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Isotope Shift in Magnesium

JOHN P. VINTI
Worcester Polytechnic Institute, Worcester, Massachusetts

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A theoretical investigation is made to see whether nuclear motion alone can account for observed fine structure in magnesium, especially for the lines $3\,{}^1S_0-3\,{}^1P_1$, $3\,{}^1S_0-3\,{}^3P_1$, $3\,{}^1P_1-3\,{}^1D_2$, $3\,{}^3P-3\,{}^3D$, and the limit of the series $3\,{}^1P_1-n\,{}^1D_2$. Both by calculation with explicit radial functions and by the choice of theoretical parameters to fit observed shifts, it is shown that the values of the core-valence parameters occurring in the theory are not at all negligible, so that a two-electron model would not be permissible. Calculations with explicit radial functions give correct signs for the specific shifts of all these lines except for the limiting shift of $3\,{}^1P_1-n\,{}^1D_2$. In the case of the line $3\,{}^1P_1-3\,{}^1D_2$ the correct sign is obtained only when one takes into account the perturbation of $(3s)\ (3d)\ {}^1D_2$ by $(3p)^2\,{}^1D_2$; however, greater accuracy in the solution of the perturbation problem could not improve the agreement very much as long as the present radial functions are used. The total shift of any member of $3\,{}^3P-3\,{}^3D$ comes out much smaller than any of the other total shifts, in agreement with Meissner's observation of the sharpness of its members. A test of the theory independent of the use of explicit radial functions is carried out by adjusting the theoretical parameters so as to give the observed shifts of the five lines mentioned. According to the theory, all these parameters are essentially positive; the necessary values of the parameters do indeed all turn out to be positive, provided that the value of Jackson and Kuhn is accepted in preference to that of Fisher for the shift of the resonance line. The shift of the line $3\,{}^1P_1-5\,{}^1S_0$ and the sharpness of the lines $3\,{}^3P-4\,{}^3S$ afford independent evidence that Fisher's value is incorrect, or else that nuclear motion is not the sole cause of the shift in the resonance line $3\,{}^1S_0-3\,{}^1P_1$. There also arises an inconsistency unless the perturbation of $(3s)\ (3d)\ {}^1D_2$ by $(3p)^2\,{}^1D_2$ is taken into account. The necessary values of the parameters are shown by the estimate of corresponding f values to be reasonable both as to their absolute and as to their relative values. With certain acceptable assumptions, it is shown that if the shifts in Mg are due to nuclear motion alone, then three relations may be deduced connecting the specific shifts. These are: (1) the specific shifts of the resonance line $3\,{}^1S_0-3\,{}^1P_1$ and of any member of $3\,{}^3P-(3p)^2\,{}^3P$ must be equal; (2) (for any members) the sum of the specific shifts of the lines $3\,{}^3D-(3p)\ (3d)\ {}^3D$ and $3\,{}^3P-3\,{}^3D$ must equal the sum of the specific shifts of the lines $(3p)^2\,{}^3P-(3p)\ (3d)\ {}^3D$ and $3\,{}^1S_0-3\,{}^1P_1$; (3) a complicated quadratic relation involving the specific shifts of the five lines $3\,{}^1S_0-3\,{}^1P_1$, $3\,{}^1S_0-3\,{}^3P_1$, $3\,{}^1P_1-3\,{}^1D_2$, $3\,{}^3P-3\,{}^3D$, and $(3p)^2\,{}^3P-(3p)\ (3d)\ {}^3D$, as well as the interaction parameter α for $3\,{}^1D_2$. With the use of known shifts, including the Jackson-Kuhn value for the resonance line, these relations lead to the prediction (for any member) of total shifts of 0.035 cm^{-1} for $\lambda2778$ to $2784=3\,{}^3P-(3p)^2\,{}^3P$, of 0.027 cm^{-1} for $\lambda3890$ to $3900=(3p)^2\,{}^3P-(3p)\ (3d)\ {}^3D$, and of 0.061 cm^{-1} for $\lambda2810$ to $2812=3\,{}^3D-(3p)\ (3d)\ {}^3D$. It is concluded that the quantum-mechanical theory of nuclear motion, without the assumption of non-Coulomb nuclear fields or of nuclear spins, gives a good qualitative explanation of fine structure in magnesium. It appears that a measurement of the shifts of lines $\lambda2778$ to 2784, $\lambda3890$ to 3900, and $\lambda2810$ to 2812 would furnish the best quantitative test.

INTRODUCTION

MAGNESIUM is known to occur in three isotopes, 24, 25, and 26, with relative abundances very close to 7 : 1 : 1. Various experimenters[1] have investigated the fine structure[2] of Mg I. Before the investigations of Meissner[1] all lines that showed fine structure were found to have two components only. Using the method of atomic beams, Meissner found, for most of the lines showing structure, three components that were practically equally spaced, the lowest frequency component being the most intense in each case and the two much weaker components of higher frequency being of about equal intensity. Meissner's results, together with the abundance ratios, point strongly to this fine structure as being purely a mass effect, i.e., as arising purely from nuclear motion and not from nuclear fields differing for each isotope or from nuclear spin. We may identify the main component in each case as due to isotope 24, and the two weaker components as due to isotopes 25 and 26, the order probably being 24, 25, 26; there seems to be no evidence of splitting due to nuclear spin even in the case of isotope 25.

For the series $3\,{}^1P_1-n\,{}^1D_2$ Meissner found $\nu_{26}-\nu_{24}$ to be $+0.0831$ cm^{-1} for $n=3$ and $+0.056$ cm^{-1} for the limit $n=\infty$; the latter figure may

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[1] R. F. Bacher and R. A. Sawyer, Phys. Rev. **47**, 587 (1935); D. A. Jackson and H. Kuhn, Proc. Roy. Soc. **A154**, 679 (1936); R. A. Fisher, Phys. Rev. **51**, 381 (1937); K. W. Meissner, Ann. d. Physik **31**, 505 (1938).

[2] The expression "fine structure" is used in the present paper to denote, without assumption as to origin, any nonelectric nonmagnetic splitting of a singlet line or of any member of a set of multiplet lines.

be regarded as the shift of a "line" $3\,^1P-3\,^2S$ (Mg II). He also found each member of $3\,^3P-3\,^3D$ and of $3\,^3P-4\,^3S$ to be sharp, so that the shifts must be very small in these cases. Bacher and Sawyer[1] found a shift of $+0.083$ cm^{-1} for the intercombination line $3\,^1S_0-3\,^3P_1$; since in those cases where Bacher and Sawyer and Meissner investigated the same lines, the shift found by Bacher and Sawyer agrees rather well with Meissner's $\nu_{26}-\nu_{24}$, we may attribute this to $\nu_{26}-\nu_{24}$. For the resonance line $3\,^1S_0-3\,^1P_1$ Fisher[1] found a shift of $+0.066$ cm^{-1} and Jackson and Kuhn[1] found $+0.033$ cm^{-1}.

Besides the work of Meissner, the general facts that no nonzero nuclear spins have been detected for elements of both even atomic number and even mass number[3] and that non-Coulomb nuclear fields have thus far been found to be of possible importance only in heavy atoms,[3] apparently leave no explanation for the shifts in Mg except nuclear motion. In this paper we shall investigate, as completely as current theory allows, whether nuclear motion does fully account for the shifts above mentioned. We shall consider especially the shifts of the lines $3\,^1S_0-3\,^1P_1$, $3\,^1S_0-3\,^3P_1$, $3\,^1P_1-3\,^1D_2$, $3\,^3P-3\,^3D$, and $3\,^3P-3\,^2S$ (Mg II); we shall also be able from the above observed shifts to predict, without the use of special radial wave functions, the shifts of the line $3\,^3P-(3p)^2\,^3P$ discovered by Bowen and Millikan[4] and of the lines $(3p)^2\,^3P-(3p)(3d)\,^3D$ and $3\,^3D-(3p)(3d)\,^3D$ discovered by Paschen.[5]

General Theory

Let H_0 and E_0 be the energy operator and a corresponding energy for a ν-electron atom, the nucleus being supposed fixed. Then the effect of nuclear motion can be expressed exactly by the addition to H_0 of a term[6]

$$G\equiv(2M)^{-1}\Big(\sum_{i=1}^{\nu}\mathbf{p}_i\Big)^2,$$

where M is the nuclear mass and $\mathbf{p}_i$ the momentum of the ith electron relative to the nucleus. We shall write $G\equiv N+\sigma$, where

$$N\equiv(2M)^{-1}\sum_{i=1}^{\nu}\mathbf{p}_i^2,\quad\text{and}\quad \sigma\equiv M^{-1}\sum_{i>j}\sum\mathbf{p}_i\cdot\mathbf{p}_j,$$

the summations being extended over all the electrons, 12 in the case of Mg **I**. N is called the "normal" term and σ the "specific" term. Suppose now that one knows the energy E_0 and the wave function of a given state for the case of a fixed nucleus ($M=\infty$); then the problem becomes one in perturbation theory, since G is small compared to H_0. Before considering the perturbation problem, however, we may mention that the effect of the term N alone can always be given exactly[6] (spin-orbit forces being left out of account): *viz.*, replace E_0 by $E_0(1+m/M)^{-1}$, where m denotes the electronic mass. This statement follows from the fact that the potential energy V is homogeneous of degree -1; i.e., $V(\xi x_1\cdots\xi z_\nu)=\xi^{-1}V(x_1\cdots z_\nu)$. Thus if $\psi(x_1\cdots z_\nu)$ satisfies the wave equation with electron mass m and energy E_0, one finds on making the transformation $x_k=\xi x_k'$ that $\psi(\xi x_1'\cdots\xi z_\nu')$ satisfies the equation with electron mass $m\xi$ and energy $E_0\xi$. Then since the effect of N is to add $1/M$ to $1/m$, we must put $\xi=M/(m+M)=(1+m/M)^{-1}$. Thus if σ were negligible, we should have, letting E denote the total energy corresponding to H_0+N: $E=E_0-(m/M)E$, so that the part of the observed total energy due to N would be given exactly by $-(m/M)E$.

