Many body single atom Hamiltonians: on the fly calculations

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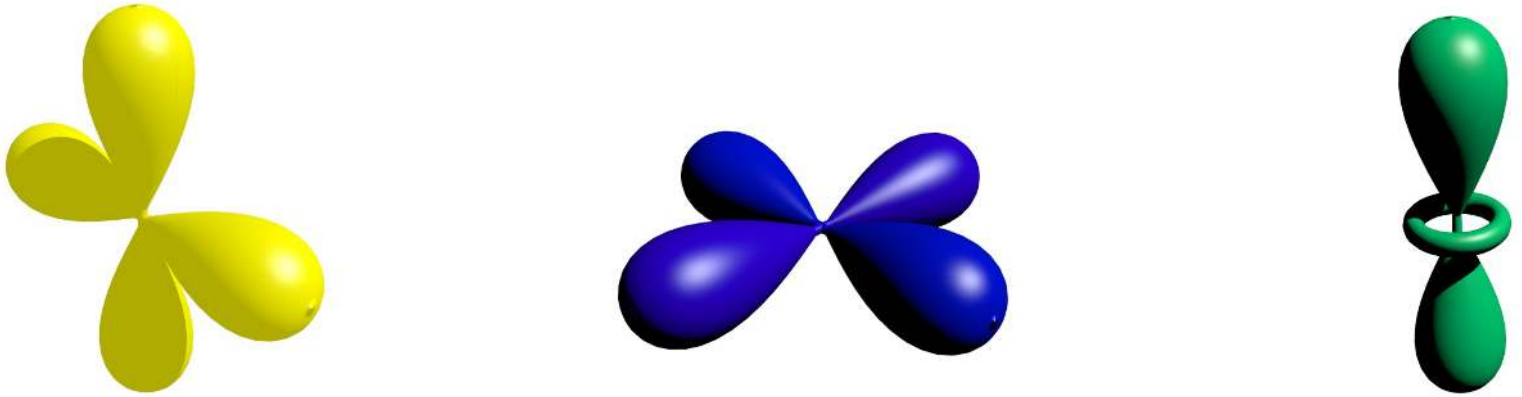
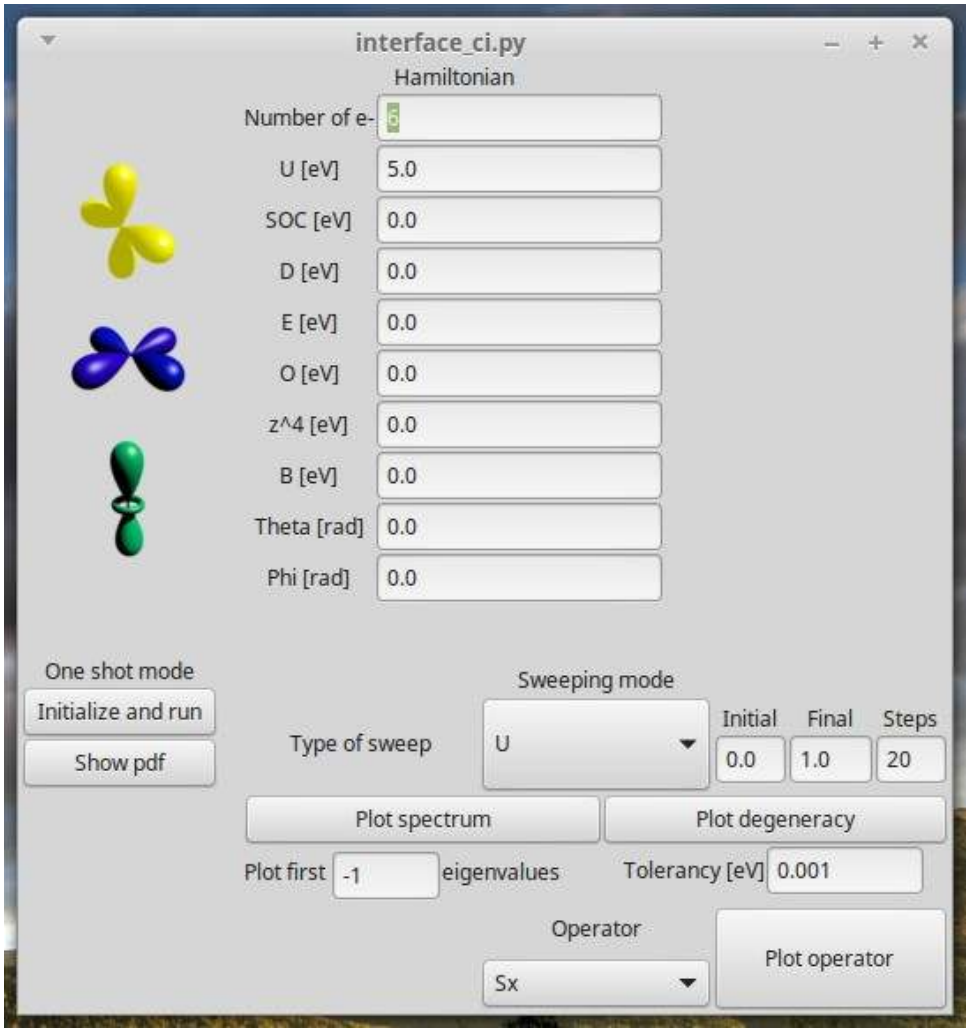


