Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information: Polaronic structure of excess electrons and holes for a series of bulk iron oxides

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Supplementary Information

Inverse Participation Ratio

A method for quantifying the extent of localisation is the inverse participation ratio (IPR), given by:

$$\mathrm{IPR} = \frac{\sum_{i=1}^{N} a_{ni}^{4}}{(\sum_{i=1}^{N} a_{ni}^{2})^{2}} \tag{1}$$

where a_{ni} is the expansion coefficient of eigenstate n for atom i. The IPR is $1/N$ for completely delocalised states, and 1 for fully localised states.

We see from Supplementary Figures 5-10 that the IPR of the hole polaron is around 1, such that the polaronic states introduced within the band gap of the semiconductor are localised to a single iron atom. The IPR of the electron polaron is around 0.5, a consequence of the localisation over two iron sites. For the goethite hole polaron, the IPR shows that the hole states are fully delocalised and no new states appear within the band gap.

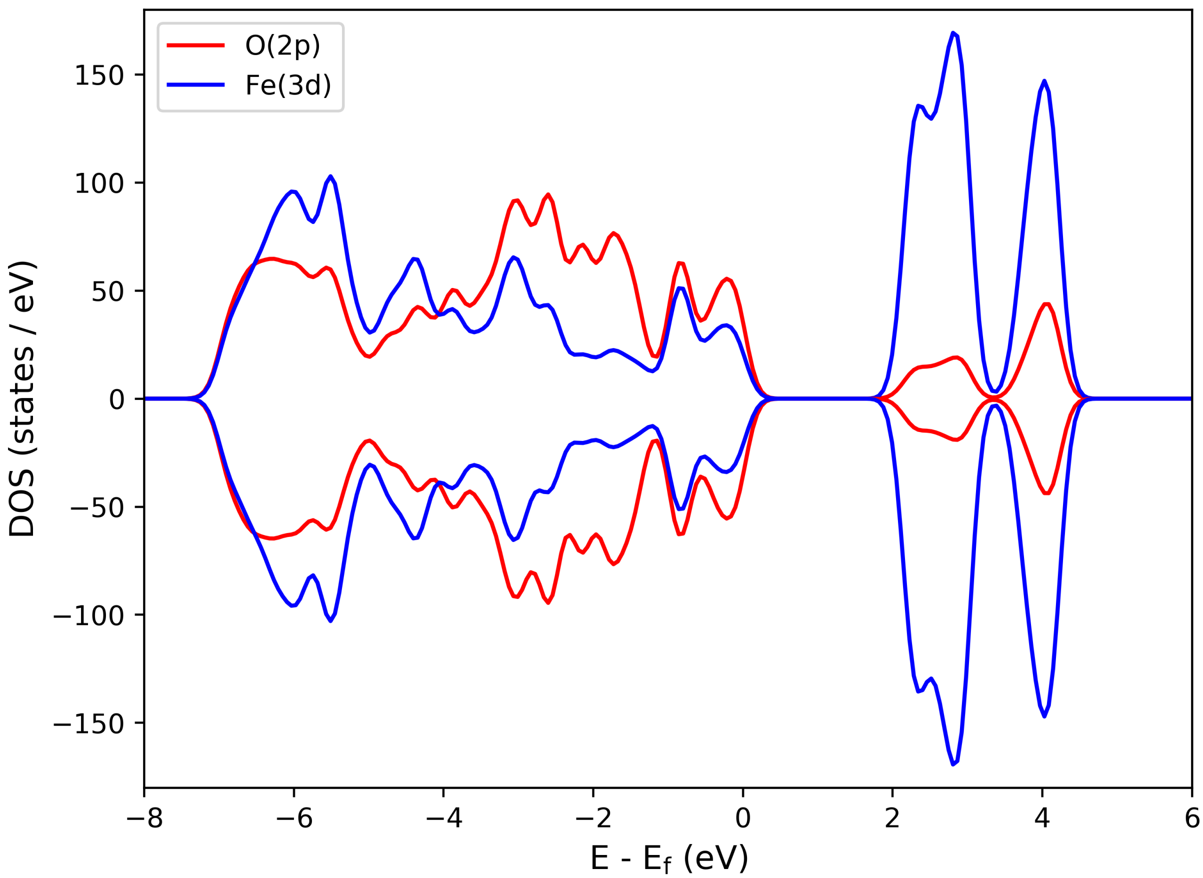
Trapping energy

In addition to the reorganisation energy $\lambda = \frac{\lambda_R + \lambda_O}{2}$ discussed in this paper, a related quantity is the trapping energy, or formation energy, of the polaron: λ_O for the electron hole polaron, and λ_R for the electron polaron.

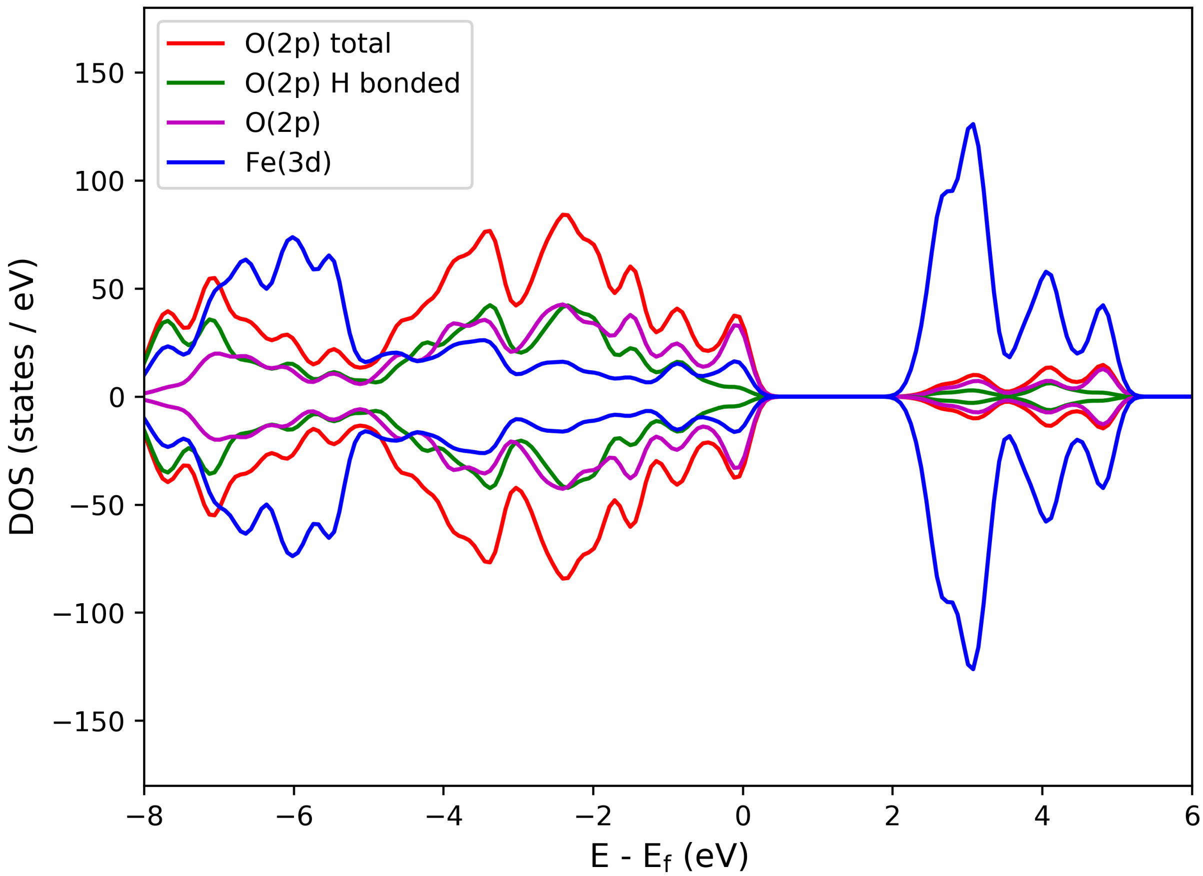
Table 1: Reorganisation energies and trapping energies for the localisation of an excess hole and electron in each iron oxide.