In the perturbation problem let us consider only the case of LS coupling, and suppose that the unperturbed wave functions make H_0 and the operators corresponding to S, L, J, and M_J diagonal. There arises a question about the degeneracy due to M_J; this difficulty is at once resolved, however, since both N and σ commute with the operators corresponding to S, L, J, and M_J. Thus N and σ are already almost diagonal with respect to the unperturbed wave functions, having no components between unperturbed states of different S, L, J, or M_J (or of different S, L, M_L, or M_S if that representation is the starting one); they may have components between states which, in an approximation in which H_0 is not diagonal, can perturb each other. They have no components between states of equal energy, so that the perturbation theory

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[3] H. A. Bethe and R. F. Bacher, Rev. Mod. Phys. **8**, 82 (1936). Cf. pp. 217 and 225.

[4] I. S. Bowen and R. A. Millikan, Phys. Rev. **26**, 150 (1925).

[5] F. Paschen, Ann. d. Physik **12**, 509 (1932).

[6] D. S. Hughes and C. Eckart, Phys. Rev. **36**, 694 (1930).

for nondegenerate systems may be applied at once. In the first order we have the familiar result that each state simply gets an additional energy equal to $\bar{N}+\bar{\sigma}$, where the bar denotes the diagonal element with respect to the unperturbed wave function. It is easily seen that the second approximation in each case leads to a correction which is smaller by a factor of the order m/M.

The term $\bar{N}$ can easily be calculated by use of the virial theorem for a Coulombian system. Since $N=(m/M)T$, where T is the operator for the kinetic energy of the electrons, we have $\bar{N}=(m/M)\bar{T}$; the virial theorem tells us that, spin-orbit forces being neglected, $\bar{T}=-E_0$, so that $\bar{N}=-(m/M)E_0$. The spin-orbit restriction means that in this approximation $\bar{N}$ has the same value for all J values of a given multiplet. We have here a check on our neglect of higher approximations in the perturbation problem: with spin-orbit neglect, an exact theory gives $-(m/M)E$ and first-order theory gives $-(m/M)E_0$ for the correction due to N; the difference is entirely negligible. We may thus feel safe in applying first-order theory also for the effect of σ.

We should now show that $\bar{\sigma}$ (as well as $\bar{N}$) has the same value for all J and M_J of a given multiplet, at least to the approximation that we shall use for our wave functions. This independence is physically reasonable, since dependence on M_J would indicate something like a Zeeman effect due to nuclear motion and dependence on J would be expected only for a perturbation like a spin-orbit interaction. To show it, suppose we start with a system of approximate wave functions, linear combinations of determinants, which form an orthonormal system and make the operators for S, L, M_L, and M_S diagonal. If there are any important configuration interactions, this system of functions is supposed to take that fact into account. Now suppose an operator K commutes with an angular momentum $\mathbf{P}$, where the eigenvalues of $\mathbf{P}^2$ are $P(P+1)h^2/4\pi^2$ and those of P_z are $M_P h/2\pi$. Then not only is K diagonal in a representation in which $\mathbf{P}^2$ and P_z are diagonal, but the diagonal components of K in such a representation are independent of M_P.[7] Now it is easily shown that σ or N commutes with any component of $\mathbf{L}$ or $\mathbf{S}$, where $\mathbf{L}$ denotes the total orbital angular momentum and $\mathbf{S}$ the total spin angular momentum. Thus we must obtain the same $\bar{\sigma}$ for all M_L and M_S of a given multiplet. Then, performing a unitary transformation to the $SLJM_J$ scheme, we easily prove that the same $\bar{\sigma}$ results for all J and M_J of the multiplet. The same argument applies to $\bar{N}$, so that the procedure for $\bar{N}$, which led to a value independent of J or M_J, is consistent with such a system of wave functions.

The above discussion covers the cases where configuration interaction is or is not negligible, and shows that in either case we may use SLM_LM_S functions rather than $SLJM_J$ functions. For the cases where configuration interaction is negligible, we shall use the Slater[8] method of diagonal sums, so that in such cases we need not find even the SLM_LM_S functions. All that we shall then need will be diagonal elements of σ with respect to certain of the determinants (slm_lm_s functions) corresponding to the multiplet.

THE MATRIX ELEMENTS

Let $A_\rho(r, \theta, \phi, \sigma_z)$ denote the total function for the ρth orbit, the product of the space function $a_\rho(r, \theta, \phi)$ and the spin function $\delta_\rho(\sigma_z)$; the functions a_ρ are supposed to form an orthonormal set. Let U be the normalized determinantal wave function corresponding to the configuration A_1, A_2, $\cdots A_r \cdots A_t \cdots A_\nu$ and U' that corresponding to A_1, A_2, $\cdots A_{r'} \cdots A_{t'} \cdots A_\nu$, so that U and U' differ by two orbits. Then, since

$$\sigma=M^{-1}\sum_{i>j}\sum \mathbf{p}_i\cdot\mathbf{p}_j,$$

and since $(a_\rho|\mathbf{p}|a_\mu)=0$ unless $l_\mu-l_\rho=\pm 1$,[9] we have:[10]

$$(U|\sigma|U)=-M^{-1}\sum_{\mu>\rho}\sum |(a_\mu|\mathbf{p}|a_\nu)|^2\delta_{\mu\rho}, \tag{1}$$

$$\begin{aligned}(U|\sigma|U')=M^{-1}[&(a_r|\mathbf{p}|a_{r'})\cdot(a_t|\mathbf{p}|a_{t'})\delta_{rr'}\delta_{tt'}\\ &-(a_r|\mathbf{p}|a_{t'})\cdot(a_t|\mathbf{p}|a_{r'})\delta_{rt'}\delta_{tr'}].\end{aligned} \tag{2}$$

In these equations $\delta_{\mu\rho}$, e.g., is a Kronecker delta on the spins of the μth and ρth orbits; in

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[7] E. U. Condon and G. S. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, 1935), p. 49.

[8] J. C. Slater, Phys. Rev. **34**, 1293 (1929).

[9] This relation holds even if a_μ and a_ρ correspond to different central fields.

[10] J. C. Slater, Phys. Rev. **38**, 1115 (1931). Reference 7, p. 173.

Eq. (1) the summations are over all occupied orbits; throughout the paper we abbreviate the scalar product of a complex vector **C** and its complex conjugate $\mathbf{C}^*$ to $|\mathbf{C}|$.[2] $(U|\sigma|U')$ is the only type of nondiagonal matrix element that we shall need, and we shall need it only in the case where configuration interaction is allowed for. In listing values of $(U|\sigma|U)$ and of $\bar{\sigma}$ we shall omit an additive term which pertains only to the neon-like core and is thus common to all spectral terms, therefore canceling out when we take differences to find shifts of lines.

We now need general formulas for the one-electron matrix elements of momentum $(nlm_l|\mathbf{p}|n'l'm_l')$. We adopt the Condon and Shortley[11] convention for the signs of the angle functions, so that the usual formulas for angular momentum operators acting on the angle functions hold for all m_l; this makes for convenience in examining wave functions for angular momentum properties in those cases where they have to be written down explicitly. We next use the formulas of Bethe[12] for the result of $\partial/\partial x$, $\partial/\partial y$, and $\partial/\partial z$ on the product of the normalized angle function and any function of the radius r, realizing that the Bethe angle function $Y_B(l, m_l)$ and the Condon-Shortley angle function $Y_C(l, m_l)$ are connected by the relation $Y_B=(-1)^{m_l}Y_C$. We of course find the selection rules $\Delta l=\pm 1$ for the matrix elements of any component of momentum, $\Delta m_l=\pm 1$ for those of p_x and p_y, and $\Delta m_l=0$ for those of p_z. We also obtain the following formulas, from which, because of the Hermitian property of the matrix of **p**, all the nonvanishing matrix elements of **p** may be found:

$$\begin{aligned}
&(n, l, m_l|p_x|n', l-1, m_l\mp 1)\\
&\quad =\pm(i/2)C_l[(l\pm m_l-1)(l\pm m_l)]^{\frac{1}{2}}\\
&\qquad\qquad \times F(n, l; n', l-1)\\
&(n, l, m_l|p_y|n', l-1, m_l\mp 1)\\
&\quad =(\tfrac{1}{2})C_l[(l\pm m_l-1)(l\pm m_l)]^{\frac{1}{2}}\\
&\qquad\qquad F(n, l; n', l-1) \qquad (3)\\
&(n, l, m_l|p_z|n', l-1, m_l)\\
&\quad =-iC_l(l^2-m_l^2)^{\frac{1}{2}}F(n, l; n', l-1),
\end{aligned}$$

where

$$C_l\equiv[(2l+1)(2l-1)]^{-\frac{1}{2}}$$

and

$$F(n, l; n', l-1)\equiv(h/2\pi)\int_0^\infty R(nl)\Big\{dR(n, l-1)/dr -[(l-1)/r]R(n, l-1)\Big\}r^2dr,$$

