Theory of Resonance Frequency Shift due to Radiation Field*

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A formalism is developed to calculate radiative processes, and applied to the shift of resonance frequency due to the radiation field itself. The zeroth approximation gives the Bohr resonance condition, while the next approximation gives a shift proportional to the photon density. The first-order shift is made of two terms: electric and magnetic. They can be interpreted as second-order Stark effect and Zeeman effect due to the oscillating field, respectively. A comparison with experimental data on the Cs atom is made. A good agreement is obtained by choosing the value of parameters suitably. These values of parameters can be checked by a future experiment.

INTRODUCTION

IN order to explain hydrogen spectral lines, Bohr[1] postulated that the absorption or emission of radiation field energy by an atom can take place when the frequency of the radiation field is equal to that of the atom which is given by the energy difference between atomic stationary states divided by the Plank constant h. This postulate was so successful that this is one of the few basic assumptions on which the entire quantum mechanics has been developed.

Each spectral line, however, has a shape, or is characterized by the width and the shift of the center frequency. Such spectral line shape is often due to interatomic interactions. When the interactions between atoms are negligible, a width of a spectral line still exists and is called its natural linewidth. A shift must also exist even when interatomic interactions are negligible. Such a shift of spectral line, which may be called the natural line shift, was first pointed out by Bloch and Seigert[2] with respect to the nuclear magnetic resonance. They showed theoretically that if one uses a linearly polarized electromagnetic wave to observe a magnetic resonance, a shift is expected compared to the case when one uses a circular polarized wave. Bloch and Siegert discussed the simplest case of spin one-half, while Salwen[3] discussed the same effect in more general cases to explain the experimental result of Heberle, Reich, and Kusch.[4]

Recently, Beehler, Snider, and Mockler[5] observed the center frequency of Cs 9-kMc/sec lines and found that it shifts when the input power of the radiation is increased. The present paper develops a general theory of the natural line shift to explain Beeler, Snider, and Mockler's result. The theory includes the Bloch-Siegert effect as a contribution, but gives a completely general formula.

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[1] N. Bohr, Phil. Mag. **26**, 1 (1913).

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

[3] H. Salwen, Phys. Rev. **101**, 623 (1956).

[4] J. Heberle, H. Reich and P. Kusch, Phys. Rev. **101**, 612 (1956).

[5] R. E. Beehler, C. S. Snider, and R. C. Mockler (private communication).

HAMILTONIAN

The Hamiltonian of our system is made of three parts, namely, that of the radiation field, that of an atom in a vacuum, and that of the interaction between them:

$$H=H_r+H_a+H_i. \tag{1}$$

The first term H_r, which is the Hamiltonian of the radiation field, can be given by the vector potential

$$\mathbf{A}(\mathbf{r},t)=\sum_{\lambda}^{2}\sum_{k}\mathbf{e}_\lambda[a_k\exp(-i\omega_k t) -a_k^*\exp(i\omega_k t)]G_k(\mathbf{r}), \tag{2}$$

where $G_k(\mathbf{r})$ is the amplitude of the kth mode of the field normalized with respect to the volume of the cavity V as

$$\int|G_k(\mathbf{r})|^2dV=V. \tag{3}$$

Note that if the cavity is infinitely large, $G_k(\mathbf{r})$ can be $\exp(i\mathbf{k}\cdot\mathbf{r})$ as given in any text books of quantum electrodynamics,[6] but for a finite cavity $G_k(\mathbf{r})$ should be real and different from such expression. $\mathbf{e}_\lambda$ is the polarization unit vector, ω_k is the frequency of the kth mode, and a_k, a_k^* are familiar annihilation and creation operators defined as

$$(n_k|a_k|n_k+1)=(n_k+1|a_k^*|n_k) =[\hbar(n_k+1)/2\omega_k\epsilon_0 V], \tag{4}$$

where n_k is the photon number of the kth mode and ϵ_0 is the capacitivity of the vacuum.

The eigenvalues of H_a, the Hamiltonian of the atom in vacuum, are very difficult to calculate but can be measured in spectroscopic experiments using Bohr's postulate.

