ment two spins flip together [$|222\rangle \rightleftarrows |311\rangle$, and $|333\rangle \rightleftarrows |422\rangle$]. In both cases all spins have a common energy level. Grant's ensemble model does not distinguish between degenerate and nondegenerate cases in which each spin flips through a different transition. The experiments presented here suggest a need for reexamination of Grant's statistical model when applied to higher-order CR processes in diluted paramagnetic salts.

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APPENDIX: MATRIX ELEMENTS OF O_{ijk} AND H_{ij}

Explicit expressions for the matrix elements necessary to determine the lattice sums of the transition operator O_{ijk} of Eqs. (11), (20), and (21) are given below.

α = Processes

$$\langle 331 | O_{ijk} | 222 \rangle = [3i/(\epsilon_3-\epsilon_2)][(b_{jk}+f_{jk}+\tfrac{1}{2}id_{jk}) \times (b_{ij}+id_{ij}+b_{ik}-f_{ik}) + (b_{ik}+f_{ik}+\tfrac{1}{2}d_{ik}) \times (b_{ik}+d_{ij}+b_{ik}-f_{jk})]. \quad \text{(A1)}$$

β = Processes

$$\langle 224 | O_{ijk} | 333 \rangle = i(9/8)[\epsilon_3-\epsilon_2]^{-1} e_{ik} e_{kj}. \quad \text{(A2)}$$

The coefficients b_{jk}, f_{jk}, etc., are those given in terms of the dipolar interaction, Eq. (14). The pertinent matrix elements of the secular part of the dipolar interaction which appear in the computation of the moments, Eq. (26), are

$$\begin{aligned}
\langle 22 | H_{ij} | 22 \rangle &= -2\,\mathrm{Re}e_{ij} + 2b_{ij}, \\
\langle 33 | H_{ij} | 33 \rangle &= (9/4) a_{ij}, \\
\langle 24 | H_{ij} | 24 \rangle &= 3\,\mathrm{Im}d_{ij}, \\
\langle 24 | H_{ij} | 42 \rangle &= \tfrac{3}{2} b_{ij}, \\
\langle 31 | H_{ij} | 31 \rangle &= -3\,\mathrm{Im}d_{ij}, \\
\langle 31 | H_{ij} | 13 \rangle &= \tfrac{3}{2} b_{ij}.
\end{aligned} \quad \text{(A3)}$$

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Some Calculations on the Jahn-Teller Effect in Octahedral Systems

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Numerical calculations for a soluble one-parameter dynamic Jahn-Teller effect in a system of octahedral symmetry are presented (vibronic coupling of a τ_{2g} vibrational mode in a Γ_8 electronic state, linear approximation). A computer subprogram for computing eigenvectors and eigenvalues is described.

INTRODUCTION

NUMERICAL solutions of the vibronic energy eigenvalue problem were presented by Moffitt and Thorson[1] and by Longuet-Higgins, Öpik, Pryce, and Sack[2] for the dynamic Jahn-Teller interaction of a doubly degenerate vibration with a doubly degenerate electronic state, as may, for example, occur in a system with a single n-fold axis, $n \geq 3$. The tractability of the problem depended upon the fact that a "vibronic angular momentum" emerged in that case as a constant of the motion. The identical dynamical problem occurs in doubly degenerate states of systems with higher symmetry (O_h). The analysis of vibronic coupling in triply degenerate states (T_1, T_2) of such systems, however, proves to be essentially more complicated.[3] Both ϵ_g (doubly degenerate) and τ_{2g} (triply degenerate) vibrational modes may interact with the triply degenerate states. The coupling of the ϵ_g modes alone is very simple, leading only to a uniform shift of all levels. On the other hand, coupling of a single τ_{2g} mode alone is not characterized by a "vibronic angular momentum"; the potential-energy hypersurfaces for nuclear motion have octahedral rather than spherical symmetry; only

* Deceased.

[1] W. Moffitt and W. Thorson, Colloq. Intern. Centre Natl. Rech. Sci. (Paris) 82, 141 (1958). Also printed in book entitled *Calcul des Fonctions d'Onde Moleculaire*, edited by R. Daudel (Centre National de la Recherche Scientifique, Paris, 1958), Reprints of French text are available from W. Thorson.

[2] H. C. Lonquet-Higgins, U. Öpik, M. H. L. Pryce, and R. A. Sack, Proc. Roy. Soc. (London) **A244**, 1 (1958).

[3] W. Moffitt and W. Thorson, Phys. Rev. **108**, 1251 (1957).

in second-order perturbation approximation an "accidental" spherical symmetry occurs. Caner and Englman[4] have computed solutions to this vibronic problem in a lattice including cubic harmonics obtained from spherical harmonics up to order 12.