$R(nl)$ being the radial function for the orbit nl, so normalized that

$$\int_0^\infty R^2r^2dr=1.$$

Eqs. (3) lead at once to Eqs. (4), which are all that we need for the case in which configuration interaction plays no role:

$$\begin{aligned}
&|(n, l, m_l|\mathbf{p}|n', l-1, m_l)|^2\\
&\quad =C_l^2(l^2-m_l^2)F(n, l; n', l-1)\\
&|(n, l, m_l|\mathbf{p}|n', l-1, m_l\mp 1)|^2\\
&\quad =(\tfrac{1}{2})C_l^2(l\pm m_l-1)(l\pm m_l)F^2(n, l; n', l-1). \qquad (4)
\end{aligned}$$

Eqs. (4) agree with the expressions developed by Bartlett and Gibbons[13] by a somewhat easier but less straightforward method. We have outlined the above derivation because we need Eqs. (3) as well as Eqs. (4), when we come to treat perturbed levels. At this point a change of units is useful; one easily shows that:

$$\begin{aligned}
F(n, l; n', l-1)&=(h/2\pi a_0)J(n, l; n', l-1)\\
&=(2mRy)^{\frac{1}{2}}J(n, l; n', l-1), \qquad (5)
\end{aligned}$$

where

$$J(n, l; n', l-1)\equiv\int_0^\infty R(nl)\left[\frac{dR(n, l-1)}{dr}-\frac{l-1}{r}R(n', l-1)\right]r^2dr,$$

where a_0 is the Bohr radius, Ry the Rydberg energy, and r is the radius expressed in units of a_0; because of this change of units $R(r)$ in Eq. (5) has a functional form different from $R(r)$ in Eq. (3).

FORMULAS FOR THE SPECIFIC SHIFT FOR CASES IN WHICH CONFIGURATION INTERACTION IS NEGLIGIBLE

We proceed to calculate $\bar{\sigma}$ in terms of the integrals $J(n, l; n', l-1)$ for those spectral terms

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[11] Reference 7, p. 52.

[12] H. A. Bethe, *Handbuch der Physik*, Vol. 24, No. 1, p. 558.

[13] J. H. Bartlett, Jr. and J. J. Gibbons, Jr., Phys. Rev. **44**, 538 (1933). There is an error in their formula for their $C(l, l-1)$, consisting of an interchange of subscripts.

for which configuration interaction may be neglected; for our present problem of magnesium this means all terms arising from 3-quantum orbits except $(3s)(3d)\ {}^1D_2$ and $(3p)^2\ {}^1D_2$. We use the Slater diagonal sum method and Eqs. (1), (4), and (5), and we write the formulas without the term common to all spectral terms.

For $(3s)^2\ {}^1S$ and $3s\ {}^2S$(MgII) the wave functions are single determinants corresponding respectively to the configurations $3s^+\ 3s^-$ and $3s^\pm$. (Superscript signs denote m_s values and subscripts where necessary denote m_l values.) The value of $\bar{\sigma}$ for $(3s)^2\ {}^1S$ comes out double that for $3s\ {}^2S$, which is

$$-M^{-1}\sum_{m_l=-1}^{+1}|(2p_{m_l}|\mathbf{p}|3s)|^2=-2(m/M)RyJ^2(2p,\,3s).$$

The configuration $(3s)(3p)$ will serve to illustrate the use of the diagonal sum method. Noting that $3s^+\ 3p_1{}^+$ belongs only to the triplet, one has for $3\ {}^3P$:

$$\bar{\sigma}=-M^{-1}\Big[\sum_{m_l=-1}^{+1}|(2p_{m_l}|\mathbf{p}|3s)|^2+\sum_{n=1}^{3}|(3p_1|\mathbf{p}|ns)|^2\Big]$$
$$=-2(m/M)Ry\Big[J^2(2p,\,3s)+\tfrac{1}{3}\sum_{n=1}^{3}J^2(3p,\,ns)\Big].$$

One also notes that $\Sigma m_s=\Sigma m_l=0$ for each of $3s^+\ 3p_0{}^-$ and $3s^-\ 3p_0{}^+$, and that these relations hold for no other choices of the m_s's and m_l's; thus each of these determinants belongs to the singlet with $M_S=M_L=0$ and to the triplet with $M_S=M_L=0$. The diagonal sum rule then tells us that the sum of the $\bar{\sigma}$'s for the singlet and the triplet is given by evaluating the sum in Eq. (1) for each of these determinants and adding the results. This sum turns out to be:

$$-4(m/M)Ry\Big[J^2(2p,\,3s)+\tfrac{1}{3}\sum_{n=1}^{2}J^2(3p,\,ns)\Big].$$

By difference we obtain for $3\ {}^1P$:

$$-2(m/M)Ry\Big[J^2(2p,\,3s)+\tfrac{1}{3}\Big\{\sum_{n=1}^{2}J^2(3p,\,ns)-J^2(3p,\,3s)\Big\}\Big].$$

For $(3s)(3d)$ the results for the singlet and the triplet come out equal, perturbation by $(3p)^2$ being left out of account. This result, which is $-2(m/M)Ry[J^2(2p,\,3s)+(\frac{2}{5})J^2(3d,\,2p)]$, we can accept only for the triplet, which is unperturbed by $(3p)^2$. For $(3p)^2$, with perturbation of the ${}^1S$ by $(3s)^2\ {}^1S$ and of the ${}^1D$ by $(3s)(3d)\ {}^1D$ left out of account, the same value is obtained for the ${}^3P$, the ${}^1S$, and the ${}^1D$, *viz.*

$$-4/3(m/M)Ry\sum_{n=1}^{2}J^2(3p,\,ns);$$

this result is acceptable for the ${}^3P$, since it is unperturbed. For $(3p)(3d)$ the values of $\bar{\sigma}$ are

$$-2(m/M)Ry\Big[\tfrac{1}{3}\sum_{n=1}^{2}J^2(3p,\,ns)+\tfrac{2}{5}J^2(3d,\,2p)+\eta J^2(3d,\,3p)\Big],$$

where for ${}^1P$, ${}^3P$, ${}^1D$, ${}^3D$, ${}^1F$, ${}^3F$ the values of η are, respectively, $-1/15$, $1/15$, $\frac{1}{5}$, $-\frac{1}{5}$, $-\frac{2}{5}$, $\frac{2}{5}$. Since $(3p)(3d)\ {}^3D$ is of odd parity, it is not perturbed by $(3s)(3d)\ {}^3D$, so that the above formula may be considered acceptable for the ${}^3D$.

THE SPECIFIC SHIFT OF $3\ {}^1D_2$

There is good evidence that the level $(3s)(3d)\ {}^1D_2$ is rather strongly perturbed by the level $(3p)^2\ {}^1D_2$. The singlet lies well below the triplet, and the work of Bacher[14] indicates that the exchange integral which should give the singlet-triplet separation (if there were no perturbation) has such a sign as to put the singlet above the triplet. Furthermore, on computing the effect of the level $(3p)^2\ {}^1D_2$ on $(3s)(3d)\ {}^1D_2$, Bacher finds that such a perturbation puts the singlet below the triplet, in fact about 2200 cm^{-1} below as compared with the observed 1550 cm^{-1}.[15]

We must thus find a wave function for $(3s)(3d)\ {}^1D$ that will allow for admixture of $(3p)^2\ {}^1D$, and calculate the corresponding specific shift. Such a wave function may be written in the form:

$$\Psi=(1+|\alpha|^2)^{-\frac{1}{2}}(\psi_1+\alpha\psi_2), \tag{6}$$

where ψ_1 and ψ_2 are normalized wave functions for $(3s)(3d)\ {}^1D$ and $(3p)^2\ {}^1D$, respectively, that do not take account of configuration interaction. The quantity α is a coefficient that will have an absolute value less than 1 for the perturbed $(3s)(3d)\ {}^1D$ and an absolute value greater than 1

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[14] R. F. Bacher, Phys. Rev. **43**, 264 (1933).
[15] R. F. Bacher, Phys. Rev. **56**, 385 (1939).

for the perturbed $(3p)^2\ {}^1D$; the factor involving α is prefixed for normalization. The usual diagonalizing process leads to the equations for α:

$$\begin{aligned} (H_{11}-E)+H_{12}\alpha&=0\\ H_{21}+(H_{22}-E)\alpha&=0, \end{aligned} \tag{7}$$

where H_{11}, H_{22}, H_{12}, and H_{21} are matrix elements of H_0 with respect to ψ_1 and ψ_2. The corresponding secular equation is:

$$\begin{vmatrix} H_{11}-E & H_{12}\\ H_{21} & H_{22}-E \end{vmatrix}=0, \tag{8}$$

the roots of which give the energies of the two perturbed ${}^1D$'s.

