Multiple Quantum Transitions of a System of Coupled Angular Momenta*†

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The transition probabilities of the multiple quantum transitions of a system of coupled angular momentum vectors in a uniform static plus perpendicular rotating magnetic field are studied both in the uncertainty width region, by time-dependent perturbation theory, and at higher amplitudes of the rotating field, by direct integration of the Schrödinger equation, in the case of well-separated resonance frequencies.

1. INTRODUCTION

A MULTIPLE quantum transition is a transition in which, in the terminology of radiation theory, several quanta supply the necessary energy so that a generalized Bohr frequency condition holds of the form

$$\bar{E}_f-\bar{E}_i=n_1\hbar\omega_1+\cdots+n_r\hbar\omega_r. \quad (1)$$

The n's are positive integers, with $\sum n_j \geqslant 2$, and the $\bar{E}$'s are the energies of the initial and final states, including energy-level shifts due to virtual absorption and emission of quanta.

The theory of two-quantum absorption and emission processes, in lowest approximation, was first discussed by Mayer.[1] Although these transitions are rare events in the optical region,[1,2] many cases of multiple-quantum transitions have recently been observed in electric and magnetic resonance transitions between hyperfine levels. The first such observation appears to have been that of Hughes and Grabner,[3] who also discussed the theory of two-quantum transitions, in lowest approximation, in the correspondence limit of unquantized electromagnetic field for the special case that the two quanta have the same frequency. Such a treatment (semiclassical radiation theory) is well justified in the hyperfine case since spontaneous emission is then a negligible process. Further observations of multiple-quantum transitions have been performed by many others.[4]

The further development of the theory was undertaken independently by Besset *et al.*,[5] Salwen,[6] and the present writer.[7] The theories of Besset *et al.* and Salwen are based on the steady state solutions[5–7] of the Schrödinger equation for a rotating magnetic field. In particular, Salwen has studied the line shapes of multiple-quantum transitions of arbitrary order in a rotating magnetic field for the case of well-separated resonance frequencies. However, it has not been well understood how the time-dependent perturbation theoretical treatment of multiple-quantum transitions, as given for two-quantum transitions by Mayer and Hughes and Grabner, is related to the theory based on the steady-state solutions. Thus, the methods used by Besset *et al.* are applicable only at higher fields, and Hughes and Geiger[4] have pointed out the necessity for a careful comparison of their own results with those of Salwen. The present paper gives a formulation of the theory which clarifies the relation of these various approaches to each other and moreover has the advantage that it can be directly extended to oscillating and multiple-frequency fields.[7,8]

2. EQUIVALENT STATIONARY PROBLEM IN THE CASE OF A ROTATING MAGNETIC FIELD

We consider a system of two coupled angular momentum vectors, **I** and **J**, with gyromagnetic ratios γ_I and γ_J, which interact with each other and also with an external magnetic field.[9] The latter consists of a rotating radio-frequency field of constant amplitude and angular velocity, $\mathcal{H}_1$ and ω, and a uniform static field, of amplitude $\mathcal{H}_0$, along the axis of rotation. With the z axis chosen in the direction of the static field and the x axis in the direction of the rotating field at time $t=0$, the Hamiltonian of the system can be written in the form

$$H=H_0+H_1, \quad (2)$$

where

$$H_0=a\mathbf{I}\cdot\mathbf{J}+\gamma_J J_z\mathcal{H}_0+\gamma_I I_z\mathcal{H}_0, \quad (3)$$

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[9] The extension to an arbitrary number of coupled angular momenta introduces nothing new in principle. On the other hand, for a single angular momentum all resonances, single- and multiple-quantum, coalesce at a single frequency.

and

$$H_1=(\gamma_J\mathbf{J}+\gamma_I\mathbf{I})\cdot[(\mathfrak{H}_1\cos\omega t)\mathbf{i}+(\mathfrak{H}_1\sin\omega t)\mathbf{j}]. \quad (4)$$