For systems with strong spin-orbit coupling and an odd number of electrons, electronic states must be categorized according to the "double-group" representations of O_h; Moffitt and Thorson[3] were able to show that for this case the vibronic coupling with a τ_{2g} mode takes on an especially symmetric form. The only states which exhibit such a coupling are the fourfold degenerate ones Γ_{8u} and Γ_{8g} in the notation of Bethe[5]; the doubly degenerate double group representations reflect only the Kramers magnetic degeneracy, which cannot be removed by the electrostatic Jahn-Teller effect. For the coupling of a mode τ_{2g} with electronic states Γ_{8u} or Γ_{8g}, the vibronic Hamiltonian is found to commute with a vibronic angular momentum, and hence eigenstates may be classified by quantum numbers for this momentum and its component on a preferred axis. Child[6] has also discussed the algebraic formulation of this problem and the solution for strong coupling. In a thorough discussion of vibronic and its applications to the vibrational spectra of higher transition-metal hexafluorides, Weinstock and Goodman[7] have treated the problem by perturbative methods for the weak-coupling limit; they treated couplings with both ϵ_g and τ_{2g} modes, a situation found experimentally in ReF_6 and isoelectronic molecules (see Discussion). In this work we present the numerical solution of the one-parameter eigenvalue problem for coupling of τ_{2g} with Γ_8, and discuss the strong-coupling limit.

ANALYSIS

A brief repetition of the fundamental analysis of Ref. 3 is our starting point. We neglect coupling with ϵ_g vibrational modes. Working in the four-dimensional electronic basis set provided by the Γ_8-type solutions to the electronic problem at the fixed O_h configuration, the nuclear-motion problem appears as a matrix equation for the nuclear motion in the three-dimensional Q space of the τ_{2g} vibration:

$$\{[-(\hbar^2/2\mu_\tau)\nabla^2+\tfrac{1}{2}k_\tau\mathbf{R}^2]\mathbf{1} + (2l\tau/\hbar)\,\boldsymbol{\varrho}_3[Q_1\mathbf{S}_1+Q_2\mathbf{S}_2+Q_3\mathbf{S}_3]\}\psi=E\psi, \quad (1)$$

where $\mathbf{R}^2=Q_1^2+Q_2^2+Q_3^2$, and ∇^2 is the Laplacian in Q space; $\mathbf{1}$ is the unit (4×4) matrix, and $\boldsymbol{\varrho}_3$, $\mathbf{S}_1$, $\mathbf{S}_2$, $\mathbf{S}_3$ are 4×4 matrices defined by Dirac,[8] and having the forms:

$$\boldsymbol{\varrho}_3=\begin{bmatrix}1&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-1\end{bmatrix};\quad \mathbf{S}_1=\tfrac{1}{2}\hbar\begin{bmatrix}0&1&0&0\\1&0&0&0\\0&0&0&1\\0&0&1&0\end{bmatrix};$$

$$\mathbf{S}_2=\tfrac{1}{2}\hbar\begin{bmatrix}0&-i&0&0\\i&0&0&0\\0&0&0&-i\\0&0&i&0\end{bmatrix};\quad \mathbf{S}_3=\tfrac{1}{2}\hbar\begin{bmatrix}1&0&0&0\\0&-1&0&0\\0&0&1&0\\0&0&0&-1\end{bmatrix}. \quad (2)$$

Now, the operator $\mathbf{S}$ acts like an "electronic angular momentum"; the electronic basis functions are eigenfunctions of $\mathbf{S}_3$ and of $\boldsymbol{\varrho}_3$, as well as of $\mathbf{S}^2$ (the eigenvalues for the last are $\frac{3}{4}\hbar^2$, for $\mathbf{S}_3$, $\pm\frac{1}{2}\hbar$, and for $\boldsymbol{\varrho}_3$, ±1). $\mathbf{S}$ has the proper commutation rules in Q space,

$$\mathbf{S}\times\mathbf{S}=i\hbar\mathbf{S}, \quad (3)$$

and in every respect is analogous to a "spin" in that space. The Hamiltonian may be written in this notation:

$$\mathsf{H}=H_0\mathbf{1}+[2(l_\tau/\hbar)]\boldsymbol{\varrho}_3[\mathbf{S}\cdot\mathbf{R}]. \quad (4)$$

H_0 is the Hamiltonian in Q space for the unperturbed three-dimensional harmonic oscillator with frequency ω_τ, previously written out in detail. The associated energy eigenvalues are $(n_\tau+\frac{3}{2})\hbar\omega_\tau$, n_τ integral, or zero, and there is as well a vibrational angular momentum $\mathbf{M}$ and its component M_3, with eigenvalues $M(M+1)\hbar^2$ for $\mathbf{M}^2$ and $M_3\hbar$ for M_3, by which the zero-order states must be categorized. M is positive or zero, has the parity of n_τ and is less than or equal to it; M_3 takes the usual $2M+1$ possible values. It is not hard to show that the definition of the vibronic angular momentum $\mathbf{J}$,

$$\mathbf{J}=\mathbf{M}+\mathbf{S}, \quad (5)$$

leads to new operators which commute with H, namely $\mathbf{J}^2$ and J_3. $\mathbf{J}$ satisfies the angular momentum commutation rules,

$$\mathbf{J}\times\mathbf{J}=i\hbar\mathbf{J}. \quad (6)$$

It may be seen that the vibronic coupling does not mix eigenfunctions with different eigenvalues of $\boldsymbol{\varrho}_3$, and that in fact for every solution to the vibronic problem with $+1$ for the ρ_3 eigenvalue, there is also one with -1 for that eigenvalue but identical values for all other eigenvalues. We shall therefore work in the reduced two-dimensional basis with $+1$ for the ρ_3 eigenvalue, $\pm\frac{1}{2}\hbar$ for the S_3 eigenvalue.

