as Dr. Aston's estimates made from incompletely resolved spectra are the only ones now available.[6] New abundances were deduced from an indirect comparison with the gadolinium, in which the densities from standard light intensities served as a reference in both cases. These new normal abundances are used in plotting the photographic density curve in Fig. 3, made from five spectra with different exposure times on one plate.

The abundances of the isotopes in the exposed sample were altered by a reduction in the isotope at mass 149 and an increase in the mass at 150. This is shown in Fig. 4 where the new abundances shown on the lines at the bottom for the five spectra are those required to make the observed densities fall on one photographic density curve. The normal abundances of Fig. 3 are shown for comparison in the top scale. Although the changes are less than in the case of gadolinium, the samarium isotope at mass 149 has become less abundant, from 12.8 to 10.0 percent, and the isotope at mass 150 has increased from 5.0 to 7.1 percent. We may conclude that the large absorption in samarium is due primarily to the isotope at mass 149.

TABLE I.

Isotope	155	156	157	158	160
Gd (normal)	15.6	20.6	16.42	23.45	20.87
Gd (altered)	13.6	22.3	9.86	30.60	20.62
Change	−2.0	+1.7	−6.6	+7.1	

The authors are indebted to Dr. L. Borst for preparing the thin deposits and exposing them in the Clinton Pile.

These observations were carried out while the authors were associated with the Metallurgical Laboratory at the University of Chicago.

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[6] F. W. Aston, Proc. Roy. Soc. A146, 46 (1934).

PHYSICAL REVIEW VOLUME 71, NUMBER 11 JUNE 1, 1947

Note on the Nuclear Electric Quadrupole Spectrum of a Homonuclear Diatomic Molecule in a Magnetic Field*

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(Received February 20, 1947)

It is shown that for very large values of the rotational quantum number J the energy of interaction of the electric quadrupole moments of a homonuclear diatomic molecule may be expressed as the sum of the energies of states of the single nucleus problem. This approximation becomes less accurate for any J value as the applied magnetic field is decreased.

THE effect of the nuclear electric quadrupole moment in the magnetic spectrum of a heteronuclear molecule has been given by Feld and Lamb.[1] In this work the molecule was treated as if the two nuclei were entirely independent. The calculations were actually carried out for the case of a single nucleus interacting with the molecular field.

In the case of a homonuclear molecule certain apparent complications arise due to the exchange degeneracy and to the fact that both nuclei are coupled to the molecular rotational angular momentum through the quadrupole interaction. The Hamiltonian expression for two nuclei with quadrupole moments in a magnetic field is

$$\mathcal{H}=\frac{e^2q_1Q_1}{2J(2J-1)I_1(2I_1-1)}\{3(\mathbf{I}_1\cdot\mathbf{J})^2+\tfrac{3}{2}(\mathbf{I}_1\cdot\mathbf{J})-\mathbf{I}_1^2\mathbf{J}^2\}+\frac{e^2q_2Q_2}{2J(2J-1)I_2(2I_2-1)}$$
$$\times\{3(\mathbf{I}_2\cdot\mathbf{J})^2+\tfrac{3}{2}(\mathbf{I}_2\cdot\mathbf{J})-\mathbf{I}_2^2\mathbf{J}^2\}+\mu_0g_1\mathbf{H}\cdot\mathbf{I}_1+\mu_0g_2\mathbf{H}\cdot\mathbf{I}_2+\mu_0g_J\mathbf{H}\cdot\mathbf{J},\quad(1)$$

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* Publication assisted by the Ernest Kempton Adams Fund for Physical Research of Columbia University, New York.

[1] B. T. Feld and W. E. Lamb, Phys. Rev. 67, 15 (1945), hereinafter referred to as FL.

in which Q_1 and Q_2 are the quadrupole moments, $\mathbf{I}_1$ and $\mathbf{I}_2$ the spin vectors of the nuclei, and q_1 and q_2 are directly related to the electric field gradients at the positions of the nuclei.[1] It is assumed that the energy of interaction between the magnetic moments of the nuclei, and of the molecular rotational magnetic field with the nuclear magnetic moments, is small compared to the quadrupole energy.

