initio calculations lead to 5π states at 60° with energies about 3 eV *above* the comparable states at 117°, the INDO calculations lead to 5π states at 60° with energies about 0 to 1 eV *below* the comparable states at 117°.

III. Discussion

The most grievious fault of INDO apparent in our calculations on ozone is the strong bias toward closed geometries,[50] even when unfavorable electron interactions should make small bond angles strictly repulsive, *e.g.*, for the $^1A_1(5\pi)$, $^3A_2(5\pi)$, $^1B_1(5\pi)$, $^3B_1(5\pi)$, and $^3B_2(6\pi)$ states. Similar problems with INDO have been found previously.[51] It appears as if INDO does not properly represent the repulsion involved when triplet-coupled electrons are forced into close proximity. In addition it appears that INDO gives rise to π bonds that are far too strong. The latter explanation would be consistent with the short bond lengths observed for $^1A_1(4\pi)$ and the large transition energies observed for the $4\pi \rightarrow 5\pi$ and $4\pi \rightarrow 6\pi$ transitions (at the calculated equilibrium geometry). Consequently, the use of INDO for calculating equilibrium geometries as in conformational studies or reaction pathways is very risky, even if correlation effects are included.

Our calculations show that INDO treats the electron correlations involved in the GVB(1) wave function fairly well, so that using such correlated wave functions will cure some of the gross errors encountered when INDO is used with the HF method. However, introduction of CI need not improve the energy spectrum obtained with INDO and, in fact, may make it worse. (See, for example, the reordering of the 5π and 6π states after CI.) Nevertheless, despite certain significant errors in describing the overall energy spectrum, INDO does reproduce many of the energy separations properly, *e.g.*, the singlet–triplet splittings of states arising from the same configurations. This indicates to us that it may be possible to develop a method on the order of INDO in complexity that would yield reliable results (comparable at least to *ab initio* MBS calculations). Work is in progress along these lines.

(50) Subsequent to submission of this paper, A. K. Q. Siu and E. F. Hayes, *Chem. Phys. Lett.*, **21**, 573 (1973), published semiempirical HF calculations on the open ($1\,^1A_1$) and ring ($2\,^1A_1$) states of ozone, in which they reported that the CNDO/2, INDO, and MINDO approximations all favored the ring state by 5 to 10 eV over the open state, in agreement with our results. Siu and Hayes also reported *ab initio* Hartree–Fock calculations, leading to the ring state about 0.36 eV above the open ground state. However, as shown earlier from *ab initio* GVB and CI calculations, HF wave functions (which exclude electron correlations) are biased in favor of the ring state by 1 eV or more, so that the *ab initio* relative energy (0.39 eV) of the ring and open states obtained by Siu and Hayes is much smaller than the real spacing between these states. Extensive DZ–CI calculations[9c] indicate that the ring state is 1.57 eV above the open ground state.

(51) M. Froimowitz and P. J. Gans, *J. Amer. Chem. Soc.*, **94**, 8020 (1972); see also T. Morton, Ph.D. Thesis, California Institute of Technology, 1972.

Symmetry Adapted Functions and Normalized Spherical Harmonic (NSH) Hamiltonians for the Point Groups O_h, T_d, D_{4h}, D_{2d}, C_{4v}, D_{2h}, C_{2v}

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Abstract: A general method is introduced for the projection of normalized spherical harmonic (NSH) Hamiltonians. Subgroups of O_h which subduce C_{2v} are specifically considered, and d^n basis functions symmetry adapted to the various groups are derived. The advantages of a symmetry-adapted basis are emphasized in the interpretation of absorption spectra of three nickel(II) systems characterized by C_{2v} effective symmetry. Symmetry-adapted representations of H_G for $G = O_h$, T_d, D_{4h}, C_{4v}, D_{2d}, D_{2h}, and C_{2v} are tabulated for the d^1 (and d^9) configuration, the spin triplet states of the d^2 (and d^8) configuration, and the spin quartet states of the d^3 (and d^7) configuration.

Although the absorption spectra of many transition metal systems have been reproduced using a ligand field Hamiltonian and l^n basis set,[1–3] calculations assuming D_{2d}, D_{2h}, or C_{2v} symmetry are not common.[4–7] Hamiltonians for D_{2h} or C_{2v} symmetry and a d^n basis set incorporate a maximum of five empirical parameters (excluding interelectronic repulsion parameters), in contrast to a maximum of three such parameters for symmetries with a fourfold axis. Spectra are therefore often interpreted assuming the symmetry of a higher point group for calculation purposes. Only in certain cases can the assumption be justified.[8] We present a method for the projection of normalized spherical harmonic (NSH) Hamiltonians which is applicable to all point group symmetries and offers not only the possibility of straightforward calculations for noncubic as well as cubic symmetries but also the possibility of

(1) R. Finkelstein and J. H. Van Vleck, *J. Chem. Phys.*, 8, 790 (1940).
(2) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962.
(3) J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, London, 1961.
(4) M. Gerloch and R. C. Slade, *J. Chem. Soc. A*, 1022 (1969).
(5) A. Flamini, L. Sestili, and C. Furlani, *Inorg. Chim. Acta*, **5**, 241 (1971).
(6) P. L. Meredith and R. A. Palmer, *Inorg. Chem.*, **10**, 1049 (1971).
(7) N. S. Hush and R. J. M. Hobbs, *Progr. Inorg. Chem.*, 10, 259 (1968).
(8) J. S. Griffith, *Mol. Phys.*, 8, 217 (1964).

standardizing correlation procedures. The empirical parameters which arise are independent of the coordinate system used for calculations and may be compared with parameters from the crystal field[9] or angular overlap model[10] to determine restrictions on parameter values. The approach parallels recent developments by Schäffer[10] and Ellzey.[11]

As illustrated in the interpretation of spectra of three nickel(II) systems characterized by C_{2v} effective symmetry, a representation of H on a basis symmetry adapted to the point group defines relationships between empirical parameters and experimental observables thus minimizing the difficulty of the parameter fitting procedure. Symmetry-adapted representations also minimize computation and provide a point group quantum number for identification of calculated energy states. A derivation of d^n basis functions symmetry adapted to point group chains[12] terminating with C_{2v} is included as are normalized spherical harmonic Hamiltonians for all point groups in the chains. Symmetry-adapted representations for d^n configurations with $n = 1, 2,$ and 3 and $G = O_h, T_d, D_{4h}, C_{4v}, D_{2d}, D_{2h},$ and C_{2v} are tabulated (Appendix).

Theory

A transition metal complex with n valence electrons is represented by an n-electron Hamiltonian of the form

$$H = H^\circ + H_G \qquad (1)$$

where H° is the free ion Hamiltonian and

$$[H^\circ, G_a] = 0; \;\; G_a \in [R(3)]^n \qquad (2)$$

$[R(3)]^n$ is the nth rank inner direct product of the rotation group in three dimensions, $R(3)$. Integers $L = 0, 1, 2, \ldots$ characterize irreducible representations of $[R(3)]^n$ and are quantum numbers for H°. H_G represents the ligand field, where

$$[H_G, G_a] = 0; \;\; G_a \in [G]^n \qquad (3)$$

and $[G]^n$ is the nth rank inner direct product of a point group G. Irreducible representations of $[G]^n$, denoted $\mathcal{A}(G)$, are quantum numbers for H. For the octahedral group, $\mathcal{A}(0) = A_1, A_2, E, T_1,$ and T_2.

The potential H_G is expanded in terms of tensor operators,[10] where

$$H_G = \sum_{i=1}^{n} P_i$$
$$P_i = \sum_L \sum_M B_M{}^L C_M{}^L \qquad (4)$$

and the $C_M{}^L$ tensors with $M = L, L-1, \ldots, -L$ are a basis for an irreducible representation of $R(3)$. Any vanishing of $B_M{}^L$ coefficients is determined not only by the symmetry of the environment of the transition metal but also by the choice of coordinate system.[10,13] Nonvanishing $B_M{}^L$ coefficients are directly related to ligand field parameters to be fitted from experiment. We choose to expand P in terms of linear combinations of tensor operators which transform according to an irreducible representation of G. The linear combinations

$$|\tau\mathcal{A}R|_G{}^L = \sum_M C_M{}^L \langle LM|\tau\mathcal{A}R\rangle_G \qquad (5)$$

are orthonormal. A degeneracy index R identifies components of the irreducible representation $\mathcal{A}(G)$ and τ distinguishes $\mathcal{A}(G)$ if more than one $\mathcal{A}$ of the same kind is subduced by L. Symmetry adaptation coefficients $\langle LM|\tau\mathcal{A}R\rangle_G$ for the octahedral group have been tabulated by Griffith.[14]

After expansion

$$P = \sum_L \sum_\tau A^{L;\tau}|\tau A_1 a_1|_G{}^L \qquad (6)$$

since only those linear combinations of tensor operators which transform as A_1 (or A_{1g}) can have nonvanishing coefficients.[11,15,16] The coefficients $A^{L;\tau}$ serve as empirical parameters to be evaluated from experiment.[17] Their magnitudes are independent of coordinate system.

