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Electron-Spin-Resonance Studies in ZnS:Ge and ZnS:Si

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Photosensitive electron-spin-resonance signals due to Ge^{3+} and Si^{3+} in ZnS are observed. These signals are much enhanced under uv excitation and quickly decreased by irradiation of light of longer wavelengths. It is found that for Ge^{3+} in cubic ZnS, $g=2.0086\pm0.0003$ and $A=305\times10^{-4}$ cm^{-1}; for Si^{3+} in cubic ZnS, $g=2.0047\pm0.0003$ and $A=654\times10^{-4}$ cm^{-1}. A molecular-orbital treatment of the unpaired-electron wave functions satisfactorily accounts for the sign and the order of magnitude of the observed g values. The correlation of the photosensitivity of resonance signals with the luminescence observed in these samples is discussed.

I. INTRODUCTION

THE optical properties of ZnS-type materials have been the subject of a number of investigations.[1] The experimental methods so far used for this purpose have been limited to studying the absorption and emission spectra and thermoluminescence. Recently, electron-spin-resonance (ESR) technique has been successfully applied to investigate the structure of activators and coactivators in ZnS and to obtain information about the role played by impurities in the process of luminescence.[2,3]

There have been several reports on the luminescent properties of ZnS phosphors activated with group IV*B* elements.[4-6] However, the structures of the luminescent centers have not been fully clarified. ZnS phosphors doped with Ge and Si in a sulfurizing atmosphere are found to show luminescence in the infrared and red regions, respectively, under excitation with uv light at 77°K.[7] In order to investigate the structures of group IV*B* impurities in ZnS and the relation of these impurities to luminescence, ZnS activated with Ge and Si is studied by the method of ESR. In both Ge- and Si-doped ZnS, we have detected extremely sharp ESR signals attributed to Ge^{3+} and Si^{3+} having the large hfs due to the nuclei of Ge^{73} and Si^{29}, respectively, under uv excitation. These resonance signals are distinctly observed only for the samples showing intense emissions. A molecular orbital treatment of the unpaired electrons satisfactorily accounts for the sign and the order of magnitude of the observed g shifts. Discussions on the correlation of these centers with luminescent processes are also included.

II. EXPERIMENTAL METHODS

Electron-spin-resonance spectra are taken with the use of a standard X-band spectrometer with 100-kc/sec magnetic-field modulation. The microwave cavity (TE_{011} mode) has a window to allow optical excitation of samples. Optical excitation or quenching of ESR signals is done by using Beckmann DU spectrometer or an ordinary 300-W tungsten lamp coupled with interference filters of various wavelengths.

Both samples of the single-crystal (wurtzite) and polycrystal (zinc blende and wurtzite) are studied in this experiment. Finely powdered ZnS of luminescent grade is vacuum sealed in quartz crucibles mixed with about 10^{-3} (mole ratio) Ge or SiS_2 and an appropriate amount of sulfur, and heated at 1050 and 950°C for the wurtzite and the zinc blende structures, respectively, for about 20 h. Then capsules are rapidly cooled to room temperature. The samples prepared in this way give rise to luminescences in the infrared and red regions for ZnS:Ge and ZnS:Si, respectively, and strong ESR absorption signals at 77°K under uv excitation. The samples slowly cooled are found to show little luminescence and only faint ESR signals. Therefore, the samples used in this experiment are all prepared by quenching. Doping of impurities into the single crystals (Eagle Picher) is done in the same way as in the powder samples. The samples of both the polycrystal and single crystal show little difference in the resonance spectra. Since the intensity of the resonance signal observed in the phosphors is larger than that in the single crystal, the g values and the hyperfine interaction constants given in this report are obtained on the powder samples. Quenching spectra are taken for the samples of the single crystal with the optically polished surfaces.

III. EXPERIMENTAL RESULTS

A. ZnS:Ge

ZnS activated with Ge in a sulfurizing atmosphere shows an emission spectrum with a peak at about 900 mμ (1.4 eV) under uv excitation at 77°K. At room temperature, no resonance signal is observed with or without optical illumination. At 77°K, this sample shows small paramagnetic absorption signals with width of about 2G in the dark. When the sample is irradiated with uv light of wavelength of around 380 mμ at 77°K, the absorption signals are much enhanced. The spectrum for the sample of zinc blende structure is shown in Fig. 1.

