Calculation of Tanabe–Sugano Diagrams by Matrix Diagonalization

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Abstract: The chemistry and spectroscopy of transition elements depend on complex interactions found for partially filled d subshells. There are complex electron–electron repulsion effects within a partially filled subshell and additional complications due to participation of some of the d orbitals in chemical bonding. The number of states involved can be quite large, and the mathematical treatment involves matrices as large as 28 by 28. The direct solution for eigenvalues and eigenvectors of matrices this large was not even attempted in the 1930s, but is well within the capabilities of current undergraduates and computers. Full matrices in the form of spreadsheets are provided in this paper for octahedral and tetrahedral symmetry for all cases from d2 through d8. Diagonalization of such matrices with MACSYMA is illustrated. Construction of full Tanabe–Sugano diagrams is possible for students for any choice of input parameters.

Introduction

The calculation of allowed energies for a free atom with a partially filled d subshell is reasonably complex. The number of quantum states involved is $10!/(n!\times(10-n)!)$, where n is the number of d electrons in the partially filled subshell. The number of states reaches 210 and 252 for $n = 4$ and $n = 5$. These possible quantum states naturally group together under different term symbols with degeneracies from 1 (^1S) to 36 (^4G). Calculating the allowed terms for different numbers of electrons in the subshell from 1 to 9 is straightforward and is a common student exercise in inorganic chemistry. The results are shown in Table 1.

The relative energies corresponding to the different terms can be expressed by two parameters describing the electron–electron repulsion within the subshell like the Racah [1–4] parameters B and C. An equally valid set of two parameters involves using the Racah B together with D, the parameter in the spin correlation stabilization energy (S.C.S.E.) equation:

$$\text{S.C.S.E.} = \text{D}^*\text{n}_\text{u}{}^*(\text{n}_\text{u} - 1) \tag{1}$$

where n_u is the number of unpaired electrons in the configuration [5–7]. The two parameter sets are related by the equation

$$C = -2.5\,B + (36/14)\,D \tag{2}$$

Calculating allowed energies for free atoms is straightforward, but not of great chemical significance, because the transition elements are normally encountered in compounds. In the most favorable geometries found in compounds, octahedral and tetrahedral, the d orbitals split into two sets with different energies that are usually described with Mulliken symbols taken from the O_h character table, t_{2g} and e_g. This introduces a third parameter, generally taken as Δ, the difference in energy between the t_{2g} and e_g orbitals. D states split similarly into T_{2g} and E_g energy levels. S and P terms become A_{1g} and T_{1g} levels respectively, but all the other free atom terms split into two to six different energies in octahedral symmetry, all of which can be assigned names from the O_h character table. Plots of the energy of these quantum states versus Δ are useful and are available as Orgel [4, 8, 9] and Tanabe–Sugano diagrams [10–12] The quantum states can be expressed as linear combinations of products of orbitals, and the orbitals themselves can be assigned energies of 0 (for t_{2g}) and $+\Delta$ (for e_g) in octahedral geometry. The lines in Orgel diagrams, however, are often curved, because the linear combinations change as functions of Δ. Even by plotting relative energies, it is not possible to show everything one wants in a two-dimensional graph, and some of the parameters must be fixed as in the assumption that

$$C/B = 3.7 \tag{3}$$

which has been used in calculating many of the Tanabe–Sugano diagrams in books. This paper shows how students can calculate these energies to check published graphs, to examine regions on a finer scale, or to make their own diagrams for different choices of the adjustable parameters.

The original calculations for Tanabe–Sugano diagrams were performed using basis functions that were eigenvectors of the orbital angular momentum operators. Students in chemistry are much more familiar with the basis functions which fit the O_h character table, d_{xz}, d_{yz}, d_{xy}, d_{zz}, and d_{xx-yy}, which we will call position orbitals. Calculations with the position orbitals are slightly more complicated for free ions [6], but are just as good for all the geometries encountered in actual solids; thus, all the calculations presented in this paper will use these five position orbitals familiar to chemists.

Two-Electron Matrix Elements with Position Orbitals

There are 45 basis functions for two electrons in the ten orbitals of a d subshell including electron spin. With modern computers, one can handle 45 × 45 matrices, but it is still advantageous to separate different spin and symmetry

