where b_0, $b_1, \ldots$ are constants and $b_3 = 0$ unless $d = 2\sigma$. It is possible to see from Joyce's work that additional logarithmic terms do appear for $d = n\sigma$, with n an integer larger than 2. These terms are, however, of higher order and they can be included formally in Eq. (A8) extending b_3 to be zero unless $d = m\sigma$, where $m = 2, 3, \ldots$

Equations (A6) and (A7) are valid in the limit of very large r. For large but finite r, the constants in these equations become functions of r and in the limit of $r \to 0$ one should expect them to go over into the constants in Eq. (A8), if $I(r, \kappa)$ has the correct dependence on κr, for small κ and any fixed r. In other words, for any fixed r, we have

$$I(r;\ \kappa r \ll 1) = f_0(r) + f_1(r)\kappa^{\sigma} + f_2(r)\kappa^{d-\sigma} + f_3(r)\kappa^{d-\sigma}\ln\kappa + \cdots , \tag{A9}$$

where $f_0(r)$, $f_1(r)$, and $f_2(r)$ are finite and nonzero for $r = 0$ and $f_3(r) = 0$ unless $d = m\sigma$, where $m = 2$, $3, \ldots$

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*Norges Teknisk-Naturvitenskapelige Forskningsråd, Postdoctoral Fellow.

†Address after October 1, 1970: Physique Théorique et Hautes Energies Bâtiment 211. Faculté des Sciences, 91-Orsay, France.

[1] J. D. Gunton and M. J. Buckingham, Phys. Rev. 166, 152 (1968).

[2] M. J. Cooper and M. S. Green, Phys. Rev. 176, 302 (1968).

[3] G. S. Joyce, Phys. Rev. 146, 349 (1966).

[4] G. Stell, Phys. Rev. 184, 135 (1969).

[5] L. S. Ornstein and F. Zernike, Proc. Acad. Sci. Amsterdam 17, 793 (1914); reprinted in *The Equilibrium Theory of Classical Fluids*, edited by H. L. Frisch and J. L. Lebowitz (Benjamin, New York, 1964).

[6] B. Widom, J. Chem. Phys. 43, 3898 (1965).

[7] L. P. Kadanoff, Physics 2, 263 (1966).

[8] T. H. Berlin and M. Kac, Phys. Rev. 86, 821 (1952).

[9] J. S. Langer, Phys. Rev. 137, A1531 (1965).

[10] H. W. Lewis and G. H. Wannier, Phys. Rev. 88, 682 (1952).

[11] J. L. Lebowitz and J. K. Percus, Phys. Rev. 144, 251 (1966).

[12] We shall not be concerned in this paper with the two-phase region where some care must be exercised in taking the thermodynamic limit of functions like $\tilde{C}(\vec{k};\Omega)$. A uniform contribution to the correlation function may come from a single term in Eq. (2.6) of the form $1 - \rho\tilde{C}(\vec{k}, \Omega) \sim O(\Omega^{-1})$, for a particular value of $\vec{k}$.

[13] M. E. Fisher, J. Appl. Phys. 38, 981 (1967).

[14] We shall not go into the difference between Eq. (3.2) and the OZ hypothesis, which has been discussed in some detail by Stell in Ref. 4.

[15] M. E. Fisher and R. J. Burford, Phys. Rev. 156, 583 (1967).

[16] J. D. Gunton and M. J. Buckingham, Phys. Rev. Letters 20, 143 (1968).

[17] M. J. Buckingham and J. D. Gunton, Phys, Rev. 178, 848 (1969); M. E. Fisher, *ibid.* 180, 594 (1969).

[18] W. K. Theumann and G. Stell, Bull. Am. Phys. Soc. 14, 368 (1969).

[19] C. C. Yan and G. H. Wannier, J. Math. Phys. 6, 1833 (1965).

[20] H. A. Gersch, Phys. Fluids 6, 599 (1963).

[21] G. N. Watson, *A Treatise on the Theory of Bessel Functions* (Cambridge U. P., Cambridge, 1958), p. 192.

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Energy Eigenvalues, Eigenfunctions, and Transition Probabilities for a Paramagnetic Ion

S. K. Gupta and M. L. Narchal

Physics Department, Punjabi University, Patiala, India

(Received 19 February 1970)

The energy eigenvalues, eigenfunctions, and radiatively induced transition probabilities are computed perturbatively for an axially symmetric paramagnetic ion for arbitrary relative orientations of the crystal symmetry axis, static magnetic field, and time-varying magnetic field. Exact calculations are also reported for a system in which $S = \frac{1}{2}$, $I = \frac{1}{2}$. The bearing of these results on dynamic-nuclear-orientation experiments in paramagnetic samples is also discussed.