	Hematite	Lepidocrocite	Goethite
Excess hole			
Reorganisation energy / eV	0.29 (221)	0.51 (313)	
	0.36 (331)	0.59 (613)	
Trapping energy / eV	0.12 (221)	0.32 (313)	
	0.17 (331)	0.44 (613)	
Excess electron			
Reorganisation energy / eV	0.19 (221)		
	0.22 (331)	0.36 (613)	0.35 (316)
Trapping energy / eV	0.10 (221)		
	0.14 (331)	0.43 (613)	0.46 (316)

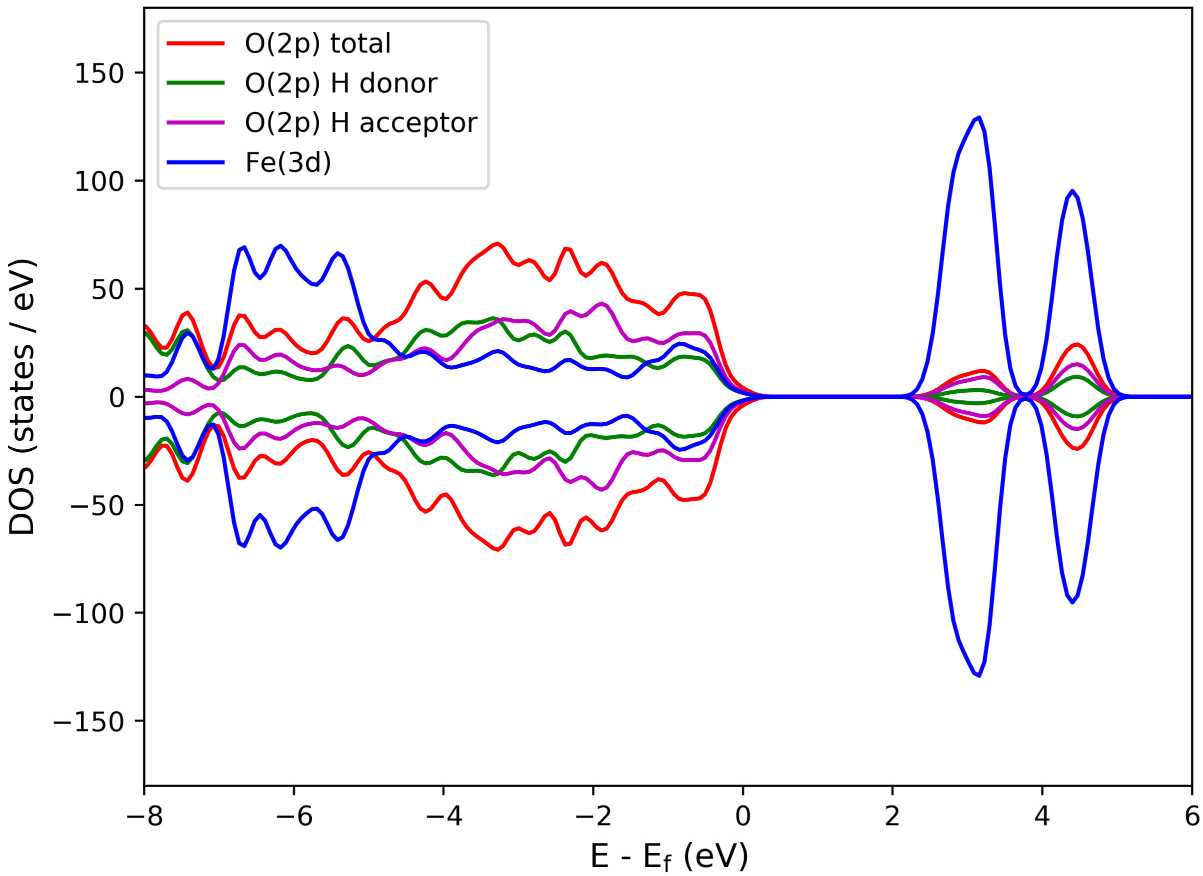
Supplementary Figures



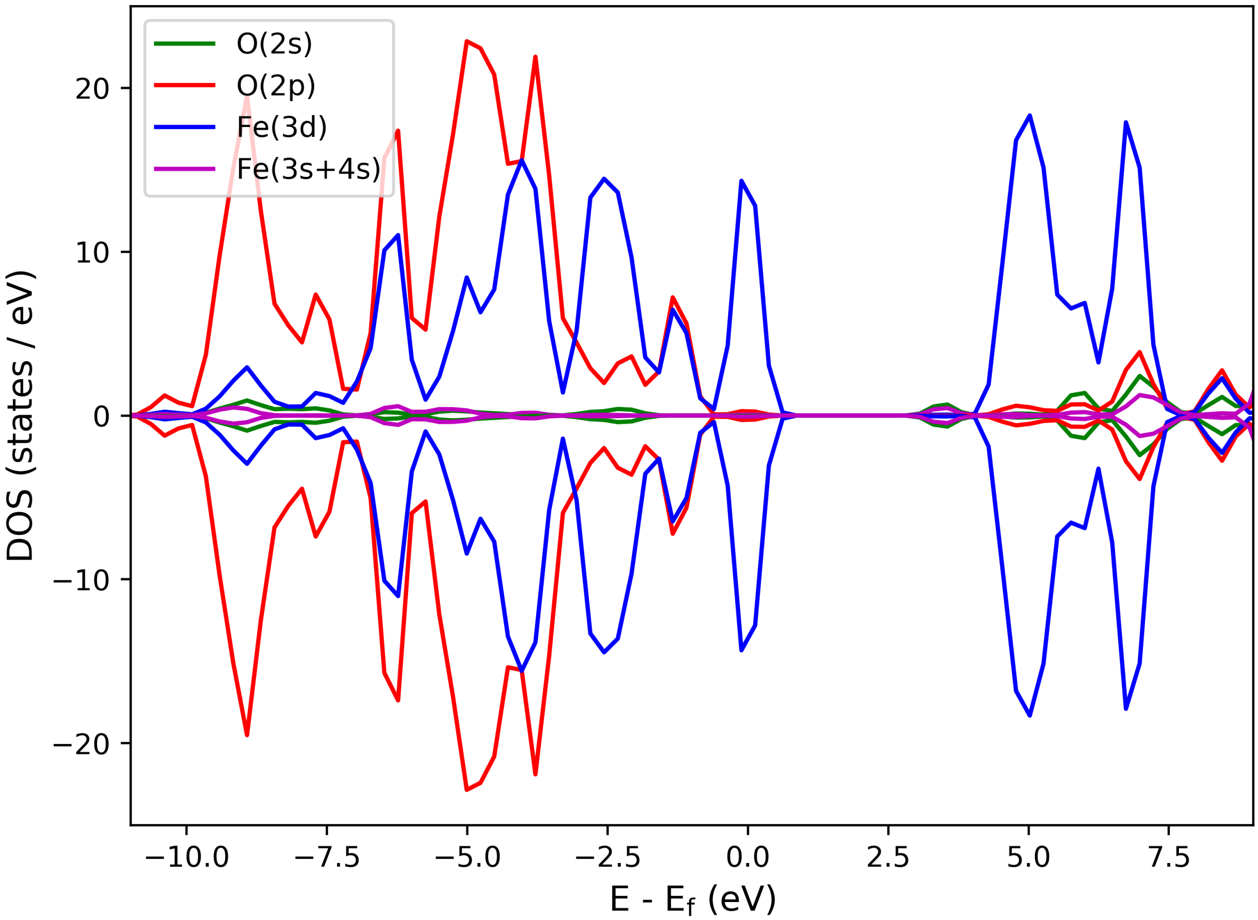
Supplementary Figure 1: Projected density of states for the hematite 331 supercell, convoluted with gaussian of width 0.2. Negative density of state values correspond to opposite spin channel.
VBM: Fe(3d) 39%, O(2p) 59%.
CBM: Fe(3d) 87%, O(2p) 9%.



