And he said, I saw all Israel scattered upon the hills, as sheep that have not a shepherd:
and the LORD said, These have no master: let them return every man to his house in peace.

- 1 Kings 22, 17

XANES spectroscopy on iron complexes

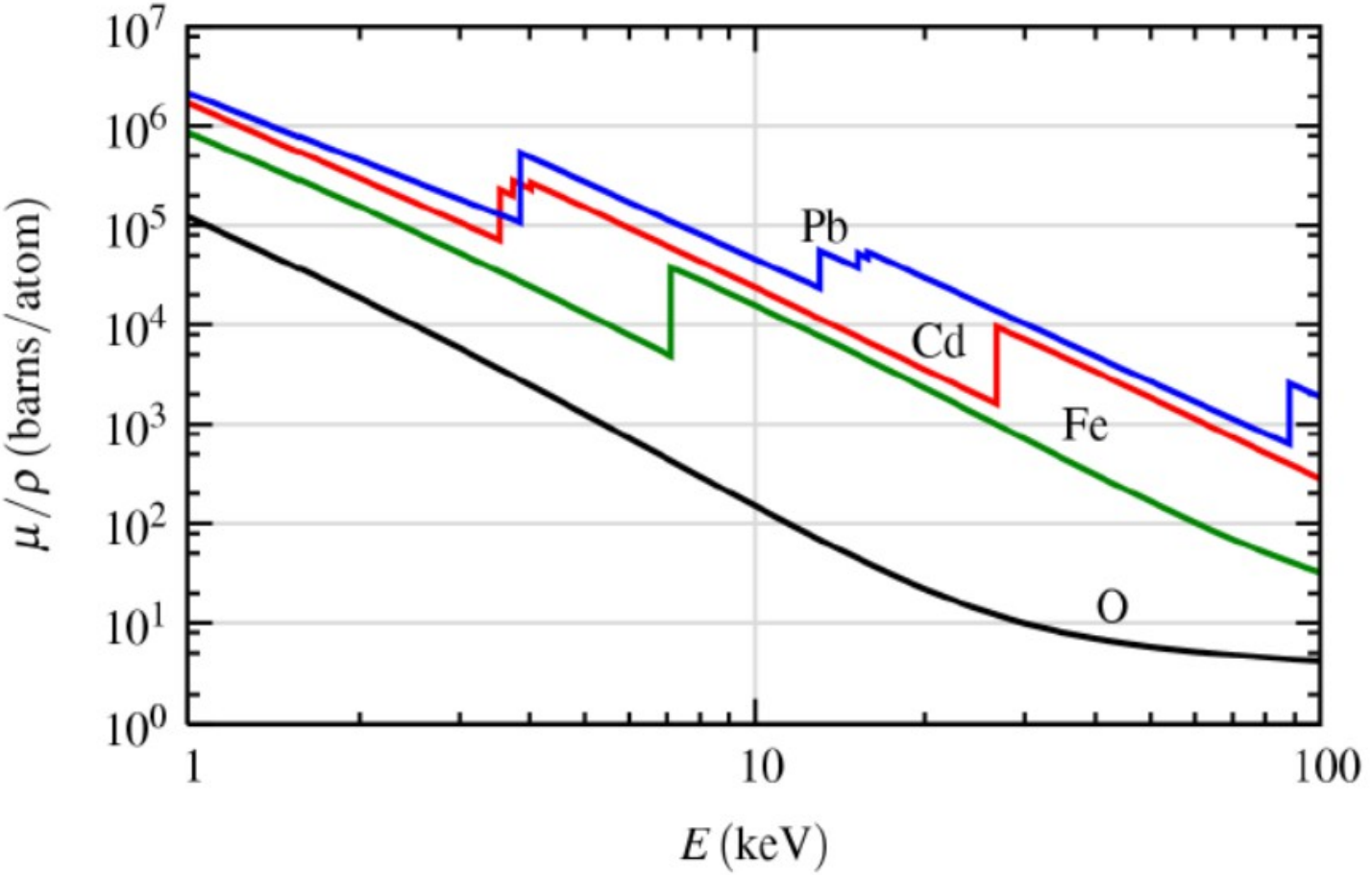
Raffaele Salvia

August 31, 2018

Part I – What is XANES

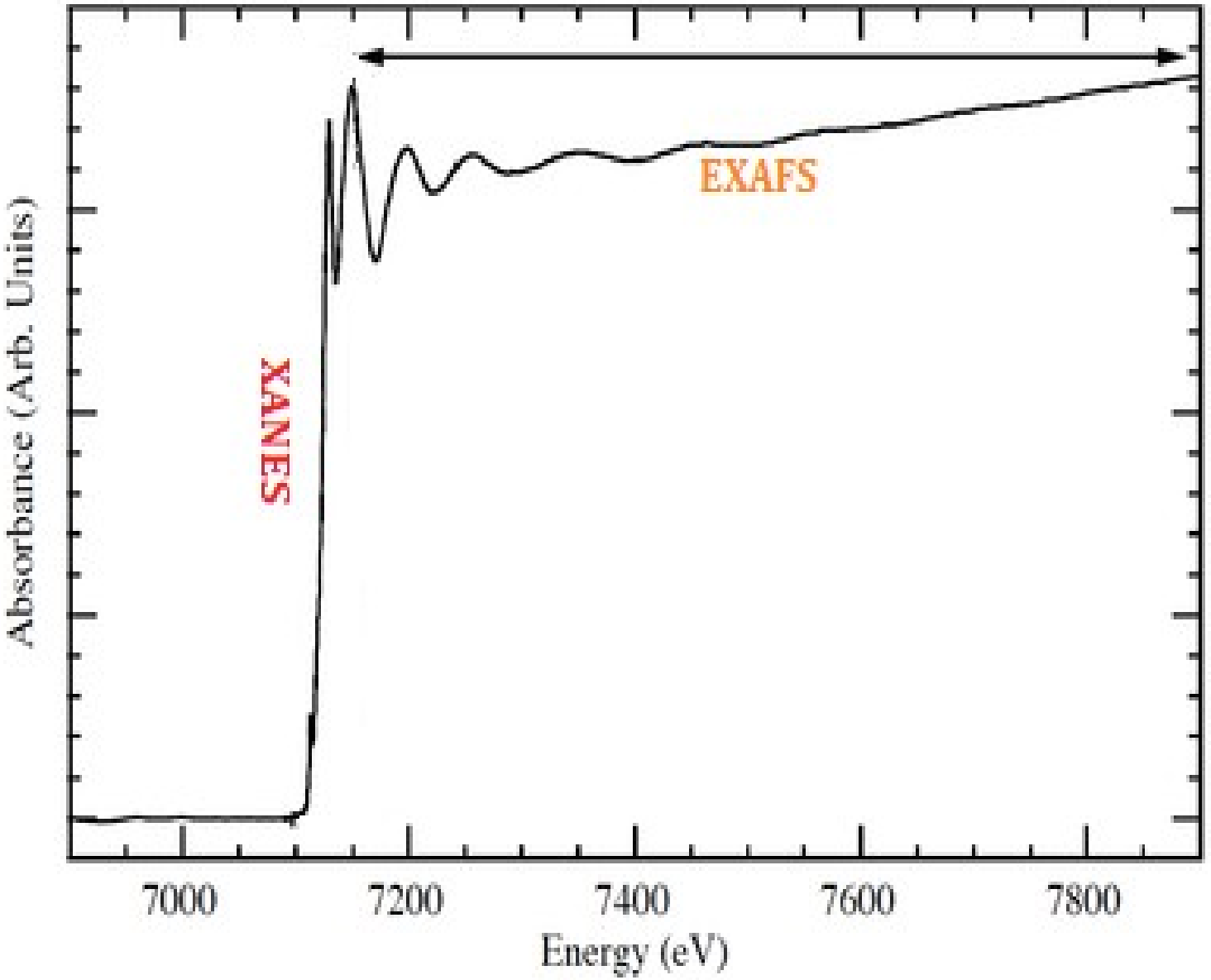
1.1. Introduction

The absorbption length ($I = I_0 e^{-\mu t}$) is roughly $\mu \approx \frac{\rho Z^4}{A E^3}$,
but with discrete edges.