I. INTRODUCTION

The EPR spectra of many paramagnetic ions that have been successfully studied experimentally[1-8] can be understood in terms of the spin Hamiltonian

$$\mathcal{H} = \beta \sum_{kl} H_k g_{kl} S_l + \sum_{kl} I_k A_{kl} S_l + g_n \beta \vec{H} \cdot \vec{I} , \tag{1.1}$$

where the symbols have their usual significance. The energy eigenvalues, eigenfunctions, and radiatively induced transition probabilities for such a system have been calculated perturbatively for

$\parallel$ and $\perp$ orientations of the crystal symmetry axis with respect to the external magnetic field.[9] In the present paper, the earlier perturbation calculations have been generalized for any arbitrary relative orientations of the crystal symmetry axis, the external static magnetic field, and the time-varying magnetic field for samples in which the hyperfine interaction dominates over the nuclear Zeeman interaction. Exact calculations for the eigenvalues, eigenfunctions, and induced transition probabilities for $S=\frac{1}{2}$, $I=\frac{1}{2}$ systems for arbitrary relative orientations are also reported. These results are compared with those obtained by Jeffries[9] and a few new significant features are brought out. The bearing of these results on dynamic-nuclear-orientation experiments in paramagnetic samples are also discussed.

II. EIGENVALUES, EIGENFUNCTIONS, AND TRANSITION PROBABILITIES FROM PERTURBATION THEORY

We consider a paramagnetic ion showing strong anisotropic hyperfine interaction so that the nuclear Zeeman term can be ignored. The Hamiltonian for such a system may be written as

$$\mathcal{H}=\beta g_{\parallel} H_z S_z+\tfrac{1}{2}\beta g_{\perp}(H_- S_+ + H_+ S_-) + A I_z S_z + \tfrac{1}{2} B(S_- I_+ + S_+ I_-), \tag{2.1}$$

where the symbols have their usual significance, and

$$H_{\pm}=H_x \pm i H_y, \quad S_{\pm}=S_x \pm i S_y, \quad I_{\pm}=I_x \pm i I_y .$$

The above Hamiltonian is written in the crystal frame whose z axis coincides with the symmetry axis of the crystal. We now introduce a new coordinate system characterized by the unit vectors:

$$\begin{aligned}\vec{i}\,' &= \vec{i}\,(g_{\parallel}\cos\theta\cos\phi/g) + \vec{j}\,(g_{\parallel}\cos\theta\sin\phi/g) - \vec{k}\,(g_{\perp}\sin\theta/g),\\ \vec{j}\,' &= -\vec{i}\sin\phi + \vec{j}\cos\phi,\\ \vec{k}\,' &= \vec{i}\,(g_{\perp}\sin\theta\cos\phi/g) + \vec{j}\,(g_{\perp}\sin\theta\sin\phi/g) + \vec{k}\,(g_{\parallel}\cos\theta/g),\end{aligned}$$

where $\vec{i}$, $\vec{j}$, $\vec{k}$ are the three-unit vectors of the crystal frame and $g^2=g_{\parallel}^2\cos^2\theta+g_{\perp}^2\sin^2\theta$, θ being the angle between the crystal symmetry axis and the direction of the static magnetic field H.

The Hamiltonian in the primed frame is

$$\begin{aligned}\mathcal{H}' = {} & g\beta H S_z' + [An^2+B(1-n^2)]S_z' I_z' + \tfrac{1}{4}(A-B)l^2 \\ & \times (S_+' I_+' + S_-' I_-') + \tfrac{1}{4}[Al^2+(2-l^2)B](S_+' I_-' + S_-' I_+') \\ & + \tfrac{1}{2} ln(A-B) S_z'(I_+' + I_-') + \tfrac{1}{2} ln(A-B)(S_+' + S_-')I_z' ,\end{aligned} \tag{2.2}$$

where $l=-g_{\perp}\sin\theta/g$, $n=g_{\parallel}\cos\theta/g$.
The second-order energy levels are

$$\begin{aligned}E(M,m) = {} & g\beta H M + [(A-B)n^2+B]Mm \\ & - \tfrac{l^4}{16}(A-B)^2(R_+^2 r_+^2 - R_-^2 r_-^2)/g\beta H \\ & - \tfrac{1}{16}[Al^2+(2-l^2)B]^2(R_+^2 r_-^2 - R_-^2 r_+^2)/g\beta H \\ & - \tfrac{1}{4} M l^2 n^2 (A-B)^2 (r_+^2 - r_-^2)/[(A-B)n^2+B] \\ & - \tfrac{1}{4} m^2 l^2 n^2 (A-B)^2 (R_+^2 - R_-^2)/g\beta H .\end{aligned} \tag{2.3}$$