Zero-order states for the vibronic problem consist,

[4] M. Caner and R. Englman, J. Chem. Phys. **44**, 4054 (1966).
[5] H. A. Bethe, Ann. Physik **3**, 133 (1929).
[6] M. S. Child, Phil. Trans. Roy. Soc. (London) **A255**, 31 (1962).
[7] B. Weinstock and G. L. Goodman, Advan. Chem. Phys. **9**, 169 (1965).
[8] P. A. M. Dirac, *Quantum Mechanics* (Oxford University Press, New York, 1947).

then, of eigenfunctions of H_0, $\mathbf{M}^2$, M_3, $\mathbf{S}^2$, and $\mathbf{S}_3$, constituted by multiplying together appropriate vibrational and electronic components. Such a basis may be called the $(n_\tau MSM_3S_3)$ representation. The constants of the motion $\mathbf{J}^2$ and J_3 are diagonalized by the usual vector-coupling transformation to the $(n_\tau MSJJ_3)$ representation. J takes the possible values $M\pm\frac{1}{2}$, except $J=\frac{1}{2}$ when $M=0$; $J_3=M_3+S_3$. The resulting secular equation does not depend on J_3, M, or S, but only on J, and has the form

$$0=\mathrm{Det}\begin{bmatrix} J+1-\lambda & [2D(J+1)]^{1/2} & 0 & 0 & 0 & 0 \\ [2D(J+1)]^{1/2} & J+2-\lambda & (2D)^{1/2} & 0 & 0 & 0 \\ 0 & (2D)^{1/2} & J+3-\lambda & [2D(J+2)]^{1/2} & 0 & 0 \\ 0 & 0 & [2D(J+2)]^{1/2} & J+4-\lambda & (4D)^{1/2}\ 0 & 0 \\ \cdots \text{ etc.,} & & & & & \end{bmatrix}, \tag{7}$$

where $D=(l_\tau^2/2\hbar\mu_\tau\omega_\tau^3)$ is a dimensionless coupling parameter, and $\lambda=(E/\hbar\omega_\tau)$. (The secular equation for $\rho_3=-1$ is obtained by replacing $\sqrt{D}$ with $-\sqrt{D}$.)

This secular equation is identical to that obtained for the two-dimensional Jahn–Teller coupling problem,[1] except that J is a half-integer instead of the integer m which appears there. The contents of two registers in the computer program for that calculation were appropriately altered and the new calculations were performed. Energy eigenvalues λ are given as a function of D in Table I.

For experimental applications it may be useful to have the eigenvectors, as well as eigenvalues. Let $u(n_\tau MSJJ_3\rho_3)$ be the basis functions in the $(n_\tau MSJJ_3)$ representation. Note that, for given (n_τ, J), M is specified, because n_τ fixes the parity of M and $S=\frac{1}{2}$. Let the eigenvectors of the secular equation be denoted $\psi(vJJ_3\rho_3)$. They can be written

$$\psi(vJJ_3\rho_3)=\sum_{n_\tau=J-1/2}^{\infty} A(vJ\rho_3;n_\tau-J+\tfrac{1}{2})\,u(n_\tau MSJJ_3\rho_3). \tag{8}$$

On written request, we will provide a listing of a FORTRAN IV subprogram which does the following: (a) Given an approximate eigenvalue (error less than 20% of adjacent eigenvalue spacing for same J), it computes exact eigenvalue by rapidly convergent method (Ref. 9). (b) It computes the normalized coefficients $A(vJ\rho_3;k)$.

Just as in the case of the two-dimensional Jahn-Teller coupling, convenient solutions may be obtained for the limiting case that D becomes very large. In such a case, the potential-energy matrix is diagonalized, and the off-diagonal terms arising from the kinetic energy are neglected. An eigenvector with given J, J_3 has components which come from Q-space vibrational functions with $M=J-\frac{1}{2}$ and those with $M=J+\frac{1}{2}$. For simplicity we shall consider the case $J_3=J$ to calculate the strong-coupling energy levels. We may thus write the most general expression for the eigenvector $\psi(v,J,J)$:

$$\psi(v,J,J)=f(J,J-\tfrac{1}{2};R)\nu(J-\tfrac{1}{2},JJ)+f(J,J+\tfrac{1}{2};R)\nu(J+\tfrac{1}{2},JJ), \tag{9}$$

where

$$\nu(J-\tfrac{1}{2},JJ)=Y(J-\tfrac{1}{2},J-\tfrac{1}{2};\theta,\phi)\Phi(+\tfrac{1}{2}),$$
$$\nu(J+\tfrac{1}{2},JJ)=-(2J+2)^{-1/2}Y(J+\tfrac{1}{2},J-\tfrac{1}{2};\theta,\phi)\Phi(+\tfrac{1}{2})+[(2J+1)/(2J+2)]^{1/2}Y(J+\tfrac{1}{2},J+\tfrac{1}{2};\theta,\phi)\Phi(-\tfrac{1}{2}); \tag{10}$$

here $\Phi(\pm\frac{1}{2})$ designates the electronic state component, and $Y(lm)$ is the spherical harmonic in the Q-space angles θ, ϕ. It is easy to show that a similarity transformation matrix $\mathbf{A}$,

$$\mathbf{A}=\begin{bmatrix} -\sin\tfrac{1}{2}\theta\exp(i\phi/2) & \cos\tfrac{1}{2}\theta\exp(-i\phi/2) \\ \cos\tfrac{1}{2}\theta\exp(i\phi/2) & \sin\tfrac{1}{2}\theta\exp(-i\phi/2) \end{bmatrix}, \tag{11}$$

