

Manipulating orbital states using LSDA+U

In this part of the tutorial, we will perform LSDA+U calculations for CuSb₂O₆ to identify the correct orbital ground state.

2.1. Setting up the calculation

Create a new directory

- Create a new directory called `lsdau`
- Copy the `=.in` and `=.dens` files from the `lda` calculation into the new directory

Main menu

- Spin sorts : 2
- Initial polarization : Check
- K-mesh subdivison : 3 3 3

```
MAIN MENU
[ ] (Q)uit/save (+) Symmetry (H)elp
GENERAL DATA
(S)pin sorts : 2 (I)nitital polarization : [X]
(K)-mesh subdivision : 3 3 3 (O)ccupied bands : -1
(N)umber of iterat. : 100 (A)ccuracy of density : 1.e-6
(T)otal energy calc. : [X] A(C)curacy of Etot : 1.e-8
Conver(G)ence condit : Density (-) Options : ...
(R)elativistic : scalar relativistic
(V)xc-version : Perdew Wang 92 (LSDA)
(F)inite nucleus : Point charge
(W) fixed spin mom. : [ ] (Y) spin moment : 1.0
RELATIVISTIC SETTINGS
Q(U)antization-axis : 0 0 1
[...]
```

Initial spin split menu

- Cu : 1, Sb and O : 0

```
INITIAL SPINSPLIT
e (X)it (H)elp
Wy-pos. element initial spin
(1) : Cu 1
(2) : Sb 0
(3) : O 0
(4) : O 0
STATUS: OK (9.09-43:M-CPA)
```

LSDA+U

- Make LSDA+U : Check
- Functional : Around mean field
- Number of definitions : 1
- Definition 1: Wyckoff position = 1, state = 3d, $F_0 = U = 8.0$ eV, $F_2 = 8.61$ eV, $F_4 = 5.39$ eV, $F_6 = 0$ eV

Remark: The fundamental quantities of the LSDA+U implementation are the Slater integrals F_0 to F_6 . The first is simply $F_0 = U$. The other three form J , depending on the angular momentum quantum number of the shell.

s-states: $J = 0$

p-states: $J = \frac{1}{5}F_2$

d-states: $J = \frac{1}{14}(F_2 + F_4)$

f-states: $J = \frac{1}{6435}(286F_2 + 195F_4 + 250F_6)$

The choice of parameter is quite simple, one can take $\frac{F_4}{F_2}$ from atomic situations, since it is a pretty local quantity. For 3d-electrons the ratio is of the order of 0.6...0.75 and a practically good choice is $\frac{F_4}{F_2} = \frac{5.39}{8.61}$ since $8.61 + 5.39 = 14$, thus $F_2 = 8.61J$, $F_4 = 5.39J$.

```
LSDA+U
e (X) it (H) elp
GENERAL CONTROL
(M)ake LSDA+U : [X]
(F)unctional : LSDA+U Around mean field (AMF/OP)
(P)rojection : orthogonal
CORRELATED STATES
(N)umber of definitions : 1
No. Wy-pos. state F0 F2 F4 F6 (eV)
(1) : 1 3d 8.0 8.61 5.39 0.
[...]
```

No.	Wy-pos.	state	F0	F2	F4	F6	(eV)
(1)	: 1	3d	8.0	8.61	5.39	0.	