In addition H is a spin free Hamiltonian[18] where

$$[H, P_a{}^{SF}] = 0; \;\; P_a{}^{SF} \in S_n{}^{SF} \qquad (7)$$

and $S_n{}^{SF}$ is the group of permutations on the spatial coordinates of the n electrons. The partitions $[\lambda]$ of $S_n{}^{SF}$ are exact quantum numbers for H and yield the multiplicity quantum number $\mathfrak{M} = 2S + 1$.

Basis Functions. A representation of H in the 5^n dimensional spin free vector space $V^{SF}(d^n)$ is a function of the ligand field parameters $A^{L;\tau}$ and the Racah parameters A, B, and C. Although eigenvalues and eigenkets can be obtained from a representation of H on the $|d^{n;\mathfrak{M}}LM\rangle$ basis of $V^{SF}(d^n)$,[19-22] a representation of H on a basis symmetry adapted to $[G]^n$ has certain advantages.[1,11,17,23] Namely, the representation is block diagonal since

$$\langle d^n;{}^{\mathfrak{M}}L;\tau^{\mathfrak{M}}\mathcal{A}R|H|d^n;{}^{\mathfrak{M}'}L';\tau'^{\mathfrak{M}'}\mathcal{A}'R'\rangle = \delta(\mathfrak{M},\mathfrak{M}')\delta(\mathcal{A},\mathcal{A}')\delta(R,R') \qquad (8)$$
$$\langle d^n;{}^{\mathfrak{M}}L;\tau^{\mathfrak{M}}\mathcal{A}R|H|d^n;{}^{\mathfrak{M}}L';\tau'^{\mathfrak{M}}\mathcal{A}R\rangle$$

and each block is identified by an irreducible representation of the point group of interest. Symmetry adaptation coefficients suitable for the projection of $|d^n;{}^{\mathfrak{M}}L;\tau^{\mathfrak{M}}\mathcal{A}R\rangle$ basis functions for O_h or D_{4h} symmetry are readily available.[14] Making use of the previously tabulated functions we project bases for d^n configura-

(9) M. T. Hutchings, *Solid State Phys.*, 16, 227 (1964).
(10) S. E. Harnung and C. E. Schäffer, *Struct. Bonding (Berlin)*, 12, 201 (1972), and references therein; C. E. Schäffer, "Wave Mechanics, the First Fifty Years," W. C. Price, S. S. Chissick, and T. Ravensdale, Ed., Butterworths, London, 1973, p 174; C. F. Schäffer, *Struct. Bonding (Berlin)*, 14, 69 (1973).
(11) M. L. Ellzey, *Int. J. Quantum. Chem.*, 7, 253 (1973).
(12) F. A. Matsen and O. R. Plummer, "Group Theory and Its Applications," E. M. Loebl, Ed., Academic Press, New York, N. Y., 1968, p 221.
(13) J. L. Prather, *Nat. Bur. Stand. (U.S.) Monogr.*, No. **19** (1961).
(14) Reference 3, Appendix 2, Table A19.
(15) Reference 3, p 202.
(16) Y. Tanabe and H. Kamimura, *J. Phys. Soc. Jap.*, **13**, 394 (1958).
(17) B. R. Hollebone, A. B. P. Lever, and J. C. Donini, *Mol. Phys.*, 22, 155 (1971).
(18) (a) F. A. Matsen and M. L. Ellzey, *J. Phys. Chem.*, 73, 2495 (1969); (b) J. C. Hempel and F. A. Matsen, *ibid.*, **73**, 2502 (1969).
(19) For a discussion of calculation techniques see, for example, (a) B. R. Judd, "Operator Techniques in Atomic Spectroscopy," McGraw-Hill, New York, N. Y., 1963; and (b) ref 3.
(20) C. W. Nielson and G. F. Koster, "Spectroscopic Coefficients for the p^n, d^n, and f^n Configurations," Technical Press, Cambridge, Mass., 1963.
(21) J. P. Jesson, *J. Chem. Phys.*, **48**, 161 (1968).
(22) J. C. Hempel, D. Klassen, W. E. Hatfield, and H. H. Dearman, *J. Chem. Phys.*, 58, 1487 (1973).
(23) J. R. Perumareddi, *Coord. Chem. Rev.*, **4**, 73 (1969).

Table I. Basis Functions and Correlation Table for the Gerade Irreducible Representations of O_h Relevant to Chains 9, 10, and 11 Terminating with C_{2v}(I)

O_h →	D_{4h} →	C_{4v} or	$D_{2d}(\mathrm{I})^a$ or	$D_{2h}(\mathrm{I})^b$ →	$C_{2v}(\mathrm{I})^c$	Bases[d]
A_{1g}	A_{1g}	A_1	A_1	A_g	A_1	R
$E_g\theta$	A_{1g}	A_1	A_1	A_g	A_1	$(2z^2 - x^2 - y^2)$
$E_g\epsilon$	B_{1g}	B_1	B_2	A_g	A_1	$\sqrt{3}(x^2 - y^2)$
A_{2g}	B_{1g}	B_1	B_2	A_g	A_1	$(x^2 - y^2)(y^2 - z^2)(z^2 - x^2)$
$T_{2g}(xy)$	B_{2g}	B_1	B_1	B_{1g}	A_2	xy
$T_{1g}(z)$	A_{2g}	A_2	A_2	B_{1g}	A_2	S_z
$T_{2g}(xz)$	$E_g(xz)$	$E(xz)$	$E(xz)$	B_{2g}	B_1	xz
$T_{1g}(y)$	$E_g(y)$	$E(y)$	$E(y)$	B_{2g}	B_1	S_y
$T_{2g}(yz)$	$E_g(yz)$	$E(yz)$	$E(yz)$	B_{3g}	B_2	yz
$T_{1g}(x)$	$E_g(x)$	$E(x)$	$E(x)$	B_{3g}	B_2	S_x

[a] $I = \{E, 2S_4, C_2(z), 2C_2', 2\sigma_h\}$. [b] $I = \{E, 3C_2, i, 3\sigma_h\}$. [c] $I = \{E, C_2(z), \sigma_h(xz), \sigma_h(yz)\}$. [d] Reference 27. S_z denotes a function which transforms like z but does not change sign under inversion.

Table II. Basis Functions and Correlation Table for the Gerade Irreducible Representations of O_h Relevant to Chains 9 and 11 Terminating with C_{2v}(II) or Chain 11 Terminating with C_{2v}(III)

O_h →	D_{4h} →	C_{4v} or	$D_{2h}(\mathrm{II})^a$ →	$C_{2v}(\mathrm{II})^b$ →	$C_{2v}(\mathrm{III})^c$	Bases[d]
A_{1g}	A_{1g}	A_1	A_g	A_1	A_1	R
$E_g\theta$	A_{1g}	A_1	A_g	A_1	A_1	$(2z^2 - x^2 - y^2)$
$T_{2g}(xy)$	B_{2g}	B_1	A_g	A_1	A_1	xy
A_{2g}	B_{1g}	B_1	B_{1g}	A_2	B_1	$(x^2 - y^2)(y^2 - z^2)(z^2 - x^2)$
$E_g\epsilon$	B_{1g}	B_1	B_{1g}	A_2	B_1	$\sqrt{3}(x^2 - y^2)$
$T_{1g}(z)$	A_{2g}	A_2	B_{1g}	A_2	B_1	S_z
$T_{1g}\tau_1$	$E_g\tau_1$	$E\tau_1$	B_{2g}	B_1	B_2	$(1/\sqrt{2})(S_x - S_y)$
$T_{2g}\tau_2$	$E_g\tau_2$	$E\tau_2$	B_{2g}	B_1	B_2	$(1/\sqrt{2})(yz + xz)$
$T_{1g}\tau_1'$	$E_g\tau_1'$	$E\tau_1'$	B_{3g}	B_2	A_2	$(1/\sqrt{2})(S_x + S_y)$
$T_{2g}\tau_2'$	$E_g\tau_2'$	$E\tau_2'$	B_{3g}	B_2	A_2	$(1/\sqrt{2})(yz - xz)$

[a] $\mathrm{II} = \{E, C_2(z), C_2(xy), C_2(\bar{x}y), i, \sigma_h(xy), \sigma_d(xy), \sigma_d(\bar{x}y)\}$. [b] $\mathrm{II} = \{E, C_2(z), \sigma_d(xy), \sigma_d(\bar{x}y)\}$. [c] $\mathrm{III} = \{E, C_2(xy), \sigma_h(xy), \sigma_d(xy)\}$; note C_{2v}(III) is not subduced by C_{4v}. [d] Reference 27.

tions which are symmetry adapted[12,17,24] to the following point group chains.[25-27]

$$O_h \longrightarrow D_{4h} \longrightarrow C_{4v} \longrightarrow C_{2v} \tag{9}$$

$$O_h \longrightarrow D_{4h} \longrightarrow D_{2d} \longrightarrow C_{2v} \tag{10}$$

$$O_h \longrightarrow D_{4h} \longrightarrow D_{2h} \longrightarrow C_{2v} \tag{11}$$

$$O_h \longrightarrow T_h \longrightarrow D_{2h} \longrightarrow C_{2v} \tag{12}$$

$$O_h \longrightarrow T_d \longrightarrow D_{2d} \longrightarrow C_{2v} \tag{13}$$

A chain is an ordering of groups in which each group contains the elements of every group lower in the chain and is a proper subgroup of every group higher in the chain. In these examples O_h is the head and C_{2v} the tail of the chain. Many noncubic molecules of interest to transition metal chemists fall into one of these chains. The threefold groups are not discussed here but can be treated in an exactly analogous manner.

