ACKNOWLEDGMENT

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[1]A. J. Coleman, Rev. Mod. Phys. 35, 668 (1963); C. Garrod and J. K. Percus, J. Math. Phys. 5, 1756 (1964).

[2]F. Bopp, Z. Physik 156, 348 (1959).

[3]T. B. Grimley and F. D. Peat, Proc. Phys. Soc. (London) 86, 249 (1965).

[4]L. J. Kijewski and J. K. Percus, Phys. Rev. A 2, 1659 (1970).

[5]A. J. Coleman, Ref. 1.

[6]Tighter restrictions on the eigenvalues apply owing to the form of some of the equality restrictions; e.g., Eq. (2.25) requires the sum of the eigenvalues of the B matrix to be not greater than $\frac{1}{18}$, and $A_{11} \leq \frac{1}{6}$. For more general discussions of linear equalities arising from the N representability of the 2 matrix, see F. Weinhold and E. B. Wilson, Jr., J. Chem. Phys. 47, 2298 (1967); H. Kummer, J. Math Phys. 8, 2063 (1967); H. W. Kuhn, Proc. Symp. Appl. Math. 10, 141 (1960); M. L. Yoseloff and H. W. Kuhn, J. Math Phys. 10, 703 (1969); E. R. Davidson, *ibid.* 10, 725 (1969).

[7]P. M. Morse, L. A. Young, and E. S. Haurwitz, Phys. Rev. 48, 948 (1935).

[8]See L. J. Kijewski and J. K. Percus, Phys. Rev. 179, 45 (1969).

[9]L. J. Kijewski, J. K. Percus, I. H. Pratt, and J. P. Tranchina, Phys. Rev. A 2, 1659 (1970).

[10]L. J. Kijewski and J. K. Percus, Intern. J. Quantum Chem. 5, 67 (1971).

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Vanishing of Dipole Matrix Elements at Level Crossings*

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The vanishing of certain coupling matrix elements at level crossings is shown to follow from angular momentum commutation relations. A magnetic dipole transition having $\Delta M = \pm 1$, induced near a crossing of the levels in a nonzero magnetic field, is found to have a dipole matrix element comparable to or smaller than the quotient of the level separation and the field. This result also applies in the analogous electric field electric dipole case.

I. INTRODUCTION

In the study of atomic systems by radio-frequency (rf) spectroscopy, transitions between unequally populated states are induced by oscillatory electric or magnetic fields. Experiments commonly involve transitions between Zeeman levels at radio frequencies or between fine-structure or hyperfine levels at microwave frequencies. In either case the order of magnitude of the coupling matrix element can be estimated by a dimensional argument if the appropriate selection rules are satisfied. Magnetic dipole matrix elements, for instance, tend to be of the order of the Bohr magneton μ_B. However, Lamb[1] has given a physical argument that magnetic dipole matrix elements may vanish at fine-structure level crossings. Casual estimates of matrix elements can therefore be seriously in error for experiments at low frequencies and high fields.

The rf Hamiltonian can be shown to have small matrix elements in two cases of transitions having $\Delta M = \pm 1$: (i) a magnetic dipole transition at low frequency, near a crossing of the levels in a nonzero static magnetic field; and (ii) an electric dipole transition near a crossing in an electric field. In the present discussion, angular momentum commutation relations are considered for a general system in an external field. The coupling matrix element is then expressed in a form displaying its variation with the level separation in the vicinity of a crossing. The magnetic dipole problem will be discussed first, because of its particular relevance to rf experiments.

II. MAGNETIC DIPOLE MATRIX ELEMENTS

A Hamiltonian of the form

$$\mathcal{H} = \mathcal{H}_0 - \mu_z H \tag{1}$$

describes an atom in a uniform static magnetic field $\vec{H}$ directed along the z axis. The term $\mathcal{H}_0$ includes the fine-structure and hyperfine interactions, and $\vec{\mu}$ denotes the magnetic dipole operator. An oscillatory magnetic field $\vec{H}_{rf}$ along the x axis can induce π transitions between a pair of states $|1\rangle$, $|2\rangle$, through the interaction