The Hamiltonian given by Eqs. (2), (3), and (4) depends explicitly on the time. However, a transformation to a coordinate system rotating with the applied radio-frequency field[10] reduces the problem to a time-independent one.[5-7] This follows with the help of the identity

$$e^{iF_z\omega t/\hbar}H_1e^{-iF_z\omega t/\hbar}=V, \quad (5)$$

where

$$V=\gamma_JJ_x\mathfrak{H}_1+\gamma_II_x\mathfrak{H}_1, \quad (6)$$

and F_z is the component of the total angular momentum, $\mathbf{F}=\mathbf{I}+\mathbf{J}$, along the direction of the static magnetic field. Equation (5) can be proved for example by observing that the derivative of the left-hand side with respect to t vanishes by virtue of the commutation relations of the angular momentum operators. The left-hand side is therefore independent of t, and since (5) clearly holds at time $t=0$, it follows that it holds generally.

The transformation to the rotating coordinate system is effected by the unitary operator $\exp(iF_z\omega t/\hbar)$ so that the transformed wave function is

$$\phi=U\psi=e^{iF_z\omega t/\hbar}\psi, \quad (7)$$

and

$$\frac{d\phi}{dt}=U\frac{d\psi}{dt}+\frac{i}{\hbar}F_z\omega U\psi$$

$$=(i\hbar)^{-1}(UHU^{-1}-\omega F_z)\phi, \quad (8)$$

where in the last line we have substituted from the Schrödinger equation for $d\psi/dt$. By virtue of Eqs. (2) and (5) and the fact that F_z commutes with H_0, we have

$$UHU^{-1}=H_0+V. \quad (9)$$

Consequently, we obtain the transformed wave equation

$$i\hbar(d\phi/dt)=W\phi, \quad (10)$$

where

$$W=H_0-\omega F_z+V \quad (11)$$

is independent of the time. In the following sections we study solutions of Eq. (10) for ω in the neighborhood of resonance frequencies of the system.

3. SOLUTION OF THE RECURSION RELATIONS OF TIME-DEPENDENT PERTURBATION THEORY FOR A CONSTANT HAMILTONIAN

Time-dependent perturbation theory starts from the equations

$$W=W_0+V, \quad W_0\psi_i=W_i\psi_i, \quad (12)$$

where the ψ_i and W_i are the eigenstates and eigenvalues of the time-independent unperturbed Hamiltonian W_0 and V is the perturbation. The wave function is expanded in the form

$$\psi_j(t)=\sum_i a_{ij}(t)e^{-iW_it/\hbar}\psi_i, \quad (13)$$

where the subscript j indicates that the initial condition is chosen, without loss of generality, as $\psi_j(0)=\psi_j$.[11] The perturbation theory consists of expanding the a_{ij} in a series

$$a_{ij}(t)=a_{ij}{}^0+a_{ij}{}^{(1)}(t)+a_{ij}{}^{(2)}(t)+\cdots, \quad (14)$$

where $a_{ij}{}^0=\delta_{ij}$, $a_{ij}{}^{(n)}(0)=0$, and the $a_{ij}{}^{(n)}(t)$ are determined by the recursion relations[12]

$$a_{ij}{}^{(n)}(t)=-\frac{i}{\hbar}\int_0^t\sum_l V_{il}e^{iW_{il}t'/\hbar}a_{lj}{}^{(n-1)}(t')dt', \quad (15)$$

where $W_{il}=W_i-W_l$. We will solve these recursion relations in the important case that V is independent of the time. In this case (15) yields for the first- and second-order transition amplitudes the well-known expressions

$$a_{ij}{}^{(1)}=-V_{ij}\left(\frac{e^{iW_{ij}t/\hbar}-1}{W_{ij}}\right), \quad (16)$$

$$a_{ij}{}^{(2)}=\sum_l V_{il}V_{lj}\left\{\frac{1}{W_{ij}W_{lj}}(e^{iW_{ij}t/\hbar}-1)\right.$$