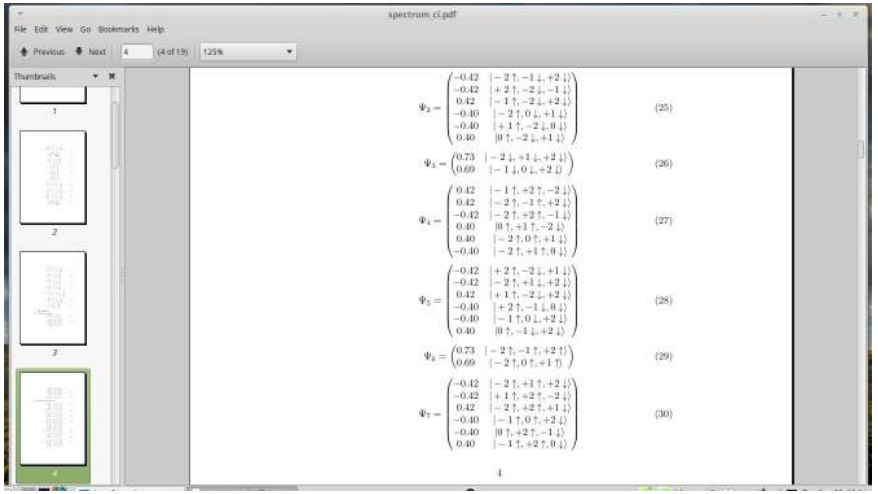
Almaden, 22th September 2015

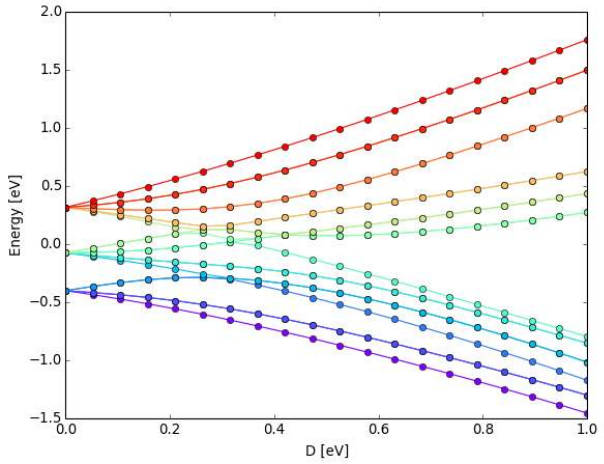
What is the goal?

- **We want a simple tool to go from a electronic system to a spin model system**
- **How does it have to be?**
  - Simple to use and understand
  - General, can be applied to different systems
  - Fast, real time calculations

The interface







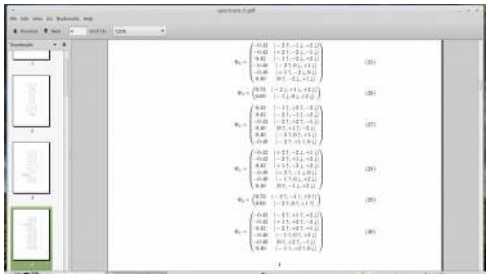
From electrons to spins

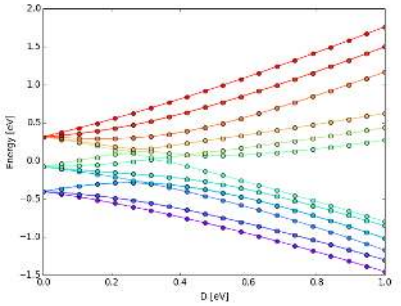
How can we extract a spin Hamiltonian from an electron Hamiltonian?