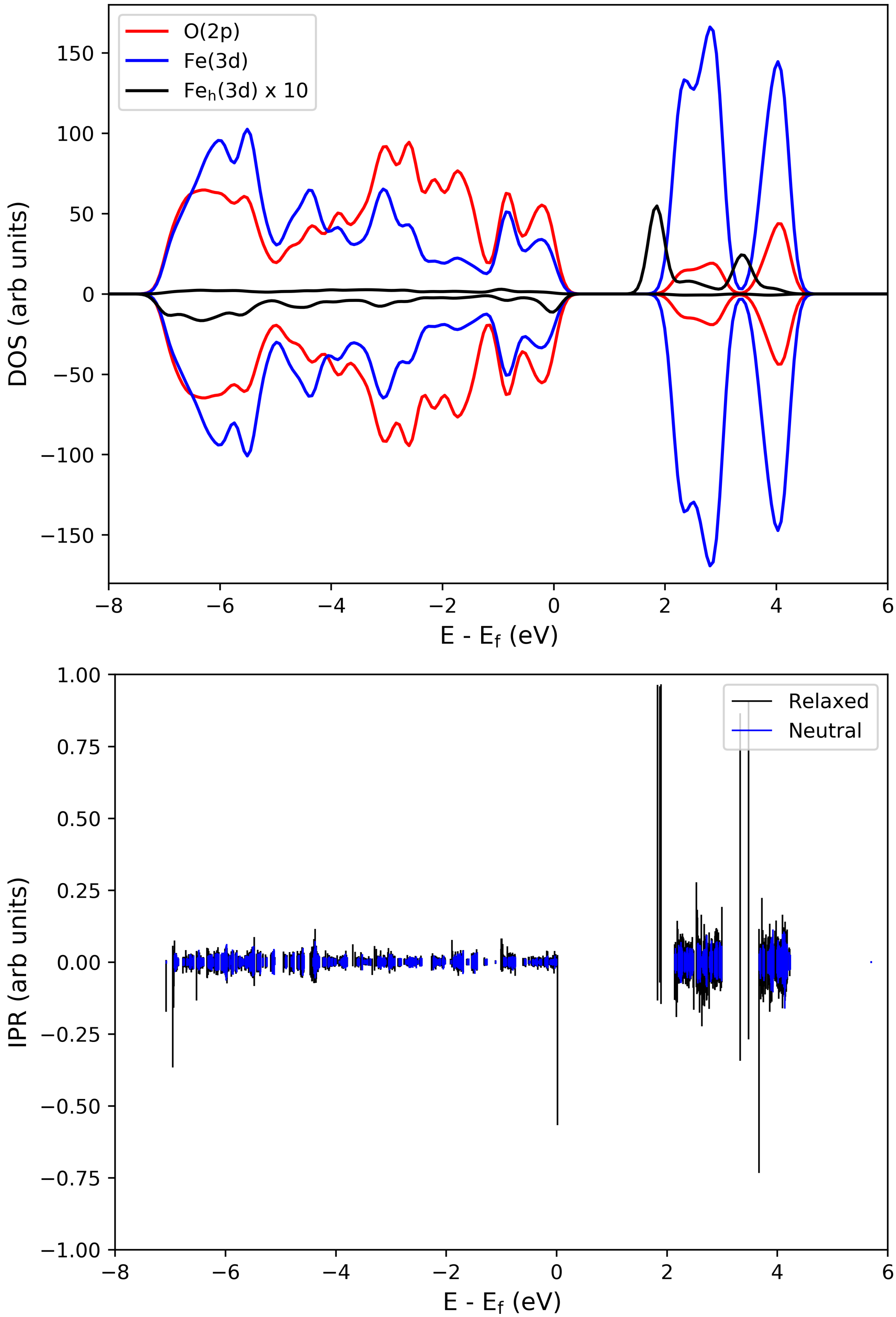
Supplementary Figure 2: Projected density of states for the lepidocrocite 316 supercell, convoluted with gaussian of width 0.2. Negative density of state values correspond to opposite spin channel.
VBM: Fe(3d) 29%, O(2p) 67%: O(2p) H bonded 6%, O(2p) non-H bonded 61%.
CBM: Fe(3d) 92%, O(2p) 4%: O(2p) H bonded 2%, O(2p) non-H bonded 3%.



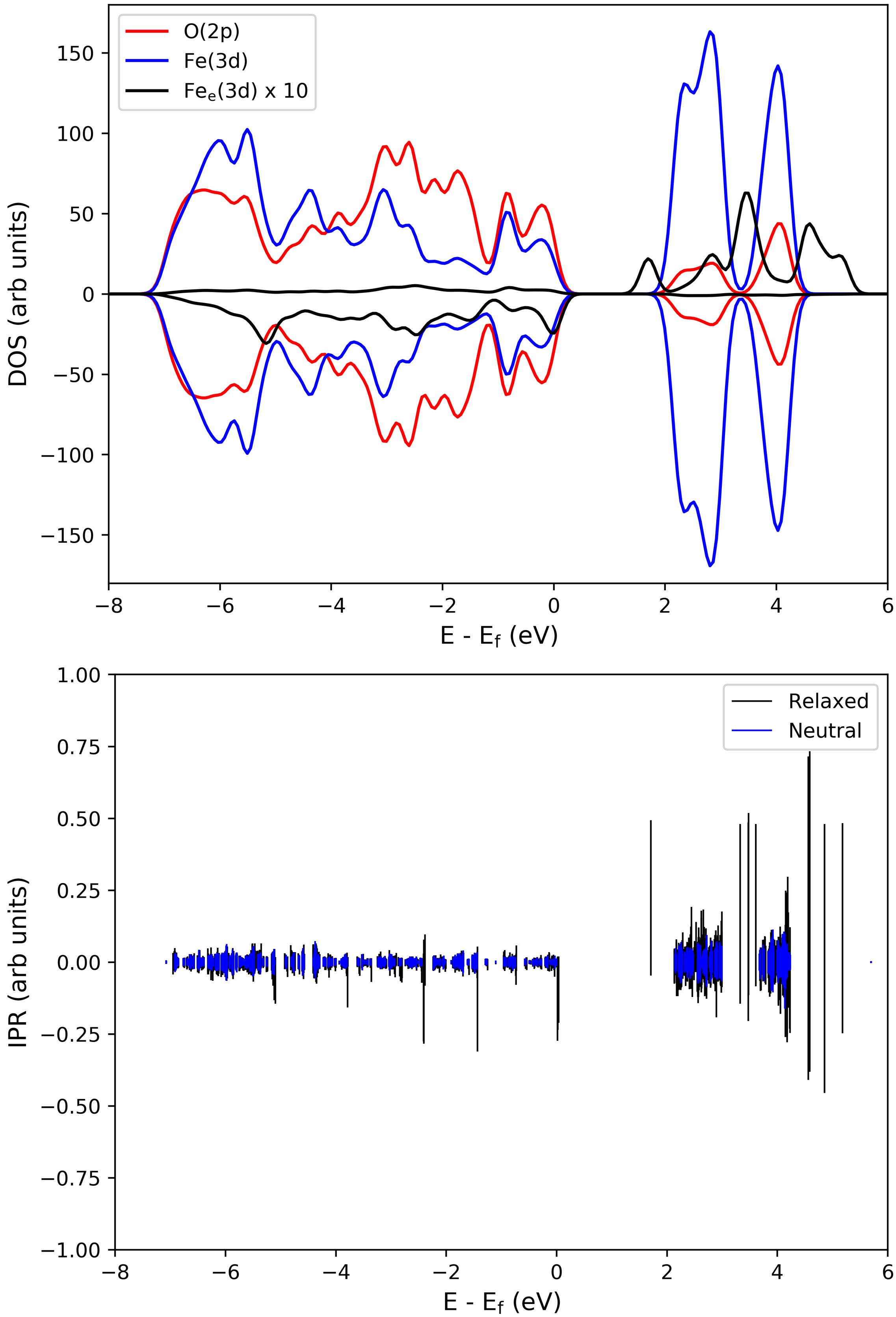
Supplementary Figure 3: Projected density of states for the goethite 613 supercell, convoluted with gaussian of width 0.2. Negative density of state values correspond to opposite spin channel.
VBM: Fe(3d) 29%, O(2p) 70%: O(2p) H donor 31%, H acceptor 39 % .
CBM: Fe(3d) 89%, O(2p) 5%: H donor 1%, H acceptor 5 % .