yields the matrix for the potential energy in diagonal form. The result of the full transformation on the Hamiltonian is a set of coupled differential equations for the component radial eigenfunctions $f(J,J\pm\frac{1}{2},R)$:

$$\left\{-\frac{\hbar^2}{2\mu R^2}\left[\frac{d}{dR}\left(R^2\frac{d}{dR}\right)\right]+\frac{(J+\frac{1}{2})^2\hbar^2}{2\mu R^2}+\tfrac{1}{2}k_\tau R^2-l_\tau R\right\}F(J;R)+\frac{(J+\frac{1}{2})\hbar^2}{2\mu R^2}G(J;R)=EF(J;R),$$

$$\left\{-\frac{\hbar^2}{2\mu R^2}\frac{d}{dR}\left(R^2\frac{d}{dR}\right)+\frac{(J+\frac{1}{2})^2\hbar^2}{2\mu R^2}+\tfrac{1}{2}k_\tau R^2+l_\tau R\right\}G(J;R)+\frac{(J+\frac{1}{2})\hbar^2}{2\mu R^2}F(J;R)=EG(J;R), \tag{12}$$

[9] J. A. Stratton, P. M. Morse, L. J. Chu, J. D. C. Little, and F. T. Corbato, *Spheroidal Wave Functions* (MIT Press, Cambridge, Mass., 1956). Especially see pages 53–62.

TABLE I. Octahedral Jahn-Teller effect (τ_{2g} with Γ_8). Eigenvalues in units of $\hbar\omega_\tau$.

	Coupling const. D				
J	0.1	0.2	0.3	0.4	0.5
1/2	1.24199337	1.03226391	0.84792711	0.67981338	0.52313780
3/2	2.11369023	1.83033900	1.59151611	1.37913241	1.18471217
5/2	3.00273355	2.66097500	2.37894656	2.13114884	1.90621990
7/2	3.90352264	3.51207551	3.19316285	2.91495820	2.66368929
9/2	4.81295071	4.37759250	4.02596631	3.72068757	3.44588604
11/2	5.72908059	5.25398209	4.87265609	4.54272892	4.24645406
13/2	6.65060743	6.13895431	5.73023694	5.37752976	5.06137674
1/2	2.51517151	2.40982380	2.25263638	2.08209708	1.91174787
3/2	3.58077637	3.39533875	3.15927048	2.92940799	2.71251987
5/2	4.60488220	4.32407797	4.02891494	3.75774136	3.50807087
7/2	5.59542039	5.23223048	4.89263745	4.58915031	4.31297059
9/2	6.56339949	6.13464842	5.75893254	5.42802252	5.12883476
11/2	7.51858522	7.03694455	6.63007902	6.27480415	5.95488969
1/2	3.30679977	3.24679484	3.22984228	3.20262991	3.14074355
3/2	4.25412589	4.28705004	4.34255127	4.31560953	4.18628618
5/2	5.23883392	5.37120258	5.44741654	5.32718363	5.10413216
7/2	6.25477085	6.46661085	6.48994443	6.24927116	5.97040709
9/2	7.29175045	7.55641322	7.45379649	7.13581341	6.82346385
1/2	4.46608173	4.30407202	4.13199301	3.98948531	3.88986466
3/2	5.49410221	5.25359028	5.03761346	4.91828963	4.90376346
5/2	6.49372647	6.18145618	5.96256967	5.94791348	6.03199840
7/2	7.47333968	7.10416477	6.94809155	7.05926701	7.19236407
1/2	5.35122877	5.32627931	5.28162334	5.18119854	5.04081558
3/2	6.33412781	6.38752164	6.34626141	6.18520066	5.98155159
5/2	7.34203984	7.45615524	7.36271749	7.12555320	6.87584701
1/2	6.43101680	6.25716390	6.12430285	6.05169841	6.01112435
3/2	7.43531734	7.19784888	7.07967564	7.07958832	7.09802328
1/2	7.38196276	7.35207441	7.25663794	7.10928105	6.95396342

	Coupling const. D				
J	0.6	0.7	0.8	0.9	1.0
1/2	0.37502665	0.23359356	0.09752131	−0.03415257	−0.16215634
3/2	1.00347078	0.83239277	0.66943250	0.51312687	0.36238674
5/2	1.69791725	1.50237385	1.31699774	1.13995141	0.96987627
7/2	2.43190352	2.21502798	2.01001766	1.81472419	1.62756500
9/2	3.19305702	2.95701340	2.73431538	2.52254337	2.31991903
11/2	3.97438548	3.72078585	3.48186119	3.25494827	3.03809269
13/2	4.77147321	4.50157928	4.24757716	4.00658055	3.77647378
1/2	1.74563697	1.58473001	1.42898699	1.27804959	1.13148108
3/2	2.50788196	2.31380017	2.12869406	1.95125331	1.78041671
5/2	3.27563084	3.05705780	2.84985413	2.65214819	2.46250791
7/2	4.05754415	3.81841119	3.59245203	3.37740259	3.17156459
9/2	4.85319433	4.59582651	4.35313294	4.12253971	3.90213409
11/2	5.66089696	5.38689035	5.12887313	4.88400877	4.65020038
1/2	3.04073657	2.91328716	2.77091886	2.62198654	2.47105229
3/2	4.00644986	3.81335422	3.61997628	3.43035041	3.24562941
5/2	4.86767826	4.63664787	4.41424545	4.20050605	3.99475222
7/2	5.70109080	5.44539868	5.20237834	4.97047557	4.74824860
9/2	6.53063099	6.25553582	5.99546712	5.74810835	5.51160801
1/2	3.82951347	3.79180357	3.75784165	3.71236804	3.64540685
3/2	4.93250970	4.95179920	4.92309901	4.82671014	4.68187922
5/2	6.10293832	6.08303976	5.94013391	5.74488080	5.53871034
7/2	7.21855281	7.04793661	6.81452969	6.57662813	6.34390844
1/2	4.88563219	4.73273536	4.59304054	4.47459355	4.38226403
3/2	5.78169584	5.61100994	5.49633817	5.45164929	5.45290751
5/2	6.66312232	6.54893627	6.55962282	6.61877232	6.67285037
1/2	5.96673952	5.89533500	5.79121407	5.66228222	5.52010713
3/2	7.06080748	6.94397516	6.77701880	6.59284712	6.40928416
1/2	6.81956095	6.71974104	6.65264000	6.60361046	6.55438158