Each group, a member of chains 9–13, can be denoted $G(S)$ where S represents the set of octahedral operations retained by G. For example, three sets of octahedral operations can be retained to generate C_{2v}.

$$\mathrm{I} = \{E, C_4^2(z), \sigma_h(xz), \sigma_h(yz)\}$$

$$\mathrm{II} = \{E, C_4^2(z), \sigma_d(xy), \sigma_d(\bar{x}y)\}$$

$$\mathrm{III} = \{E, C_2'(xy), \sigma_h(xy), \sigma_d(xy)\}$$

(24) Reference 2, Chapter 1.
(25) M. Hamermesh, "Group Theory and Its Application to Physical Problems," Addison-Wesley, Reading, Mass., 1962.
(26) L. Jansen and M. Boon, "Theory of Finite Groups," Interscience, New York, N. Y., 1967.
(27) G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, "Properties of the Thirty-Two Point Groups," MIT Press, Cambridge, Mass., 1963.

Each $C_{2v}(S)$, where S = I, II, or III, retains a C_4^2 or C_2' operation from the $3C_2$ or $6C_2'$ classes of O_h, two mutually perpendicular reflection planes whose line of intersection is the twofold axis, and the identity operation. Symmetry operations of O_h are defined with respect to the symmetry axes of an octahedron which pass through the ligands of a six coordinate O_h system. A right-handed coordinate system is assumed. When the basis of an irreducible representation[26] of O_h, denoted $\mathcal{A}(O_h)$, is symmetry adapted to chain 10, for example, it is also a basis for one or more irreducible representations of D_{4h}, D_{2d}, and C_{2v}. The matrices $D(G_a) \in \mathcal{A}(O_h)$ for the operations of the octahedral group retained by $G = D_{4h}$, D_{2d}, or C_{2v} have a block diagonal form with each irreducible representation of G subduced corresponding to one such block. Basis functions and correlation tables for the gerade irreducible representations of O_h symmetry adapted to chains 9, 10, or 11 terminating with C_{2v}(I) are given in Table I. These bases are also symmetry adapted to chain 12. Correlation tables are included in Tables II and III for a basis symmetry adapted to chain 9 terminating with C_{2v}(II), chain 11 terminating with C_{2v}(II) or C_{2v}(III), and chain 13 terminating with C_{2v}(II). Also included in Tables I–III are definitions of S for $D_{2d}(S)$, S = I and II, and $D_{2h}(S)$, S = I and II.

Symmetry properties of basis elements are summarized as functions of x, y, and z. The $D(G_a) \in \mathcal{A}(O_h)$ for $\mathcal{A} = A_{1g}, A_{2g}, E_g, T_{1g}$, or T_{2g} can therefore be reconstructed since by definition[26]

$$G_a\phi_i = \sum_{j=1}^{N} D_{ji}(G_a)\phi_j \tag{14}$$

where $B_N = \{\phi_i; i = 1, N\}$ is the basis of $\mathcal{A}(O_h)$ and

Table III. Basis Functions and Correlation Table for the Gerade Irreducible Representations of O_h Relevant to Chain 13

O_h →	T_d →	D_{2d}(II)[a] →	C_{2v}(II)[b]	Bases[c]
A_{1g}	A_1	A_1	A_1	R
$E_g\theta$	$E\theta$	A_1	A_1	$(2z^2 - x^2 - y^2)$
$T_{2g}(xy)$	$T_2(xy)$	B_2	A_1	xy
A_{2g}	A_2	B_1	A_2	$(x^2 - y^2)(y^2 - z^2)\cdot(z^2 - x^2)$
$E_g\epsilon$	$E\epsilon$	B_1	A_2	$\sqrt{3}(x^2 - y^2)$
$T_{1g}(z)$	$T_1(z)$	A_2	A_2	S_z
$T_{1g}\tau_1$	$T_1\tau_1$	$E\tau_1$	B_1	$(1/\sqrt{2})(S_x - S_y)$
$T_{2g}\tau_2$	$T_2\tau_2$	$E\tau_2$	B_1	$(1/\sqrt{2})(yz + xz)$
$T_{1g}\tau_1'$	$T_1\tau_1'$	$E\tau_1'$	B_2	$(1/\sqrt{2})(S_x + S_y)$
$T_{2g}\tau_2'$	$T_2\tau_2'$	$E\tau_2'$	B_2	$(1/\sqrt{2})(yz - xz)$

[a] II = $\{E, 2S_4, 3C_2, 2\sigma_d\}$. [b] II = $\{E, C_2(z), \sigma_d(xy), \sigma_d(\bar{x}y)\}$. [c] Reference 27.

$D_{ji}(G_a)$ is an element of the matrix $D(G_a)$. Tables I–III were obtained by bringing $\mathcal{a}(O_h)$ for a previously reported basis[27] to the appropriate block diagonal form and relating any similarity transformations required to basis transformations.[26]

Linear combinations of tensor components symmetry adapted to O_h and characterized by the symmetry of the basis functions given in Table I have been reported previously by Griffith[14] for $L = 0, 1, \ldots, 6$. The symmetry adaptation coefficients tabulated yield either gerade or ungerade functions since the inversion symmetry of the projected function reflects the inversion symmetry of its tensor components. One-electron tensor operators are g if L is even and u if L is odd. Components of a $|d^{n;\mathfrak{M}}LM\rangle$ basis are always g.

Given $L = 2$ functions tabulated by Griffith and Table I, we deduce

$$|E_g\theta;\ A_{1g};\ A_1;\ A_1\rangle = |20\rangle$$

$$|E_g\epsilon;\ B_{1g};\ B_2;\ A_1\rangle = \frac{1}{\sqrt{2}}\{|22\rangle + |2\bar{2}\rangle\}$$

$$|T_{2g}(yz);\ E_g(yz);\ E(yz);\ B_2\rangle = i/\sqrt{2}\{|2\bar{1}\rangle + |21\rangle\} \quad (15)$$

$$|T_{2g}(xz);\ E_g(xz);\ E(xz);\ B_1\rangle = 1/\sqrt{2}\{|2\bar{1}\rangle - |21\rangle\}$$

$$|T_{2g}(xy);\ B_{2g};\ B_1;\ A_2\rangle = -i/\sqrt{2}\{|22\rangle - |2\bar{2}\rangle\}$$

where the functions are identified by an irreducible representation and degeneracy index for the groups O_h, D_{4h}, D_{2d}(I), and C_{2v}(I), respectively. Symmetry-adapted functions for a chain terminating with C_{2v}(II) are obtained as linear combinations of the tabulated functions. For $L = 2$

$$|E_g\theta;\ A_{1g};\ A_g;\ A_1\rangle = |20\rangle$$

$$|E_g\epsilon;\ B_{1g};\ B_{1g};\ A_2\rangle = 1/\sqrt{2}\{|22\rangle + |2\bar{2}\rangle\}$$

$$|T_{2g}\tau_2;\ E_g\tau_2;\ B_{2g};\ B_1\rangle = {}^1/_2\{a|2\bar{1}\rangle + b|21\rangle\} \quad (16)$$

$$|T_{2g}\tau_2';\ E_g\tau_2';\ B_{3g};\ B_2\rangle = {}^1/_2\{b|2\bar{1}\rangle + a|21\rangle\}$$

$$|T_{2g}(xy);\ B_{2g};\ A_g;\ A_1\rangle = i/\sqrt{2}\{|22\rangle - |2\bar{2}\rangle\}$$

where $a = i + 1$ and $b = i - 1$, and functions are identified by irreducible representations of O_h, D_{4h}, D_{2h}(II), and C_{2v}(II), respectively. Therefore, given the information in Tables I–III and previously tabulated[14] symmetry adaptation coefficients for O_h, $|d^n;{}^{\mathfrak{M}}L;\tau^{\mathfrak{M}}\mathcal{a}R\rangle$ basis functions and ligand field operators are readily generated for the point group symmetries of interest.

