PHYSICAL REVIEW VOLUME 170, NUMBER 2 10 JUNE 1968

Exact Solution for an N-Molecule–Radiation-Field Hamiltonian

Michael Tavis and Frederick W. Cummings
University of California, Riverside, California

(Received 8 December 1967)

The exact solution for a problem of N identical two-level molecules interacting through a dipole coupling with a single-mode quantized radiation field at resonance is given. Approximate expressions for the eigenvectors and eigenvalues for the ground and low-lying excited states, as well as the most highly excited states, are developed and compared with the exact results.

I. INTRODUCTION

ALMOST fifteen years ago, Dicke[1] pointed out the importance of treating a gas of radiating molecules as a single quantum system, in that the molecules are interacting with a common radiation field and should not be treated as independent. An independent molecule picture is wrong in principle as are many results obtained from it. Dicke's results were obtained in first-order perturbation theory; many subsequent authors have considered other approximations to the N-molecule–radiation-field problem.[2–4]

Exact solutions to model problems have historically provided much insight into realistic physical systems, as well as affording a standard of comparison for approximation techniques. Further, the states obtained can be used as a basis set in which the state of a more realistic model may be expanded. For example, a recent analysis of a quantum coherent device by Scully and Lamb[5] describes the system of N molecules by a 2×2 matrix, instead of by one of dimension 2^N; the states obtained in the present work may provide a convenient basis for an N-molecule analysis along similar lines, although no applications are given in the present paper.

Quantum electrodynamics has historically been developed in terms of the stationary number states of the free radiation-field Hamiltonian. The classical limit of quantum electrodynamics is one in which the quantum numbers are typically large as well as uncertain, and the photon number states are not a natural basis in this case. Glauber[6] has discussed quantum states which form an overcomplete set which are well suited to treatment of the classical region. These states have a "classical" dispersion in photon number, where the dispersion is equal to the average photon number. It is interesting to see the same classical dispersion for many of the eigenstates of an N-molecule–radiation Hamiltonian as in the present analysis.

II. FORMULATION OF PROBLEM

The Hamiltonian which describes the interaction of N-identical two-level systems with a single-mode radiation field is taken as

$$H=R_3+a^\dagger a-\kappa^* aR_+-\kappa a^\dagger R_- \tag{2.1a}$$

$$=H_0-\kappa^* aR_+-\kappa a^\dagger R_-. \tag{2.1b}$$

The N identical two-level systems (TLS) are assumed to have nonoverlapping space functions, and the energy separation of each TLS is equal to the mode frequency ($\hbar=1$) of the electromagnetic field. $\kappa=|\kappa|e^{-i\phi_1}$ is the complex coupling constant divided by the mode frequency. The TLS are coupled to the single-mode radiation field in the dipole approximation, and all TLS are further assumed to be located at equivalent, fixed mode positions, or to be all confined to a container whose dimensions are small compared to the radiation wavelength. Terms have already been ignored in the dipole coupling in Eq. (2.1) which do not conserve energy in the first order of perturbation; their contribution is very small except for very high intensity fields.[7] Their contribution can be considered as a perturbation after the eigenstates of H are found.

States of the noninteracting system are defined[1] such that

$$H_0|n\rangle|r,m\rangle=(m+n)|n\rangle|r,m\rangle, \tag{2.2a}$$

$$R_3|r,m\rangle=\sum_{j=1}^{N}R_{j3}|r,m\rangle=m|r,m\rangle, \tag{2.2b}$$

$$R_\pm|r,m\rangle=\sum_{j=1}^{N}R_{j\pm}|r,m\rangle =e^{\pm i\phi_2}[r(r+1)-m(m\pm1)]^{1/2}|r,m\pm1\rangle, \tag{2.2c}$$

$$a|n\rangle=e^{i\phi_3}\sqrt{n}|n-1\rangle. \tag{2.2d}$$

The eigenstates of H_0 have been chosen to be simultaneous eigenstates of $R^2\equiv R_3^2+(R_+R_-+R_-R_+)/2$,

---

[1] R. H. Dicke, Phys. Rev. **93**, 99 (1954).

[2] J. P. Gordon, L. R. Walker, and W. H. Louiselle, Phys. Rev. **130**, 806 (1963). These authors include a long list of references.

[3] A. E. Glassgold and D. Holliday, Phys. Rev. **139**, A1717 (1965).

[4] J. A. Fleck, Phys. Rev. **149**, 309 (1966).

[5] M. O. Scully and W. E. Lamb, Jr., Phys. Rev. **159**, A208 (1967).