$$\left.-\frac{1}{W_{il}W_{lj}}(e^{iW_{il}t/\hbar}-1)\right\}. \quad (17)$$

The solution of the recursion relations (15) to all orders can be described as follows for the case of a constant Hamiltonian. In Fig. 1 the labels at the right designate the initial, final, and intermediate states, and the sequences of arrows are all possible ways of jumping upwards from state j to state i. If a single arrow in one of these sequences connects a lower state s to an upper state p and passes over states $r, \cdots, q$ on the way, we associate with it a factor

$$1/(W_{ps}W_{qs}\cdots W_{rs}).$$

If p happens to be the final state, we adjoin an additional factor $(e^{iW_{ps}t/\hbar}-1)$. For each sequence of arrows we take the product of all such factors, multiply by the product of matrix elements $V_{il}\cdots V_{mj}$, and sum over all intermediate states. The rule for obtaining the sign of each term is explained below. In this way, for

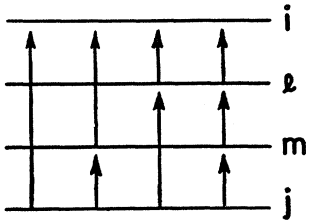

FIG. 1. Diagram for construction of the third-order transition amplitude.

[10] Rabi, Ramsey, and Schwinger, Revs. Modern Phys. **26**, 167 (1954).

[11] The solution satisfying the most general initial condition $\psi(0)=\sum_j c_j\psi_j$ is clearly $\psi(t)=\sum_j c_j\psi_j(t)$ (reference 12).

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the third-order case illustrated in Fig. 1, we arrive at the following transition amplitude:

$$a_{ij}^{(3)}=\sum_{l,m} V_{il}V_{lm}V_{mj}\left\{-\frac{1}{W_{ij}W_{lj}W_{mj}}(e^{iW_{ij}t/\hbar}-1)\right.$$
$$+\frac{1}{W_{im}W_{lm}}\cdot\frac{1}{W_{mj}}(e^{iW_{im}t/\hbar}-1)$$
$$+\frac{1}{W_{il}}\cdot\frac{1}{W_{lj}W_{mj}}(e^{iW_{il}t/\hbar}-1)$$
$$\left.-\frac{1}{W_{il}}\cdot\frac{1}{W_{lm}}\cdot\frac{1}{W_{mj}}(e^{iW_{il}t/\hbar}-1)\right\}.$$

The diagram for order $n+1$ gives 2^n terms and can be constructed from the diagram for order n by (1) continuously extending the final arrows one level higher (no new arrows) and (2) adding a new row of arrows across the top of the diagram for order n. The sign rule is then as follows: The 2^{n-1} terms corresponding to (1) arise from the exponential terms of the preceding order n and get an additional minus sign when the corresponding terms of order $n+1$ are obtained from Eq. (15). Their signs are therefore opposite to the signs in the preceding order. The 2^{n-1} terms corresponding to (2) come from the minus one terms of the preceding order, and this minus sign together with the one from Eq. (15) gives no net sign change so that the signs are the same as in the preceding order. (The sign is negative for $n=1$.)

The prescription given above can be proved by mathematical induction. It is obviously valid for $n=1$. We now assume its validity for n and prove its validity for $n+1$. For a term arising from an exponential, say $e^{iW_{lp}t/\hbar}$, the multiplication by $e^{iW_{il}t/\hbar}$ in (15), and integration, gives a factor $(e^{iW_{ip}t/\hbar}-1)/W_{ip}$, which is just the additional factor needed according to the above prescription for the term arising from continuously extending the final arrow of the corresponding sequence of the nth order diagram. For a term arising from a minus one, the multiplication by $e^{iW_{il}t/\hbar}$, and integration, gives a factor $(e^{iW_{il}t/\hbar}-1)/W_{il}$, which is just the additional factor needed for the term arising from adding an arrow to the top of the corresponding nth order sequence. Thus (15) establishes the validity of the procedure for $n+1$ if it holds for n; since it holds for $n=1$, it therefore holds for all n.