XANES spectroscopy on iron complexes

1.1. Introduction



XANES spectroscopy on iron complexes

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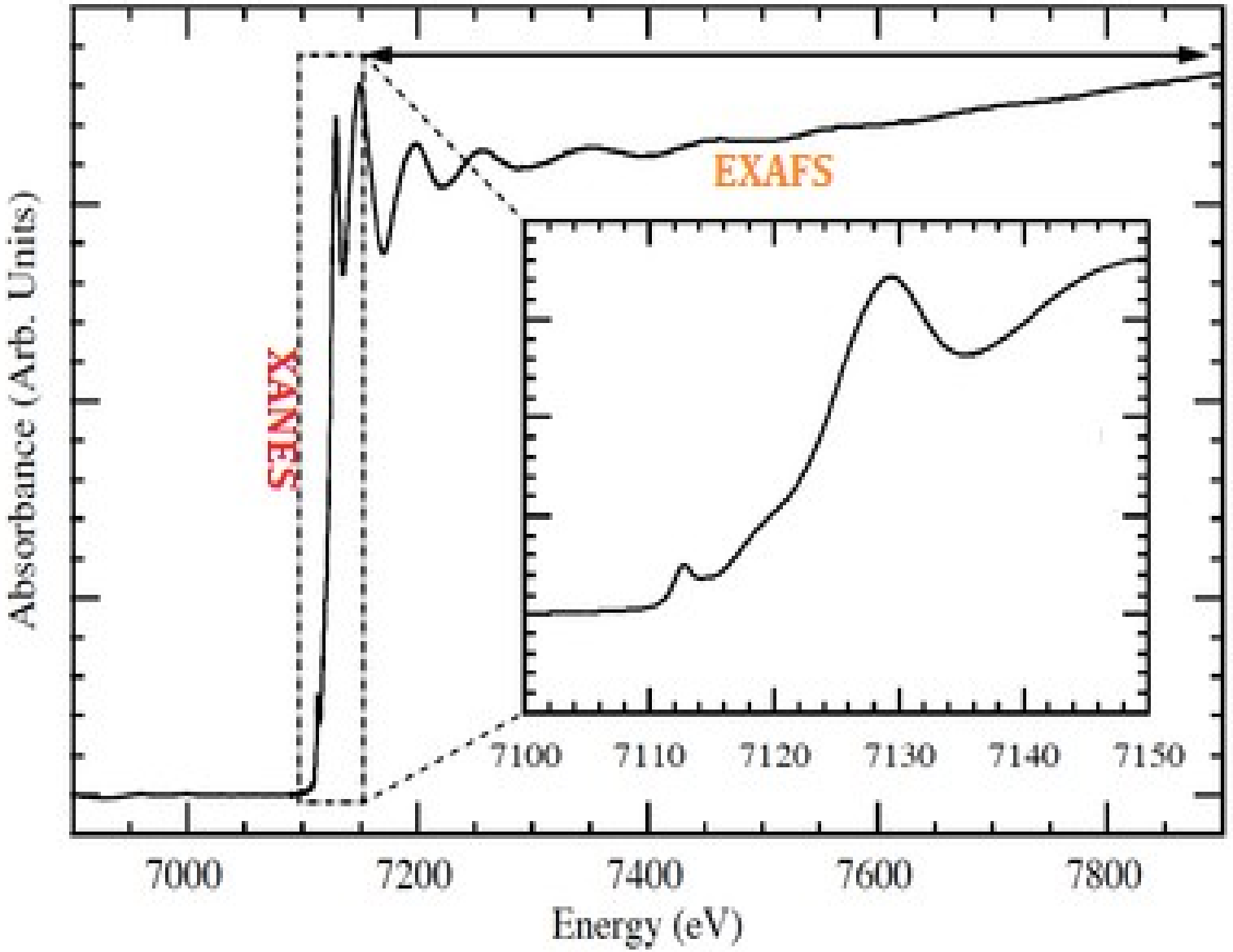

XANES spectroscopy on iron complexes

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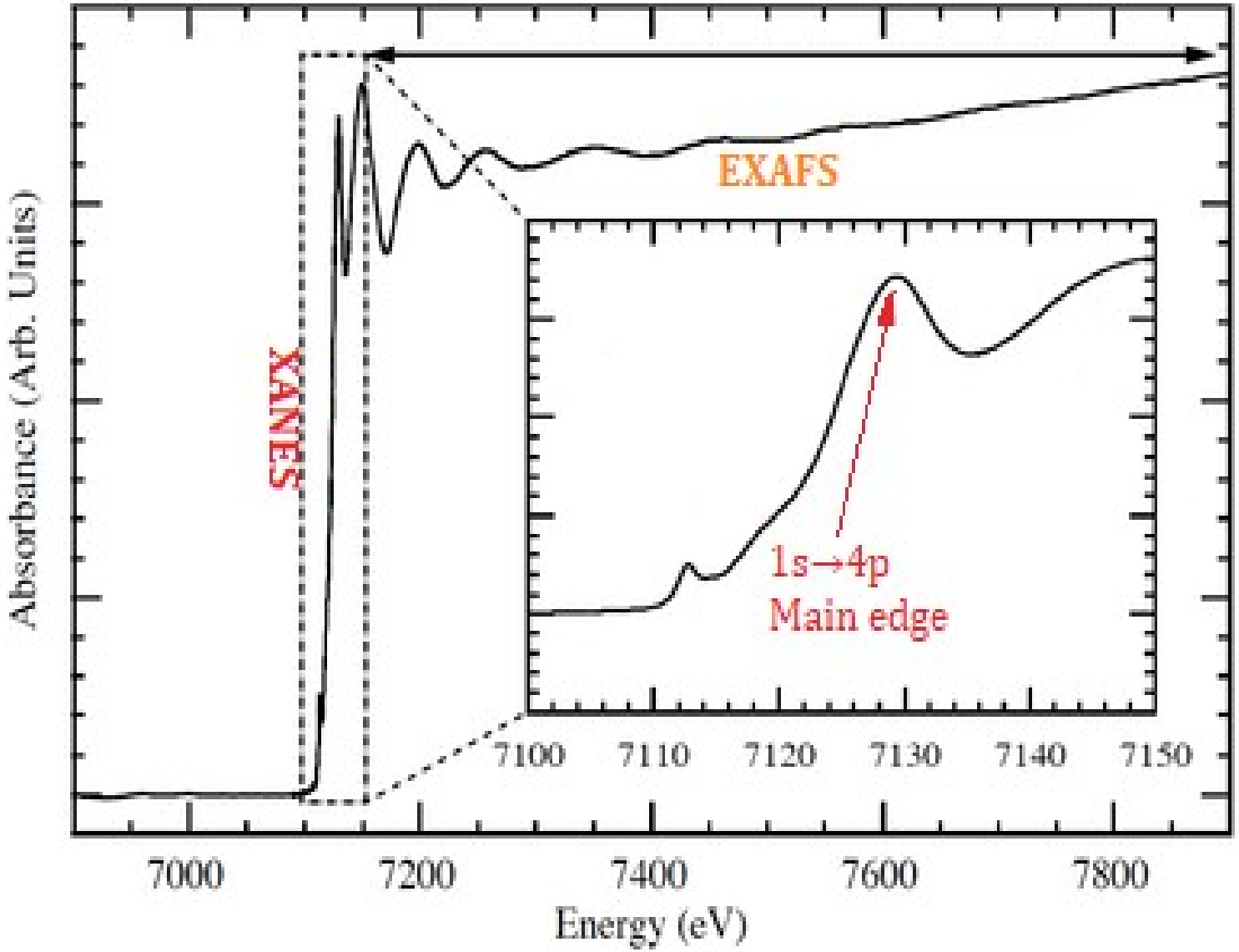

XANES spectroscopy on iron complexes

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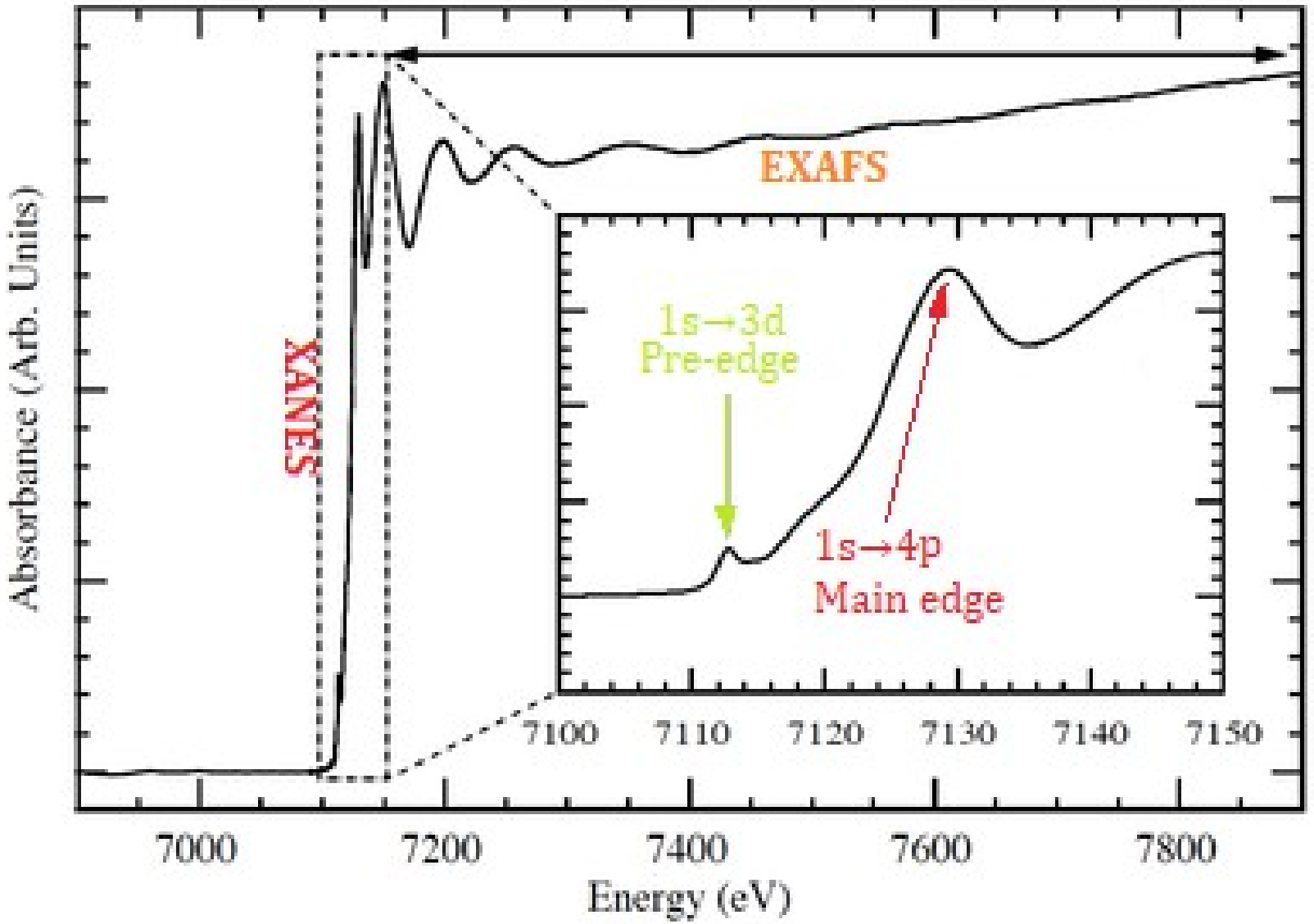