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[5] N. W. Smit and F. A. Kröger, J. Opt. Soc. Am. **39**, 661 (1949).

[6] Y. Mita, J. Phys. Soc. Japan **20**, 1822 (1965).

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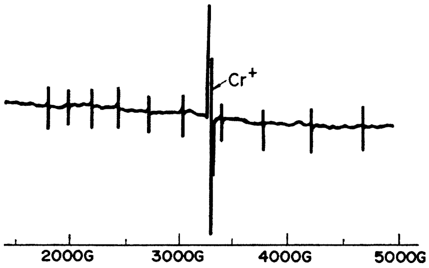

FIG. 1. The electron-spin-resonance spectrum for cubic ZnS:Ge^{3+}.

After the irradiation is stopped, the decrease in the intensity of the signals is hardly recognized for an hour at 77°K. When the sample is irradiated with light of longer wavelengths, the magnitude of the absorption signals is quickly decreased. The decrease of the intensity of ESR signals as a function of wavelength of the irradiated light is shown in Fig. 2. The quenching is most efficient when the sample is irradiated with light of around 490 mμ (2.5 eV).

In Fig. 1, a very strong main line is seen at the center due to the isotope having zero nuclear spin, accompanied with 10 smaller hfs lines with large separation due to the hyperfine interaction with the nuclear spin of Ge^{73} ($I=\frac{9}{2}$, 7.61% abundant). The central line is about 120 times as strong as hfs lines. This is in good agreement with the calculated intensity ratio 121 from the natural abundance and the nuclear-spin quantum number. No difference in the resonance spectrum is observed between the cubic and the hexagonal samples except for the very small anisotropy of g value in the hexagonal ones. Therefore, the discussions will be confined to the results obtained on the cubic samples.

The resonance spectrum can be described by the following spin Hamiltonian:

$$\mathcal{H}=g\beta\mathbf{S}\cdot\mathbf{H}+A\mathbf{I}\cdot\mathbf{S} \tag{1}$$

with $S=\frac{1}{2}$. The second term gives the hyperfine interaction of the electron spin with the nuclear spin of Ge^{73}. Since the hyperfine interaction is very large in this case, we use the following resonance condition solved to the second order

$$h\nu=g\beta H+Am+[I(I+1)-m^2]A^2/2h\nu. \tag{2}$$

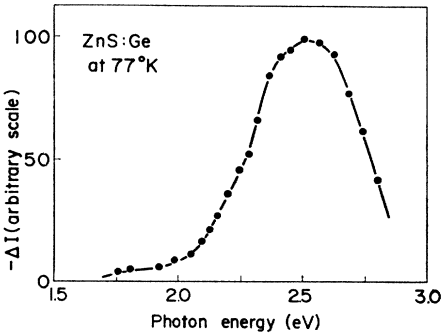

FIG. 2. The quenching of resonance signal for ZnS:Ge^{3+}. The change of signal intensity versus the energy of irradiated light on the excited sample is plotted.

TABLE I. The observed parameters. The small anisotropy of g values in hexagonal sample is calculated from the analysis of powder pattern.[a]

		ZnS:Ge	ZnS:Si
$\|A\|$	(10^{-4} cm^{-1})	305	654
g	(cubic)	2.0086±0.0003	2.0047±0.0003
$g_{\parallel}$	(hexagonal)	2.0087±0.0003	2.0045±0.0005
$g_{\perp}$		2.0096±0.0003	2.0062±0.0002

[a] See F. K. Kneubuhl, J. Chem. Phys. 33, 1074 (1960).

The observed values are given in Table I. The isotropic hfs constant, A, can be written in the form,

$$A=(8/3)\pi g\beta g_n\beta_n\rho_s(0), \tag{3}$$

where $\rho_s(0)$ is the unpaired spin density at the impurity nucleus. The value of $\rho_s(0)$ is given in Table II. Besides the resonance lines attributed to Ge, a very small line due to a trace of Cr$^+$ impurity is observed at $g=1.9993$.[8]

TABLE II. Comparison of the observed spin densities and the calculated densities for neutral atom from Hartree-Fock wave functions.