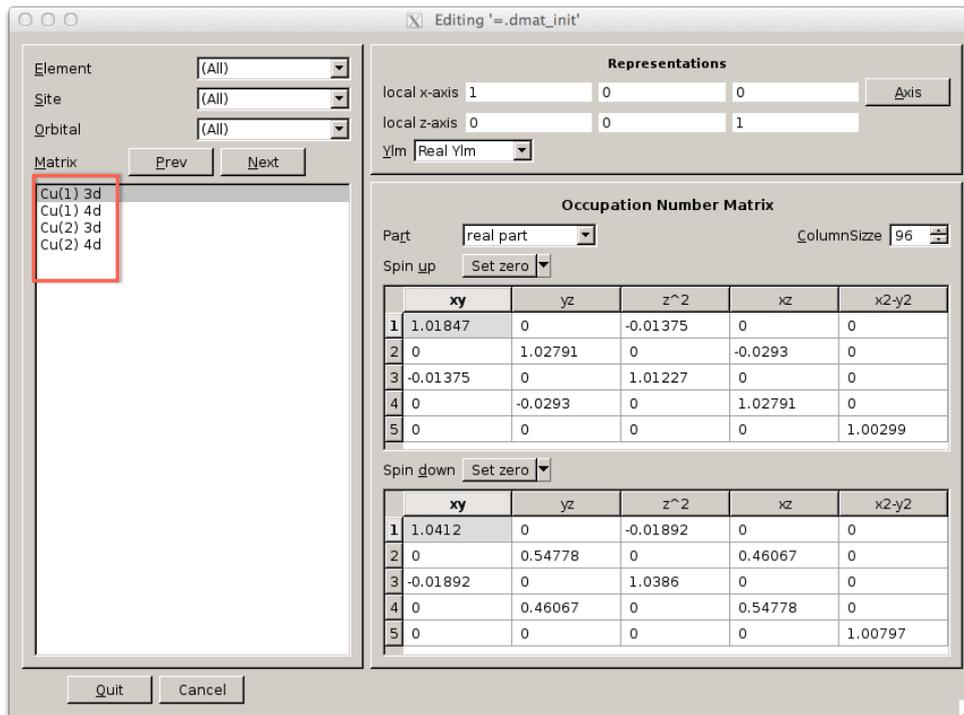
```
STATUS: OK (9.09-43:M-CPA)
```

2.2. Run the self consistent calculation

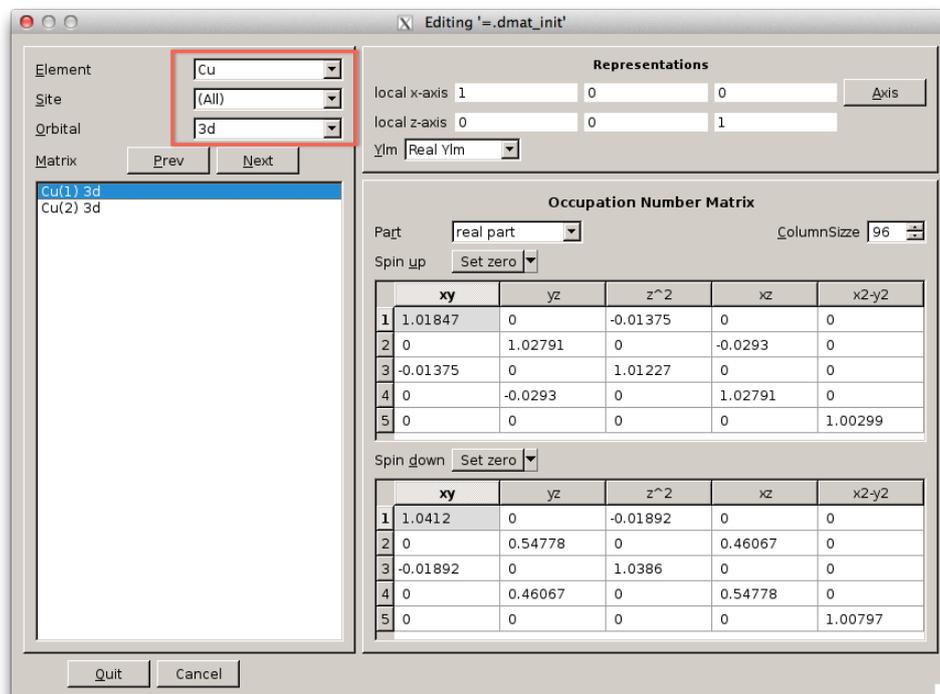
- `fplo9.09-43-x86_64 > out` (≈ 10 mins)
- Check if the calculation is converged: `grep "st de" out`
- Check if a gap has been opened: `grep gap out`
- Converged energy : ≈ -30115.272149 Ha (`grep EE out`)

2.3. Analyze the Cu-3d occupation matrix (density matrix)

- Save the calculation for later use: `cp -r lsdau lsdau_backup`
- The file `=.dmat_init` has the density matrices (orbital occupation numbers) for the "correlated" orbitals. To view it, from within the `lsdau` directory, type `dmatedit`. This opens an editor which displays the 5x5 matrices of the spin-up and spin-down contribution. On the lower left panel, we can select between Cu(1) or Cu(2) and as well as 3d or 4d.

