# Spin-Orbit Coupling in Tetragonal d³ Systems

Patrick E. Hoggard

Department of Chemistry, North Dakota State University, Fargo, North Dakota

Z. Naturforsch. **36a**, 1276–1288 (1981); received March 18, 1981

The complete set of energy matrices for tetragonal $d^3$ systems, including spin-orbit coupling, has been constructed within the framework of the Angular Overlap Model. Examples are presented of the variation in energy of the intraconfigurational ($t_{2g}^3$) doublets as a function of spin-orbit coupling (appropriate to first row metal ions) and ligand field asymmetry. It is seen that asymmetry in $Dq$ values is much less important than the relative partitioning of $Dq$ into $e_\sigma$ and $e_\pi$. The use of spin-orbit matrix elements in the calculation of intensities of spin-forbidden transitions is also illustrated.

## 1. Introduction

The $d^3$ configuration is unique among d-electron systems in that, for six-coordinate complexes, several spin-forbidden intraconfigurational ($t_{2g}^3$) electronic transitions occur which are up to two orders of magnitude narrower than the broad bands typical of most electronic spectra. The electronic excited states responsible for these transitions comprise, depending on symmetry, as many as five doublets, which are often the lowest excited states, and three more doublets which are higher in energy, but very frequently in the visible range of the spectrum. In favorable cases, all eight of these may be observed in absorption or excitation spectra, accompanied by associated vibronic structure [1, 2].

A few of these doublets may also be observed in luminescence spectra. In manganese (IV) or chromium (III) complexes, one or another of the lower energy group will be lowest in energy, and chiefly responsible for the observed emission spectrum (in the red or near infrared region) including extensive vibronic structure [3, 4]. Rhenium (IV) complexes, on the other hand, have been found to emit in the visible region from the higher group of doublets, as well as from the lower doublets in the infrared [5].

The precision with which the doublet band positions may be measured has not been matched by the several versions of ligand field theory used so successfully to understand broad band spectra [6]. One may note, for example, that to first order all five of the lower group of doublets in tetragonal ($C_{4v}$ or $D_{4h}$) complexes have the same energy, while experimentally there are nearly always five distinct bands. Jørgensen [7] has offered formulas to approximate the configuration interaction with higher doublets, which does lead to some splitting of the doublets. A much more satisfactory step in this direction was taken by Perumareddi [8], who published wave functions and matrices with which full interaction within the $d^3$ configuration may be taken into account.

Still, the fitting of doublet spectra remained elusive [9]. There are still a number of factors which may be important at the 1 $cm^{-1}$ level (the approximate precision of band peak measurements). Perumareddi's treatment did not take spin-orbit coupling into account, which especially for the second and third transition series complexes is indispensable. Other factors may include deviations from 90° bond angles, variations in bond lengths and bond angles within the molecule, and the effects of the counterions present.

For many complexes, the most important of these considerations is spin-orbit coupling. The effects, as far as the doublets in question are concerned, are expected to be subtle, since only two of them, both in the upper group (from the octahedral $^2T_{2g}$ state) are affected in first order. Configuration interaction, however, both with quartets and higher doublets, is extensive. A very interesting question concerns the extent to which the asymmetry of the complex may lead to larger spin-orbit effects, and how the asymmetry is to be defined.

This problem has been addressed by Güdel [10] and by Flint [11], who have reported results from calculations which have included spin-orbit coupling. There is a considerable advantage, however, in having an actual set of wavefunctions and matrix

Reprint requests to Herrn P. E. Hoggard, Department of Chemistry, North Dakota State University, Fargo/North Dakota 58105, U.S.A.

0340-4811 / 81 / 1200-1276 $ 01.00/0. — Please order a reprint rather than making your own copy.

Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung") beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition "no derivative works"). This is to allow reuse in the area of future scientific usage.

elements at hand, especially with respect to consistency in sign among ligand field, interelectronic repulsion, and spin-orbit contributions. Perumareddi's matrices, for example, contain some errors in signs of a few single-term off-diagonal elements [12]. Since the Hamiltonian matrix is symmetric this does not affect the eigenvalues. In combination with a spin-orbit term, however, an out-of-phase interelectronic repulsion term will lead to errors.

Thus we have derived the complete ligand field energy matrices for the tetragonal $d^3$ configuration, including interelectronic repulsion and spin-orbit coupling. We have used a strong field basis set, and have employed an Angular Overlap Model treatment of the ligand field potential, which we feel leads to a parameter set of more physical significance than the $Dq$, $Ds$, and $Dt$ of conventional ligand field theory.

## 2. Wave Functions and Energy Matrices

We have used basically the strong field wave functions of Perumareddi [8], modified such that the two components of degenerate $E$ representations be consistently connected in phase, and adapted to the spinor group $D_4^*$ as in Table 1. The phase of the $E_a$ and $E_b$ components was selected such that $C_4(E_a) = -E_b$ and $C_4(E_b) = E_a$, with $C_4$ defined as $C_4(x, y, z) = (-y, x, z)$.

All wavefunctions for an odd-electron system under $D_4^*$ symmetry must belong to the $E'$ or $E''$ representations. The spin functions $(+\frac{1}{2}, -\frac{1}{2})$ and $(+\frac{3}{2}, -\frac{3}{2})$ form bases for the $E'$ and $E''$ representations, respectively, and we have labelled their components with the corresponding spin functions. The $D_{4h}$ basis functions may be symmetry adapted to $D_4^*$ as in Table 1, where all of the spin components of each quartet and doublet state are listed together with the $D_4^*$ label. These spin components may be derived from each other in the usual way, using spin raising and lowering operators.

Table 1. Symmetry adaptation of $d^3$ wavefunctions in $D_4^*$ [a].

| $D_{4h}$ | $D_4^*$ | $D_{4h}$ | $D_4^*$ |
|---|---|---|---|
| ${}^4A_{2(3/2)}$ | $E''_{3/2}$ | ${}^4(E_a - iE_b)_{3/2}$ | $E'_{1/2}$ |
| ${}^4A_{2(1/2)}$ | $E'_{1/2}$ | ${}^4(E_a - iE_b)_{1/2}$ | $E'_{-1/2}$ |
| ${}^4A_{2(-1/2)}$ | $E'_{-1/2}$ | ${}^4(E_a - iE_b)_{-1/2}$ | $E''_{-3/2}$ |
| ${}^4A_{2(-3/2)}$ | $E''_{-3/2}$ | ${}^4(E_a - iE_b)_{-3/2}$ | $E''_{3/2}$ |
| ${}^4B_{1(3/2)}$, ${}^4B_{2(3/2)}$ | $E'_{-1/2}$ | ${}^2A_{1(1/2)}$, ${}^2A_{2(1/2)}$ | $E'_{1/2}$ |
| ${}^4B_{1(1/2)}$, ${}^4B_{2(1/2)}$ | $E''_{-3/2}$ | ${}^2A_{1(-1/2)}$, ${}^2A_{2(-1/2)}$ | $E'_{-1/2}$ |
| ${}^4B_{1(-1/2)}$, ${}^4B_{2(-1/2)}$ | $E''_{3/2}$ | ${}^2B_{1(1/2)}$, ${}^2B_{2(1/2)}$ | $E''_{-3/2}$ |
| ${}^4B_{1(-3/2)}$, ${}^4B_{2(-3/2)}$ | $E'_{1/2}$ | ${}^2B_{1(-1/2)}$, ${}^2B_{2(-1/2)}$ | $E''_{3/2}$ |
| ${}^4(E_a + iE_b)_{3/2}$ | $E''_{-3/2}$ | ${}^2(E_a + iE_b)_{1/2}$ | $E''_{3/2}$ |
| ${}^4(E_a + iE_b)_{1/2}$ | $E''_{3/2}$ | ${}^2(E_a + iE_b)_{-1/2}$ | $E'_{1/2}$ |
| ${}^4(E_a + iE_b)_{-1/2}$ | $E'_{1/2}$ | ${}^2(E_a - iE_b)_{1/2}$ | $E'_{-1/2}$ |
| ${}^4(E_a + iE_b)_{-3/2}$ | $E'_{-1/2}$ | ${}^2(E_a - iE_b)_{-1/2}$ | $E''_{-3/2}$ |

[a] The fractions following the representation label denote the spin associated with a state in $D_{4h}$; in $D_4^*$ they designate a particular component of the spinor representation. $E_a$ and $E_b$ are defined such that $C_4(E_a) = -E_b$ and $C_4(E_b) = E_a$ for the operation $C_4(x, y, z) = (-y, x, z)$.

Adapting Perumareddi's functions as in Table 1, $D_4^*$ wave functions are listed in the Appendix. Some of these were chosen with imaginary coefficients so that the energy matrix would be real. The $D_{4h}$ and $O_h$ parentage of each function is also given, as well as the $d^2$ $O_h$ fractional parentage when necessary to distinguish otherwise similar functions.

From the wavefunctions listed in the Appendix, energy matrices were constructed for $E'$ and $E''$ states, using a Hamiltonian,

$$H = V_{\mathrm{LF}} + \sum_{i>j} e^2/r_{ij} + \sum_i \xi l_i s_i$$

omitting the central field portion.

The Angular Overlap Model (AOM) treatment of the ligand field potential, $V_{\mathrm{LF}}$, was used [13]. In tetragonal symmetry, the AOM potential is diagonal in the strong field basis set:

$$\langle z^2 | V | z^2 \rangle = e_{\sigma z} + \tfrac{1}{4}(e_{\sigma x} + e_{\sigma y}),$$
$$\langle x^2 - y^2 | V | x^2 - y^2 \rangle = \tfrac{3}{4}(e_{\sigma x} + e_{\sigma y}),$$
$$\langle xy | V | xy \rangle = 2(e_{\pi x} + e_{\pi y}),$$
$$\langle xz | V | xz \rangle = 2(e_{\pi x} + e_{\pi z}),$$
$$\langle yz | V | yz \rangle = 2(e_{\pi y} + e_{\pi z}).$$

Here $e_{\sigma x}$ and $e_{\pi x}$, for example, represent the sums of the $\sigma$ and $\pi$ destabilization parameters, respectively, of the two ligands on the $x$ axis.

The interelectronic repulsion part of the Hamiltonian is spherically symmetric, and could be carried over from the octahedral case [14], except for the problem of phase in the descent from $O_h$ to $D_4^*$ symmetry. Thus all elements were derived by standard methods [11, 12] for the set of wavefunctions in Appendix I. The spin-orbit coupling terms were derived using matrix elements of the one-electron operator $\xi \mathbf{l} \cdot \mathbf{s}$ [15], which for d electrons may be written

$$\langle m_l m_s | \xi \mathbf{l} \cdot \mathbf{s} | m_l m_s \rangle = \zeta m_l m_s,$$
$$\langle \overset{+}{m_l} | \xi \mathbf{l} \cdot \mathbf{s} | m_l + 1 \rangle = \tfrac{1}{2}\sqrt{(2 - m_l)(3 + m_l)}\,\zeta,$$
$$\langle \overset{-}{m_l} | \xi \mathbf{l} \cdot \mathbf{s} | \overset{+}{m_l} - 1 \rangle = \tfrac{1}{2}\sqrt{(\tfrac{1}{4} + m_l)(3 - m_l)}\,\zeta.$$

Table 2. One-Electron spin-orbit coupling matrix elements for the real d wave functions (in units of $\zeta$).

| | $\overset{+}{xy}$ | $\overset{+}{xz}$ | $\overset{+}{yz}$ | $\overset{+}{x^2-y^2}$ | $\overset{+}{z^2}$ | $\overset{-}{xy}$ | $\overset{-}{xz}$ | $\overset{-}{yz}$ | $\overset{-}{x^2-y^2}$ | $\overset{-}{z^2}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $\overset{+}{xy}$ | 0 | 0 | 0 | $i$ | 0 | 0 | $-i/2$ | $\frac{1}{2}$ | 0 | 0 |
| $\overset{+}{xz}$ | 0 | 0 | $-i/2$ | 0 | 0 | $i/2$ | 0 | 0 | $-1/2$ | $\sqrt{3}/2$ |
| $\overset{+}{yz}$ | 0 | $i/2$ | 0 | 0 | 0 | $-1/2$ | 0 | 0 | $-i/2$ | $-\sqrt{3}i/2$ |
| $\overset{+}{x^2-y^2}$ | $-i$ | 0 | 0 | 0 | 0 | 0 | $1/2$ | $i/2$ | 0 | 0 |
| $\overset{+}{z^2}$ | 0 | 0 | 0 | 0 | 0 | 0 | $-\sqrt{3}/2$ | $\sqrt{3}i/2$ | 0 | 0 |
| $\overset{-}{xy}$ | 0 | $-i/2$ | $-1/2$ | 0 | 0 | 0 | 0 | 0 | $-i$ | 0 |
| $\overset{-}{xz}$ | $i/2$ | 0 | 0 | $1/2$ | $-\sqrt{3}/2$ | 0 | 0 | $i/2$ | 0 | 0 |
| $\overset{-}{yz}$ | $1/2$ | 0 | 0 | $-i/2$ | $-\sqrt{3}i/2$ | 0 | $-i/2$ | 0 | 0 | 0 |
| $\overset{-}{x^2-y^2}$ | 0 | $-1/2$ | $i/2$ | 0 | 0 | | 0 | 0 | 0 | 0 |
| $\overset{-}{z^2}$ | 0 | $\sqrt{3}/2$ | $\sqrt{3}i/2$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

For the latter two equations, $m_s$ is indicated as $+\frac{1}{2}$ or $-\frac{1}{2}$ by the sign over the wavefunction (represented by the $m_l$ number). The one electron spin-orbit coupling matrix is shown in Table 2.

The complete set of matrix elements for $E'$ and $E''$ states is listed in the Appendix. As mentioned above, the wave functions have been chosen so that all elements are real. The matrices are, of course, symmetric.

The spin-orbit matrix elements were calculated by hand and also by computer. A further check on the accuracy of the wave functions and matrix elements is the attainment of the appropriate degeneracies among the eigenvalues in the limits of zero spin-orbit coupling and/or octahedral symmetry.