The interaction between the field and the atom is

$$H_i=-\sum_i[(e_i/\mu_i)\mathbf{P}_i\cdot\mathbf{A}_i-(e_i^2/2\mu_i)\mathbf{A}_i^2 +(e_i/\mu_i)\mathbf{s}_i\cdot(\nabla\times\mathbf{A}_i)], \tag{5}$$

where e_i, μ_i, $\mathbf{s}_i$, and $\mathbf{P}_i$ are the charge, mass, spin, and momentum of the ith particle of the atom, and $\mathbf{A}_i$ is

[6] For example, W. Heitler, *The Quantum Theory of Radiation* (Oxford University Press, New York, 1954).

the vector potential at the position of the ith particle. Since we are interested in modes with wavelength very much larger than the atomic dimension, we can approximate (5) as

$$H_i=(e/\mu)\mathbf{P}\cdot\mathbf{A}_0-(Ze^2/2\mu)\mathbf{A}_0^2 -i(e/2\mu)(\mathbf{L}+2\mathbf{S})\cdot(\nabla\times\mathbf{A})_0, \quad (6)$$

where e and μ are charge and mass of the electron, Z is the total number of electrons, $\mathbf{P}$, $\mathbf{L}$, and $\mathbf{S}$ are total linear momentum, total orbital angular momentum, and total spin angular momentum of electrons, respectively. Subscript 0 means to take values at the position of the atom. It was shown by Power and Zienau[7] that in our case the first two terms in (6) can be replaced by

$$\sum_k i\omega_k \mathbf{e}_\lambda\cdot\mathbf{M}_e(a_k-a_k^*)G_{k0}, \quad (7)$$

where $\mathbf{M}_e$ is the dipole moment of the atom.

In a representation in which both H_r and H_a are diagonal, we have

$$\begin{aligned}(n_k a|H_r|n_k a)&=n_k\hbar\omega_k,\\ (n_k a|H_a|n_k a)&=W_a,\end{aligned} \quad (8)$$

where W_a is the energy of the atom in its ath state. Nondiagonal matrix elements are:

$$(n_k a|H_i|n_k+1b)=-i(e/2\mu)(\mathbf{e}_\lambda\times V G_{k0}) \cdot(a|\mathbf{L}+2\mathbf{S}|b)[\hbar(n_k+1)/2\omega_k\epsilon_0 V]^{1/2}, \quad (9)$$

$$(n_k|H_i|n_k+1c) =i\omega_k G_{k0}(a|\mathbf{e}_\lambda\cdot\mathbf{M}_e|c)[\hbar(n_k+1)/2\omega_k\epsilon_0 V]^{1/2}. \quad (10)$$

Atomic states a and b can be the same, but state c is different from them.

TIME DEVELOPMENT OPERATOR

The Schrödinger equation

$$i\hbar\dot{\psi}=H\psi \quad (11)$$

is formally solved as

$$\psi(t)=\exp(-iHt/\hbar)\psi(0), \quad (12)$$

where $\exp(-iHt/\hbar)$ is called the time development operator. The transition probability for $i\to f$ can be defined as

$$S(i\to f)=\lim_{t\to\infty}|(f|\exp(-iHt/\hbar)|i)|^2/t. \quad (13)$$

We are interested in the emission of a photon where

$$|i)=|n\alpha) \quad (14)$$

$$|f)=|n+1\beta) \quad (15)$$

in the same notation as in the previous section.

As a result of the interaction term H_i, wave functions (14) and (15) are not eigenfunctions of the Hamiltonian H. If H_i can be assumed to be small, however, the perturbation method can be used to obtain eigenfunctions. Thus the first approximation is obtained as

$$|n\alpha)=\varphi_n+(n+1\beta|H_i|n\alpha) \times(E_{n+1}-E_n)^{-1}\varphi_{n+1}+\textstyle\sum_m\xi_m\varphi_m, \quad (16)$$

$$|n+1\beta)=\varphi_{n+1}-(n\alpha|H_i|n+1\beta) \times(E_{n+1}-E_n)^{-1}\varphi_n+\textstyle\sum_m\xi_m\varphi_m, \quad (17)$$