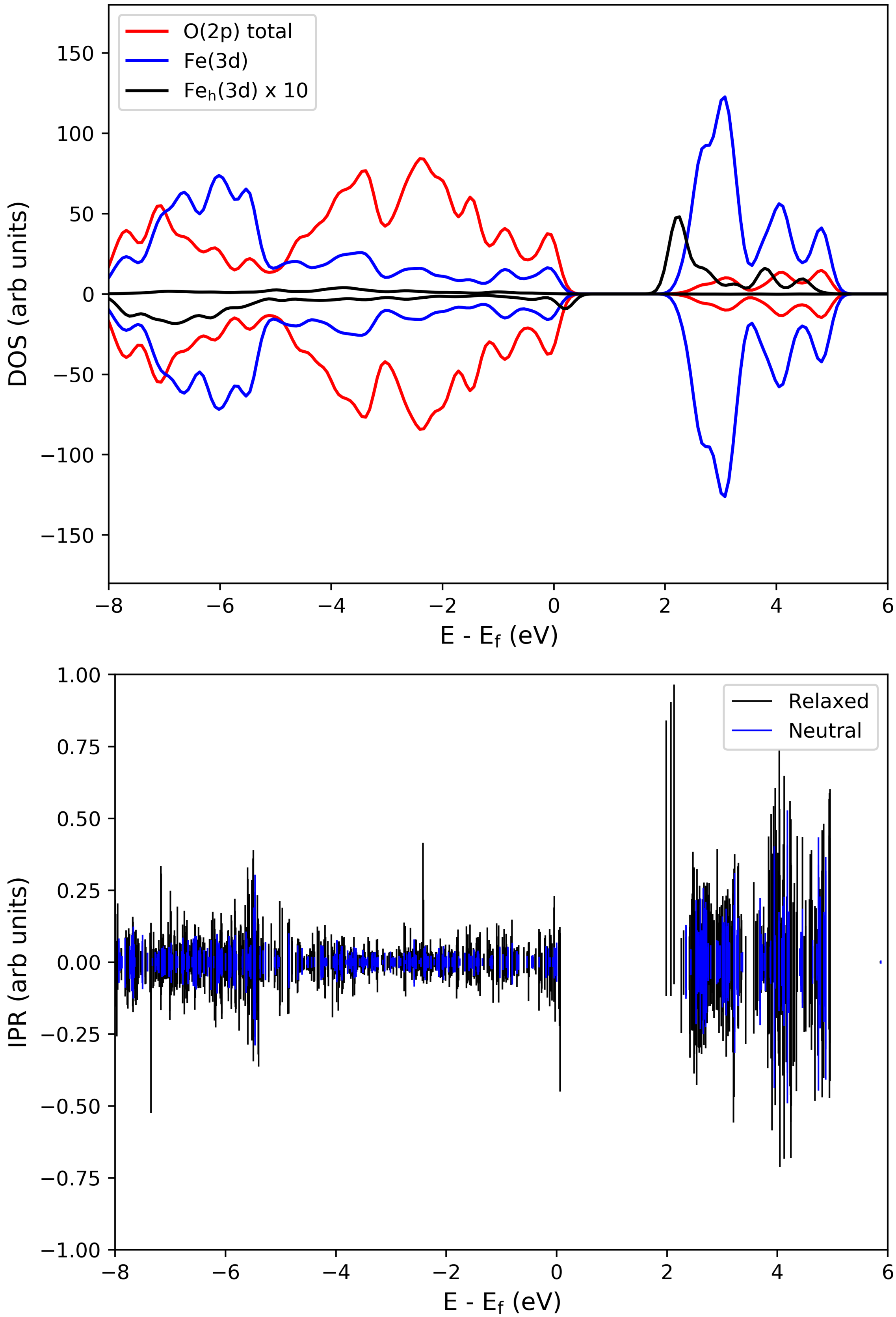
Supplementary Figure 4: Projected density of states for the white rust 332 supercell, convoluted with gaussian of width 0.3. Negative density of state values correspond to opposite spin channel.
VBM: Fe(3d) 96%, O(2p) 2%.
CBM: Fe(3s+4s) 38%, O(2s) 56%.



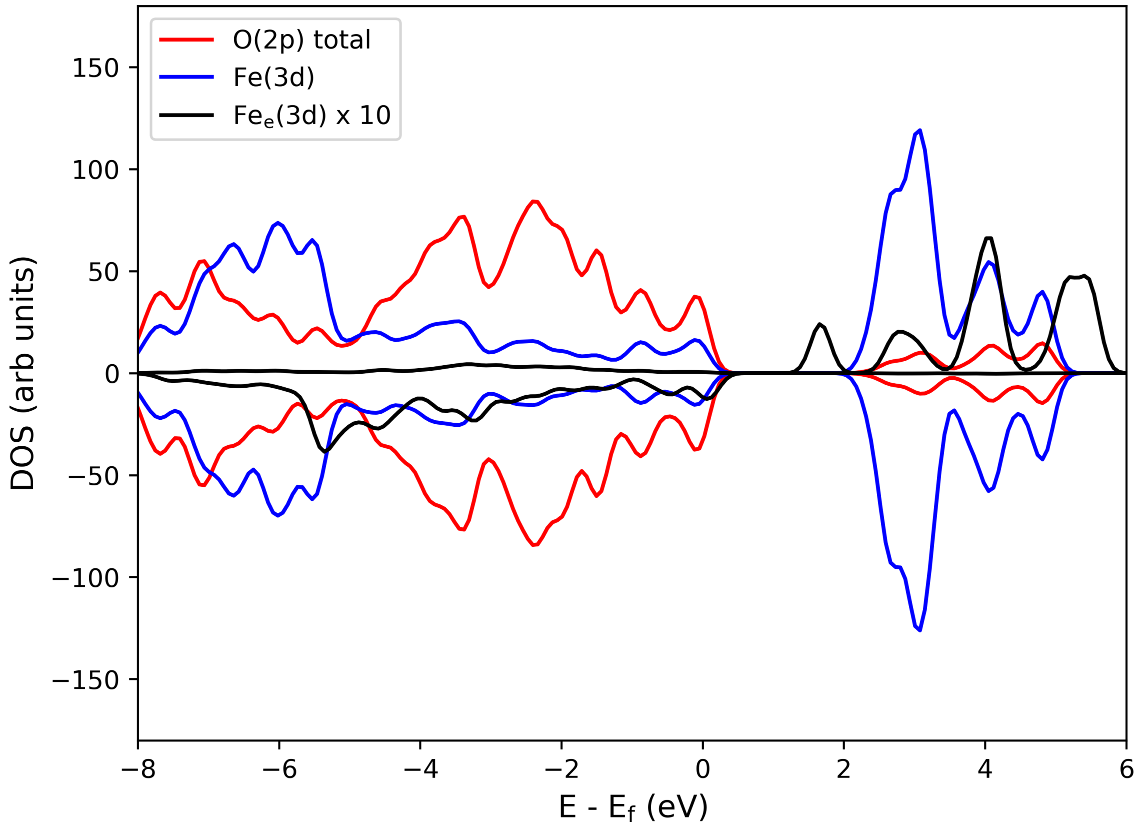
Supplementary Figure 5: Projected density of states for a relaxed electron hole polaron in the hematite 331 supercell (top). IPR for neutral, and relaxed electron hole polaron (bottom).