## 3. Applications

### *A) Energy Level Calculations*

Since spin-orbit coupling has been (of necessity) often ignored in $d^3$ energy level calculations [8], it is certainly of interest to see how valid the approximation is. The free-ion value of the spin-orbit coupling parameter $\zeta$ for Cr (III) is 273 $cm^{-1}$ [14], and consequently it is generally expected that spin-orbit effects in electronic spectra can be neglected for chromium complexes. This is certainly a good approximation for the excited quartets, and an even better one for the ground state quartet [6], but the spin-orbit effects can rival those of low symmetry fields within the sharp-line doublets.

As indicated in the Introduction, we are primarily interested in the eight doublet levels which share the $t_{2g}^3$ electronic configuration of the ground state, upon whose energies the effects of moderate spin-orbit coupling are expected to be the most pronounced (in relation to the band widths). A point of particular interest is the extent to which low symmetry and spin-orbit effects reinforce each other. For moderate coupling, this is primarily a question of low symmetry enhancing spin-orbit effects, rather than vice versa.

We may illustrate the effects of introducing a moderate amount of spin-orbit coupling (appropriate to a V (II) or Cr (III) complex) to a tetragonal system with fairly disparate ligand fields in Figure 1. In this example the angular overlap parameters would be appropriate to a tetraamine complex with two strong $\pi$-donor ligands in *trans* positions. The effect of spin-orbit coupling on the non-degenerate doublet levels is seen to be minimal. The $^2A_1$ and $^2B_1$ (again, we are using $D_4$ or $C_{4v}$ symmetry labels) levels are, in this example, accidentally degenerate (vide infra), and this degeneracy is not appreciably disturbed by spin-orbit coupling.

The $^2E$ levels, on the other hand, are split into diverging $E'$ and $E''$ components, the splitting at $\zeta = 300$ $cm^{-1}$ in this case not approaching that achieved through the low symmetry field, but still quite marked. It would be very difficult to estimate the extent of this splitting without using the full $d^3$ matrices. The increase in energy of the $E''$ com-

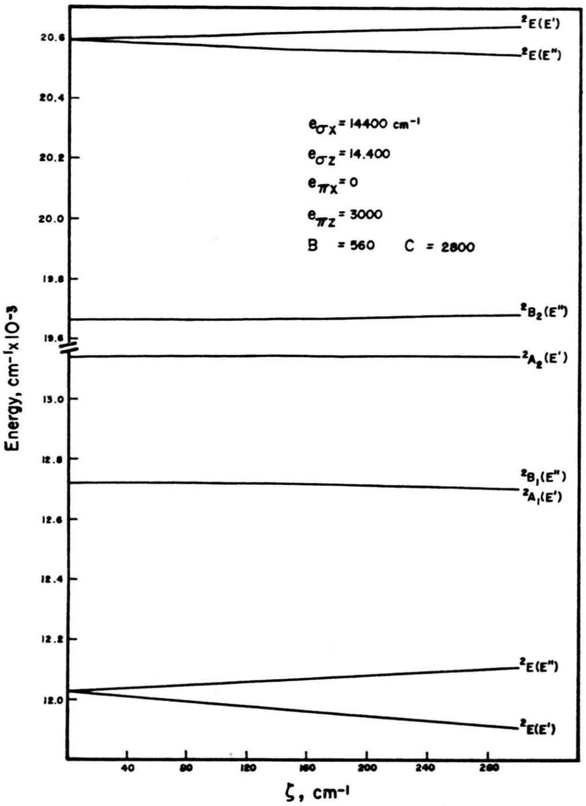


Fig. 1. Variation in transition energies with spin-orbit coupling for the eight intraconfigurational doublets of a tetragonal $d^3$ complex. Note the discontinuity in the ordinate.

ponent of the lower $^2E$ state relative to the ground state is due neither to a first-order (diagonal) perturbation, nor a second-order interaction: There are no non-zero matrix elements connecting the five lowest doublets to the ground state. It should instead be viewed as a relatively greater decrease in energy of the ground state, due to spin-orbit coupling, than of the $^2E(E'')$ excited state.

The splitting of the lower $^2E$ state at $\zeta = 250\ cm^{-1}$ is 165 $cm^{-1}$ under the conditions of Figure 1. For a similar, but octahedral complex ($e_\sigma = 14{,}400$, $e_\pi = 1500\ cm^{-1}$) the calculated splitting of the corresponding $^2T_{1g}(O_h)$ state is just 60 $cm^{-1}$.

We obtain another picture of the influence of spin-orbit coupling and low symmetry fields on each other by holding the spin-orbit coupling fixed and varying the ligand field parameters. This can be done in a large number of ways. Figure 2 illustrates the behavior of the doublet levels for a *trans*-$MA_4B_2$ complex in which $A$ and $B$ have the same $Dq$, but the distribution ($10Dq = 3e_\sigma - 4e_\pi$) between $e_\sigma$ and $e_\pi$ of the ligand $B$ is varied. The effects are seen to be substantial, and it should be emphasized that the range of $e_{\pi z}$ envisioned in Fig. 2 ($e_{\pi z} = 2e_{\pi B}$) is not at all unreasonable. The conditions of Fig. 1 correspond to the crossing point at $e_{\pi z} = -1500\ cm^{-1}$ in Fig. 2, which produces the degeneracy noted above.

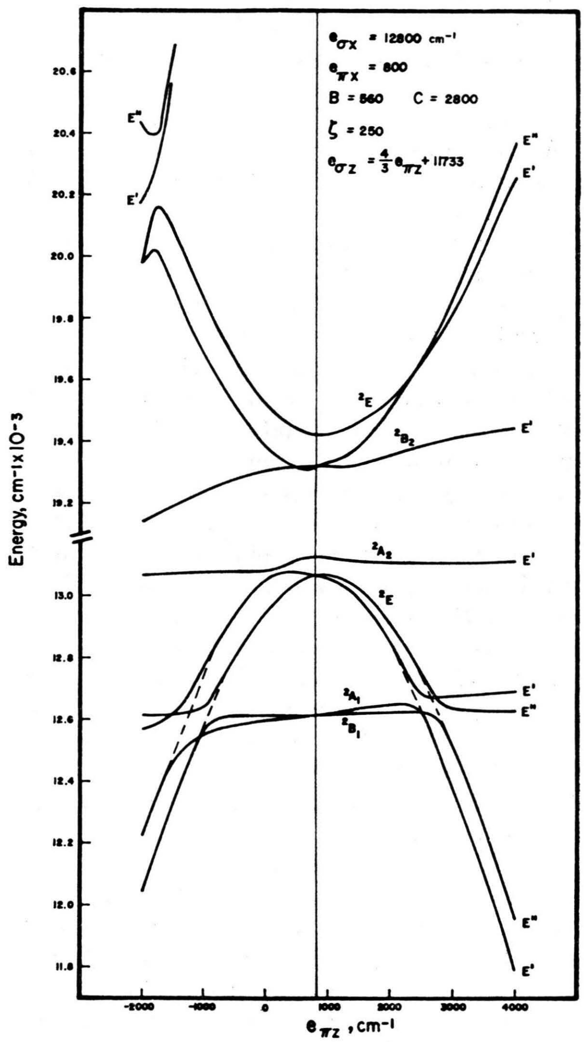


Fig. 2. Doublet transition energies for a trans-$MA_4B_2$ complex, in which $A$ and $B$ have the same ligand field strength, $Dq$. The $e_\pi$ angular overlap parameter of the $B$ ligand is varied, $e_\sigma$ being simultaneously adjusted to keep $Dq$ constant. The vertical line indicates the pseudo-octahedral situation in which the ligands have identical $e_\sigma$ and $e_\pi$ values. The $E'$ and $E''$ states in the upper left corner represent quartet states which are crossing the highest doublets at that point. Note the discontinuity in the ordinate.

There is some problem in retaining the single group representation labels past the crossover points on the right and left sides of the diagram. At these relatively small values of $\zeta$, we have felt justified in using them as if the states had crossed. Thus, as we did in Fig. 1, we consider the lower $E'$ and $E''$ states past the crossover points to be components of the $^2$E state, which is reasonable in that these levels collapse as $\zeta$ approaches zero. Nevertheless, a reasonable amount of ambiguity regarding the spinless state parentages must exist in the crossover regions themselves, making such complexes an interesting area for experimental study.

Another area in which the ($D_{4h}$, $C_{4v}$) labels become ambiguous is near octahedral symmetry. For example, the components of the octahedral $^2T_{1g}$ state converge to $E'$ and $O$ states, which are linear combinations of the tetragonal $A_2(E')$, $E(E')$, and $E(E'')$ components. The upper state, $E'(O^*)$, cannot be identified with the $A_2(E')$ state in the $D_4^*$ basis. Nevertheless, as diagrams similar to Fig. 1 make clear, away from octahedral conditions the splitting of the $^2T_{1g}(O_h)$ state is occasioned primarily by the low symmetry field, and the upper state is reasonably represented as $A_2(C_{4v})$.

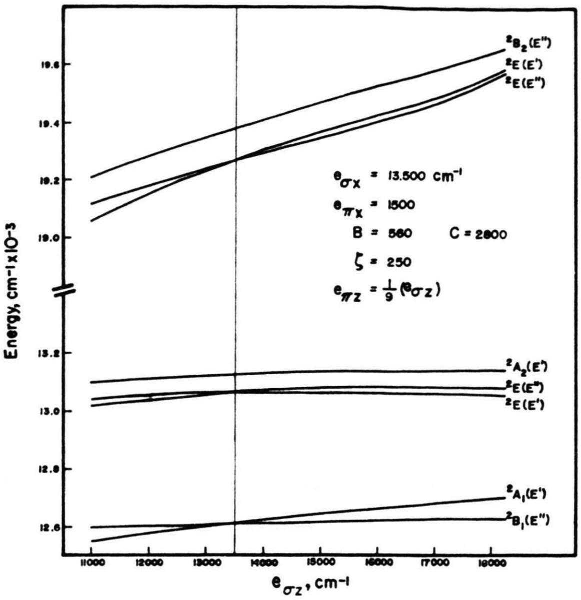


Fig. 3. Doublet transition energies for a trans-$MA_4B_2$ complex, for which $Dq$ of the $B$ ligand is varied while maintaining $e_\sigma$ and $e_\pi$ in a ratio identical to that of $A$. The vertical line indicates the octahedral parameter set. Note the ordinate discontinuity.

Figure 3 shows a different view of the effects of low symmetry fields on the spin-orbit split doublets. In this case, again for a hypothetical *trans*-$MA_4B_2$ complex, $Dq$ of ligand $B$ is varied. There are, of course many things which might be held constant in such a diagram. We have chosen to keep a constant $e_\sigma/e_\pi$ ratio (identical with that of the ligand $A$), which perhaps best serves to isolate the effects of $Dq$ differences alone. In the $Dq$, $Ds$, $Dt$ parameterization, this is equivalent to varying $Dt$ while holding $Ds$ at a constant ratio to $Dt$.

It is seen in Fig. 3 that the effects of $Dq$ differences are actually rather slight, so that the largest effects operating on a system with only moderate spin-orbit coupling are concerned with the distribution of the ligand field between $e_\sigma$ and $e_\pi$.

The preceding diagrams point towards a method of fitting and assigning doublet spectra. Quite frequently, $Dq$ values are the easiest to assign to each ligand. From Figs. 1 and 3, it is seen that errors in assuming $Dq$ and $\zeta$ values will not be serious. A diagram along the lines of Fig. 2 may then be constructed, varying $e_\pi$ of one axis while keeping $Dq$ of all ligands constant. The observed spectrum can then be fitted to this diagram and corresponding electronic assignments made. In such a procedure, $Dq$ of one ligand or axis must be arbitrarily partitioned between $e_\sigma$ and $e_\pi$. Exact values cannot be determined spectroscopically, but frequently reasonable estimates can be made, based, for example, on an assignment of $e_\pi(NH_3) = 0$.

In the above discussion we have not mentioned the ground state splitting. As predicted by several investigators [6, 16], we find this splitting to be quite small, when $\zeta$ is near 250 cm$^{-1}$ no more than 0.3 cm$^{-1}$ within the ranges of Figures 1—3.

### *B) Intensities of Spin-Forbidden Transitions*

It is, of course, spin-orbit coupling which allows observation of spin-forbidden bands, of which transitions to the eight doublets discussed above are examples. The wave function of a doublet state is perturbed through spin-orbit coupling with nearby quartets, and if the matrix element, $\langle\Psi'_D \mid H_{SO} \mid \Psi_Q\rangle$, representing this interaction is **a**, then if **a** is small, a good approximation is that the doublet eigenfunction will include a term $\mathbf{a}\Psi_Q/\Delta E$ where $\Delta E$ is the energy difference between the quartet and doublet states. As long as the perturbations are small, interactions with several quartets are additive,

$$\Psi'_D \cong \Psi_D + \left(\frac{a_1}{\Delta E_1}\right)\Psi_{Q_1} + \left(\frac{a_2}{\Delta E_2}\right)\Psi_{Q_2} + \cdots. \quad (1)$$

It is the squares of these mixing coefficients which are proportional to the absorption intensity [15]. These should properly be weighted by the intensities or oscillator strengths of the transitions to each of quartets involved, which in turn depend on a number of other factors. But a simple approximation to the relative intensities of the $d^3$ doublets might be in terms of the sum of the squares of the mixing coefficients:

$$I = \sum_i \left(\frac{a_i}{\Delta E_i}\right)^2. \quad (2)$$

The matrix elements, $\mathbf{a}_i$, are simply those listed in the Appendix. In Table 3 we tabulate the matrix elements between the first five doublets and the $^4A_{2g}$, $^4T_{2g}$, and $^4T_{1g}$ states (in $O_h$ notation), which contribute the most heavily to spin-mixing in the doublets. Three of the doublets interact with pairs of states from the same ($D_4$) quartet, for which cases the value of $\mathbf{a}_i$ was taken as the square root of the sum of the squares of the coefficients.

As an example, we might look at data from the complexes $[Cr(en)_2F_2]^+$ and $[Cr(IDA)_2]^-$, where en = ethylenediamine and IDA = iminodiacetate. These complexes are unusual in that the $^2E$ (from $O_h$ $^2T_{1g}$) state is the lowest excited doublet [3, 17, 18]. They are also unusual in that the absorption intensities of the $^2E$ bands are much smaller than for the other doublets — a factor of 10 smaller for $Na[Cr(IDA)_2]$, while the $^2E$ levels were not detected at all for $[Cr(en)_2F_2]ClO_4$, though at least one was observed in luminescence [17]. This has led to misassignments of the electronic origins [19].