where

$$H\varphi_n=E_n\varphi_n, \quad (18)$$

$$H\varphi_{n+1}=E_{n+1}\varphi_{n+1}, \quad (19)$$

and

$$H\varphi_m=E_m\varphi_m. \quad (20)$$

From (13) we have

$$\begin{aligned}&S(n\alpha\to n+1\beta)\\ &=\lim_{t\to\infty}|(n+1\beta|H_i|n\alpha)|^2|\exp(-iE_nt/\hbar)\\ &\qquad-\exp(-iE_{n+1}t/\hbar)|^2/(E_n-E_{n+1})^2t\\ &=(2\pi/\hbar^2)|(n+1\beta|H_i|n\alpha)|^2\delta[(E_n-E_{n+1})/\hbar],\end{aligned} \quad (21)$$

which gives the resonance condition

$$E_n=E_{n+1}. \quad (22)$$

Since the first approximation to the eigenvalues gives

$$E_n\cong n\hbar\omega+W_\alpha, \quad (23)$$

$$E_{n+1}=(n+1)\hbar\omega+W_\beta \quad (24)$$

according to (8); the resonance condition (22) is

$$\hbar\omega=W_\alpha-W_\beta, \quad (25)$$

which is the Bohr resonance condition.

FREQUENCY SHIFT

The deviation from the Bohr resonance condition (25) can be obtained by calculating the eigenvalues E_n and E_{n-1} to a higher order of approximation. For our case where the degeneracy exists due to the condition (22), we see the Van Vleck transformation[8] is most suitable to calculate such improvement. Thus we obtain

$$E_n=n\hbar\omega+W_\alpha+\sum_{n',\gamma}|(n\alpha|H_i|n'\gamma)|^2/ [(n-n')\hbar\omega+W_\alpha-W_\gamma], \quad (26)$$

$$E_{n+1}=(n+1)\hbar\omega+W_\beta+\sum_{n',\gamma}|(n+1\beta|H_i|n'\gamma)|^2/ [(n-1-n')\hbar\omega+W_\beta-W_\gamma], \quad (27)$$

where

$$\gamma\neq\alpha,\quad \text{nor } \beta. \quad (28)$$

From (22) the resonance condition is now

$$\hbar\omega=W_\alpha-W_\beta+\Omega, \quad (29)$$

[7] E. A. Power and S. Zienau, Phil. Trans. Roy. Soc. (London) A251, 427 (1959).

[8] J. H. Van Vleck, Phys. Rev. 33, 467 (1929).

where the shift Ω is, from (9), (10), and (27),

$$\Omega=n\hbar[\sum_\gamma|(\alpha|D|\gamma)|^2\{(\hbar\omega+W_\alpha-W_\gamma)^{-1}+(-\hbar\omega+W_\alpha-W_\gamma)^{-1}\}-\sum_\gamma|(\beta|D|\gamma)|^2\{(\hbar\omega+W_\alpha-W_\gamma)^{-1}+(-\hbar\omega+W_\alpha-W_\gamma)^{-1}\}]/2\omega\epsilon_0V, \quad (30)$$

where γ does not include α nor β, and

$$D=(e/2\mu)(\mathbf{e}_\lambda\times\nabla G)_0\cdot(\mathbf{L}+2\mathbf{S})+\omega G_0\mathbf{e}_\lambda\cdot\mathbf{M}_e. \quad (31)$$

In (30) we neglected one compared to n.

Because of the selection rule, the shift (30) can be expressed as a simple sum of terms called electric shift and magnetic shift, respectively:

$$\Omega=\Omega_e+\Omega_m, \quad (32)$$

where

$$\Omega_e=(n\hbar\omega G_0^2/2\epsilon_0V)[\sum_\gamma|(\alpha|\mathbf{e}_\lambda\cdot\mathbf{M}_e|\gamma)|^2\times\{(\hbar\omega+W_\alpha-W_\gamma)^{-1}+(-\hbar\omega+W_\alpha-W_\gamma)^{-1}\}-\sum_\gamma|(\beta|\mathbf{e}_\lambda\cdot\mathbf{M}_e|\gamma)|^2\times\{(\hbar\omega+W_\beta-W_\gamma)^{-1}+(-\hbar\omega+W_\beta-W_\gamma)^{-1}\}], \quad (33)$$

and a similar expression for Ω_m which is obtained from the first term of (31).