Hamiltonians. Those d^n compounds characterized by the point group symmetry of a member of the chains terminating with C_{2v} require ligand field Hamiltonians of the following form

$$H_G = V \quad (17)$$

when $G = O_h$ and T_d

$$H_G = V + V' \quad (18)$$

when $G = D_{4h}$, C_{4v}, D_{2d}(I), and D_{2d}(II)

$$H_G = V + V' + V'' \quad (19)$$

when $G = D_{2h}$(I) and C_{2v}(I)

$$H_G = V + V' + V''' \quad (20)$$

when $G = D_{2h}$(II), C_{2v}(II), and C_{2v}(III)

where

$$V = DQ|A_{1g}|_{O_h}{}^4 \quad (21)$$

$$V' = DS|E_g\theta|_{O_h}{}^2 + DT|E_g\theta|_{O_h}{}^4 \quad (22)$$

$$V'' = DU|E_g\epsilon|_{O_h}{}^2 + DV|E_g\epsilon|_{O_h}{}^4 \quad (23)$$

$$V''' = DM|T_{2g}(xy)|_{O_h}{}^2 + DN|T_{2g}(xy)|_{O_h}{}^4 \quad (24)$$

O_h quantum numbers identify linear combinations of tensor operators which transform as A_1 (or A_{1g}) of G (see Table I). $A^{L;\tau}$ coefficients (eq 6) are called DQ, DS, DT, DU, and DV by analogy to previously defined[28] parameters Dq, Ds, and Dt. Although A_{2g} of O_h subduces A_1 of D_{2h}(I) and C_{2v}(I), no functions of this form appear in eq 19 since Hamiltonians for d^n configurations can be projected from even tensors of rank four or less,[2,3] and irreducible representations of $R(3)$ with $L = 0, 2, 4$ do not subduce A_{2g} of O_h.[3,27] Symmetry adapted expansions are given in Table IV.[14]

Table IV. Operator Expansions Symmetry Adapted[a] to O_h

$\lvert A_{1g}\rvert_{O_h}{}^{L=0} = C_0{}^0$
$\lvert E_g\theta\rvert_{O_h}{}^2 = C_0{}^2$
$\lvert E_g\epsilon\rvert_{O_h}{}^2 = (1/\sqrt{2})(C_2{}^2 + C_{-2}{}^2)$
$\lvert T_2(xy)\rvert_{O_h}{}^2 = (-i/\sqrt{2})(C_2{}^2 - C_{-2}{}^2)$
$\lvert A_{1g}\rvert_{O_h}{}^4 = (7/12)^{1/2}C_0{}^4 + (5/24)^{1/2}(C_4{}^4 + C_{-4}{}^4)$
$\lvert E_g\theta\rvert_{O_h}{}^4 = (-5/12)^{1/2}C_0{}^4 + (7/24)^{1/2}(C_4{}^4 + C_{-4}{}^4)$
$\lvert E_g\epsilon\rvert_{O_h}{}^4 = (1/\sqrt{2})(C_2{}^4 + C_{-2}{}^4)$
$\lvert T_2(xy)\rvert_{O_h}{}^4 = (-i/\sqrt{2})(C_2{}^4 - C_{-2}{}^4)$

[a] Reference 14.

The A_{1g} component arising from $L = 0$ contributes equally to the energy of each state of a d^n configuration and is not included in the ligand field operator. As indicated, the Hamiltonians for D_{4h}, C_{4v}, and D_{2d} are indistinguishable. Similarly, the Hamiltonian for D_{2h}(I) is indistinguishable from that for C_{2v}(I) (see Table I). Nonzero matrix elements of V, V', V'', and V''' on a d orbital basis symmetry adapted to the appropriate chain, eq 15 or 16, are given in Table V. The matrix elements for V and V' relate DS, DT, and DQ parameters to the previously defined[28] parameters Ds, Dt, and Dq where

$$DQ = 6(21)^{1/2}Dq - {}^7/_2(21)^{1/2}Dt \quad (25)$$

$$DT = {}^7/_2(15)^{1/2}Dt \quad (26)$$

$$DS = -7Ds \quad (27)$$

(28) Reference 2, p 101.

Table V. Nonzero Matrix Elements for Empirical Ligand Field Operators on the d^1 Basis Symmetry Adapted to C_{2v}(I), C_{2v}(II), and C_{2v}(III)

$\mathcal{A}(C_{2v}(S))$ S^a I	II	III	$\mathcal{A}(O_h)R$	Operator^b	$\mathcal{A}'(O_h)R'$	$\langle d^1;{}^2\mathcal{A}(O_h)R;{}^2\mathcal{A}(C_{2v}(S))\|\text{operator}^b\|d^1;{}^2\mathcal{A}'(O_h)R';{}^2\mathcal{A}(C_{2v}(S))\rangle$ DQ	DS	DT	DU	DV	DM	DN
A_1	A_1	A_1	$E_g\theta$	$V + V'$	$E_g\theta$	$\left(\frac{1}{21}\right)^{1/2}$	$\frac{2}{7}$	$-\frac{5}{7}\left(\frac{1}{15}\right)^{1/2}$				
A_1			$E_g\theta$	V''	$E_g\epsilon$				$\frac{1}{7}(2)^{1/2}$	$-\frac{5}{14}\left(\frac{2}{15}\right)^{1/2}$		
	A_1	A_1	$E_g\theta$	V'''	$T_{2g}(xy)$						$\frac{1}{7}(2)^{1/2}$	$-\frac{5}{14}\left(\frac{2}{15}\right)^{1/2}$
A_1	A_2	B_1	$E_g\epsilon$	$V + V'$	$E_g\epsilon$	$\left(\frac{1}{21}\right)^{1/2}$	$-\frac{2}{7}$	$\frac{5}{7}\left(\frac{1}{15}\right)^{1/2}$				
A_2	A_1	A_1	$T_{2g}(xy)$	$V + V'$	$T_{2g}(xy)$	$-\frac{2}{3}\left(\frac{1}{21}\right)^{1/2}$	$-\frac{2}{7}$	$-\frac{20}{21}\left(\frac{1}{15}\right)^{1/2}$				
B_1			$T_{2g}(xz)$	$V + V' + V''$	$T_{2g}(xz)$	$-\frac{2}{3}\left(\frac{1}{21}\right)^{1/2}$	$\frac{1}{7}$	$\frac{10}{21}\left(\frac{1}{15}\right)^{1/2}$	$\frac{1}{7}(3)^{1/2}$	$\frac{10}{21}\left(\frac{1}{5}\right)^{1/2}$		
B_2			$T_{2g}(yz)$	$V + V' + V''$	$T_{2g}(yz)$	$-\frac{2}{3}\left(\frac{1}{21}\right)^{1/2}$	$\frac{1}{7}$	$\frac{10}{21}\left(\frac{1}{15}\right)^{1/2}$	$-\frac{1}{7}(3)^{1/2}$	$-\frac{10}{21}\left(\frac{1}{5}\right)^{1/2}$		
	B_1	B_2	$T_{2g}\tau_2$	$V + V' + V'''$	$T_{2g}\tau_2$	$-\frac{2}{3}\left(\frac{1}{21}\right)^{1/2}$	$\frac{1}{7}$	$\frac{10}{21}\left(\frac{1}{15}\right)^{1/2}$			$\frac{1}{7}(3)^{1/2}$	$\frac{10}{21}\left(\frac{1}{5}\right)^{1/2}$
	B_2	A_2	$T_{2g}\tau_2'$	$V + V' + V'''$	$T_{2g}\tau_2'$	$-\frac{2}{3}\left(\frac{1}{21}\right)^{1/2}$	$\frac{1}{7}$	$\frac{10}{21}\left(\frac{1}{15}\right)^{1/2}$			$-\frac{1}{7}(3)^{1/2}$	$-\frac{10}{21}\left(\frac{1}{15}\right)^{1/2}$

[a] Defined in Tables I and II. [b] Defined by eq 20 and 24.

Note that in the *octahedral limit* $DQ = 6(21)^{1/2}Dq$. Note also that for a Hamiltonian of the form $V + V'$ the center of gravity rule holds within the e_g and t_{2g} levels of a d^1 system for *DS and DT* energy components, an observation which is independent of the d basis used for calculations. See Appendix.

Six-Coordinate Systems

Ligand substitutions and angular distortions leading to a first coordination sphere characterized by C_{2v} symmetry are summarized in Table VI and Figure 1.

Table VI. Mixed Ligand Six-Coordinate Systems Which Can Exhibit C_{2v} Symmetry

	Highest available point group symmetry[a]		Possible C_{2v} distortion patterns[b]
MA_6		O_h	I, II, III
MA_4XY	Trans	C_{4v}	I, II
MA_4B_2	Trans	D_{4h}	I, II, III
	Cis	C_{2v}	III
MA_2B_2XY	Trans	C_{2v}	I
$MA_2B_2C_2$	Trans	D_{2h}	I
	Cis	C_{2v}	III
MA_3B_3	Equatorial	C_{2v}	I
$M(A{-}A)_2XY$	Trans	C_{2v}	II
$M(A{-}A)_2B_2$	Trans	C_{2v}	II, III
$M(A{-}A')_2B_2$	Trans	C_{2v}	III

[a] Corresponds to the symmetry of an octahedral angular configuration. [b] As defined by Figure 1.

Although mixed ligand systems may exhibit angular distortions, the highest symmetry available to each corresponds to the symmetry of an octahedral angular configuration. For example, the limiting symmetry for *trans*-MA_4B_2 is D_{4h} while that for *cis*-MA_4B_2 is C_{2v} (Table VI). Any distortion of the octahedral angular configuration lifts the D_{4h} symmetry of the trans system, while the cis system retains C_{2v} symmetry for a C_{2v}(III) angular configuration, as defined by Figure 1.