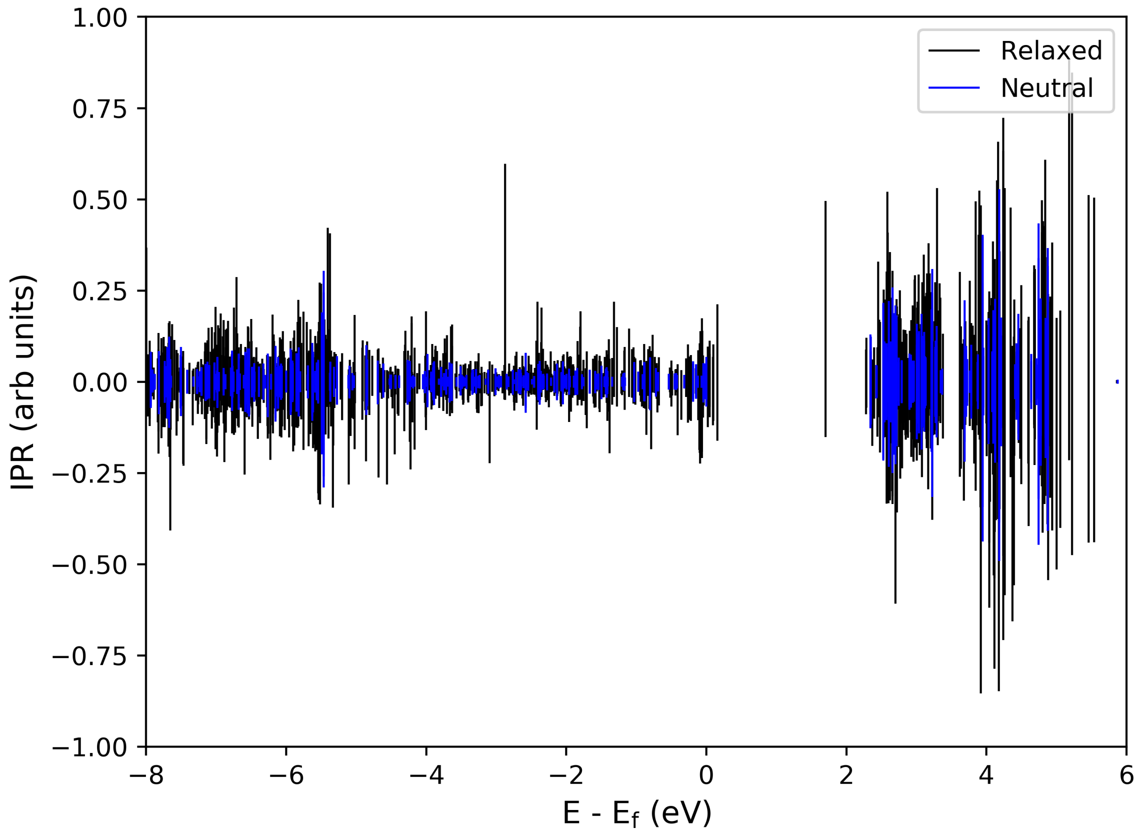


Supplementary Figure 6: Projected density of states for a relaxed electron polaron in the hematite 331 supercell (top). IPR for neutral, and relaxed electron polaron (bottom).

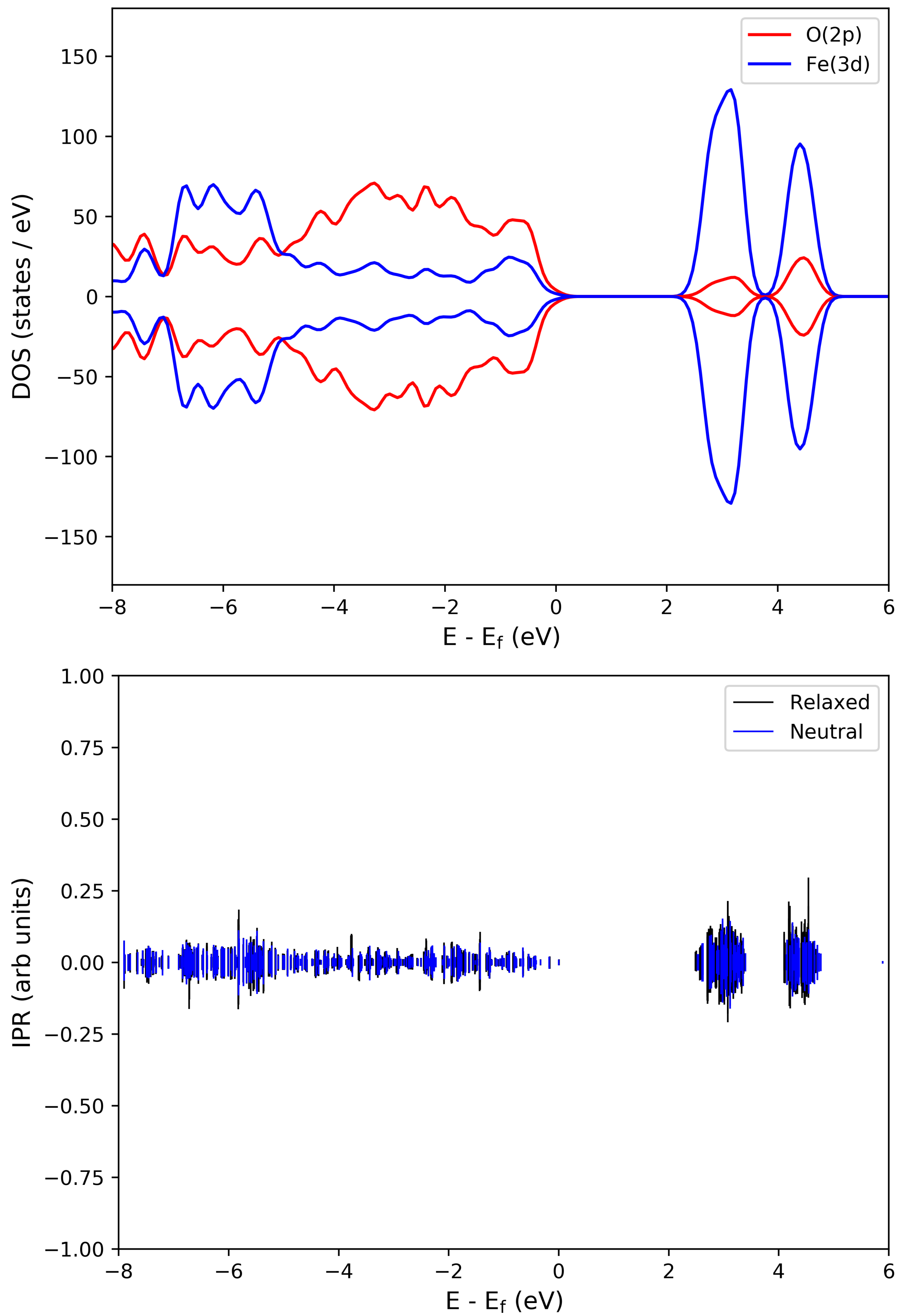


Supplementary Figure 7: Projected density of states for a relaxed electron hole polaron in the lepidocrocite 613 supercell (top). IPR for neutral, and relaxed electron hole polaron (bottom).