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Table 1. Allowed Energy Levels for Partially Filled d Subshells for Free Atoms

subshell	Number of quantum states	Number of energy levels	Term Symbols
d^1	10	1	^{2}D
d^2	45	5	^{3}F, ^{3}P, ^{1}G, ^{1}D, ^{1}S
d^3	120	8	^{4}F, ^{4}P, ^{2}H, ^{2}G, ^{2}F, ^{2}D, ^{2}D, ^{2}P
d^4	210	16	^{5}D, ^{3}H, ^{3}G, ^{3}F, ^{3}F, ^{3}D, ^{3}P, ^{3}P, ^{1}I, ^{1}G, ^{1}G, ^{1}F, ^{1}D, ^{1}D, ^{1}S, ^{1}S
d^5	252	16	^{6}S, ^{4}G, ^{4}F, ^{4}D, ^{4}P, ^{2}I, ^{2}H, ^{2}G, ^{2}G, ^{2}F, ^{2}F, ^{2}D, ^{2}D, ^{2}D, ^{2}P, ^{2}S
d^6	210	16	^{5}D, ^{3}H, ^{3}G, ^{3}F, ^{3}F, ^{3}D, ^{3}P, ^{3}P, ^{1}I, ^{1}G, ^{1}G, ^{1}F, ^{1}D, ^{1}D, ^{1}S, ^{1}S
d^7	120	8	^{4}F, ^{4}P, ^{2}H, ^{2}G, ^{2}F, ^{2}D, ^{2}D, ^{2}P
d^8	45	5	^{3}F, ^{3}P, ^{1}G, ^{1}D, ^{1}S
d^9	10	1	^{2}D
d^{10}	1	1	^{1}S

Table 2. Basis Functions with aas Symmetry and the 3 ´ 3 Matrix for the d^2 Case with Parallel Spins and Parameters D = 1688, Δ = 18500, A = –926, B = 700, and C = 2,590.57, All in Units of Kaysers or cm^{-}1

basis functions		Matrix (numeric)	
| xzα yzα >	–4426.	0.	–4200.
| xyα zzα >	0.	11974.	0.
| xyα xx-yyα >	–4200.	0.	20374.
basis functions		Matrix (functional form)	
| xzα yzα >	A–5*B	0.	–6*B
| xyα zzα >	0.	A–8*B+Δ	0.
| xyα xx-yyα >	–6*B	0.	A+4*B+Δ
eigenvalues		eigenvectors	
-5117.982	| 0.98670	0.	0.16257>
11974.	| 0.	1.	0.>
21065.982	| -0.16257	0.	0.98670>

functions. For example, there are only ten basis functions with positive spin for both electrons, and the ten divide into three groups of three and a 1 × 1 matrix when one considers symmetry on reflection in the three σ_h planes, *yz*, *xz*, and *xy*. The four symmetries can be described as aas, asa, saa, and sss if one uses the letters a and s for antisymmetric and symmetric with respect to reflection in the planes perpendicular to the *x*, *y*, and z axes, respectively. One can classify basis functions into these four classes easily by counting the number of *x*'s, *y*'s, and *z*'s in the subscripts, and seeing if the numbers are odd or even. If all three numbers are even, one has sss symmetry as for $|d_{zz}\alpha\, d_{xx\text{-}yy}\alpha\rangle$, where the greek letter α is used to designate a spin of +1/2. Similarly $|d_{xz}\alpha\ d_{yz}\alpha\rangle$ is seen to have aas symmetry.

Table 2 shows the three $\alpha\alpha$ basis functions with aas symmetry and the nine matrix elements for Δ = 17,100 cm^{-1}; *D* = 1,688; and the Racah parameters, *A* = –926, *B* = 700, and *C* = 2,590.57. This 3 × 3 matrix has eigenvalues of –5,117.982, 11,974.000, and 21,065.982. The predicted absorption peaks for these three energy levels are at 17,092 and 26,184 cm^{-1}. These are not unreasonable parameters for the blue $V(H_2O)_6^{3+}$ ion, for which the observed absorption peaks [13, 14] are at 17,100 and 25,000 cm^{-1}.

If Δ is set to zero the eigenvalues are –6,526, –6,526, and 3,974, the energies of the two triplet states for a d^2 system with these values of the parameters. The values for the free ion are *A* – 8 × *B* = –6,526 and *A* + 7 × *B* = 3,974 for the ^{3}F and ^{3}P states respectively. Note that the energy difference is a function of the parameter *B*: 3,974 – (–6,526) = 10,500 cm^{-1} = 15 × *B*. The parameter *D* specifies (by eq 1) the difference between the average energies of all states and all states with the maximum multiplicity. The parameter *B* determines the energy difference between the states of maximum multiplicity, which is 15 × *B* for d^2, d^3, d^7, and d^8.

There are 25 basis functions in d^2 of the $\alpha\beta$ type, with spin up for the first electron and down for the second. Seven of these are of sss symmetry and are shown in Table 3. The three other symmetry classes each have six basis functions. There is no particular reason to remain with cm^{-1} as the energy unit or with values chosen for a particular oxidation state of vanadium. Thus, a more general set of parameters, *B* = 10, *D* = 24.111111, and *C* = 37 is used for Table 3.