Now

$$\rho_e=n\hbar\omega G_0^2/2V \quad (34)$$

is the time average of the electric field energy density at the position of the atom. On the other hand, the average electric field strength at the position of the atom $\mathcal{E}_0$ is given by

$$\rho_e=\epsilon_0\mathcal{E}_0^2/2 \quad (35)$$

so that (33) can be written as

$$\Omega_e=(\mathcal{E}_0^2/2)[\sum_\gamma|(\alpha|\mathbf{e}_\lambda\cdot\mathbf{M}_e|\gamma)|^2\{(\hbar\omega+W_\alpha-W_\gamma)^{-1}+(-\hbar\omega+W_\alpha-W_\gamma)^{-1}\}-\sum_\gamma|(\beta|\mathbf{e}_\lambda\cdot\mathbf{M}_e|\gamma)|^2\times\{(\hbar\omega+W_\beta-W_\gamma)^{-1}+(-\hbar\omega+W_\beta-W_\gamma)^{-1}\}] \quad (36)$$

which shows that the electric shift Ω_e can be interpreted as a second-order Stark effect due to the average electric field of the radiation. Note, however, that the matrix element $(\alpha|\mathbf{e}_\lambda\cdot\mathbf{M}_e|\beta)$ does not contribute to the shift.

The same interpretation can be done about the magnetic shift Ω_m. If we define the average magnetic flux density at the position of the atom B_0 by

$$\rho_m=B_0^2/2\mu_0, \quad (37)$$

where ρ_m is the time average of the magnetic field energy density at the position of the atom, and μ_0 is the permeability of the vacuum, we see that

$$\Omega_m=(B_0^2/2)[\sum_\gamma|(\alpha|\mathbf{e}_\lambda'\cdot\mathbf{M}_m|\gamma)|^2\times\{(\hbar\omega+W_\alpha-W_\gamma)^{-1}+(-\hbar\omega+W_\alpha-W_\gamma)^{-1}\}-\sum_\gamma|(\beta|\mathbf{e}_\lambda'\cdot\mathbf{M}_m|\gamma)|^2\times\{(\hbar\omega+W_\beta-W_\gamma)^{-1}+(-\hbar\omega+W_\beta-W_\gamma)^{-1}\}], \quad (38)$$

where

$$\mathbf{M}_m=(e/2\mu)(L+2S) \quad (39)$$

is the magnetic dipole moment of the atom. Again the summation over γ should exclude both α and β.

APPLICATION TO Cs 9-KMC/SEC LINES

The ground state of the Cs atom is $2S_{1/2}$ and the nuclear spin of $\frac{7}{2}$ splits it into $F=4$ and $F=3$ states. The $F=4$ state is higher in energy than the $F=3$ state by about 9 kMc/sec. Beehler, Snider, and Mockler[5] observed the change of the resonance frequency due to the field in tensity. In their experiment a static magnetic field B is applied to remove the degeneracy. The transition $F=4\leftrightarrow3$ is the magnetic dipole transition.

The magnetic component of the microwave can be either parallel or perpendicular to the static magnetic field. They are called π and σ cases, respectively. The selection rules for the magnetic dipole transition are

$$\begin{aligned}&\Delta M=0 \quad \text{for } \pi \text{ case},\\ &\Delta M=\pm1 \quad \text{for } \sigma \text{ case}.\end{aligned} \quad (40)$$

Let us consider the electric shift first. Since the microwave frequency is very low compared to any resonance frequency of electric dipole transition, we can use experimental data of the Stark effect with static field, which are given by

$$\Delta E_\alpha=\mathcal{E}^2\sum_\gamma|(\alpha|\mathbf{e}_\lambda\cdot\mathbf{M}_e|\gamma)|^2(W_\alpha-W_\gamma)^{-1}$$

and

$$\Delta E_\beta=\mathcal{E}^2\sum_\gamma|(\beta|\mathbf{e}_\lambda\cdot\mathbf{M}_e|\gamma)|^2(W_\beta-W_\gamma)^{-1}. \quad (41)$$

