

Supporting Information

Valence-band hybridization in sulphides

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AUTOMATED INTENSITY AND ENERGY POSITION DETERMINATION

Band structures, (projected) density of states (PDOS), and calculated spectra are first loaded for all $U_{d,eff}$ and $U_{p,eff}$. In the first step of the automated evaluation illustrated in Figure S1, the centre energies E_1 and E_2 between the “S 3 derived” (short “3s”), “metal d derived” (short “d”), and “S 3p derived” (short “3p”) bands, as well as the electronic band gap energy E_{Gap} are determined. In the second step, these energies are used to determine the intensities

$$I_{3s,SL} = \sum_{E=E_{min}}^{E_1} I_{SL}(E), \quad I_{d,SL} = \sum_{E=E_1}^{E_2} I_{SL}(E)$$
$$I_{d,SK} = \sum_{E=E_1}^{E_2} I_{SK}(E), \quad \text{and} \quad I_{3p,SK} = \sum_{E=E_2}^0 I_{SK}(E).$$

Likewise, the centre of mass energies E_{COM} are determined as:

$$E_{3s,COM,SL} = \sum_{E=E_{min}}^{E_1} I_{SL}(E) \cdot E / I_{3s,SL}, \quad E_{d,COM,SL} = \sum_{E=E_1}^{E_2} I_{SL}(E) \cdot E / I_{d,SL}$$

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$$E_{d,COM,SK} = \sum_{E=E_1}^{E_2} I_{SK}(E) \cdot E / I_{d,SK}, \text{ and } E_{3p,COM,SK} = \sum_{E=E_2}^0 I_{SK}(E) \cdot E / I_{3p,SK}.$$

In the third step, the spectra are broadened with a Voigt function, using Gaussian and Lorentzian widths adjusted to best reproduce the experimental spectra. Then, the maxima in the regions defined by E_1 and E_2 give the respective $E_{I_{max}}$ energies.