4. MULTIPLE QUANTUM TRANSITIONS IN THE UNCERTAINTY WIDTH REGION

The time-independent transformed Hamiltonian W [Eq. (11)] can be split up into an unperturbed Hamiltonian W_0 and a perturbation V proportional to the amplitude of the rotating magnetic field,

$$W=W_0+V, \tag{18}$$

where

$$W_0=H_0-\omega F_z, \tag{19}$$

and

$$V=\gamma_J J_x \mathcal{H}_1+\gamma_I I_x \mathcal{H}_1. \tag{20}$$

W_0 is diagonal in the representation determined by the eigenstates ψ_i of the commuting Hermitian operators H_0 and F_z, and we have

$$W_0\psi_i=W_i\psi_i=(E_i-M_i\hbar\omega)\psi_i,$$

where E_i and $M_i\hbar$ are the eigenvalues of H_0 and F_z, and W_i is the eigenvalue of W_0, in the eigenstate ψ_i. Thus

$$W_{ij}=W_i-W_j=\hbar(\omega_{ij}-[M_i-M_j]\omega), \tag{21}$$

where $\omega_{ij}=(E_i-E_j)/\hbar$. Also we define matrix elements A_{ij} by

$$V_{ij}=(\psi_i,V\psi_j)=\hbar A_{ij}. \tag{22}$$

Since the ψ_i are eigenstates of F_z, the M_i selection rules are the same as in the F, M_F representation,[13] namely,

$$A_{ij}=0 \quad \text{unless} \quad M_i=M_j\pm 1. \tag{23}$$

For an ordinary allowed transition, with $M_i=M_j\pm 1$, the first order of perturbation theory gives for the transition amplitude

$$a_{ij}^{(1)}=-A_{ij}\frac{e^{i(\omega_{ij}\mp\omega)t}-1}{\omega_{ij}\mp\omega}, \tag{24}$$

and therefore for the transition probability

$$P^{(1)}(i\leftrightarrow j)=4A_{ij}^2\frac{\sin^2[\frac{1}{2}(\omega\mp\omega_{ij})t]}{(\omega\mp\omega_{ij})^2}. \tag{25}$$

If E_i-E_j and $M_i-M_j(=\pm 1)$ have the same sign, we obtain a resonance for $\omega=|E_i-E_j|/\hbar$. If, on the other hand, E_i-E_j and M_i-M_j have opposite sign, then there is no resonance for any positive value of ω. The physical basis of this situation is the fact that for the positive direction of rotation of the radio-frequency field, the absorption (emission) of a photon increases (decreases) angular momentum as well as energy, so that both angular momentum and energy can be conserved in the first case but not in the second. However, in order to obtain a resonance in the second case, it is only necessary to choose the opposite direction of rotation.

For a two-quantum transition,[1,3] insertion of Eqs. (21) and (22) into (17) gives

$$a_{ij}^{(2)}=\sum_l A_{il}A_{lj}\left\{\frac{e^{i(\omega_{ij}\mp 2\omega)t}-1}{(\omega_{ij}\mp 2\omega)(\omega_{lj}\mp\omega)}\right.$$
$$\left.-\frac{e^{i(\omega_{il}\mp\omega)t}-1}{(\omega_{il}\mp\omega)(\omega_{lj}\mp\omega)}\right\} \tag{26}$$

[13] E. U. Condon and G. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1953), p. 61.

for $M_i=M_j\pm 2$. The summation over l may be restricted to intermediate states for which $M_l=M_j\pm 1$, as otherwise $A_{il}A_{lj}$ vanishes. The first term in the braces exhibits a resonance at

$$\omega=\pm(E_i-E_j)/2\hbar. \tag{27}$$

Similarly, making use of the solution developed in the preceding section, we see that for given I and J, multiple quantum transitions are possible of orders $n=2$ up to $n=2(I+J)=\max(M_i-M_j)$ at resonance frequencies given by the generalized Bohr condition

$$\omega=\pm(E_i-E_j)/n\hbar. \tag{28}$$

For well-separated resonance frequencies and for ω in the neighborhood of the value (28), we have