The Stark effect depends on the angle between the electric field and the quantization axis, and in Beehler, Snider, and Mockler's experiment the electric component of the microwave is perpendicular to the static magnetic field. Haun and Zacharias[9] observed the Stark effect of $(F=3,\ M=0)\leftrightarrow(F=4,\ M=0)$ transition in the same situation and obtained

$$-2.9\times10^{-2}\mathcal{E}^2 \text{ cps}, \quad (42)$$

where $\mathcal{E}$ is in V/m. We thus expect

$$\begin{aligned}\Omega_e(0\leftrightarrow0)/h&=-2.9\times10^{-2}\rho_e/\epsilon_0 \text{ cps}\\ &=-3.3\times10^9\rho_e \text{ cps}\end{aligned} \quad (43)$$

for $M=0\leftrightarrow0$ transition. ρ_e is in J/m^3.

Since each of (41) will be expressed as $(\Delta E_0-\Delta E_1M^2)\mathcal{E}^2$ we expect the electric shift for other transitions as

$$\Omega_e(M\leftrightarrow M)/h=(-3.3\times10^9+DM^2)\rho_e \text{ cps}, \quad (44)$$

$$\Omega_e(F=3,\ M\leftrightarrow F=4,\ M\pm1)/h=(-3.3\times10^9+C\pm2CM+DM^2)\rho_e \text{ cps}, \quad (45)$$

where C and D are constants.

In calculating the magnetic shift, we can restrict ourselves to the transitions among the electronic ground state since magnetic excitations to any other electronic states will have only a negligible contributions due to

[9] R. D. Haun, Jr., and J. R. Zacharias, Phys. Rev. **107**, 107 (1957).

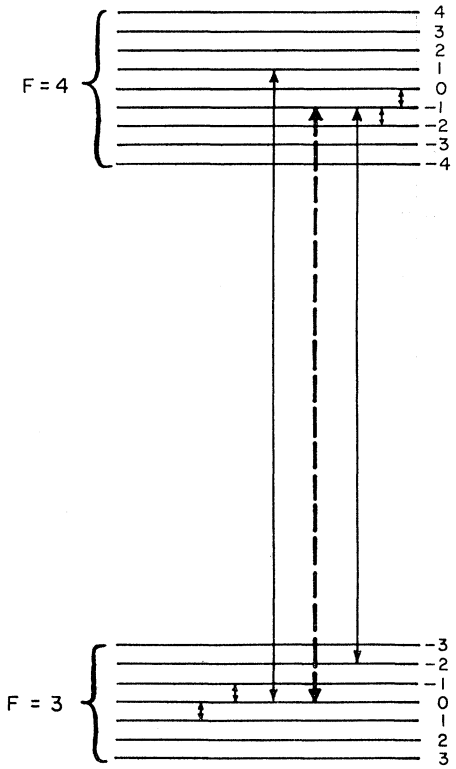

FIG. 1. Magnetic dipole transitions perturbing frequency of $(F=3, M=0) \rightarrow (F=4, M=-1)$.

high excitation energies. We see immediately that under such approximation

$$\Omega_m(M \leftrightarrow M)=0 \tag{46}$$

for all π-type transitions.

In the σ-type transitions, on the other hand, the selection rule makes the magnetic shift important (Fig. 1). If the microwave is linearly polarized, as in the present case, the transition $(F=3, M) \leftrightarrow (F=4, M+1)$, for example, is perturbed by the transitions $(F=3, M) \leftrightarrow (F=4, M-1)$ and $(F=3, M+2) \leftrightarrow (F=4, M+1)$ very strongly, since denominators in (38) are quite small for these terms. Other transitions $(F=3, M) \leftrightarrow (F=3, M-1)$, $(F=3, M) \leftrightarrow (F=4, M+2)$ also contribute to Ω_m to some, but to a much smaller extent.

Since the external field B gives additional energy

$$-B(eh/\mu)M/8 \quad \text{for } F=3 \text{ states}, \tag{47}$$

$$B(eh/\mu)M/8 \quad \text{for } F=4 \text{ states}, \tag{48}$$

the frequency of $(F=3, M) \leftrightarrow (F=4, M+1)$ transition is $\omega_0+B(e/8\mu)$ $(2M+1)$ is the zeroth approximation.