At this point we must decide on what radial functions to use for $3s$, $3p$, and $3d$. The only available functions are those given by Bacher.[14] We write them below with slight corrections in the normalizations and with the constant exponentials in the 3d function expressed numerically; also our R's are such that

$$\int_0^\infty R^2r^2dr=1.$$

The unit of length is the Bohr radius a_0.

$$\begin{aligned} R(3s)&=(2.8191)^{-1}(-e^{-0.95r}r^2\\ &\qquad+11.96e^{-3.92r}r-6.86e^{-11.70r}),\\ R(3p)&=(2.3526)^{-1}(e^{-1.00r}r^2-10.43e^{-3.90r}r),\\ R(3d)&=-10^{-3}(52.155e^{-0.70r}r^2\\ &\qquad+7.0691e^{-0.35r}r^2). \end{aligned} \tag{9}$$

Since these functions are admittedly none too accurate, we shall not use them in a straightforward way to calculate α, but shall determine the quantities involved as much as possible by the use of experimental data. By the usual spectral theory one has for the energy of $(3s)(3d)\ {}^3D$, which is unperturbed by $(3p)^2$, the expression $F_1-\frac{1}{5}R_b$, and for H_{11} the expression $F_1+\frac{1}{5}R_b$, where F_1 is a constant that does not concern us, and R_b is one of Bacher's integrals, $\frac{1}{5}R_b$ being the usual singlet-triplet exchange integral. Using $R_b=+10{,}190$ cm^{-1} as determined from the above radial functions and the observed energy of $(3s)(3d)\ {}^3D=-13{,}715$ cm^{-1}, the ionization limit being taken as the zero, we obtain $H_{11}=-9639$ cm^{-1}. Again, from the Slater theory for p^2, we have $H_{22}=F_2+(1/25)R_e$, and the energy of $(3p)^2\ {}^3P$ (which is unperturbed by $(3s)(3d)$) $=F_2-(\frac{1}{5})R_e$. F_2 is a constant that does not concern us, and R_e, one of Bacher's integrals, comes out $+29{,}940$ cm^{-1} with the above radial functions; equating $F_2-(\frac{1}{5})R_e$ to the observed energy of $(3p)^2\ {}^3P$, *viz.* -3819 cm^{-1}, we find $H_{22}=+3367$ cm^{-1}. For E we use the observed value for $(3s)(3d)\ {}^1D$, *viz.* $-15{,}269$ cm^{-1}. With these values for H_{11}, H_{22}, and E, Eq. (8) gives $|H_{12}|=10{,}240$ cm^{1}. Direct calculation of H_{12} with the same choice of constant phases for ψ_1 and ψ_2 that we later use and the same choice of signs for the radial functions as in Eqs. (9) leads to a positive real value for H_{12}; thus $H_{12}=+10{,}240$ cm^{-1}, so $H_{21}=H_{12}$, and α comes out real. Eqs. (7) now readily give $\alpha=-0.550$. From Eq. (6) we have:

$$\begin{aligned} \bar{\sigma}\equiv(\Psi|\sigma|\Psi)=(1+\alpha^2)^{-1}[(\psi_1|\sigma|\psi_1)\\ +\alpha^2(\psi_2|\sigma|\psi_2)+\alpha(\psi_1|\sigma|\psi_2)+\alpha(\psi_2|\sigma|\psi_1)]. \end{aligned} \tag{10}$$

Also, one easily verifies by applying the proper angular momentum operators that:

$$\begin{aligned} \psi_1&=2^{-\frac{1}{2}}\,(U_1-U_2)\\ \psi_2&=U_3, \end{aligned} \tag{11}$$

where U_1, U_2, and U_3 are the normalized determinants corresponding, respectively, to $3s^+3d_2^-$, $3s^-3d_2^+$, and $3p_1^+\,3p_1^-$. From Eqs. (11), (1), and (2) we obtain:

$$\begin{aligned} (\psi_1|\sigma|\psi_1)=-M^{-1}[\sum_{m_l}|(2p_{m_l}|\mathbf{p}|3s)|^2\\ +\sum_{m_l}|(3d_2|\mathbf{p}|2p_{m_l})|^2], \end{aligned} \tag{12a}$$

$$(\psi_2|\sigma|\psi_2)=-2M^{-1}\sum_{n=1}^{2}|(3p_1|\mathbf{p}|ns)|^2, \tag{12b}$$

$$\begin{aligned} (\psi_1|\sigma|\psi_2)=(\psi_2|\sigma|\psi_1)^*=2^{\frac{1}{2}}M^{-1}(3s|\mathbf{p}|3p_1)\\ \cdot(3d_2|\mathbf{p}|3p_1). \end{aligned} \tag{12c}$$

Eqs. (12a) and (12b), by the use of Eqs. (4) and (5), and Eq. (12c), by the use of Eqs. (3) and (5), can be expressed as:

$$\begin{aligned} (\psi_1|\sigma|\psi_1)&=-2(m/M)Ry[J^2(2p,\,3s)\\ &\qquad+(2/5)J^2(3d,\,2p)],\\ (\psi_2|\sigma|\psi_2)&=-4/3(m/M)Ry\sum_{n=1}^{2}J^2(3p,\,ns),\\ (\psi_1|\sigma|\psi_2)+(\psi_2|\sigma|\psi_1)&=(8)(15)^{-\frac{1}{2}}(m/M)Ry\\ &\qquad\times J(3p,\,3s)J(3d,\,3p). \end{aligned} \tag{13}$$

Equations (10) and (13) then give for the perturbed $3\,{}^1D$:

$$\bar{\sigma}=-2(m/M)Ry(1+\alpha^2)^{-1}[J^2(2p,\,3s)$$

$$+(2/5)J^2(3d,\,2p)+(2/3)\alpha^2\sum_{n=1}^{2}J^2(3p,\,ns)$$

$$-4(15)^{-\frac{1}{2}}\alpha J(3p,\,3s)J(3d,\,3p)].\quad(14)$$

We now collect in Table I the formulas already obtained for the specific shift; we here list the formulas for the quantity k, where $\bar{\sigma}\equiv-2(m/M)\times Ryk$. In the case of $3s\,{}^2S$(Mg II) we put a prime on the $3s$ to indicate that it would be desirable to use a different $R(3s)$ in this case in computing $J(2p,\,3s)$. We also include $4\,{}^3S$ and $5\,{}^1S$ in the table for later purposes.

NUMERICAL CALCULATIONS

Suppose we have a line due to the transition $A\rightarrow B$. Let the total energy of state A be E_A, its electronic kinetic energy T_A, term value τ_A, the normal shift of an isotope of mass M (as compared with a nucleus of infinite mass) $N_A(M)$, the specific shift (as compared with that of $M=\infty$) $\sigma_A(M)$; also let $N_A(26)-N_A(24)\equiv\delta N_A$ and $\sigma_A(26)-\sigma_A(24)\equiv\delta\sigma_A$. Now, using the definition of N and the virial theorem and putting the energy difference equal to the term value difference with reversed sign, we have:

$$N_A(M)-N_B(M)=(m/M)(T_A-T_B)$$
$$=(m/M)(E_B{}^0-E_A{}^0)=(m/M)(\tau_A-\tau_B).\quad(15)$$

Also, using $\bar{\sigma}\equiv-2(m/M)Ryk$, we have

$$\sigma_A(M)-\sigma_B(M)=-2(m/M)Ry(k_A-k_B).\quad(16)$$

Now, expressing both ν's and E's in cm^{-1}, we have:

$$E_A(26)-E_A(24)=\delta N_A+\delta\sigma_A,\quad \nu_{26}=E_A(26)-E_B(26),$$

etc., from which

$$\Delta\nu\equiv\nu_{26}-\nu_{24}=\delta(N_A-N_B)+\delta(\sigma_A-\sigma_B).\quad(17)$$

TABLE I. *Formulas for the specific shifts in terms of the integrals J (n, l; n′, l−1).*

TERM	k (IN $\bar{\sigma}\equiv-2(m/M)Ryk$)
$3s\,{}^2S$(Mg II)	$J^2(2p,\,3s')$
$(3s)^2\,{}^1S$	$2J^2(2p,\,3s)$
$(3s)(3p)$	$J^2(2p,\,3s)+(1/3)\left[\sum_{n=1}^{2}J^2(3p,\,ns)+\eta J^2(3p,\,3s)\right]$, where $\eta=+1$ for ${}^3P$ and -1 for ${}^1P$.
$(3s)(3d)\,{}^3D$	$J^2(2p,\,3s)+(2/5)J^2\,(3d,\,2p)$
$(3s)(3d)\,{}^1D$	$(1+\alpha^2)^{-1}\left[J^2(2p,\,3s)+(2/5)J^2(3d,\,2p)+(2/3)\alpha^2\sum_{n=1}^{2}J^2(3p,\,ns)-4(15)^{-\frac{1}{2}}J(3p,\,3s)J(3d,\,3p)\right]$
$(3p)^2\,{}^3P$	$(2/3)\,[J^2(3p,\,1s)+J^2(3p,\,2s)]$
$(3p)(3d)$	$1/3\sum_{n=1}^{2}J^2(3p,\,ns)+(2/5)J^2(3d,\,2p)+\eta J^2(3d,\,3p)$, where the values of η are given below*
$(3s)(4s)\,{}^3S$	$J^2(2p,\,3s)+J^2(2p,\,4s)$
$(3s)(5s)\,{}^1S$	$J^2(2p,\,3s)+J^2(2p,\,5s)$

* ${}^1P=-1/15$, ${}^3P=1/15$, ${}^1D=1/5$, ${}^3D=-1/5$, ${}^1F=-2/5$, and ${}^3F=2/5$.

