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Resonance Transitions Induced by Perturbations at Two or More Different Frequencies

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Resonance transition probabilities for a system in the presence of oscillatory perturbations at two or more different frequencies are discussed. It is shown that if resonance transitions are induced by a perturbation at one frequency, then the presence of the other perturbations at nonresonant frequencies alters the resonance frequency for the first perturbation. Theoretical expressions for the alteration of the resonance frequency are derived. Various applications of the derived formulas are discussed, including resonance experiments with more than one oscillatory field, molecular beam experiments in a nonuniform constant field, evaluation of "collision-narrowing" effects in nuclear paramagnetic resonance, etc. The effects of the extraneous oscillatory perturbations are shown to be especially important if their frequencies are close to Bohr frequencies for the perturbation.

I. INTRODUCTION

IN many cases, resonance transitions are studied in the presence of more than one oscillatory field. For example, in nuclear resonance experiments the transitions are often induced by a high harmonic of an oscillator at a low fundamental frequency. In such a case the other harmonics are often also present and the question arises as to the effects that the oscillatory magnetic fields of the other harmonics may have on the apparent resonance frequency. Likewise, in a molecular beam experiment, the transitions are induced by an applied oscillatory field while the molecules pass through a fixed field. If the fixed field is not completely uniform, the motion of the molecule through the varying field gives rise to an apparent oscillatory field at the molecule in addition to the one specifically applied.[1] As a still different example, if a molecule is subjected to many collisions, the magnetic field of say one nucleus at the position of the other fluctuates in time and one Fourier component of this fluctuating field will appear as an oscillating magnetic field; if an externally produced oscillating field is produced to induce a resonance transition, the transition then actually occurs in the presence of perturbations at more than one frequency.

One special case of the simultaneous presence of two perturbations has been discussed by Bloch and Siegert,[2] Stevenson,[3] and Winter[4]: that of a magnetic moment acted upon by two fields rotating at equal frequencies but with opposite directions of rotation. The more general results derived in the present paper will be shown to agree with those of Bloch and Siegert in the special case to which their result applies.

In the present paper, it will be shown that if resonance transitions are induced by a perturbation at one frequency, then the presence of the other perturbations at nonresonant frequencies will alter the resonance frequency for the first perturbation. Since most resonance experiments involve only single quantum transitions rather than the multiple quantum transitions that have occasionally been discussed,[4-10] the present discussion will be limited to single quantum transitions, i.e., the assumption will be made that one of the oscillatory perturbations is approximately at the resonance frequency of an allowed transition while the other perturbations are not at resonance frequencies.

The results reported here were first obtained in 1950 and have been privately circulated[5] and quoted in various publications.[1,5-7] The present report is the subsequent paper promised in one of these earlier publications.

II. MAGNETIC MOMENT IN TWO ROTATING FIELDS

A particularly easy case to discuss is that of a magnetic moment $\gamma\hbar\mathbf{I}$ acted upon by a fixed field H_0 about which as an axis two fields H_1 and H_2, perpendicular to H_0, rotate with angular velocities $-\omega$ and $-\omega_2$.

In the absence of H_2, the magnetic resonance frequency for ω would be equal to the Larmor frequency,

$$\omega_0 = \gamma H_0. \tag{1}$$

It now remains to see how the presence of H_2 rotating at frequency $-\omega_2$ affects the position of the resonance frequency for ω. This problem can easily be analyzed by the use of a rotating coordinate system.[11]

Consider the problem from the point of view of a coordinate system rotating with angular velocity $-\omega_2$. Then, as discussed by Rabi, Ramsey, and Schwinger,[11]

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[1] Kolsky, Phipps, Ramsey, and Silsbee, Phys. Rev. **81**, 106 (1951); **87**, 400 (1952).

[2] F. Bloch and A. Siegert, Phys. Rev. **57**, 522 (1940).

[3] A. J. Stevenson, Phys. Rev. **58**, 1061 (1940).

[4] N. Winter (private communication). Dr. Winter's calculations were made without his knowledge of the existence of the work reported in the present paper. Dr. Winter's results will be reported in *Comptes rendus hebdomadaires des séances de l'académie des sciences, Paris*.