The first-order eigenfunctions are

$$\begin{aligned}\psi(M,m) = {} & |M,m\rangle' - \frac{l^2}{g\beta H}\left(\frac{A-B}{4}\right)\{r_+ R_+ |M+1,\ m+1\rangle' - R_- r_- |M-1,\ m-1\rangle'\} - \left[\frac{Al^2+(2-l^2)B}{4g\beta H}\right] \\ & \times\{R_+ r_- |M+1,\ m-1\rangle' - R_- r_+ |M-1,\ m+1\rangle'\} - \frac{ln(A-B)}{2(An^2+(1-n^2))}\{r_+ |M,\ m+1\rangle' - r_- |M,\ m-1\rangle'\} \\ & - \frac{mln(A-B)}{2g\beta H}\{R_+ |M+1,\ m\rangle' - R_- |M-1,\ m\rangle'\},\end{aligned} \tag{2.4}$$

where $|M,m\rangle'$ is a simultaneous eigenfunction of S_z' and I_z' corresponding to eigenvalues M and m, respectively, and

$$R_{\pm}=[(S\mp M)(S\pm M+1)]^{1/2}, \quad r_{\pm}=[(I\mp m)(I\pm m+1)]^{1/2}.$$

The various radiatively induced transition probabilities are shown in Table I. The above results and those of Table I are the generalization of Jeffries results[9] and reduce to them in appropriate limits.

III. EXACT CALCULATIONS FOR $S=\frac{1}{2}$, $I=\frac{1}{2}$ SYSTEMS

We consider an $S=\frac{1}{2}$, $I=\frac{1}{2}$ system described by the spin Hamiltonian (2.1). The matrix elements of the Hamiltonian in $|M,m\rangle$ representation are

TABLE I. Transition probability per sec W between states ψ_1 (M, m) and ψ_2 induced by a rf field $\vec{\mathrm{H}}_1$ applied to a system represented by the $\mathcal{H}$ of Eq. (2.2).

ψ_2	W sec^{-1}
$M\pm1,\ m$	$(Cg^2/g^2H^2\sin^2\theta)[g_{\parallel}^2\cos^2\theta\{\vec{\mathrm{H}}_1\cdot\vec{\mathrm{H}}-(\vec{\mathrm{H}}_1\cdot\vec{\mathrm{k}})(\vec{\mathrm{H}}\cdot\vec{\mathrm{k}})\}^2+g^2\{(\vec{\mathrm{H}}\times\vec{\mathrm{H}}_1)\cdot\vec{\mathrm{k}}\}]R^2{}_{\pm}/4$
$M\pm1,\ m\mp1$	$C\{(A-B)l^2+2B\}[\vec{\mathrm{H}}_1\cdot\vec{\mathrm{H}}g_{\perp}^2-(\vec{\mathrm{H}}_1\cdot\vec{\mathrm{k}})(\vec{\mathrm{H}}\cdot\vec{\mathrm{k}})(g_{\parallel}^2-g_{\perp}^2)]^2R_{\pm}^2r_{\mp}^2/16g^2\beta^2H^2$
$M\pm1,\ m\pm1$	$C(A-B)^2l^4[(\vec{\mathrm{H}}_1\cdot\vec{\mathrm{H}})g_{\perp}^2+(g_{\parallel}^2-g_{\perp}^2)(\vec{\mathrm{H}}_1\cdot\vec{\mathrm{k}})(\vec{\mathrm{H}}\cdot\vec{\mathrm{k}})]^2R_{\pm}^2r_{\pm}^2/16g^2\beta^2H^2$
$M,\ m\pm1$	$(Cg_{\perp}^2/g^2H^2\sin^2\theta)[g_{\parallel}^2\cos^2\theta\{\vec{\mathrm{H}}_1\cdot\vec{\mathrm{H}}-(\vec{\mathrm{H}}\cdot\vec{\mathrm{k}})(\vec{\mathrm{H}}_1\cdot\vec{\mathrm{k}})\sec^2\theta\}^2\{2(A-B)l^2+2B\}^2$ $+g^2\{(\vec{\mathrm{H}}\times\vec{\mathrm{H}}_1)\cdot\vec{\mathrm{k}}\}^2(2B)^2M^2r_{\pm}^2/16g^2\beta^2H^2$, where $C=g(\nu)\beta^2/4\hbar^2$

$$H_{11}=-\tfrac{1}{2}\beta g_{\parallel}H_z+\tfrac{1}{4}A,\quad H_{12}=H_{14}=H_{34}=0,$$

$$H_{13}=H_{24}=\tfrac{1}{2}\beta g_{\perp}H_+,\quad H_{22}=-\tfrac{1}{2}\beta g_{\parallel}H_z-\tfrac{1}{4}A,$$

$$H_{23}=\tfrac{1}{2}B,$$

$$H_{33}=\tfrac{1}{2}\beta g_{\parallel}H_z-\tfrac{1}{4}A,\quad H_{44}=\tfrac{1}{2}g_{\parallel}\beta H_z+\tfrac{1}{4}A,$$

and

$$H_{ij}=H_{ji}^*.$$

The characteristic equation of this matrix is

$$\lambda^4-A'\lambda^2+B'\lambda+C'=0, \tag{3.1}$$

where

$$A'=\tfrac{1}{8}(A^2+2B^2)+\tfrac{1}{2}g^2\beta^2H^2,$$

$$B'=\tfrac{1}{8}AB^2,$$

$$C'=(A^2/256)(A^2-4B^2)+\tfrac{1}{16}(g\beta H)^4$$
$$+\tfrac{1}{32}\beta^2A^2g^2H^2+\tfrac{1}{16}(B^2-A^2)\beta^2g_{\parallel}^2H^2.$$