	ZnS:Ge	ZnS:Si
$\rho_s(0)_{\mathrm{obs}}$ (10^{24} cm^{-3})	39.4	14.9
$\|\psi_s(0)\|^2_{\mathrm{free}}$ (10^{24} cm^{-3})	64.6	25.7

B. ZnS:Si

ZnS doped with Si in a sulfurizing atmosphere shows strong ESR signals with width of about 1G under excitation of light of around 380 mμ at 77°K. Before the optical excitation, the signals are very small. The sample shows an emission spectrum with a peak at about 1.7 eV under uv excitation at 77°K. A strong line at the center and much weaker 2 lines with large separation are observed as shown in Fig. 3. The weaker lines are identified to be hfs originating from Si^{29} ($I=\frac{1}{2}$,

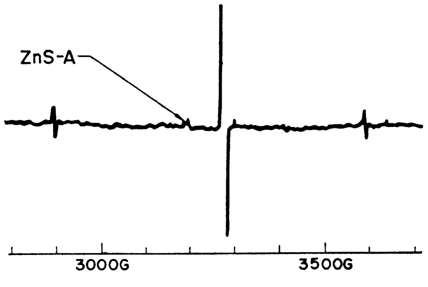

FIG. 3. The electron-spin-resonance spectrum for cubic ZnS:Si^{3+}.

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[8] R. S. Title, Phys. Rev. 131, 623 (1963).

4.70% abundant). The observed intensity ratio (~40) of the central line to the weaker lines is in good agreement with the calculated value. The intensity is much decreased by the irradiation of light of around 560 mμ (2.2 eV). The resonance spectrum can be described by Eq. (1) in which the second term is replaced with $I=\frac{1}{2}$ for Si^{29}. The observed parameters are summarized in Table I. When the sample is excited with light of near 365 mμ, a much weaker broad resonance line is also observed, which has been attributed to the so-called ZnS-*A* center.[2]

IV. PHENOMENOLOGICAL THEORY FOR *g* SHIFT

The observed hyperfine interaction constants are very large and isotropic, implying that the wave functions of the unpaired electrons are of *s* type. Therefore, it may be reasonably assumed that the unpaired electrons are in the 4*s* and the 3*s* orbitals for Ge and Si, respectively, that is, the excited impurity ions are trivalent.

The observed *g* shifts are very small and isotropic. This seems to be obvious since the ground states of Ge^{3+} and Si^{3+} are ^2S states. In both samples of ZnS:Ge and ZnS:Si, definitely positive *g* shifts are observed. If one considers the *p* states in the impurity atom as the excited state which gives rise to a *g* shift through the spin-orbit interaction, a negative shift will be expected. This is not the case. Fidone and Stevens[9] proposed the idea that the effect of covalent bonding can give a contribution to a *g* shift through the spin-orbit interaction. Watanabe[10] has developed this idea of charge transfer mechanism into a more detailed theory of a *g* shift for Fe^{3+} in II–VI compounds. We will derive the expression for Δg of $\mathrm{ZnS{:}Ge}^{3+}$ and $\mathrm{ZnS{:}Si}^{3+}$ by using the theory based on this charge-transfer mechanism. We will start with the following Hamiltonian[11] for an unpaired electron in an external magnetic field

$$\mathcal{H}=2.0023\beta\mathbf{S}\cdot\mathbf{H}+\frac{eh}{2m^2c^2}\mathbf{S}\cdot\left[\mathbf{E}\times\left(\mathbf{p}+\frac{e}{c}\mathbf{A}\right)\right]+\frac{e}{2mc}(\mathbf{p}\cdot\mathbf{A}+\mathbf{A}\cdot\mathbf{p}),\quad(4)$$

where the second term gives the spin-orbit interaction in which **A** is the vector potential that gives a static magnetic field externally applied, and **p** is the linear momentum operator, **E** is an electric field in which an electron moves. The third term describes the orbital Zeeman interaction. The *g* shift caused by the combined effect of the spin-orbit and the orbital Zeeman coupling is given by[11]

$$\Delta g_z=\frac{e}{m^2c^2}\cdot\frac{1}{H_0}\times\sum{}'\frac{\langle0|(\mathbf{E}\times\mathbf{p})_z|n\rangle\langle n|(\mathbf{p}\cdot\mathbf{A}+\mathbf{A}\cdot\mathbf{p})_z|0\rangle}{E_0-E_n},\quad(5)$$

where H_0 denotes the magnitude of the external magnetic field.