[5] N. F. Ramsey (private communications and public lectures, 1950) (unpublished).

[6] H. Silsbee, Ph.D. thesis, Harvard University, 1950.

[7] N. F. Ramsey, *Molecular Beams* (Oxford University Press, Oxford, 1955).

[8] P. Kusch, Phys. Rev. **93**, 1022 (1954).

[9] Brossel, Cagnac, and Kastler, Comptes rend. **237**, 984 (1953).

[10] Besset, Horowitz, Messiah, and Winter, J. phys. radium **15**, 251 (1954).

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

on this rotating coordinate system the effective magnetic field H_{er} from H_0, H_2, and the rotation will have the magnitude

$$H_{er}=[(H_0-\omega_2/\gamma)^2+H_2^2]^{\frac{1}{2}}. \tag{2}$$

However, on this rotating coordinate system the apparent rotational frequency of H_1 will be $-(\omega-\omega_2)$. Hence, if the magnitude of $H_0-\omega_2/\gamma$ is much greater than either H_2 or H_1, the resonance frequency will be at

$$\omega-\omega_2=\gamma H_{er}=\gamma[(H_0-\omega_2/\gamma)^2+H_2^2]^{\frac{1}{2}} \tag{3}$$

or for $\omega_0-\omega\gg\gamma H_2$

$$\begin{aligned}\omega&=\omega_0+(\omega_0-\omega_2)\{[1+(\gamma H_2)^2/(\omega_0-\omega_2)^2]^{\frac{1}{2}}-1\}\\&=\omega_0+(\gamma H_2)^2/2(\omega_0-\omega_2).\end{aligned} \tag{4}$$

Consequently it is apparent that the presence of the perturbation of amplitude γH_2 shifts the resonance away from the Larmor frequency ω_0.

The special case considered by Bloch and Siegert[2] and by Stevenson[4] was that for which $\omega_2=-\omega_0$ and $H_2=H_1$, in which case the above reduces to

$$\omega=\omega_0+(\gamma H_1)^2/4\omega_0, \tag{5}$$

which is just the result of Bloch and Siegert. It is also apparent from Eq. (4) that the selection of $\omega_2=-\omega_0$ is one for which the extra oscillatory field is particularly ineffective, in agreement with the conclusion of Bloch and Siegert that their term was ordinarily small. On the other hand, if $\omega_2\approx\omega_0$ the shift of the resonance frequency can become significant in some cases.

III. GENERAL CASE FOR TWO EIGENSTATES

The discussion in the preceeding section was limited to a magnetic moment in a magnetic field. In the present section the result will be generalized to transitions involving any two eigenstates p and q. However, the discussion in this section will be limited to the case of only two levels being involved. In the next section, the effects of the presence of more than two eigenstates will be considered.

The calculation can be performed in several different ways. One is to consider directly a case for which the result is relevant, namely the case of the separated oscillatory field method of molecular beam resonance described in a previous paper.[12] The calculation is thereby simplified since the two oscillatory fields can be considered to be applied at separate times, yet the results for the shift in resonance frequency is applicable equally to the case when the two perturbing frequencies are applied simultaneously since for levels of fixed separation the resonance frequency in the separated oscillatory field method is the same[12] as in the method with a single oscillatory field. Consideration of the separated oscillatory field problem in this section has the further advantage that the results show the consistency of the conclusions of the present section with those of the preceding section for which the perturbations are simultaneously applied.