The roots of this equation give the energy eigenvalues of the system

$$\lambda_{1,2}=\tfrac{1}{2}[-a\mp(a^2-4b)^{1/2}], \tag{3.2}$$

$$\lambda_{3,4}=\tfrac{1}{2}[a\mp(a^2-4e)^{1/2}], \tag{3.3}$$

where

$$a^2=(-x+\sqrt{y})^{1/2}+(-x-\sqrt{y})^{1/2}+\tfrac{2}{3}A',$$

$$x=\tfrac{1}{2}(\tfrac{2}{27}A'^3-\tfrac{8}{3}A'C'-B'^2),\quad y=x^2-(\tfrac{1}{9}A'^2+\tfrac{4}{3}C')^3,$$

and

$$b=\tfrac{1}{2}(-A'+a^2-B'/a),\quad e=(-A'+a^2+B'/a),$$

where any value of the cube root may be taken. Corresponding to the eigenvalue λ_k the eigenfunction is

$$\psi_k=\sum_{j=1}^{4}C_{kj}\phi_j, \tag{3.4}$$

where $\phi_1=|-\tfrac{1}{2},\tfrac{1}{2}\rangle$, $\phi_2=|-\tfrac{1}{2},-\tfrac{1}{2}\rangle$,

$$\phi_3=|\tfrac{1}{2},-\tfrac{1}{2}\rangle,\quad \phi_4=|\tfrac{1}{2},\tfrac{1}{2}\rangle,$$

and $C_{k1}=(2G_k/\beta g_{\perp}H_{\perp}^2)H_+C_{k4}$,

$$C_{k2}=-(\beta g_{\perp}H_+^2/BT_k)(\tfrac{1}{2}\beta g_{\perp}-2F_kG_k/\beta g_{\perp}H_{\perp}^2)C_{k4},$$

$$C_{k3}=-(2H_+/B)(\tfrac{1}{2}\beta g_{\perp}-2F_kG_k/\beta g_{\perp}H_{\perp}^2)C_{k4},$$

$$C_{k4}=\{[(16/B^2\beta^2g^2H^2T_k^2)(\tfrac{1}{16}B^2\beta^2g_{\perp}^2H_{\perp}^2T_k^2$$
$$+\tfrac{1}{4}\beta^2g_{\perp}^2H_{\perp}^2(\tfrac{1}{4}\beta^2g_{\perp}^2H_{\perp}^2-F_kG_k)^2+\tfrac{1}{4}B^2T_k^2G_k^2$$
$$+T_k^2(\tfrac{1}{4}\beta^2g_{\perp}^2H_{\perp}^2-F_kG_k)^2)]^{1/2}\}^{-1},$$

where $F_k=\lambda_k-H_{22}$, $G_k=\lambda_k-H_{44}$, $T_k=\lambda_k-H_{11}$, and $H_{\perp}^2=H_x^2+H_y^2$. We apply an rf field represented by the perturbation Hamiltonian

$$\mathcal{H}_{\mathrm{rf}}=g_{\parallel}\beta H_{1z}S_z+\tfrac{1}{2}g_{\perp}\beta(H_{1-}S_++H_{1+}S_-),$$

where $H_{1\pm}=H_{1x}\pm iH_{1y}$. The transition probability W_{ij} between the eigenstates λ_i and λ_j is given by

$$W_{ij}=(g(\nu_{ij})/4\hbar^2)C_{i4}^2C_{j4}^2(4/B^2)^2(T_i^2T_j^2)^{-1}(4/\beta^2g_{\perp}^2H_{\perp}^2)^2[\tfrac{1}{4}g_{\parallel}^2\beta^2H_{1z}^2\{(-\tfrac{1}{4}\beta^2g_{\perp}^2H_{\perp}^2+T_iT_j)P_iP_j$$
$$+\tfrac{1}{4}B^2T_iT_j(-G_iG_j+\tfrac{1}{4}g_{\perp}^2H_{\perp}^2\beta^2)\}^2+\tfrac{1}{2}g_{\parallel}\beta^2H_{1z}g_{\perp}(\vec{\mathrm{H}}\cdot\vec{\mathrm{H}}_1-(\vec{\mathrm{H}}\cdot\vec{\mathrm{k}})(\vec{\mathrm{H}}_1\cdot\vec{\mathrm{k}}))\{(-\tfrac{1}{4}\beta^2g_{\perp}^2H_{\perp}^2+T_iT_j)$$
$$\times P_iP_j+\tfrac{1}{4}[B^2T_iT_j(-G_iG_j+\tfrac{1}{4}\beta^2g_{\perp}^2H_{\perp}^2)\}\{\tfrac{1}{2}\beta g_{\perp}P_iP_j(T_i+T_j)+\tfrac{1}{8}\beta g_{\perp}T_iT_jB^2(G_j+G_i)\}+\tfrac{1}{4}g_{\perp}^2\beta^2$$