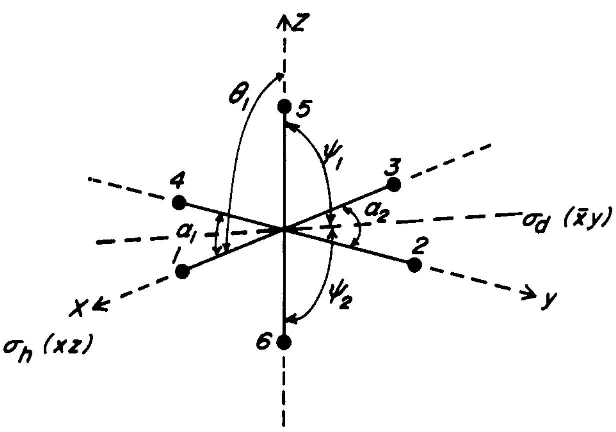

Figure 1. Definitions of the angular configuration for (1) O_h (axes pass through ligand positions; $\alpha_1 = \alpha_2 = 90°$; $\theta_i = 90°$; $\psi_1 = \psi_2 = 90°$); (2) C_{2v}(I) (I = $\{E, C_2(z), \sigma_h\,(xz), \sigma_h\,(yz)\}$; ligands 5 and 6 lie on the z axis; $\alpha_1 = \alpha_2 = 90°$; $\theta_1 = \theta_3$, $\theta_2 = \theta_4$, and $0° < \theta_1$ and $\theta_2 < 180°$; $\psi_1 = \psi_2 = 90°$); (3) C_{2v}(II) (II) = $\{E, C_2(z), \sigma_d(xy), \sigma_d(\bar{x}y)\}$; ligands 5 and 6 lie on the z axis; $0° < \alpha_1 = \alpha_2 \leq 90°$, $\theta_i = \theta$ for $0° < \theta < 180°$; $\psi_1 = \psi_2 = 90°$); (4) C_{2v}(III) (III = $\{E, C_2'(xy), \sigma_h(xy), \sigma_d(xy)\}$; ligands 1, 2, 3, and 4 lie in the xy plane; $0° < \alpha_1, \alpha_2, \leq 180°$; $\theta_i = 90°$; $0° < \psi_1 = \psi_2 \leq 90°$).

Parameters suitable for empirical ligand field calculations on a d^n basis are specified in eq 17–24. The number of parameters required for each symmetry is dictated by the symmetry and the choice to restrict consideration to states arising from a d^n configuration. That is to say

$$N_p = \sum_{L=2,4} f^{L;A_1} \tag{28}$$

where $f^{L;A_1}$ is the number of times L subduces A_1 (or A_{1g}) of the point group of interest. However, assuming ligand additivity and an average electrostatic effect for

Table VII. Nonzero Matrix Elements of the C_{2v}(I) Hamiltonian for the Triplet States of a d^2 Basis Symmetry Adapted to C_{2v}(I)

$\alpha(C_{2v}(I))$	$^3L;\tau$	$^3L';\tau'$	$\langle d^2;{}^3L;\tau\,{}^3\alpha(C_{2v}(I))\vert H^\circ + H_{C_{2v}(I)}\vert d^2;{}^3L';\tau'\,{}^3\alpha(C_{2v}(I))\rangle$					
			B	DQ	DS	DT	DU	DV
A_1	$F;1$	$F;1$		0.43644				
A_2	$P;1$	$P;1$	15		−0.40000			
	$P;1$	$F;1$		0.14548	−0.34286	−0.12295		
	$P;1$	$F;2$					−0.25555	0.16496
	$F;1$[a]	$F;1$		−0.21822	0.11429	0.18443		
	$F;1$	$F;2$					−0.12778	0.08248
	$F;2$	$F;2$		0.07274		−0.43033		
B_1[b]	$P;1$	$P;1$	15		0.20000		0.34641*	
	$P;1$	$F;1$		0.14548	0.17143	0.06148	0.29692*	0.10648*
	$P;1$	$F;2$			−0.22131*	0.14286*	0.12778	−0.08248
	$F;1$	$F;1$		−0.21822	−0.05714	−0.09221	−0.09897*	−0.15972*
	$F;1$	$F;2$			−0.11066*	0.07143*	0.06389	−0.04124
	$F;2$	$F;2$		0.07274		0.21517		0.37268*

[a] The $\vert d^2;{}^3F;1\alpha(C_{2v}(I))\rangle$ for $\alpha = A_2, B_1, B_2$ arise from $\alpha(O_h) = T_{1g}$. [b] The nonzero matrix elements for the $^3B_2$ states are derived from the matrix elements tabulated for the $^3B_1$ states using the negative of the starred (*) multipliers and the other multipliers as tabulated.

different ligands, assumptions implicit in most applications of empirical crystal field theory,[8-10,29] certain systems require fewer than N_p parameters.

By relating empirical crystal field parameters[9] for the six-coordinate molecules in Table VI to the empirical $A^{L;\tau}$ parameters, one finds that

$$DU = (R_1 + R_3)\sin^2\theta_1 - (R_2 + R_4)\sin^2\theta_2$$
$$DM = (R_1 + R_4)\sin(90 - \alpha_1)\sin^2\theta + (R_2 + R_3)\sin(90 - \alpha_2)\sin^2\theta \qquad (29)$$

where R_i is an empirical radial parameter for ligand i, and the angles θ_i, α_1, and α_2 are defined in Figure 1. Therefore, DM (and DN) always go to zero when a C_{2v}(II) or C_{2v}(III) system (Table VI) retains an octahedral angular configuration ($\theta = \alpha = 90°$) and ligand additivity is assumed. Similarly, DU (and DV) go to zero when a *trans*-MA_4XY C_{2v}(I) system is characterized by $\theta_1 = 90 - \delta$ and $\theta_2 = 90 + \delta$. In such a case $H_{C_{2v}}$ has exactly the same form as H_G where $G = D_{4h}$, C_{4v}, and D_{2d}. These compounds may therefore be described with a Hamiltonian of higher symmetry than C_{2v} and reflect a property previously termed intermediate symmetry by Griffith.[8] The equatorial (meridional) configuration of a MA_3B_3 system (C_{2v}(I) symmetry) can also display a type of intermediate symmetry. When the system retains an octahedral angular configuration, DS and DT go to zero and the system can be described with the parameters DU, DQ, and DV

To demonstrate the utility of this procedure, it is applied in the analysis of three nickel complexes whose polarized crystal spectra have been published. It is a feature of the spectra of noncubic complexes of the twofold groups that the selection rules are in general not so well obeyed as those for representative examples from the fourfold groups. For this reason the assignments cannot be considered so secure; application of the tensor Hamiltonian technique will serve to provide an additional means of verifying assignments through correlation of parameter values.

Octahedral nickel(II) systems (d^8) have an orbitally nondegenerate $^3A_{2g}$ ground state. Three relatively intense bands are observed in the absorption spectrum of an octahedral complex and may be assigned to the $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3T_{1g}(F)$, and $^3T_{1g}(P)$ transitions of increasing energy, respectively. In a complex of C_{2v} symmetry, the orbital degeneracy of the excited triplet states is lifted and there are nine possible spin-allowed transitions. The x, y, and z components of the electric dipole vector transform as B_1, B_2, and A_1, respectively, for C_{2v} symmetry where x, y, and z refer to the symmetry axes for C_{2v}.[30]

D_{2h}(I) and C_{2v}(I). Polarized single crystal electronic spectra of bis(diethylenetriamine)nickel(II) chloride monohydrate have been reported by Fereday and Hathaway.[31] The tridentate ligand diethylenetriamine (den) coordinates equatorially.[32] Secondary nitrogens, which lie trans to one another, define a C_2 axis and the N–Ni–N angle made by the primary nitrogens within a den ring is ~162°. Although the nickel(II) cation as a whole does not have a C_2 axis, polarized absorption spectra indicate an effective symmetry higher than the C_1 crystallographic site symmetry. Three absorption bands are observed in each of three crystal orientations with the electric field vector essentially along x, y, and z symmetry axes of C_{2v} or D_{2h}.[30] An assumption of D_{2h} symmetry, suggested by Fereday and Hathaway,[31] predicts[33] the observation of nine triplet–triplet bands. $H_{D_{2h}(I)}$ is indistinguishable in form from $H_{C_{2v}(I)}$ (eq 19) and the x, y, and z components of the electric dipole vector transform as b_{3u}, b_{2u}, and b_{1u} for D_{2h} symmetry.[30]

The representation of H (eq 1) for D_{2h}(I) symmetry on a basis symmetry adapted to C_{2v}(I) is given in Table VII for the triplet states of a d^2 configuration. See Appendix. Since the trace of a matrix is invariant under diagonalization, various combinations of the experimentally observed transition energies are directly related to traces of blocks of the representation and can be used to establish relationships between B, DQ, DS, DT, DU, and DV. For example

$$\frac{2}{7}\sqrt{3}DU + \frac{4}{21}\sqrt{5}DV = \mathrm{Tr}(^3B_{2g}) - \mathrm{Tr}(^3B_{3g}) \qquad (30)$$

where $\mathrm{Tr}(^3\alpha(D_{2h}))$ refers to the sum of the energies of transitions from the ground state to excited triplet

(29) G. Maki, *J. Chem. Phys.*, 28, 651 (1958).