The problem then is that of an atom or molecule with energy eigenvalues W_p and W_q which is first perturbed for a time τ by a perturbation of the form

$$V_{pq}=\hbar be^{i\omega t},\quad V_{qp}=\hbar be^{-i\omega t},\quad V_{pp}=V_{qq}=0, \tag{6}$$

where the notation here and subsequently is that of reference 12. Then the atom enters a region where (unlike the usual case[12]) it is subjected to a perturbation

$$V_{pq}=\hbar b_2e^{i(\omega_2+\phi)},\quad V_{qp}=\hbar b_2e^{-i(\omega_2+\phi)},\quad V_{pp}=V_{qq}=0, \tag{7}$$

for the time T. Finally the atom is again perturbed as in Eq. (6) for a time τ. Without loss of generality in the calculation of the shift of resonance frequency, τ (but not $b\tau$) can be taken as very small and $|2b|\gg|\omega_0-\omega$. For simplicity, it will be assumed that $|\omega_0-\omega_2|\gg 2b_2$ though some generality is lost by this assumption. At time $t=0$ the system will be assumed to be in the state $C_q=0$, $C_p=1$.

For these assumptions, $\sin\Theta=1$, $\cos\Theta=0$, $\sin\Theta_2=0$, $\cos\Theta_2=1$, and $a=2b$, so the equations analogous to Eqs. (8a–f) of reference 12 become the following:

$$\begin{aligned}C_p(\tau)&=\cos b\tau,\\C_q(\tau)&=-i\sin b\tau,\\C_p(\tau+T)&=[i\sin\tfrac{1}{2}a_2T+\cos\tfrac{1}{2}a_2T]C_p(\tau)\\&\qquad\times\exp\{i[\tfrac{1}{2}\omega_2-(W_p+W_q)/2\hbar]T\}\\&=C_p(\tau)\exp\{i[\tfrac{1}{2}a_2+\tfrac{1}{2}\omega_2\\&\qquad-(W_p+W_q)/2\hbar]T\},\\C_q(\tau+T)&=[-i\sin\tfrac{1}{2}a_2T+\cos\tfrac{1}{2}a_2T]C_q(\tau)\\&\qquad\times\exp\{i[-\tfrac{1}{2}\omega_2-(W_p+W_q)/2\hbar]T\}\\&=C_q(\tau)\exp\{i[-\tfrac{1}{2}a_2-\tfrac{1}{2}\omega_2\\&\qquad-(W_p+W_q)/2\hbar]T\},\\C_p(2\tau+T)&=\cos b\tau C_p(\tau+T)\\&\qquad-i\sin b\tau\exp(i\omega T)C_q(\tau+T),\\C_q(2\tau+T)&=-i\sin b\tau\exp(-i\omega T)C_p(\tau+T)\\&\qquad+\cos b\tau C_q(\tau+T).\end{aligned} \tag{8}$$

The nonappearence of ϕ in the above equations can be seen from the equivalence of ϕ to ωt_1 in reference 12 and from the fact that ωt_1 terms do not appear in Eq. (4) of reference 12 with the above assumption of $\sin\Theta_2=0$. Therefore,

$$\begin{aligned}C_q(2\tau+T)&=-i\sin b\tau\cos b\tau\exp\{i[\tfrac{1}{2}a_2+\tfrac{1}{2}\omega_2\\&\qquad-\omega-(W_p+W_q)/2\hbar]T\}-i\sin b\tau\cos b\tau\\&\qquad\times\exp\{i[-\tfrac{1}{2}a_2-\tfrac{1}{2}\omega_2-(W_p+W_q)/2\hbar]T\}\\&=-2i\sin b\tau\cos b\tau\cos\tfrac{1}{2}\lambda_2T\\&\qquad\times\exp\{-[\omega+(W_p+W_q)/\hbar]T/2\},\end{aligned} \tag{9}$$

where

$$\lambda_2=a_2+\omega_2-\omega. \tag{10}$$

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[12] N. F. Ramsey, Phys. Rev. 78, 695 (1950).