$$a_{ij}^{(n)}\simeq(-1)^n \times\sum_{l,m,\cdots,r}\frac{A_{il}A_{lm}\cdots A_{rj}[e^{i(\omega_{ij}\mp n\omega)t}-1]}{(\omega_{ij}\mp n\omega)[\omega_{lj}\mp(n-1)\omega]\cdots(\omega_{rj}\mp\omega)} \tag{29}$$

for $M_i=M_j\pm n$. The summations over intermediate states l, m, $\cdots$, r can be restricted to states satisfying $M_l=M_j\pm(n-1)$, $M_m=M_j\pm(n-2)$, $\cdots$, $M_r=M_j\pm 1$ as otherwise the product of matrix elements in the numerator of (29) vanishes. Thus

$$P^{(n)}(i\leftrightarrow j)\simeq\frac{\omega_1^2}{(\omega-\omega_0)^2}\sin^2[\tfrac{1}{2}n(\omega-\omega_0)t], \tag{30}$$

where

$$\omega_1=\frac{2}{n}\sum_{l,m,\cdots,r}\times\frac{A_{il}A_{lm}\cdots A_{rj}}{[\omega_{lj}\mp(n-1)\omega][\omega_{mj}\mp(n-2)\omega]\cdots(\omega_{rj}\mp\omega)} \tag{31}$$

and

$$\omega_0=\pm\omega_{ij}/n. \tag{32}$$

This result already accounts for the principal observed characteristics of the multiple-quantum transitions. Resonance occurs at the frequency given by the generalized Bohr condition (28) and with an uncertainty width of the order of $\Delta\omega=2\pi/nt$.[14] It is clear that the intensity of the transition depends on the relative locations of the intermediate states, falling off, as observed by Kusch,[4] as the locations of the intermediate states become much different from equally spaced points between the terminal states of the transition. Since the matrix elements in the numerator of (31) are proportional to the amplitude $\mathfrak{IC}_1$ of the rotating field, the leading term of the transition probability for an n-quantum transition goes as the $(2n)$th power of $\mathfrak{IC}_1$.

[14] The narrowing of the uncertainty width with increasing n is by no means in conflict with the energy-time uncertainty principle. In fact, by (28) the uncertainty in the measured energy difference is $n\hbar$ times larger than $\Delta\omega$, so that $\Delta E\cdot t\sim h$.

5. EXTENSION TO HIGHER RADIO-FREQUENCY FIELDS

As the rotating field amplitude $\mathfrak{IC}_1$ is increased, the lowest nonvanishing order of time-dependent perturbation theory ceases to be a good approximation and higher order corrections must be taken into account. The result that for well-separated resonance frequencies a formula of the Rabi type holds [Eq. (53) below] was first proved by Salwen[6] for multiple quantum transitions in a rotating radio-frequency field. We derive this formula here under the same assumptions by a simpler and more direct method which is also applicable to oscillating and multiple-frequency fields.

We consider first the simplest case of coupled angular momenta, $I=J=\frac{1}{2}$, and afterwards treat the general case of arbitrary I and J. In the $I=J=\frac{1}{2}$ case the time-dependent Schrödinger equation becomes

$$\begin{aligned} ida_i/dt&=A_{il}e^{i(\omega_{il}-\omega)t}a_l+A_{im}e^{i(\omega_{im}-\omega)t}a_m,\\ ida_l/dt&=A_{li}e^{i(\omega_{li}+\omega)t}a_i+A_{lj}e^{i(\omega_{lj}-\omega)t}a_j,\\ ida_m/dt&=A_{mi}e^{i(\omega_{mi}+\omega)t}a_i+A_{mj}e^{i(\omega_{mj}-\omega)t}a_j,\\ ida_j/dt&=A_{jl}e^{i(\omega_{jl}+\omega)t}a_l+A_{jm}e^{i(\omega_{jm}+\omega)t}a_m, \end{aligned} \tag{33}$$

where the second subscript on the a's, which would denote the fixed initial state, is suppressed, and the basis states ψ_i are labeled as follows according to the (F,M_F) quantum numbers of the states into which the ψ_i go over continuously as

$$\mathfrak{IC}_0\to 0:\quad i\text{—}(1,1),\quad l\text{—}(1,0),\quad m\text{—}(0,0),\quad j\text{—}(1,-1).$$