We assume that the wave function of the ground state for the unpaired electron can be constructed as a linear combination of the *s* orbital of the impurity with the orbitals of the neighboring sulfur atoms. In T_d symmetry, a possible molecular orbital combination is given as follows

$$\Psi_0=N\{\phi_0-\rho(1/2)[\sigma_0(\mathrm{S}^1)+\sigma_0(\mathrm{S}^2)+\sigma_0(\mathrm{S}^3)+\sigma_0(\mathrm{S}^4)]\},\quad(6)$$

where ϕ_0 denotes the *s* orbital of the impurity atom and $\sigma_0(\mathrm{S}^i)$ is the σ orbital of the *i*th sulfur atom directed toward the impurity atom. The σ orbital is assumed to be constructed from the sp^3 hybridized orbitals. In the above expression, we denote the antibonding orbital by positive ρ. The normalization factor *N* is given as

$$N=[1+\rho^2-2\rho S_0]^{-1/2},\quad(7)$$

where S_0 is the group overlap integral between ϕ_0 and the ligand orbitals. On the other hand, there will be a bonding orbital occupied with two electrons, which is orthogonal to Ψ_0. This bonding orbital may not connect with the antibonding one through the spin-orbit interaction. The excited states are supposed to be the bonding and the antibonding molecular orbitals as approximation to the localized valence and conduction-band states, respectively. They are assumed to be constructed by the following linear combination of the σ orbitals of the neighboring sulfur atoms and those of the second-nearest-neighbor zinc atoms

$$\Psi^a(i,j)=N_-[(1-\alpha^2)^{1/2}\sigma_j(\mathrm{S}^i)-\alpha\sigma_i(\mathrm{Zn}^j)],\quad(8)$$

$$\Psi^b(i,j)=N_+[\alpha\sigma_j(\mathrm{S}^i)+(1-\alpha^2)^{1/2}\sigma_i(\mathrm{Zn}^j)],\quad(9)$$

$$i=1,2,3,4,$$

$$j=1,2,3,$$

where α^2 is the ionicity in the bond between Zn and S in the neighborhood of the impurity, and $\sigma_i(\mathrm{Zn}^j)$ is the σ orbital of the *j*th Zn atom pointing to the *i*th S atom. Normalization factors $N_\mp$ are given as

$$N_\mp=[1\mp2\alpha(1-\alpha^2)^{1/2}S_1]^{-1/2},\quad(10)$$

with

$$S_1=\langle\sigma_j(\mathrm{S}^i)|\sigma_i(\mathrm{Zn}^j)\rangle.\quad(11)$$

The states of Ψ^a and Ψ^b may be considered to contain no electron and two, respectively. When the excited states of Ψ^a are formed by promoting an electron from Ψ_0 into one of these states, a negative *g* shift may be

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[9] I. Fidone and K. W. H. Stevens, Proc. Phys. Soc. (London) **73**, 116 (1959).

[10] H. Watanabe, J. Phys. Chem. Solids **25**, 1471 (1964).

[11] C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row Publishers, Inc., New York, 1963), Chap. 7.

expected. On the other hand, transfer of a hole from Ψ_0 into one of the excited states of Ψ^b may lead to a positive g shift.[12] We will consider only the states of Ψ^a and Ψ^b as excited state. Since the electric field is large only near the nuclei of the impurity atom and ligand atoms, we may neglect the overlap between the impurity and the ligand atoms in evaluation of the spin-orbit matrix elements. The orbital angular-momentum matrix elements of (5) are readily evaluated by making an appropriate gauge transformation and neglecting certain overlap terms.[11] Substituting Eqs. (8) and (9) into Eq. (5), we obtain the following expression for Δg