$$\mathcal{H}' = -\mu_x H_{rf} \ , \tag{2}$$

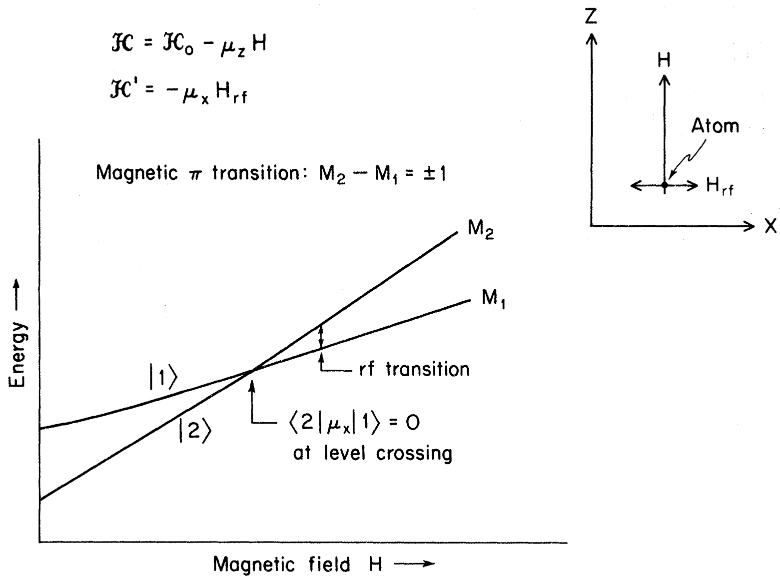

FIG. 1. Field configuration and level scheme for a transverse-field rf-resonance experiment in the vicinity of a level crossing.

as indicated in Fig. 1. In the following analysis, attention will be focused on the dipole coupling matrix element $\langle 2|\mu_x|1\rangle$ and its behavior near a nonzero-field crossing of the levels.

The total angular momentum

$$\vec{J} = \sum_n \vec{j}^n \tag{3}$$

is the sum of orbital and spin contributions due to all the particles of the system, where the symbol $\vec{j}^n$ denotes either an orbital or a spin angular momentum for a constituent particle. The corresponding magnetic moment is given by

$$\vec{\mu} = \sum_k \gamma_k \vec{j}^k \ , \tag{4}$$

where γ_k is the gyromagnetic ratio associated with $\vec{j}^k$. Application of the commutation rule for angular momenta relates μ_x to the commutator of J_y and μ_z:

$$\begin{aligned}\mu_x &= \sum_k \gamma_k j_x^k \\ &= \sum_{k,n} \gamma_n \frac{[j_y^k, j_z^n]}{i\hbar} \\ &= \frac{[J_y, \mu_z]}{i\hbar} \ .\end{aligned} \tag{5}$$

Since $\vec{J}$ commutes with $\mathcal{H}_0$, Eqs. (1) and (5) imply

$$\mu_x = [\mathcal{H}, J_y]/i\hbar H \ . \tag{6}$$

A useful expression follows for the matrix elements of μ_x between eigenstates of $\mathcal{H}$:

$$\begin{aligned}\langle 2|\mu_x|1\rangle &= \frac{\langle 2|[\mathcal{H}, J_y]|1\rangle}{i\hbar H} \\ &= \frac{E_2 - E_1}{H} \frac{\langle 2|J_y|1\rangle}{i\hbar} \ ,\end{aligned} \tag{7}$$

where state $|i\rangle$ has energy E_i.

From Eq. (7) it is apparent that $\langle 2|\mathcal{H}'|1\rangle$ passes through zero at a nonzero-field level crossing, where $E_1 = E_2$. Near the zero-field crossing of adjacent Zeeman levels, the energy difference $E_2 - E_1$ is proportional to H. The right-hand side of Eq. (7) thus remains finite for Zeeman transitions in the zero-field region, as it does for other allowed transitions, which have $\langle 2|J_y|1\rangle$ proportional to H at low fields. At nonzero values of H, an approximate upper bound for the dipole matrix element is given by the relation

$$|\langle 2|\mu_x|1\rangle| \lesssim |E_2 - E_1|/H \ , \tag{8}$$

where it is assumed that the second factor in Eq. (7) is of order unity or smaller. This limitation becomes significant near level crossings and in other situations where the transitions are of low frequency. Figure 2 illustrates the characteristic variation of $\langle 2|\mu_x|1\rangle$ with magnetic field for the $\Delta M = 1$ crossing in a ^2P system.

The vanishing of the μ_x matrix element at a level crossing can be interpreted in the context of a small static transverse-field perturbation H_x. This is the approach taken in the comments by Lamb.[1] A nonvanishing matrix element would imply such nonphysical results as first-order level shifts and anticrossing of the levels.