Therefore, the transition probability is

$$P_{p,q}=4\sin^2 b\tau\cos^2 b\tau\cos^2(\tfrac{1}{2}\lambda_2 T)$$
$$=\sin^2(2b\tau)\cos^2(\tfrac{1}{2}\lambda_2 T). \quad (11)$$

It is apparent from Eq. (11) that the transition probability of Eq. (11) will be a maximum for $\lambda_2=0$. A discussion of the effect of a molecular beam velocity distribution on a function of this form is given in reference 12, Eq. (14), ff. The resonance frequency ω for maximum transition probability, from Eq. (10) above and from Eq. (5) of reference 12, then is

$$\begin{aligned}\omega&=a_2+\omega_2=[(\omega_0-\omega_2)^2+(2b_2)^2]^{\frac{1}{2}}+\omega_2\\&=\omega_0+(\omega_0-\omega_2)\{[1+(2b_2)^2/(\omega_0-\omega_2)^2]^{\frac{1}{2}}-1\}\\&=\omega_0+(2b_2)^2/2(\omega_0-\omega_2).\end{aligned} \quad (12)$$

In the special case of magnetic moments,[12] $2b_2=\gamma H_2$ and the above reduces to Eq. (4), which was derived for magnetic moments only but with the two perturbations applied simultaneously instead of successively as in the separated oscillatory field method.

If $|\omega_0|\gg|\omega_2|$, Eq. (12) can also be written as

$$\omega=\omega_0+(2b_2)^2/2\omega_0+(2b_2)^2\omega_2/2\omega_0^2+(2b_2)^2\omega_2^2/2\omega_0^3. \quad (12a)$$

On the other hand, if $|\omega_0|\ll|\omega_2|$,

$$\omega=\omega_0-(2b_2)^2/2\omega_2+(2b_2)^2\omega_0/2\omega_2^2. \quad (12b)$$

From these equations it is apparent, when oscillatory instead of rotating fields are used and when ω_2 is far from ω_0, that the first terms dependent on ω_2 are mutually cancelled by the positive and negative rotating components into which the oscillatory field can be resolved.[2] Nearer the resonance frequency, however, this partial cancellation is much less complete.

IV. MORE THAN TWO EIGENSTATES

Now consider the case of four levels p, q, r, and s with the primary resonance observed at frequency ω being that for transitions from p to q while there are also present nonresonant perturbations with the matrix elements

$$\begin{aligned}V_{pr}&=\hbar b_r e^{i(\omega_r t+\phi_r)},\\V_{sq}&=\hbar b_s e^{i(\omega_s t+\phi_s)},\end{aligned} \quad (13)$$

between the levels p and r and between the levels s and q. ω_r and ω_s could of course be equal and for a two-frequency problem they would have to be, with the two frequencies being ω and $\omega_1=\omega_r=\omega_s$.

With the same approximations as in the preceding section, this problem can be solved as in that section; in fact the same Eqs. (8) apply except that the middle two equations are replaced by

$$\begin{aligned}C_p(\tau+T)&=C_p(\tau)\exp\{i[\tfrac{1}{2}a_r+\tfrac{1}{2}\omega_r-(W_p+W_r)/2\hbar]T\},\\C_q(\tau+T)&=C_q(\tau)\exp\{i[-\tfrac{1}{2}a_s-\tfrac{1}{2}\omega_s-(W_s+W_q)/2\hbar]T\}.\end{aligned} \quad (14)$$

Consequently, Eq. (9) is replaced by

$$\begin{aligned}C_q(2\tau+T)&=-i\sin b\tau\cos b\tau\exp\{i[\tfrac{1}{2}a_r+\tfrac{1}{2}\omega_r-\omega-(W_p+W_r)/2\hbar]T\}-i\sin b\tau\cos b\tau\\&\quad\times\exp\{i[-\tfrac{1}{2}a_s-\tfrac{1}{2}\omega_s-(W_s+W_q)/2\hbar]T\}\\&=2i\sin b\tau\cos b\tau\cos\tfrac{1}{2}\lambda_{rs}T\\&\quad\times\exp\{-i[\omega+\tfrac{1}{2}(a_s-a_r)+\tfrac{1}{2}(\omega_s-\omega_r)+(W_p+W_s+W_r+W_q)/2\hbar]T/2\},\end{aligned} \quad (15)$$

where

$$\lambda_{rs}=\tfrac{1}{2}(a_r+a_s)+\tfrac{1}{2}(\omega_r+\omega_s)-\omega-(W_p-W_q+W_r-W_s)/2\hbar. \quad (16)$$