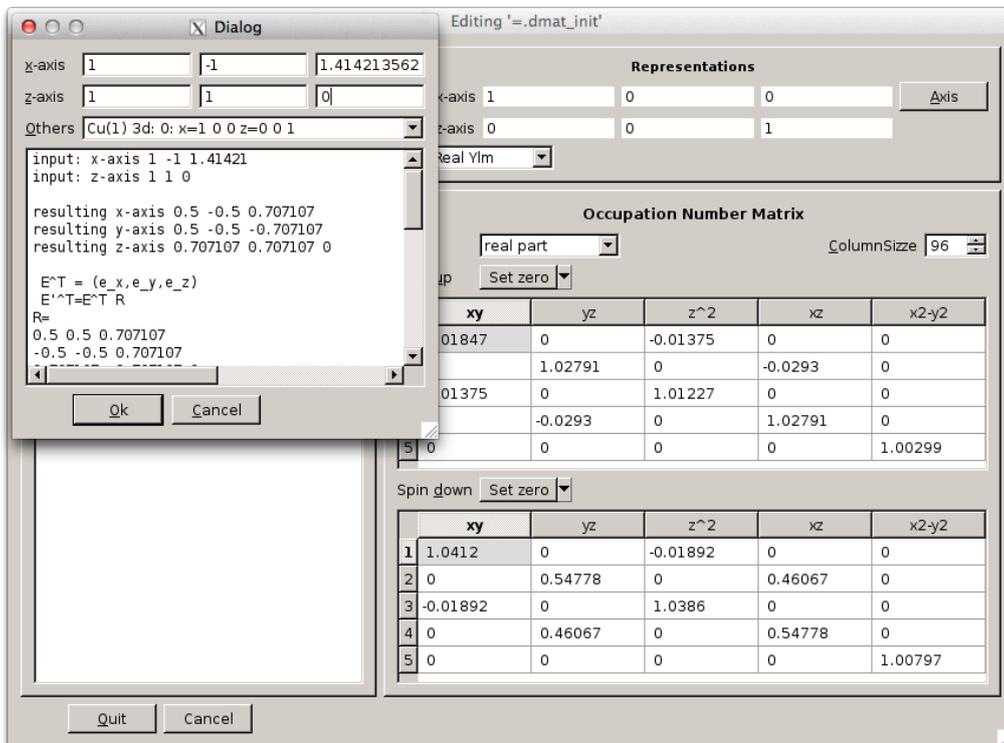


- We will minimize the display to just the 3d density matrices by selecting "Element" = Cu and "Orbital" = 3d.