The 7 × 7 matrix with Δ = 300 shown in Table 3 has eigenvalues of 848.575, 662.805, 662.805, 506.778, 237.981, 68.751, and 68.751, corresponding to the $^1A_1$, ^{1}E, $^3A_2$, $^1A_1$, and ^{1}E states, respectively, recognizing that each E state must be present twice.

Changing the Δ value simply requires adjusting the diagonal matrix elements. For Δ = 0 the diagonal becomes 137.777778, 137.777778, 137.777778, 137.777778, –16.222222, –16.222222, 137.777778. The matrix for Δ = 0 has eigenvalues of 385.778, 100.778, 100.778, 100.778, 30.778, 30.778, and –93.222, giving the energies of all the free-ion singlet states along with the ^{3}F energy from the $^3A_2$ line. Note that the $^3A_2$ state has an eigenvalue of –93.222 + 2 Δ in both calculations. With the basis set in Table 3, the $^3A_2$ eigenvector is |0, 0, 0, 0, –0.7071, 0.7071, 0>.

It is very easy to make a mistake in one or more of 49 matrix elements in a 7 × 7 matrix, and it is quite gratifying to get close enough to get even one eigenvalue and eigenvector that one can recognize is correct like the –93.222 + 600 = 506.778 value above. Furthermore the d^2 calculations are relatively easy compared to the d^4 and d^5 cases; thus, it is desirable to have the full matrices available in spreadsheet and word-processor forms, ready for student use, and one of the aims of this paper is to make these available.

For some purposes, it would be desirable to have the full 45 × 45 matrix for the d^2 case, but it requires many pages to print over 2000 values most of which are zero. Rounding to the nearest integer, as in one version of Table 4, still leaves the 45 × 45 matrix nearly unreadable. A more convenient representation is created in a spreadsheet, and Table 4 is available in the spreadsheet d2p.wb2 in cell positions a129 through ax176. If you wish to have the full matrix for other values of the parameters, the entries in cells b3 through b6 can be adjusted. The 10 × 10 and 25 × 25 portions of this matrix are shown with double spacing and extra labels in the intermediate sections of the spreadsheet, cells a73 through p99 and a1 through ak71, respectively, and they are presented in printed form for the particular choice of *B* = 10, *D* = 21.014,

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Table 3. Basis Functions with sss Symmetry and the 7 ´ 7 Matrix for the d2 Case with Opposite Spins and Parameters D = 24.111, Δ = 300, A = –13.222, B = 10, and C = 37

basis function	Matrix						
| xzα xzβ >	137.778	67.	67.	47.	17.3205	17.3205	67.
| yzα yzβ >	67.	137.778	67.	47.	–17.3205	–17.3205	67.
| xyα xyβ >	67.	67.	137.778	77.	0.	0.	37.
| zzα zzβ >	47.	47.	77.	737.778	0.	0.	77.
| zzα xx-yyβ >	17.3205	–17.3205	0.	0.	583.778	77.	0.
| xx-yyα zzβ >	17.3205	–17.3205	0.	0.	77.	583.778	0.
|xx-yyα xx-yyβ >	67.	67.	37.	77.	0.	0.	737.778

C = 29.036, and A = –7.028 in Tables 5 and 6. A printed version of these sections of the spreadsheet takes seven pages, but is very useful to have available because these two-electron matrix elements appear in calculations for the d^3 through d^9 cases as well.

Note that Tables 4, 5, and 6 are supplied both in spreadsheet (d2p.wb2) and in two text forms, one printed from the spreadsheet and with rounded values in typed tables.

These matrix elements can all be expressed in analytical form in the Racah parameters and are easily programmed into the spreadsheet. The diagonal terms are all of the form

$$A + (n/2)B + mC + p\Delta \qquad (4)$$

where n, m, and p are integers. The value of p is obtained by counting the number of higher-energy d orbitals present in the basis function, and can vary from 0 to 2. The tetrahedral case can be handled using a negative value for Δ and adjusting A, or by making a different spreadsheet.

There are four different types of off-diagonal matrix elements, 0, $q \times 3^{(1/2)} \times B$, $r \times B$, and $s \times t \times B + t \times C$, where q, r, s, and t are integers, and t can be only +1 or –1. The allowed values of r are –6, –3, +3, and +6. Similarly, s can be 0, 1, 3, or 4, and q ranges from –3 to +3 with +5 and –5 also allowed when there are more than two d electrons. One is tempted to develop rules or special tables to show when these different values are found, but my personal experience has been that it is best to rely on the full 10 × 10 and 25 × 25 matrices in Tables 5 and 6 when the value of a particular two-electron matrix element is needed.

