

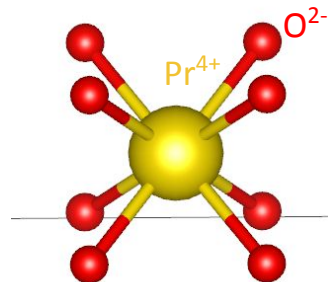
The Cubic Model As A Starting Point For CF Analysis

Jensen Kaplan
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What is the Crystal Field

- The Crystal Field is an electric field experienced by a central ion due to the surrounding ligand environment in a crystalline system.
- I use PrO_2 as a benchmark for calculating starting crystal field parameters. PrO_2 has been characterized by Boothroyd (DOI: [10.1103/PhysRevLett.86.2082](https://doi.org/10.1103/PhysRevLett.86.2082)).
- Here the oxygens each produce a field which is felt by the Pr^{4+} central ion.
- The general Crystal Field Hamiltonian in Stevens' convention is:

$$H_{\text{CEF}} = \sum_n \sum_m B_n^m \hat{O}_n^m(J, J_z)$$



- The Crystal Field Hamiltonian uses a few common conventions:
Stevens' Operators or Wybourne Operators.
 - Boothroyd's paper was written using Wybourne's convention but it's more common nowadays to use Stevens' convention.
 - There are tables used to convert Wybourne's Coefficients to Stevens' and vice versa.
- The B's are scalar coefficients with units being energy.
- The O's are operators which are derived from a mess of spherical harmonics.
- There can be a total of 15 terms; symmetry groups determine which of the 15 are needed.
- **The crystal field splits degeneracies in the energy levels of the central ion.**

The Characteristics of PrO_2

The crystal lattice structure is cubic, a very simple model. The Hamiltonian only requires 4 terms. It is further simplified with cubic constraints between the coefficients, meaning the CF Hamiltonian only needs 2 independent parameters.

The cubic hamiltonian is:

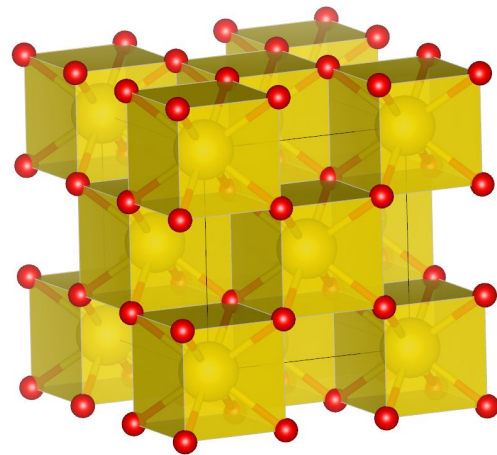
$$H_{CUB} = B_4^0 \hat{O}_4^0 + B_4^4 \hat{O}_4^4 + B_6^0 \hat{O}_6^0 + B_6^4 \hat{O}_6^4$$

With the constraints:

$$\begin{aligned} B_4^4 &= 5 * B_4^0 \\ B_6^4 &= -21 * B_6^0 \end{aligned}$$

We get:

$$H_{CUB} = B_4(\hat{O}_4^0 + 5\hat{O}_4^4) + B_6(\hat{O}_6^0 - 21\hat{O}_6^4)$$



The Characteristics of PrO_2

The central ion is Pr in its oxidized state Pr^{4+} . The Pr^{4+} ions are distanced far enough from each other that single ion properties can be assumed.

Pr is a rare earth ion which has a large magnetic moment and allows us to use dipole approximations.

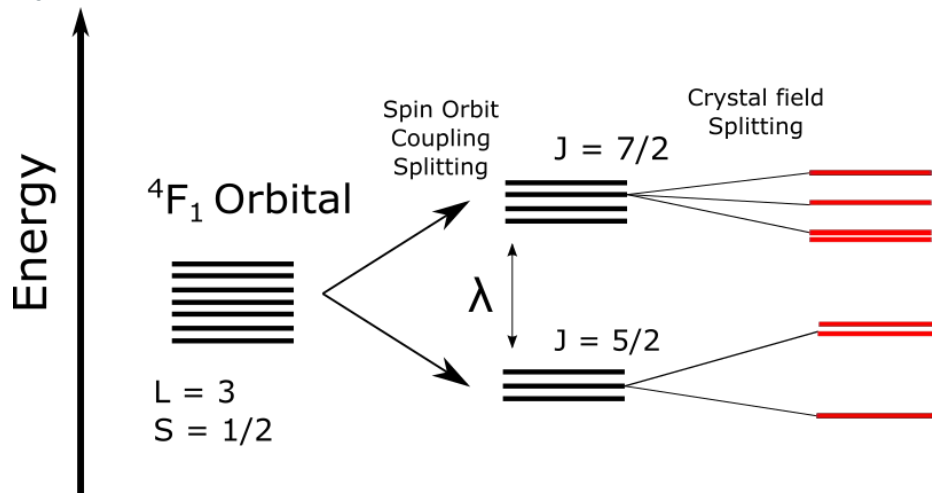
Pr^{4+} is in the $4f_1$ electronic configuration.
It's a single electron $L = 3$, $S = \frac{1}{2}$ problem.