Table 3. Spin-orbit interaction energies of the five lowest $d^3$ doublets with nearest quartets in units of $\zeta$[a].

| | Ground ($^4A_{2g}$) | $^4T_{2g}$ | | $^4T_{1g}$ | |
|---|---|---|---|---|---|
| | $^4B_1$ | $^4B_2$ | $^4E$ | $^4A_2$ | $^4E$ |
| $E'$ $^2A_1$ ($^2E_g$) | 0 | 0 | 1.115 | 0 | 0 |
| $E''$ $^2B_1$ ($^2E_g$) | 0 | 0.943 | 0.667 | 0 | 0 |
| $E'$ $^2A_2$ ($^2T_{1g}$) | 0 | 0 | 0.577 | 0 | 1.000 |
| $E'$ $^2E$ ($^2T_{1g}$) | 0 | 0.500 | 0.408 | 0.500 | 0.707 |
| $E'$ $^2E$ ($^2T_{1g}$) | 0 | 0.289 | 0.408 | 0.866 | 0.707 |

[a] Doublets are identified with $D_4^*$ and $C_{4v}$ labels, $O_h$ labels in parantheses; Quartets are identified with $C_{4v}$ labels, with $O_h$ parents above.

Table 4. Doublet intensities, relative to $^2A_1$ (tetragonal), for some Chromium (III) complexes.

| State[a] | $[Cr(en)_2F_2]ClO_4$ calc.[b] | $[Cr(en)_2F_2]ClO_4$ exptl.[c] | $Na[Cr(IDA)_2]$ exptl.[d] |
|---|---|---|---|
| $^2A_1$ | 1.0 | 1.0 | 1.0 |
| $^2B_1$ | 0.58 | 0.75 | [f] |
| $^2E_a$ ($E'$) | 0.15 | [e] | 0.13 |
| $^2E_b$ ($E''$) | 0.14 | [e] | 0.04 |
| $^2A_2$ | 0.37 | 0.29 | 0.85 |

| State[g] | $K_3[Cr(NCS)_6]$ calc.[h] | $K_3[Cr(NCS)_6]$ exptl.[i] |
|---|---|---|
| $2A_1$ ($^2E_g$) | 1.0 | 1.0 |
| $^2E_a$ ($^2T_{1g}$) | 0.58 | 0.62 |
| $^2E_b$ ($^2T_{1g}$) | 0.69 | |
| $^2A_2$ ($^2T_{1g}$) | 0.84 | 0.61 |

[a] $D_4$ labels, $D_4^*$ in parentheses.
[b] Based on quartet energies from Ref. [17], doublet energies from Ref. [14].
[c] Ref. [14].
[d] Ref. [15]. Energies of quartet components are not known; they are similar, however, to $[Cr(en)_2F_2]^+$.
[e] Not observed.
[f] Not resolved from $^2A_1$.
[g] $O_h$ labels in parentheses.
[h] Based on quartet energies from A.B.P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 1968; doublet energies from Ref. [18].
[i] Ref. [18].

We have used the assignments of Flint [17] for the energies of the doublet levels of $[Cr(en)_2F_2]^+$, and of Dubicki and Day [20], for the quartet levels, and Table 4 shows the relative intensities calculated from (2). Considering the level of approximation, the agreement with the experimental absorption intensities is quite good. Table 4 also contains the experimental data [18] for $Na[Cr(IDA)_2]$. We have not calculated relative intensities, because the quartet components have not been resolved for this complex. The energy levels are, however, expected to resemble those of $[Cr(en)_2F_2]ClO_4$ [17].

Table 4 also contains calculated and experimental [21] relative intensities for $[Cr(NCS)_6]^{3-}$, which are more representative of intensities seen in other chromium (III) complexes. Again the agreement is good.

*Acknowledgements*

The support of this work by the Research Corporation through a Cottrell Research Grant is gratefully acknowledged, as is support from the National Institutes of Health (GM 26570).

## Appendix

Table I. $D_4^*$ spin-orbit wavefunctions for the $d^3$ configuration.

*$E'_{1/2}$ Functions*

$$\Psi_1(^4B_1;\, ^4A_{2g}\, t_{2g}^3) = (\overline{xy})(\overline{xz})(\overline{yz}), \quad \Psi_2(^4B_2;\, ^4T_{2g}\, t_{2g}^2\, e_g) = i(\overline{xz})(\overline{yz})(\overline{x^2-y^2}),$$

$$\Psi_3(^4A_2;\, ^4T_{1g}\, t_{2g}^2\, e_g) = \frac{i}{\sqrt{3}}[(xz)(yz)(\overline{z^2}) + (xz)(\overline{yz})(z^2) + (\overline{xz})(yz)(z^2)],$$

$$\Psi_4(^4A_2;\, ^4T_{1g}\, t_{2g}\, e_g^2) = \frac{i}{\sqrt{3}}[(xy)(z^2)(\overline{x^2-y^2}) + (xy)(\overline{z^2})(x^2-y^2) + (\overline{xy})(z^2)(x^2-y^2)],$$

$$\begin{aligned}\Psi_5(^4E;\, ^4T_{2g}\, t_{2g}^2\, e_g) = \frac{1}{\sqrt{24}}[&-(\overline{yz})(\overline{xy})(x^2-y^2) - (\overline{yz})(xy)(\overline{x^2-y^2}) - (yz)(\overline{xy})(\overline{x^2-y^2})\\ &+\sqrt{3}(\overline{yz})(\overline{xy})(z^2) + \sqrt{3}(\overline{yz})(xy)(\overline{z^2}) + \sqrt{3}(yz)(\overline{xy})(\overline{z^2})\\ &- i(\overline{xy})(\overline{xz})(x^2-y^2) - i(\overline{xy})(xz)(\overline{x^2-y^2}) - i(xy)(\overline{xz})(\overline{x^2-y^2})\\ &- \sqrt{3}i(\overline{xy})(\overline{xz})(z^2) - \sqrt{3}\,i(\overline{xy})(xz)(\overline{z^2}) - \sqrt{3}\,i(xy)(\overline{xz})(\overline{z^2})],\end{aligned}$$

$$\Psi_6(^4E;\, ^4T_{2g}\, t_{2g}^2\, e_g) = \frac{1}{\sqrt{8}}[-(yz)(xy)(x^2-y^2) + \sqrt{3}(yz)(xy)(z^2) + i(xy)(xz)(x^2-y^2) + \sqrt{3}\,i(xy)(xz)(z^2)],$$

$$\begin{aligned}\Psi_7(^4E;\, ^4T_{1g}\, t_{2g}^2\, e_g) = \frac{1}{\sqrt{24}}[&-\sqrt{3}(\overline{yz})(\overline{xy})(x^2-y^2) - \sqrt{3}(\overline{yz})(xy)(\overline{x^2-y^2}) - \sqrt{3}(yz)(\overline{xy})(\overline{x^2-y^2})\\ &- (\overline{yz})(\overline{xy})(z^2) - (\overline{yz})(xy)(\overline{z^2}) - (yz)(\overline{xy})(\overline{z^2})\\ &- \sqrt{3}\,i(\overline{xy})(\overline{xz})(x^2-y^2) - \sqrt{3}\,i(\overline{xy})(xz)(\overline{x^2-y^2}) - \sqrt{3}\,i(xy)(\overline{xz})(\overline{x^2-y^2})\\ &+ i(\overline{xy})(\overline{xz})(z^2) + i(\overline{xy})(xz)(\overline{z^2}) + i(xy)(\overline{xz})(\overline{z^2})],\end{aligned}$$

$$\Psi_8(^4E;\, ^4T_{1g}\, t_{2g}^2\, e_g) = \frac{1}{\sqrt{8}}[-\sqrt{3}(yz)(xy)(x^2-y^2) - (yz)(xy)(z^2) + \sqrt{3}\,i(xy)(xz)(x^2-y^2) - i(xy)(xz)(z^2)],$$

$$\begin{aligned}\Psi_9(^4E;\, ^4T_{1g}\, t_{2g}\, e_g^2) = \frac{1}{\sqrt{6}}[&(\overline{xz})(\overline{z^2})(x^2-y^2) + (\overline{xz})(z^2)(\overline{x^2-y^2}) + (xz)(\overline{z^2})(\overline{x^2-y^2})\\ &- i(\overline{yz})(\overline{z^2})(x^2-y^2) - i(\overline{yz})(z^2)(\overline{x^2-y^2}) - i(yz)(\overline{z^2})(\overline{x^2-y^2})],\end{aligned}$$

$$\Psi_{10}(^4E;\, ^4T_{1g}\, t_{2g}\, e_g^2) = \frac{1}{\sqrt{2}}[(xz)(z^2)(x^2-y^2) + i(yz)(z^2)(x^2-y^2)],$$

$$\begin{aligned}\Psi_{11}(^2A_1;\, ^2A_{1g}\, t_{2g}^2\, e_g) = \frac{1}{\sqrt{12}}[&-2(xy)(\overline{xy})(z^2) + (yz)(\overline{yz})(z^2) + (xz)(\overline{xz})(z^2)\\ &+\sqrt{3}(xz)(\overline{xz})(x^2-y^2) - \sqrt{3}(yz)(\overline{yz})(x^2-y^2)],\end{aligned}$$

$$\Psi_{12}(^2A_1;\, ^2E_g\, t_{2g}^3) = \frac{1}{\sqrt{2}}[(xy)(xz)(\overline{yz}) - (xy)(\overline{xz})(yz)],$$

$$\Psi_{13}(^2A_1;\, ^2E_g\, t_{2g}^2(^1A_{1g})\, e_g) = \frac{1}{\sqrt{3}}[(xy)(\overline{xy})(z^2) + (xz)(\overline{xz})(z^2) + (yz)(\overline{yz})(z^2)],$$

$$\begin{aligned}\Psi_{14}(^2A_1;\, ^2E_g\, t_{2g}^2(^1E_g)\, e_g) = \frac{1}{\sqrt{12}}[&-2(xy)(\overline{xy})(z^2) + (xz)(\overline{xz})(z^2) + (yz)(\overline{yz})(z^2)\\ &- \sqrt{3}(xz)(\overline{xz})(x^2-y^2) + \sqrt{3}(yz)(\overline{yz})(x^2-y^2)],\end{aligned}$$

$$\Psi_{15}(^2A_1;\, ^2E_g\, e_g^3) = (z^2)(x^2-y^2)(\overline{x^2-y^2}),$$

$$\Psi_{16}(^2A_2;\, ^2T_{1g}\, t_{2g}^3) = \frac{i}{\sqrt{2}}[(xz)(\overline{xz})(xy) - (yz)(\overline{yz})(xy)],$$

$$\Psi_{17}(^2A_2;\, ^2T_{1g}\, t_{2g}^2(^3T_{1g})\, e_g) = \frac{i}{\sqrt{6}}[-2(xz)(yz)(\overline{z^2}) + (xz)(\overline{yz})(z^2) + (\overline{xz})(yz)(z^2)],$$

$$\Psi_{18}(^2A_2;\, ^2T_{1g}\, t_{2g}^2(^1T_{2g})\, e_g) = \frac{i}{\sqrt{2}}[(xz)(\overline{yz})(x^2-y^2) - (\overline{xz})(yz)(x^2-y^2)],$$

$$\Psi_{19}(^2A_2;\, ^2T_{1g}\, t_{2g}\, e_g^2(^3A_{2g})) = \frac{i}{\sqrt{6}}[-2(\overline{xy})(z^2)(x^2-y^2) + (xy)(z^2)(\overline{x^2-y^2}) + (xy)(\overline{z^2})(x^2-y^2)],$$

$$\Psi_{20}(^2A_2;\, ^2T_{1g}\, t_{2g}\, e_g^2(^1E_g)) = \frac{i}{\sqrt{2}}[(\overline{xy})(\overline{z^2})(x^2-y^2) - (xy)(z^2)(\overline{x^2-y^2})],$$

$$\Psi_{21}(^2E;\, ^2T_{1g}\, t_{2g}^3) = \tfrac{1}{2}[(yz)(\overline{yz})(\overline{xz}) - (xy)(\overline{xy})(\overline{xz}) - i(xy)(\overline{xy})(\overline{yz}) + i(xz)(\overline{xz})(\overline{yz})],$$

$$\begin{aligned}\Psi_{22}(^2E;\, ^2T_{1g}\, t_{2g}^2(^3T_{1g})\, e_g) = \frac{1}{\sqrt{48}}[&(yz)(\overline{xy})(\overline{z^2}) + (\overline{yz})(xy)(\overline{z^2}) - 2(\overline{yz})(\overline{xy})(z^2)\\ &+\sqrt{3}(yz)(\overline{xy})(\overline{x^2-y^2}) + \sqrt{3}(\overline{yz})(xy)(\overline{x^2-y^2}) - 2\sqrt{3}(\overline{yz})(\overline{xy})(x^2-y^2)\\ &- i(xy)(\overline{xz})(\overline{z^2}) - i(\overline{xy})(xz)(\overline{z^2}) + 2i(\overline{xy})(\overline{xz})(z^2)\\ &+\sqrt{3}\,i(xy)(\overline{xz})(\overline{x^2-y^2}) + \sqrt{3}\,i(\overline{xy})(xz)(\overline{x^2-y^2}) - 2\sqrt{3}\,i(\overline{xy})(\overline{xz})(x^2-y^2)],\end{aligned}$$

$$\begin{aligned}\Psi_{23}(^2E;\, ^2T_{1g}\, t_{2g}^2(^1T_{2g})\, e_g) = \tfrac{1}{4}[&-(yz)(\overline{xy})(\overline{x^2-y^2}) + (\overline{yz})(xy)(\overline{x^2-y^2}) + \sqrt{3}(yz)(\overline{xy})(\overline{z^2}) - \sqrt{3}(\overline{yz})(xy)(\overline{z^2})\\ &+ i(xy)(\overline{xz})(\overline{x^2-y^2}) - i(\overline{xy})(xz)(\overline{x^2-y^2}) - \sqrt{3}\,i(\overline{xy})(xz)(\overline{z^2}) + \sqrt{3}\,i(xy)(\overline{xz})(\overline{z^2})],\end{aligned}$$