XANES spectroscopy on iron complexes

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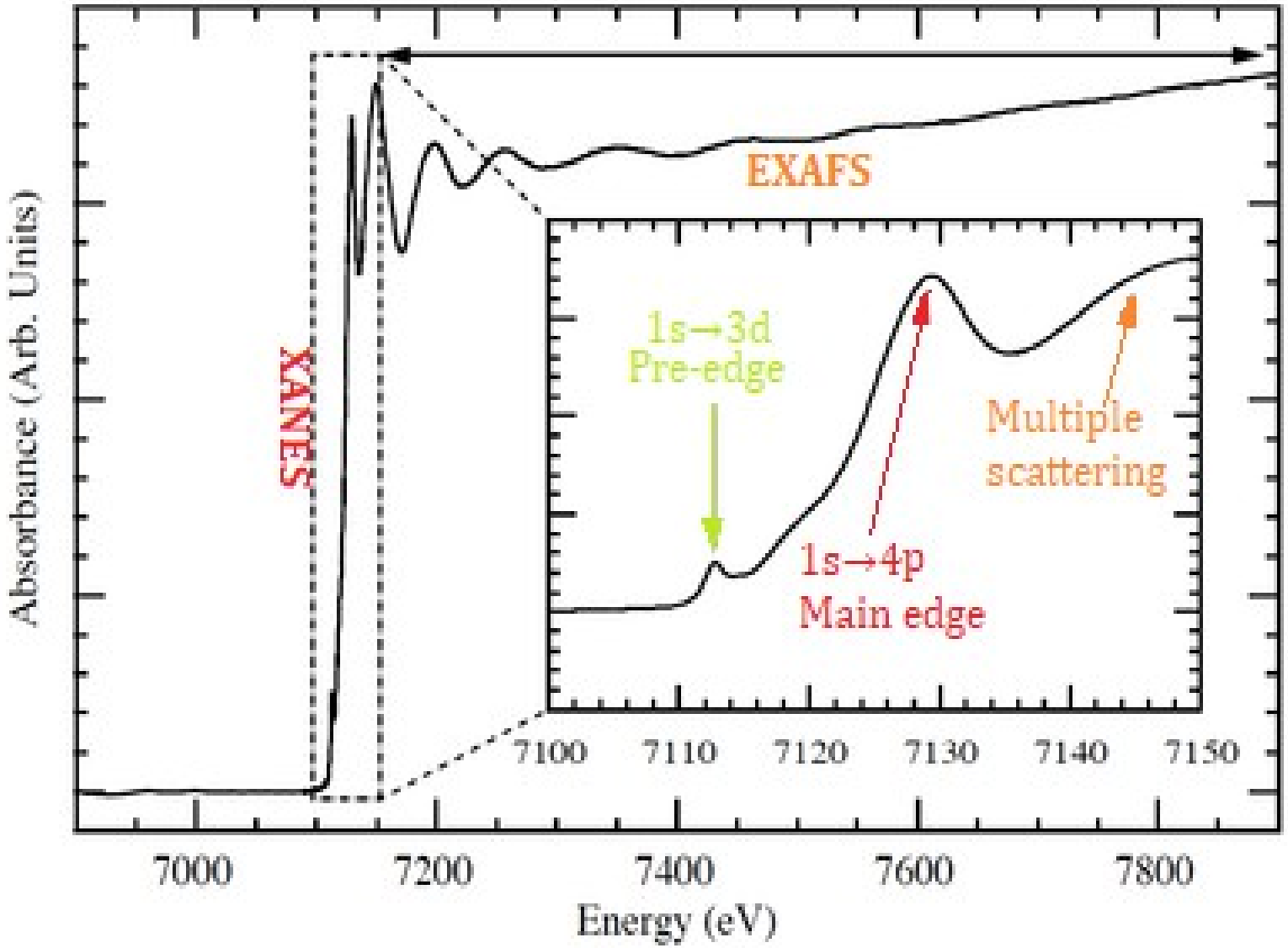

XANES spectroscopy on iron complexes

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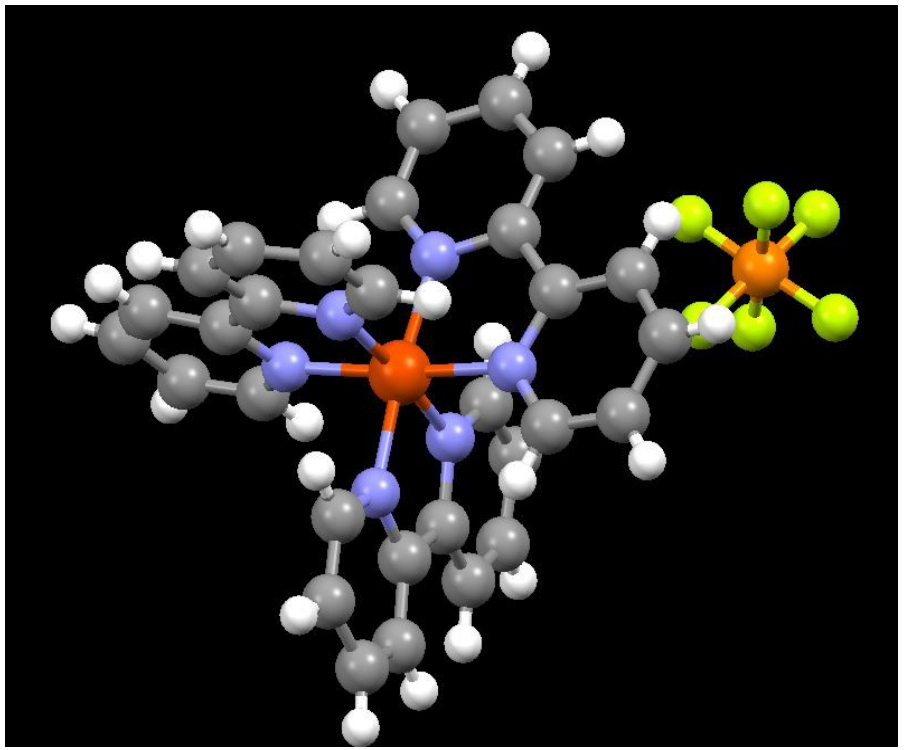
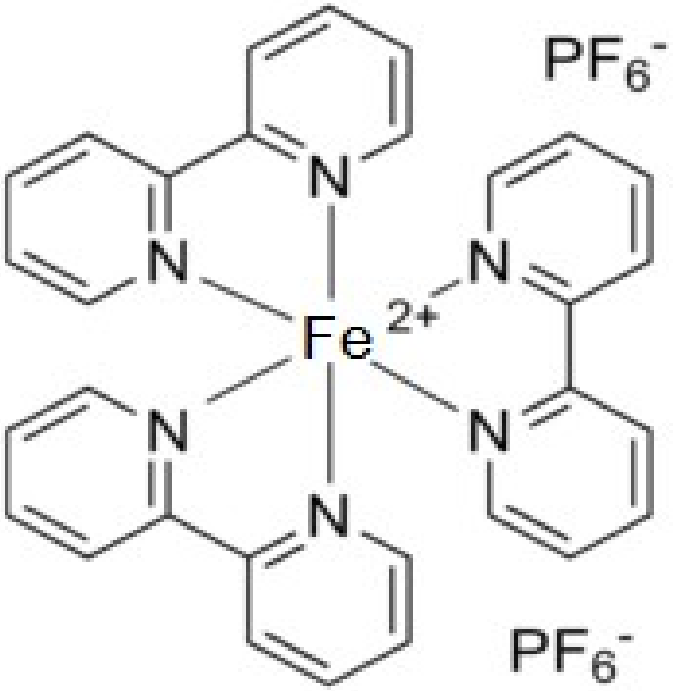
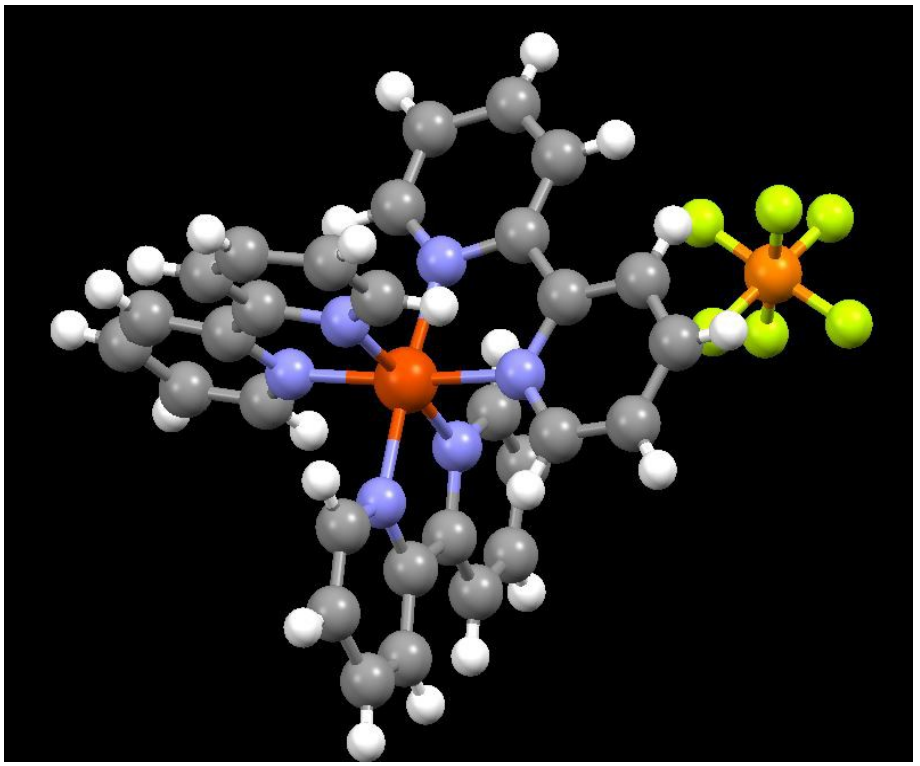
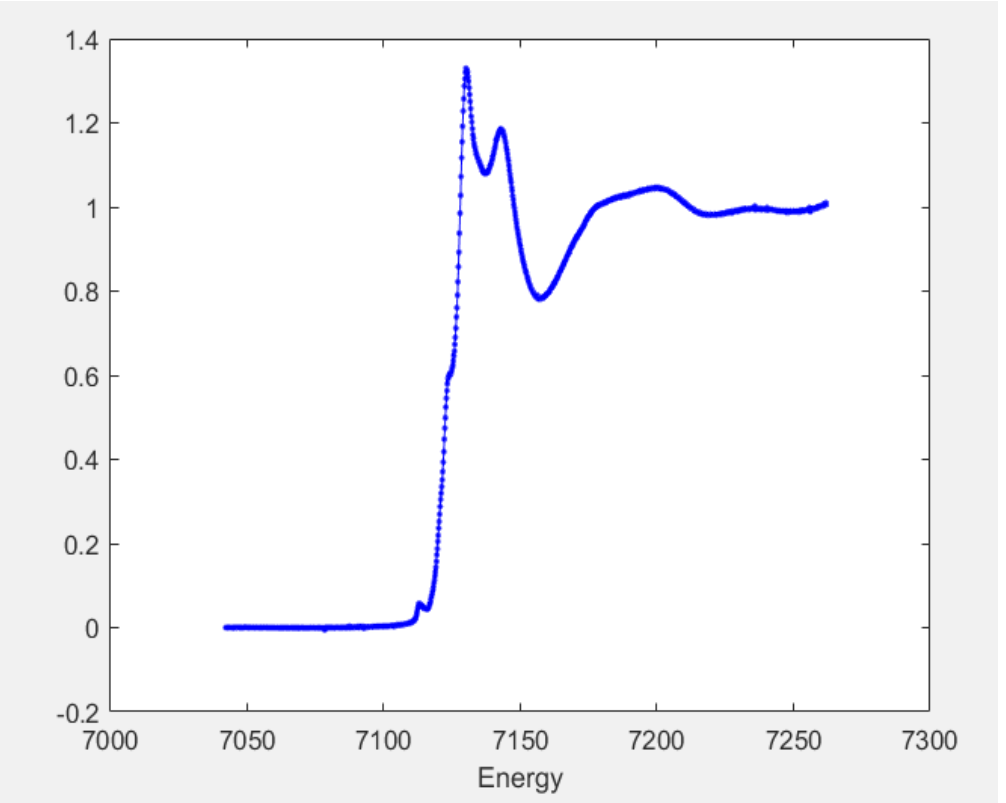