[6] R. J. Glauber, Phys. Rev. **131**, 2766 (1963).

[7] E. T. Jaynes and F. W. Cummings, Proc. IEEE **51**, 89 (1963) have shown that the "counter-rotating" terms in the complete dipole interaction, namely the terms proportional to R_+a^+ and R_-a, are very small at resonance except for extremely high intensity fields.

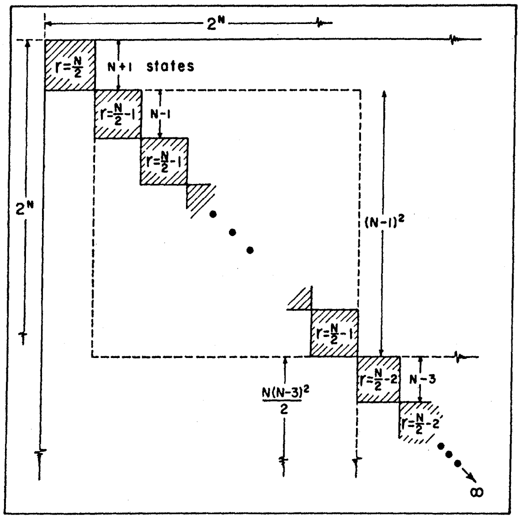

FIG. 1. Schematic of matrix representation of H.

analogous to the angular momentum formalism. The "cooperation number" r satisfies

$$R^2 \,|\, r, m\rangle = r(r+1) \,|\, r, m\rangle, \qquad (2.3)$$

with

$$|\, m \,| \leq r \leq N/2, \qquad (2.4)$$

where r and m are either integers or half-integers. The operators in Eq. (2.1) also satisfy the commutation relations

$$[R_3, R_\pm] = \pm R_\pm, \qquad (2.5a)$$

$$[R_+, R_-] = 2R_3, \qquad (2.5b)$$

$$[a, a^\dagger] = 1. \qquad (2.5c)$$

Since both R^2 and H_0 commute with H, the eigenstates of H may be chosen to be eigenstates of these two operators as well, and the eigenstates may be labeled by r, the cooperation number, and c, the eigenvalue of H_0. For a given r and c, the (in general) $2r+1$ energy eigenvalues will then be symmetrically displaced about this constant c, where $-r \leq c < \infty$.

It is helpful to display the elements

$$\langle n \,|\langle r, m \,|\, H \,|\, r', m'\rangle|\, n'\rangle$$

as a matrix, where there is a grouping into an infinite number of blocks of dimension 2^N along the main diagonal. Each 2^N dimensional block in turn breaks up into smaller blocks along the main diagonal, their number and dimension determined according to the irreducible representations of the group $SU(2)$. This is shown schematically in Fig. 1. Only the shaded blocks have nonzero elements. There are $N!(2r+1)/[(N/2+r+1)!(N/2-r)!]$ identical blocks for each value of r, and each smaller block is of dimension $2r+1$. The values of r range from $N/2$ for the largest single shaded block at the top left-hand corner of the figure, down to either $r=0$, or $r=\frac{1}{2}$ depending on whether N is even or odd. For a given value of r, an integer change in c corresponds to a change to an adjacent block of dimension 2^N.

Figure 2 shows the elements of one of the shaded blocks of Fig. 1 of a particular r value. The block has nonzero entries only along the diagonal and immediately adjacent to it. If the value of c is such that $c<r$, then the block will have dimension less than $2r+1$ and will be of dimension $c+r+1$ instead; thus, besides having an infinite number of blocks of dimension 2^N, there will also be N large blocks of dimension smaller than 2^N.

Denote eigenstates of H as $|\, r, c, j\rangle$. Then

$$H \,|\, r, c, j\rangle = \lambda_{r,c,j} \,|\, r, c, j\rangle, \qquad (2.6)$$

where j takes on the $2r+1$ values $0, 1, 2, \cdots, 2r$, if $c \geq r$, or the $c+r+1$ values $0, 1, \cdots, c+r$ if $c<r$. Recalling that the states $|\, r, c, j\rangle$ are eigenstates of H, H_0, and R^2, and that $m=c-n$ varies between r and $-r$,

$$|\, r, c, j\rangle = \sum_{n=c-r}^{c+r} A_n^{(r,c,j)} \,|\, n\rangle|\, r, c-n\rangle, \qquad (2.7)$$

where, from Eqs. (2.1), (2.2), and (2.5) the $A_n^{(r,c,j)}$ satisfy the difference equation