$$\Psi_{24}(^2E;\, ^2T_{1g}\, t_{2g}\, e_g^2(^3A_{2g})) = \frac{1}{\sqrt{12}} [2(xz)(\overline{z^2})(\overline{x^2-y^2}) - (\overline{xz})(z^2)(\overline{x^2-y^2}) - (\overline{xz})(\overline{z^2})(x^2-y^2) - 2i(yz)(\overline{z^2})(\overline{x^2-y^2}) + i(\overline{yz})(z^2)(\overline{x^2-y^2}) + i(\overline{yz})(\overline{z^2})(x^2-y^2)]$$

$$\Psi_{25}(^2E;\, ^2T_{1g}\, t_{2g}\, e_g^2(^1E_g)) = \tfrac{1}{4}[(\overline{xz})(z^2)(\overline{x^2-y^2}) - (\overline{xz})(\overline{z^2})(x^2-y^2) + \sqrt{3}(\overline{xz})(z^2)(\overline{z^2}) - \sqrt{3}(\overline{xz})(x^2-y^2)(\overline{x^2-y^2}) - i(\overline{yz})(z^2)(\overline{x^2-y^2}) + i(\overline{yz})(\overline{z^2})(x^2-y^2) - \sqrt{3}i(\overline{yz})(x^2-y^2)(\overline{x^2-y^2}) + \sqrt{3}i(\overline{yz})(z^2)(\overline{z^2})]$$

$$\Psi_{26}(^2E;\, ^2T_{2g}\, t_{2g}^3) = \tfrac{1}{2}[(yz)(\overline{yz})(\overline{xz}) + (xy)(\overline{xy})(\overline{xz}) + i(xy)(\overline{xy})(\overline{yz}) + i(xz)(\overline{xz})(\overline{yz})]$$

$$\Psi_{27}(^2E;\, ^2T_{2g}\, t_{2g}^2(^3T_{1g})\, e_g) = \frac{1}{\sqrt{48}} [(yz)(\overline{xy})(\overline{x^2-y^2}) + (\overline{yz})(xy)(\overline{x^2-y^2}) - 2(\overline{yz})(\overline{xy})(x^2-y^2) - \sqrt{3}(yz)(\overline{xy})(\overline{z^2}) - \sqrt{3}(\overline{yz})(xy)(\overline{z^2}) + 2\sqrt{3}(\overline{yz})(\overline{xy})(z^2) + i(xy)(\overline{xz})(\overline{x^2-y^2}) + i(\overline{xy})(xz)(\overline{x^2-y^2}) - 2i(\overline{xy})(\overline{xz})(x^2-y^2) + \sqrt{3}\,i(xy)(\overline{xz})(\overline{z^2}) + \sqrt{3}\,i(\overline{xy})(xz)(\overline{z^2}) - 2\sqrt{3}\,i(\overline{xy})(\overline{xz})(z^2)],$$

$$\Psi_{28}(^2E;\, ^2T_{2g}\, t_{2g}^2(^1T_{2g})\, e_g) = \tfrac{1}{4}[-(yz)(\overline{xy})(\overline{z^2}) + (\overline{yz})(xy)(\overline{z^2}) - \sqrt{3}(yz)(\overline{xy})(\overline{x^2-y^2}) + \sqrt{3}(\overline{yz})(xy)(\overline{x^2-y^2}) - i(xy)(\overline{xz})(\overline{z^2}) + i(\overline{xy})(xz)(\overline{z^2}) + \sqrt{3}\,i(xy)(\overline{xz})(\overline{x^2-y^2}) - \sqrt{3}\,i(\overline{xy})(xz)(\overline{x^2-y^2})],$$

$$\Psi_{29}(^2E;\, ^2T_{2g}\, t_{2g}\, e_g^2(^1A_{1g})) = \tfrac{1}{2}[(\overline{xz})(z^2)(\overline{z^2}) + (\overline{xz})(x^2-y^2)(\overline{x^2-y^2}) + i(\overline{yz})(z^2)(\overline{z^2}) + i(\overline{yz})(x^2-y^2)(\overline{x^2-y^2})],$$

$$\Psi_{30}(^2E;\, ^2T_{2g}\, t_{2g}\, e_g^2(^1E_g)) = \tfrac{1}{4}[-(\overline{xz})(z^2)(\overline{z^2}) + (\overline{xz})(x^2-y^2)(\overline{x^2-y^2}) + \sqrt{3}(\overline{xz})(z^2)(\overline{x^2-y^2}) - \sqrt{3}(\overline{xz})(\overline{z^2})(x^2-y^2) + i(\overline{yz})(x^2-y^2)(\overline{x^2-y^2}) - i(\overline{yz})(z^2)(\overline{z^2}) - \sqrt{3}\,i(\overline{yz})(z^2)(\overline{x^2-y^2}) + \sqrt{3}\,i(\overline{yz})(\overline{z^2})(x^2-y^2)].$$

*$E''_{3/2}$ Functions*

$$\Psi_1(^4B_1;\, ^4A_{2g}\, t_{2g}^3) = \frac{1}{\sqrt{3}} [(xy)(\overline{xz})(\overline{yz}) + (\overline{xy})(xz)(\overline{yz}) + (\overline{xy})(\overline{xz})(yz)],$$

$$\Psi_2(^4B_2;\, ^4T_{2g}\, t_{2g}^2\, e_g) = \frac{i}{\sqrt{3}} [(xz)(\overline{yz})(\overline{x^2-y^2}) + (\overline{xz})(yz)(\overline{x^2-y^2}) + (\overline{xz})(\overline{yz})(x^2-y^2)],$$

$$\Psi_3(^4A_2;\, ^4T_{1g}\, t_{2g}^2\, e_g) = i(xz)(yz)(z^2), \quad \Psi_4(^4A_2;\, ^4T_{1g}\, t_{2g}\, e_g^2) = i(xy)(z^2)(x^2-y^2),$$

$$\Psi_5(^4E;\, ^4T_{2g}\, t_{2g}^2\, e_g) = \frac{1}{\sqrt{24}} [-(yz)(xy)(\overline{x^2-y^2}) - (yz)(\overline{xy})(x^2-y^2) - (\overline{yz})(xy)(x^2-y^2) + \sqrt{3}(yz)(xy)(\overline{z^2}) + \sqrt{3}(yz)(\overline{xy})(z^2) + \sqrt{3}(\overline{yz})(xy)(x^2-y^2) - i(xy)(xz)(\overline{x^2-y^2}) - i(xy)(\overline{xz})(x^2-y^2) - i(\overline{xy})(xz)(x^2-y^2) - \sqrt{3}\,i(xy)(xz)(\overline{z^2}) - \sqrt{3}\,i(xy)(\overline{xz})(z^2) - \sqrt{3}\,i(\overline{xy})(xz)(z^2)],$$

$$\Psi_6(^4E;\, ^4T_{2g}\, t_{2g}^2\, e_g) = \frac{1}{\sqrt{8}} [-(\overline{yz})(\overline{xy})(\overline{x^2-y^2}) + \sqrt{3}(\overline{yz})(\overline{xy})(\overline{z^2}) + i(\overline{xy})(\overline{xz})(\overline{x^2-y^2}) + \sqrt{3}\,i(\overline{xy})(\overline{xz})(\overline{z^2})],$$

$$\Psi_7(^4E;\, ^4T_{1g}\, t_{2g}^2\, e_g) = \frac{1}{\sqrt{24}} [-(yz)(xy)(\overline{z^2}) - (yz)(\overline{xy})(z^2) - (\overline{yz})(xy)(z^2) - \sqrt{3}(yz)(xy)(\overline{x^2-y^2}) - \sqrt{3}(yz)(\overline{xy})(x^2-y^2) - \sqrt{3}(\overline{yz})(xy)(x^2-y^2) - i(xy)(xz)(\overline{z^2}) + i(xy)(\overline{xz})(z^2) + i(\overline{xy})(xz)(z^2) - \sqrt{3}\,i(xy)(xz)(\overline{x^2-y^2}) - \sqrt{3}\,i(xy)(\overline{xz})(x^2-y^2) - \sqrt{3}\,i(\overline{xy})(xz)(x^2-y^2)],$$

$$\Psi_8(^4E;\, ^4T_{1g}\, t_{2g}^2\, e_g) = \frac{1}{\sqrt{8}} [-(\overline{yz})(\overline{xy})(\overline{z^2}) - \sqrt{3}(\overline{yz})(\overline{xy})(\overline{x^2-y^2}) - i(\overline{xy})(\overline{xz})(\overline{z^2}) + \sqrt{3}\,i(\overline{xy})(\overline{xz})(\overline{x^2-y^2})],$$

$$\Psi_9(^4E;\, ^4T_{1g}\, t_{2g}\, e_g^2) = \frac{1}{\sqrt{6}} [(xz)(z^2)(\overline{x^2-y^2}) + (xz)(\overline{z^2})(x^2-y^2) + (\overline{xz})(z^2)(x^2-y^2) - i(yz)(z^2)(\overline{x^2-y^2}) - i(yz)(\overline{z^2})(x^2-y^2) - i(\overline{yz})(z^2)(x^2-y^2)],$$

$$\Psi_{10}(^4E;\, ^4T_{1g}\, t_{2g}\, e_g^2) = \frac{1}{\sqrt{2}} [(\overline{xz})(\overline{z^2})(\overline{x^2-y^2}) + i(\overline{yz})(\overline{z^2})(\overline{x^2-y^2})],$$

$$\Psi_{11}(^2B_1;\, ^2A_{2g}\, t_{2g}^2(^1E_g)\, e_g) = \frac{1}{\sqrt{12}} [-2(xy)(\overline{xy})(\overline{x^2-y^2}) + (xz)(\overline{xz})(\overline{x^2-y^2}) + (yz)(\overline{yz})(\overline{x^2-y^2}) - \sqrt{3}(xz)(\overline{xz})(\overline{z^2}) + \sqrt{3}(yz)(\overline{yz})(\overline{z^2})],$$

$$\Psi_{12}(^2B_1;\, ^2E_g\, t_{2g}^3) = \frac{1}{\sqrt{6}} [2(xy)(\overline{xz})(\overline{yz}) - (\overline{xy})(xz)(\overline{yz}) - (\overline{xy})(\overline{xz})(yz)],$$

$$\Psi_{13}(^2B_1;\, ^2E_g\, t_{2g}^2(^1A_{1g})\, e_g) = \frac{1}{\sqrt{3}} [(xy)(\overline{xy})(\overline{x^2-y^2}) + (xz)(\overline{xz})(\overline{x^2-y^2}) + (yz)(\overline{yz})(\overline{x^2-y^2})],$$

$$\Psi_{14}(^2B_1;\, ^2E_g\, t_{2g}^2(^1E_g)\, e_g) = \frac{1}{\sqrt{12}} [-2(xy)(\overline{xy})(\overline{x^2-y^2}) + (xz)(\overline{xz})(\overline{x^2-y^2}) + (yz)(\overline{yz})(\overline{x^2-y^2}) + \sqrt{3}(xz)(\overline{xz})(\overline{z^2}) - \sqrt{3}(yz)(\overline{yz})(\overline{z^2})],$$

$$\Psi_{15}(^2B_1;\, ^2E_g\, e_g^3) = (z^2)(\overline{z^2})(\overline{x^2-y^2}),$$

$$\Psi_{16}({}^2\mathrm{B}_2;\ {}^2\mathrm{T}_{2g}\,\mathrm{t}_{2g}^3) = \frac{i}{\sqrt{2}}\,[(xz)(\overline{xz})(\overline{xy}) + (yz)(\overline{yz})(\overline{xy})],$$

$$\Psi_{17}({}^2\mathrm{B}_2;\ {}^2\mathrm{T}_{2g}\,\mathrm{t}_{2g}^2({}^3\mathrm{T}_{1g})\,\mathrm{e}_g) = \frac{i}{\sqrt{6}}\,[-(xz)(\overline{yz})(\overline{x^2-y^2}) - (\overline{xz})(yz)(\overline{x^2-y^2}) + 2(\overline{xz})(\overline{yz})(x^2-y^2)],$$

$$\Psi_{18}({}^2\mathrm{B}_2;\ {}^2\mathrm{T}_{2g}\,\mathrm{t}_{2g}^2({}^1\mathrm{T}_{2g})\,\mathrm{e}_g) = \frac{i}{\sqrt{2}}\,[(xz)(\overline{yz})(\overline{z^2}) - (\overline{xz})(yz)(\overline{z^2})],$$

$$\Psi_{19}({}^2\mathrm{B}_2;\ {}^2\mathrm{T}_{2g}\,\mathrm{t}_{2g}\,\mathrm{e}_g^2({}^1\mathrm{A}_{1g})) = \frac{i}{\sqrt{2}}\,[(\overline{xy})(z^2)(\overline{z^2}) + (\overline{xy})(x^2-y^2)(\overline{x^2-y^2})],$$

$$\Psi_{20}({}^2\mathrm{B}_2;\ {}^2\mathrm{T}_{2g}\,\mathrm{t}_{2g}\,\mathrm{e}_g^2({}^1\mathrm{E}_g)) = \frac{i}{\sqrt{2}}\,[(\overline{xy})(z^2)(\overline{z^2}) - (\overline{xy})(x^2-y^2)(\overline{x^2-y^2})],$$

$$\Psi_{21}({}^2\mathrm{E};\ {}^2\mathrm{T}_{1g}\,\mathrm{t}_{2g}^3) = \tfrac{1}{2}[(yz)(\overline{yz})(xz) - (xy)(\overline{xy})(xz) - i(xy)(\overline{xy})(yz) + i(xz)(\overline{xz})(yz)],$$

$$\begin{aligned}\Psi_{22}({}^2\mathrm{E};\ {}^2\mathrm{T}_{1g}\,\mathrm{t}_{2g}^2({}^3\mathrm{T}_{1g})\,\mathrm{e}_g) = \frac{1}{\sqrt{48}}\,&[2(yz)(xy)(\overline{z^2}) - (yz)(\overline{xy})(z^2) - (\overline{yz})(xy)(z^2)\\ &+ 2\sqrt{3}(yz)(xy)(\overline{x^2-y^2}) - \sqrt{3}(yz)(\overline{xy})(x^2-y^2) - \sqrt{3}(\overline{yz})(xy)(x^2-y^2)\\ &- 2i(xy)(xz)(\overline{z^2}) + i(xy)(\overline{xz})(z^2) + i(\overline{xy})(xz)(z^2)\\ &+ 2\sqrt{3}\,i(xy)(xz)(\overline{x^2-y^2}) - \sqrt{3}\,i(xy)(\overline{xz})(x^2-y^2) - \sqrt{3}\,i(\overline{xy})(xz)(x^2-y^2)],\end{aligned}$$