TABLE II. *Uncorrected values of the J′s, calculated from radial functions.*

$nl;\,n',\,l-1$	$J'(n,\,l;\,n',\,l-1)$	$J'^2(n,\,l;\,n',\,l-1)$
$2p3s$	-0.2606	0.0679
$3p1s$	0.3911	0.1529
$3p2s$	-0.2911	0.0848
$3p3s$	0.2918	0.0851
$3d2p$	0.1148	0.01319
$3d3p$	0.4700	0.2209
$2p1s$	-3.125	
$2p2s$	-1.014	

Eqs. (15) and (16) give:

$$(\Delta\nu)_N\equiv\delta(N_A-N_B)=(1/26-1/24)(1838)^{-1}(\tau_A-\tau_B)$$
$$=(\tau_B-\tau_A)/573{,}460\text{ cm}^{-1},\quad(18)$$

$$(\Delta\nu)_\sigma\equiv\delta(\sigma_A-\sigma_B)=-(1/26-1/24)(1838)^{-1}2Ry(k_A-k_B)$$
$$=0.3827(k_A-k_B)\text{ cm}^{-1}.\quad(19)$$

To compute the k's we must compute the integrals $J(n,\,l;\,n',\,l-1)$; to do this we must have radial functions for $1s$, $2s$, and $2p$, besides those for $3s$, $3p$, and $3d$ given in Eqs. (9). Morse, Young, and Haurwitz[16] have obtained such functions for Mg^{++} by a variational method; we shall use their functions, thus making the assumption that the core functions are not appreciably affected by the presence of electrons in the M shell. They are:

$$R(1s)=2(\mu a)^{\frac{3}{2}}e^{-\mu ar},$$
$$R(2s)=2(\mu^5/3N_2)^{\frac{1}{2}}(e^{-\mu r}r-3A/\mu e^{-\mu br}),\quad(20)$$
$$R(2p)=2(\mu^5c^5/3)^{\frac{1}{2}}e^{-\mu cr}r,$$

where $a=3.21$, $\mu a=11.75$, $b=3.00$, $\mu b=10.96$, $2c\mu=7.55$, and $2\mu=7.31$. Also $A=(a+b)^3/(1+a)^4$ and $N_2=1-48A/(1+b)^4+3A^2/b^3$. The parameter A is so chosen that $R(2s)$ is orthogonal to $R(1s)$. The Bohr radius a_0 is the unit of length and the functions are so normalized that

$$\int_0^\infty R^2r^2dr=1.$$

However, our above $R(3s)$ is not quite orthogonal to $R(1s)$ or to $R(2s)$ nor $R(3p)$ to $R(2p)$. Since our fundamental equations (1) and (2) for the matrix elements are true only if the single electron functions form an orthonormal set, we shall have to correct for this lack of orthogonality. We denote values of $J(n,\,l;\,n',\,l-1)$ calculated from Eq. (5) with the use of Eqs. (9) and (20), and thus uncorrected for this lack of orthogonality, by adding primes as superscripts. Some elementary integrations then lead to Table II for $J'(n,\,l;\,n',\,l-1)$.

To make the corrections for lack of orthogonality, note that we start from slm_lm_s functions in the form of determinants; since the value of a determinant is not changed by adding a constant times a given row to another row, we may subtract from the $3p$ function enough of the $2p$ to produce orthogonality of $3p$ to $2p$ and from the $3s$ enough of the $1s$ and the $2s$ to produce orthogonality of $3s$ to $1s$ and $2s$. Let us denote the corresponding normalized orthogonalized radial functions by $R^0(3p)$ and $R^0(3s)$. Then, using these latter functions, the others being

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[16] Morse, Young, and Haurwitz, Phys. Rev. **48**, 948 (1935).

TABLE III. *Corrected values of the J's, calculated from radial functions.*

$n, l; n', l-1$	$J(n, l; n', l-1)$	$J^2(n, l; n', l-1)$
$2p3s$	-0.2772	0.0768
$3p1s$	0.4011	0.1609
$3p2s$	-0.2812	0.0791
$3p3s$	0.2879	0.0829
$3d2p$	0.1148	0.01319
$3d3p$	0.4689	0.2199

$J^2(3p, 1s)+J^2(3p, 2s)=0.2399$

unchanged, we shall have a right to apply the fundamental analysis resulting in Table I. We find:

$$R(3p)=c_1[R(3p)+\rho_1 R(2p)],$$
$$R(3s)=c_2[R(3s)+\rho_2 R(1s)+\rho_3 R(2s)],$$

where

$$c_1=1.0001,\quad c_2=1.0002,\quad \rho_1=-0.00984,$$
$$\rho_2=-0.001531,\quad \text{and}\quad \rho_3=0.02102.$$

The corrected J's are then easily expressed in terms of the uncorrected J's (including those for $2p\,1s$ and $2p\,2s$, for which reason we have inserted the values of the latter in Table II). The corrected J's are given in Table III; Tables I and III together give numerical values for the k's, listed in Table IV. In Table IV the value of k in the case $(3s)(3d)\,{}^1D$ is given for several values of α. The value $\alpha=0$ corresponds to no interaction with $(3p)^2\,{}^1D$ and the value $\alpha=-0.550$ to the interaction that we have actually found. It is seen that interaction increases the value of k. Since, however, our solution of the interaction problem may be somewhat in error, it is of interest also to know what is the largest value that interaction can give to k. This cannot be found by varying α arbitrarily and thus finding the maximum k, since only values $|\alpha|\leqq 1$ correspond to the term that we call $(3s)(3d)\,{}^1D$. Furthermore our analysis shows that α must be negative, and a simple calculation shows that k increases monotonically as α varies from 0 to -1; however, a value as large as 1 for $|\alpha|$ would undoubtedly be a good deal too large, since it would give equal importance to both configurations.

Using values of k from Table IV, observed term values [17] τ, and Eqs. (18) and (19), we obtain Table V below, giving a comparison of observed[18] and calculated total shifts and observed and calculated specific shifts for all lines arising from 3-quantum configurations for which the shifts have been measured. The observed specific shifts are obtained by subtracting the normal shifts (as calculated from Eq. (18)) from the observed total shifts. In regard to the line $3\,{}^3P-3\,{}^3D$ it is well to mention that Meissner was able to resolve this line so as to obtain the members corresponding to the triplet structure, but was unable to obtain any further resolution; the figure 0 is accordingly entered for $(\Delta\nu)_{\text{obs}}$ for this line. The high resolution which Meissner was able to obtain, as indicated by his success with the singlets and the small probable errors which he gives, leads one to believe that it must actually be zero at least to two decimal places. The line $3\,{}^1S-S\,{}^3P_1$ is an intercombination line, depending for its existence on departure from LS coupling; there is thus some question as to the applicability of the theory in this case, but since intercombination lines in Mg are weak compared to permitted lines, the departure from LS coupling is probably small, so we include this line also in our table. It may be noted also that values of $(\Delta\nu)_\sigma$ calculated from values of k obtained by neglecting the core-valence J's, and using only $J(3p, 3s)$ and $J(3d, 3p)$, disagree markedly with the calculated values of $(\Delta\nu)_\sigma$ in Table V. (In some cases they would lead to better agreement, in others to worse.) We may therefore conclude that a two-electron model is not permissible for calculating isotope shift in magnesium; any agreement thus obtained with experiment would be quite misleading.

A comparison of columns (5) and (6) of Table V shows that for the five lines calculated the calculated $\Delta\nu$ has the right order of magnitude for all but the first and last lines, being too small by a factor of about 2 for the first line and about $2\frac{1}{2}$ for the last line; it is interesting to note that the calculated $\Delta\nu$ for $3\,{}^3P-3\,{}^3D$, all members of which are sharp, comes out much smaller than the other $\Delta\nu$'s. A more severe test is obtained by comparing columns (3) and (7) for the specific

TABLE IV. *Values of k in* $\bar{\sigma}\equiv-2(m/M)Ry\,k$, *calculated from radial functions.*

TERM	k	
$3s\,{}^2S(\text{MgII})$	0.0768	
$(3s)^2\,{}^1S$	0.1537	
$(3s)(3p)\,{}^3P$	0.1844	
$(3s)(3p)\,{}^1P$	0.1292	
$(3s)(3d)\,{}^3D$	0.0821	
$(3s)(3d)\,{}^1D$	$(1+\alpha^2)^{-1}[0.0821-0.1394\alpha+0.1599\alpha^2]$	
	0.0821	(for $\alpha=0$)
	0.1591	(for $\alpha=-0.550$)
	0.1970	(for $\alpha=-1$)

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[17] The term values are taken from Bacher and Goudsmit, *Atomic Energy States*, except in the cases of $(3p)^2\,{}^3P$ and $(3p)(3d)\,{}^3D$, which are taken from Paschen, reference 5. The center of gravity is used for triplet levels.

[18] In the column for observed shifts, M= Meissner, F= Fisher, JK= Jackson and Kuhn, BS= Bacher and Sawyer, the references being given in footnote 1.