Experimental spectrum of iron tris-(2,2)bipyridine ($[Fe(bpy)_3]^{2+}$)

1.1. Introduction





Experimental spectrum of iron tris-(2,2)bipyridine ($FeBpy_3$)

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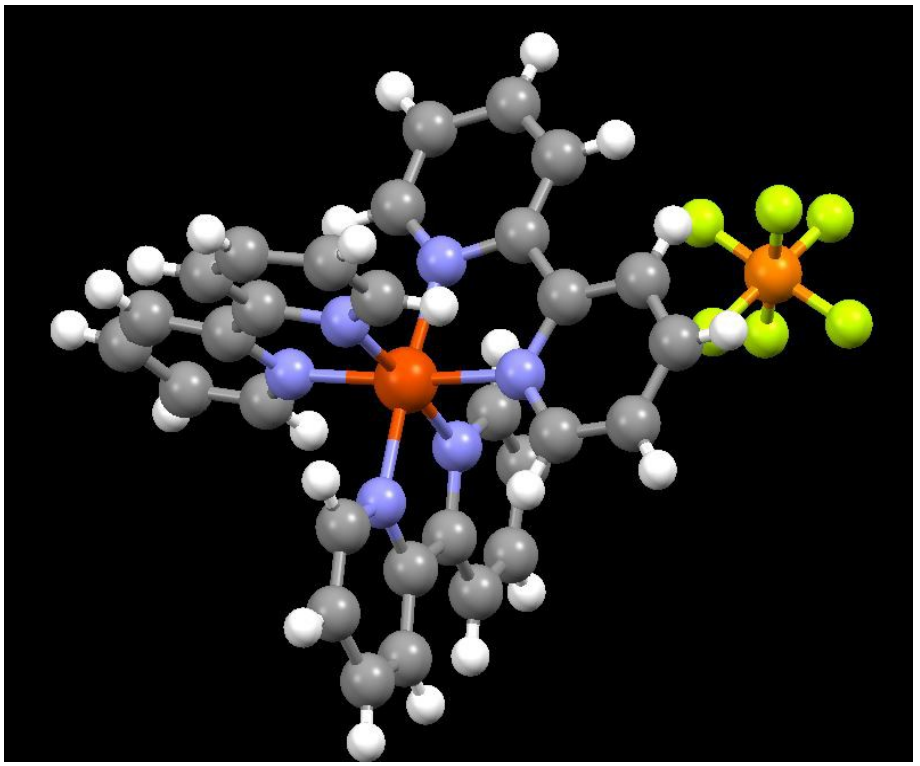
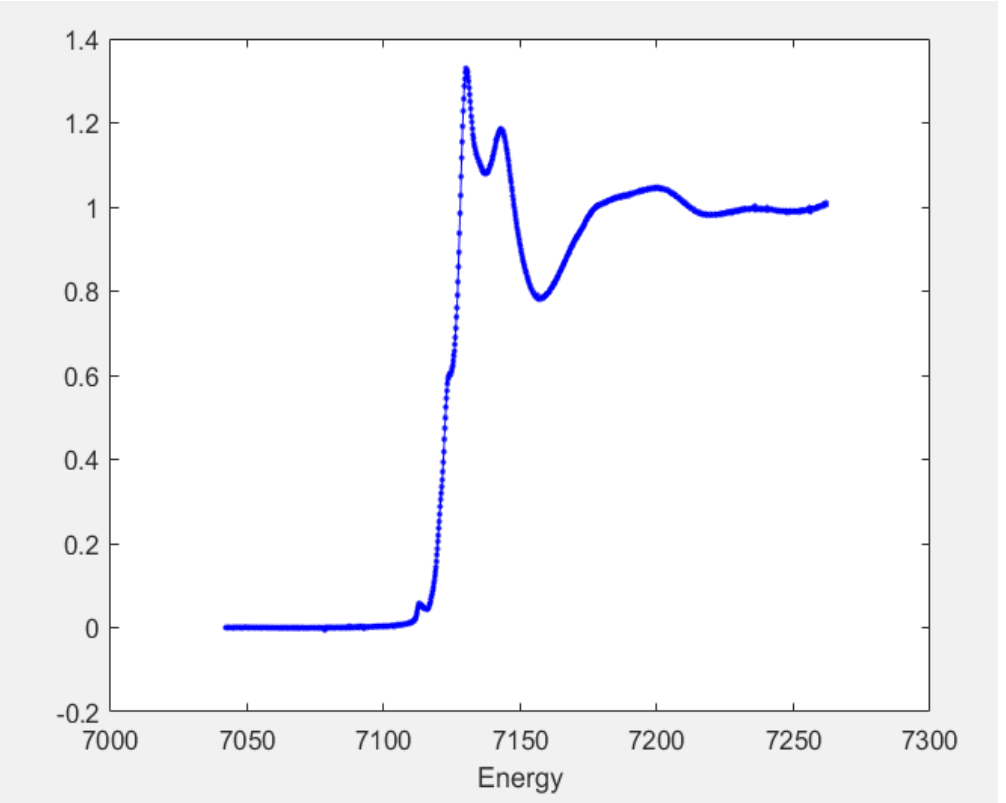
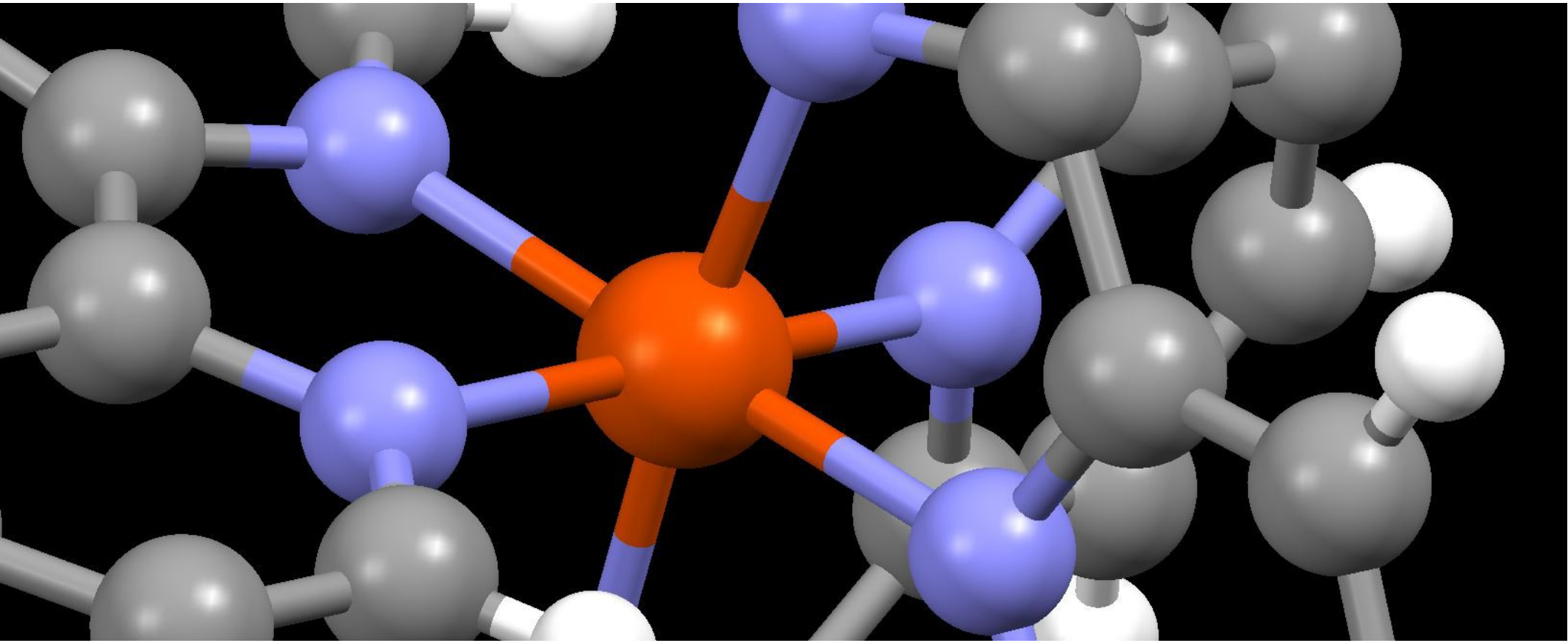