The order of the basis functions in tables like Table 4 is extremely important, but it is more or less arbitrary. It is desirable to place all the ones with the same number of e_g orbitals together and to group orbitals with the same symmetries together. Where these are inconsistent, either way can be chosen, and the choices in this paper are not completely consistent. In general a priority order of d_{xz}, d_{yz}, d_{xy}, d_{zz}, and finally $d_{xx–yy}$ has been used, but this has been violated to keep functions like $|xz\alpha\, zz\beta>$ and $|zz\alpha\, xz\beta>$ together. It is hoped that the order in Table 6 and the double spacing in the six-page version will be helpful to students needing to look up particular d^2 matrix elements.

To get all the energies for an Orgel diagram for the d^2 case, the 7 × 7 matrix can be diagonalized and any one of the 6 × 6 matrices for two electrons of opposite spin extracted from Table 6. The thirteen eigenvalues are listed in Table 7 for Δ = 300 and for the two limiting cases of Δ = 0 and the strong-field limit, Δ approaching infinity. Table 8 is an older version of this table with different values for A, C, and D.

The strong-field limits are obtained by diagonalizing a block-diagonal matrix with all matrix elements between terms for different Δ values set to zero. Table 9 shows the form taken by the asa 6 × 6 matrix in this limit. The eigenvalues of this matrix are –63.222, 70.778, 206.778, 326.778, 360.778, and 400.778, corresponding to the $^3T_1$, $^1T_2$, $^3T_2$, $^3T_1$, $^1T_2$, and $^1T_1$ states, respectively. The 326.778 eigenvector, |0. 0. –0.612 0.612 0.353 –0.353> can be seen to be a triplet from the pattern of equal values and opposite signs for pairs of basis functions with forms like $|xz\alpha\, zz\beta>$ and $|zz\alpha\, xz\beta>$. Deciding which ones are T_1 and which are T_2 is complicated in this case by the fact that 90-degree rotation about the y axis thoroughly mixes the zz and $xx–yy$ orbitals. The easiest way to make the assignments is by the symmetry of the aas eigenvectors to C_{4z}, but it can be done using the matrix for C_{4y} in Table 10. The orbital d_{yy}, which is completely symmetric to rotations about the y axis, is the linear combination, $d_{yy} = 0.866 \times d_{zz} - 0.500 \times d_{xx-yy}$, and it is this pattern of constants related by a factor of minus one over the square root of 3 which appears in the T_1 eigenvectors. Thus $^1T_1$ = |400.778> = |0. 0. 0.612 0.612 –0.353 –0.353>.

The 326.778 eigenvector is found to have $^3T_1$ symmetry, and the energy is at $A + 4 \times B + \Delta$. Finding the analytic form from a numerical value is somewhat easier if C is not an integer; thus, while the choice A = –13.222222, B = 10, D = 24.111111, and C = 37 is useful for checking literature plots constructed for C/B = 3.7, most of this paper uses a different choice for the parameters, A = –7.028, B = 10, C = 29.036, and D = 21.014. With this choice, two-electron matrix elements of 29.036, 39.036, 59.026, and 69.036 are easily recognized as $C + s \times B$ with s values from 0 to 4.

Matrix Elements for the d^3 Case

There are only two basis functions for three d electrons that have aas symmetry, have two spins up and one down, and which do not use any e orbitals. They can be written as

$$|11> = |xz\alpha\, xy\alpha\, xz\beta> \text{ and}$$

$$|12> = |yz\alpha\, xy\alpha\, yz\beta>$$

The diagonal matrix elements are sums of three two-electron integrals; thus,

$$<11|11> = <xz\alpha\, xy\alpha|xz\alpha\, xy\alpha> + <xz\alpha\, xz\beta|xz\alpha\, xz\beta> + <xy\alpha\, xz\beta|xy\alpha\, xz\beta>$$

Looking up the three two-electron integrals in Tables 4 and 5 gives: <11|11> = –57.028 + 120.08 + 2.008 = 65.06

Table 4. The Full 45 × 45 Matrix for d2, Rounded to Integers. The Parameters $A = 0$, $B = 10$, $C = 29.036$, $D = 21.014$, and $\Delta = 300$ are used. See the spreadsheet d2p.wb2 in Positions a129 to ax176 for an Alternative Form of This Table