The transition probability $P_{p,q}$ is then given by

$$P_{p,q}=\sin^2(2b\tau)\cdot\cos^2(\tfrac{1}{2}\lambda_{rs}T). \quad (17)$$

Just as in the previous section then, the resonance frequency is

$$\begin{aligned}\omega&=\tfrac{1}{2}[a_r+\omega_r-(W_p+W_r)/\hbar]+\tfrac{1}{2}[a_s+\omega_s-(W_q+W_s)/\hbar]\\&=(W_q-W_p)/\hbar+\tfrac{1}{2}\{(W_r-W_p)/\hbar-\omega_r\}\\&\quad\times\{[1+(2b_r)^2/((W_r-W_p)/\hbar-\omega_r)^2]^{\frac{1}{2}}-1\}\\&\quad+\tfrac{1}{2}\{(W_q-W_s)/\hbar-\omega_s\}\\&\quad\quad\times\{[1+(2b_s)^2/((W_q-W_s)/\hbar-\omega_s)^2]^{\frac{1}{2}}-1\}\\&=\omega_0+(2b_r)^2/4[(W_r-W_p)/\hbar-\omega_r]\\&\quad+(2b_s)^2/4[(W_q-W_s)/\hbar-\omega_s].\end{aligned} \quad (18)$$

It is of interest to note that Eq. (18) equals Eq. (12) in the case that $W_p=W_s$, $W_q=W_r$, and $\omega_2=\omega_r=\omega_s$.

Equations (12) and (18) may be combined to provide the net resonance frequency in the general case of the presence of several nonresonant perturbations to different eigenstates. Let ω be the resonance transition frequency between the two levels p and q. Let the level p be perturbed by a matrix element to the state r at frequency ω_i such as

$${}_iV_{pr}=\hbar\;{}_ib_{pr}\,e^{i(\omega_i t+{}_i\phi_{pr})}, \quad (19)$$

while q is perturbed by

$${}_iV_{rq}=\hbar\;{}_ib_{rq}\,e^{i(\omega_i t+{}_i\phi_{rq})}. \quad (20)$$

Then, from Eqs. (12) and (18),

$$\begin{aligned}\omega-\omega_0&=\textstyle\sum_i(2\;{}_ib_{pq})^2/2(\omega_0-\omega_i)\\&\quad+\textstyle\sum_i\sum_r{}''(2\;{}_ib_{pr})^2/4[(W_r-W_p)/\hbar-\omega_i]\\&\quad+\textstyle\sum_i\sum_r{}''(2\;{}_ib_{rq})^2/4[(W_q-W_r)/\hbar-\omega_i],\end{aligned} \quad (21)$$

where the symbol $\sum_r{}''$ indicates that the summation does not include $r=p$ or q. Expansions similar to Eqs. (12a) and (12b) can also be made for Eq. (21) when desired.

V. APPLICATIONS

The relations derived above are applicable to a number of different present and contemplated experiments. In molecular-beam magnetic-resonance experiments, the oscillatory magnetic fields are often produced as high harmonics of a much lower frequency fundamental. In such experiments undesired harmonics are often present along with the fundamental. Equation (21) can then be used to estimate the distortion caused by the unwanted oscillations. As shown by the above formulas, these effects can be serious if the unwanted frequency is at all close to a Bohr frequency of the system. It should be noted in the application of Eqs. (12) and (21) that for perturbation frequencies far from resonance, the positive and negative rotating components partially cancel each other as discussed in conjunction with Eqs. (12a) and (12b); however, this is not true for the components closer to the resonance condition.

