger + c_2^\dagger b^\dagger c_3) \quad (4.3)$$

where a, b are photon annihilation operators obeying boson commutation relations; c_1, c_2, c_3 are the annihilation operators for the molecular levels obeying fermion commutation and anticommutation relations. The coupling constants κ_a, κ_b are proportional to μ_{12}, μ_{23} —the matrix elements of the dipole moments between levels 1 and 2, and 2 and 3 respectively.

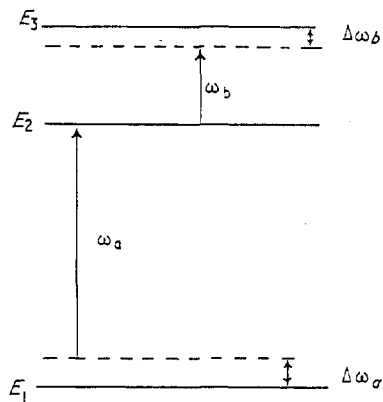


Figure 2. Three-level molecule interacting with two electromagnetic field modes.

We proceed as in § 2 by constructing the following two operators

$$I_0 = \hbar(\omega_1 + \Delta\omega_a)c_1^\dagger c_1 + \hbar\omega_2 c_2^\dagger c_2 + \hbar(\omega_3 - \Delta\omega_b)c_3^\dagger c_3 + \hbar\omega_a a^\dagger a + \hbar\omega_b b^\dagger b \quad (4.4)$$

$$I_1 = H_1 - \hbar\Delta\omega_a c_1^\dagger c_1 + \hbar\Delta\omega_b c_3^\dagger c_3 \quad (4.5)$$

where

$$\Delta\omega_a = \omega_{12} - \omega_a \quad \Delta\omega_b = \omega_{23} - \omega_b$$

such that

$$H = I_0 + I_1. \quad (4.6)$$

The following commutation relations are easily verified

$$[I_0, I_1] = [I_0, H] = [I_1, H] = 0. \quad (4.7)$$

Thus I_0 and I_1 are constants of the motion and since they commute a representation may be found in which the total Hamiltonian H is diagonal.

We choose as a set of basis states

$$\psi^\dagger = (|1, n_a + 1, n_b + 1\rangle, |2, n_a, n_b + 1\rangle, |3, n_a, n_b\rangle) \quad (4.8)$$

where n_a, n_b are the number states for the photon fields and 1, 2, 3 refer to the molecular level occupied. These three states form a complete set of basis states for the system.

The Schrödinger equation in the interaction picture now becomes

$$I_1 \psi = \hbar A \psi \quad (4.9)$$

where A is the 3×3 matrix

$$A = \begin{pmatrix} -\Delta\omega_a & g_a & 0 \\ g_a & 0 & g_b \\ 0 & g_b & \Delta\omega_b \end{pmatrix} \quad (4.10)$$

where

$$g_a = (n_a + 1)^{1/2} \kappa_a \quad g_b = (n_b + 1)^{1/2} \kappa_b.$$

The eigenstates and eigenvalues of the system are obtained from the diagonalization of the matrix A . The eigenvalues are given by the roots of the cubic equation

$$\lambda^3 + (\Delta\omega_a - \Delta\omega_b)\lambda^2 - \lambda(g_a^2 + g_b^2 + \Delta\omega_a\Delta\omega_b) + g_a^2\Delta\omega_b - g_b^2\Delta\omega_a = 0. \quad (4.11)$$

The solutions of this equation cannot be expressed in closed form except when

$$\Delta\omega_a + \Delta\omega_b = 0. \quad (4.12)$$

This occurs for example in the Raman effect for Stokes scattering from a three-level molecule. This case has been previously studied (Shimoda 1969, 1970, Walls 1971).

The condition (4.12) does not generally hold. However for $g_b \ll g_a$ a solution may be found correct to first order in g_b . This situation occurs for example in an experiment where there is a strong pump field applied between levels 1 and 2 and a weak signal between levels 2 and 3. If the molecule is initially in state $|3\rangle$ the transition probability for the one-quantum transition to state $|2\rangle$ is found to be

$$P_{32}(t) = \frac{|g_b|^2}{4G^2(\Omega^2 - G^2)^2} |2G(\Delta\omega_a + \Delta\omega_b) e^{i\Omega t} - 2G(\Delta\omega_a + \Delta\omega_b) \cos Gt - i(2G^2 + \Delta\omega_a\Omega) \sin Gt|^2. \quad (4.13)$$

The corresponding transition probability for the two-quantum transition to state $|1\rangle$ is

$$P_{31}(t) = \frac{|g_a|^2 |g_b|^2}{G^2(\Omega^2 - G^2)^2} |G \cos Gt + i\Omega \sin Gt - G e^{i\Omega t}|^2 \quad (4.14)$$

where

$$G = \left\{ \left(\frac{\Delta\omega_a}{2} \right)^2 + g_a^2 \right\}^{1/2} \quad (4.15)$$

and

$$\Omega = \Delta\omega_b + \frac{\Delta\omega_a}{2}. \quad (4.16)$$

These results are almost identical to the results obtained by the semiclassical calculations of Javan (1957) and Macke *et al.* (1969). The important difference is the $(n_a + 1)^{1/2}$ and $(n_b + 1)^{1/2}$ factors in g_a and g_b . The +1 allows for spontaneous emission from levels $3 \rightarrow 2$ and $2 \rightarrow 1$. When the radiation field is treated classically spontaneous emission is not included.

We note that in the presence of a strong pumping field between levels 1 and 2 the absorption line between levels 2 and 3 appears as a doublet. The magnitude of the splitting of the doublet is $2G$. An interference effect between the two components of the doublet may be neglected for high saturating power (see Javan 1957). This is the effect first observed in the resonant modulation experiment of Autler and Townes (1950). The presence of the pumping field gives rise to a modulation of the wavefunction between the two states 2 and 3 at an angular frequency G .

The above results give the effect of the application of the electromagnetic fields on the dynamic state of the molecule. The effects of molecular collisions may be

superposed on these results (Javan 1957, Macke *et al.* 1969). The experiments of Macke *et al.* (1969) studying the rotational transitions in sulphur dioxide show a satisfactory agreement with theory.

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