sym.	orbitals		matrix																																												
	α	β																																													
a a s	xz yz		-57	0	-60	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
a a s	xy zz		0	213	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
a a s	xy xx-yy		-60	0	333	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
a s a	yz xy		0	0	0	-57	-52	30	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
a s a	xz zz		0	0	0	-52	303	-52	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
a s a	xz xx-yy		0	0	0	30	-52	243	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
s a a	xz xy		0	0	0	0	0	0	-57	-52	-30	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
s a a	yz zz		0	0	0	0	0	0	-52	303	52	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
s a a	yz xx-yy		0	0	0	0	0	0	-30	52	243	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
s s s	zz xx-yy		0	0	0	0	0	0	0	0	0	513	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
s s s	xz	xz	0	0	0	0	0	0	0	0	0	0	120	59	59	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	39	17	17	59	0	0	0	0	0	0	0	0	0	0
s s s	yz	yz	0	0	0	0	0	0	0	0	0	0	59	120	59	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	39	-17	-17	59	0	0	0	0	0	0	0	0	0	0
s s s	xy	xy	0	0	0	0	0	0	0	0	0	0	59	59	120	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	69	0	0	29	0	0	0	0	0	0	0	0	0	0
a a s	xz	yz	0	0	0	0	0	0	0	0	0	0	0	0	0	2	59	0	0	0	0	17	17	-30	30	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
a a s	yz	xz	0	0	0	0	0	0	0	0	0	0	0	0	0	59	2	0	0	0	0	17	17	30	-30	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
a s a	yz	xy	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2	59	0	0	0	0	0	0	-35	17	0	-30	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
a s a	xy	yz	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	59	2	0	0	0	0	0	0	17	-35	-30	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
s a a	xz	xy	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2	59	0	0	0	0	0	0	0	0	-35	17	0	30	0	0	0	0	0	0	0	0	0	0	0	0	0	0
s a a	xy	xz	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	59	2	0	0	0	0	0	0	0	0	17	-35	30	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
a a s	xy	zz	0	0	0	0	0	0	0	0	0	0	0	0	0	17	17	0	0	0	0	282	69	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
a a s	zz	xy	0	0	0	0	0	0	0	0	0	0	0	0	0	17	17	0	0	0	0	69	282	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
a a s	xy	xx-yy	0	0	0	0	0	0	0	0	0	0	0	0	0	-30	30	0	0	0	0	0	0	362	29	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
a a s	xx-yy	xy	0	0	0	0	0	0	0	0	0	0	0	0	0	30	-30	0	0	0	0	0	0	29	362	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
a s a	xz	zz	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-35	17	0	0	0	0	0	0	342	39	-35	17	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
a s a	zz	xz	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	17	-35	0	0	0	0	0	0	39	342	17	-35	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
a s a	xz	xx-yy	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-30	0	0	0	0	0	0	-35	17	302	59	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
a s a	xx-yy	xz	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-30	0	0	0	0	0	0	0	17	-35	59	302	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
s a a	yz	zz	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-35	17	0	0	0	0	0	0	0	0	342	39	35	-17	0	0	0	0	0	0	0	0	0	0	0	0	0	0
s a a	zz	yz	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	17	-35	0	0	0	0	0	0	0	0	39	342	-17	35	0	0	0	0	0	0	0	0	0	0	0	0	0	0
s a a	yz	xx-yy	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	30	0	0	0	0	0	0	0	0	35	-17	302	59	0	0	0	0	0	0	0	0	0	0	0	0	0	0
s a a	xx-yy	yz	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	30	0	0	0	0	0	0	0	0	0	-17	35	59	302	0	0	0	0	0	0	0	0	0	0	0	0	0	0
s s s	zz	zz	0	0	0	0	0	0	0	0	0	0	39	39	69	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	720	0	0	69	0	0	0	0	0	0	0	0	0	0
s s s	zz	xx-yy	0	0	0	0	0	0	0	0	0	0	17	-17	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	582	69	0	0	0	0	0	0	0	0	0	0	0

Table 4. The Full 45 × 45 Matrix for d2, Rounded to Integers. The Parameters $A = 0$, $B = 10$, $C = 29.036$, $D = 21.014$, and $\Delta = 300$ are used. See the spreadsheet d2p.wb2 in Positions a129 to ax176 for an Alternative Form of This Table (continued)

sym.	orbitals α	β	matrix																																												
s s s	xx-yy	zz	0	0	0	0	0	0	0	0	0	0	17	-17	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	69	582	0	0	0	0	0	0	0	0	0	0	0
s s s	xx-yy	xx-yy	0	0	0	0	0	0	0	0	0	0	59	59	29	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	69	0	0	720	0	0	0	0	0	0	0	0	0	0
a a s	xz	yz	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-57	0	-60	0	0	0	0	0	0	0
a a s	xy	zz	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	213	0	0	0	0	0	0	0	0
a a s	xy	xx-yy	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-60	0	333	0	0	0	0	0	0	0
a s a	yz	xy	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-57	-52	30	0	0	0	0
a s a	xz	zz	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-52	303	-52	0	0	0	0
a s a	xz	xx-yy	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	30	-52	243	0	0	0	0
s a a	xz	xy	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-57	-52	-30	0
s a a	yz	zz	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-52	303	52	0
s a a	yz	xx-yy	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-30	52	243	0
s s s	zz	xx-yy	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	513