$$-|\,\kappa\,|\, e^{i\phi} n^{1/2} C_{r,c-n} A_{n-1}^{(r,c,j)} + (c-\lambda_{r,c,j}) A_n^{(r,c,j)}$$
$$-|\,\kappa\,|\, e^{-i\phi} (n+1)^{1/2} C_{r,c-n-1} A_{n+1}^{(r,c,j)} = 0, \qquad (2.8)$$

where

$$\phi \equiv \phi_1 + \phi_2 + \phi_3 \qquad (2.9a)$$

and

$$C_{r,c-n} \equiv [r(r+1) - (c-n)(c-n+1)]^{1/2}. \qquad (2.9b)$$

The $A_n^{(r,c,j)}$ satisfy the end conditions

$$A_{r+c+1}^{(r,c,j)} = A_{c-r-1}^{(r,c,j)} = 0 \qquad c \geq r \qquad (2.10a)$$

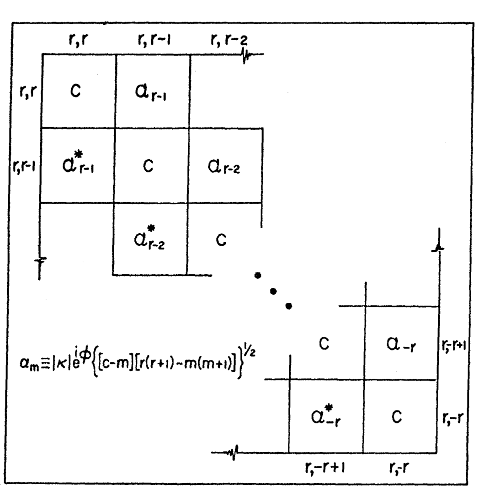

FIG. 2. Submatrix for given r and c.

and

$$A_{r+c+1}{}^{(r,c,j)}=A_{-1}{}^{(r,c,j)}=0 \qquad c<r. \qquad (2.10\text{b})$$

It is very convenient to define B_n's so that

$$A_n=\frac{(qe^{i\phi})^n B_n}{\sqrt{(n!)}\,C_{c-1}C_{c-2}\cdots C_{c-n}} \qquad c<r \qquad (2.11\text{a})$$

and

$$A_n=\frac{(qe^{i\phi})^n B_n}{\sqrt{(n!)}\,C_{r-1}C_{r-2}\cdots C_{c-n}}, \qquad c\geq r \qquad (2.11\text{b})$$

where

$$q=(c-\lambda)/2\,|\,\kappa\,|, \qquad (2.12)$$

and the superscripts (subscripts) (r,c,j) have been dropped for simplicity whenever this does not cause confusion. Only the r subscript will be suppressed in the $C_{r,c-n}$ to conform to Fig. 2. The q's are now the effective eigenvalues, the largest value of q for a given value of r and c corresponding to the ground state of the system. B_n satisfies the difference equation

$$q^2B_{n+1}-2q^2B_n+nC_{c-n}{}^2B_{n-1}=0. \qquad (2.13)$$

III. EXACT SOLUTION

The exact solution of Eq. (2.13) (non-normalized) can be seen to be

$$B_n=2^n\sum_{l=0}^{n/2}(2q)^{-2l}\mathcal{S}_l{}^{(n-1)}(-1)^l, \qquad c\leq r \qquad (3.1\text{a})$$

$$B_n=2^nq^{r-c}\sum_{l=0}^{(r+n-c)/2}(2q)^{-2l}\mathcal{S}_l{}^{(n-1)}(-1)^l \qquad c>r. \qquad (3.1\text{b})$$

The $\mathcal{S}_l{}^{(n-1)}$ are the sums of all products of $\mathcal{C}_m$'s where $\mathcal{C}_m\equiv mC_{c-m}{}^2$, l at a time, $\mathcal{C}_{n-1}$ being the maximum, and no "nearest neighbors" are included in the products. This definition may be clarified by the examples

$$\mathcal{S}_3{}^{(6)}=\mathcal{C}_1\mathcal{C}_3\mathcal{C}_5+\mathcal{C}_1\mathcal{C}_3\mathcal{C}_6+\mathcal{C}_1\mathcal{C}_4\mathcal{C}_6+\mathcal{C}_2\mathcal{C}_4\mathcal{C}_6,$$

$$\mathcal{S}_3{}^{(5)}=\mathcal{C}_1\mathcal{C}_3\mathcal{C}_5, \qquad \mathcal{S}_2{}^{(4)}=\mathcal{C}_1\mathcal{C}_3+\mathcal{C}_1\mathcal{C}_4+\mathcal{C}_2\mathcal{C}_4,$$

$\mathcal{S}_0{}^{(n)}\equiv 1$, and $\mathcal{S}_l{}^{(n)}=0$ if $l>\frac{1}{2}(n+1)$, e.g., $\mathcal{S}_3{}^{(4)}=0$.