For the discussion of the energy levels of a homonuclear molecule it is convenient to employ a "strong-field" representation, in which the rotational angular momentum, the spins of the individual nuclei, and the components of each of these quantities in the direction of the magnetic field are diagonal matrices. In the absence of the quadrupole interaction all states with the same value of m_J and of M_S, the component of total nuclear spin in the magnetic field direction, are degenerate.

If the wave function representing a nucleus with z component of spin given by i is α_i, then the part of the total nuclear wave function which depends on the nuclear spin coordinates may be written $\alpha_i(1)\cdot\alpha_k(2)$ where $i+k=M_S$. It is useful to alter the representation by forming the symmetric and antisymmetric combinations of these functions

$$\Gamma_{ik}^{\pm}=\frac{1}{\sqrt{2}}\{\alpha_i(1)\cdot\alpha_k(2)\pm\alpha_k(1)\alpha_i(2)\},\quad \Gamma_{ii}=\alpha_i(1)\cdot\alpha_i(2).$$

The magnetic terms in the Hamiltonian are diagonal in this representation with energy values

$$g_I M_S H_z + g_J m_J H_z.$$

The matrix elements of the quadrupole interaction for an individual nucleus have been given by Kellogg, Rabi, Ramsey, and Zacharias.[2] Non-vanishing matrix elements exist between states with the following relationships of quantum numbers

$$\begin{array}{ll}
\Delta m_S=0 & \Delta m_J=0\\
\Delta m_S=+1 & \Delta m_J=-1\\
\Delta m_S=-1 & \Delta m_J=+1\\
\Delta m_S=+2 & \Delta m_J=-2\\
\Delta m_S=-2 & \Delta m_J=+2
\end{array}$$

In the case of a homonuclear diatomic molecule there are no matrix elements of the two quadrupole terms between the states defined in the Γ representation having a common value of M_S. Thus if the quadrupole interaction is considered to be a small perturbation (strong-field condition), the Γ representation is the correct set of wave functions in first-order approximation. The diagonal matrix element of the quadrupole operator for a single nucleus is given by

$$F_{im_J}^{im_J}=\tfrac{1}{2}[3i^2-I_1(I_1+1)][3m_J^2-J(J+1)].\tag{2}$$

For two identical nuclei in the Γ representation the diagonal element is

$$F_{im_J}^{im_J}+F_{km_J}^{km_J}=[\tfrac{3}{2}i^2+\tfrac{3}{2}k^2-I_1(I_1+1)][3m_J^2-J(J+1)].\tag{3}$$

The total nuclear spin is not diagonal in the Γ_{ik} functions, that is, the wave functions in terms of which the quadrupole energy is a diagonal matrix consist of combinations of functions corresponding to different values of total nuclear spin. The first-order quadrupole energy consists simply of the sum of the energies of two individual nuclei. It will be shown below that if the rotational angular momentum is very large the eigenvalues of the magnetic and quadrupole energies may always be expressed as the sum of two eigenvalues of the individual nucleus problem.[1]

The Hamiltonian of Eq. (1) may be written as

$$\mathcal{H}=H_1(I_1JH)+H_2(I_2JH).\tag{4}$$

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[2] J. M. B. Kellogg, I. I. Rabi, N. F. Ramsey, and J. R. Zacharias, Phys. Rev. **57**, 677 (1940).