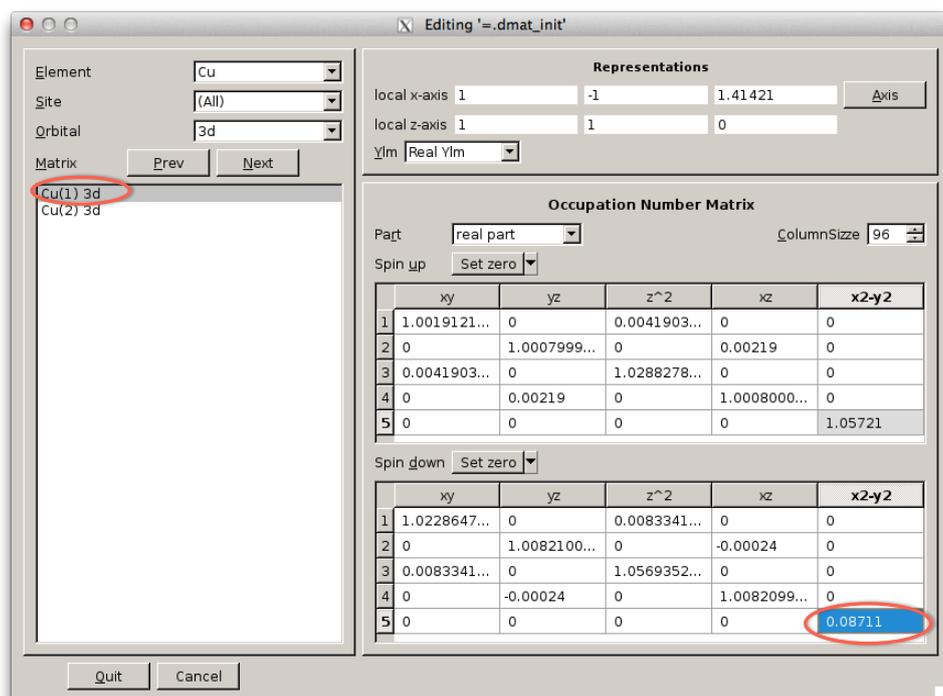


- The density matrices are presently displayed in the standard coordinate system. *i.e.* the x- and z-axis are along the global cartesian coordinate axes. Notice that the spin-up states are fully occupied with one electron in each 3d orbital. The remaining four electrons are distributed in the spin-down states. Notice the lack of "integer" occupation and the existence of sizable off-diagonal elements. This arises due to the difference of the Cu(1)'s local coordinate system from the global

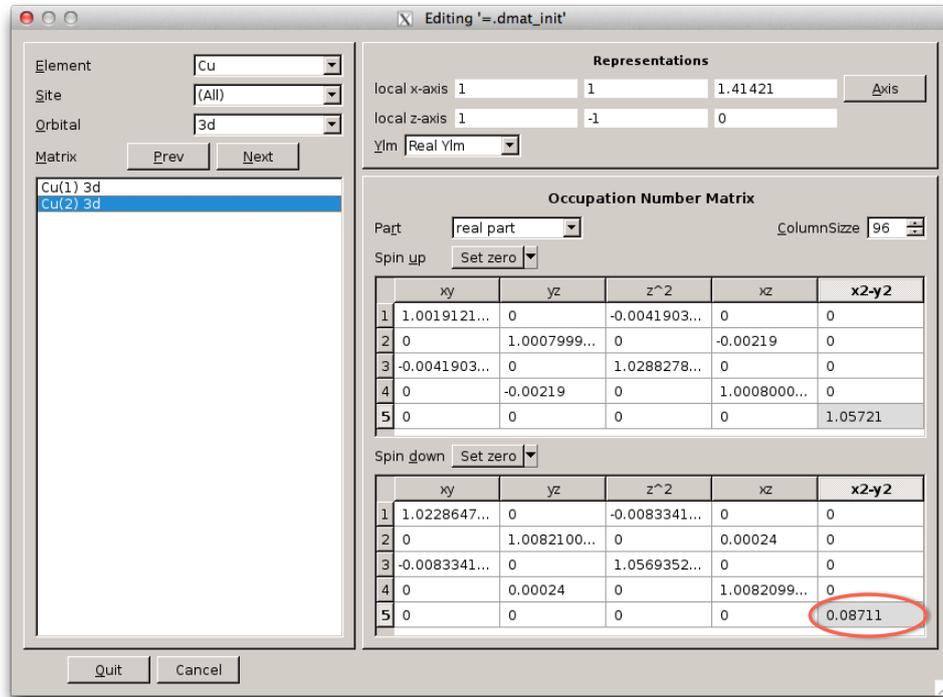
axis. We now transform the quantization axis into the local coordinate system. For Cu(1), it is: local x-axis = 1, -1, 1.414213562 and local z-axis = 1, 1, 0. Click on the Axis button and enter these values.



- Click Ok. The transformed density matrix will now be displayed. Notice that the spin-up matrix which was fully occupied and diagonal, remains so. The spin-down matrix is now diagonal and has four orbitals with integer occupation and the $d_{x^2-y^2}$ is empty. *i.e.* the Cu(1)- $3d_{x^2-y^2}$ orbital manifold is half-filled.