The $\mathcal{S}_l{}^{(n)}$ can be seen to obey, by induction or inspection, the useful recursion relation

$$\mathcal{S}_l{}^{(n)}=\mathcal{S}_l{}^{(n-1)}+\mathcal{C}_n\mathcal{S}_{l-1}{}^{(n-2)}. \qquad (3.2)$$

The exact eigenvalues, or equivalently the q's are determined from the conditions

$$B_{r+c+1}=B_{c-r-1}=0, \qquad c\geq r \qquad (3.3\text{a})$$

$$B_{r+c+1}=B_{-1}=0 \qquad c<r. \qquad (3.3\text{b})$$

These are polynomials in $2q$ of degree $2r+1$ ($2r$ if r is an integer) if $c\geq r$ (and there is one root $q=0$ if r is an integer) and of degree $r+c+1$ ($r+c$ if r is an integer) if $c<r$ (and again there is a root $q=0$ if r is an integer). Whenever r is an integer, the solution corresponding to $q=0$ is to be found directly from the equation for the A_n, and is given by

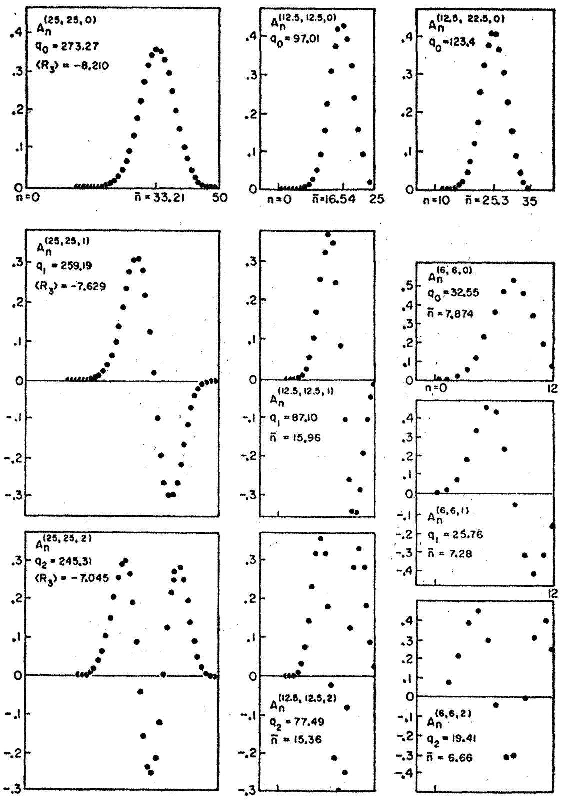

FIG. 3. Selected eigenvectors $A_n{}^{(r,c,j)}$.

$$A_n=(-1)^{n/2}\mathcal{S}_{n/2}{}^{(n-1)}/\sqrt{(n!)}\,C_{c-1}C_{c-2}\cdots C_{c-n},$$
$$n\text{ even, } 0\leq n\leq c+r \qquad (3.4\text{a})$$

$$A_n=0, \qquad n\text{ odd, } 0\leq n\leq c+r \qquad (3.4\text{b})$$

and

$$A_n=(-1)^{(r+n-c)/2}\mathcal{S}_{(r+n-c)/2}{}^{(n-1)}/\sqrt{(n!)}\,C_{r-1}C_{r-2}\cdots C_{c-n},$$
$$n-(c-r)\text{ even, } c-r\leq n\leq c+r \qquad (3.4\text{c})$$

$$A_n=0, \qquad n-(c-r)\text{ odd, } c-r\leq n\leq c+r. \qquad (3.4\text{d})$$

A high speed computer was used to calculate $A_n{}^{(r,c,j)}$. Figure 3 shows $A_n{}^{(r,c,j)}$ as a function of n for several representative values of r, c, and j. The value $j=0$ corresponds to the ground state, $j=1$ to the first excited state, and $j=2r$ to the most highly excited state. The value q_0 corresponds to the ground state, and is the largest value of q. The q's are such that $q_{2r}=-q_0$, $q_{2r-1}=-q_1$, and so on, symmetrically displacing the q-values about zero. The states $A_n{}^{(j)}$, $j=2r$, $2r-1$, $\cdots$, $r+1$, if r is an integer (or $r+\frac{1}{2}$ if r is an half-integer) are found from the states $A_n{}^{(j)}$, $j=0$, 1, $\cdots$, $r-1$ (or $r-\frac{1}{2}$ if r is a half-integer) by replacing q by $-q$