Table 5. The 10 × 10 Matrix for d^2 for Parallel Spins. The Parameters $A = 0$, $B = 10$, $C = 29.036$, D = 21.014, and $\Delta = 300$ Are Used. See the Spreadsheet d2p.wb2 in Positions a72 to p99 for an Alternative Form of This Table

| xzαyzα >	-57.028	0	-60	0	0	0	0	0	0	0
| xyαzzα >	0	212.972	0	0	0	0	0	0	0	0
| xyαxx-yyα >	-60	0	332.972	0	0	0	0	0	0	0
| yzαxyα >	0	0	0	-57.028	-51.962	30	0	0	0	0
| xzαzzα >	0	0	0	-51.962	302.972	-51.962	0	0	0	0
| xzαxx-yyα >	0	0	0	30	-51.962	242.972	0	0	0	0
| xzαxyα >	0	0	0	0	0	0	-57.028	-51.962	-30	0
| yzαzzα >	0	0	0	0	0	0	-51.962	302.972	51.962	0
| yzαxx-yyα >	0	0	0	0	0	0	-30	51.962	242.972	0
| xx-yyαxx-yyα >	0	0	0	0	0	0	0	0	0	512.972

Table 6. The 25 × 25 Matrix for d^2 for Opposed Spins. The Parameters $A = 0$, $B = 10$, $C = 29.036$, $D = 21.014$, and $\Delta = 300$ Are Used. See the Spreadsheet d2p.wb2 in Positions a11 to ak68 for an Alternative Form of This Table with Less Round Off and Double Spacing

| xzα. xzβ>	120	59	59	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	39	17	17	59
| yzα. yzβ>	59	120	59	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	39	-17	-17	59
| xyα. xyβ>	59	59	129	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	69	0	0	29
| xzα. yzβ>	0	0	0	2	59	0	0	0	0	17	17	-30	30	0	0	0	0	0	0	0	0	0	0	0	0
| yzα. xzβ>	0	0	0	59	2	0	0	0	0	17	17	30	-30	0	0	0	0	0	0	0	0	0	0	0	0
| yzα. xyβ>	0	0	0	0	0	2	59	0	0	0	0	0	0	-34.6	17	0	-30	0	0	0	0	0	0	0	0
| xyα. yzβ>	0	0	0	0	0	59	2	0	0	0	0	0	0	170	-34.6	-30	0	0	0	0	0	0	0	0	0
| xzα. xyβ>	0	0	0	0	0	0	0	2	59	0	0	0	0	0	0	0	0	-34.6	17	0	30	0	0	0	0
| xyα. xzβ>	0	0	0	0	0	0	0	59	2	0	0	0	0	0	0	0	0	17	-34.6	30	0	0	0	0	0
| xyα. zzβ>	0	0	0	17	17	0	0	0	0	282	69	0	0	0	0	0	0	0	0	0	0	0	0	0	0
| zzα. xyβ>	0	0	0	17	17	0	0	0	0	69	282	0	0	0	0	0	0	0	0	0	0	0	0	0	0
| xyα. xx-yyβ>	0	0	0	-30	30	0	0	0	0	0	0	362	29	0	0	0	0	0	0	0	0	0	0	0	0
| xx-yyα. xyβ>	0	0	0	30	-30	0	0	0	0	0	0	29	362	0	0	0	0	0	0	0	0	0	0	0	0
| xzα. zzβ>	0	0	0	0	0	-34.6	17	0	0	0	0	0	0	342	39	-34.6	17	0	0	0	0	0	0	0	0
| zzα. xzβ>	0	0	0	0	0	17	-34.6	0	0	0	0	0	0	39	342	17	-34.6	0	0	0	0	0	0	0	0
| xzα. xx-yyβ>	0	0	0	0	0	0	-30	0	0	0	0	0	0	-34.6	17	302	59	0	0	0	0	0	0	0	0
| xx-yyα. xzβ>	0	0	0	0	0	-30	0	0	0	0	0	0	0	17	-34.6	59	302	0	0	0	0	0	0	0	0
| yzα. zzβ>	0	0	0	0	0	0	0	-34.6	17	0	0	0	0	0	0	0	0	342	39	34.6	-17	0	0	0	0
| zzα. yzβ>	0	0	0	0	0	0	0	17	-34.6	0	0	0	0	0	0	0	0	39	342	-17	34.6	0	0	0	0
| yzα. xx-yyβ>	0	0	0	0	0	0	0	0	30	0	0	0	0	0	0	0	0	34.6	-17	302	59	0	0	0	0
| xx-yyα. yzβ>	0	0	0	0	0	0	0	30	0	0	0	0	0	0	0	0	0	-17	34.6	59	302	0	0	0	0
| zzα. zzβ>	39	39	69	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	720	0	0	69
| zzα. xx-yyβ>	17	-17	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	582	69	0
| xx-yyα. zzβ>	17	-17	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	69	582	0
| xx-yyα. xx-yyβ>	59	59	29	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	69	0	0	720