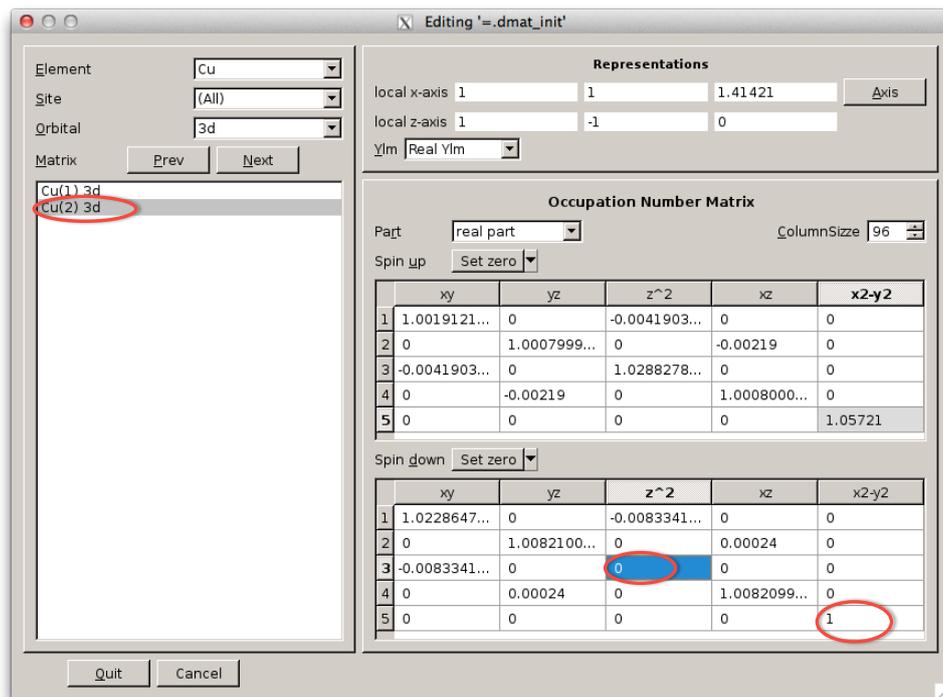
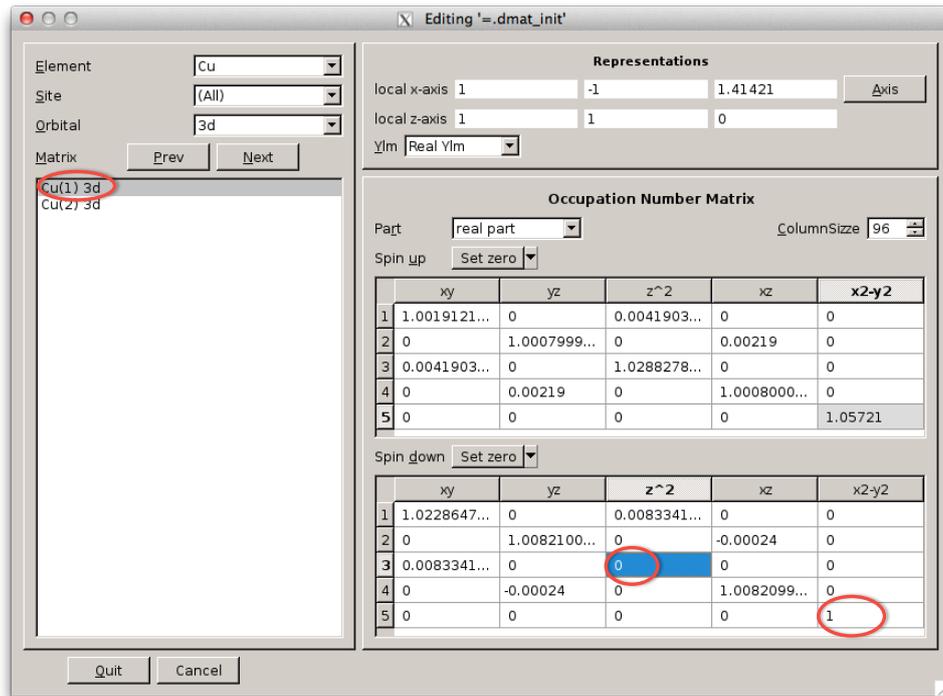


- Bearing in mind that Cu(1) and Cu(2) have different local coordinate systems, let's now analyze Cu(2)'s density matrix in its corresponding local axis: local x-axis = 1, 1, 1.414213562 and local z-axis = 1, -1, 0. Here too, we notice that the Cu(2)- $3d_{x^2-y^2}$ orbital manifold is half-filled.