TABLE V. *A comparison of observed shifts with shifts calculated from radial wave functions.*

LINE	λ IN A	$(\Delta\nu)_{\sigma\text{CALC}}$ CM^{-1}	$(\Delta\nu)_N$ CM^{-1}	$(\Delta\nu)_{\text{CALC}}$ CM^{-1}	$(\Delta\nu)_{\text{OBS}}$ CM^{-1}	$(\Delta\nu)_{\sigma\text{OBS}}$ CM^{-1}
$3\,{}^1P-3s\,{}^2S$(MgII)		-0.0200	0.0464	0.0264	0.056(M) 0.066(F)	0.010 0.005(F)
$3\,{}^1S_0-3\,{}^1P_1$	2852	-0.0094	0.0611	0.0517	0.033(JK)	-0.028(JK)
$3\,{}^1S_0-3\,{}^3P_1$	4571	0.0118	0.0382	0.0499	0.083(BS)	0.045
$3\,{}^3P-3\,{}^3D$	3829 to 3838	-0.0392	0.0455	0.0063	0(M)	-0.045
$3\,{}^1P_1-3\,{}^1D_2$	8807	-0.0180 $(\alpha=0)$ 0.0114 $(\alpha=-0.55)$ 0.0236 $(\alpha=-1)$	0.01980	0.0018 $(\alpha=0)$ 0.0312 $(\alpha=-0.55)$ 0.0434 $(\alpha=-1)$	0.0831(M)	0.0633
$3\,{}^3P-(3p)^2\,{}^3P$	2778 to 2784		0.0627			
$(3p)^2\,{}^3P-(3p)(3d)\,{}^3D$	3890 to 3900		0.0448			
$3\,{}^3D-(3p)(3d)\,{}^3D$	2810 to 2812		0.0620			
$3\,{}^3P-4\,{}^3S$	5167 to 5184		0.0337		0(M)	-0.0337
$3\,{}^1P_1-5\,{}^1S_0$	5711		0.0305		0.0543(M)	0.0238

shifts alone. Even then, however, the sign comes out correct for all the lines but the first, provided that we accept the Jackson-Kuhn value for $3\,{}^1S_0-3\,{}^1P_1$, and we shall see that there is evidence for their value rather than Fisher's. In the case of the first "line" $3\,{}^2S(\text{Mg II})\rightarrow 3\,{}^1P$, for which the sign of the specific shift comes out wrong, we may attribute at least part of the discrepancy to the error made in using the same radial function for the $3s'$ of $3s\,{}^2S$(Mg II) as for the $3s$ in $(3s)(3p)$. In the case of the line $3\,{}^1P_1-3\,{}^1D_2$, it is seen that perturbation of $(3s)(3d)$ by $(3p)^2$ must be taken into account to get the correct sign for the specific shift, but that greater accuracy in the solution of the interaction problem cannot lead to a good numerical agreement, i.e., with the radial functions above used.

ANOTHER TEST OF THE THEORY

The test of the theory just given depends on the use of explicit radial functions, which are probably not very accurate. There is another method of testing the theory which does not depend on such explicit use of radial functions. We may calculate what values of the J^2's are necessary to give the observed shifts and then test the reasonableness of the J^2's by finding what f values they give.

Let us introduce the abbreviations $J^2(2p,3s')\equiv b_0$, $J^2(2p,3s)\equiv b_1$, $J^2(3p,1s)+J^2(3p,2s)\equiv b_2$, $J^2(3p,3s)\equiv b_3$, $J^2(3d,2p)\equiv b_4$, $J^2(3d,3p)\equiv b_5$, $J^2(2p,4s)\equiv b_6$, $J^2(2p,5s)\equiv b_7$, and let us denote the specific shifts of the lines $3\,{}^1P-3s\,{}^2S$(Mg II), $3\,{}^1S_0-3\,{}^1P_1$, $3\,{}^1S_0-3\,{}^3P_1$, $3\,{}^3P-3\,{}^3D$, $3\,{}^1P_1-3\,{}^1D_2$, $3\,{}^3P-(3p)^2\,{}^3P$, $(3p)^2\,{}^3P-(3p)(3d)\,{}^3D$, $3\,{}^3D-(3p)(3d)\,{}^3D$, $3\,{}^3P-4\,{}^3S$, and $3\,{}^1P_1-5\,{}^1S_0$ by $s_0, s_1, s_2, s_3, s_4, s_5, s_6, s_7, s_8$, and s_9, respectively. (Of these s_5, s_6, and s_7 are not yet known, but as we wish to predict them we include equations for them also). Then, putting $0.3827\equiv\gamma$ for short, we find from Eq. (19) and Table I:

$$b_0-b_1-(\tfrac{1}{3})b_2+(\tfrac{1}{3})b_3=s_0/\gamma, \tag{21.0}$$

$$-b_1+(\tfrac{1}{3})b_2-(\tfrac{1}{3})b_3=s_1/\gamma, \tag{21.1}$$

$$-b_1+(\tfrac{1}{3})b_2+(\tfrac{1}{3})b_3=s_2/\gamma, \tag{21.2}$$

$$-(\tfrac{1}{3})b_2-(\tfrac{1}{3})b_3+(\tfrac{2}{5})b_4=s_3/\gamma, \tag{21.3}$$

$$(1+\alpha^2)^{-1}[b_1+(\tfrac{2}{5})b_4+(\tfrac{2}{3})\alpha^2b_2-(4\alpha)(15)^{-\frac{1}{2}}(b_3b_5)^{\frac{1}{2}}]-b_1-(\tfrac{1}{3})b_2+(\tfrac{1}{3})b_3=s_4/\gamma, \tag{21.4}$$

$$-b_1+(\tfrac{1}{3})b_2-(\tfrac{1}{3})b_3=s_5/\gamma, \tag{21.5}$$

$$-(\tfrac{1}{3})b_2+(\tfrac{2}{5})b_4-(\tfrac{1}{5})b_5=s_6/\gamma, \tag{21.6}$$

$$-b_1+(\tfrac{1}{3})b_2-(\tfrac{1}{5})b_5=s_7/\gamma, \tag{21.7}$$

$$-(\tfrac{1}{3})b_2-(\tfrac{1}{3})b_3+b_6=s_8/\gamma, \tag{21.8}$$

$$-(\tfrac{1}{3})b_2+(\tfrac{1}{3})b_3+b_7=s_9/\gamma. \tag{21.9}$$

We evaluate b_1, b_2, b_3, b_4, b_5 from Eqs. (21.0) to (21.4). Eqs. (21.1) and (21.2) at once give $b_3=\frac{3}{2}(s_2-s_1)/\gamma=0.286$, provided the Jackson-Kuhn value is used for s_1. To go further we have to make an assumption about b_0; if we assume as before that $R(3s')=R(3s)$, then $b_0=b_1$, and we can evaluate the rest of the b's. Eqs. (21.0) and (21.1) then give $b_1 = -(s_0 + s_1)/\gamma$. The Jackson-Kuhn value for s_1 then gives $b_1 = 0.047$, while the Fisher value gives -0.039. Since the b's must all be positive, this fact appears to be against the Fisher value, unless one is willing to admit that nuclear motion is not the only factor producing shift in the resonance line $3\,^1S_0 - 3\,^1P_1$. It is true, of course, if one takes into account that b_0 may differ somewhat from b_1, that the value of b_1 deduced from Fisher's s_1 might conceivably be increased from -0.039 to a positive value. But there is other evidence against Fisher's value, independent of any assumption about b_0. If one subtracts Eq. (21.8) from Eq. (21.9) and Eq. (21.1) from Eq. (21.2), one obtains:

$$(s_9 - s_8)/\gamma = (\tfrac{2}{3})b_3 + b_7 - b_6$$
$$(s_2 - s_1)/\gamma = (\tfrac{2}{3})b_3.$$

Now very probably[19] $J^2(2p, 5s) < J^2(2p, 4s)$, so that $b_7 < b_6$; thus we must have $s_9 - s_8 < s_2 - s_1$. Now $s_9 - s_8 = 0.058$ cm^{-1}, while $s_2 - s_1 = 0.040$ cm^{-1} with Fisher's s_1 and 0.073 cm^{-1}, with the Jackson-Kuhn s_1. We again reach the conclusion that *if Fisher's value for the shift of the resonance line is correct, then such a shift cannot be due to nuclear motion alone.* Since other evidence in Mg I points against such a conclusion, we prefer to decide tentatively in this paper for the Jackson-Kuhn value for s_1. We can also see that Eqs. (21.1) to (21.4) are not compatible if $\alpha = 0$: if we put $\alpha = 0$ in Eq. (21.4) and subtract it from Eq. (21.3), we obtain $(\tfrac{2}{3})b_3 = (s_4 - s_3)/\gamma$, while by subtracting Eq. (21.1) from Eq. (21.2) we obtained $(\tfrac{2}{3})b_3 = (s_2 - s_1)/\gamma$. Thus $\alpha = 0$ would require that $s_4 + s_1 = s_3 + s_2$; Table V gives $s_3 + s_2 = 0$ and $s_4 + s_1 = 0.035$ cm^{-1} with the Jackson-Kuhn value for s_1, and 0.068 cm^{-1} with the Fisher value. Thus the observed shifts point directly to the interaction of $(3s)(3d)\,^1D$ with $(3p)^2\,^1D$ as being very important. We now readily finish solving Eqs. (21.0) to (21.4), using $\alpha = -0.550$, obtaining Table VI for the values of $J^2(nl; n', l-1)$ necessary to account for the observed shifts. The magnitude of the core-valence J^2's again shows that a two-electron model would not be permissible.