- Focus on d electrons (but can be generalized to f)
- Single atom picture
- Full many body space for the d levels

What can we calculate?

- **Many body electron Hamiltonian: crystal fields, SOC and electronic interactions**
- **One shot mode (generates a pdf):**
  - Spectrum
  - Manifolds
  - Operator projections





- **Sweep mode (generates graphs):**
  - Evolution of the spectra/degeneracies/operator values with respect a certain parameter

What are the different parameters?

- **Simplified vision: They are only numbers in a toy model, with a value in a reasonable range**
- **More practical: can be extracted from experiment/DFT**
- **Lets take a look to each one**

Electron number

- **Strongly dependent on the environment**
  - Are there covalent bonds?
  - Are the surroundings a metal?
  - What is the oxidation state?
- **DFT can give a good estimation**

One body terms

- **Crystal fields: come from environment**
  - Electric like + hybridization
  - Taylor expansion of V(x,y,z)
  - Isomorphism between $L_x \leftrightarrow x^2$
- **Spin orbit coupling**
  - Depend on the row (3d,4d,5d)
  - Effective value slightly dependent on environment

Electron-electron interaction

- **Can we know the value?**
  - Dependent on row (3d,4d,5d)
  - Dependent on surroundings (are there covalent bonds?)
  - Hard to compute (double counting uncertainties)
- **Good idea to use as a parameter, in a interval of reasonable values**
- **Currently just one parameter (controls U and J simultaneously), this will be soon improved**

Take home

- **Simple and fast way to understand multielectronic single atom systems**
- **Take every number as a parameter in a toy model, meaningful values could be extracted from DFT**

Some examples!

- **We will try to understand single electron terms (crystal field and SOC)**
- **Afterwards we move to many electron states**
- **Keep in mind that the following are just warm up examples!**

Octahedral: eg VS t2g

Octahedral crystal field

Manifold	Degeneracy	ΔE (eV)	Energy (eV)
GS	6	0.000	1.800
Excited #1	4	0.600	2.400

Ground state manifold

$$\Psi_1 = (\ \ |-1\downarrow\rangle)$$

$$\Psi_2 = \begin{pmatrix} \frac{1}{\sqrt{2}} & |-2\downarrow\rangle \\ -\frac{1}{\sqrt{2}} & |+2\downarrow\rangle \end{pmatrix}$$

$$\Psi_3 = (\ \ |-1\uparrow\rangle)$$

$$\Psi_4 = \begin{pmatrix} \frac{1}{\sqrt{2}} & |-2\uparrow\rangle \\ -\frac{1}{\sqrt{2}} & |+2\uparrow\rangle \end{pmatrix}$$

$$\Psi_5 = (\ \ |+1\downarrow\rangle)$$

$$\Psi_6 = (\ \ |+1\uparrow\rangle)$$

Excited state manifold #1

$$\Psi_1 = (\ \ |0\downarrow\rangle)$$

$$\Psi_2 = \begin{pmatrix} \frac{1}{\sqrt{2}} & |+2\downarrow\rangle \\ \frac{1}{\sqrt{2}} & |-2\downarrow\rangle \end{pmatrix}$$

$$\Psi_3 = (\ \ |0\uparrow\rangle)$$

$$\Psi_4 = \begin{pmatrix} \frac{1}{\sqrt{2}} & |+2\uparrow\rangle \\ \frac{1}{\sqrt{2}} & |-2\uparrow\rangle \end{pmatrix}$$

Pure spin orbit coupling

Manifold	Degeneracy	ΔE (eV)	Energy (eV)
GS	4	0.000	-0.300
Excited #1	6	0.500	0.200