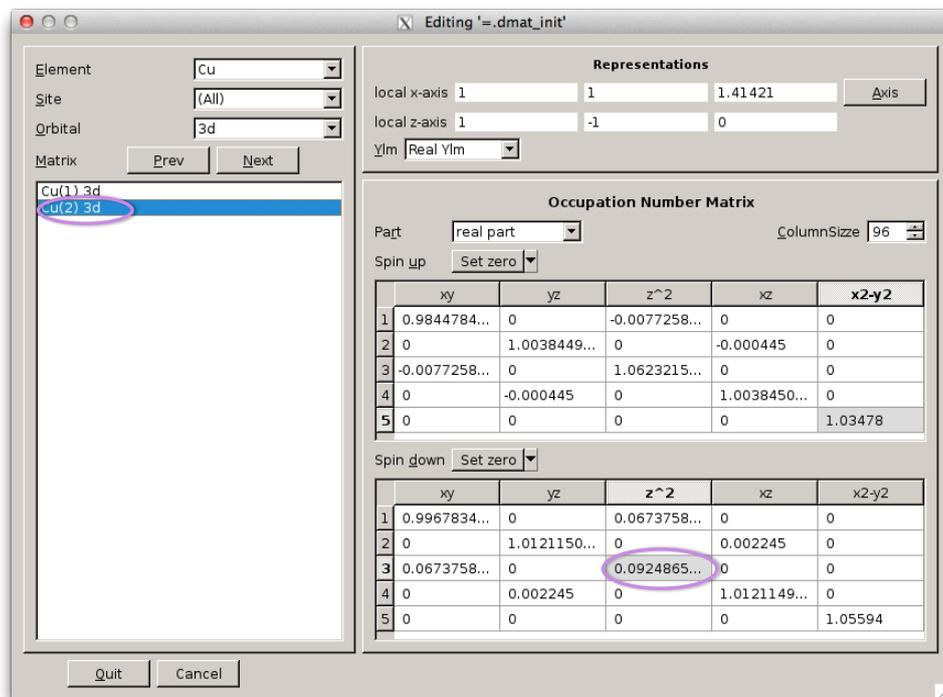
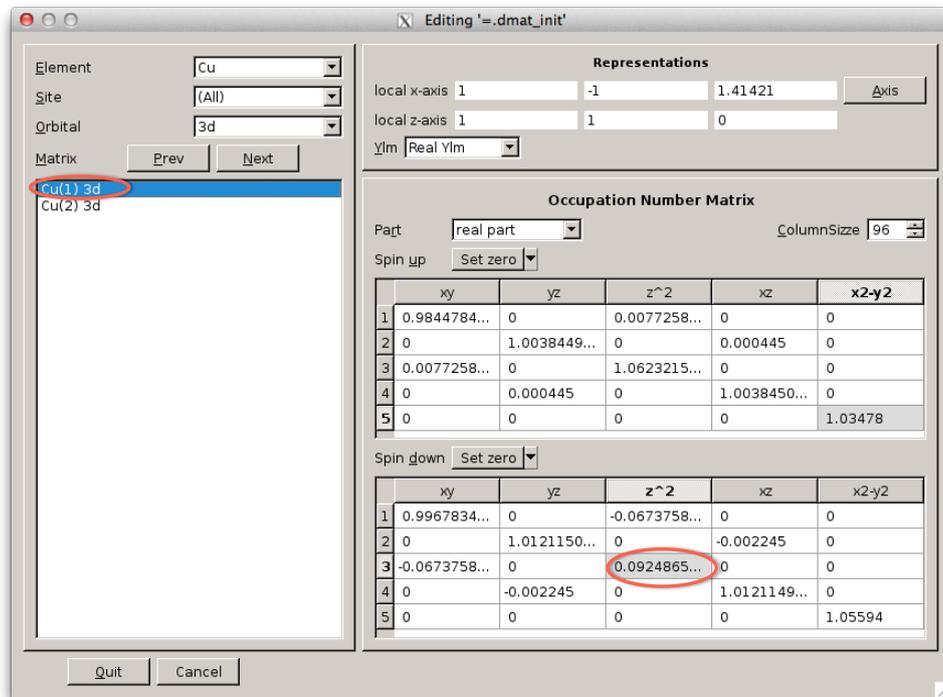
2.4. What happens if $3d_{3z^2-r^2}$ is half filled ?