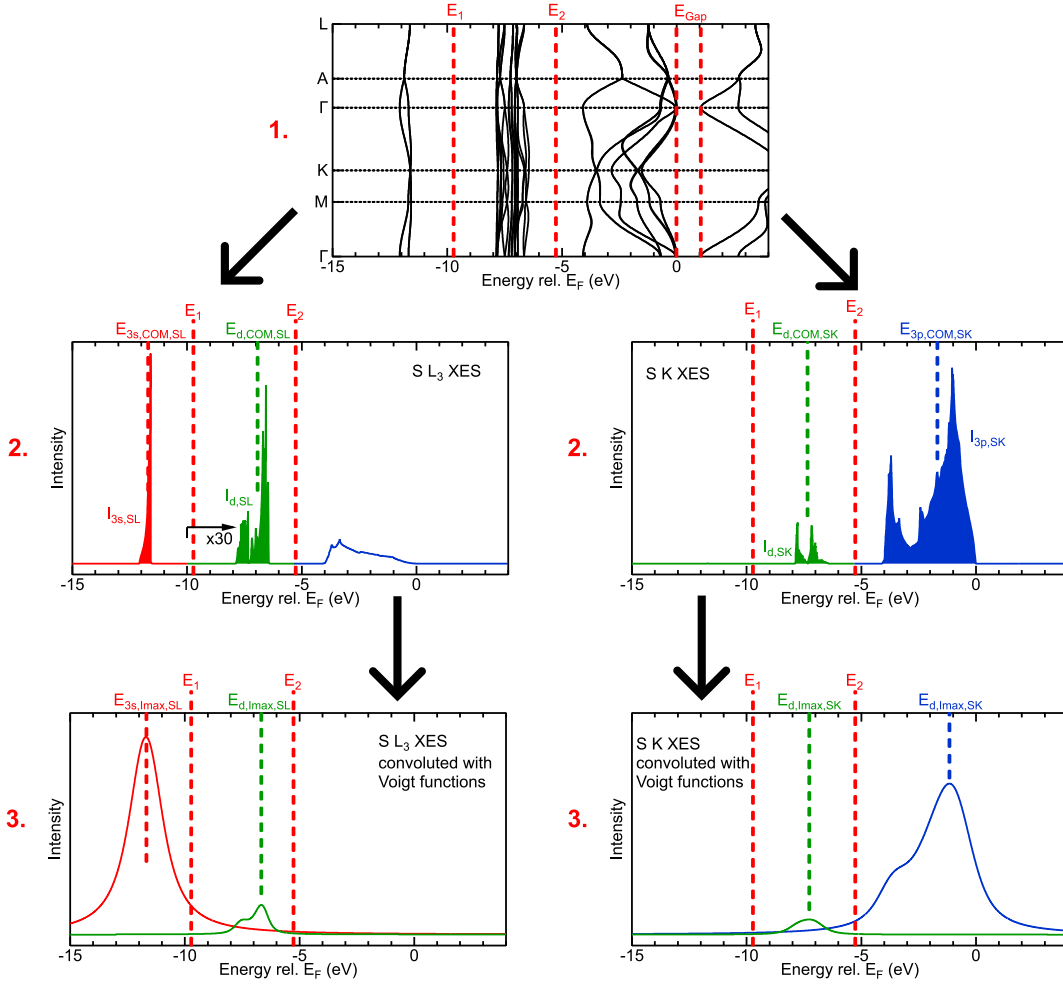


Figure S1: Illustration of steps 1 to 3 of the automated evaluation of the DFT calculation data for S L_{2,3} (left) and S K (right) XES.

TWO STATE HYBRIDIZATION MODEL

As a simple model, we describe the hybrid *bands* as hybrid *orbitals* formed by hybridization of “atomic” S 3s, S 3p, and metal d orbitals with wave functions $\varphi_{S\ 3s}$, $\varphi_{S\ 3p}$, and φ_d , respectively. We limit the model to hybrid orbitals formed by two separate orbital “pairs”, i.e., S 3s with metal d and metal d with S 3p, respectively. Analogous to the treatment of the hydrogen molecule by Heitler and London¹, we then assume that the wave

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function ψ_x of the hybrid orbital x can be described as a linear combination of the “atomic” orbitals. For hybridization between the S 3s and metal d orbitals, this gives us $\psi_x = c_1\varphi_{S\ 3s} + c_2\varphi_d$. With the Schrödinger equation, the Hamiltonian \hat{H} of the system, and the energy E_x of the hybrid orbital x , we obtain

$$\langle \psi_x | \hat{H} | \psi_x \rangle = \langle \psi_x | E_x | \psi_x \rangle$$

$$E_x = \frac{\langle \psi_x | \hat{H} | \psi_x \rangle}{\langle \psi_x | \psi_x \rangle} = \frac{\langle c_1\varphi_{S\ 3s} + c_2\varphi_d | \hat{H} | c_1\varphi_{S\ 3s} + c_2\varphi_d \rangle}{\langle c_1\varphi_{S\ 3s} + c_2\varphi_d | c_1\varphi_{S\ 3s} + c_2\varphi_d \rangle} = \frac{c_1^2\epsilon_{S\ 3s} + 2c_1c_2\beta + c_2^2\epsilon_d}{(c_1^2 + 2c_1c_2S + c_2^2)}$$

with the Coulomb integrals $\langle \varphi_i | H | \varphi_i \rangle = \epsilon_i$, the resonance integrals $\langle \varphi_i | H | \varphi_j \rangle = \beta_{ij}$, and the overlap integrals $\langle \varphi_i | \varphi_j \rangle = S_{ij}$ (with $S_{ii} = 1$). To find values for c_1 and c_2 that minimize the energy E_x , we use the variational Ritz method² by setting the partial derivatives to 0:

$$\frac{\partial E_x}{\partial c_1} = 0: c_1(\epsilon_{S\ 3s} - E_x) + c_2(\beta_{3s\ d} - E_x S_{3s\ d}) = 0 \quad (1)$$

$$\frac{\partial E_x}{\partial c_2} = 0: c_1(\beta_{3s\ d} - E_x S_{3s\ d}) + c_2(\epsilon_d - E_x) = 0 \quad (2)$$

This homogeneous system of linear equations only has a non-trivial solution if the determinant is zero, i.e., if

$$(\epsilon_{S\ 3s} - E_x)(\epsilon_d - E_x) - (\beta_{3s\ d} - E_x S_{3s\ d})^2 = 0.$$

As expected, this gives us two solutions for E_x , i.e., two hybrid orbitals which we name according to Figure 6 in the main paper. Since we do not require an explicit form of the energies, they can be given in a compact implicit form:

$$E_{ds} = \epsilon_d + \frac{(\beta_{S\ 3s\ d} - E_{ds} S_{S\ 3s\ d})^2}{E_{ds} - \epsilon_{S\ 3s}}$$

$$E_{sd} = \epsilon_{S\ 3s} - \frac{(\beta_{S\ 3s\ d} - E_{sd} S_{S\ 3s\ d})^2}{\epsilon_d - E_{sd}}$$