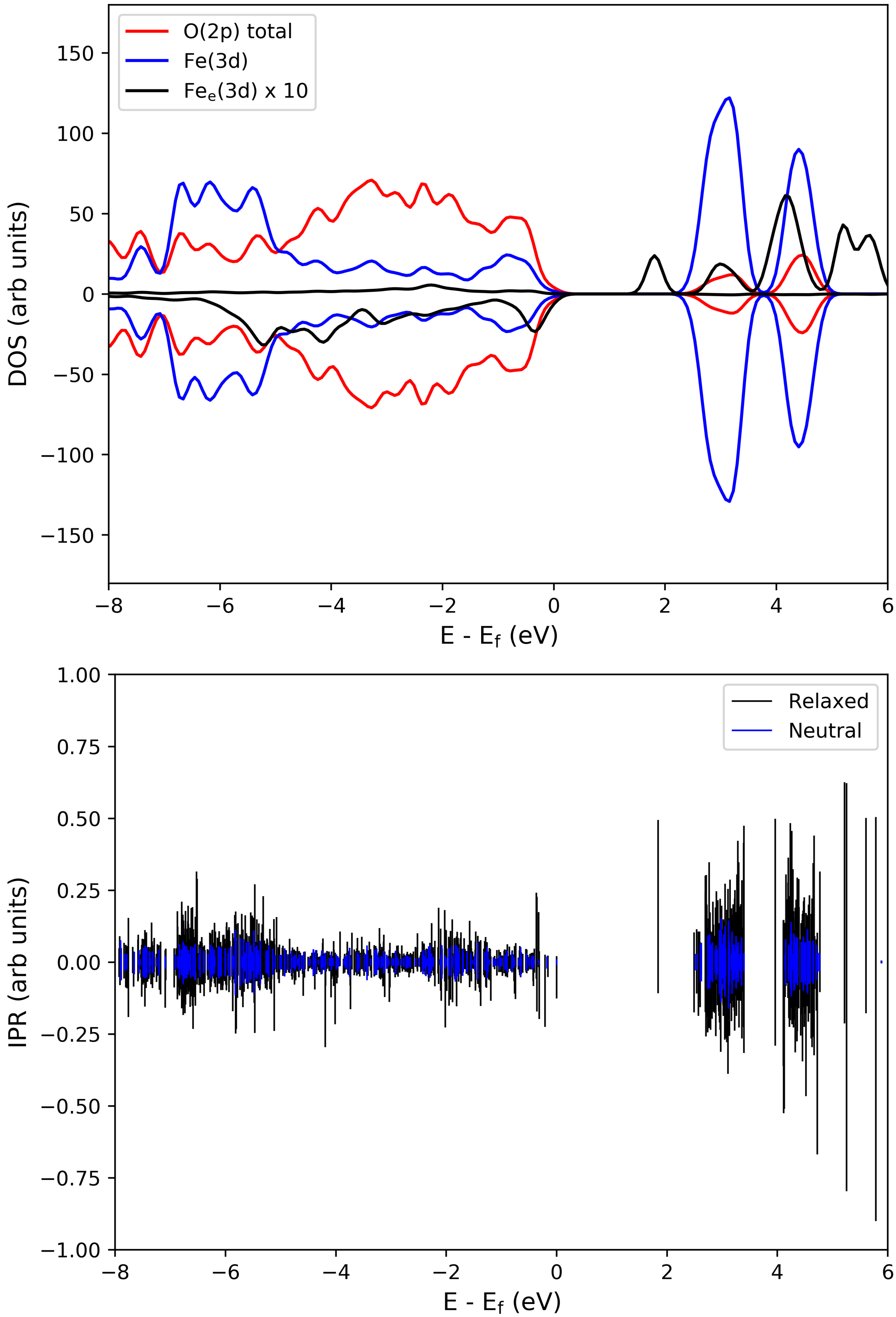




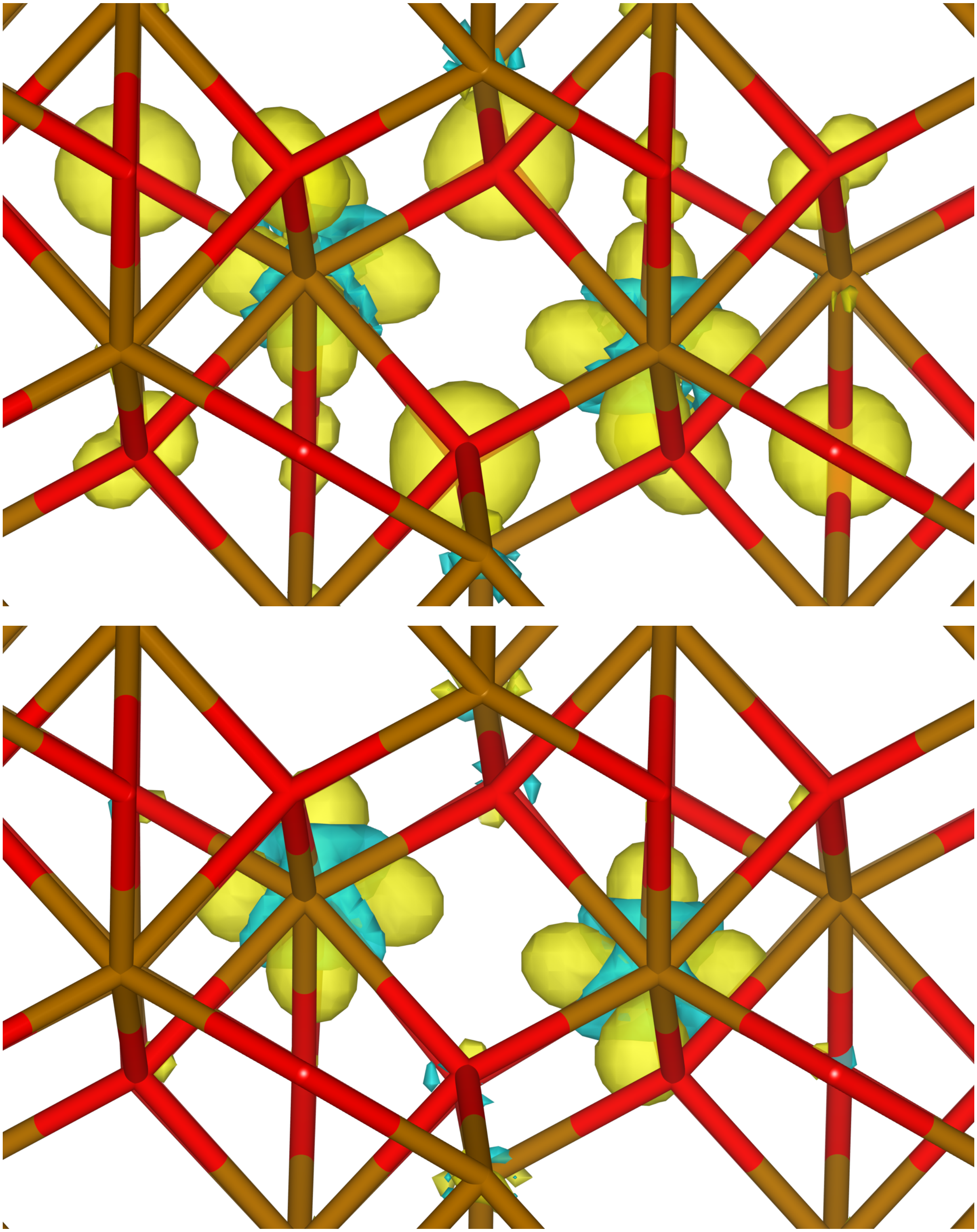
Supplementary Figure 8: Projected density of states for a relaxed electron polaron in the lepidocrocite 613 supercell (top). IPR for neutral, and relaxed electron polaron (bottom).