$$\Delta g \approx \frac{\rho^2\zeta}{1+\rho^2-2\rho S_0}\left[\frac{\alpha^2+\alpha(1-\alpha^2)^{1/2}S_1}{\Delta E^b[1+2\alpha(1-\alpha^2)^{1/2}S_1]} - \frac{1-\alpha^2-\alpha(1-\alpha^2)^{1/2}S_1}{\Delta E^a[1-2\alpha(1-\alpha^2)^{1/2}S_1]}\right], \quad (12)$$

where ΔE^b and ΔE^a are the hole-transfer and electron-transfer energies to the surrounding sulfur atoms, respectively, and ζ is the one-electron spin-orbit interaction parameter for the $3p$ orbital of S^{--}. Strictly speaking, the spin-orbit parameter is different in the cases of an electron transfer and a hole transfer, but this may not be an important factor in the present calculation.

V. DISCUSSIONS

Before uv excitation, the ESR signal is very small and most of the impurity may be divalent or tetravalent. The ESR signal and emission spectrum are hardly observed in the sample which is treated only with impurity, while in the sample prepared in a sulfurizing atmosphere, the strong resonance signal is observed. Therefore, it may be reasonably assumed that the impurity atom is originally substituted for a zinc atom. As the sample is prepared in a highly sulfurizing atmosphere, we assume that most of the impurities are tetravalent, that is, the impurity ion is compensated with a zinc vacancy. This assumption seems not to conflict with the absence of dark conductivity in these samples. A plausible mechanism of the enhancement and the quenching of the ESR signal may be as follows. Illumination with uv light near 380 $m\mu$ may be considered to excite an electron from the valence band to the tetravalent impurity level. At liquid-nitrogen temperature, the excited electron may remain steady because the level is deep. Under the illumination with light of longer wavelengths, the electron at the impurity level may be further excited to the conduction band, leading to a decrease in the intensity of the ESR signal. Luminescence observed in the sample is believed to be caused by an electron transition from the trivalent impurity level to the valence band.

TABLE III. The values of the parameters used for estimation of Δg and comparison between the calculated and observed Δg's.

	ZnS:Ge	ZnS:Si
Emission energy (eV)	1.4	1.7
Quenching energy (eV)	2.5	2.2
Overlap integral S_0	0.897	0.753
Overlap integral S_1	0.351	0.351
Δg_{cal}	+0.0077	+0.0040
Δg_{obs}	+0.0063	+0.0024

We will now discuss Δg observed for ZnS:Ge and ZnS:Si by using Eq. (10). For this purpose, it is necessary to estimate the excitation energy ΔE; the mixing coefficient ρ; the ionicity α^2; and the spin-orbit parameter ζ. It is difficult to estimate the precise value of α^2. We assume that this is not appreciably different from the ionicity in an unperturbed ZnS crystal, that is, we neglect the polarization effect in Zn–S bond caused by the substitution of a trivalent impurity ion for a divalent zinc ion. There have been many discussions about the ionicity for the bond in ZnS crystal. The reported values are somewhat scattered. Birman[13] assumed that about $\frac{1}{3}$ covalent character is reasonable for the bond in ZnS. This value is used in our calculation. By noting that Fe^{3+} substituted for ZnS has about 20% covalent character for a Fe–S bond[8] and that Ge^{3+} and Si^{3+} have approximately the same electronegativity[14] as Fe^{3+}, it may be assumed that the covalency $\rho^2/(1+\rho^2)$ for a Ge–S or a Si–S bond is about 20% ($\rho^2=0.25$). The value of ζ is not available for S^{--}. In the case of $2p$ shell atoms, such as O and F, the spin-orbit parameters of the sequences of O, O^+, O^{2+} and of F, F^+, F^{3+} are known.[15] The values of the parameters of O^{--} and F^{--} may be extrapolated from the sequences. They are about 70% of those of the neutral atoms. Therefore, the value of ζ of S^{--} may be put to be 0.7 times the value of free neutral atom[16] ($\zeta=0.032$ eV). The overlap integrals are evaluated with Slater radial functions. In our model, ΔE^a and ΔE^b may be assumed to be equal to the quenching and the emission energies. The values of the parameters used in the estimation of Δg and the calculated Δg's are summarized in Table III. The calculated Δg for ZnS:Ge is larger than that for ZnS:Si in agreement with experimental observations. If we assume that the impurity is originally substituted for zinc atom as divalent ion and the quenching is caused by a hole transition from the impurity to valence band, the value of Δg calculated for ZnS:Ge is found to be much smaller than that for

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[12] G. D. Watkins and J. W. Corbett, Phys. Rev. **121**, 1001 (1961).