Ground state manifold

$$J_z = \begin{pmatrix} -\frac{3}{2} & 0 & 0 & 0 \\ 0 & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & \frac{1}{2} & 0 \\ 0 & 0 & 0 & \frac{3}{2} \end{pmatrix}$$

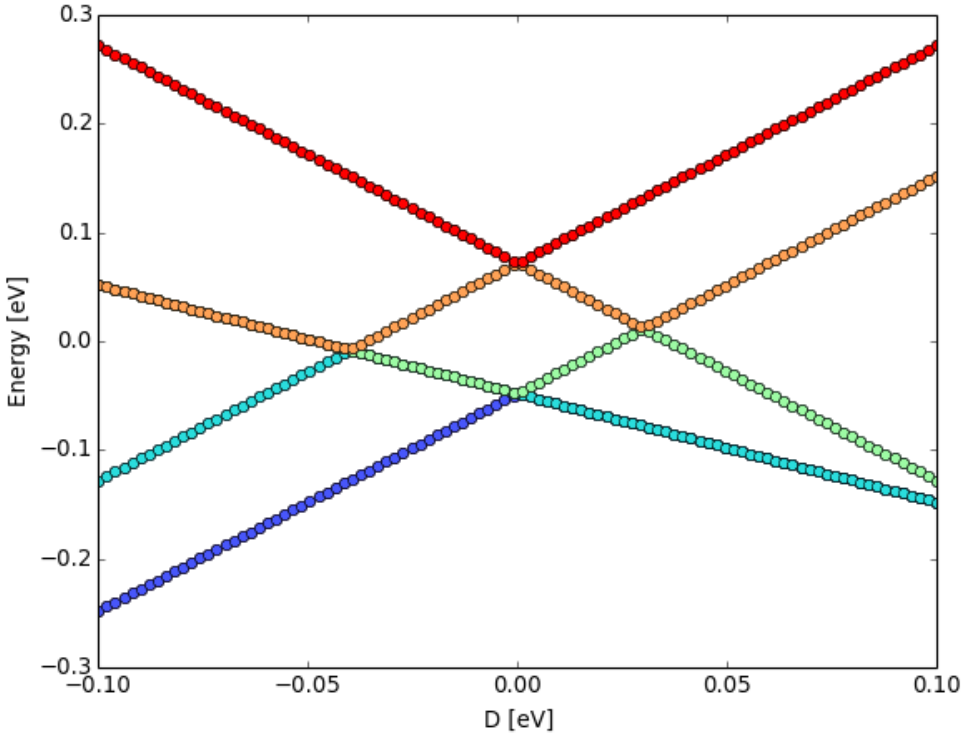
$$\Psi_1 = \begin{pmatrix} 0.89 & |-2\uparrow\rangle \\ -0.45 & |-1\downarrow\rangle \end{pmatrix}$$

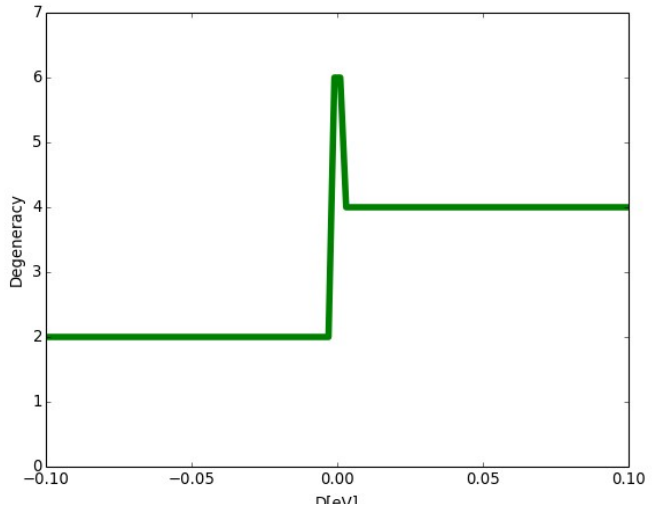
$$\Psi_2 = \begin{pmatrix} 0.77 & |-1\uparrow\rangle \\ -0.63 & |0\downarrow\rangle \end{pmatrix}$$