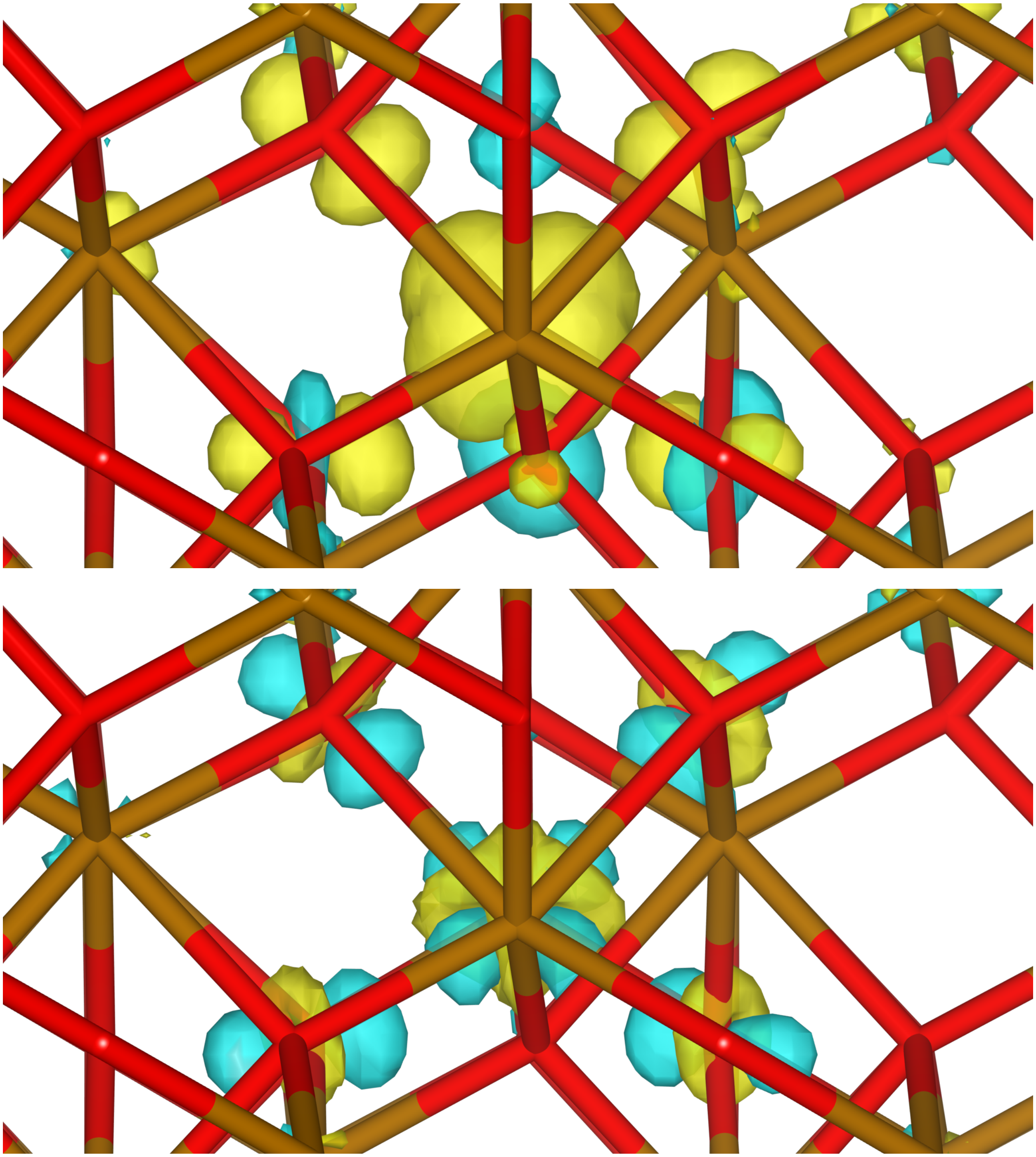
Supplementary Figure 9: Projected density of states for a relaxed electron hole polaron in the goethite 316 supercell (top). IPR for neutral, and relaxed electron hole polaron (bottom).



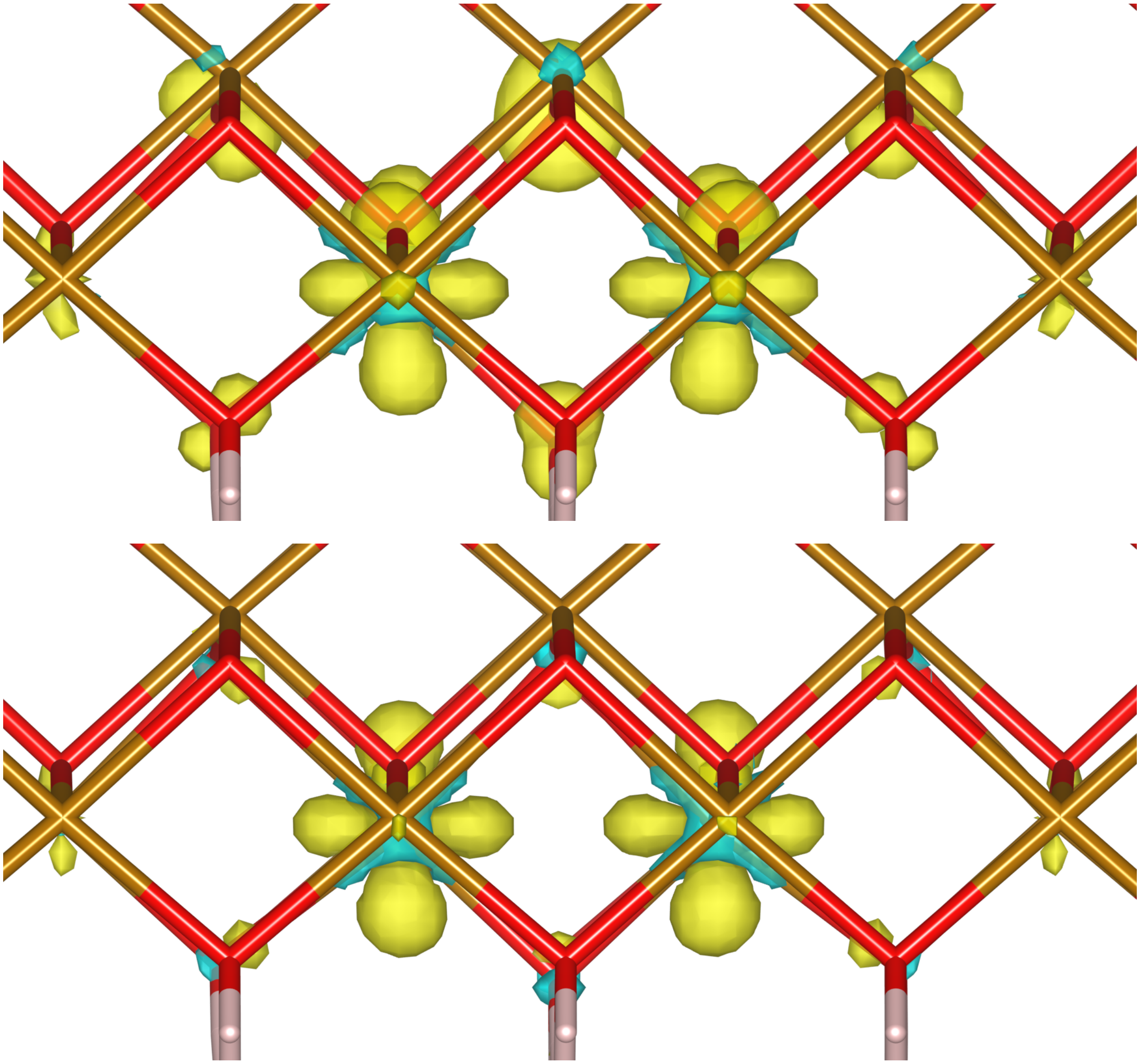
Supplementary Figure 10: Projected density of states for a relaxed electron polaron in the goethite 316 supercell (top). IPR for neutral, and relaxed electron polaron (bottom).