[13] J. L. Birman, Phys. Rev. **109**, 810 (1958).

[14] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, New York, 1960), 3rd ed., Chap. 3.

[15] M. Blume and R. E. Watson, Proc. Roy. Soc. (London) **A271**, 565 (1963).

[16] *Atomic Energy Levels*, edited by C. E. Moore, Natl. Bur. Std. (U. S.) Circ. No. 467 (U. S. Government Printing Office, Washington, D. C., 1949).

ZnS:Si. This is contradictory to the experimental results. The agreement between the calculated and the observed Δg's seems fairly good. Although this is perhaps fortuitous because of the crudeness of the parameters used, the sign and the order of magnitude of the g shifts seems to be interpreted qualitatively on the theory based on our proposed model.

The observed spin densities, $\rho_s(0)$, are extremely large. We will tentatively compare the observed values with those of the s orbitals of the free atoms. Available values of $|\psi_s(0)|^2_{\text{free}}$ of neutral atoms[17,18] calculated from Hartree-Fock wave functions are also listed in Table II. The observed densities are approximately 60% of those of free atoms. Any quantitative discussion of these values could hardly be fruitful from (10) in our crude one-electron linear-combination-of-atomic-orbitals approximation. Quantitative calculations of the unpaired spin densities would require the detailed knowledge of wave function for unpaired electron and of the inner core polarization.

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Effects of Atomic Degeneracy and Cavity Anisotropy on the Behavior of a Gas Laser

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Expressions are developed in this paper which describe the behavior of a gas laser having generalized polarization characteristics. It is found that degeneracies of the atomic energy levels play an important part in determining the behavior of such a laser since significant terms occur in the nonlinear polarization which are attributable to an oscillatory mixing of these levels. As a result, it is found, for example, that for single-mode operation the field intensity is greatest for either plane or circular polarization depending upon whether a $\Delta j = \pm 1$ or $\Delta j = 0$ atomic transition is involved in the laser action. For two-mode operation, on the other hand, the behavior depends in a complicated way both on the polarization states of the oscillations and on the degree of degeneracy of the energy levels. This behavior is discussed in a number of special cases.

I. INTRODUCTION

In this paper, we extend Lamb's theory of an optical maser[1] to cover systems involving degenerate atomic energy levels and optical oscillations having arbitrary states of polarization. Our treatment is specifically aimed at determining the output characteristics of gas lasers which utilize generalized anisotropic resonant cavities. Such lasers are of interest because of the unambiguous control of their frequency and polarization characteristics which is made possible by the use of nonresonant intra-cavity anisotropic components. In addition to forming the basis for a number of practical devices,[2,3] this control is quite useful in the study of the fundamental atomic phenomena governing laser behavior.

A recent theoretical and experimental study of the properties of a Fabry-Perot resonator containing an array of retardation plates and Faraday rotators has established that each longitudinal mode of such a cavity is split into two distinct resonances.[3] The frequency separation between these resonances is dependent upon the strength of the anisotropic effects and their preferred states of polarization are in general elliptical and orthogonal. The introduction of anisotropic losses into such a resonator can furthermore break down the orthogonality of the preferred polarization states and, in extreme cases, can restrict oscillation to a single polarization. In the discussion below, we will thus give particular attention to lasers whose oscillations belong to two distinct, but not necessarily orthogonal, states of polarization.

Our theoretical approach is quite similar to that of Lamb, the chief distinctions being our explicit treatment of the vectorial nature of the electromagnetic field and of the degeneracies of the atomic system. In the sections below, the reader will thus be referred to Lamb's work for more detailed discussions of some of the conditions of the problem and for treatment of those calculative details which are common to the two works. It should

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[1] Willis E. Lamb, Jr., Phys. Rev. **134**, A1429 (1964).
[2] W. M. Doyle, W. D. Gerber, P. M. Sutton, and M. B. White, IEEE J. Quantum Electron. **QE-1**, 181 (1965).
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