(30) For a definition of these symmetry axes see (a) character tables given in ref 27 or (b) A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier, Amsterdam, 1968.

(31) R. J. Fereday and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 197 (1972).

(32) S. Biagini and M. Cannas, *J. Chem. Soc. A*, 2398 (1970).

(33) Note that ref 31 incorrectly assumes the $^3A_{2g}(O_h)$ state to subduce a $^3B_{1g}(D_{2h})$ state.

states characterized by the quantum number $\mathcal{A}(D_{2h})$. Similarly

$$\frac{3}{7}DS + \frac{6}{21}\sqrt{\frac{5}{3}}\ DT = \frac{1}{2}\ \mathrm{Tr}(^3\mathrm{B}_{2g}) + \frac{1}{2}\ \mathrm{Tr}(^3\mathrm{B}_{3g}) - \mathrm{Tr}(^3\mathrm{B}_{1g}) \quad (31)$$

$$15B - \frac{20}{3\sqrt{21}}\ DQ = \frac{1}{3}\mathrm{Tr}(^3\mathrm{B}_{1g}) + \frac{1}{3}\mathrm{Tr}(^3\mathrm{B}_{2g}) + \frac{1}{3}\ \mathrm{Tr}(^3\mathrm{B}_{3g}) - 3\mathrm{Tr}(^3\mathrm{A}_g) \quad (32)$$

Therefore, when nine triplet–triplet transitions are observed, there are three independent variables to be fitted from experiment: B (or DQ), DU (or DV), and DS (or DT). Transitions calculated with B = 780, DS = −435, DU = −100, DQ = −32,215, DT = 370, DV = 350 cm^{-1}, and a d^2 basis are compared with experimental values for $[\mathrm{Ni(den)_2}]^{2+}$ in Table VIII. The parameters reported exactly reproduce the $^3\mathrm{A}_g \rightarrow {}^3\mathrm{B}_{1g}$ transition energies as well as the trace (or sum) of the $^3\mathrm{A}_g \rightarrow {}^3\mathrm{B}_{3g}$ transition energies and the trace of the $^3\mathrm{A}_g \rightarrow {}^3\mathrm{B}_{2g}$ transition energies. Although the first excited triplet state is calculated to have the same point group quantum number as the highest excited triplet state for all parameter sets which reproduce the traces, this is not observed experimentally.

Table VIII. Calculated and Experimental Spin-Allowed Transitions for $[\mathrm{Ni(den)_2}]^{2+}$

Exptl[a] Energy	Exptl[a] Polarization	Assignment D_{2h}(I)	Assignment C_{2v}(I)	Calcd[b] energy
11,200	x	$^3\mathrm{A}_g \rightarrow {}^3\mathrm{B}_{3g}$	$^3\mathrm{A}_1 \rightarrow {}^3\mathrm{B}_2$	11,659
11,600	z	B_{1g}	A_2	11,556
11,600	y	B_{2g}	B_1	11,925
18,100	y	B_{2g}	B_1	18,077
18,300	z	B_{1g}	A_2	18,343
18,600	x	B_{3g}	B_2	18,152
28,700	x	B_{3g}	B_2	28,688
28,700	z	B_{1g}	A_2	28,700
28,900	y	B_{2g}	B_1	28,597

[a] Reference 31. [b] B = 780 cm^{-1}, DS = −435, DU = −100, DQ = −32,215, DT = 370, and DV = 350 cm^{-1} and a d^2 basis.

An interpretation of the polarized single crystal spectra of $[\mathrm{Ni(den)_2}]^{2+}$ assuming D_{2h} symmetry implies that the angular distortion revealed by the X-ray structure study[32] does not determine the effective symmetry of the system. Assumption of C_{2v}(I) symmetry is consistent with the angular distortion and implies only that the primary nitrogens of the den ligand are distinct, which may reflect the small bond length difference obtained in the X-ray structure determination and/or a small deviation in the N–Ni–N angles within the two den rings.

C_{2v}(**III**). Polarized single crystal absorption spectra for bis(DL-histidinato)nickel(II) monohydrate have been reported by Meredith and Palmer.[6] The tridentate histidine molecules bond through three inequivalent functional groups and coordinate facially.[34] Oxygens from the carboxy group and nitrogens from the α-amino group of each ligand lie in a plane with an O–Ni–O angle of 100.3° and an O–Ni–N$_\mathrm{A}$ angle of 79.7°. The two remaining bonds, imidazole nitrogen–nickel bonds, deviate from colinearity by 2.4°. The site symmetry of the nickel atoms is C_2.[34]

Eight of nine possible spin-allowed triplet–triplet transitions are observed in x, y, and z polarizations[30] with some of the transitions forbidden (not observed) in each polarization. Meredith and Palmer assumed C_{2v}(III) symmetry, the symmetry of the first coordination sphere of the nickel ion, in an interpretation of the spectra. A full calculation for C_{2v} symmetry was carried out within the d^2 configuration using an empirical Hamiltonian in the form of eq 4. The coordinate system used by Meredith and Palmer to define the tensor operators lies with its z axis bisecting the O–Ni–O angle and its x axis bisecting the N$_\mathrm{A}$–Ni–O angle. For this choice of coordinate system nonzero B_M^L coefficients multiply only those C_M^L operators with $L = 2$, $M = 0$, ± 2 and $L = 4$, $M = 0, \pm 2, \pm 4$.[10,13] It should be noted, however, that the coordinate systems with x, y, and z labels permuted correspond to Hamiltonians of the same form. The coordinate choice is fixed only by the assignment of the point group symmetry quantum number associated with each calculated energy state. That is to say, the form of the projection operators[35] or symmetry adapted basis functions used to determine $\mathcal{A}(G)$ reflects the coordinate system choice. Therefore, a fitting procedure which reproduces energy level splittings by adjustment of B_M^L parameters for $L = 2$, $M = 0, \pm 2$ and $L = 4$, $M = 0, \pm 2, \pm 4$ can be expected to find a number of equivalent fits. B_M^L coefficients reported by Meredith and Palmer convert to DQ = −31504, DS = −1955, DT = 2155, DM = 3409, and DN = −5149 cm^{-1}. These $A^{L;\tau}$ parameters, defined by eq 23, reproduce the energy level splittings and assignments given in Table IX (with B = 783 cm^{-1}) in *any* coordinate system.

Table IX. Calculated and Experimental Spin-Allowed Transitions for $[\mathrm{Ni(DL\text{-}his)_2}]$

Assignment C_{2v}(III)	Energy, cm^{-1}: Calcd, 6 variables[a,b]	Calcd, 5 variables[c]	Exptl[a]
$^3\mathrm{B}_1 \rightarrow {}^3\mathrm{A}_1(x)$[d]	10,706	10,615	10,600 (xz)[e]
$\rightarrow {}^3\mathrm{B}_2$	11,300	11,456	
$\rightarrow {}^3\mathrm{A}_2(y)$	11,884	11,649	11,400 (y)
$\rightarrow {}^3\mathrm{B}_2$	16,472	16,500	16,500 (xy)
$\rightarrow {}^3\mathrm{B}_1(z)$	18,848	18,881	18,800 (xz)
$\rightarrow {}^3\mathrm{A}_2(y)$	19,244	18,692	19,000 (y)
$\rightarrow {}^3\mathrm{A}_2$	27,213	27,404	27,300 (y)
$\rightarrow {}^3\mathrm{B}_1(z)$	28,751	28,863	28,900 (z)
$\rightarrow {}^3\mathrm{B}_2$	29,608	29,588	29,600 (xy)

[a] Reference 6. [b] B = 783, DM = 3409, DN = −5149, DS = −1955, DT = 2155, and DQ = −31,504 cm^{-1}. [c] B = 820, DM = 3000 (DN = −3955), DS = −3000, DT = 1859, and DQ = −31,069 cm^{-1}. [d] Allowed polarization C_{2v} symmetry. [e] Polarizations observed.

A representation of H for C_{2v}(III) symmetry on a d^2 basis symmetry adapted to C_{2v}(III) is given in Table X

(34) K. A. Fraser and M. M. Harding, *J. Chem. Soc. A*, 415 (1967).

(35) S. R. Polo, "National Technical Information Service," U. S. Dept. of Commerce, AD282493, 1961.