$$\begin{aligned}\Psi_{23}({}^2\mathrm{E};\ {}^2\mathrm{T}_{1g}\,\mathrm{t}_{2g}^2({}^1\mathrm{T}_{2g})\,\mathrm{e}_g) = \tfrac{1}{4}&[-(yz)(\overline{xy})(x^2-y^2) + (\overline{yz})(xy)(x^2-y^2) + \sqrt{3}(yz)(\overline{xy})(z^2)\\ &- \sqrt{3}(\overline{yz})(xy)(z^2) + i(xy)(\overline{xz})(x^2-y^2) - i(\overline{xy})(xz)(x^2-y^2)\\ &- \sqrt{3}\,i(\overline{xy})(xz)(z^2) + \sqrt{3}\,i(xy)(\overline{xz})(z^2)],\end{aligned}$$

$$\begin{aligned}\Psi_{24}({}^2\mathrm{E};\ {}^2\mathrm{T}_{1g}\,\mathrm{t}_{2g}\,\mathrm{e}_g^2({}^3\mathrm{A}_{2g})) = \frac{1}{\sqrt{12}}\,&[-2(\overline{xz})(z^2)(x^2-y^2) + (xz)(\overline{z^2})(x^2-y^2) + (xz)(z^2)(\overline{x^2-y^2})\\ &+ 2i(\overline{yz})(z^2)(x^2-y^2) - i(yz)(\overline{z^2})(x^2-y^2) - i(yz)(z^2)(\overline{x^2-y^2})],\end{aligned}$$

$$\begin{aligned}\Psi_{25}({}^2\mathrm{E};\ {}^2\mathrm{T}_{1g}\,\mathrm{t}_{2g}\,\mathrm{e}_g^2({}^1\mathrm{E}_g)) = \tfrac{1}{4}&[(xz)(z^2)(\overline{x^2-y^2}) - (xz)(\overline{z^2})(x^2-y^2) + \sqrt{3}(xz)(z^2)(\overline{z^2})\\ &- \sqrt{3}(xz)(x^2-y^2)(\overline{x^2-y^2}) - i(yz)(z^2)(\overline{x^2-y^2}) + i(yz)(\overline{z^2})(x^2-y^2)\\ &- \sqrt{3}\,i(yz)(x^2-y^2)(\overline{x^2-y^2}) + \sqrt{3}\,i(yz)(z^2)(\overline{z^2})],\end{aligned}$$

$$\Psi_{26}({}^2\mathrm{E};\ {}^2\mathrm{T}_{2g}\,\mathrm{t}_{2g}^3) = \tfrac{1}{2}[(yz)(\overline{yz})(xz) + (xy)(\overline{xy})(xz) + i(xy)(\overline{xy})(yz) + i(xz)(\overline{xz})(yz)],$$

$$\begin{aligned}\Psi_{27}({}^2\mathrm{E};\ {}^2\mathrm{T}_{2g}\,\mathrm{t}_{2g}^2({}^3\mathrm{T}_{1g})\,\mathrm{e}_g) = \frac{1}{\sqrt{48}}\,&[2(yz)(xy)(\overline{x^2-y^2}) - (yz)(\overline{xy})(x^2-y^2) - (\overline{yz})(xy)(x^2-y^2)\\ &- 2\sqrt{3}(yz)(xy)(\overline{z^2}) + \sqrt{3}(yz)(\overline{xy})(z^2) + \sqrt{3}(\overline{yz})(xy)(z^2)\\ &+ 2i(xy)(xz)(\overline{x^2-y^2}) - i(xy)(\overline{xz})(x^2-y^2) - i(\overline{xy})(xz)(x^2-y^2)\\ &+ 2\sqrt{3}\,i(xy)(xz)(\overline{z^2}) - \sqrt{3}\,i(xy)(\overline{xz})(z^2) - \sqrt{3}\,i(\overline{xy})(xz)(z^2)],\end{aligned}$$

$$\begin{aligned}\Psi_{28}({}^2\mathrm{E};\ {}^2\mathrm{T}_{2g}\,\mathrm{t}_{2g}^2({}^1\mathrm{T}_{2g})\,\mathrm{e}_g) = \tfrac{1}{4}&[-(yz)(\overline{xy})(z^2) + (\overline{yz})(xy)(z^2) - \sqrt{3}(yz)(\overline{xy})(x^2-y^2)\\ &+ \sqrt{3}(\overline{yz})(xy)(x^2-y^2) - i(xy)(\overline{xz})(z^2) + i(\overline{xy})(xz)(z^2)\\ &+ \sqrt{3}\,i(xy)(\overline{xz})(x^2-y^2) - \sqrt{3}\,i(\overline{xy})(xz)(x^2-y^2)],\end{aligned}$$

$$\Psi_{29}({}^2\mathrm{E};\ {}^2\mathrm{T}_{2g}\,\mathrm{t}_{2g}\,\mathrm{e}_g^2({}^1\mathrm{A}_{1g})) = \tfrac{1}{2}[(xz)(z^2)(\overline{z^2}) + (xz)(x^2-y^2)(\overline{x^2-y^2}) + i(yz)(z^2)(\overline{z^2}) + i(yz)(x^2-y^2)(\overline{x^2-y^2})],$$

$$\begin{aligned}\Psi_{30}({}^2\mathrm{E};\ {}^2\mathrm{T}_{2g}\,\mathrm{t}_{2g}\,\mathrm{e}_g^2({}^1\mathrm{E}_g)) = \tfrac{1}{4}&[-(xz)(z^2)(\overline{z^2}) + (xz)(x^2-y^2)(\overline{x^2-y^2}) + \sqrt{3}(xz)(z^2)(\overline{x^2-y^2})\\ &- \sqrt{3}(xz)(\overline{z^2})(x^2-y^2) + i(yz)(x^2-y^2)(\overline{x^2-y^2}) - i(yz)(z^2)(\overline{z^2})\\ &- \sqrt{3}\,i(yz)(z^2)(\overline{x^2-y^2}) + \sqrt{3}\,i(yz)(\overline{z^2})(x^2-y^2)].\end{aligned}$$

Table II. $E'_{1/2}$ and $E''_{3/2}$ nonzero tetragonal d³ matrix elements (wave functions are numbered as in Table I; matrices are symmetric).

| $E'_{1/2}$ Matrix | $E'_{1/2}$ Matrix | $E'_{1/2}$ Matrix |
|---|---|---|
| $\langle 1\|1\rangle = 4e_{\pi x} + 2e_{\pi z} - 15B$ | $\langle 2\|23\rangle = -\zeta/4$ | $\langle 3\|6\rangle = -\zeta/\sqrt{8}$ |
| $\langle 1\|2\rangle = \zeta$ | $\langle 2\|24\rangle = \zeta/2$ | $\langle 3\|7\rangle = \zeta/\sqrt{18}$ |
| $\langle 1\|5\rangle = -2\zeta/\sqrt{6}$ | $\langle 2\|26\rangle = -\zeta/2$ | $\langle 3\|8\rangle = \zeta/\sqrt{24}$ |
| $\langle 1\|26\rangle = \zeta$ | $\langle 2\|27\rangle = -\zeta/\sqrt{48}$ | $\langle 3\|9\rangle = 2\zeta/\sqrt{18}$ |
| $\langle 1\|27\rangle = -2\zeta/\sqrt{3}$ | $\langle 2\|28\rangle = -3\zeta/\sqrt{48}$ | $\langle 3\|10\rangle = \zeta/\sqrt{6}$ |
| $\langle 2\|2\rangle = \frac{3}{2}e_{\sigma x} + 2e_{\pi x} + 2e_{\pi z} - 15B$ | $\langle 2\|29\rangle = -\zeta/2$ | $\langle 3\|11\rangle = -\zeta/3$ |
| $\langle 2\|5\rangle = \zeta/\sqrt{24}$ | $\langle 2\|30\rangle = -\zeta$ | $\langle 3\|13\rangle = -2\zeta/3$ |
| $\langle 2\|7\rangle = \zeta/\sqrt{8}$ | $\langle 3\|3\rangle = \frac{1}{2}e_{\sigma x} + e_{\sigma z} + 2e_{\pi x} + 2e_{\pi z} - 3B$ | $\langle 3\|14\rangle = -\zeta/3$ |
| $\langle 2\|9\rangle = -\zeta/\sqrt{2}$ | | $\langle 3\|21\rangle = \zeta/2$ |
| $\langle 2\|21\rangle = -\zeta/2$ | $\langle 3\|4\rangle = 6B$ | $\langle 3\|22\rangle = \zeta/12$ |
| $\langle 2\|22\rangle = -\zeta/4$ | $\langle 3\|5\rangle = -\zeta/\sqrt{6}$ | $\langle 3\|23\rangle = -\zeta/4$ |

Table II. Continued.