TABLE I. (*Continued*).

J	Coupling const. D 1.1	1.2	1.3	1.4	1.5
1/2	−0.28705632	−0.40930290	−0.52926075	−0.64722972	−0.76345950
3/2	0.21637567	0.07443489	−0.06396518	−0.19925773	−0.33180226
5/2	0.80573445	0.64671198	0.49215666	0.34153644	0.19441064
7/2	1.44733453	1.27308949	1.10407542	0.93967779	0.77938820
9/2	2.12509010	1.93700000	1.75480464	1.57781711	1.40546959
11/2	2.82981014	2.62894195	2.43456320	2.24592168	2.06239590
13/2	3.55565138	3.34286104	3.13710361	2.93756689	2.74358009
1/2	0.98885136	0.84976560	0.71387108	0.58085612	0.45044606
3/2	1.61532395	1.45527159	1.29967816	1.14805776	1.0000000(!)
5/2	2.27981362	2.10317246	1.93185994	1.76527908	1.60293139
7/2	2.97362796	2.78255816	2.59752185	2.41783636	2.24293431
9/2	3.69045027	3.48633631	3.28886777	3.09728961	2.91097580
11/2	4.42584702	4.20969407	4.00073690	3.79815639	3.60127438
1/2	2.32045009	2.17134220	2.02428402	1.87951252	1.73709536
3/2	3.06597620	2.89119961	2.72098871	2.55500485	2.39291823
5/2	3.79619189	3.60407903	3.41775215	3.23663617	3.06023382
7/2	4.53447594	4.32814271	4.12840574	3.93456005	3.74601128
9/2	5.28449263	5.06557803	4.85390004	4.64866320	4.44920315
1/2	3.55407806	3.44214580	3.31606985	3.18154741	3.04250938
3/2	4.51563858	4.34219324	4.16749520	3.99403219	3.82286160
5/2	5.33301775	5.13100201	4.93355342	4.74080133	4.55260089
7/2	6.11809088	5.89920252	5.68683750	5.48049289	5.27967179
1/2	4.31503764	4.26556953	4.22351883	4.17875949	4.12284761
3/2	5.46642396	5.46632657	5.42888933	5.34065985	5.21218095
5/2	6.67800997	6.58818676	6.42895746	6.24593941	6.05704417
1/2	5.37404204	5.23080855	5.09572022	4.97358733	4.86863764
3/2	6.23774119	6.09121414	5.98727309	5.93572689	5.92280537
1/2	6.49009921	6.40302728	6.29366022	6.16779365	6.03222914

J	Coupling const. D 1.6	1.7	1.8	1.9	2.0
1/2	−0.87816030	−0.99151076	−1.10366386	−1.21475152	−1.32488823
3/2	−0.46190089	−0.58981024	−0.71575047	−0.83991179	−0.96246000
5/2	0.05040950	−0.09078077	−0.22942911	−0.36576800	−0.50000000
7/2	0.62278048	0.46949324	0.31921685	0.17168383	0.02666113
9/2	1.23728634	1.07286417	0.91185784	0.75396905	0.59893805
11/2	1.88346543	1.70868927	1.53768998	1.37014149	1.20575989
13/2	2.55458164	2.37009584	2.18971559	2.01308928	1.83991081
1/2	0.32229865	0.19649972	0.07255916	−0.04959237	−0.17010641
3/2	0.85515501	0.71322154	0.57393856	0.43707779	0.30243845
5/2	1.44439570	1.28931239	1.13737161	0.98830416	0.84187438
7/2	2.07233814	1.90564148	1.74249516	1.58259656	1.42568138
9/2	2.72940052	2.55211705	2.37874218	2.20894418	2.04243366
11/2	3.40952192	3.22241618	3.03954331	2.86054535	2.68511033
1/2	1.59700943	1.45918367	1.32352281	1.18992076	1.05826817
3/2	2.23442194	2.07923597	1.92710721	1.77780764	1.63113195
5/2	2.88811437	2.71991350	2.55527424	2.39393955	2.23564602
7/2	3.56225390	3.38285429	3.20743755	3.03567713	2.86728664
9/2	4.25495878	4.06545134	3.88026868	3.69905307	3.52149166
1/2	2.90141310	2.75974352	2.61838985	2.47788192	2.33853130
3/2	3.65441282	3.48882232	3.32608456	3.16612433	3.00883335
5/2	4.36870959	4.18885764	4.01277714	3.84021419	3.67093311
7/2	5.08391535	4.89281029	4.70598793	4.52312019	4.34391486
1/2	4.05022008	3.95940421	3.85270455	3.73418742	3.60777806
3/2	5.06230151	4.90306477	4.74034081	4.57691080	4.41413575
7/2	5.86803601	5.68095814	5.49657750	5.31515889	5.13674927
1/2	4.78319489	4.71600059	4.66209497	4.61450913	4.56602254
3/2	5.92541061	5.92447973	5.90253663	5.84357041	5.74406805
1/2	5.89259703	5.75318512	5.61746467	5.48862752	5.36988792