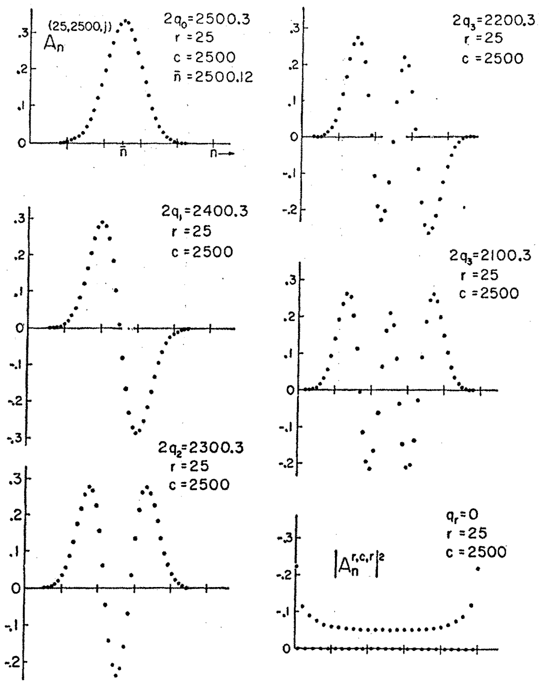

FIG. 4. $A_n^{(25,2500,j)}$, $j=0, 1, \cdots, 4$; and $|A_n^{(25,2500,25)}|^2$.

(or ϕ by $\phi+\pi$) in Eq. (2.11). The phase ϕ has been taken as zero for the plots of Figs. 3 and 4. Approximate analytical expressions will now be obtained for the eigenvalues and eigenvectors and compared with the exact results of this section.

IV. APPROXIMATE ANALYTICAL SOLUTIONS

In this section, approximate expressions will be obtained which are quite accurate for the ground and low-lying excited states (and, because of the symmetry about $q=0$, for the most highly excited states and eigenvalues as well). Toward this end Eq. (2.13) may be rewritten in the form

$$B_{n+1}+B_{n-1}-2B_n+\{(nC_{c-n}{}^2-q^2)/q^2\}B_{n-1}=0. \quad (4.1)$$

If $\Delta B_n \equiv B_{n+1}-B_n$, then $\Delta^2 B_n=B_{n+2}+B_n-2B_{n+1}$, so that (4.1) is written as

$$\Delta^2 B_{n-1}+\{(nC_{c-n}{}^2-q^2)/q^2\}B_{n-1}=0. \quad (4.2)$$

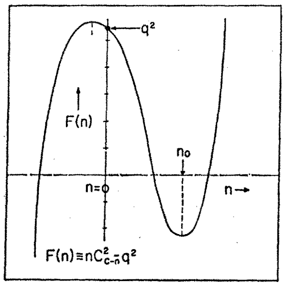

FIG. 5. Schematic of cubic $F(n)$ versus n.

Two different approximations will be made at this point. First, let $\Delta^2 \to d^2/dn^2$, which will be accurate for large enough values of r, when n takes on a sufficient number of values to make this replacement sensible—clearly it will not be for $r=\frac{1}{2}$, for example, when there are only two values of n for a given c. Also this approximation is not expected to be accurate for large j when B_n oscillates rapidly as n varies; for example, from Eq. (3.4a) it can be seen that A_n changes sign on every other value of n for the eigenvalue corresponding to $j=r$.

The second approximation which is made in Eq. (4.2) is most easily seen by reference to Fig. 5. This figure shows the cubic equation, considered as a continuous function of n:

$$F(n)=-nC_{c-n}{}^2+q^2=n^3-(2c+1)n^2 \\ -[r(r+1)-c(c+1)]n+q^2. \quad (4.3)$$

The minimum of $F(n)$ is at n_0, obtained from $F'(n_0)=0$, namely

$$n_0=\tfrac{1}{3}(2c+1)+\tfrac{1}{3}[3r(r+1)+c(c+1)+1]^{1/2}. \quad (4.4)$$

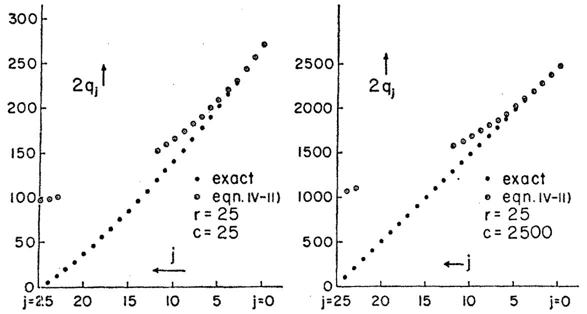

FIG. 6. Eigenvalues.