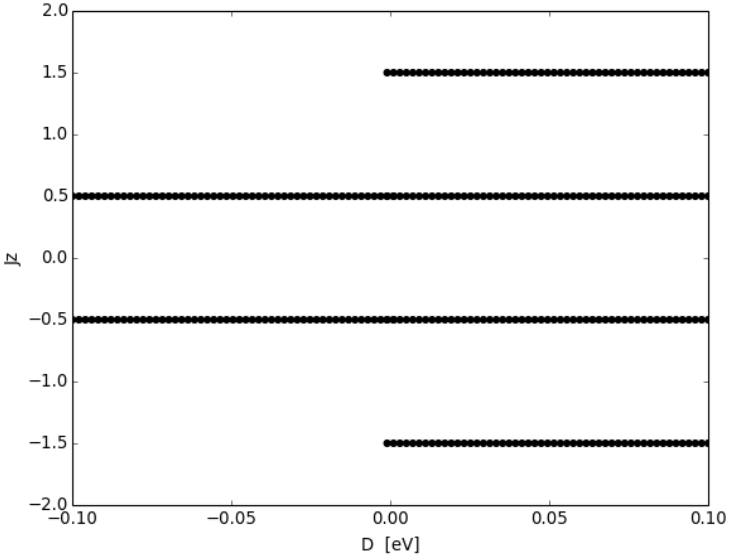
$$\Psi_3 = \begin{pmatrix} 0.77 & |+1\downarrow\rangle \\ -0.63 & |0\uparrow\rangle \end{pmatrix}$$

$$\Psi_4 = \begin{pmatrix} -0.89 & |+2\downarrow\rangle \\ 0.45 & |+1\uparrow\rangle \end{pmatrix}$$

Tetragonal distortion in octahedral field







CF with axial symmetry

Manifold	Degeneracy	ΔE (eV)	Energy (eV)
GS	2	0.000	0.000
Excited #1	4	0.200	0.200
Excited #2	4	0.800	0.800

Ground state manifold

$$\Psi_1 = (\quad |0\downarrow\rangle)$$

$$\Psi_2 = (\quad |0\uparrow\rangle)$$

Excited state manifold #1

$$\Psi_1 = (\quad |-1\downarrow\rangle)$$

$$\Psi_2 = (\quad |-1\uparrow\rangle)$$

$$\Psi_3 = (\quad |+1\downarrow\rangle)$$

$$\Psi_4 = (\quad |+1\uparrow\rangle)$$

Excited state manifold #2

$$\Psi_1 = (\quad |-2\downarrow\rangle)$$

$$\Psi_2 = (\quad |-2\uparrow\rangle)$$

$$\Psi_3 = (\quad |+2\downarrow\rangle)$$

$$\Psi_4 = (\quad |+2\uparrow\rangle)$$

Out of the game dz2

Manifold	Degeneracy	ΔE (eV)	Energy (eV)
GS	8	0.000	-0.400
Excited #1	2	0.400	0.000

$$\vec{L}^{(i)} \cdot \vec{S}^{(i)} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{2} & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

Ground state manifold

$$\Psi_1 = (\quad |-2\downarrow\rangle)$$

$$\Psi_2 = (\quad |-1\downarrow\rangle)$$

$$\Psi_3 = (\quad |-2\uparrow\rangle)$$

$$\Psi_4 = (\quad |-1\uparrow\rangle)$$

$$\Psi_5 = (\quad |+1\downarrow\rangle)$$

$$\Psi_6 = (\quad |+1\uparrow\rangle)$$

$$\Psi_7 = (\quad |+2\downarrow\rangle)$$

$$\Psi_8 = (\quad |+2\uparrow\rangle)$$

Mn in vacuum (5e)

Manifold	Degeneracy	ΔE (eV)	Energy (eV)
GS	6	0.000	144.330
Excited #1	36	3.160	147.490
Excited #2	12	3.680	148.010
Excited #3	20	3.900	148.230