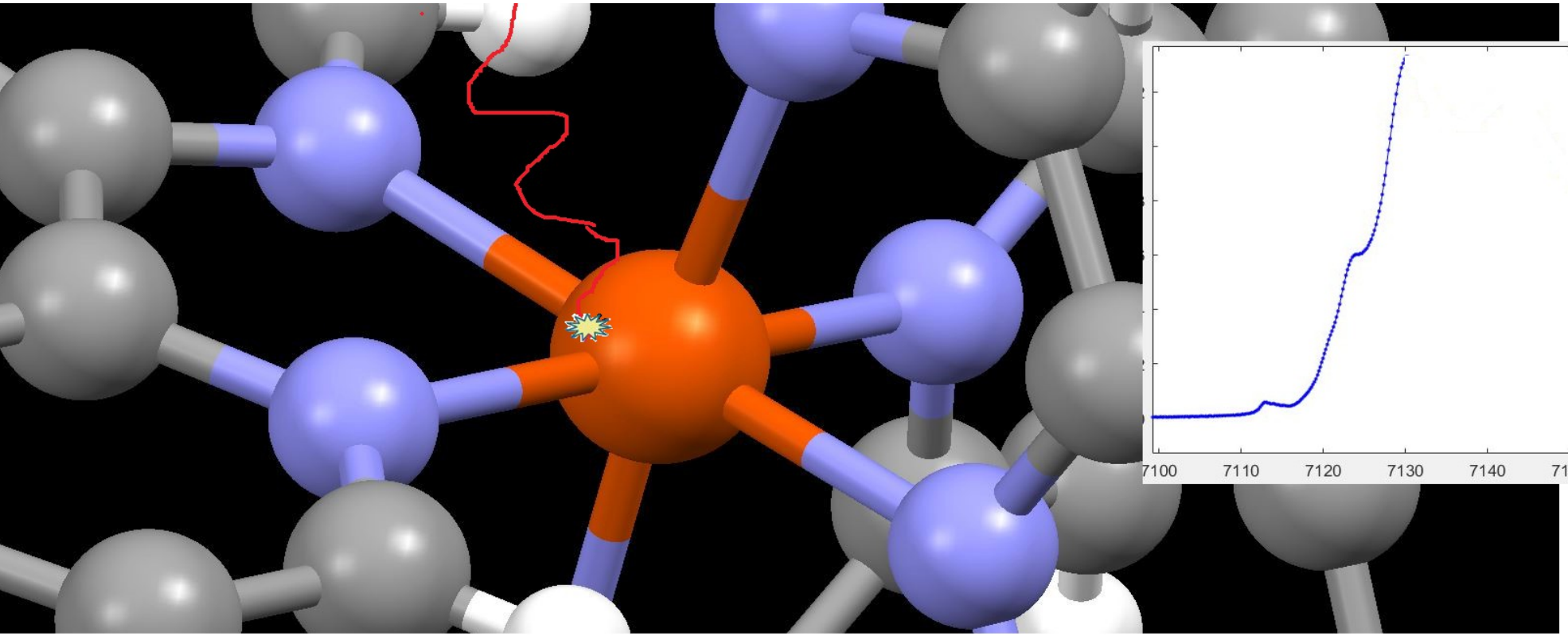
Experimental spectrum of iron tris-(2,2)bipyridine ($FeBpy_3$)

1.2. Why two peaks?



XANES spectroscopy on iron complexes

1.2. Why two peaks?



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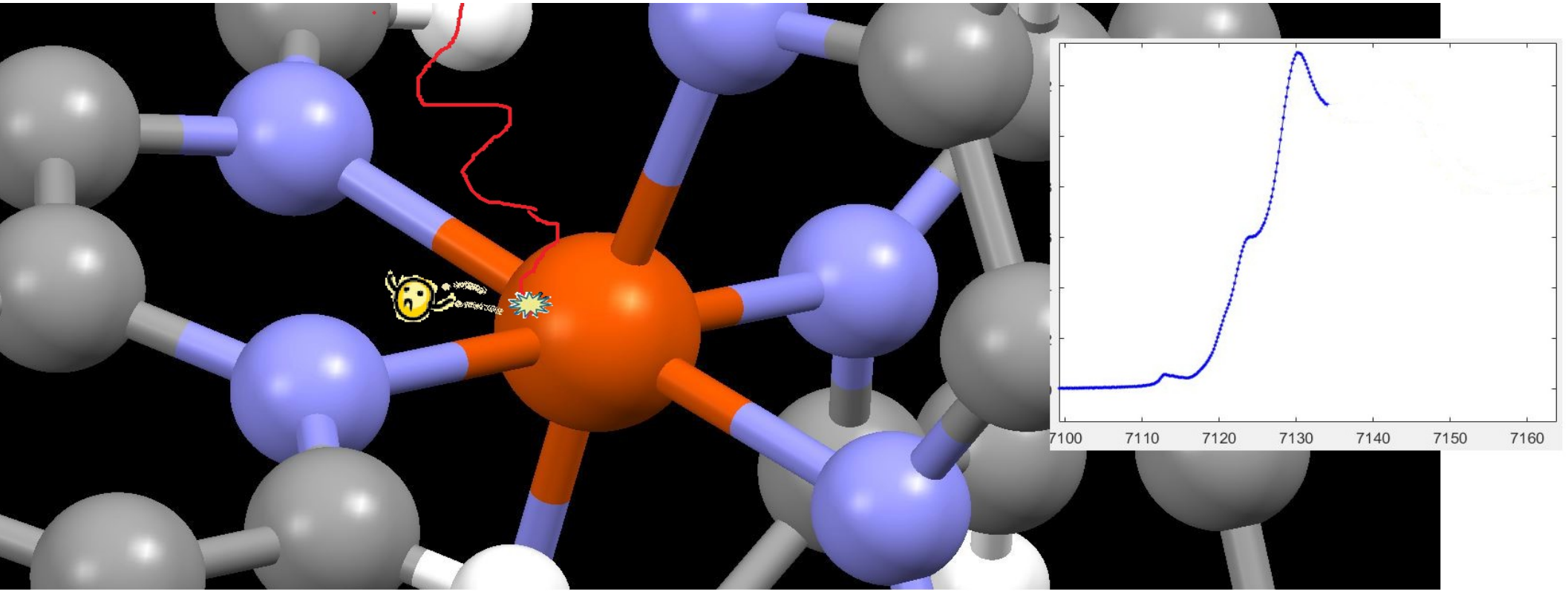