Table X. Nonzero Matrix Elements of the $C_{2v}(S)$ Hamiltonian for the Triplet States of a d^2 Basis Symmetry Adapted to $C_{2v}(S)$, S = II and III

$\mathcal{A}(C_{2v}(S))$				$\langle d^2;{}^3L;\tau\,{}^3\mathcal{A}(C_{2v}(S))\|H^\circ + H_{C_{2v}(S)}\|d^2;{}^3L';\tau'\,{}^3\mathcal{A}(C_{2v}(S))\rangle$					
II	III	$^3L;\tau$	$^3L';\tau'$	B	DQ	DS	DT	DM	DN
A_1	A_1	$F;1$	$F;1$		0.07274		−0.43033		
B_1[a]	A_2[a]	$P;1$	$P;1$	15		0.20000		−0.34641*	
		$P;1$	$F;1$		0.14548	0.17143	0.06148	0.19795*	−0.05324*
		$P;1$	$F;2$			−0.22131*	0.14286*	0.25555	0.12372
		$F;1$[b]	$F;1$		−0.21822	−0.05714	−0.09221	−0.02474*	−0.31944*
		$F;1$	$F;2$			−0.11066*	0.07143*	−0.03194	0.16496
		$F;2$	$F;2$		0.07274		0.21517	0.12372*	0.10648*
A_2	B_1	$P;1$	$P;1$	15		−0.40000			
		$P;1$	$F;1$		0.14548	−0.34286	−0.12295		
		$P;1$	$F;2$					−0.25555	0.16496
		$F;1$	$F;1$		−0.21822	−0.11429	0.18443		
		$F;1$	$F;2$					−0.12778	0.08248
		$F;2$	$F;2$		0.43644				
B_2[a]	B_2[a]								

[a] The nonzero matrix elements for the $^3B_2$ states are derived from the matrix elements tabulated for the $^3B_1$ (or $^3A_2$) states using the negative of the starred (*) multipliers and the other multipliers as tabulated. [b] The $|d^2,{}^3F;1\mathcal{A}(C_{2v}(\mathrm{II}))\rangle$ for a = B_1, A_2, and B_2 arise from $\mathcal{A}(O_h)$ = T_{1g}.

for the spin triplet states. See Appendix. The following relationships are deduced from Table X

$$\frac{2}{7}(3)^{1/2}DM + \frac{4}{21}(5)^{1/2}DN = \mathrm{Tr}(^3B_2) - \mathrm{Tr}(^3A_2) \quad (33)$$

$$-\frac{2}{7}DS + \frac{8}{7}\left(\frac{5}{3}\right)^{1/2}DT + 15B = \mathrm{Tr}(^3B_1) - 3\mathrm{Tr}(^3A_1) \quad (34)$$

$$\frac{3}{7}DS - \frac{1}{21}DT - \frac{5}{3\sqrt{21}}DQ = \frac{1}{2}\mathrm{Tr}(^3A_2) + \frac{1}{2}\mathrm{Tr}(^3B_2) - \mathrm{Tr}(^3B_1) \quad (35)$$

where $\mathrm{Tr}(^3\mathcal{A}(C_{2v}(\mathrm{III}))$ refers to the sum of the energies of transitions from the ground state to excited triplet states characterized by $\mathcal{A}(C_{2v}(\mathrm{III}))$. When nine spin-allowed triplet–triplet transitions are observed, the energies of the triplet states can be specified with four independent variables, for example, B, DM (or DN), DS (or DT), and DQ. Transitions calculated with B = 820, DM = 3000, DN = −3955, DS = −3000, DT = 1859, and DQ = −31069 cm^{-1} are compared with experimental values for [Ni(DL-his)$_2$] in Table IX. This fit, which retains the C_{2v} assignments made by Meredith and Palmer, exactly reproduces the $^3B_1 \rightarrow {}^3B_1$ and $^3B_1 \rightarrow {}^3A_1$ transition energies as well as the trace of the $^3B_1 \rightarrow {}^3A_2$ transitions. Since one $^3B_1 \rightarrow {}^3B_2$ transition is not observed experimentally, five variables were allowed to vary independently in the fitting procedure. The fit compares favorably with that of Meredith and Palmer, in which six parameters were varied independently.

A scissoring distortion in the xz plane[30] can be measured in units of 2β, where $\angle$O–Ni–O = 90° − 2β and $\angle$O–Ni–N$_A$ = 90° + 2β. Relating $A^{L;\tau}$ parameters to empirical crystal field parameters one finds that

$$[\cos(4\beta)]DN = [-\sin(2\beta)]\{\sqrt{5/21}\,DQ + \sqrt{1/3}\,DT\} \quad (36)$$

where $-2\beta \simeq 18°$ for Meredith and Palmer's fit[6] of the experimental spectrum and $-2\beta \simeq 14°$ for the fit obtained with five independent variables. From the X-ray structure determination[34] one would expect $-2\beta \simeq 10.3°$. The $A^{L;\tau}$ parameters obtained for Ni(DL-his)$_2$ therefore not only adequately reproduce the absorption spectrum but can be used to predict a distortion observed experimentally. Although electric dipole selection rules for C_{2v} symmetry are not strictly obeyed, all predicted transitions are observed.

Four-Coordinate Systems

Many ML$_4$ systems exhibit one of the two limiting symmetries available to a four-coordinate system: D_{4h} (square planar) or T_d (tetrahedral).[7] Equations 29 relate empirical crystal field parameters for four-coordinate systems to parameters DU and DM defined by the chains incorporating D_{4h}. With the assumption of ligand additivity, DM (and DN) go to zero for the D_{4h} angular configuration of *cis*-MA$_2$B$_2$ (θ = α = 90°) and the system exhibits intermediate symmetry.[8,29] Similarly, one finds that the D_{4h} angular configuration of *trans*-MA$_2$B$_2$ can be described with DQ, DU, DV, DS, and $DT = \frac{1}{2}(5/7)^{1/2}DQ$ and the D_{4h} angular configuration of MA$_4$ with DS, DQ, and $DT = \frac{1}{2}(5/7)^{1/2}DQ$.

Projections of ligand position vectors are defined to lie on 45° diagonals in the xy plane for T_d symmetry in contrast to the D_{4h} system, where symmetry axes pass through ligand positions. For this reason a C_{2v}(II) distortion of the T_d configuration is equivalent to a C_{2v}(I) distortion of the D_{4h} configuration. Parameters which indicate the distortion from T_d symmetry arise in the first approach while parameters which indicate the distortion from D_{4h} symmetry arise in the second. DM for chain 13, incorporating T_d, is given by

$$DM = 2R_A \sin^2\theta_1 - 2R_B \sin^2\theta_2 \quad (37)$$

where R_A and R_B are the empirical radial parameters for ligands in positions 1 and 3 and 2 and 4, respectively. Ligand positions are indexed by the spherical coordinates (θ_i, ϕ_i) with ϕ_1 = 45°, $\phi_{i+1} = \phi_i$ + 90°, and $\theta_1 = \theta_3$, $\theta_2 = \theta_4$. The T_d angular configuration of MA$_2$B$_2$, characterized by C_{2v}(II), can be described with DM, DN, and DQ when an assumption of ligand additivity holds.

We have restricted consideration to MA$_4$ and MA$_2$B$_2$ systems, systems which can exhibit C_{2v} symmetry and which require Hamiltonians and basis functions symmetry adapted to chains 9, 10, 11, or 13. The theory and techniques outlined are applied to a four-coordi-

Table XI. Calculated and Experimental Spin-Allowed Transitions for Ni(i-Pr-sal)$_2$

Obsd[a] energy, cm^{-1}	Assignment D_{2d}(II)	Assignment C_{2v}(II)	Calcd energy, cm^{-1}	
	$^3A_2 \rightarrow {}^3E(xy)$[b]	$^3A_2 \rightarrow {}^3B_1, {}^3B_2(xy)$[b]	910[c]	382[d]
6,000	$^3E(xy)$	$^3B_1, {}^3B_2(xy)$	5,796	3,007
	$^3B_2$	$^3A_1$	9,078	3,880
14,280	$^3B_1(z)$	$^3A_2(z)$	14,208	6,917
17,500	$^3A_2$	$^3A_2(z)$	17,572	14,544
19,000	$^3E(xy)$	$^3B_1, {}^3B_2(xy)$	19,076	14,593

[a] References 4 and 36. [b] Allowed polarization. [c] B = 835, C = 2,700, DS = 2,200, DT = $-4{,}982$, and DQ = 20,000 cm^{-1}. [d] Reference 4: B = 790, C = 3160, DS = 132, DT = -1350, and DQ = 9947 cm^{-1}.

Gerloch and Slade[4] report an extensive oriented single crystal magnetic susceptibility study of Ni(i-Pr-sal)$_2$ for $T \geq 80$°K in which they conclude that the effective symmetry of the system is D_{2d}. Magnetic susceptibilities were calculated using an empirical crystal field Hamiltonian incorporating spin–orbit and Zeeman terms with $\lambda \simeq -100$ cm^{-1} and k = 0.4. Converting empirical crystal field parameters used in the magnetic susceptibility fitting procedure to $A^{L;\tau}$ parameters, one obtains DS = 132, DT = -1350, and DQ = 9947 cm^{-1}. Triplet–triplet transition energies calculated with these parameters (and B = 790 cm^{-1}) are compared with experimental values in Table XI. It should be noted that the bands at ~17,500 and

Table XII. Empirical Ligand Field Parameters from Polarized Single Crystal Studies of Nickel(II) Systems

System	Symmetry	B	DQ	DS	DT	DM	DN	Ref
Ni^{2+}:MgO	O_h	815	$-22{,}408$					41
$Ni(NH_3)_4(NCS)_2$	D_{4h}	847	$-29{,}814$	-770	216			42
Ni(DL-his)$_2$	C_{2v}(III)	783	$-31{,}504$	-1955	2155	3409	-5149	6
		820	$-31{,}069$	-3000	1859	3000	-3955	This work
						DU	DV	
$[Ni(den)_2]Cl_2 \cdot H_2O$	C_{2v}(I)	780	$-32{,}215$	-435	370	-100	350	This work
Ni^{2+}:ZnO	T_d	795	11,135					41
Ni(i-Pr-sal)$_2$·	D_{2d}	790	9,947	132	-1350			4
		835	20,000	2200	-4982			This work

Parameters,[a] cm^{-1}: B, DQ, DS, DT, DM, DN.