In order to treat the two-quantum resonance transition between states i and j, we take as initial condition $\psi(0)=\psi_i$ or

$$a_i(0)=1,\quad a_l(0)=a_m(0)=a_j(0)=0. \tag{34}$$

We are interested in the solution of (33) subject to the initial condition (34) for ω in the neighborhood of the two-quantum resonance frequency

$$\omega_0=(\tilde{E}_i-\tilde{E}_j)/2\hbar. \tag{35}$$

Integration by parts of the second equation of (33) gives

$$\begin{aligned} a_l=&\frac{A_{li}}{\omega_{il}-\omega}e^{i(\omega_{li}+\omega)t}a_i-\frac{A_{li}}{\omega_{il}-\omega}\\ &-\frac{A_{li}}{\omega_{il}-\omega}\int_0^t e^{i(\omega_{li}+\omega)t}\frac{da_i}{dt}dt+\frac{A_{lj}}{\omega_{jl}+\omega}e^{i(\omega_{lj}-\omega)t}a_j\\ &-\frac{A_{lj}}{\omega_{jl}+\omega}\int_0^t e^{i(\omega_{lj}-\omega)t}\frac{da_j}{dt}dt, \end{aligned} \tag{36}$$

and similarly for a_m. We assume that the separations of the resonance frequencies are large compared to the widths of allowed transitions. To the lowest order in the rotating-field amplitude, we may neglect the inte-

grals involving da_i/dt and da_j/dt in (36). We may also neglect the constant term, since on substitution of (36) and the corresponding equation for a_m into the first and last equations of (33), it will be multiplied by exponential factors which oscillate rapidly for ω in the neighborhood of (35). With these approximations we obtain

$$\begin{aligned} ida_i/dt&=\epsilon a_i+\gamma e^{-i\Omega t}a_j,\\ ida_j/dt&=\eta a_j+\delta e^{+i\Omega t}a_i, \end{aligned} \tag{37}$$

where

$$\Omega=2\omega-\omega_{ij}, \tag{38}$$

and

$$\begin{aligned} \epsilon&=\frac{A_{il}A_{li}}{\omega_{il}-\omega}+\frac{A_{im}A_{mi}}{\omega_{im}-\omega}, & \gamma&=\frac{A_{il}A_{lj}}{\omega_{jl}+\omega}+\frac{A_{im}A_{mj}}{\omega_{jm}+\omega},\\ \eta&=\frac{A_{jl}A_{lj}}{\omega_{jl}+\omega}+\frac{A_{jm}A_{mj}}{\omega_{jm}+\omega}, & \delta&=\frac{A_{jl}A_{li}}{\omega_{il}-\omega}+\frac{A_{jm}A_{mi}}{\omega_{im}-\omega}. \end{aligned} \tag{39}$$

The diagonal coefficients ϵ and η correspond to energy level shifts due to virtual emission followed by absorption, and the opposite order, respectively. The off-diagonal coefficients determine the peak intensity at low fields and the resonance width at higher fields. In the neighborhood of the resonance frequency (35) we can make the approximation $\delta\simeq\gamma$. In terms of

$$b_i=e^{i\epsilon t}a_i, \quad b_j=e^{i\eta t}a_j, \tag{40}$$

we then have

$$idb_i/dt=\delta e^{-i\Omega' t}b_j, \quad idb_j/dt=\delta e^{+i\Omega' t}b_i, \tag{41}$$

where

$$\Omega'=\Omega-\epsilon+\eta. \tag{42}$$

The solution of (41) which satisfies the initial condition (34) is

$$\begin{aligned} b_i(t)&=(p_+/d)e^{ip_-t}-(p_-/d)e^{ip_+t},\\ b_j(t)&=(p_+p_-/d\delta)e^{i\Omega' t}(e^{ip_+t}-e^{ip_-t}), \end{aligned} \tag{43}$$

where

$$p_\pm=-\tfrac{1}{2}\Omega'\pm\tfrac{1}{2}d, \quad d=(\Omega'^2+4\delta^2)^{\frac{1}{2}}. \tag{44}$$