From equations (1) and (2), we derive the following conditions for the coefficients:

$$c_1 = c_2 \frac{\beta_{S\ 3s\ d} - E_{ds} S_{S\ 3s\ d}}{E_{ds} - \epsilon_{S\ 3s}} \quad \text{and} \quad c_2 = c_1 \frac{\beta_{S\ 3s\ d} - E_{sd} S_{S\ 3s\ d}}{\epsilon_d - E_{sd}}$$

Introducing normalization factors N_{ds} and N_{sd} , we can now write the wave functions of the two hybrid orbitals:

$$\psi_{ds} = N_{ds} \left(\frac{\beta_{S\ 3s\ d} - E_{ds} S_{S\ 3s\ d}}{E_{ds} - \epsilon_{S\ 3s}} \varphi_{S\ 3s} + \varphi_d \right)$$

$$\psi_{sd} = N_{sd} \left(\varphi_{S\ 3s} - \frac{\beta_{S\ 3s\ d} - E_{sd} S_{S\ 3s\ d}}{\epsilon_d - E_{sd}} \varphi_d \right)$$

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In the same way, we derive the energies and wave functions for hybridization of the metal d with the S 3p levels:

$$E_{dp} = \epsilon_d - \frac{(\beta_{S\ 3p\ d} - E_{dp} S_{S\ 3p\ d})^2}{\epsilon_{S\ 3p} - E_{dp}}$$

$$E_{pd} = \epsilon_{S\ 3p} + \frac{(\beta_{S\ 3p\ d} - E_{pd} S_{S\ 3p\ d})^2}{E_{pd} - \epsilon_d}$$

$$\psi_{dp} = N_{dp} \left(\varphi_d - \frac{\beta_{S\ 3p\ d} - E_{dp} S_{S\ 3p\ d}}{\epsilon_{S\ 3p} - E_{dp}} \varphi_{S\ 3p} \right)$$

$$\psi_{pd} = N_{sd} \left(\frac{\beta_{S\ 3p\ d} - E_{pd} S_{S\ 3p\ d}}{E_{pd} - \epsilon_d} \varphi_d + \varphi_{S\ 3p} \right)$$

The emission intensity of photons of energy E generated by transitions from an initial state $|i\rangle$ to a final state $|f\rangle$ is proportional to $E^3 |\langle f|\hat{x}|i\rangle|^2$, as derived by Dirac^{3,4}. With the S 2p wave function $\varphi_{S\ 2p}$, the ‘‘S 3s bands’’ represented by the ‘‘sd’’ orbital, the ‘‘metal d bands’’ by the ‘‘ds’’ and ‘‘dp’’ orbitals, and the ‘‘S 3p bands’’ by the ‘‘pd’’ orbital, we can now simulate the area ratios within our model. For S L_{2,3} XES, this gives

$$\frac{I_{d,SL}}{I_{3s,SL}} \approx \frac{I_{ds} + I_{dp}}{I_{sd}} = \frac{(E_{ds} - E_{S\ 2p})^3 |\langle \psi_{ds} | \hat{x} | \varphi_{S\ 2p} \rangle|^2 + (E_{dp} - E_{S\ 2p})^3 |\langle \psi_{dp} | \hat{x} | \varphi_{S\ 2p} \rangle|^2}{(E_{sd} - E_{S\ 2p})^3 |\langle \psi_{sd} | \hat{x} | \varphi_{S\ 2p} \rangle|^2}$$

$$= \frac{(E_{ds} - E_{S\ 2p})^3 N_{ds}^2 \left| \left\langle \frac{\beta_{S\ 3s\ d} - E_{ds} S_{S\ 3s\ d}}{E_{ds} - \epsilon_{S\ 3s}} \varphi_{S\ 3s} + \varphi_d \right| \hat{x} \left| \varphi_{S\ 2p} \right\rangle \right|^2 + (E_{dp} - E_{S\ 2p})^3 N_{dp}^2 \left| \left\langle \varphi_d - \frac{\beta_{S\ 3p\ d} - E_{dp} S_{S\ 3p\ d}}{\epsilon_{S\ 3p} - E_{dp}} \varphi_{S\ 3p} \right| \hat{x} \left| \varphi_{S\ 2p} \right\rangle \right|^2}{(E_{sd} - E_{S\ 2p})^3 N_{sd}^2 \left| \left\langle \varphi_{S\ 3s} - \frac{\beta_{S\ 3s\ d} - E_{sd} S_{S\ 3s\ d}}{\epsilon_d - E_{sd}} \varphi_d \right| \hat{x} \left| \varphi_{S\ 2p} \right\rangle \right|^2}$$