[a] For energy levels calculated with a d^2 basis.

nate nickel system characterized by an approximately tetrahedral configuration. A tetrahedral nickel(II) system is expected to exhibit three spin-allowed absorption bands, assigned as $^3T_1(F) \rightarrow {}^3T_2(F)$, $^3A_2(F)$, and $^3T_1(P)$. In C_{2v} symmetry the orbital degeneracy of the states is removed and there exists the possibility of observing nine triplet–triplet transitions. However, if the distortion from T_d symmetry is small, the two levels arising from the ground state lie at very low energies.

C_{2v}**(II).** Polarized single crystal spectra for bis-(N-isopropylsalicylaldiminato)nickel(II) have been reported by Basu and Belford[36] and by Gerloch and Slade.[4] The conformation of the first coordination sphere corresponds very nearly to the C_{2v}(II) distortion of a tetrahedral configuration.[37] Planar isopropylsalicylaldimine (i-Pr-sal) ligands bond through an imine nitrogen and a hydroxy oxygen with an O(1)–Ni–O(2) angle of ~125° and a N(1)–Ni–N(2) angle of ~121°. The ligand planes intersect at an angle of 82°. The system contains discrete molecules characterized by a triplet ground state.[37,38]

Six bands are observed in the absorption spectrum of Ni(i-Pr-sal)$_2$ with the electric field vector parallel to b and to c crystal axes.[4,36] One band (~11,000 cm^{-1}) is weak and sharp, characteristic of a spin-forbidden band. Another (~22,400 cm^{-1}) is relatively very intense. The four remaining bands (at ~6000, 14,280, 17,500, and 19,000 cm^{-1}) are of comparable intensity, characteristic of spin-allowed d–d bands.[39]

(36) G. Basu and R. L. Belford, *J. Mol. Spectrosc.*, 17, 167 (1965).
(37) M. R. Fox, P. L. Oriolo, E. C. Lingafelter, and L. Sacconi, *Acta Crystallogr.*, 17, 1159 (1964).
(38) L. Sacconi, P. L. Orioli, P. Paoletti, and M. Ciampolini, *Proc. Chem. Soc., London*, 7, 255 (1962).
(39) L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Amer. Chem. Soc.*, **85**, 411 (1963).

19,000 cm^{-1} are disregarded in the interpretation of data proposed by Gerloch and Slade. Triplet–triplet transitions calculated with B = 835, DS = 2200, DT = -4982, and DQ = 20,000 cm^{-1} are also given in Table XI. These parameters reproduce all observed transitions and preliminary calculations[40] indicate that the parameters will reproduce the susceptibility data for $T \geq 80$°K with λ = 140 cm^{-1} and $k \simeq 0.58$. The assumption of D_{2d} symmetry requires that the imine nitrogens and hydroxy oxygens be indistinguishable for symmetry purposes. A full polarization study of the absorption spectrum has not been done due to the unfavorable placement of nickel centers in the single crystal.[37] Ni(i-Pr-sal)$_2$ could be characterized by a small splitting in the $^3A_2 \rightarrow {}^3E$ bands. In such a case the assumption of C_{2v} symmetry predicts the four observed triplet–triplet bands. One of the bands is forbidden in D_{2d} symmetry (see Table XI). The low-lying spin-forbidden transition observed experimentally is essentially independent of crystal field strength and a C value consistent with its observation is included in the footnote to Table XI for each interpretation of the absorption spectrum.

Discussion

$A^{L;\tau}$ parameters for three nickel(II) systems characterized by a C_{2v} effective symmetry are compared with parameters for other[41,42] six-coordinate and four-coordinate nickel systems in Table XII. As indicated, the relative magnitudes of DQ parameters for the six-coordinate species reflect an increase in ligand field

(40) J. C. Hempel, to be submitted for publication.
(41) R. Pappalardo, D. L. Wood, and R. C. Linares, Jr., *J. Chem. Phys.*, 35, 1460 (1961).
(42) A. B. P. Lever, *Coord. Chem. Rev.*, 3, 119 (1968).

"strength" for ligands which coordinate through nitrogen over that of an oxygen ligand in MgO. This observation tends to support the proposed interpretation of the Ni(i-Pr-sal)$_2$ spectrum which indicates an increase in ligand "strength," as measured by DQ, over that of the oxygen ligand in the tetrahedral ZnO matrix. The magnitudes of parameters DS and DT for the various systems, as well as DM and DN or DU and DV, appear to reflect ligand substitution more sensitively than angular distortion. For example, DM for a six-coordinate C_{2v}(II) molecule is found to be much larger in absolute magnitude than DU for a C_{2v}(I) molecule. DM is predicted to correspond to a sum and DU to a difference of empirical radial parameters (eq 29).

If it is assumed that the potential due to the ligands is the sum of a potential due to each ligand and that similar ligands are indistinguishable, certain deductions can be made concerning the symmetry of the various systems. For example, since DS and DT are nonzero for Ni(i-Pr-sal)$_2$, the system is not characterized by a T_d angular configuration and since DM and DN are nonzero for Ni(DL-his)$_2$, the system is not characterized by an O_h angular configuration. These deductions do correlate with X-ray structure determinations.[34,37] Further, the magnitude of a distortion in the first coordination sphere of Ni(DL-his)$_2$ can be deduced from $A^{L;\tau}$ parameters DQ, DT, and DN using a relation applicable to all six-coordinate systems charterized by C_{2v}(III) symmetry.

The nine triplet–triplet transitions of a nickel(II) system can be described with three independent parameters for C_{2v}(I) symmetry and with four independent parameters for C_{2v}(II) or C_{2v}(III) symmetry. Nine triplet–triplet transitions observed for Ni(den)$_2^{2+}$ were fitted with three independent parameters (B, DS, and DU), while the eight triplet–triplet transitions observed for Ni(DL-his)$_2$ were fitted with five independent parameters (B, DQ, DS, DT, and DM). The four triplet–triplet bands observed for Ni(i-Pr-sal)$_2$ were fitted with B, DQ, DS, and DT (with $DM = DN = 0$). For each of these systems, all triplet–triplet transitions predicted assuming C_{2v} symmetry are observed. Results of this study imply that the angular configuration of the first coordination sphere determines the effective symmetry of the system and that predictions based on an assumption of ligand additivity hold.

Summary and Conclusion

The utility of normalized spherical harmonic Hamiltonians may be summarized as follows.

(i) Their adoption would provide a standard and systematic procedure for generating ligand field Hamiltonians in the noncubic point groups.

(ii) The scalar parameters generated with these NSH Hamiltonians are truly spherical and are therefore independent of coordinate axis choice. We have chosen in this article to expand all the tensor components along the same axes, *i.e.*, a right-hand coordinate system quantized along the $C_4(z)$ octahedral axis, irrespective of the symmetry axes of the molecule concerned. In the threefold groups the same choice may be made but it may be computationally more favorable to utilize a set quantized along $C_3(xyz)$ (O_h). In either event the magnitudes of the scalar parameters obtained will be the same.

(iii) Clearly within a group of molecules belonging to the same point group, the variation of a given parameter, such as DS, as a function of the ligand or metal, may be compared and contrasted. It may also be useful to include, within this comparison, complexes of other stereochemistries whose point groups lie within the same subduction chain and whose Hamiltonians contain the same tensor component. In this way a *systematic* body of knowledge concerning the noncubic point groups can be amassed. Series of DS or DT paralleling the spectrochemical series of Dq could be generated. These would differ from the spectrochemical series in that the latter, for a given metal, is a function of only one ligand, while the former would be at least two dimensional being a function normally of at least two ligands. For this reason, a melding of this tensor technique with the orbital angular overlap model will probably prove beneficial.[10]

This model provides an alternative to that based on the Gerloch and Slade[43] C_p parameter.

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Appendix

Tabulated Symmetry-Adapted Representations. Table V contains the nonzero matrix elements of a representation of H, eq 1, for $G = O_h$, T_d, D_{4h}, D_{2h}, D_{2d}, and C_{2v} on d^1 bases symmetry adapted to C_{2v}(I), C_{2v}(II), and C_{2v}(III). To determine which matrix elements are required for the point group of interest refer to eq 17–24 to determine the form of H_G. Tables VII and X contain the nonzero matrix elements of H for the spin triplet states of a d^2 basis symmetry adapted to C_{2v}(I) and C_{2v}(III), respectively. Tables VII and X also apply to the spin quartet states of a d^7 basis. The representation of H_G for d^{10-n} is in each case the negative of the representation for d^n. The representation of $H°$ does not change sign.

(43) M. Gerloch and R. C. Slade, "Ligand Field Parameter," Cambridge University Press, London, 1973.