Note that the minimum position does not depend on the eigenvalue q. Writing $F(n)$ as a function of $(n-n_0)$ gives

$$F(n)=-\alpha_1+q^2+\alpha_2(n-n_0)^2+(n-n_0)^3, \quad (4.5)$$

where the α's are defined by

$$\alpha_1=n_0C_{c-n_0}{}^2, \quad (4.6a)$$

$$\alpha_2=[3r(r+1)+c(c+1)+1]^{1/2}. \quad (4.6b)$$

For all $(n-n_0)$ such that $|n-n_0| \ll \alpha_2$, discarding the cubic term will be a good approximation. For example, it turns out that the dispersion of the ground state is less than $\sqrt{n_0}$, which means that the maximum $|n-n_0|$ is about $\sqrt{n_0}$; but α_2 is of order n_0 (or greater) so that for large n_0 this is clearly a valid approximation, at least for the ground state, and, as it develops, for a number of the first excited states as well.

With these two approximations, Eq. (4.2) becomes

$$\frac{d^2B_{n-1}}{dn^2}+\left\{\frac{\alpha_1-q^2}{q^2}-\frac{\alpha_2}{q^2}(n-n_0)^2\right\}B_{n-1}=0. \quad (4.7)$$

TABLE I. Some limiting cases.

	$c=-r+\epsilon$ $r\gg\epsilon\gg1$	$r\gg c\gg1$	$r=c\gg1$	$c\gg r\gg1$
α_2	$2r(1-\frac{1}{4}\epsilon/r)$	$\sqrt{3}r(1+\frac{1}{6}c^2/r^2)$	$2c$	$c(1+\frac{3}{2}r^2/c^2)$
n_0	$\frac{1}{2}\epsilon$	$(r/\sqrt{3})(1+2c/\sqrt{3}r)$	$\frac{4}{3}c$	$c(1+\frac{1}{2}r^2/c^2)$
C_{c-n_0}	$[\epsilon(r-\frac{1}{3}\epsilon)]^{1/2}$	$(\frac{2}{3})^{1/2}r(1+c/2\sqrt{3}r)$	$\frac{2}{3}\sqrt{2}c$	r
α_1	$\frac{1}{2}\epsilon^2(r-\frac{1}{3}\epsilon)$	$(2/3\sqrt{3})r^3(1+\sqrt{3}c/r)$	$(32/27)c^3$	$r^2c(1+\frac{1}{2}r^2/c^2)$
q_0	$\epsilon[\frac{1}{2}(r-\frac{1}{3}\epsilon)]^{1/2}$	$3^{1/4}(\frac{1}{3}\sqrt{2})r^{3/2}$	$\frac{4}{3}(\frac{2}{3})^{1/2}c^{3/2}$	$rc^{1/2}$
σ^2	$\frac{1}{3}n_0$	$n_0(1+\sqrt{6})$	$n_0/(1+2\sqrt{3})$	$\frac{1}{2}r$

Making the change of variable,

$$t=(\alpha_2/q^2)^{1/4}(n-n_0) \tag{4.8}$$

in Eq. (4.7) gives

$$\left\{\frac{d^2}{dt^2}+\left[\frac{\alpha_1-q^2}{(\alpha_2)^{1/2}q}-t^2\right]\right\}B(t)=0. \tag{4.9}$$

This is in standard form for the harmonic oscillator,[8] and if we apply the usual boundary condition that B vanish as $t\rightarrow\pm\infty$, then

$$\begin{aligned}&(\alpha_1-q^2)/(\alpha_2)^{1/2}q=2j+1,\\ &\qquad j=0, 1, \cdots, r-1, \quad r \text{ integer}\\ &\qquad j=0, 1, \cdots, r-\tfrac{1}{2}, \quad r \text{ half-integer}.\end{aligned} \tag{4.10}$$

Solving the quadratic for q,

$$q_j=-(\alpha_2)^{1/2}(j+\tfrac{1}{2})+[(j+\tfrac{1}{2})^2\alpha_2+\alpha_1]^{1/2}, \tag{4.11}$$

which gives the approximate eigenvalues for j positive, $\leq r$. For $j>r$, the eigenvalues are again to be given as explained below Eq. (3.4d); they are the negative of the values for $j<r$.