The above formulas can also be applied to the case of a molecular beam resonance experiment for which the constant magnetic field is not exactly uniform and unidirectional. By field measurements, the fluctuating magnetic field components perpendicular to $\mathbf{H}_0$ can be estimated as well as the characteristic cyclic distances d_2 for the variation of the direction of these components. If v is the velocity of the molecule, then the characteristic frequencies for the fluctuating components are v/d_2. Equations (4), (12), or (21) can then be used to evaluate the displacement of the resonance frequency. For the molecular beam case, in the averaging of such relations as Eq. (11) over the molecular beam velocity to obtain the experimental line shape, it should be noted that ω_2 and hence λ_2 are velocity-dependent. In the frequently occurring case that expansions such as Eq. (12a) are applicable, the $\cos^2(\frac{1}{2}\lambda_2 T)$ of Eq. (11) becomes for a particular velocity v and for $T=L/v$,

$$\begin{aligned}\cos^2(\tfrac{1}{2}\lambda_2 T) &= \cos^2\{\tfrac{1}{2}[\omega_0-\omega+(2b_2)^2/2\omega_0+(2b_2)^2 v/2\omega_0{}^2 d_2 \\ &\qquad +(2b_2)^2 v^2/2\omega_0{}^2 d_2{}^2+\cdots\} \\ &= \cos^2\{\tfrac{1}{2}[\omega_0+(2b_2)^2/2\omega_0-\omega]L/v \\ &\qquad +(2b_2)^2 L/2\omega_0{}^2 d_2 \\ &\qquad +(2b_2)^2 Lv/2\omega_0{}^2 d_2{}^2+\cdots\}. \qquad (22)\end{aligned}$$

From this, it is apparent that the first term in Eq. (12a) that is dependent on the frequency ω_2 becomes a velocity-independent phase shift $(2b_2)^2 L/2\omega_0{}^2 d_2$ in Eq. (22). The effects of such velocity-independent phase shifts on the average resonance line shape have been discussed by Ramsey and Silsbee.[13]

The above formulas may also be applied to a discussion of "collision narrowing" in nuclear paramagnetic resonance.[14] In a free molecule, the nuclear magnetic. resonance frequency depends on the orientation state of the molecule, due to the various magnetic interactions within the molecule. Furthermore, because of the even-order perturbations of these interactions, the average frequency of the resonance lines in the vicinity of the nuclear Larmor frequency is not equal to the Larmor frequency in the average magnetic field at the nucleus (the external magnetic field corrected for the magnetic shielding of the molecule). The average nuclear resonance frequency for the free molecule is in fact closer to the Larmor frequency in the average magnitude of the field at the nucleus rather than in the magnitude of the average field (these differ since the internal fields are not always parallel to the external field). If the molecule on the other hand is subjected to many collisions which change the molecular orientation, the separate resonance lines are averaged to a single one by the process[14] of "collision narrowing." However, it is not immediately obvious that the collision-narrowed line is at the Larmor frequency of the nucleus in the magnitude of the average field at the nucleus rather than in the average magnitude of the field; indeed, the latter corresponds more nearly to the average of the resonance frequencies for the free molecule.

The discussion of the previous sections can be applied to show that it is the magnitude of the average field rather than the average of the magnitudes that is relevant when the molecule is subject to frequent collisions. Although the collisions cause a randomly fluctuating field, the field can be Fourier-analyzed into components at angular frequency ω_i, where ω_i is of the order of the collision frequency or of the inverse of the correlation time[15] τ_c. Then the nondiagonal matrix elements can be taken to be of the form of Eqs. (19) and (20), and Eq. (21) applies. However, in most cases of collision narrowing,

$$\omega_i \gg (W_r - W_p)/\hbar \gg 2\; {}_i b_{pr} \approx \gamma H_\sigma,$$

where H_σ is a typical instantaneous component of the molecular magnetic field perpendicular to the direction of the external field H_0. Consequently, in this limit, $\omega=\omega_0$. On the other hand, in the absence of collisions a typical frequency ω_i would be the Larmor precession frequency of the molecular rotational magnetic moment; this is not necessarily larger than $(W_r-W_p)/\hbar$ so the terms on the right side of Eq. (21) become important and $\omega\neq\omega_0$.

Finally, it should be added that there are resonance experiments in which several different oscillatory frequencies are deliberately, instead of accidentally, introduced. In such cases, the formulas of the preceding sections may be directly applied to estimate the shifts of the resonance frequencies. In some precision experiments, these shifts can be important.

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[15] N. F. Ramsey, Phys. Rev. **58**, 226 (1940).