J vs LS Basis

- Typically the Crystal Field Hamiltonian is written in the total angular momentum J basis.
- In the case where $H_{\text{Coulomb}} \gg H_{\text{SOC}} \gg H_{\text{CF}}$ we need to use the LS basis.

- $J = L \pm S$: Therefore we have two J manifolds that are split by spin-orbit coupling. In the picture this effect is characterized by the spin orbit coupling strength λ .
- The multiplets are then further split by the crystal field.



Boothroyd's Results

Boothroyd reports the 2 independent coefficients and the spin orbit coupling strength of Pr^{4+}

$$B_0^4 = -776 \text{ meV}$$

$$B_0^6 = 207 \text{ meV}$$

$$\lambda = 100 \text{ meV}$$

To the right I confirm that PCF's calculation accurately reflect the physics and observed results.

Using Boothroyd's results I produce an ground-state quartet as well as the 130meV, 332meV, 368meV, and 729meV modes.

```
#Define coupling strength, as given by paper
LS = 100
#B40 and B60 are reported in the paper. We use Ce3+ as a central ion because it is electronically equivalent to Pr4+.
#The orbital parameters for Pr4+ have not been tabulated / integrated into PCF.
Stev = cef.WybourneToStevens('Ce3+', {'B40':-776, 'B60':207}, LS=True)
#These are cubic symmetry relations for stevens operators
Stev['B44'] = 5*Stev['B40']
Stev['B64'] = -21*Stev['B60']
#Create the LS_CFlevels object for Pr central ion and print the eigenvalues/eigenvectors
Pr = cef.LS_CFlevels.Bdict(Bdict=Stev, L=3, S=0.5, SpinOrbitCoupling=LS)
Pr.printEigenvectors()
```

```
0.00000 | [ 0. -0.856 0.312 0. 0. 0. 0. 0. 0. -0.268
0.312 0. 0. 0. ] |
0.00000 | [ 0. 0. 0. 0. 0.312 -0.268 0. 0. 0. 0.
0. 0.312 -0.856 0. ] |
0.00000 | [ 0.053 0. 0. 0. 0. 0. 0. 0. -0.687 0.725 0.
0. 0. 0. 0. ] |
0.00000 | [ 0. 0. 0. 0. 0. 0. -0.725 0.687 0. 0. 0.
0. 0. 0. -0.053 ] |
130.59742 | [ 0. 0. 0. 0. -0.604 0.615 0. 0. 0. 0. 0.
0. -0.174 -0.476 0. ] |
130.59742 | [ 0. -0.476 -0.174 0. 0. 0. 0. 0. 0. 0. 0.615
-0.604 0. 0. ] |
332.82442 | [0.645 0. 0. 0. 0. 0. 0. 0.577 0.5 0. 0.
0. 0. ] |
332.82442 | [ 0. 0. 0. 0. 0. 0. -0.5 -0.577 0. 0. 0.
0. 0. -0.645 ] |
368.66515 | [ 0. 0. 0. -0.486 -0.715 0. 0. 0. 0. 0.
0. -0.486 -0.13 0. ] |
368.66515 | [ 0. -0.13 -0.486 0. 0. 0. 0. 0. 0. -0.715
-0.486 0. 0. ] |
368.66515 | [ 0.762 0. 0. 0. 0. 0. 0. -0.442 -0.474 0.
0. 0. 0. ] |
368.66515 | [ 0. 0. 0. 0. 0. 0. 0.474 0.442 0. 0. 0.
0. 0. -0.762 ] |
728.89290 | [ 0. 0.152 0.798 0. 0. 0. 0. 0. 0. -0.196
-0.55 0. 0. ] |
728.89290 | [ 0. 0. 0. 0.55 0.196 0. 0. 0. 0. 0.
0. -0.798 -0.152 0. ] |
```

Building On Boothroyd's Results

Because of the simple Hamiltonian that is brought about by cubic symmetry, I wish to use this as a base case for other compounds.