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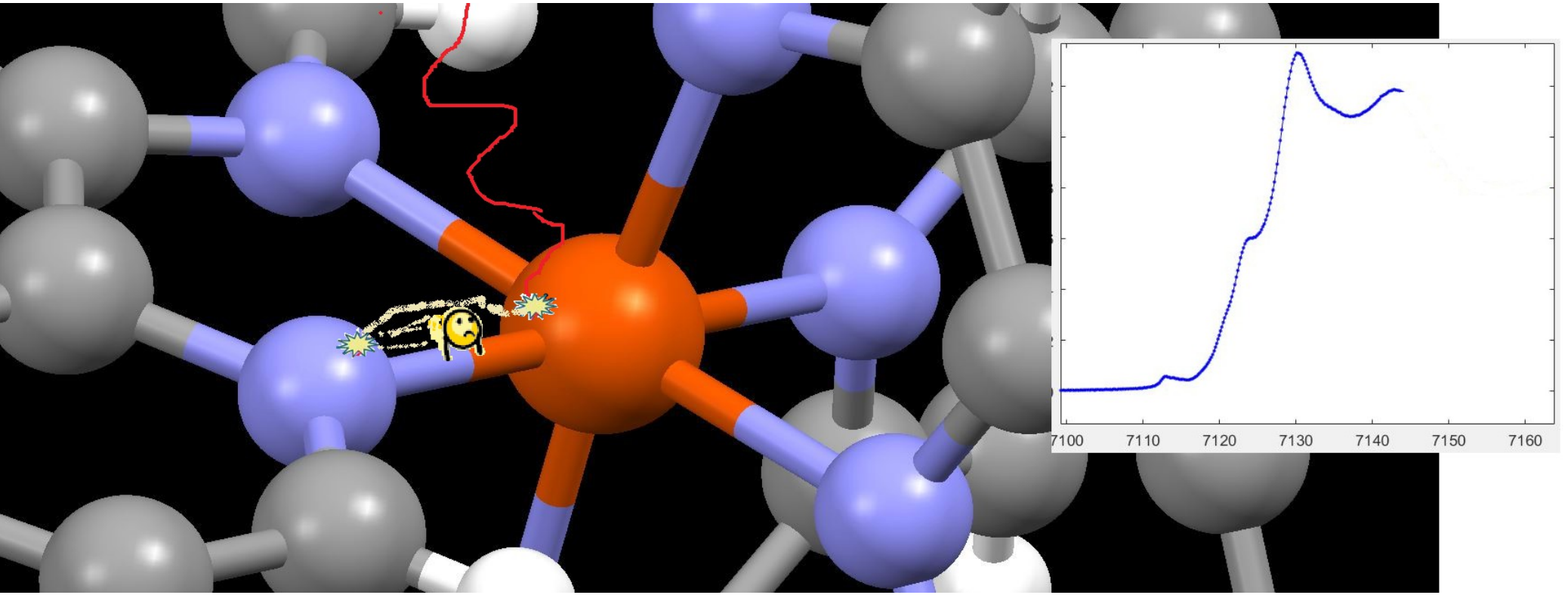

1.3. The EXAFS equation

By the Fermi golden rule $\mu(E) \propto |\langle i|\mathcal{H}|f\rangle|^2$

The final state $|f\rangle$ is perturbed by the neighboring atoms:

$$|f\rangle = |f_0\rangle + |\Delta f\rangle$$

Expanding,

$$\mu(E) \propto |\langle i|\mathcal{H}|f_0\rangle|^2 \left[1 + \langle i|\mathcal{H}|\Delta f\rangle \frac{\langle f_0|\mathcal{H}|i\rangle^*}{|\langle i|\mathcal{H}|f_0\rangle|^2} + C.C\right]$$

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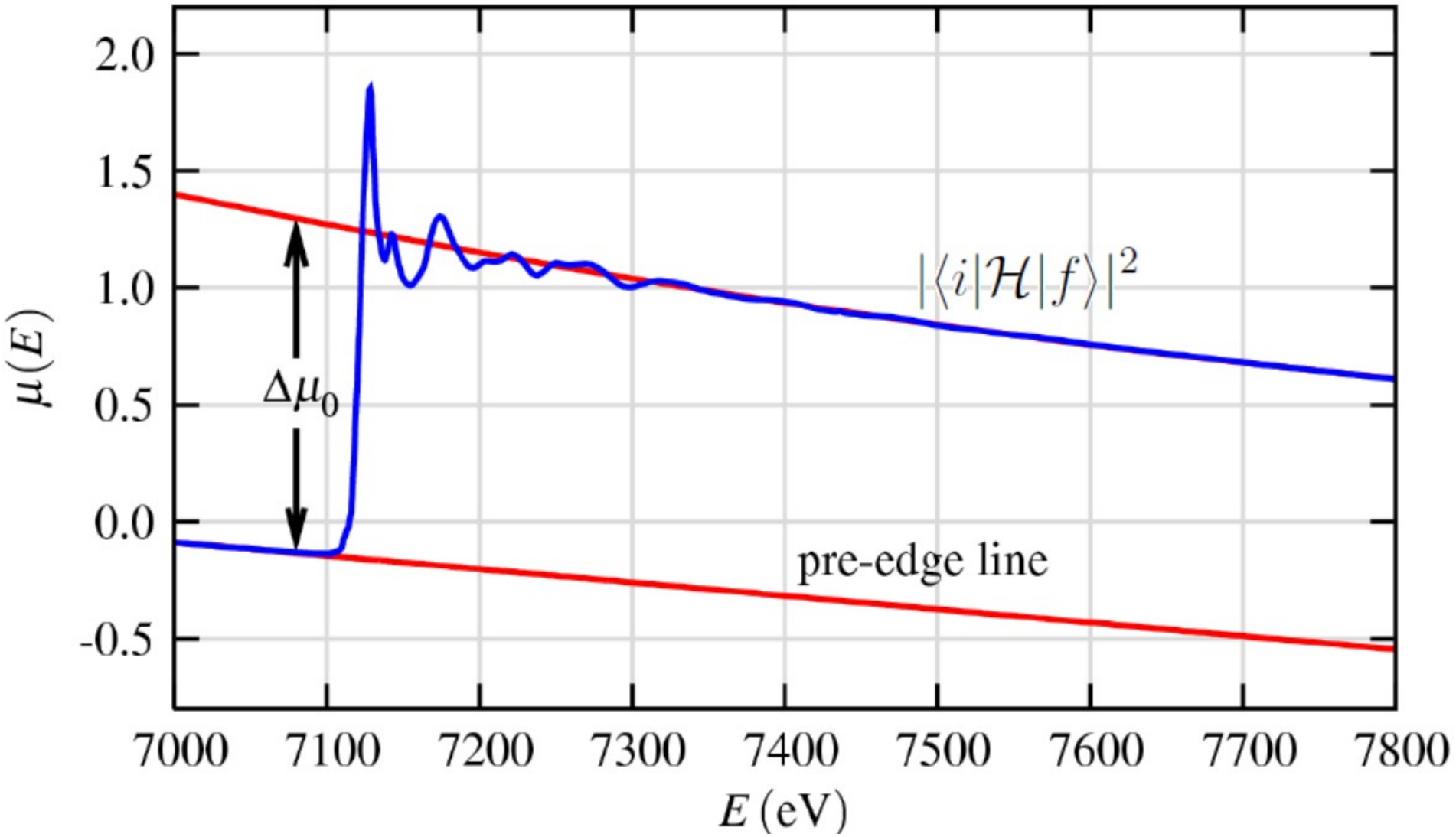
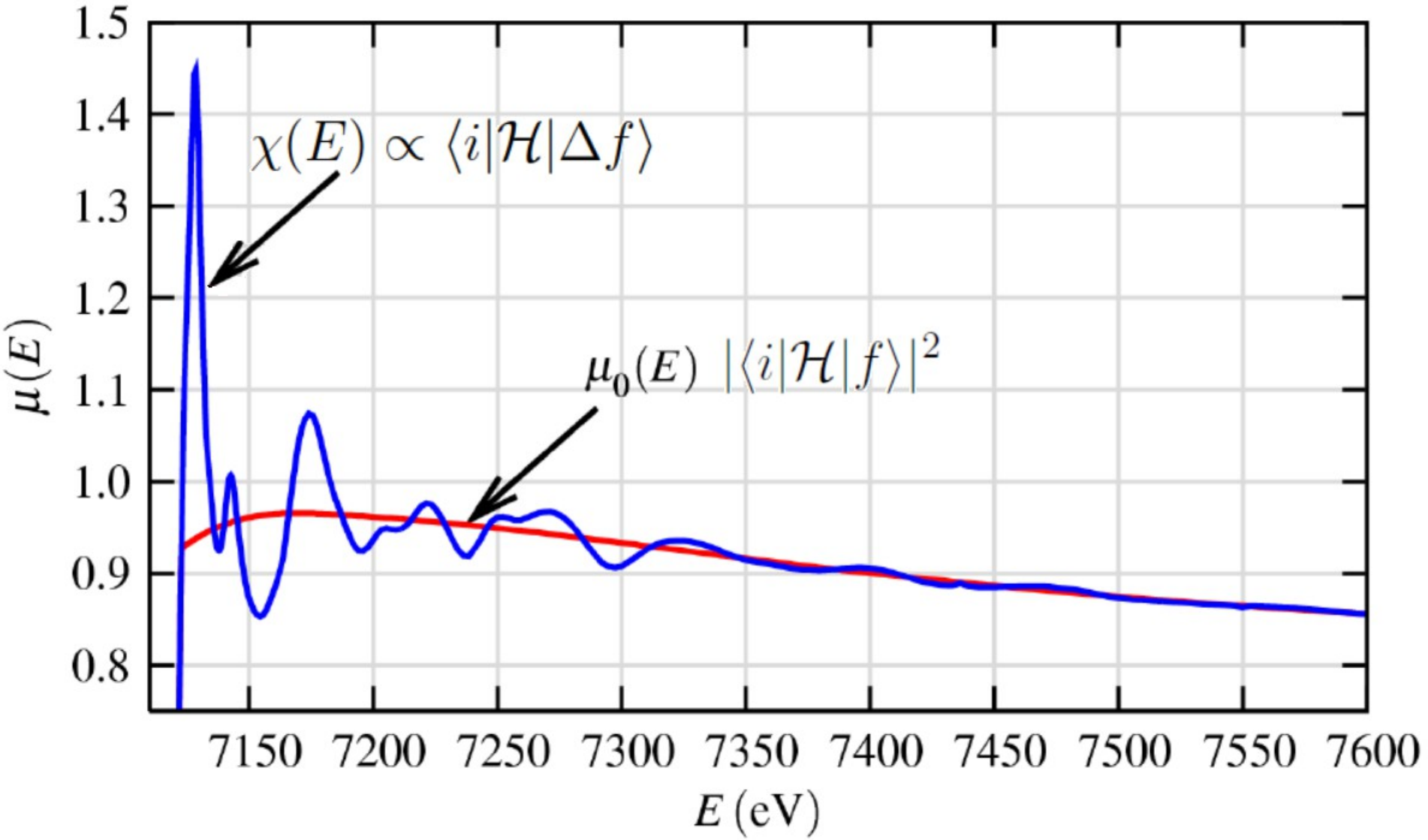
$$\mu(E) = \mu_0(E)[1 + \chi(E)]$$