III. TORQUES AND GENERAL FIELDS

The preceding remarks can be extended to the general case of arbitrary external electric and magnetic fields $\vec{\mathcal{E}}, \vec{H}$, and the inclusion in $\mathcal{H}$ of multipole terms of all orders:

$$\mathcal{H} = \mathcal{H}_0 - \vec{d} \cdot \vec{\mathcal{E}} - \vec{\mu} \cdot \vec{H} + \text{quadrupole terms} + \cdots \ , \tag{9}$$

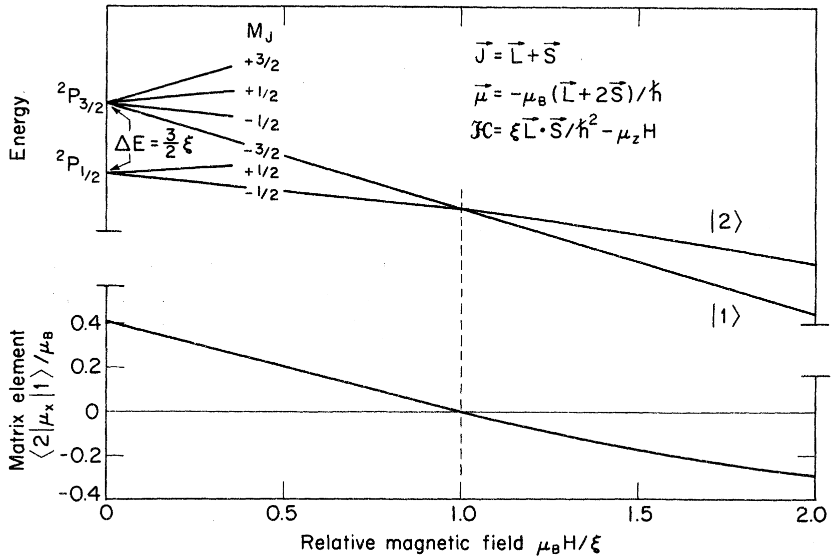

FIG. 2. Magnetic field dependence of ^2P energy levels and of the coupling matrix element for a transition having $\Delta M_J = 1$. The matrix element passes through zero where the levels cross.

where $\vec{d}$ is the total electric dipole moment.[2] The torque operator, defined by

$$\vec{\tau} = i[\mathcal{H}, \vec{J}]/\hbar \quad , \tag{10}$$

has vanishing matrix elements between states of equal total energy. When the commutator is expanded, operator analogs of the classical torque terms are obtained:

$$\vec{\tau} = \vec{d} \times \vec{\mathcal{E}} + \vec{\mu} \times \vec{H} + \cdots \quad . \tag{11}$$

Up to this point the discussion has emphasized the important special case $\vec{\tau} = \vec{\mu} \times \vec{H}$. If only an electric field $\vec{\mathcal{E}}$ is present, interacting with a dipole moment $\vec{d}$, the matrix elements of $\vec{d}$ are seen to satisfy the condition

$$\langle 2|\vec{d}|1\rangle \times \vec{\mathcal{E}} = i(E_2 - E_1)\langle 2|\vec{J}|1\rangle/\hbar \quad , \tag{12}$$

and consequently an upper bound analogous to that of Eq. (8) can be estimated for the components of $\langle 2|\vec{d}|1\rangle$ perpendicular to $\vec{\mathcal{E}}$:

$$|\langle 2|d_\perp|1\rangle| \lesssim |E_2 - E_1|/\mathcal{E} \quad . \tag{13}$$

Accordingly, small electric dipole matrix elements are to be expected in the case of low-frequency transitions induced between Stark-shifted levels of opposite parity.

This treatment can readily be applied to matrix elements arising from other multipole terms, and to combinations of terms in Eq. (11).

IV. CONCLUSIONS

In rf experiments at high magnetic fields, where Eq. (8) applies, the matrix element of μ_x may be much smaller than the Bohr magneton. For example, it is three orders of magnitude smaller than μ_B if the transition frequency is 1 MHz at a field of 1 kG. Under these circumstances the rf power requirement varies roughly as the inverse square of the level separation. At 1 MHz the minimum power can be expected to be 10^6 times that required at microwave frequencies (where a high-Q resonator permits further reduction of the oscillator power). A corresponding conclusion follows from Eq. (13) for the electric field case. It is evident that intense rf fields are necessary if coupling of the states is to be achieved near a nonzero-field crossing.

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[1]W. E. Lamb, Jr., Phys. Rev. 105, 559 (1957), especially pp. 568, 569.

[2]Techniques for determining eigenvalues due to double perturbations are discussed by W. Lichten [Phys. Rev. A 3, 594 (1971)].