$$\times\{H_{1\perp}^2 H_\perp^2 (\tfrac{1}{2}\beta g_\perp T_i P_i P_j + \tfrac{1}{8} g_\perp \beta B^2 T_i T_j G_j)^2 + (\tfrac{1}{2}\beta g_\perp T_j P_i P_j + \tfrac{1}{8} B^2 \beta g_\perp T_i T_j G_i)^2\} + 2\{(\vec{\mathrm{H}}\cdot\vec{\mathrm{H}}_1 - (\vec{\mathrm{H}}_1\cdot\vec{\mathrm{k}})$$
$$\times(\vec{\mathrm{H}}\cdot\vec{\mathrm{k}}))^2 - ((\vec{\mathrm{H}}\times\vec{\mathrm{H}}_1)\cdot\vec{\mathrm{k}})^2\}\,\{\tfrac{1}{2}\beta g_\perp T_j (P_i P_j + \tfrac{1}{4} G_j B^2 T_j)\}\,\{\tfrac{1}{2}\beta g_\perp T_i (P_i P_j + \tfrac{1}{4} G_i B^2 T_i)\}, \qquad (3.5)$$

where $P_i = \frac{1}{4}\beta^2 g_\perp^2 H_\perp^2 - F_i G_i$ and $g(\nu_{ij})$ is the line-shape function corresponding to the frequency $\nu_{ij} = |\lambda_i - \lambda_j|h$, where h is Planck's constant. Equations (3.2)–(3.5) reduce to their respective perturbation limits in the high-field region ($H \geq 300$ Oe).

The eigenvalues and radiatively induced probabilities for paramagnetic ($\Delta M = \pm 1$, $\Delta m = 0$), flip-flip ($\Delta M = \pm 1$, $\Delta m = \pm 1$), and flip-flop ($\Delta M = \pm 1$, $\Delta m = \mp 1$) transitions are plotted as function of the static magnetic field on a double log scale for various relative orientations of relevant directions in Figs. 1–4 for a hypothetical sample with $S = \frac{1}{2}$, $I = \frac{1}{2}$ having $g_\parallel = 0.362$, $g_\perp = 2.702$, $A = 0.0052$ cm^{-1} and $B = 0.0312$ cm^{-1}, which actually correspond to a Nd^{3+} ion in $\mathrm{La_2Mg_3(NO_3)_{12}\cdot 24H_2O}$. The following conclusions may be drawn from an analysis of the curves.

A. Eigenvalues

The shape of the curves (Fig. 1) is more or less independent of the direction of the static magnetic field relative to the crystal symmetry axis. For very low fields ≤ 50 Oe or so, the energy levels are independent of the orientations and are very unequally spaced. When the orientation of the static field is parallel to crystal symmetry axis,