1.3. The EXAFS equation



1.3. The EXAFS equation



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$$\chi(E) \propto \langle i|\mathcal{H}|\Delta f\rangle$$

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Using $\psi(k,r) = \frac{e^{ikr}}{kr}$ we obtain

$$\chi(k) \propto \psi_{\text{scatt}}(k, r=0) = \frac{e^{ikR}}{kR}\left[2kf(k)e^{i\delta(k)}\right]\frac{e^{ikR}}{kR} + C.C.$$

$$= \frac{f(k)}{kR^2}\sin[2kR + \delta(k)]$$

1.3. The EXAFS equation

$$\chi(E) \propto \langle i|\mathcal{H}|\Delta f\rangle$$

- Let the initial, buond state be δ(x)
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$$\chi(E) \propto \int dr\delta(r)e^{ikr}\psi_{\text{scatt}}(r) = \psi_{\text{scatt}}(0)$$

Using $\psi(k,r) = \frac{e^{ikr}}{kr}$ we obtain

$$\chi(k) = \sum_j \frac{N_j e^{-2k^2\sigma_j^2} f_j(k)}{kR_j^2} \sin[2kR_j + \delta_j(k)]$$

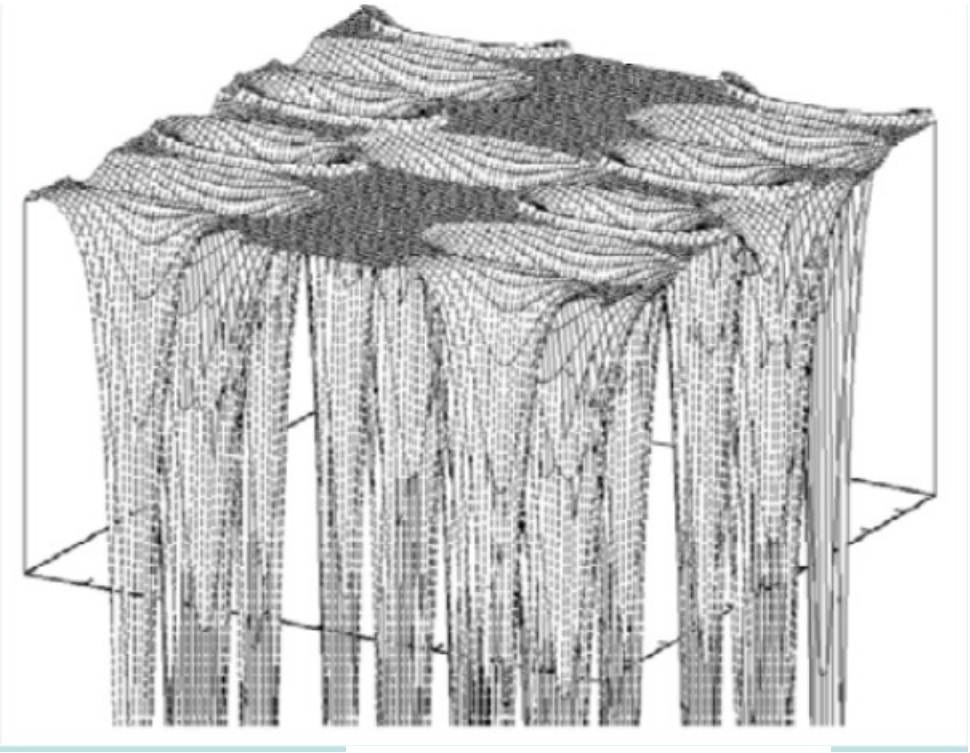
(summing over the atoms)

Part II – Theoretical calculations

2. Methods for calculation

"Muffin Tin" approximation:

- Constant potential outside the atoms
- Spherical symmetry inside the atoms



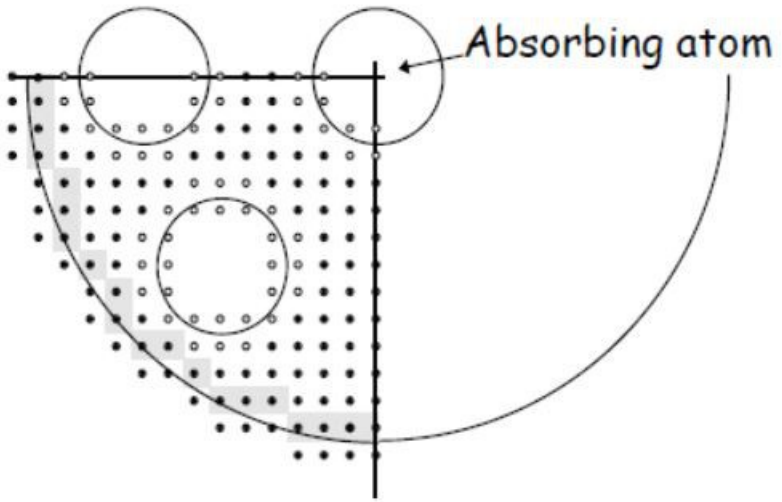
Solvable using Green funtionals

2. Methods for calculation

Finite Differences Method:

Approximates Schrödinger equation with discrete second derivative.

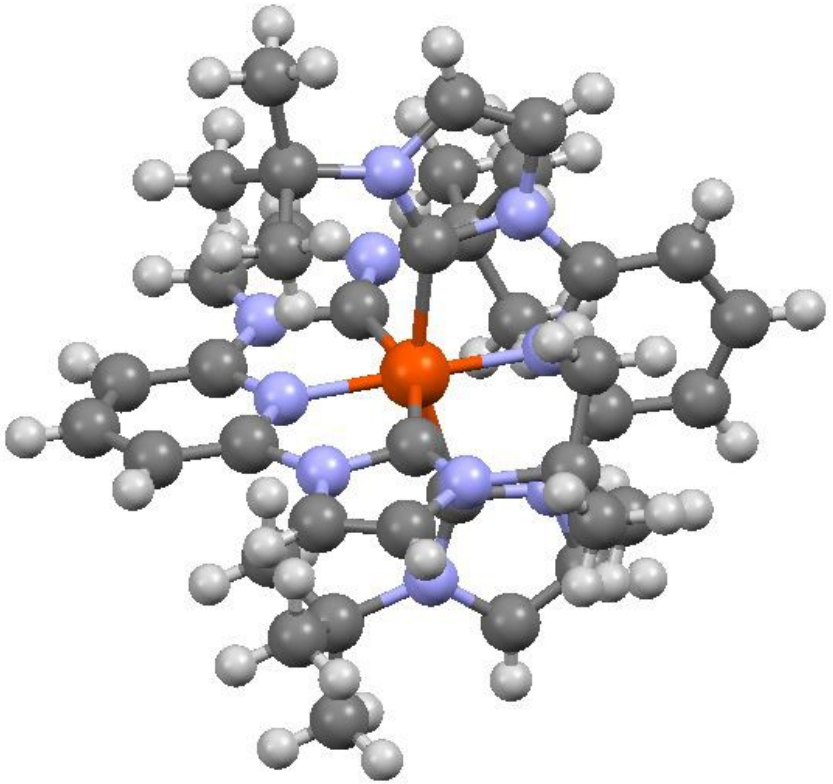
The problem is reduced to a linear system.

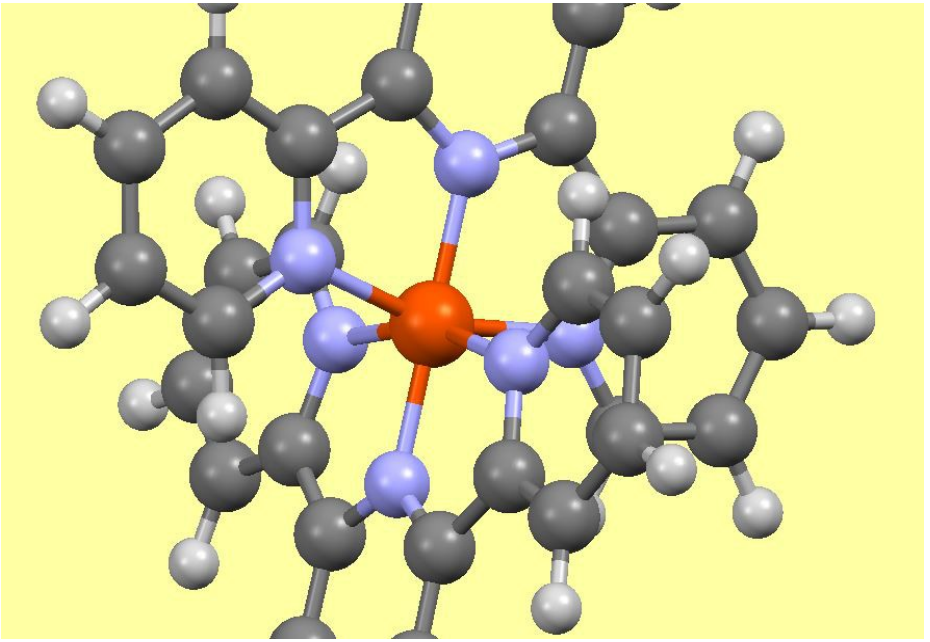


This method is more costly in terms of time (expecially with large cluster sizes), but allows an arrbitrary potential.