The contribution of transition $(F=3, M) \leftrightarrow (F=4, M-1)$ to the magnetic shift Ω_m of the above frequency is, according to (38),

$$(\rho_m\mu_0/64)(4-M)(5-M)(eh/\mu^2) \times[(4\mu/Be)-(2\omega_0)^{-1}], \tag{49}$$

where ρ_m is the magnetic field energy density. In the same way, the contribution of transition $(F=3, M+2) \leftrightarrow (F=4, M+1)$ is obtained as

$$-(\rho_m\mu_0/64)(2-M)(3-M)(eh/\mu)^2 \times[(4\mu/Be)+(2\omega_0)^{-1}]. \tag{50}$$

Adding (49) and (50) together, and neglecting $(2\omega_0)^{-1}$ terms, we have

$$\Omega_m/h=1100(\rho_m/B)(7-2M) \text{ cps}, \tag{51}$$

where ρ_m and B are given in the mks unit.

The same consideration gives the following formula for the magnetic shift of $(F=3, M) \leftrightarrow (F=4, M-1)$ transition:

$$\Omega_m/h=-1100(\rho_m/B)(7+2M) \text{ cps}. \tag{52}$$

COMPARISON WITH EXPERIMENT

Theoretical shifts for all transitions are tabulated in Table I.

TABLE I. Theoretical shifts in cps. ρ and B_0 are in kms units.

$M(F=3)$	$M(F=4)$	Electric	Magnetic
0	0	$-3.3\times10^9\rho_e$	0
±1	±1	$(-3.3\times10^9+D)\rho_e$	0
±2	±2	$(-3.3\times10^9+4D)\rho_e$	0
±3	±3	$(-3.3\times10^9+9D)\rho_e$	0
±3	±2	$(-3.3\times10^9-5C+9D)\rho_e$	$\pm1.43\times10^4(\rho_m/B_0)$
±2	±1	$(-3.3\times10^9-3C+4D)\rho_e$	$\pm1.21\times10^4(\rho_m/B_0)$
±1	0	$(-3.3\times10^9-C+D)\rho_e$	$\pm0.99\times10^4(\rho_m/B_0)$
0	±1	$(-3.3\times10^9+C)\rho_e$	$\pm0.77\times10^4(\rho_m/B_0)$
±1	±2	$(-3.3\times10^9+3C+D)\rho_e$	$\pm0.55\times10^4(\rho_m/B_0)$
±2	±3	$(-3.3\times10^9+5C+4D)\rho_e$	$\pm0.33\times10^4(\rho_m/B_0)$
±3	±4	$(-3.3\times10^9+7C+9D)\rho_e$	$\pm0.11\times10^4(\rho_m/B_0)$

In Beeler, Snider, and Mockler's experiment[5] input power was measured, but the energy densities ρ_e and ρ_m in the cavity were not. It is assumed here that these energy densities are both proportional to the input power.

Experimental data are tabulated in Table II and

TABLE II. Theoretical result with parameters given by (54), (55), and (56).

$M(F=3)$	$M(F=4)$	B_0	Shift/input (cps/mW)
0	0	...	(<1/50)
1	1	...	+1.9
0	1	2.50×10^{-5}	+1.5
1	0	2.50×10^{-5}	−1.0
0	1	0.95×10^{-5}	+8.5
−2	−3	0.71×10^{-5}	−14.0
3	4	0.73×10^{-5}	−3.0

given in Fig. 2. Straight lines in Fig. 2 are theoretical ones obtained by choosing the values of parameters as