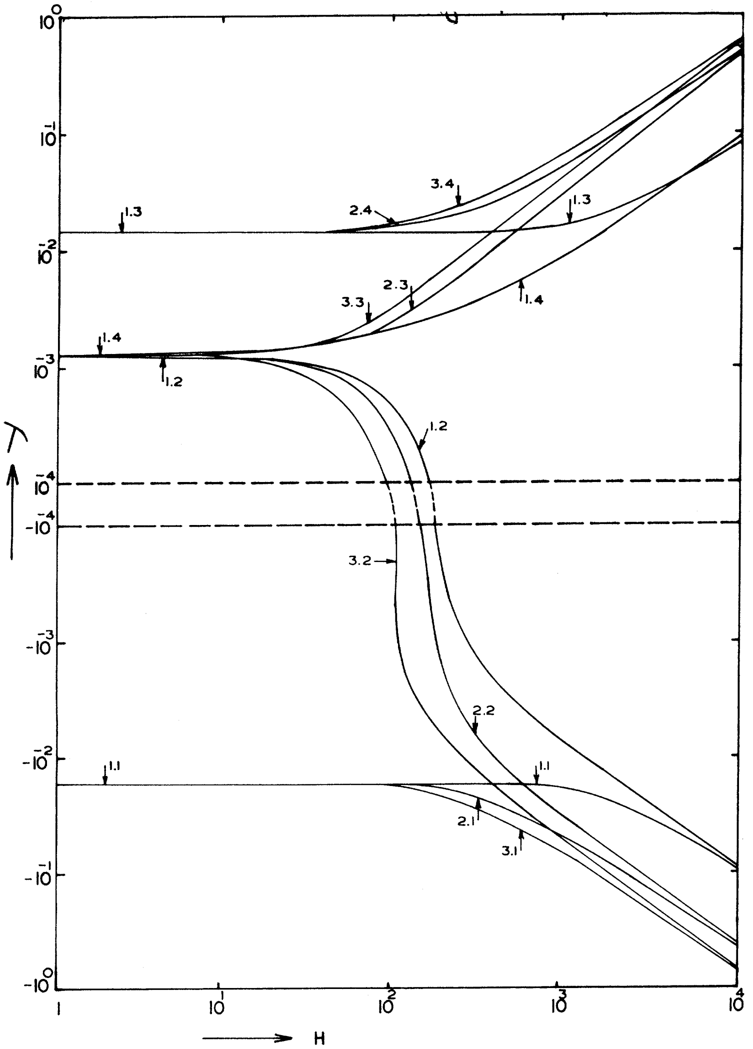

FIG. 1. Curves showing the relation between energy eigenvalues (cm^{-1}) and the static magnetic field (Oe). These curves are numbered as $a.b$, where $a = 1, 2, 3$ stands for three values of $\theta = 0°, 45°$, and $90°$, respectively, and $b = 1, 2, 3, 4$ stands for level $|-\frac{1}{2}, \frac{1}{2}\rangle$, $|-\frac{1}{2}, -\frac{1}{2}\rangle$, $|\frac{1}{2}, -\frac{1}{2}\rangle$, and $|\frac{1}{2}, \frac{1}{2}\rangle$, respectively, as represented in the perturbation limit.

the levels 2 and 4 are pure states and are represented exactly by wave functions $|-\frac{1}{2}, -\frac{1}{2}\rangle$ and $|\frac{1}{2}, \frac{1}{2}\rangle$, respectively. When the static field is applied ⊥ to crystal axis and hf constant $B=0$, the levels 1, 2 and 3, 4 become degenerate having eigenvalues $-\frac{1}{2}(\beta^2 g^2 H^2 + A/4)^{1/2}$ and $\frac{1}{2}(\beta^2 g^2 H^2 + A^2/4)^{1/2}$, respectively.

B. Transition Probabilities

The radiativity induced transition probabilities (Fig. 2–4) are in general dependent on the angle θ_1 between the direction of the crystal symmetry axis and the static magnetic field, the angle θ_1, between the direction of the time varying field and the crystal symmetry axis, and also the angle ϕ_1 between $\vec{H}_\perp$ and $\vec{H}_{1\perp}$.

When the static field is along the crystal symmetry axis, the flip-flip transition is always forbidden. The probabilities for paramagnetic and flip-flip transitions are independent of ϕ_1 and are more or less constant for fields ≤300 Oe. The paramagnetic (cross) transition probability has a maximum (minimum) and minimum (maximum) magnitude when the time-varying field is applied ⊥(∥) and ∥(⊥) to the crystal axis.

When the static field is applied either at an angle of 45° or at an angle of 90° to the crystal axis, the magnitude of the transition probabilities in most of the cases is the same for $\phi_1 = 0$ and $\phi_1 = \pi$. The paramagnetic transition probabilities for $\phi_1 = \pi/2$ are in general about an order of magnitude greater than the corresponding values for $\phi_1 = 0$, π. The reverse is true for cross relaxations.

When the static field and the crystal axis are inclined at an angle of 45° and the time-varying field is applied ∥ to crystal axis, all the transition probabilities are independent of ϕ_1, irrespective of the field strength, and the paramagnetic transition probability is also field independent.

For ⊥ orientation the paramagnetic (cross) transition is forbidden when the time-varying field is applied ⊥(∥) to the crystal axis.

The above results have an important bearing on dynamic-nuclear-orientation experiments. An