Up to this point we have made no assumption whatever as to whether the various electrons move in different central fields or all move in the same central field. If we now assume that they all move in the same central field with potential energy $V(r)$, we have (Appendix I):

$$J(n, l; n', l-1) = (\tfrac{1}{2})[\epsilon(n', l-1) - \epsilon(nl)] \times r(nl; n', l-1), \tag{22}$$

where

$$r(n, l; n'l') \equiv \int_0^\infty R(nl)R(n'l')r^3 dr,$$

the unit of length being a_0 and where $\epsilon(nl)$ is the energy of the electron in the orbit nl, expressed in Rydberg units. This assumption of the same central field for each electron was made by Slater[8] in his paper on complex spectra and is approximately borne out by Hartree's calculations. The various electrons according to the Hartree method move in only slightly different fields; our ϵ's are thus essentially the energies which would be given by the Hartree method. We may thus look on $\epsilon(nl)$ as the energy which would be required to remove the nl electron from the atom, if exchange were not operative. If the above assumption as to central fields were not made, Eq. (22) would have to contain an additive term proportional to

$$\int_0^\infty [V_{nl}(r) - V_{n',\,l-1}(r)]R(nl)R(n'l-1)r^3 dr;$$

we may regard Hartree's calculations as showing the unimportance of this term. However, this assumption about central fields is used only in this section in judging the reasonableness of the J^2's and is not used in the previous direct calcula-

TABLE VI. *Values of the J^2's calculated from observed shifts, assuming $R(3s') = R(3s)$ and the Jackson-Kuhn value for the resonance line.*

$nl; n', l-1$	$J(nl; n', l-1)$	$J^2(nl; n', l-1)$
$2p3s$		0.047
$3p1s$		$J^2(3p, 1s) + J^2(3p, 2s) = 0.208$
$3p2s$		
$3p3s$	0.535	0.286
$3d2p$		0.118
$3d3p$	0.351	0.123

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[19] See Eq. (26) below; although $|\epsilon(2p) - \epsilon(5s)| > |\epsilon(2p) - \epsilon(4s)|$, f values fall off so rapidly that $|f(2p \rightarrow 5s)| \ll |f(2p \rightarrow 4s)|$, so that $J^2(2p, 5s) < J^2(2p, 4s)$. Considerations of overlapping of $2p$ with $4s$ or with $5s$ also lead to the conclusion that $r^2(2p, 5s) \ll r^2(2p, 4s)$, so that $J^2(2p, 5s) < J^2(2p, 4s)$. (See Eq. (22) below.)

tions with wave functions or in the section where we predict shifts for other lines.

Now, using atomic units, with $l'=l\pm 1$, we have:[20]

$$f(nl\rightarrow n'l')\equiv(1/3)(2l'+1)^{-1}[\epsilon(nl)-\epsilon(n'l')]\times\sum_{m_l m_l'}\sum|(nlm_l|\mathbf{r}|n'l'm_l')|^2, \quad (23)$$

$$=(1/3)(2l'+1)^{-1}\max(l,l')\times[\epsilon(nl)-\epsilon(n'l')]r^2(nl;n'l'). \quad (24)$$

Thus

$$f(nl\rightarrow n',l-1)=(1/3)l(2l-1)^{-1}\times[\epsilon(nl)-\epsilon(n',l-1)]r^2(nl;n',l-1). \quad (25)$$

Comparison of Eqs. (25) and (22) leads to the relation:

$$f(nl\rightarrow n',l-1)=(4/3)[\epsilon(nl)-\epsilon(n',l-1)]^{-1}\times l(2l-1)^{-1}J^2(nl;n',l-1). \quad (26)$$

The ϵ's can be estimated for $1s$, $2s$, and $2p$ from x-ray data, and for $3s$, $3p$, and $3d$ from term values in Mg I and Mg II; the details are given in Appendix II. The results are $\epsilon(1s)=-96.0$, $\epsilon(2s)=-4.58$, $\epsilon(2p)=-3.65$, $\epsilon(3s)=-0.764$, $\epsilon(3p)=-0.299$, $\epsilon(3d)=-0.106$. Using these values for the ϵ's, the J^2's in Table VI, and Eq. (26), we obtain Table VII for the f values.

Note that the (3, 3) f values are of the same order of magnitude and are large compared to the (3, 2) f values, which are all of the same order, being in turn large compared to the (3, 1) f value. These relative values are to be expected and help to show the reasonableness of the f's. For an actual comparison with experimental data we must remember that these f values are for the system of one electron moving in the effective Hartree field of the rest of the Mg atom, and as such could not be directly compared with f values in Mg I, even if the latter were known. They may, however, be compared for order of magnitude with f values in Na I. In Na I, theoretical calculations by Trumpy[21] and by Prokofjew[21] give 0.98 for $f(3p\rightarrow 3s)$, while various experiments[21] give values ranging from 0.97 to 1.16; according to the Kuhn-Reiche sum rule we should expect a value less than 1. For $f(3d\rightarrow 3p)$ calculations by Prokofjew[21] give 0.832 and for $f(2p\rightarrow 3s)$ calculations by Sugiura[22] give -0.043. These theoretical calculations are all based on radial functions obtained by numerical integration, the field being chosen with the aid of a W. K. B. modified Bohr quantum condition so as to reproduce observed term values; as such they are probably quite reliable. We see that our f values are of the correct order of magnitude, with $f(3p\rightarrow 3s)$ and $f(3d\rightarrow 3p)$ both ~ 1, with $f(3p\rightarrow 3s)>f(3d\rightarrow 3p)$ as in Na I, and with $f(2p\rightarrow 3s)$ about half that for Na I; the parallelism with Na f values is remarkable. Thus we have a confirmation of the reasonableness of the J^2's and the consequent likelihood of the essential correctness of the theory.

TABLE VII. *f values calculated from J^2's that give the observed shifts.*

$nl, n', l-1$	$f(nl\rightarrow n', l-1)$
$2p3s$	-0.022
$3p1s$	<0.0029
$3p2s$	<0.065
$3d2p$	0.0296
$3p3s$	0.820
$3d3p$	0.566

PREDICTIONS OF THE SHIFTS OF OTHER LINES

Equations (21) are capable of yielding still other interesting results. Comparison of Eqs. (21.5) and (21.1) gives $s_5=s_1$ as a requirement of the theory; this result is independent of any assumption as to the relative magnitudes of b_0 and b_1. In words, if the shifts in Mg are due to nuclear motion alone, then the specific shifts of the resonance line $3\,{}^1S_0-3\,{}^1P_1$ and of any member of $3\,{}^3P-(3p)^2\,{}^3P$ must be equal. Also, if one tries to solve Eqs. (21.1), (21.2), (21.3), (21.6), and (21.7) for b_1, b_2, b_3, b_4, b_5, one finds that the determinant of the coefficients of the b's vanishes, so that these equations are not independent; one readily finds that $s_7+s_3=s_6+s_1$. Thus, nuclear motion alone being effective, the sum of the specific shifts of the lines $3\,{}^3D-(3p)(3d)\,{}^3D$ and $3\,{}^3P-3\,{}^3D$ must equal the sum of the specific shifts of the lines $(3p)^2\,{}^3P-(3p)(3d)\,{}^3D$

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[20] H. A. Bethe, *Handbuch der Physik*, Vol. 24, No. 1, p. 435.

[21] Cf. S. A. Korff and G. Breit, Rev. Mod. Phys. **4**, 499 (1932) for a tabulation of f values with references.

[22] Y. Sugiura, Phil. Mag. **4**, 495 (1927). This f value corresponds to a line forbidden by the Pauli principle, but was calculated by Sugiura for a check of his f values by the Kuhn-Reich sum rule.

and $3\,{}^1S_0-3\,{}^1P_1$. Suppose now that one tries to solve Eqs. (21.1), (21.2), (21.3), (21.4), and (21.6) for b_1, b_2, b_3, b_4, b_5; one readily solves for b_3 and b_5 and for b_4 and b_2 in terms of b_1. One then inserts these values of b_2, b_3, b_4, b_5 into Eq. (21.4) to solve for b_1, but b_1 at once cancels out, leaving the general relation:

$$(1+\alpha^2)(s_4-s_2)+s_1=s_3-2\alpha[(s_2-s_1)^2+2(s_2-s_1)(s_3-s_6)]^{\frac{1}{2}}. \qquad (27.3)$$

The other relations are:

$$s_5=s_1, \qquad (27.1)$$

$$s_7+s_3=s_6+s_1. \qquad (27.2)$$

Thus of the seven equations (21.1) to (21.7) only four are independent. The relations (27) are independent of any assumption as to the relative magnitude of b_0 and b_1; they do depend on: (1) having the same radial function for a given 3-quantum orbit in all configurations involving two 3-quantum electrons, (2) having *LS* coupling, (3) having the perturbation of $(3s)(3d)$ by $(3p)^2$ as the only important perturbation. Eq. (27.3) is an equation quadratic in the specific shifts of all the lines $3\,{}^1S_0-3\,{}^1P_1$, $3\,{}^1S_0-3\,{}^3P_1$, $3\,{}^3P-3\,{}^3D$, $3\,{}^1P_1-3\,{}^1D_2$, and $(3p)^2\,{}^3P-(3p)(3d)\,{}^3D$. Using the Jackson-Kuhn value for s_1 and the value $\alpha=-0.550$, we obtain from Eqs. (27): $s_5=-0.028$ cm^{-1}, $s_6=-0.018$ cm^{-1}, and $s_7=-0.001$ cm^{-1}. The corresponding normal shifts are 0.063 cm^{-1}, 0.045 cm^{-1}, and 0.062 cm^{-1}, respectively, leading to total shifts of 0.035 cm^{-1}, 0.027 cm^{-1}, 0.061 cm^{-1} for any member of the sets of lines λ2778 to $2784=3\,{}^3P-(3p)^2\,{}^3P$, λ3890 to $3900=(3p)^2\,{}^3P-(3p)(3d)\,{}^3D$, and λ2810 to $2812=3\,{}^3D-(3p)(3d)\,{}^3D$, respectively. It appears that measurement of the shifts of these lines would afford the best quantitative test of the idea that nuclear motion is alone responsible for fine structure in magnesium.