Table 7. Eigenvalues for Δ Values of 0, 300, and ∞ from the 25 × 25 Matrix for d2 with A = -7.028, B = 10., and C = 29.036

State	Δ 0	300	infinite	Analytic form
$^1A_1$	336.224	814.163	2*Δ + 189.116	A + 8*B + 4*C +2*Δ
^1E	91.044	653.071	2*Δ + 51.044	A + 2*C + 2*Δ
$^3A_2$	-87.028	512.972	2*Δ - 87.028	A - 8*B + 2*Δ
$^1T_1$	91.044	391.044	Δ + 91.044	A + 4*B + 2*C + Δ
$^1T_2$	91.044	355.124	Δ + 51.044	A + 2*C + Δ
$^3T_1$	62.972	341.944	Δ + 32.972	A + 4*B + Δ
$^3T_2$	-87.028	212.972	Δ - 87.028	A - 8*B + Δ
$^1A_1$	91.044	213.105	238.152	A + 10*B + 5*C
^1E	21.044	59.017	61.044	A + B + 2*C
$^1T_2$	21.044	56.963	61.044	A + B + 2*C
$^3T_1$	-87.028	-66.050	-57.028	A - 5*B

The other diagonal term, <12|12>, is the sum of the same three numbers. The off-diagonal element is the two-electron integral, <*xzα xzβ|yzα yzβ*> = 59.036. One always gets a single two-electron term if two and only two of the pieces in the two basis functions are different. One of the basis functions may need to be rearranged to see the match, but if there are three or more differences, the matrix element must be zero.

This 2 × 2 matrix is shown in Table 11. It has eigenvalues, eigenvectors, and symmetries as shown in the lower part of the table. Note that C_{4z} takes |11> into –|12> so that the sum, 0.707 |11> + 0.707 |12> is antisymmetric to this rotation and thus $^1T_2$. These two energy eigenvalues, 6.024 and 124.096 in the strong field limit, can be written as $3A - 6B + 3C$ and $3A + 5C$.

For the d3 case at +1Δ and aas symmetry there are six basis functions and thus a 6 × 6 matrix to be diagonalized, as shown in Table 12. The diagonal elements are again sums of three d^2 diagonal terms from Tables 4 and 5. Here, off the diagonal, we have a few terms like <*xzα zzα yzβ|yzα xx–yyα xzβ*> that are zero because there are three differences. Most cases of terms with only one difference are zero from symmetry, but if the difference is changing *zz* to *xx–yy*, there is no symmetry change and a sum must be calculated. For example,

<xzα zzα yzβ|xzα xx–yyα yzβ> = <xzα zzα|xzα xx–yyα> + <zzα yzβ|xx–yyα yzβ> = –51.9615 + 34.641 = –17.3205

Table 12 also gives the eigenvalues and term symbols for the six states. The quartets, $^4T_2$ at Δ – 171.084 and $^4T_1$ at Δ – 51.084, are easily written as $3A - 15B + \Delta$ and $3A - 3B + \Delta$. For the doublets, however, there are two terms of each symmetry that mix, and the calculated eigenvalues are valid only for the particular value of C/B used in constructing the matrix. It is helpful to have the eigenvalues for the strong-field limit so that the 6 × 6 portion of the full 13 × 13 matrix can be checked.

Full calculations for the d^3 case require an 11 × 11 matrix for sss symmetry and three 13 × 13 matrices for the three other symmetries. All of these are available in the spreadsheet d3orb.wb2, and separately in Tables 13 through 16 in the form required by MACSYMA for reading in matrices. It is not necessary to examine all the large tables provided with the rest of this paper. In general, they are not necessary for understanding, but they will be useful whenever further calculations are required on a particular system. Table 13 contains our first example of an off diagonal element of $-86.6025 = -5 \times 3^{0.5} \times B$. It appears as the matrix element <*xz zz xz| xz xx–yy xz*> which must be evaluated as a sum

<xzα zzα xzβ|xzα xx–yyα xzβ> = <xzα zzα|xzα xx–yyα>+ <zzα xzβ|xx–yyα xzβ> = –51.9615 – 34.641 = –86.6025

Table 17 gives the eigenvalues for the d^3 case with C/B = 2.9036 and four values for Δ including both the free atom and strong-field limits. Where the strong-field limit can be expressed analytically as a sum of the form $3A + bB + cC + d\Delta$, the values for b, c, and d are included in Table 17.