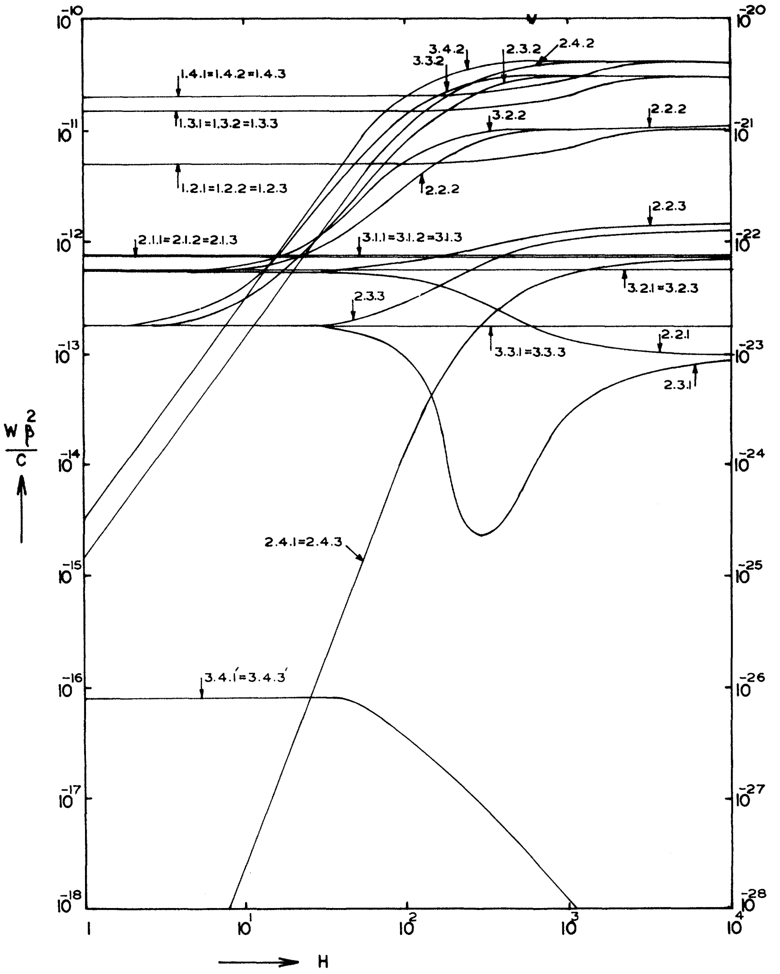

FIG. 2. Curves showing the relation between $W\beta^2/c$ (erg^2 sec) for paramagnetic transitions and the static magnetic field (oersteds). The curves are numbered as $a.b.c$, where $a=1,2,3$, stands for $\theta=0°, 45°$, and 90°, respectively, $b=1,2,3,4$ stands for $\theta_1 = 0°, 30°, 60°$, and 90°, respectively, and $c=1,2,3$ stands for $\phi_1 = 0, \pi/2, \pi$, respectively. The primed curves are plotted on the scale marked on the right.

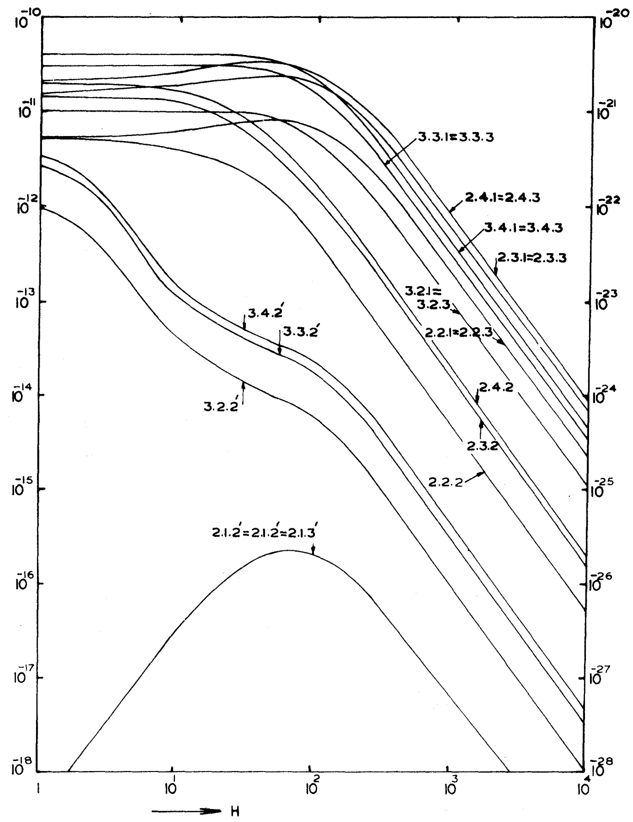

FIG. 3. Curves showing the relation between $W\beta^2/c$ (erg^2 sec) for flip-flip transitions and the static magnetic field (oersteds). "*a.b.c*" has the same meaning as in Fig. 2. The primed curves are plotted on the scale marked on the right.