By parameterizing the Hamiltonian as

$$H = PF * (O_4^0 + 5O_4^4) + PF * x * (O_6^0 - 21O_6^4)$$

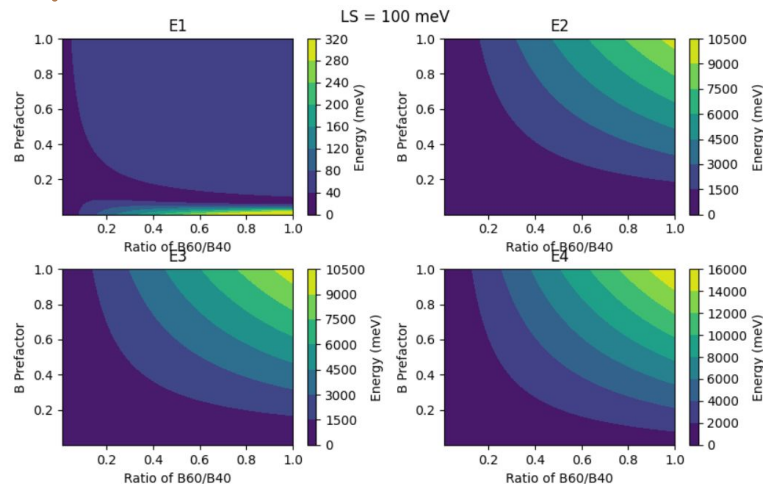
with

$$x = B_6^0/B_4^0$$

I create a grid search to determine the starting parameters for unknown compounds, these will then be fit to data to determine the true coefficients.

I create a few different files for $LS = [50,150]$ in increments of 10 meV.

By searching for compatibility in each energy band I see that with only 2.5% tolerance between measured and calculated energy, I only get correct energy values for PrO_2 at the reported $LS = 100$ level.



```
Parameter search for: Compound: PrO2_new at LS = 100 meV with 0.025 tolerance.
With x = 0.03487437185929648 and bpf = 0.38754773869346737
E1 = 128.23272053214646 meV
E2 = 333.7748264614862 meV
E3 = 367.3364892553882 meV
E4 = 725.7733656324108 meV

With x = 0.03487437185929648 and bpf = 0.4076281407035176
E1 = 132.0784011970664 meV
E2 = 333.01470996063415 meV
E3 = 368.395911838139 meV
E4 = 748.2034104112804 meV
```

Building On Boothroyd's Results

Now by using one of the compatible (x,bpf) pairs I compute the Hamiltonian and see good agreement with the results reported by Boothroyd.

By using this cubic grid search with allowable tolerance, I can find a starting guess for B_4^0 and B_6^0 . Then I can lift cubic constraints, allow more Stevens' terms and perform a non-linear least square fit. By treating the cubic system perturbatively I should be able to capture the physics exhibited by compounds of different, non-cubic structures.

```
For PrO2_new at x[5] = 0.0349 and bpf[77] = 0.3875
E2 = 333.7748264614862
Using these values lets see if degeneracies are protected.
```

Eigenvalues	Eigenvectors
0.00000	[0. 0. 0. 0.314 -0.265 0. 0. 0. 0. 0. 0.]
0. 0.314 -0.856 0.]	
0.00000	[0. -0.856 0.314 0. 0. 0. 0. 0. 0. 0. -0.265
0.314 0. 0.]	
0.00000	[-0.05 0. 0. 0. 0. 0. 0. 0. 0.685 -0.727 0.
0. 0. 0.]	
0.00000	[0. 0. 0. 0. 0. 0. -0.727 0.685 0. 0. 0.
0. 0. 0.]	
128.23272	[0. -0.476 -0.174 0. 0. 0. 0. 0. 0. 0. 0.615
-0.604 0. 0.]	
128.23272	[0. 0. 0. -0.604 0.615 0. 0. 0. 0. 0. 0.
0. -0.174 -0.476 0.]	
333.77483	[-0.645 0. 0. 0. 0. 0. 0. 0. -0.577 -0.5 0.
0. 0. 0.]	
333.77483	[0. 0. 0. 0. 0. 0. -0.5 -0.577 0. 0. 0.
0. 0. 0.]	
367.33649	[0.762 0. 0. 0. 0. 0. 0. 0. -0.444 -0.471 0.
0. 0. 0.]	
367.33649	[0. 0. 0. -0.484 -0.716 0. 0. 0. 0. 0. 0.
0. -0.484 -0.134 0.]	
367.33649	[0. 0. 0. 0. 0. 0. 0.471 0.444 0. 0. 0.
0. 0. 0.]	
367.33649	[0. -0.134 -0.484 0. 0. 0. 0. 0. 0. 0. -0.716
-0.484 0. 0.]	
725.77337	[0. 0.152 0.798 0. 0. 0. 0. 0. 0. 0. -0.196
-0.549 0. 0.]	
725.77337	[0. 0. 0. 0.549 0.196 0. 0. 0. 0. 0.
0. -0.798 -0.152 0.]	