(The rotational moment term is not important for the following discussion.) The matrix elements for an individual nucleus in the strong-field representation are

$$V_{Q_j}{}^{i}R_{m_{J'}}^{m_J}\delta_{m_{J'},\, m_J+i-l}+V_{M_j}{}^{i}\delta_{i,\, j} \tag{5}$$

in which $V_{M_j}{}^{i}$ is the magnetic interaction energy (diagonal), and $V_{Q_J}{}^{i}R_{m_{J'}}^{m_J}\delta_{m_{J'},\, m_J+i-l}$ is the quadrupole matrix element between nuclear spin states i and j and rotational states m_J and $m_{J'}$. The energy matrix of Eq. (4) in the Γ representation is then

$$H_{nlm_{J'}}^{ikm_J}=V_{Q_n}{}^{i}R_{m_{J'}}^{m_J}\delta_{k,\, l}\delta_{m_{J'},\, m_J+i-n}+V_{M_n}{}^{i}\delta_{i,\, n}\delta_{k,\, l}+V_{Q_l}{}^{k}\delta_{1,\, n}R_{m_{J'}}^{m_J}\delta_{m_{J'},\, m_J+k-l}+V_{M_l}{}^{k}\delta_{k,\, l}\delta_{1,\, n}. \tag{6}$$

In this matrix non-zero elements appear only between states of equal values of M, the z component of total angular momentum. Within each sub-matrix for any value of M there are no matrix elements between states of the same M_S. In such a sub-matrix the value of the rotational magnetic quantum number has at most $4I_1+1$ values distributed in the interval $M-2I_1\leq m_J\leq M+2I_1$. If J is very large compared to I_1, the variation of the matrix elements $R_{m_{J'}}^{m_J}$ with m_J, with $m_J-m_{J'}$ fixed, will be small in this interval. (This will not be the case for the small fraction of states in which m_J or $J-m_J$ is comparable with I_1.) If this variation be neglected $R_{m_{J'}}^{m_J}$ depends only on

$$m_J-m_{J'}=n-i \quad \text{or} \quad m_J-m_{J'}=l-k$$

and the matrix element Eq. (5) may be written $V_j{}^i$. The homonuclear matrix element of Eq. (6) becomes

$$H_{nl}^{ik}=V_n{}^i\delta_{k,\, l}+V_l{}^k\delta_{1,\, n}. \tag{7}$$

In the matrix element $V_n{}^i$ the rotational matrix element $R_{m_{J'}}^{m_J}$ may be set equal to its average value for which m_J is equal to M.

We assume that the energy matrix of the individual nucleus problem is brought into diagonal form by a transformation matrix A. Thus $W=AVA^{-1}$ in which W is a diagonal matrix. The direct product matrix

$$\mathcal{A}=A\times A \quad \text{or} \quad \alpha_{ik}{}^{mt}=a_i{}^m a_k{}^t \tag{8}$$

is to be applied to the complete energy matrix of Eq. (7)

$$\begin{aligned} H'^{mt}_{pq}&=\sum_{nl}\sum_{ik}\alpha_{ik}^{mt}H_{nl}^{ik}(\alpha^{-1})_{pq}^{nl}\\ &=\sum_{nl}\sum_{ik}a_i{}^m a_k{}^t\{V_n{}^i\delta_{k,\, l}+V_l{}^k\delta_{in}\}(a^{-1})_p{}^n(a^{-1})_q{}^l \\ &=W_p{}^m\delta_{t,\, q}\delta_{m,\, p}+W_q{}^t\delta_{m,\, p}\delta_{t,\, q}. \end{aligned} \tag{9}$$

Thus the transformation matrix $\mathcal{A}$ diagonalizes the energy matrix, and the diagonal values are just the sums of eigenvalues of the individual nucleus problem.

It is clear that any system consisting of two (or more) parts, the energy matrix of which can be put into the form of Eq. (7), will show this same additivity of the energies of the individual parts. Thus a heteronuclear molecule of large rotational angular momentum, and with quadrupole interactions, will yield eigenvalues expressible as the sums of the energies of the individual nuclei. The inclusion of an interaction between the nuclei will of course destroy the form of the energy matrix of Eq. (7).