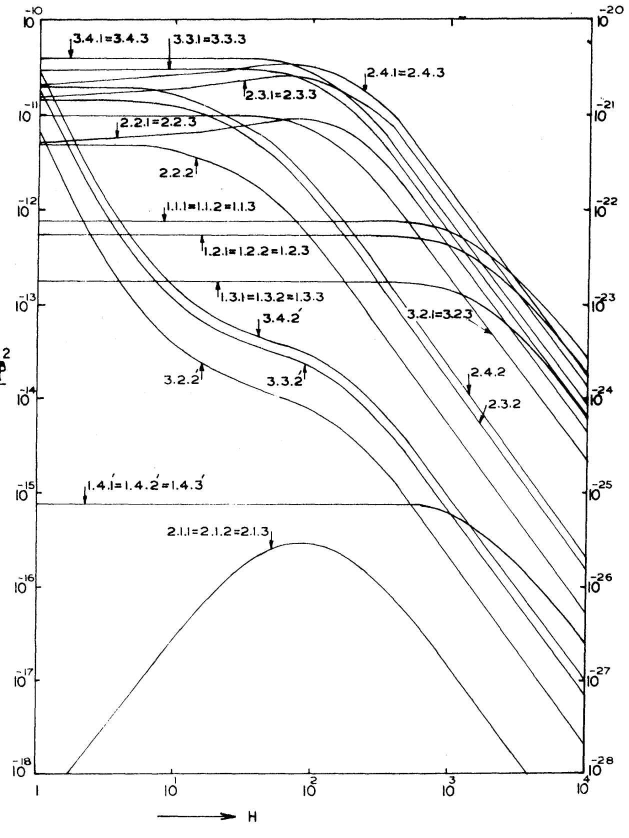

FIG. 4. Curves showing the relation between $W\beta^2/c$ for flip-flop transitions and the static magnetic field. *a.b.c* has the same meaning as in Fig. 2. The primed curves are plotted on the scale marked on the right.

Overhauser[10] dynamic-nuclear-orientation experiment can best be performed when the static field and the time-varying field are applied parallel and perpendicular to the crystal axis, respectively. The best scheme for the Jeffries[11]–Abragam-Proctor[12] effect with noncompeting pumps[13] is $\parallel$ orientation with time-varying field also applied $\parallel$ to crystal axis. The Jeffries–Abragam-Proctor effect with competing pumps[13] can best be obtained when the static and the time-varying fields are applied at angles of 45° and 90°, respectively, with $\phi_1 = 0$ or π.

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[1] K. D. Bowers and J. Owen, Rept. Progr. Phys. 18, 304 (1955).

[2] J. W. Orton, Rept. Progr. Phys. 22, 204 (1959).

[3] J. D. Axe, H. J. Stapleton, and C. D. Jeffries, Phys. Rev. 121, 1630 (1961).

[4] F. M. Pipkin, Phys. Rev. 112, 935 (1958).

[5] F. M. Pipkin and J. W. Culvhouse, Phys. Rev. 109, 1423 (1959).

[6] R. Kyi, Phys. Rev. 128, 151 (1962).

[7] M. M. Abragam, R. A. Weeks, G. W. Clark, and C. B. Finch, Phys. Rev. 148, 350 (1966).

[8] D. H. Lyons and R. W. Kedzie, Phys. Rev. 145, 148 (1966).

[9] C. D. Jeffries, Phys. Rev. 117, 1056 (1960).

[10] A. W. Overhauser, Phys. Rev. 89, 689 (1953); 92, 411 (1953).

[11] C. D. Jeffries, Phys. Rev. 106, 164 (1957).

[12] A. Abragam and W. G. Proctor, Compt. Rend. 246, 2253 (1958).

[13] K. L. Bhatia and M. L. Narchal, Appl. Opt. 5, 1075 (1966).

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Electron Correlation in Ferromagnetism. II. Hybridization of *s* and *d* Bands

R. Kishore and S. K. Joshi

Physics Department, University of Roorkee, Roorkee, India

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The problem of electron correlation in the ferromagnetism of transition metals is investigated by taking an approximate model Hamiltonian which takes into account the hybridization of the *s* and *d* bands. The Green's-function technique is used to obtain the self-consistent ferromagnetic solutions within the Hartree-Fock approximation. An approximate solution of the correlation problem is obtained. The ferromagnetic solutions for which the correlation effects are taken into account are compared with those in the Hartree-Fock approximation. The model is used to investigate the role of the *s-d* interaction in metal-nonmetal transitions. It is also possible to understand the difficulty of observing pressure-induced nonmetal-metal transition.

I. INTRODUCTION

In recent years, much attention has been devoted to the theory of electron correlations in relation to the magnetic properties of transition metals.[1] The electron correlations in the *d* band of transition metals have been studied by Kanamori,[2] Gutzwiller,[3] and Hubbard.[4] These authors based their theories on the assumption that the only interaction responsible for the magnetic properties is the intra-atomic interaction between opposite spin-*d* electrons. Recently, Richmond and Sewell,[5] Pratt and Caron,[6] and Kishore and Joshi[7] took into account the interatomic interaction also. All these investigations completely neglect the presence of the *s* band of conduction electrons.

Anderson's theory[8] of dilute alloys of the transition metals is able to explain the occurrence of the localized magnetic moment on transition-metal impurities dissolved in nonmagnetic metals. In Anderson's model, the band states of the host metal are treated as independent quasiparticles. The impurity is introduced as an extra-localized orbital which is mixed with the band states by a hybrid matrix element. All two-body Coulomb interactions are neglected except the Coulomb interaction between the opposite-spin electrons on the localized orbital. As an extension of this model,