$$D\rho_e/\text{inp.}=1.9 \text{ cps/mW}, \tag{53}$$

$$C\rho_e/\text{inp.}=-3.2 \text{ cps/mW}, \tag{54}$$

$$\rho_m/\text{inp.}=1.2\times10^{-8} \text{ J/m}^3 \text{ mW}, \tag{55}$$

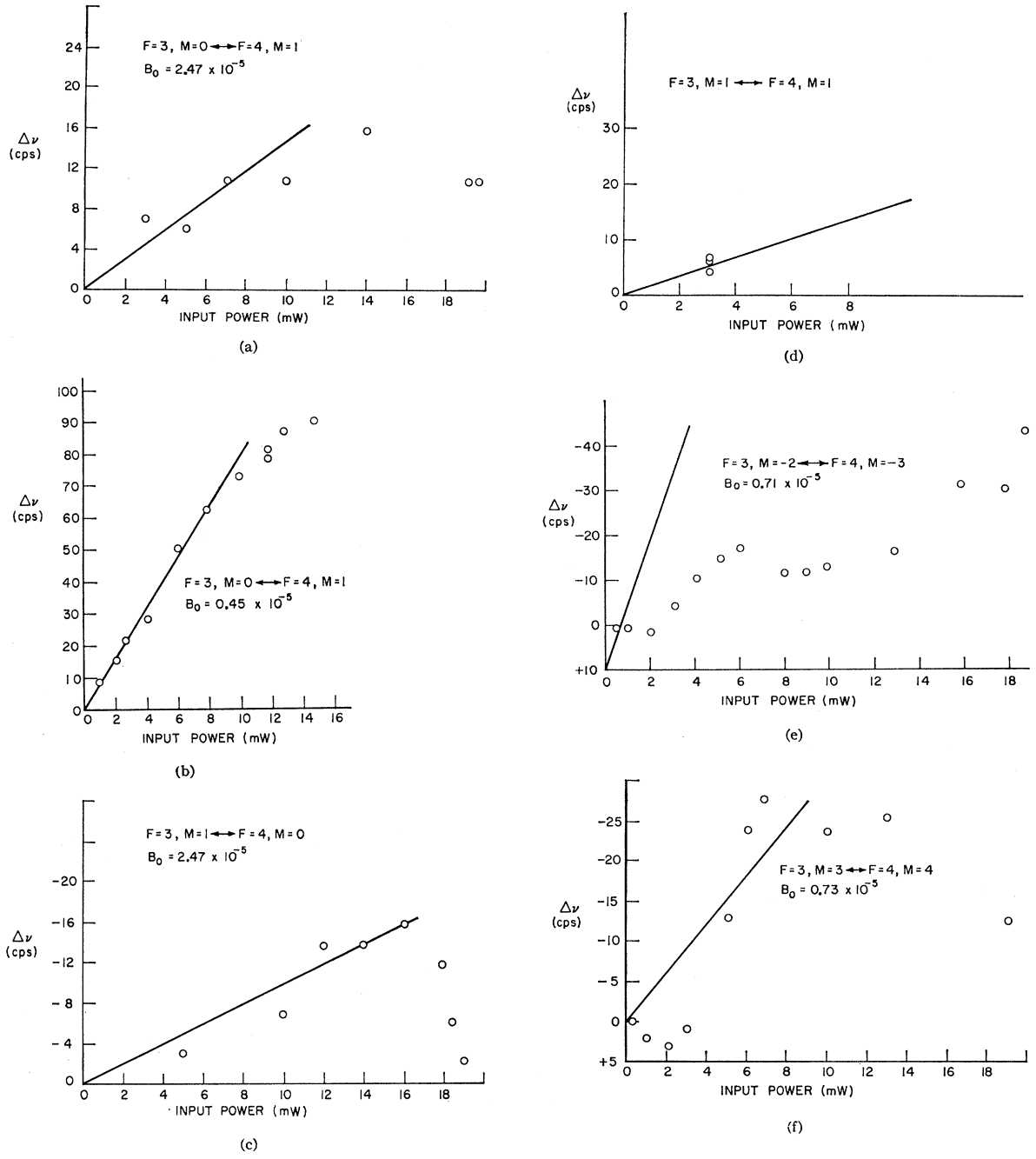

FIG. 2. Comparison of theoretical and experimental shifts.

where inp. means the input power in mW. Since they found no shift for the $M=0\leftrightarrow 0$ transition within the experimental accuracy we see

$$\rho_e/\text{inp.}<10^{-10}\ \text{J/m}^3\ \text{mW}. \tag{56}$$

Values for the energy densities are reasonable compared to estimations given by characteristics of the apparatus.

In the higher input regions experiment shows large deviations from linear behavior. A large disagreement is also seen in transition $(F=4, M=-2)\leftrightarrow(F=3, M=-3)$.

The effect of the molecular velocity is neglected in the present theory. The experiment by Beeler, Snider, and Mockler was with an atomic beam from an oven of about 150°C. The deviations of the experimental data from the theoretical lines can be due to the molecular velocity.