| $E'_{1/2}$ Matrix | $E'_{1/2}$ Matrix | $E'_{1/2}$ Matrix |
|---|---|---|
| $\langle 3\|24\rangle = \zeta/6$ | $\langle 7\|13\rangle = -\zeta/\sqrt{18}$ | $\langle 11\|20\rangle = -\zeta/\sqrt{6}$ |
| $\langle 3\|25\rangle = \zeta/\sqrt{3}$ | $\langle 7\|14\rangle = -\zeta/\sqrt{72}$ | $\langle 11\|21\rangle = -\zeta$ |
| $\langle 3\|26\rangle = \zeta/2$ | $\langle 7\|16\rangle = -\zeta/2$ | $\langle 11\|22\rangle = \zeta/3$ |
| $\langle 3\|27\rangle = -\zeta/\sqrt{48}$ | $\langle 7\|17\rangle = -\zeta/12$ | $\langle 11\|24\rangle = \zeta/3$ |
| $\langle 3\|28\rangle = \zeta/\sqrt{48}$ | $\langle 7\|18\rangle = \zeta/4$ | $\langle 11\|25\rangle = \zeta/\sqrt{3}$ |
| $\langle 3\|29\rangle = \zeta/2$ | $\langle 7\|19\rangle = -\zeta/6$ | $\langle 12\|12\rangle = 4e_{\pi x} + 2e_{\pi z} - 6B + 3C$ |
| $\langle 4\|4\rangle = 2e_{\sigma x} + e_{\sigma z} + 2e_{\pi x} - 12B$ | $\langle 7\|20\rangle = -\zeta/\sqrt{3}$ | $\langle 12\|13\rangle = -6\sqrt{2}B$ |
| $\langle 4\|5\rangle = 2\zeta/\sqrt{6}$ | $\langle 7\|21\rangle = -\zeta/\sqrt{2}$ | $\langle 12\|14\rangle = -3\sqrt{2}B$ |
| $\langle 4\|6\rangle = \zeta/\sqrt{2}$ | $\langle 7\|22\rangle = -\zeta/\sqrt{72}$ | $\langle 12\|18\rangle = -\zeta$ |
| $\langle 4\|7\rangle = 2\zeta/\sqrt{18}$ | $\langle 7\|23\rangle = \zeta/\sqrt{8}$ | $\langle 12\|23\rangle = -\zeta/\sqrt{2}$ |
| $\langle 4\|8\rangle = \zeta/\sqrt{6}$ | $\langle 7\|24\rangle = -\zeta/\sqrt{18}$ | $\langle 12\|26\rangle = -\zeta/\sqrt{2}$ |
| $\langle 4\|9\rangle = -2\zeta/\sqrt{18}$ | $\langle 7\|25\rangle = -2\zeta/\sqrt{6}$ | $\langle 12\|27\rangle = -\zeta/\sqrt{6}$ |
| $\langle 4\|10\rangle = -\zeta/\sqrt{6}$ | $\langle 7\|26\rangle = \zeta/\sqrt{2}$ | $\langle 13\|13\rangle = \frac{1}{2}e_{\sigma x} + e_{\sigma z} + \frac{8}{3}e_{\pi x}$ |
| $\langle 4\|11\rangle = 2\zeta/3$ | $\langle 7\|27\rangle = -\zeta/\sqrt{24}$ | $+ \frac{4}{3}e_{\pi z} + 8B + 6C$ |
| $\langle 4\|13\rangle = -2\zeta/3$ | $\langle 7\|28\rangle = \zeta/\sqrt{24}$ | $\langle 13\|14\rangle = \frac{2}{3}(e_{\pi z} - e_{\pi x}) + 10B$ |
| $\langle 4\|14\rangle = 2\zeta/3$ | $\langle 7\|29\rangle = \zeta/\sqrt{2}$ | $\langle 13\|15\rangle = \sqrt{3}(2B + C)$ |
| $\langle 4\|15\rangle = -2\zeta/\sqrt{3}$ | $\langle 8\|8\rangle = \frac{5}{4}e_{\sigma x} + \frac{1}{4}e_{\sigma z} + 3e_{\pi x}$ | $\langle 13\|17\rangle = -2\zeta/\sqrt{18}$ |
| $\langle 4\|22\rangle = \zeta/6$ | $+ e_{\pi z} - 3B - \zeta/4$ | $\langle 13\|19\rangle = \zeta/\sqrt{18}$ |
| $\langle 4\|23\rangle = -\zeta/2$ | $\langle 8\|10\rangle = 6B - \zeta/2$ | $\langle 13\|20\rangle = \zeta/\sqrt{6}$ |
| $\langle 4\|24\rangle = \zeta/3$ | $\langle 8\|11\rangle = \zeta/\sqrt{6}$ | $\langle 13\|22\rangle = -\zeta/3$ |
| $\langle 4\|27\rangle = \zeta/\sqrt{12}$ | $\langle 8\|13\rangle = -\zeta/\sqrt{6}$ | $\langle 13\|24\rangle = \zeta/6$ |
| $\langle 4\|28\rangle = -\zeta/\sqrt{12}$ | $\langle 8\|14\rangle = -\zeta/\sqrt{24}$ | $\langle 13\|25\rangle = \zeta/\sqrt{12}$ |
| $\langle 5\|5\rangle = \frac{3}{4}e_{\sigma x} + \frac{3}{4}e_{\sigma z} + 3e_{\pi x}$ | $\langle 8\|16\rangle = 3\zeta/\sqrt{12}$ | $\langle 13\|26\rangle = -\zeta$ |
| $+ e_{\pi z} - 15B + \zeta/12$ | $\langle 8\|17\rangle = \zeta/\sqrt{48}$ | $\langle 13\|27\rangle = \zeta/\sqrt{3}$ |
| $\langle 5\|7\rangle = (3(e_{\sigma x} - e_{\sigma z}) - \zeta)/\sqrt{48}$ | $\langle 8\|18\rangle = -3\zeta/\sqrt{48}$ | $\langle 13\|29\rangle = \zeta/2$ |
| $\langle 5\|9\rangle = \zeta/\sqrt{12}$ | $\langle 8\|19\rangle = \zeta/\sqrt{12}$ | $\langle 13\|30\rangle = -\zeta/2$ |
| $\langle 5\|12\rangle = \zeta/\sqrt{3}$ | $\langle 8\|20\rangle = \zeta$ | $\langle 14\|14\rangle = e_{\sigma x} + \frac{1}{2}e_{\sigma z} + \frac{8}{3}e_{\pi x}$ |
| $\langle 5\|13\rangle = \zeta/\sqrt{6}$ | $\langle 9\|9\rangle = 2e_{\sigma x} + e_{\sigma z} + e_{\pi x}$ | $+ \frac{4}{3}e_{\pi z} - B + 3C$ |
| $\langle 5\|14\rangle = -\zeta/\sqrt{24}$ | $+ e_{\pi z} - 12B + \zeta/6$ | $\langle 14\|15\rangle = 2\sqrt{3}B$ |
| $\langle 5\|16\rangle = \zeta/\sqrt{12}$ | $\langle 9\|11\rangle = -2\zeta/\sqrt{18}$ | $\langle 14\|16\rangle = -\zeta/\sqrt{2}$ |
| $\langle 5\|17\rangle = \zeta/\sqrt{48}$ | $\langle 9\|13\rangle = -\zeta/\sqrt{18}$ | $\langle 14\|17\rangle = -\zeta/\sqrt{18}$ |
| $\langle 5\|18\rangle = \zeta/\sqrt{48}$ | $\langle 9\|14\rangle = \zeta/\sqrt{18}$ | $\langle 14\|19\rangle = -\zeta/\sqrt{18}$ |
| $\langle 5\|19\rangle = -\zeta/\sqrt{12}$ | $\langle 9\|15\rangle = -\zeta/\sqrt{6}$ | $\langle 14\|20\rangle = -\zeta/\sqrt{6}$ |
| $\langle 5\|21\rangle = -\zeta/\sqrt{6}$ | $\langle 9\|17\rangle = -\zeta/6$ | $\langle 14\|21\rangle = -\zeta/2$ |
| $\langle 5\|22\rangle = -\zeta/\sqrt{24}$ | $\langle 9\|18\rangle = \zeta/2$ | $\langle 14\|22\rangle = -\zeta/6$ |
| $\langle 5\|23\rangle = -\zeta/\sqrt{24}$ | $\langle 9\|19\rangle = -\zeta/3$ | $\langle 14\|24\rangle = -\zeta/6$ |
| $\langle 5\|24\rangle = \zeta/\sqrt{6}$ | $\langle 9\|22\rangle = -\zeta/\sqrt{18}$ | $\langle 14\|25\rangle = -\zeta/\sqrt{12}$ |
| $\langle 5\|26\rangle = \zeta/\sqrt{6}$ | $\langle 9\|23\rangle = \zeta/\sqrt{2}$ | $\langle 14\|26\rangle = \zeta/2$ |
| $\langle 5\|27\rangle = \zeta/\sqrt{72}$ | $\langle 9\|24\rangle = -2\zeta/\sqrt{18}$ | $\langle 14\|27\rangle = -\zeta/\sqrt{12}$ |
| $\langle 5\|28\rangle = \zeta/\sqrt{8}$ | $\langle 9\|27\rangle = \zeta/\sqrt{6}$ | $\langle 14\|29\rangle = \zeta/2$ |
| $\langle 5\|29\rangle = \zeta/\sqrt{6}$ | $\langle 9\|28\rangle = -\zeta/\sqrt{6}$ | $\langle 14\|30\rangle = -\zeta/2$ |
| $\langle 5\|30\rangle = 2\zeta/\sqrt{6}$ | $\langle 10\|10\rangle = 2e_{\sigma x} + e_{\sigma z} + e_{\pi x}$ | $\langle 15\|15\rangle = \frac{7}{8}e_{\sigma x} + e_{\sigma z} - 8B + 4C$ |
| $\langle 6\|6\rangle = \frac{3}{4}e_{\sigma x} + \frac{3}{4}e_{\sigma z} + 3e_{\pi x}$ | $+ e_{\pi z} - 12B + \zeta/2$ | $\langle 15\|19\rangle = \zeta/\sqrt{6}$ |
| $+ e_{\pi z} - 15B + \zeta/4$ | $\langle 10\|11\rangle = -2\zeta/\sqrt{6}$ | $\langle 15\|20\rangle = \zeta/\sqrt{2}$ |
| $\langle 6\|8\rangle = \sqrt{3}(e_{\sigma x} - e_{\sigma z} - \zeta)/4$ | $\langle 10\|13\rangle = -\zeta/\sqrt{6}$ | $\langle 15\|24\rangle = \zeta/\sqrt{12}$ |
| $\langle 6\|10\rangle = 3\zeta/\sqrt{12}$ | $\langle 10\|14\rangle = \zeta/\sqrt{6}$ | $\langle 15\|25\rangle = \zeta/2$ |
| $\langle 6\|12\rangle = \zeta$ | $\langle 10\|15\rangle = -\zeta/\sqrt{2}$ | $\langle 15\|29\rangle = -3\zeta/\sqrt{12}$ |
| $\langle 6\|13\rangle = \zeta/\sqrt{2}$ | $\langle 10\|17\rangle = \zeta/\sqrt{12}$ | $\langle 15\|30\rangle = -3\zeta/\sqrt{12}$ |
| $\langle 6\|14\rangle = -\zeta/\sqrt{8}$ | $\langle 10\|18\rangle = -3\zeta/\sqrt{12}$ | $\langle 16\|16\rangle = 4e_{\pi x} + 2e_{\pi z} - 6B + 3C$ |
| $\langle 6\|16\rangle = -\zeta/2$ | $\langle 10\|19\rangle = \zeta/\sqrt{3}$ | $\langle 16\|17\rangle = 3B$ |
| $\langle 6\|17\rangle = -\zeta/4$ | $\langle 11\|11\rangle = e_{\sigma x} + \frac{1}{2}e_{\sigma z} + \frac{8}{3}e_{\pi x}$ | $\langle 16\|18\rangle = -3B$ |
| $\langle 6\|18\rangle = -\zeta/4$ | $+ \frac{4}{3}e_{\pi z} - 11B + 3C$ | $\langle 16\|20\rangle = -2\sqrt{3}B$ |
| $\langle 6\|19\rangle = \zeta/2$ | $\langle 11\|13\rangle = \frac{2}{3}(e_{\pi z} - e_{\pi x})$ | $\langle 16\|22\rangle = \zeta/\sqrt{8}$ |
| $\langle 7\|7\rangle = \frac{5}{4}e_{\sigma x} + \frac{1}{4}e_{\sigma z} + 3e_{\pi x}$ | $\langle 11\|14\rangle = \frac{2}{3}(e_{\pi x} - e_{\pi z}) + \frac{1}{2}(e_{\sigma z} - e_{\sigma x})$ | $\langle 16\|23\rangle = -\zeta/\sqrt{8}$ |
| $+ e_{\pi z} - 3B - \zeta/12$ | $\langle 11\|16\rangle = \zeta/\sqrt{2}$ | $\langle 16\|26\rangle = \zeta/\sqrt{2}$ |
| $\langle 7\|9\rangle = 6B - \zeta/6$ | $\langle 11\|17\rangle = -\zeta/\sqrt{18}$ | $\langle 16\|27\rangle = -\zeta/\sqrt{24}$ |
| $\langle 7\|11\rangle = \zeta/\sqrt{18}$ | $\langle 11\|19\rangle = -\zeta/\sqrt{18}$ | $\langle 16\|28\rangle = 3\zeta/\sqrt{24}$ |

Table II. Continued.

$E'_{1/2}$ Matrix

$\langle 17|17\rangle = \frac{1}{2}e_{\sigma x} + e_{\sigma z} + 2e_{\pi x} + 2e_{\pi z} + 3C$
$\langle 17|18\rangle = -3B$
$\langle 17|19\rangle = -3B$
$\langle 17|20\rangle = -3\sqrt{3}B$
$\langle 17|21\rangle = \zeta/\sqrt{8}$
$\langle 17|22\rangle = \zeta/\sqrt{18}$
$\langle 17|23\rangle = \zeta/\sqrt{8}$
$\langle 17|24\rangle = -5\zeta/\sqrt{72}$
$\langle 17|25\rangle = \zeta/\sqrt{6}$
$\langle 17|26\rangle = \zeta/\sqrt{8}$
$\langle 17|27\rangle = -\zeta/\sqrt{6}$
$\langle 17|28\rangle = -\zeta/\sqrt{24}$
$\langle 17|29\rangle = \zeta/\sqrt{8}$
$\langle 18|18\rangle = \frac{3}{2}e_{\sigma x} + 2e_{\pi x} + 2e_{\pi z} - 6B + 3C$
$\langle 18|19\rangle = 3B$
$\langle 18|20\rangle = \sqrt{3}B$
$\langle 18|21\rangle = -\zeta/\sqrt{8}$
$\langle 18|22\rangle = \zeta/\sqrt{8}$
$\langle 18|24\rangle = -\zeta/\sqrt{8}$
$\langle 18|26\rangle = -\zeta/\sqrt{8}$
$\langle 18|27\rangle = \zeta/\sqrt{24}$
$\langle 18|29\rangle = -\zeta/\sqrt{8}$
$\langle 18|30\rangle = -\zeta/\sqrt{2}$
$\langle 19|19\rangle = 2e_{\sigma x} + e_{\sigma z} + 2e_{\pi x} - 6B + 3C$
$\langle 19|20\rangle = 2\sqrt{3}B$
$\langle 19|22\rangle = -5\zeta/\sqrt{72}$
$\langle 19|23\rangle = -\zeta/\sqrt{8}$
$\langle 19|24\rangle = \zeta/\sqrt{18}$
$\langle 19|27\rangle = -5\zeta/\sqrt{24}$
$\langle 19|28\rangle = -\zeta/\sqrt{24}$
$\langle 20|20\rangle = 2e_{\sigma x} + e_{\sigma z} + 2e_{\pi x} - 2B + 3C$
$\langle 20|22\rangle = \zeta/\sqrt{6}$
$\langle 20|25\rangle = \zeta/\sqrt{8}$
$\langle 20|28\rangle = \zeta/\sqrt{2}$
$\langle 20|30\rangle = 3\zeta/\sqrt{24}$
$\langle 21|21\rangle = 4e_{\pi x} + 2e_{\pi z} - 6B + 3C$
$\langle 21|22\rangle = 3B - \zeta/4$
$\langle 21|23\rangle = -3B + \zeta/4$
$\langle 21|25\rangle = -2\sqrt{3}B$
$\langle 21|26\rangle = e_{\pi z} - e_{\pi x} + \zeta/2$
$\langle 21|27\rangle = -\zeta/\sqrt{48}$
$\langle 21|28\rangle = 3\zeta/\sqrt{48}$
$\langle 22|22\rangle = \frac{5}{4}e_{\sigma x} + \frac{1}{4}e_{\sigma z} + 3e_{\pi x} + e_{\pi z} + 3C - \zeta/6$
$\langle 22|23\rangle = -3B - \zeta/4$
$\langle 22|24\rangle = -3B + 5\zeta/12$
$\langle 22|25\rangle = -3\sqrt{3}B - \zeta/\sqrt{12}$
$\langle 22|26\rangle = \zeta/4$
$\langle 22|27\rangle = (3(e_{\sigma x} - e_{\sigma z}) - 2\zeta)/\sqrt{48}$
$\langle 22|28\rangle = -\zeta/\sqrt{48}$
$\langle 22|29\rangle = \zeta/4$
$\langle 23|23\rangle = \frac{3}{4}e_{\sigma x} + \frac{3}{4}e_{\sigma z} + 3e_{\pi x} + e_{\pi z} - 6B + 3C$
$\langle 23|24\rangle = 3B + \zeta/4$
$\langle 23|25\rangle = \sqrt{3}B$
$\langle 23|26\rangle = -\zeta/4$
$\langle 23|27\rangle = \zeta/\sqrt{48}$
$\langle 23|28\rangle = 3(e_{\sigma x} - e_{\sigma z})/\sqrt{48}$
$\langle 23|29\rangle = -\zeta/4$
$\langle 23|30\rangle = -\zeta/2$
$\langle 24|24\rangle = 2e_{\sigma x} + e_{\sigma z} + e_{\pi x} + e_{\pi z} - 6B + 3C - \zeta/6$
$\langle 24|25\rangle = 2\sqrt{3}B$
$\langle 24|27\rangle = -5\zeta/\sqrt{48}$
$\langle 24|28\rangle = -\zeta/\sqrt{48}$
$\langle 25|25\rangle = 2e_{\sigma x} + e_{\sigma z} + e_{\pi x} + e_{\pi z} - 2B + 3C - \zeta/4$
$\langle 25|28\rangle = \zeta/2$
$\langle 25|29\rangle = 3(e_{\sigma z} - e_{\sigma x})/\sqrt{12}$
$\langle 25|30\rangle = 3\zeta/\sqrt{48}$
$\langle 26|26\rangle = 4e_{\pi x} + 2e_{\pi z} + 5C$
$\langle 26|27\rangle = 3\sqrt{3}B + \zeta/\sqrt{48}$
$\langle 26|28\rangle = -5\sqrt{3}B - 3\zeta/\sqrt{48}$
$\langle 26|29\rangle = 4B + 2C$
$\langle 26|30\rangle = -2B$
$\langle 27|27\rangle = \frac{3}{4}e_{\sigma x} + \frac{3}{4}e_{\sigma z} + 3e_{\pi x} + e_{\pi z} - 6B + 3C + \zeta/6$
$\langle 27|28\rangle = -3B - \zeta/4$
$\langle 27|29\rangle = 3\sqrt{3}B + \zeta/\sqrt{48}$
$\langle 27|30\rangle = -3\sqrt{3}B + \zeta/\sqrt{12}$
$\langle 28|28\rangle = \frac{5}{4}e_{\sigma x} + \frac{1}{4}e_{\sigma z} + 3e_{\pi x} + e_{\pi z} + 4B + 3C$
$\langle 28|29\rangle = -\sqrt{3}B - 3\zeta/\sqrt{48}$
$\langle 28|30\rangle = -\sqrt{3}B$
$\langle 29|29\rangle = 2e_{\sigma x} + e_{\sigma z} + e_{\pi x} + e_{\pi z} + 6B + 5C - \zeta/2$
$\langle 29|30\rangle = \frac{1}{2}(e_{\sigma x} - e_{\sigma z}) - 10B$
$\langle 30|30\rangle = 2e_{\sigma x} + e_{\sigma z} + e_{\pi x} + e_{\pi z} - 2B + 3C + \zeta/4$