Also $B_j(t)=e^{-t^2/2}H_j(t)$, where $H_j(t)$ is the Hermite polynomial of order j. Then

$$\begin{aligned}B_{n-1}^{(j)}=&\{\exp[-(\alpha_2)^{1/2}(n-n_0)^2/2q_j]\}\\ &\times H_j[(\alpha_2/q_j^2)^{1/4}(n-n_0)].\end{aligned} \tag{4.12}$$

All graphs which show eigenvectors are computed from the exact results and are normalized. The phase ϕ has been set equal to zero. In Fig. 6, exact eigenvalues are compared with those computed from Eq. (4.11). The lack of agreement between the exact and the approximate results in the region $j\sim r$ is due to the use of harmonic-oscillator boundary conditions [below Eq. (4.9)] and the replacement of the second difference by the second differential, rather than neglect of the cubic term in Eq. (4.5). A second-order perturbation calculation on the cubic term indicates that inclusion of this term will correct the eigenvalues in the wrong direction and by a negligible amount.

For all values of c and r ($r\gg1$) except for c of the order of r, the eigenvalues are very closely linear in the index j, and the eigenvectors resemble the familiar harmonic-oscillator eigenfunctions for all states (Fig. 4, especially the lower right-hand corner which gives the squared eigenvector for $j=25$). The expression $q_0=-\frac{1}{2}(\alpha_2)^{1/2}+(\frac{1}{4}\alpha_2+\alpha_1)^{1/2}$ is accurate to about 0.1% for all cases considered.

In all cases, the average value $\langle R_3\rangle$ is negative in the ground state for specified r and c, and approaches zero for $c\gg r\gg1$.

V. DISPERSION IN PHOTON NUMBER IN THE GROUND STATE

Table I lists limiting forms for ready reference of several previously defined quantities, as well as σ^2, the dispersion in the ground state. From the Table, it is readily seen, for all four limiting regions considered, that q_0/C_{c-n_0} is very closely equal to $(n_0)^{1/2}$. This is also a statement that $\alpha_2\ll\alpha_1$, for these limits, and so $q_0=-\frac{1}{2}(\alpha_2)^{1/2}+(\frac{1}{4}\alpha_2+\alpha_1)^{1/2}\approx(\alpha_1)^{1/2}$. Then q_0 can also be written as $q_0=\sqrt{2}n_0\{[(r+\frac{1}{2})^2+n_0^2]^{1/2}-n_0\}^{1/2}$ from which it is clear that $q_0\lesssim(2r+1)^{1/2}n_0$. For the first two columns of Table 1, this is a good approximation. For $c\gg r\gg1$, $C_{c-n_0}\rightarrow r$, and then $q_0\rightarrow(n_0)^{1/2}r$. In the ground state, with negligible approximation, the product of C_n's which appear in the denominator of Eq. (2.11) can be written

$$C_{c-1}C_{c-2}\cdots C_{c-n}\approx C_{c-n_0}{}^n\propto C_{r-1}C_{r-2}\cdots C_{c-n}. \tag{5.1}$$

So now the non-normalized $A_n{}^{(r,c,0)}$ [since $H_0(t)=1$] are

$$A_n{}^{(0)}\cong\frac{(q_0/C_{c-n_0})^n e^{in\phi}}{(n!)^{1/2}}\exp[-(n-n_0)^2(\alpha_2)^{1/2}/2q_0]. \tag{5.2}$$

Since $q_0/C_{c-n_0}\cong(n_0)^{1/2}\gg1$, this may be well approximated by

$$A_n{}^{(0)}\cong\exp\left\{-\frac{(n-n_0)^2}{4n_0}\left[1+\frac{2(\alpha_2)^{1/2}n_0}{q_0}\right]\right\}e^{in\phi}. \tag{5.3}$$

Then the dispersion in photon number in the ground

---

[8] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Co., New York, 1955).

state is

$$\sigma^2=\langle(n-n_0)^2\rangle=\sum|A_n^{(0)}|^2(n-n_0)^2/\sum|A_n^{(0)}|^2,$$

or, using Eq. (5.3),

$$\sigma^2=\frac{n_0}{1+2(\alpha^2)^{1/2}n_0/q_0}. \tag{5.4}$$

The bottom row of Table I shows σ^2 for four limiting cases. The dispersion [Eq. (5.4)] is in every case smaller than the classical dispersion obtained from a Poisson distribution, namely $\sigma^2=n_0$,[6] although for $r\gtrsim c$ the dispersion is of order n_0, the average photon number. When the amount of energy in the electromagnetic field greatly exceeds the amount of energy available to the uncoupled atoms, $c\gg r$, then the dispersion is much less than the average photon number, $n_0\cong c$, and is $\sim r$ instead.