TABLE I. (*Continued*).

J	Coupling const. D 2.1	2.2	2.3	2.4	2.5
1/2	−1.43417383	−1.54269579	−1.65053105	−1.75774754	−1.86440539
3/2	−1.08354037	−1.20328105	−1.32179560	−1.43918515	−1.55554014
5/2	−0.63230278	−0.76283317	−0.89173138	−1.01911858	−1.14510904
7/2	−0.11605565	−0.25664699	−0.39527308	−0.53207696	−0.66718681
9/2	0.44563700	0.29656479	0.14884281	0.00321169	−0.14047152
11/2	1.04429622	0.88553068	0.72926817	0.57533449	0.42357344
13/2	1.66991177	1.50285520	1.33853079	1.17675077	1.01734674
1/2	−0.28911898	−0.40675271	−0.52311850	−0.63831696	−0.75243963
3/2	0.16984283	0.03913270	−0.08983344	−0.21718281	−0.34303026
5/2	0.69787467	0.55612098	0.41644924	0.27871247	0.14277843
7/2	1.27151723	1.11989840	0.97064189	0.82358397	0.67857747
9/2	1.87895644	1.71828777	1.56022779	1.40459789	1.25123763
11/2	2.51296412	2.34386475	2.17759703	2.01396878	1.85280745
1/2	0.92845670	0.80038140	0.67394190	0.54904300	0.42559477
3/2	1.48689504	1.34492970	1.20508453	1.06722197	0.93121678
5/2	2.08016886	1.92730762	1.77688277	1.62873277	1.48271171
7/2	2.70201341	2.53963311	2.37994567	2.22277166	2.06794951
9/2	3.34730909	3.17626150	3.00813157	2.84272501	2.67986695
1/2	2.20051510	2.06392625	1.92880443	1.79515528	1.66296266
3/2	2.85408933	2.70176618	2.55173946	2.40388922	2.25810141
5/2	3.50471763	3.34137001	3.18070982	3.02257246	2.86680756
7/2	4.16811122	3.99547577	3.82579881	3.65889127	3.49458215
1/2	3.47648069	3.24326908	3.20681652	3.07072127	2.93467063
3/2	4.25270088	4.09295083	3.93504968	3.77906162	3.62499407
5/2	4.96129585	4.78869986	4.61884262	4.45159881	4.28684329
1/2	4.51016858	4.44205318	4.35928057	4.26228232	4.15347455
3/2	5.61571408	5.47171514	5.32023269	5.16547568	5.00961226
1/2	5.26434069	5.17417735	5.09951029	5.03776255	4.98427061

where

$$F(J;R)=f(J,J+\tfrac{1}{2})+f(J,J-\tfrac{1}{2}),\qquad(13)$$
$$G(J;R)=f(J,J-\tfrac{1}{2})-f(J,J+\tfrac{1}{2}).$$

If now we imagine l_τ to be large, and neglect the coupling term in G, the equation for F becomes that for motion on a potential surface whose minimum is displaced from $R=0$; its minimum energy is lowered by the amount $D\hbar\omega_\tau$. F represents motion on the lower potential sheet, G that on an excited sheet. The approximate equation for F is very similar to that of the vibrating rotor, analyzed by Dunham.[10] The limiting energy levels may be expressed in terms of the vibrational quantum number v, and J are

$$\begin{aligned}E(v,J,J_3)&=\hbar\omega_\tau\{-D+(v+\tfrac{1}{2})+(J+\tfrac{1}{2})^2[(1/4D)+(15/32D^2)]\\&+(3/8D^2)(v+\tfrac{1}{2})(J+\tfrac{1}{2})^2+(15/32D^3)(v+\tfrac{1}{2})^2(J+\tfrac{1}{2})^2\\&-[(1/16D^3)+(163/512D^5)](J+\tfrac{1}{2})^4\}.\qquad(14)\end{aligned}$$

A curious phenomenon occurs in the behavior of eigenvalues emanating from a given zero-order level of the unperturbed system. For the level with zero-order energy $(n_\tau+\frac{3}{2})\hbar\omega_\tau$ allowed values of J are $\frac{1}{2}$, $\frac{3}{2}$, $\cdots(n_\tau+\frac{1}{2})$. As implied by Eq. (14) the eigenvalue spectrum for large D is that of a vibrating rotor, but before this limiting behavior is obtained the eigenvalues perform a sequence of curious oscillations about the "baseline" value $[(n_\tau+\frac{3}{2})\hbar\omega_\tau-D\hbar\omega_\tau]$. Figure 1 illustrates the behavior in question for the zero-order level with $n_\tau=6$. The "adjusted" eigenvalues $E(J)+D\hbar\omega_\tau$ are plotted versus D. As is shown in Fig. 1, the eigenvalues for $J=\frac{1}{2}, \cdots\frac{13}{2}$ fan out from the baseline value of $7.5\hbar\omega_\tau$; the level $\frac{13}{2}$ drops monotonically towards its

[10] J. L. Dunham, Phys. Rev. **41**, 721 (1932).