A weak oscillating magnetic field $\mathbf{H}'$ introduces a perturbation of the form

$$\mathcal{H}' = \mu_0 g_I \mathbf{H}' \cdot \mathbf{I}_1 + \mu_0 g_I \mathbf{H}' \cdot \mathbf{I}_2$$

leading to transitions between the levels given by Eq. (9). From the properties of the matrix $\mathcal{A}$ it may be shown that the possible transitions are restricted to changes in the value of only one of the terms of Eq. (9), and the selection rules for these transitions are identical with those in the spectrum of a single nucleus. Subject to the approximation that the rotational angular momentum is large, we have the general rule: the magnetic nuclear spectrum of a homonuclear diatomic molecule, including electric quadrupole interaction, is identical with that of a single nucleus with the same spin. This rule is not in agreement with the recent results of Feld.[3]

The physical meaning of Eqs. (3) and (6) may be expressed quite simply. In a strong magnetic field the two spin vectors and the rotational angular momentum are decoupled and precess independently in the field. Equation (3) expresses the fact that the energies of the precessing spin vectors are additive. As the field is reduced to zero, the spin vectors are each coupled to the rotational angular momentum through the quadrupole interaction, and the three vectors form a resultant total angular momentum. If the rotational vector $\mathbf{J}$ is very large the spin vectors may be considered to be precessing about $\mathbf{J}$. In this case the rotational vector has the role of a strong applied field and the energies are additive (Eq. (6)).

The effect of a finite value of rotational angular momentum is to make important the variation of the rotational matrix elements with m_J within a group of states of fixed M. In this case the complete matrix of Eq. (6) may not be diagonalized by a transformation of the form $\mathcal{A} = A \times A$ with eigenvalues expressed simply as sums of eigenvalues of the individual nucleus problem. The strong field first-order solution of Eq. (3), however, shows the additive property even for small values of J, and it is clear from the foregoing discussion that the deviations from additivity become more important in higher approximations. To investigate the maximum effect we proceed directly to the zero-field case. The following discussion will deal only with the quadrupole interaction in zero field. In this case we may use a representation in which F, m_F, I, J, I_1, I_2 are diagonal. F is the quantum number of total angular momentum, and m_F is its component on a fixed space axis. I is the total nuclear spin. The matrix elements of the quadrupole interaction are given for reference in the Appendix. Non-zero matrix elements exist between states differing in total spin by $\Delta I = 0 \pm 2$. For any value of $i_0 = F - J$ the states of total spin values $I \geq i_0$ must be diagonalized. The combinations of total spin wave functions in which the quadrupole perturbation is diagonal for any value of i_0, are the same as the total spin combinations in the strong field case for an identical value of M_S.

For a single nucleus, in the zero-field case, Feld and Lamb gave an expression (FL III 7) for the energy which is accurate for large J values

$$E_Q = e^2 qQ[3i_1^2 - I_1(I_1+1)]/4I_1(2I_1-1), \quad i_1 = F - J. \tag{10}$$

These authors also gave the exact solution of the single nucleus problem (FL III 5). The eigenvalue solution in the homonuclear problem described above may be expressed as the sum of two expressions of the type of Eq. (10) for large J values, in accordance with the general rule (Eq. (9)). For smaller J values, and particularly for large values of nuclear spin, deviations from simple additivity will occur. Investigation of several special cases indicates that these deviations are of the same magnitude as, though not identical with, the differences between the exact single nucleus solution (FL III 5) and the values given by Eq. (10). For nuclear spins as large as $I = 5$ and with $J = 20$ these deviations are important, and the simple formula of Eq. (10) will not apply accurately in either the homonuclear or heteronuclear case.

The author wishes to thank Professor I. I. Rabi for several interesting discussions of this problem.

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[3] B. T. Feld, Phys. Rev. **70**, 112A (1946).