With $\langle \varphi_{S\ 3p} | \hat{x} | \varphi_{S\ 2p} \rangle = 0$ due to the dipole selection rules and assuming $\langle \varphi_d | \hat{x} | \varphi_{S\ 2p} \rangle \ll \langle \varphi_{S\ 3s} | \hat{x} | \varphi_{S\ 2p} \rangle$, as also suggested by the vanishing contribution of d symmetry to the S PDOS, we obtain

$$\frac{I_{d,SL}}{I_{3s,SL}} \approx \frac{(E_{ds} - E_{S\ 2p})^3 N_{ds}^2 \left(\frac{\beta_{S\ 3s\ d} - E_{ds} S_{S\ 3s\ d}}{E_{ds} - \epsilon_{S\ 3s}} \right)^2 |\langle \varphi_{S\ 3s} | \hat{x} | \varphi_{S\ 2p} \rangle|^2}{(E_{sd} - E_{S\ 2p})^3 N_{sd}^2 |\langle \varphi_{S\ 3s} | \hat{x} | \varphi_{S\ 2p} \rangle|^2} = \frac{(E_{ds} - E_{S\ 2p})^3 N_{ds}^2 (\beta_{S\ 3s\ d} - E_{ds} S_{S\ 3s\ d})^2}{(E_{sd} - E_{S\ 2p})^3 N_{sd}^2 (E_{ds} - \epsilon_{S\ 3s})^2}.$$

Within our model, we approximate $dE_{COM} \approx E_{ds} - E_{sd}$ for the S L_{2,3} emission, and thus

$$E_{ds} - \epsilon_{S\ 3s} = E_{ds} - E_{sd} - \frac{(\beta_{S\ 3s\ d} - E_{sd} S_{S\ 3s\ d})^2}{\epsilon_d - E_{sd}} \approx dE_{COM} - \frac{(\beta_{S\ 3s\ d} - E_{sd} S_{S\ 3s\ d})^2}{\epsilon_d - E_{sd}}.$$

We further approximate $\frac{(\beta_{S\ 3s\ d} - E_{sd} S_{S\ 3s\ d})^2}{\epsilon_d - E_{sd}} = \Delta E_{sd}$ to be independent of dE_{COM} and derive

$$\frac{I_{d,SL}}{I_{3s,SL}} \approx \frac{(E_{ds} - E_{S\ 2p})^3 N_{ds}^2 (\beta_{S\ 3s\ d} - E_{ds} S_{S\ 3s\ d})^2}{(E_{sd} - E_{S\ 2p})^3 N_{sd}^2 (dE_{COM} - \Delta E_{sd})^2}.$$

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We now define the constant $C_{ds} = \frac{N_{ds}^2}{N_{sd}^2} (\beta_{S3sd} - E_{ds} S_{S3sd})^2$. Using the Hückel approximation ($S_{S3sd} = 0$) this simplifies to $C_{ds} \approx \frac{N_{ds}^2}{N_{sd}^2} \beta_{S3sd}^2$, which we assume to be mostly independent of dE_{COM} . C_{ds} contains the wave function normalization constants and the resonance integral β_{S3sd} , which might be interpreted as a measure for the bonding strength between S 3s and the metal d states. Furthermore, we approximate $\frac{(E_{ds} - E_{S2p})^3}{(E_{sd} - E_{S2p})^3} \approx 1 + 3 \frac{dE_{COM}}{E_{sd} - E_{S2p}} \approx 1$, giving

$$\frac{I_{d,SL}}{I_{3s,SL}} \approx \frac{C_{ds}}{(dE_{COM} - \Delta E_{sd})^2}.$$

Similarly, we derive an approximation for the intensity ratio of the “metal d bands” and the “S 3p bands” in the S K emission:

$$\frac{I_{d,SK}}{I_{3p,SK}} \approx \frac{C_{dp}}{(dE_{COM} - \Delta E_{pd})^2}.$$

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