This gives for the transition probability

$$P(i\to j)\simeq\frac{\delta^2}{d^2}4\sin^2(\tfrac{1}{2}dt), \tag{45}$$

or, if we recall the definitions of Ω, Ω', and d and put

$$\omega_1=\delta, \quad \omega_0=\tfrac{1}{2}(\omega_{ij}+\epsilon-n), \tag{46}$$

$$P(i\to j)\simeq\frac{\omega_1^2}{(\omega-\omega_0)^2+\omega_1^2}\sin^2[(\omega-\omega_0)^2+\omega_1^2]^{\frac{1}{2}}t. \tag{47}$$

Equation (47) extends the previous result (30) to higher radio-frequency fields, for the case $I=J=\frac{1}{2}$ and $n=2$. In the case of arbitrary I and J, the Schrödinger equation becomes

$$ida_i/dt=\textstyle\sum_l A_{il}e^{i(\omega_{il}\mp\omega)t}a_l \tag{48}$$

for $i=1, 2, \cdots, (2I+1)\times(2J+1)$ and where the $-$ or $+$ sign is to be taken according as $M_i=M_l+1$ or $M_i=M_l-1$, respectively. The summation can be restricted to states satisfying $M_l=M_i\pm1$ as otherwise A_{il} vanishes. For an n-quantum transition $i\to j$ where $M_i=M_j\pm n$ we obtain, integrating the preceding equations successively by parts and making the same approximations as before,

$$\begin{aligned} ida_i/dt&=\epsilon a_i+\gamma e^{-i\Omega t}a_j,\\ ida_j/dt&=\eta a_j+\delta e^{+i\Omega t}a_i, \end{aligned} \tag{49}$$

where

$$\Omega=\pm n\omega-\omega_{ij} \tag{50}$$

and

$$\begin{aligned} \epsilon&=\sum_{M_l=M_i-1}\frac{A_{li}^2}{\omega_{il}-\omega}+\sum_{M_l=M_i+1}\frac{A_{li}^2}{\omega_{il}+\omega},\\ \eta&=\sum_{M_l=M_j-1}\frac{A_{lj}^2}{\omega_{jl}-\omega}+\sum_{M_l=M_j+1}\frac{A_{lj}^2}{\omega_{jl}+\omega},\\ \gamma&=(-1)^{n-1}\sum_{l,m,\cdots,r}\\ &\quad\times\frac{A_{il}A_{lm}\cdots A_{rj}}{[\omega_{lj}\mp(n-1)\omega][\omega_{mj}\mp(n-2)\omega]\cdots(\omega_{rj}\mp\omega)},\\ \delta&=(-1)^{n-1}\sum_{l,m,\cdots,r}\\ &\quad\times\frac{A_{jr}\cdots A_{ml}A_{li}}{[\omega_{ri}\pm(n-1)\omega]\cdots(\omega_{mi}\pm2\omega)(\omega_{li}\pm\omega)}. \end{aligned} \tag{51}$$

Equations (49) are of the form (37) already considered, and we can again make the approximation $\gamma\simeq\delta$ in the neighborhood of resonance since the A_{ij} can be chosen symmetric and

$$\begin{aligned} \omega_{qj}\mp(n-p)\omega&\simeq\omega_{qj}-[(n-p)/n]\omega_{ij}\\ &\simeq\omega_{qi}\pm p\omega. \end{aligned} \tag{52}$$

We can thus immediately apply the previous formula (45), where d is defined as before [Eq. (44), with Ω' given by (42) and (50)]. Thus

$$P_{i\to j}\simeq\frac{\omega_1^2}{(\omega-\omega_0)^2+\omega_1^2}\sin^2\{\tfrac{1}{2}n[(\omega-\omega_0)^2+\omega_1^2]^{\frac{1}{2}}t\}, \tag{53}$$

where

$$\omega_1=2\delta/n, \quad \omega_0=\pm(1/n)(\omega_{ij}+\epsilon-n). \tag{54}$$

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