$E''_{3/2}$ Matrix

$\langle 1|1\rangle = 4e_{\pi x} + 2e_{\pi z} - 15B$
$\langle 1|2\rangle = \zeta/3$
$\langle 1|5\rangle = -4\zeta/\sqrt{18}$
$\langle 1|6\rangle = 2\zeta/\sqrt{6}$
$\langle 1|16\rangle = 2\zeta/\sqrt{6}$
$\langle 1|17\rangle = -4\zeta/\sqrt{18}$
$\langle 1|26\rangle = \zeta/\sqrt{3}$
$\langle 1|27\rangle = -2\zeta/3$
$\langle 2|2\rangle = \frac{3}{2}e_{\sigma x} + 2e_{\pi x} + 2e_{\pi z} - 15B$
$\langle 2|5\rangle = \zeta/\sqrt{18}$
$\langle 2|6\rangle = \zeta/\sqrt{24}$
$\langle 2|7\rangle = \zeta/\sqrt{6}$
$\langle 2|8\rangle = \zeta/\sqrt{8}$
$\langle 2|9\rangle = -2\zeta/\sqrt{6}$
$\langle 2|10\rangle = -\zeta/\sqrt{2}$
$\langle 2|11\rangle = -\zeta/3$
$\langle 2|12\rangle = -4\zeta/\sqrt{18}$
$\langle 2|13\rangle = -2\zeta/3$
$\langle 2|14\rangle = -\zeta/3$
$\langle 2|21\rangle = -\zeta/\sqrt{12}$
$\langle 2|22\rangle = -\zeta/\sqrt{48}$
$\langle 2|23\rangle = -\zeta/\sqrt{48}$
$\langle 2|24\rangle = \zeta/\sqrt{12}$
$\langle 2|26\rangle = -\zeta/\sqrt{12}$
$\langle 2|27\rangle = -\zeta/12$
$\langle 2|28\rangle = -\zeta/4$
$\langle 2|29\rangle = -\zeta/\sqrt{12}$
$\langle 2|30\rangle = -\zeta/\sqrt{3}$
$\langle 3|3\rangle = \frac{1}{2}e_{\sigma x} + e_{\sigma z} + 2e_{\pi x} + 2e_{\pi z} - 3B$
$\langle 3|4\rangle = 6B$
$\langle 3|5\rangle = -\zeta/\sqrt{8}$
$\langle 3|7\rangle = \zeta/\sqrt{24}$
$\langle 3|9\rangle = \zeta/\sqrt{6}$
$\langle 3|21\rangle = 3\zeta/\sqrt{12}$
$\langle 3|22\rangle = \zeta/\sqrt{48}$
$\langle 3|23\rangle = -3\zeta/\sqrt{48}$
$\langle 3|24\rangle = \zeta/\sqrt{12}$
$\langle 3|25\rangle = \zeta$
$\langle 3|26\rangle = 3\zeta/\sqrt{12}$
$\langle 3|27\rangle = -\zeta/4$
$\langle 3|28\rangle = \zeta/4$
$\langle 3|29\rangle = 3\zeta/\sqrt{12}$
$\langle 4|4\rangle = 2e_{\sigma x} + e_{\sigma z} + 2e_{\pi x} - 12B$
$\langle 4|5\rangle = \zeta/\sqrt{2}$
$\langle 4|7\rangle = \zeta/\sqrt{6}$
$\langle 4|9\rangle = -\zeta/\sqrt{6}$
$\langle 4|22\rangle = \zeta/\sqrt{12}$
$\langle 4|23\rangle = -3\zeta/\sqrt{12}$
$\langle 4|24\rangle = \zeta/\sqrt{3}$
$\langle 4|27\rangle = \zeta/2$
$\langle 4|28\rangle = -\zeta/2$
$\langle 5|5\rangle = \frac{3}{4}e_{\sigma x} + \frac{3}{4}e_{\sigma z} + 3e_{\pi x} + e_{\pi z} - 15B - \zeta/12$
$\langle 5|7\rangle = (3(e_{\sigma x} - e_{\sigma z}) + \zeta)/\sqrt{48}$
$\langle 5|9\rangle = -\zeta/\sqrt{12}$
$\langle 5|11\rangle = \zeta/\sqrt{18}$
$\langle 5|12\rangle = -\zeta/3$
$\langle 5|13\rangle = -\zeta/\sqrt{18}$
$\langle 5|14\rangle = -\zeta/\sqrt{72}$
$\langle 5|16\rangle = \zeta/\sqrt{12}$
$\langle 5|17\rangle = \zeta/12$
$\langle 5|18\rangle = \zeta/4$

Table II. Continued.

| $E''_{3/2}$ Matrix | $E''_{3/2}$ Matrix | $E''_{3/2}$ Matrix |
|---|---|---|
| $\langle 5\vert 19\rangle = \zeta/\sqrt{12}$ | $\langle 9\vert 18\rangle = \zeta/\sqrt{12}$ | $\langle 14\vert 22\rangle = -\zeta/\sqrt{12}$ |
| $\langle 5\vert 20\rangle = \zeta/\sqrt{3}$ | $\langle 9\vert 22\rangle = -\zeta/\sqrt{18}$ | $\langle 14\vert 24\rangle = -\zeta/\sqrt{12}$ |
| $\langle 5\vert 21\rangle = -\zeta/\sqrt{6}$ | $\langle 9\vert 23\rangle = \zeta/\sqrt{2}$ | $\langle 14\vert 25\rangle = -\zeta/2$ |
| $\langle 5\vert 22\rangle = -\zeta/\sqrt{24}$ | $\langle 9\vert 24\rangle = -2\zeta/\sqrt{18}$ | $\langle 14\vert 26\rangle = -\zeta/\sqrt{12}$ |
| $\langle 5\vert 23\rangle = -\zeta/\sqrt{24}$ | $\langle 9\vert 27\rangle = \zeta/\sqrt{6}$ | $\langle 14\vert 27\rangle = \zeta/6$ |
| $\langle 5\vert 24\rangle = \zeta/\sqrt{6}$ | $\langle 9\vert 28\rangle = -\zeta/\sqrt{6}$ | $\langle 14\vert 29\rangle = -\zeta/\sqrt{12}$ |
| $\langle 5\vert 26\rangle = \zeta/\sqrt{6}$ | $\langle 10\vert 10\rangle = 2e_{\sigma x} + e_{\sigma z} + e_{\pi x}$ | $\langle 14\vert 30\rangle = \zeta/\sqrt{12}$ |
| $\langle 5\vert 27\rangle = \zeta/\sqrt{72}$ | $+ e_{\pi z} - 12B - \zeta/2$ | $\langle 15\vert 15\rangle = \frac{5}{2}e_{\sigma x} + 2e_{\sigma z} - 8B + 4C$ |
| $\langle 5\vert 28\rangle = \zeta/\sqrt{8}$ | $\langle 10\vert 13\rangle = -\zeta/\sqrt{2}$ | $\langle 15\vert 19\rangle = -\zeta/\sqrt{2}$ |
| $\langle 5\vert 29\rangle = \zeta/\sqrt{6}$ | $\langle 10\vert 14\rangle = -\zeta/\sqrt{2}$ | $\langle 15\vert 20\rangle = -\zeta/\sqrt{2}$ |
| $\langle 5\vert 30\rangle = 2\zeta/\sqrt{6}$ | $\langle 10\vert 15\rangle = -3\zeta/\sqrt{6}$ | $\langle 15\vert 24\rangle = -\zeta/2$ |
| $\langle 6\vert 6\rangle = \frac{3}{4}e_{\sigma x} + \frac{3}{4}e_{\sigma z} + 3e_{\pi x}$ | $\langle 10\vert 17\rangle = \zeta/2$ | $\langle 15\vert 25\rangle = -3\zeta/\sqrt{12}$ |
| $+ e_{\pi z} - 15B - \zeta/4$ | $\langle 10\vert 18\rangle = -\zeta/2$ | $\langle 15\vert 29\rangle = -\zeta/2$ |
| $\langle 6\vert 8\rangle = 3(e_{\sigma x} - e_{\sigma z} + \zeta)/\sqrt{48}$ | $\langle 11\vert 11\rangle = e_{\sigma x} + \frac{1}{2}e_{\sigma z} + \frac{8}{3}e_{\pi x}$ | $\langle 15\vert 30\rangle = -\zeta/2$ |
| $\langle 6\vert 10\rangle = -3\zeta/\sqrt{12}$ | $+ \frac{4}{3}e_{\pi z} + 9B + 3C$ | $\langle 16\vert 16\rangle = 4e_{\pi x} + 2e_{\pi z} + 5C$ |
| $\langle 6\vert 11\rangle = \zeta/\sqrt{6}$ | $\langle 11\vert 13\rangle = \frac{2}{3}(e_{\pi z} - e_{\pi x})$ | $\langle 16\vert 17\rangle = 3\sqrt{3}B$ |
| $\langle 6\vert 12\rangle = -\zeta/\sqrt{3}$ | $\langle 11\vert 14\rangle = \frac{1}{2}(e_{\sigma x} - e_{\sigma z})$ | $\langle 16\vert 18\rangle = -5\sqrt{3}B$ |
| $\langle 6\vert 13\rangle = -\zeta/\sqrt{6}$ | $+ \frac{2}{3}(e_{\pi x} - e_{\pi z})$ | $\langle 16\vert 19\rangle = 4B + 2C$ |
| $\langle 6\vert 14\rangle = -\zeta/\sqrt{24}$ | $\langle 11\vert 16\rangle = -\zeta/\sqrt{6}$ | $\langle 16\vert 20\rangle = -2B$ |
| $\langle 6\vert 16\rangle = -\zeta/2$ | $\langle 11\vert 17\rangle = \zeta/\sqrt{18}$ | $\langle 16\vert 21\rangle = -\zeta/\sqrt{2}$ |
| $\langle 6\vert 17\rangle = -\zeta/\sqrt{48}$ | $\langle 11\vert 19\rangle = -\zeta/\sqrt{6}$ | $\langle 16\vert 22\rangle = -\zeta/\sqrt{8}$ |
| $\langle 6\vert 18\rangle = -3\zeta/\sqrt{48}$ | $\langle 11\vert 20\rangle = \zeta/\sqrt{6}$ | $\langle 16\vert 23\rangle = \zeta/\sqrt{8}$ |
| $\langle 6\vert 19\rangle = -\zeta/2$ | $\langle 11\vert 26\rangle = \zeta/\sqrt{3}$ | $\langle 16\vert 27\rangle = \zeta/\sqrt{24}$ |
| $\langle 6\vert 20\rangle = -\zeta$ | $\langle 11\vert 27\rangle = -\zeta/3$ | $\langle 16\vert 28\rangle = -3\zeta/\sqrt{24}$ |
| $\langle 7\vert 7\rangle = \frac{5}{4}e_{\sigma x} + \frac{1}{4}e_{\sigma z} + 3e_{\pi x}$ | $\langle 11\vert 29\rangle = \zeta/\sqrt{3}$ | $\langle 17\vert 17\rangle = \frac{3}{2}e_{\sigma x} + 2e_{\pi x}$ |
| $+ e_{\pi z} - 3B + \zeta/12$ | $\langle 11\vert 30\rangle = -\zeta/\sqrt{3}$ | $+ 2e_{\pi z} - 6B + 3C$ |
| $\langle 7\vert 9\rangle = 6B + \zeta/6$ | $\langle 12\vert 12\rangle = 4e_{\pi x} + 2e_{\pi z} - 6B + 3C$ | $\langle 17\vert 18\rangle = -3B$ |
| $\langle 7\vert 13\rangle = -\zeta/\sqrt{6}$ | $\langle 12\vert 13\rangle = -6\sqrt{2}B$ | $\langle 17\vert 19\rangle = 3\sqrt{3}B$ |
| $\langle 7\vert 14\rangle = \zeta/\sqrt{24}$ | $\langle 12\vert 14\rangle = +3\sqrt{2}B$ | $\langle 17\vert 20\rangle = -3\sqrt{3}B$ |
| $\langle 7\vert 16\rangle = -\zeta/2$ | $\langle 12\vert 16\rangle = -\zeta/\sqrt{3}$ | $\langle 17\vert 21\rangle = \zeta/\sqrt{24}$ |
| $\langle 7\vert 17\rangle = \zeta/\sqrt{48}$ | $\langle 12\vert 17\rangle = -\zeta/3$ | $\langle 17\vert 22\rangle = \zeta/\sqrt{6}$ |
| $\langle 7\vert 18\rangle = -\zeta/\sqrt{48}$ | $\langle 12\vert 23\rangle = 3\zeta/\sqrt{6}$ | $\langle 17\vert 23\rangle = -\zeta/\sqrt{24}$ |
| $\langle 7\vert 19\rangle = -\zeta/2$ | $\langle 12\vert 26\rangle = -\zeta/\sqrt{6}$ | $\langle 17\vert 24\rangle = 5\zeta/\sqrt{24}$ |
| $\langle 7\vert 21\rangle = -\zeta/\sqrt{2}$ | $\langle 12\vert 27\rangle = -\zeta/\sqrt{18}$ | $\langle 17\vert 26\rangle = \zeta/\sqrt{24}$ |
| $\langle 7\vert 22\rangle = -\zeta/\sqrt{72}$ | $\langle 13\vert 13\rangle = \frac{3}{2}e_{\sigma x} + \frac{8}{3}e_{\pi x}$ | $\langle 17\vert 27\rangle = \zeta/\sqrt{18}$ |
| $\langle 7\vert 23\rangle = \zeta/\sqrt{8}$ | $+ \frac{4}{3}e_{\pi z} + 8B + 6C$ | $\langle 17\vert 28\rangle = -\zeta/\sqrt{8}$ |
| $\langle 7\vert 24\rangle = -\zeta/\sqrt{18}$ | $\langle 13\vert 14\rangle = \frac{2}{3}(e_{\pi z} - e_{\pi x}) - 10B$ | $\langle 17\vert 29\rangle = \zeta/\sqrt{24}$ |
| $\langle 7\vert 25\rangle = -2\zeta/\sqrt{6}$ | $\langle 13\vert 15\rangle = \sqrt{3}(2B + C)$ | $\langle 17\vert 30\rangle = \zeta/\sqrt{6}$ |
| $\langle 7\vert 26\rangle = \zeta/\sqrt{2}$ | $\langle 13\vert 16\rangle = -2\zeta/\sqrt{6}$ | $\langle 18\vert 18\rangle = \frac{1}{2}e_{\sigma x} + e_{\sigma z} + 2e_{\pi x}$ |
| $\langle 7\vert 27\rangle = -\zeta/\sqrt{24}$ | $\langle 13\vert 17\rangle = 2\zeta/\sqrt{18}$ | $+ 2e_{\pi z} + 4B + 3C$ |
| $\langle 7\vert 28\rangle = \zeta/\sqrt{24}$ | $\langle 13\vert 19\rangle = \zeta/\sqrt{6}$ | $\langle 18\vert 19\rangle = -\sqrt{3}B$ |
| $\langle 7\vert 29\rangle = \zeta/\sqrt{2}$ | $\langle 13\vert 20\rangle = -\zeta/\sqrt{6}$ | $\langle 18\vert 20\rangle = -\sqrt{3}B$ |
| $\langle 8\vert 8\rangle = \frac{5}{4}e_{\sigma x} + \frac{1}{4}e_{\sigma z} + 3e_{\pi x}$ | $\langle 13\vert 22\rangle = \zeta/\sqrt{3}$ | $\langle 18\vert 21\rangle = -3\zeta/\sqrt{24}$ |
| $+ e_{\pi z} - 3B + \zeta/4$ | $\langle 13\vert 24\rangle = -\zeta/\sqrt{12}$ | $\langle 18\vert 22\rangle = \zeta/\sqrt{24}$ |
| $\langle 8\vert 10\rangle = 6B + \zeta/2$ | $\langle 13\vert 25\rangle = -\zeta/2$ | $\langle 18\vert 24\rangle = \zeta/\sqrt{24}$ |
| $\langle 8\vert 13\rangle = -\zeta/\sqrt{2}$ | $\langle 13\vert 26\rangle = -\zeta/\sqrt{3}$ | $\langle 18\vert 25\rangle = -\zeta/\sqrt{2}$ |
| $\langle 8\vert 14\rangle = \zeta/\sqrt{8}$ | $\langle 13\vert 27\rangle = \zeta/3$ | $\langle 18\vert 26\rangle = -3\zeta/\sqrt{24}$ |
| $\langle 8\vert 16\rangle = 3\zeta/\sqrt{12}$ | $\langle 13\vert 29\rangle = \zeta/\sqrt{12}$ | $\langle 18\vert 27\rangle = -\zeta/\sqrt{8}$ |
| $\langle 8\vert 17\rangle = -\zeta/4$ | $\langle 13\vert 30\rangle = -\zeta/\sqrt{12}$ | $\langle 18\vert 29\rangle = -3\zeta/\sqrt{24}$ |
| $\langle 8\vert 18\rangle = \zeta/4$ | $\langle 14\vert 14\rangle = e_{\sigma x} + \frac{1}{2}e_{\sigma z} + \frac{8}{3}e_{\pi x}$ | $\langle 19\vert 19\rangle = 2e_{\sigma x} + e_{\sigma z}$ |
| $\langle 8\vert 19\rangle = 3\zeta/\sqrt{12}$ | $+ \frac{4}{3}e_{\pi z} - B + 3C$ | $+ 2e_{\pi x} + 6B + 5C$ |
| $\langle 9\vert 9\rangle = 2e_{\sigma x} + e_{\sigma z} + e_{\pi x}$ | $\langle 14\vert 15\rangle = -2\sqrt{3}B$ | $\langle 19\vert 20\rangle = e_{\sigma z} - e_{\sigma x} - 10B$ |
| $+ e_{\pi z} - 12B - \zeta/6$ | $\langle 14\vert 16\rangle = -\zeta/\sqrt{6}$ | $\langle 19\vert 22\rangle = -\zeta/\sqrt{8}$ |
| $\langle 9\vert 13\rangle = -\zeta/\sqrt{6}$ | $\langle 14\vert 17\rangle = \zeta/\sqrt{18}$ | $\langle 19\vert 23\rangle = \zeta/\sqrt{8}$ |
| $\langle 9\vert 14\rangle = -\zeta/\sqrt{6}$ | $\langle 14\vert 19\rangle = -\zeta/\sqrt{6}$ | $\langle 19\vert 27\rangle = \zeta/\sqrt{24}$ |
| $\langle 9\vert 15\rangle = -\zeta/\sqrt{2}$ | $\langle 14\vert 20\rangle = \zeta/\sqrt{6}$ | $\langle 19\vert 28\rangle = -3\zeta/\sqrt{24}$ |
| $\langle 9\vert 17\rangle = -\zeta/\sqrt{12}$ | $\langle 14\vert 21\rangle = -3\zeta/\sqrt{12}$ | $\langle 19\vert 29\rangle = -\zeta/\sqrt{2}$ |