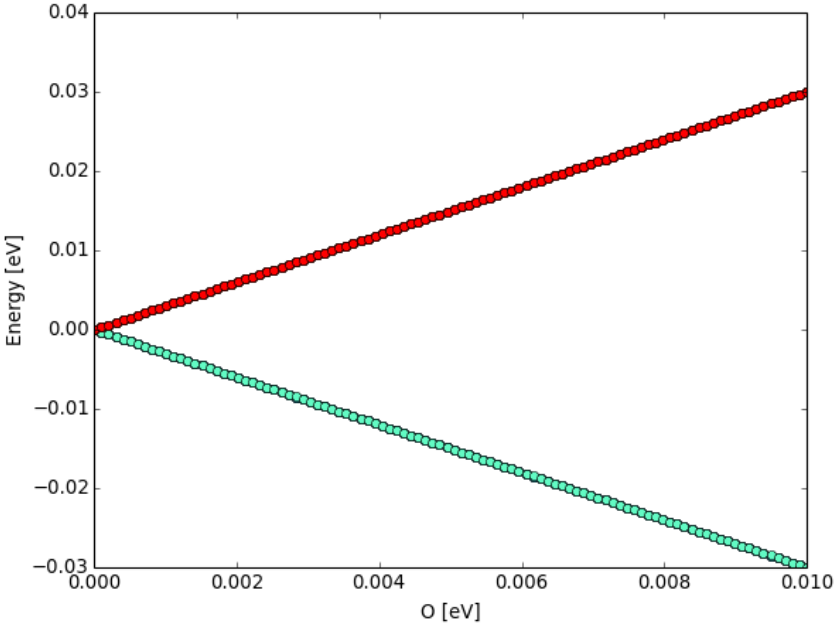
$$S_z = \begin{pmatrix} -\frac{5}{2} & 0 & 0 & 0 & 0 & 0 \\ 0 & -\frac{3}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{3}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{5}{2} \end{pmatrix}$$

Fe@MgO (6e)

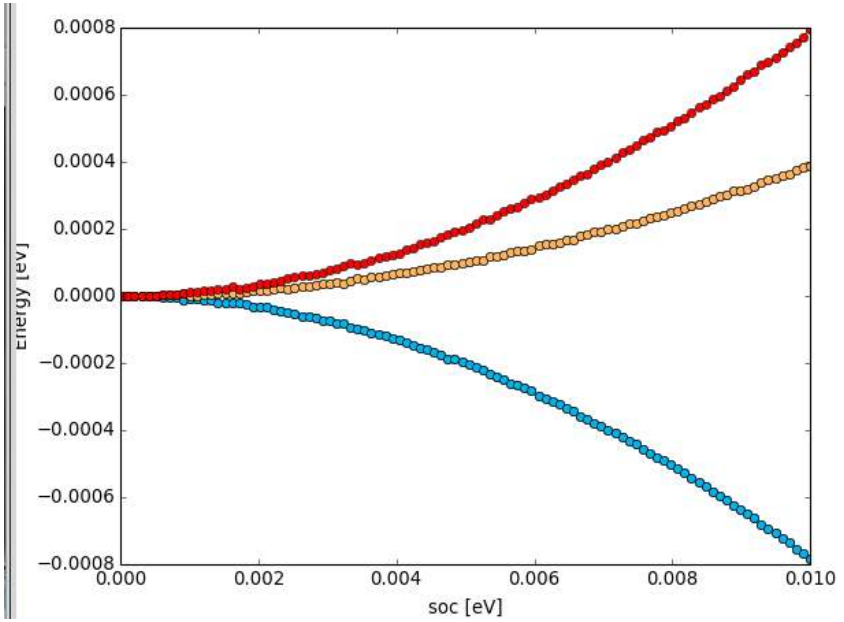
Axial

Manifold	Degeneracy	ΔE (eV)	Energy (eV)
GS	10	0.000	219.890
Excited #1	10	0.300	220.190
Excited #2	5	0.400	220.290

Octahedral



SOC



V (3e) with axial CF>0 (not MgO!)

Manifold	Degeneracy	ΔE (eV)	Energy (eV)
GS	8	0.000	43.320
Excited #1	8	0.100	43.420
Excited #2	12	0.140	43.460
Excited #3	4	1.450	44.770
Excited #4	2	1.710	45.030
Excited #5	4	1.720	45.040

$$\vec{L}^{(i)} \cdot \vec{S}^{(i)} = \begin{pmatrix} \frac{3}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{3}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\frac{3}{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{3}{2} \end{pmatrix}$$

$$X^4 + Y^4 + Z^4 = \begin{pmatrix} 63 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 63 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 63 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 63 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 63 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 63 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 63 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 63 \end{pmatrix}$$