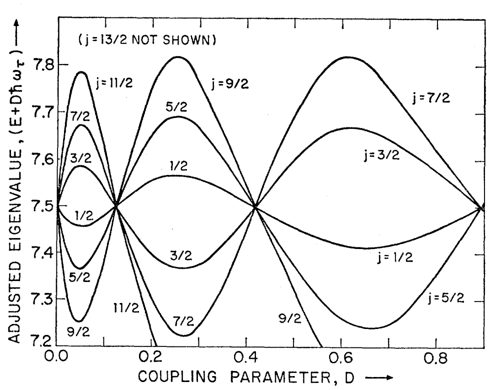

FIG. 1. Nodal degeneracy phenomenon. Oscillation of the eigenvalues for the zero-order level with $n_\tau=6$.

TABLE II. Discrepancies in the nodal degeneracy phenomenon [for each node, n_τ, and j value, the value of D_c such that $E_j + D_c\hbar\omega = (n_\tau+\frac{3}{2})\hbar\omega_\tau$].

n_τ	j	First node D_c	Second node D_c	Third node D_c	Fourth node D_c	Fifth node D_c
2	1/2	0.265025				
	3/2	0.270196				
3	1/2	0.205246	0.712189			
	3/2	0.207607	0.714163			
	5/2	0.211816	...			
4	1/2	0.167566	0.574538	1.259788		
	3/2	0.168840	0.575335	1.256415		
	5/2	0.171059	0.576149	...		
	7/2	0.174389	...	...		
5	1/2	0.141612	0.482345	1.043725	1.872713	
	3/2	0.142377	0.482741	1.041389	1.863562	
	5/2	0.143693	0.483183	1.036336	...	
	7/2	0.145626	0.483252	...	...	
	9/2	0.148286	...	...	...	
6	1/2	0.122635	0.416015	0.893288	1.581563	2.532009
	3/2	0.123131	0.416241	0.891684	1.575564	2.517175
	5/2	0.123976	0.416511	0.888493	1.563914	...
	7/2	0.125202	0.416636	0.882858	...	...
	9/2	0.126858	0.416280	...	...	...
	11/2	0.129020	...	...	...	...

limiting place as a rotational component for $v=0$ in Eq. (14), but the remaining $(n_\tau-1)$ eigenvalues again converge towards each other and the baseline and at a certain critical D value appear to be simultaneously degenerate with the baseline value $E(J)+D\hbar\omega_\tau = 7.50\,\hbar\omega_\tau$. For increasing D they again diverge, the level $J=\frac{11}{2}$ drops monotonically towards its place in the rotational structure for $v=1$, and the remaining $(n_\tau-2)$ levels again converge on an apparent nodal degeneracy at the baseline at a second critical D value. For increasing D this pattern is repeated, with the level of highest remaining J value "peeling off" each time, until only the level $J=\frac{1}{2}$ remains to cross the baseline and join the rotational structure for $v=n_\tau$. This behavior is quite systematic; it occurs $(n_\tau-1)$ times for the zero-order level $(n_\tau+\frac{3}{2})\hbar\omega_\tau$. Surmising that such "accidental" degeneracy could not truly be accidental, we performed extensive exploration of the regions of nodal degeneracy. The result of this exploration is stranger still: *The degeneracy is not quite exact.* Table II lists the values of D, for each nodal region and each J value, for which $E_J+D\hbar\omega_\tau=(n_\tau+\frac{3}{2})\hbar\omega_\tau$. It will be seen that although these D values are clustered closely, there is a finite spread in each case, ranging from 1×10^{-4} to 2×10^{-2}; nor is it true that a nodal degeneracy occurs at any point *off* the baseline value.

Obviously, results like this could be attributed to systematic errors in the computer program, and we have gone over the computation exhaustively, with this in mind. However, we are now convinced that the computation is accurate to at least one part in 10^9, for a number of reasons:

(1) At least one eigenvalue and its eigenvector have been calculated to *nine decimal place agreement,* using (a) a desk calculator, (b) the computer program listed here, and (c) UNIVAC I at Harvard, using a somewhat different computational procedure. Also, complete nine-figure agreement between results of (b) and (c) was observed in every case tested.

(2) The results are independent of the point of truncation, agreeing to 1×10^{-12}, whether one uses 200 or 400 terms in the recursion process.

(3) The precision of computed eigenvalues is of this order, too; there is no ambiguity or "wandering" of $E_J(D)$ as function of D; the plots are cleanly defined and unambiguously "miss" the nodal degeneracy by the amounts given in Table II.

(4) All computation is done in double precision (IBM 360); we found the perturbations due to deliberate underspecification of parameter precision, to single precision, to be in the *sixth* decimal place.

(5) The eigenvector expansion converges unambiguously and in every case we evaluated the coefficients out to magnitudes 1×10^{-12}.