Note added in proof. Figure 3 should have $2q$ everywhere instead of q, as in Fig. 4. Also, Fig. 5 defines $-F(n)$, not $F(n)$.

ACKNOWLEDGMENTS

We wish to thank James Johnston for many helpful discussions. One of us (M.T.) would like to thank Aerospace Corp., San Bernardino, Calif., for financial assistance during this work. F.W.C. would like to thank the Aspen Institute, where part of this work was carried out, for their hospitality.

PHYSICAL REVIEW VOLUME 170, NUMBER 2 10 JUNE 1968

Nonexponential Spin-Lattice Relaxation of Protons in Solid CH_3CN and Solid Solutions of CH_3CN in CD_3CN[*]

Michael F. Baud[†] and Paul S. Hubbard
Department of Physics, University of North Carolina, Chapel Hill, North Carolina 27514

(Received 25 January 1968)

The proton spin-lattice relaxation in solid CH_3CN, and in 1:6 and 1:10 solid solutions of CH_3CN in CD_3CN, has been measured by pulsed NMR techniques at a frequency of 30.0 MHz, for temperatures between 79.5 and 173°K. The relaxation is nonexponential at the higher temperatures, and exponential only at the lowest temperature. The experimental results for 1:6 solutions are compared with the relaxation previously predicted by a calculation based on the assumptions that (1) the relaxation is due to intramolecular dipole-dipole interactions between protons, which are time-dependent because of hindered rotations of the methyl groups, (2) the axes of hindered rotation are randomly oriented, and (3) the correlation time for reorientation is the same for all methyl groups at the same temperature. The distinctly nonexponential relaxation predicted by the theory is due to the inclusion of the effects of the cross correlations of the intramolecular dipole-dipole interactions. The agreement between the experimental results and the calculations is fairly good, the discrepancy being attributable to the effects of other relaxation mechanisms, such as intermolecular dipole-dipole interactions. The results provide the first experimental evidence of nonexponential spin-lattice relaxation produced by the effects of cross correlations of dipole-dipole interactions.

I. INTRODUCTION

The nuclear magnetic relaxation of spin-$\frac{1}{2}$ nuclei is due in many cases mainly to nuclear magnetic dipole-dipole interactions, which are time-dependent as a result of the motion of the nuclei. The calculation of the nuclear magnetic relaxation involves certain correlation functions of each dipole-dipole interaction with itself (autocorrelations) and with other dipole-dipole interactions (cross correlations). If the cross-correlation terms are omitted, the calculated relaxations of the longitudinal and transverse components of the nuclear magnetization are simple exponential decays.[1] If the cross-correlation terms are included in the calculation, the longitudinal relaxation is found, in general, to be the sum of more than one decaying exponential.

Calculations of the relaxation of systems of three and four identical spin-$\frac{1}{2}$ nuclei in molecules undergoing isotropic rotational Brownian motion have shown that there is little difference in the relaxation predicted when cross correlations are included and the exponential relaxation predicted when cross correlations are omitted.[2–6]

One situation for which the inclusion of cross correlations in the calculation has led to the prediction of a distinctly nonexponential spin-lattice relaxation is the case of three identical spin-$\frac{1}{2}$ nuclei at the corners of an equilateral triangle which undergoes hindered rotations

---

[*] Research supported in part by the National Science Foundation and the Advanced Research Projects Agency.

[†] Present address: Great Lakes Research Corporation, Elizabethton, Tenn.

[1] P. S. Hubbard, Rev. Mod. Phys. **33**, 249 (1961).

[2] P. S. Hubbard, Phys. Rev. **109**, 1153 (1958); **111**, 1746 (1958).

[3] P. S. Hubbard, Phys. Rev. **128**, 650 (1962).

[4] G. W. Kattawar and M. Eisner, Phys. Rev. **126**, 1054 (1962).

[5] P. M. Richards, Phys. Rev. **132**, 27 (1963).

[6] L. K. Runnels, Phys. Rev. **134**, A28 (1964).