Table II. Continued.

| $E''_{3/2}$ Matrix | $E''_{3/2}$ Matrix | $E''_{3/2}$ Matrix |
|---|---|---|
| $\langle 20 \vert 20\rangle = 2e_{\sigma x} + e_{\sigma z}$ | $\langle 22 \vert 28\rangle = \zeta/\sqrt{48}$ | $\langle 25 \vert 30\rangle = -3\zeta/\sqrt{48}$ |
| $+ 2e_{\pi x} - 2B + 3C$ | $\langle 22 \vert 29\rangle = -\zeta/4$ | $\langle 26 \vert 26\rangle = 4e_{\pi x} + 2e_{\pi z} + 5C$ |
| $\langle 20 \vert 23\rangle = \zeta/\sqrt{2}$ | $\langle 23 \vert 23\rangle = \frac{3}{4}e_{\sigma x} + \frac{3}{4}e_{\sigma z} + 3e_{\pi x}$ | $\langle 26 \vert 27\rangle = 3\sqrt{3}B - \zeta/\sqrt{48}$ |
| $\langle 20 \vert 25\rangle = -3\zeta/\sqrt{24}$ | $+ e_{\pi z} - 6B + 3C$ | $\langle 26 \vert 28\rangle = -5\sqrt{3}B + 3\zeta/\sqrt{48}$ |
| $\langle 20 \vert 27\rangle = \zeta/\sqrt{6}$ | $\langle 23 \vert 24\rangle = 3B - \zeta/4$ | $\langle 26 \vert 29\rangle = 4B + 2C$ |
| $\langle 20 \vert 30\rangle = \zeta/\sqrt{8}$ | $\langle 23 \vert 25\rangle = \sqrt{3}B$ | $\langle 26 \vert 30\rangle = -2B$ |
| $\langle 21 \vert 21\rangle = 4e_{\pi x} + 2e_{\pi z} - 6B + 3C$ | $\langle 23 \vert 26\rangle = \zeta/4$ | $\langle 27 \vert 27\rangle = \frac{3}{4}e_{\sigma x} + \frac{3}{4}e_{\sigma z} + 3e_{\pi x}$ |
| $\langle 21 \vert 22\rangle = 3B + \zeta/4$ | $\langle 23 \vert 27\rangle = -\zeta/\sqrt{48}$ | $+ e_{\pi z} - 6B + 3C - \zeta/6$ |
| $\langle 21 \vert 23\rangle = -3B - \zeta/4$ | $\langle 23 \vert 28\rangle = \sqrt{3}(e_{\sigma x} - e_{\sigma z})/4$ | $\langle 27 \vert 28\rangle = -3B + \zeta/4$ |
| $\langle 21 \vert 25\rangle = -2\sqrt{3}B$ | $\langle 23 \vert 29\rangle = \zeta/4$ | $\langle 27 \vert 29\rangle = 3\sqrt{3}B - \zeta/\sqrt{48}$ |
| $\langle 21 \vert 26\rangle = e_{\pi z} - e_{\pi x} - \zeta/2$ | $\langle 23 \vert 30\rangle = \zeta/2$ | $\langle 27 \vert 30\rangle = -3\sqrt{3}B - \zeta/\sqrt{12}$ |
| $\langle 21 \vert 27\rangle = \zeta/\sqrt{48}$ | $\langle 24 \vert 24\rangle = 2e_{\sigma x} + e_{\sigma z} + e_{\pi x}$ | $\langle 28 \vert 28\rangle = \frac{5}{4}e_{\sigma x} + \frac{1}{4}e_{\sigma z} + 3e_{\pi x}$ |
| $\langle 21 \vert 28\rangle = -3\zeta/\sqrt{48}$ | $+ e_{\pi z} - 6B + 3C + \zeta/6$ | $+ e_{\pi z} + 4B + 3C$ |
| $\langle 22 \vert 22\rangle = \frac{5}{4}e_{\sigma x} + \frac{1}{4}e_{\sigma z} + 3e_{\pi x}$ | $\langle 24 \vert 25\rangle = 2\sqrt{3}B$ | $\langle 28 \vert 29\rangle = -\sqrt{3}B + 3\zeta/\sqrt{48}$ |
| $+ e_{\pi z} + 3C + \zeta/6$ | $\langle 24 \vert 27\rangle = 5\zeta/\sqrt{48}$ | $\langle 28 \vert 30\rangle = -\sqrt{3}B$ |
| $\langle 22 \vert 23\rangle = -3B + \zeta/4$ | $\langle 24 \vert 28\rangle = \zeta/\sqrt{48}$ | $\langle 29 \vert 29\rangle = 2e_{\sigma x} + e_{\sigma z} + e_{\pi x}$ |
| $\langle 22 \vert 24\rangle = -3B - 5\zeta/12$ | $\langle 25 \vert 25\rangle = 2e_{\sigma x} + e_{\sigma z} + e_{\pi x}$ | $+ e_{\pi z} + 6B + 5C + \zeta/2$ |
| $\langle 22 \vert 25\rangle = -3\sqrt{3}B + \zeta/\sqrt{12}$ | $+ e_{\pi z} - 2B + 3C + \zeta/4$ | $\langle 29 \vert 30\rangle = \frac{1}{2}(e_{\sigma x} - e_{\sigma z}) - 10B$ |
| $\langle 22 \vert 26\rangle = -\zeta/4$ | $\langle 25 \vert 28\rangle = -\zeta/2$ | $\langle 30 \vert 30\rangle = 2e_{\sigma x} + e_{\sigma z} + e_{\pi x}$ |
| $\langle 22 \vert 27\rangle = (3(e_{\sigma x} - e_{\sigma z}) + 2\zeta)/\sqrt{48}$ | $\langle 25 \vert 29\rangle = \sqrt{3}(e_{\sigma z} - e_{\sigma x})/2$ | $+ e_{\pi z} - 2B + 3C - \zeta/4$ |

[1] O. S. Mortensen, J. Chem. Phys. **47**, 4215 (1967).
[2] R. W. Schwartz, Inorg. Chem. **15**, 2817 (1976).
[3] H.-H. Schmidtke and P. E. Hoggard, Chem. Phys. Lett. **20**, 119 (1973).
[4] A. M. Black and C. D. Flint, J. Chem. Soc. Dalton Trans. 977 (1974).
[5] (a) A. R. Reinberg and S. G. Parker, Phys. Rev. **B1**, 2085 (1971). (b) C. D. Flint and A. G. Paulusz, Chem. Phys. Lett. **62**, 259 (1979).
[6] R. M. Macfarlane, J. Chem. Phys. **47**, 2066 (1967).
[7] C. K. Jørgensen, Advan. Chem. Phys. **5**, 33 (1963).
[8] J. R. Perumareddi, Coordin. Chem. Rev. **4**, 73 (1969).
[9] R. K. Lowry, Jr., and J. R. Perumareddi, J. Phys. Chem. **74**, 1371 (1970).
[10] S. Decurtins, H. U. Güdel, and K. Neuenschwander, Inorg. Chem. **16**, 796 (1977).
[11] C. D. Flint, A. P. Matthews, and P. J. O'Grady, J. Chem. Soc. Faraday II, **73**, 655 (1977).
[12] For example, in Appendix B of Ref. [8], the (2, 3) element of the $^2B_1$ matrix should be $6\sqrt{2}\,B$ rather than $-6\sqrt{2}\,B$, using the wavefunctions from Appendix A.
[13] C. E. Schaeffer and C. K. Jørgensen, Kgl. Danske Videnskab. Selskab. Mat. Fys. Medd. **34**, No. 13 (1965).
[14] J. S. Griffith, The Theory of Transition-Metal Ions, Cambridge University Press, London 1961.
[15] C. J. Ballhausen, Introduction to Ligand Field Theory, McGraw-Hill, New York 1962.
[16] H. Hartmann and H.-H. Schmidtke, Z. Phys. Chem. Frankfurt (Main) **19**, 43 (1959).
[17] C. D. Flint and A. P. Matthews, J. Chem. Soc. Faraday II **70**, 1307 (1974).
[18] C. D. Flint and A. P. Matthews, J. Chem. Soc. Faraday II **71**, 379 (1975).
[19] P. E. Hoggard and H.-H. Schmidtke, Ber. Bunsenges. Phys. Chem. **76**, 1013 (1972).
[20] L. Dubicki, M. A. Hitchman, and P. Day, Inorg. Chem. **9**, 188 (1970).
[21] C. D. Flint and A. P. Matthews, J. Chem. Soc. Faraday II **70**, 1301 (1974).