It is our view that exact degeneracy does not, in fact, occur, though we have no explanation either for the "near-miss" situation observed, nor for the existence of even *approximate* degeneracies.

(Pragmatically, we may note that in the presence of even a very weak additional perturbation *not* diagonal in J, the eigenvalues near a nodal degeneracy will exhibit first-order shifts; this renders the issue a purely formal, academic one.)

[For anyone interested in pursuing the formal problem, we may write the Hamiltonian most compactly as

$$\mathsf{H}=\hbar\omega_\tau\mathbf{1}\{\tfrac{1}{2}(\boldsymbol{\alpha}^\dagger\cdot\boldsymbol{\alpha}+\boldsymbol{\alpha}\cdot\boldsymbol{\alpha}^\dagger)-i(\sqrt{D})\boldsymbol{\sigma}\cdot(\boldsymbol{\alpha}^\dagger-\boldsymbol{\alpha})\},\tag{15}$$

where

$$\boldsymbol{\alpha}^\dagger=(2m\hbar\omega_\tau)^{-1/2}[\mathbf{P}+im\omega_\tau\mathbf{R}]\qquad \boldsymbol{\alpha}=(\boldsymbol{\alpha}^\dagger)^*,\tag{16}$$

and $\boldsymbol{\sigma}$ is the (vector) Pauli spin matrices. The orbital angular momentum $\mathbf{R}\times\mathbf{P}$ is given by $\mathbf{M}=-i\hbar[\boldsymbol{\alpha}^\dagger\times\boldsymbol{\alpha}]$, and the operator $\mathsf{J}=\mathbf{M}+(\frac{1}{2}\hbar)\boldsymbol{\sigma}$ commutes with H. The point to be proved (if possible) is that there exist critical D values and n_τ values such that $(\mathsf{H}+D\hbar\omega_\tau\mathbf{1})$ has a multiply degenerate eigenvalue $[(n_\tau+\frac{3}{2})\hbar\omega_\tau]$.]

DISCUSSION

The eigenvalue computations presented were originally performed on the UNIVAC I Computer at the

Harvard University Computation Laboratory. The details of computation are analogous to those described in Ref. 1. While the dynamic Jahn-Teller effect is nearly as elusive as ever, there has been an increasing amount of work concerned with it, particularly in solid state physics.

Some molecules and certain complex ions in solids are known to have Γ_8 ground states. A Γ_8 state can arise either from an orbital doublet (E state) with spin $\frac{1}{2}$, or from the manifold of states produced from an orbital triplet (T state) with half-integral spin and strong spin-orbit coupling.

In solids, the first case is the one encountered in every known example to date, and it is also found that in these systems which appear to exhibit dynamic Jahn-Teller coupling it is always the doubly-degenerate mode ϵ_g which is strongly coupled, that to the τ_{2g} mode being apparently negligible. For the second case to occur, strong spin-orbit coupling would be essential to split the Γ_8 component from other multiplets of the same term by separations large compared to the vibronic perturbations; this situation could be found in the heavier elements, as it is for molecules.[11]

In molecules, the case of a Γ_8 ground state arising from an orbital triplet is known experimentally. Weinstock and Goodman[7] analyzed the vibrational spectra of ReF_6 and TcF_6 by treating the coupling of both ϵ_g and τ_{2g} modes with the Γ_8 electronic state, using perturbation methods. In both cases, though the ϵ_{2g} splitting is larger than that due to τ_{2g}, the dimensionless parameter D is larger for the latter mode than for the former because of the much lower frequency of the trigonal bending mode relative to the tetragonal (stretching) mode. However, both are important, and vibronic interactions quadratic in the vibration coordinates (not considered in our calculations) seem to play a significant part.[12]

The case we have treated here, which assumes coupling only to the τ_{2g} mode and restricts that to linear terms, remains without direct applications. It may be instructive, however, as an exact solution against which approximate methods can be checked. With this in mind, we have written a FORTRAN IV computer subprogram to compute normalized eigenvectors of this problem; this makes the computation of reduction factors and other experimentally useful quantities quite simple. The program simultaneously refines the accuracy of approximately known eigenvalues, enabling rapid interpolation from Table I to any desired coupling parameter. Also, merely by changing the angular momentum quantum number from an odd half-integer to an integer, the program computes solutions for the much more common case discussed in Refs. 1 and 2.

It should be pointed out that by far the greater amount of literature on the Jahn-Teller effect and its applications has appeared since 1959. The articles by Liehr[13,14] and by Weinstock and Goodman,[7] and the volume by Herzberg,[15] provide a good picture of the work done relevant to molecules. An extensive discussion dealing particularly with the effects of Jahn-Teller coupling on optical and paramagnetic resonance spectra has been given by Ham.[16] Ham's paper is also very useful for its literature citations on solids. More recently, an excellent review article on the dynamic Jahn-Teller effect in solids has been written by Sturge,[17] with a comprehensive bibliography.

ACKNOWLEDGMENTS

This work was done in collaboration with the late William Moffitt, Professor of Chemistry at Harvard until his untimely death in 1958. It is only appropriate that his influence be acknowledged by listing him as co-author. I am also indebted to Dr. F. S. Ham for helpful comments and recent literature citations.

[11] We are indebted to Dr. F. S. Ham (private communication) for comments on the experimental situation with respect to Γ_8 states in solids.

[12] Dr. G. L. Goodman (private communication) has drawn this point to our attention.

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