- We now want to stabilize the half-filling of the $3d_{3z^2-r^2}$ orbital. We will manipulate the density matrices such that we make $3d_{3z^2-r^2}$ orbital as half-filled for both Cu(1) and Cu(2). To facilitate that, let's modify the density matrix that we presently have. For Cu(1) and Cu(2), change the spin-down $3d_{3z^2-r^2} = 0$ and $3d_{x^2-y^2} = 1$. (FPLO reads the =dmat_init file at the start of a LSDA+U calculation and thus a good initial guess can direct the convergency in the desired direction)



- Clicking now on **Quit** will save the updated density matrices back in the `=.dmat_init` file. There is no need to change the matrices back into the global axes, since the `dmatedit` program remembers the various settings and conversions. **Note:** Clicking on **Cancel** will not make any updates to the `=.dmat_init` file.
- `fedit9.09-43-x86_64` - Turn OFF the Initial polarization
- `Run fplo9.09-43-x86_64 > out` (≈ 10 mins)
- Check if the calculation is converged: `grep "st de" out`
- Check if a gap has been opened: `grep gap out`

- Converged energy : ≈ -30115.281658 Ha (grep EE out) - Notice that this energy is lower than the previous one wherein the $3d_{x^2-y^2}$ orbital was half-filled.
- Call `dmatedit` again and check if the converged density matrices still have $3d_{3z^2-r^2}$ as half-filled for both Cu(1) and Cu(2). Notice that the program remembers the local axes !! (locally in a file called `dmatedit.ini`)



2.5. Results

- The presence of a nearly regular CuO_6 octahedron results in a competition between the two e_g states in CuSb_2O_6 . LSDA+ U calculations indicate that a hole in the $\text{Cu-}3d_{3z^2-r^2}$ orbital is

energetically more favorable, in contrast to almost all other cuprates, where the $d_{x^2-y^2}$ orbital is half-filled

- LSDA+ U is prone to multiple solutions. It can be directed toward a given solution by manipulating the density matrix. In systems with orbital degeneracy, it is often necessary (and recommended) to check the energetics of the various orbital ground states and compare their relative energies to identify the actual ground state. For CuSb_2O_6 , since both local e_g bands are present at E_F and nearly degenerate, it is imperative that we check the energy of a calculation where $3d_{3z^2-r^2}$ is half-filled. Otherwise, we end up with the hole in the $d_{x^2-y^2}$ orbital, which is not the actual ground state.
- Now back to the orbital energies: our Wannier function analysis has shown that $\varepsilon_{x^2-y^2} > \varepsilon_{3z^2-r^2}$, but in LSDA+ U the situation is opposite. Is it a contradiction? Not at all. We use different approximations (standard LDA vs. LSDA+ U) and, therefore, arrive at different conclusions. The LSDA+ U solution should be closer to reality, because we took into account the “correlations” (Hubbard U), and indeed CuSb_2O_6 features a hole in the $d_{3z^2-r^2}$ orbital. On the other hand, Wannier functions tell us how the system behaves without correlations. Then we can conclude that the on-site Hubbard repulsion (U) plays crucial role in stabilizing the $d_{3z^2-r^2}$ orbital state in CuSb_2O_6 .