The author wishes to express his gratitude to Professor Breit for the original suggestion of this problem and for valuable advice during the investigation.

APPENDIX I

To show that

$$\int_0^\infty R(nl)\left[\frac{dR(n',l-1)}{dr}-\frac{(l-1)}{r}R(n',l-1)\right]r^2dr$$
$$=\tfrac{1}{2}[\epsilon(n',l-1)-\epsilon(nl)]\int_0^\infty R(nl)R(n',l-1)r^3dr,$$

we resort to the following argument. With a_0 as the unit of length and the Rydberg constant as the unit of energy, with $S(nl)\equiv rR(nl)$, and with the superscript primes denoting differentiation with respect to r, we have:

$$S''(nl)+[\epsilon(nl)-V-l(l+1)/r^2]S(nl)=0, \qquad \text{(I)}$$

$$S''(n'l')+[\epsilon(n'l')-V-l'(l'+1)/r^2]S(n'l')=0. \qquad \text{(II)}$$

Multiply (I) by $rS(n'l')$, (II) by $rS(nl)$, take the difference, express $S(n'l')S''(nl)-S''(n'l')S(nl)$ as $(d/dr)[S(n'l')S'(nl)-S'(n'l')S(nl)]$, integrate from $r=0$ to $r=\infty$, put

$$\int_0^\infty S(n'l')S'(nl)dr=-\int_0^\infty S(nl)S'(n'l')dr,$$

and then replace the S's by the R's. The result is:

$$2\int_0^\infty R(nl)\frac{dR(n'l')}{dr}r^2dr=[\epsilon(n'l')-\epsilon(nl)]\int_0^\infty R(nl)R(n'l')r^3dr$$
$$+[l(l+1)-l'(l'+1)-2]\int_0^\infty R(nl)R(n'l')rdr. \qquad \text{(III)}$$

If now in (III) we put $l'=l-1$, we at once obtain the desired relation.

APPENDIX II: ESTIMATES OF THE ϵ'S

To estimate the ϵ's for 1*s*, 2*s*, and 2*p* we take $-\epsilon$ as corresponding, respectively, to the term values of the x-ray absorption limits K, L_{I}, and a mean of L_{II} and L_{III}, without making corrections to "reduced" term values, these corrections being small. From Ase[23] we have the *K*-absorption limit at 9.496A and from Skinner and Johnston[24] we have the L_{I} limit at 62.0 volts and the L_{II} and L_{III} limits at 49.5 and 49.2 volts. We obtain $\epsilon(1s)=-96.0$, $\epsilon(2s)=-4.58$, and $\epsilon(2p)=-3.65$.

For the 3-quantum orbits the ϵ's can be estimated from term values in Mg I and Mg II. E.g. for the 3*d*, the value of $\epsilon(3d)$ as determined from the configuration $(3s)(3d)$, which is the only configuration in our problem involving 3*d*, must correspond to a mean of the singlet and triplet term values; the mean must be taken in order to avoid the effect of exchange, since these ϵ's are supposed to be Hartree energies. Also, for the singlet, in order to avoid the effect of perturbation by $(3p)^2$, one should use the value before deduced, *viz.* 9639 cm^{-1}, corresponding to no perturbation by $(3p)^2$. On averaging this with the triplet term value, one obtains $-\epsilon(3d)=11{,}677$ cm$^{-1}=0.106$ *Ry.*

For the 3*p*, the singlet-triplet mean for $(3s)(3p)$ gives 33,201 cm^1. One can also obtain a value from the $(3p)^2\,{}^1D$, which if unperturbed by $(3s)(3d)$ we saw before would have a term value of -3367 cm^{-1}; we wish to include the effect of this configuration because it occurs in our perturbed $(3s)(3d)\,{}^1D$. By adding -3367 cm^{-1} to 121, 267 cm^{-1}, the term value of $3s\,{}^2S$ of Mg. II, one obtains the work required to strip the atom to the neon-like core; then on subtracting from this the term value 85, 537 cm^{-1} of $3p\,{}^2P$ in Mg II, one obtains the network to remove a 3*p* electron from

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[23] See M. Siegbahn, *Spektroskopie der Roentgenstrahlen*, second edition (Springer, 1931), p. 265.

[24] H. W. B. Skinner and J. E. Johnston, Proc. Roy. Soc. **A161**, 420 (1937).

$(3p)^2\,{}^1D$, leaving another $3p$ electron behind; this procedure gives 32,363 cm^{-1}. The mean of these values from $(3s)(3p)$ and $(3p)^2$ gives $-\epsilon(3p)=32{,}782\ \text{cm}^{-1}=0.299\ Ry$.

For the $3s$, the configurations $(3s)^2$ and $3s$ give at once 61,672 cm^{-1} and 121,267 cm^{-1}, respectively, there being no exchange correction to be made in these cases. For $(3s)(3p)$ we add the singlet-triplet mean 33,201 cm^{-1} to 121,267 cm^{-1} to find the work to strip down to the core, and subtract from this the term value 85,537 cm^{-1} of $3p\,{}^2P$ in Mg II, to find the net work required to remove the $3s$, leaving behind the $3p$; this gives 68,931 cm^{-1}. A similar procedure for $(3s)(3d)$, with the use of the above 11,677 cm^{-1} for the singlet-triplet mean term value, leads to 83,167 cm^{-1}. The deviation of the value computed from the configuration $3s$ (alone) from the other three values illustrates the error probably made in putting $R(3s')=R(3s)$. However, a mean of the four values gives $-\epsilon(3s)=83{,}759\ \text{cm}^{-1}=0.764Ry$.

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The Dielectric Constants of Ammonia, Nitrogen, and Carbon Dioxide at Ultra-High Frequency

Gerald W. Fox and Alden H. Ryan*
Physics Laboratory, Iowa State College, Ames, Iowa

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The heterodyne beat method has been used to determine the dielectric constants of nitrogen, carbon dioxide, and ammonia at a frequency of 56 megacycles in the temperature range of 22°C to 45°C. The method proved to be entirely satisfactory showing that the techniques customarily applied in making measurements at the lower frequencies are applicable in the ultra-high frequencies as well. The dielectric constants of nitrogen and ammonia at 56 megacycles agree with the values found at low frequencies. In the case of carbon dioxide, an anomaly was observed, the value of the constant rising from its normal value to a maximum at about 39°C and then decreasing. This variation is briefly discussed.

Introduction

With the growing use of the ultra-high frequencies in applied physics, redetermination of the dielectric constants of gases appears desirable at these frequencies. The purpose of the present investigation was twofold: (1) To determine whether the heterodyne beat method could be used successfully at frequencies up to 56 megacycles per second. (2) To determine the dielectric constant of three typical gases (nitrogen, ammonia, and carbon dioxide) at a frequency around 56 mc, as a preliminary to future work at still higher frequencies.

Experimental Method

In the heterodyne method, two oscillators are used, one of fixed frequency, and one whose frequency depends in part on a condenser to which the material under study can be admitted. As this capacity is altered, the frequency of the circuit of which it is a part changes and this shift appears as a change in the beat note between the two oscillators.

Hector and Schultz[1] pointed out the experimental difficulties of this method. These are: to maintain the frequency stability of the fixed oscillator; to prevent synchronization of the two oscillators when the beat frequency approaches zero; and to prevent changes in the frequency of the variable oscillator, except as produced by admitting the material to the condenser.

In the present apparatus, the first difficulty was reduced by using a crystal-controlled oscillator, operating on a frequency of 14.18 mc. A second stage quadrupled this to 56.76 mc. The crystal was a Bliley B5 low drift crystal, and for further stability, it was enclosed in a crystal oven.

The second difficulty was eliminated by thoroughly shielding both oscillators and their batteries, and by coupling the oscillators very weakly to the detector by radiation. The use of high frequency reduced synchronization, since the beat frequency change was much larger than

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* Now Westinghouse Research Fellow, East Pittsburgh, Pennsylvania.

[1] L. G. Hector and H. L. Schultz, Physics **7**, 133–136 (1936).