APPENDIX

The matrix elements of the quadrupole interaction in Eq. (1) in the weak-field representation in which F, m_F, I, I_1, I_2, J are diagonal are given here. The matrix elements of $(\mathbf{I}_1\cdot\mathbf{J})$ are[4]

$$
\begin{aligned}
(JIF|\mathbf{I}_1\cdot\mathbf{J}|JIF) &= \frac{1}{2}\,\frac{I_1(I_1+1)-I_2(I_2+1)+I(I+1)}{2I(I+1)}\{F(F+1)-I(I+1)-J(J+1)\},\\
(JIF|\mathbf{I}_1\cdot\mathbf{J}|JI-1F) &= \frac{1}{2}\left\{\frac{(I-I_1+I_2)(I+I_1-I_2)(I_1+I_2+I+1)(I_1+I_2-I+1)}{4I^2(2I-1)(2I+1)}\right\}^{\frac{1}{2}}\\
&\qquad\times\{(F+I-J)(F+J-I+1)(F+I+J+1)(I+J-F)\}^{\frac{1}{2}}\\
&= (JI-1F|\mathbf{I}_1\cdot\mathbf{J}|JIF),\\
(JIF|\mathbf{I}_1\cdot\mathbf{J}|JI+1F) &= \frac{1}{2}\left\{\frac{(I+1-I_1+I_2)(I+1+I_1-I_2)(I_1+I_2+I+2)(I_1+I_2-I)}{4(I+1)^2(2I+1)(2I+3)}\right\}^{\frac{1}{2}}\\
&\qquad\times\{(F+I+1-J)(F+J-I)(F+I+J+2)(I+1+J-F)\}^{\frac{1}{2}}\\
&= (JI+1F|\mathbf{I}_1\cdot\mathbf{J}|JIF).
\end{aligned}
$$

The off diagonal elements for $(\mathbf{I}_2\cdot\mathbf{J})$ are minus the corresponding elements in $(\mathbf{I}_1\cdot\mathbf{J})$.

In the homonuclear case $I_1=I_2$, and the matrix elements of the quadrupole terms of Eq. (1) are obtained by matrix multiplication:

$$
\begin{aligned}
(JIF|H_Q|JIF) &= \frac{e^2qQ}{2J(2J-1)I_1(2I_1-1)}\Big\{\tfrac{3}{8}[F(F+1)-I(I+1)-J(J+1)]^2\\
&\quad+\frac{3}{8}\,\frac{(2I_1+1)^2-I^2}{4I^2-1}(F+I-J)(F+J-I+1)(F+I+J+1)(I+J-F)\\
&\quad+\frac{3}{8}\,\frac{(2I_1+1)^2-(I+1)^2}{(2I+1)(2I+3)}(F+I+1-J)(F+J-I)(F+I+J+2)(I+1+J-F)\\
&\quad+\tfrac{3}{4}[F(F+1)-I(I+1)-J(J+1)]-2I_1(I_1+1)J(J+1)\Big\},\\
(JIF|H_Q|JI+2F) &= \frac{3e^2qQ}{2J(2J-1)I_1(2I_1-1)}\Big\{\frac{(2I_1+1)^2-(I+1)^2}{4(2I+1)(2I+3)}(F+I+1-J)(F+J-I)\\
&\quad\times(F+I+J+2)(I+J+1-F)\Big\}^{\frac{1}{2}}\Big\{\frac{(2I_1+1)^2-(I+2)^2}{4(2I+3)(2I+5)}(F+I+2-J)\\
&\quad\times(F+J-I-1)(F+I+J+3)(I+2+J-F)\Big\}^{\frac{1}{2}}\\
&= (JI+2F|H_Q|JIF),\\
(JIF|H_Q|JI-2F) &= \frac{3e^2qQ}{2J(2J-1)I_1(2I_1-1)}\Big\{\frac{(2I_1+1)^2-I^2}{4(4I^2-1)}(F+I-J)(F+J-I+1)(F+I+J+1)\\
&\quad\times(I+J-F)\Big\}^{\frac{1}{2}}\Big\{\frac{(2I_1+1)^2-(I-1)^2}{4(2I-3)(2I-1)}(F+I-J-1)(F+J-I)(F+J+I)(I+J-F-1)\Big\}^{\frac{1}{2}}.
\end{aligned}
$$

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[4] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, 1935), p. 71.