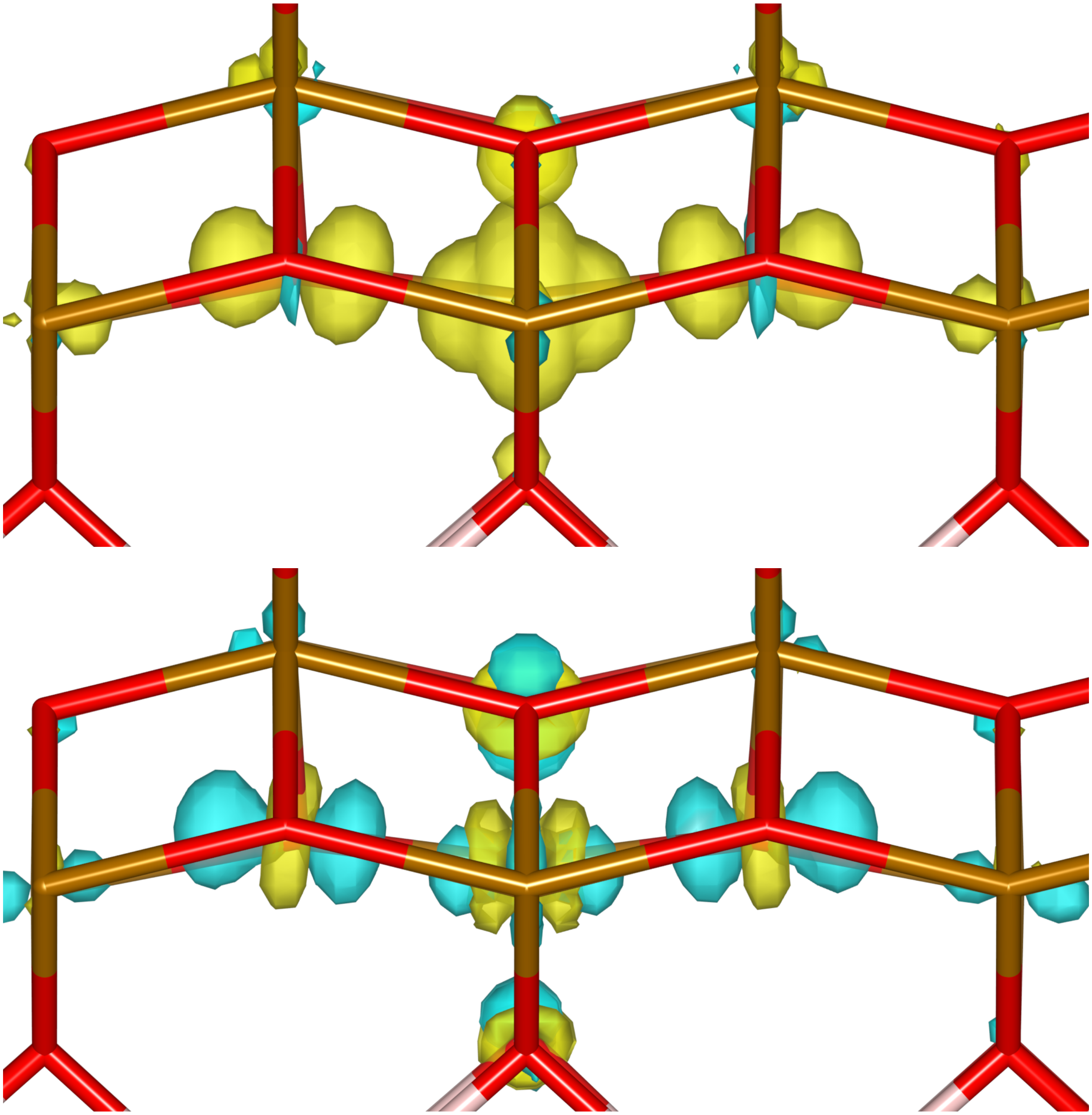
Supplementary Figure 11: Alternate view for the hematite electron polaron, 331 supercell. Top spin density difference, bottom electron density difference.



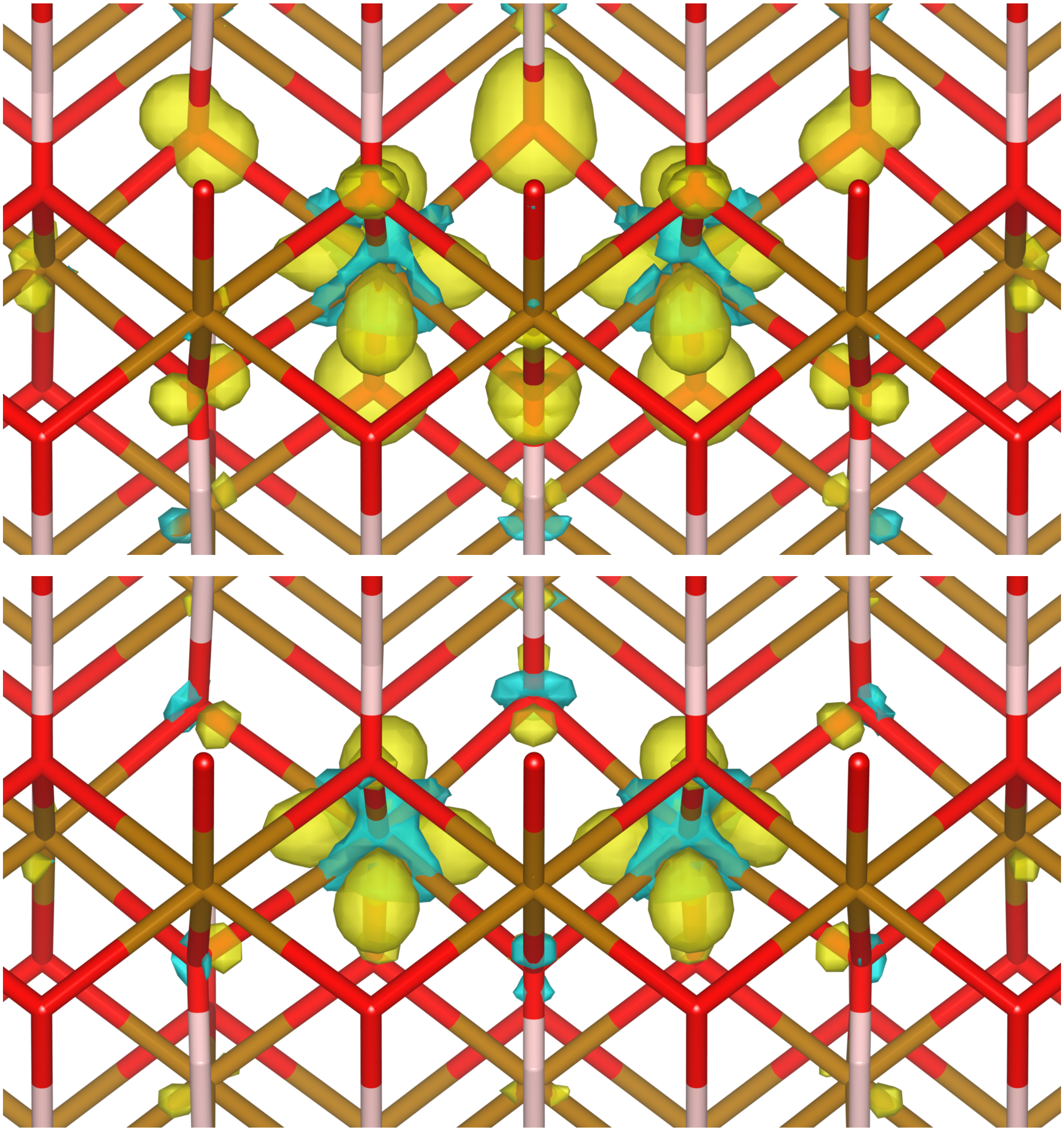
Supplementary Figure 12: Alternate view for the hematite hole polaron, 331 supercell. Top spin density difference, bottom electron density difference.



Supplementary Figure 13: Alternate view for the lepidocrocite electron polaron, 613 supercell. Top spin density difference, bottom electron density difference.



Supplementary Figure 14: Alternate view for the lepidocrocite hole polaron, 613 supercell. Top spin density difference, bottom electron density difference.



Supplementary Figure 15: Alternate view for the goethite electron polaron, 316 supercell. Top spin density difference, bottom electron density difference.