Spreadsheets and Tables for d^4 through d^8

The form used in the spreadsheet d3orb.wb2 can be expanded to include the 28 × 28 and 24 × 24 matrices required for d^4, d^5, and d^6 calculations. These are provided in spreadsheets d4orb.wb2, d5orb.wb2, and d6orb.wb2, respectively. The d^7 and d^8 matrices are essentially the same as d^3 and d^2, but they are provided as d7orb.wb2 and d8orb.wb2 for completeness. Tables 18 through 23 give eigenvalues calculated from these matrices for d^4 through d^9 in the same form as Table 17. A large, essentially complete set of matrices for the d^3, d^4 and d^5 cases is provided in Tables 24 through 34. The d^6 through d^8 cases can be handled by reusing the d^4 through d^2 matrices, because all off-diagonal matrix elements are unchanged on substituting holes for electrons. Nevertheless, the spreadsheets for d^7 and d^8 are provided as d7orb.wb2 and d8orb.wb2 respectively. Two of the d^7 tables are included as Tables 35 and 36.

It is very difficult to calculate values for a large matrix without making some errors. Troubleshooting the 28 × 28 matrices of sss symmetry is aided by the fact that at every stage in the calculation there are e orbitals which must come in pairs with equal eigenvalues. Thus, the most difficult ones are the 24 × 24 matrices for T states in d^4 and d^5. It is very helpful to approach constructing these matrices in steps. The strong field eigenvalues are extremely useful in the first step of getting the block-diagonal matrices error free. The pieces of these are 10 × 10 or smaller. The rest of the off-diagonal terms can be added in groups; thus, for the d^4 case, I added them starting with the 2 × 10 group mixing tttt with ttee. This was followed by 8 × 10, 4 × 10, 8 × 4, and 2 × 8 groups, one at a time. At each stage, the patterns of T_1 and T_2 symmetries are conserved if and only if there are no errors in the group added. A similar order of addition for d^5 would be 1 × 10, 6 × 10, 1 × 6, 10 × 1,

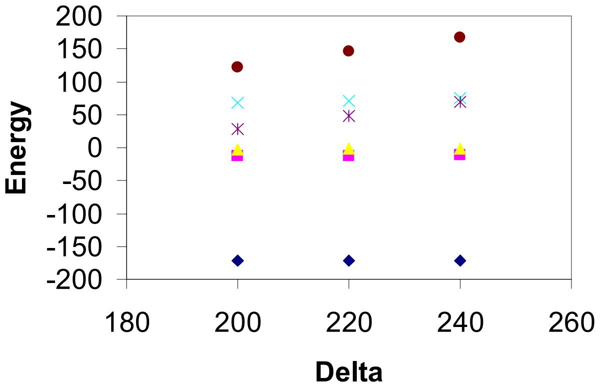

Figure 1. Energy versus delta for the lower energy orbitals in the d3 case for delta values between 200 and 240 with A = -7.028, B = 10, and C = 29.036.

10 × 6, 6 × 1, and finally the 6 × 6. Table 37 gives the eigenvalues after each of these additions for one particular set of parameters.

Calculations for Varying Values of Δ

Figure 1 shows a plot of the energy of the lowest lying orbitals in the d^3 case for Δ values from 200 to 240. Such calculations are easily performed by making changes in the diagonal matrix elements of the d^3 aas and d^3 sss matrices. This type of calculation is easily handled by students, and the construction of a full Orgel diagram is easily possible for a class.

Extension for D_{4h} Symmetry

For high spin d^4 ions with octahedral geometry, there is a single electron in the e orbitals;. thus, one expects a Jahn–Teller distortion so that one of the e orbitals, usually d_{zz}, is lowered in energy. This gives one D_{4h} symmetry instead of O_h. If we introduce an additional parameter, *d*, so that the energy of the e orbitals are $\Delta - d$ and $\Delta + d$ for d_{zz} and d_{xx-yy} respectively, it is a simple matter to calculate the energy, the diagonal terms, for the full 100 basis functions in d4orb.wb2. In fact, this spreadsheet has been modified to include the additional parameter, *d*, in cell D6 of the spreadsheet. The matrices with all four symmetries are shown in Table 38 and the file d4h180.wpd for one choice of the parameters with $\Delta - d = 173$ and $\Delta + d = 187$. The 18 lowest eigenvalues are reported in Table 39 with the appropriate term symbols so that the corresponding orbital and spin degeneracies are clear. Table 39 also shows the corresponding values for octahedral symmetry.

Supporting Material. Tables 8–41 (WordPerfect format) and 11 Quattro Pro files are available in a single compressed Zip file available at (http://dx.doi.org/10.1007/s00897000462b).

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