2. Methods for calculation

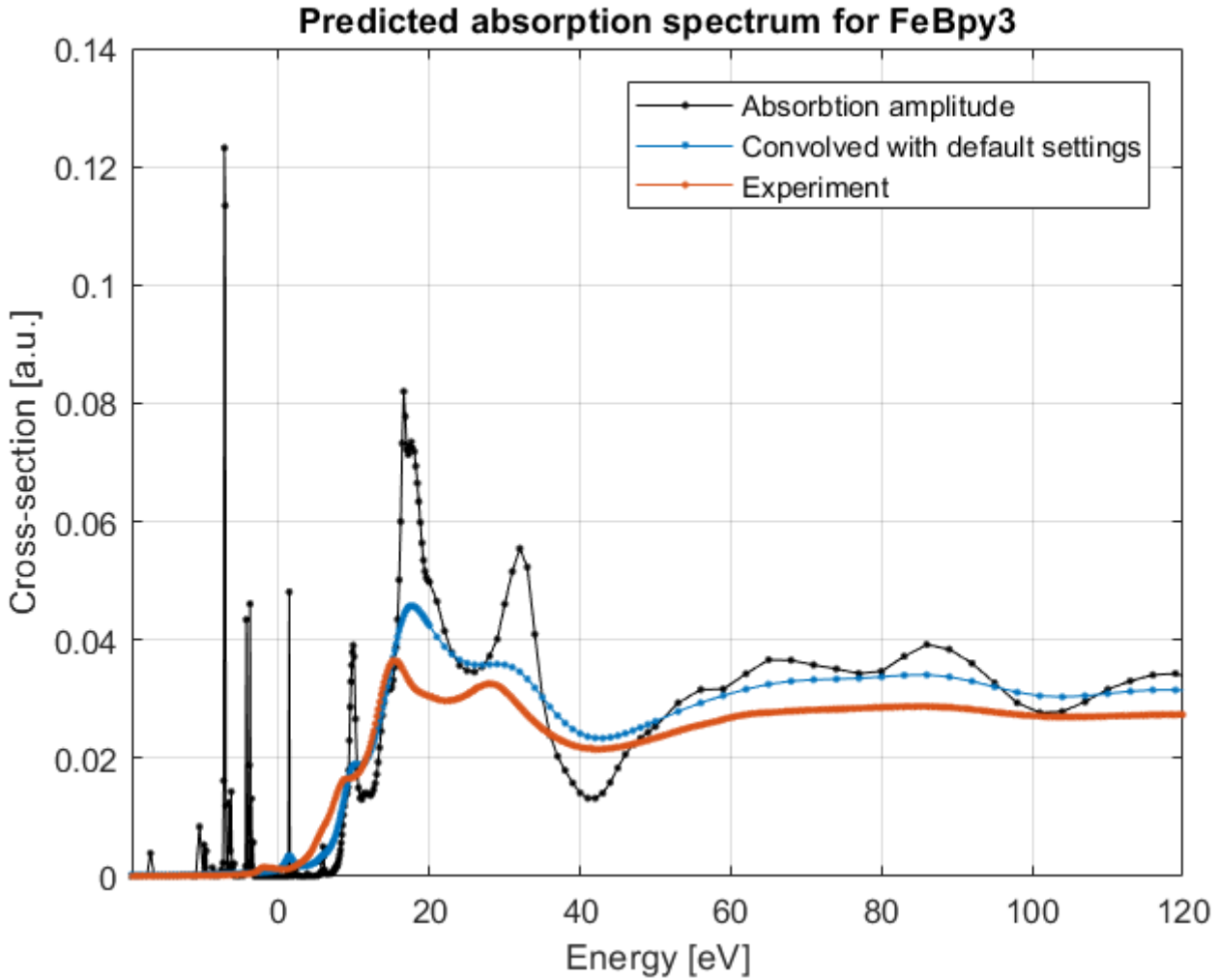
Once chosen the method, we have to specify the position of the atoms. This can be done via density functional theory (DFT), or with a crystallographic structure.





2. Methods for calculation

The resulting spectra has to be convolved.



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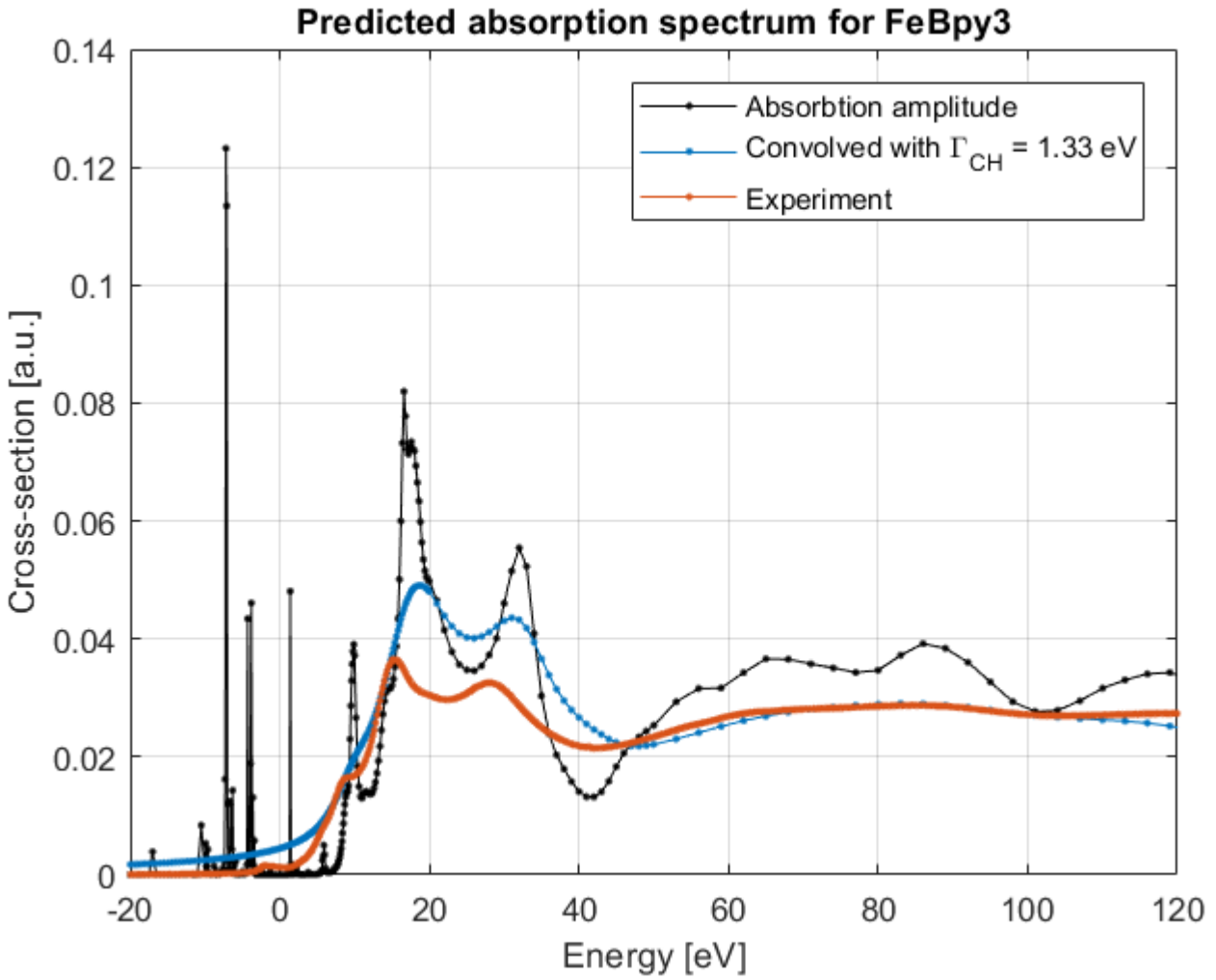
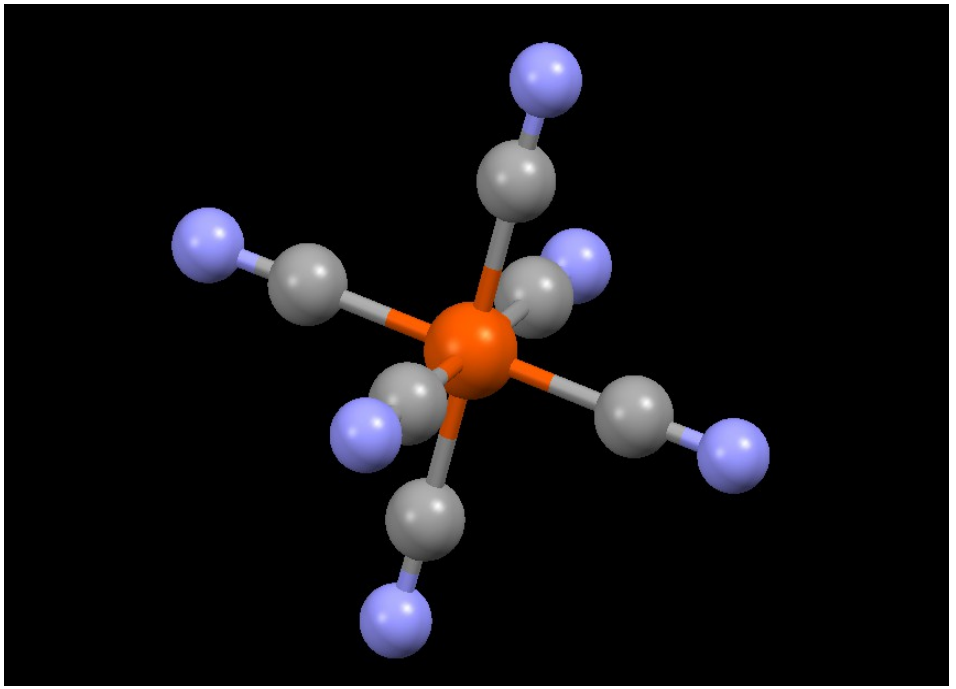
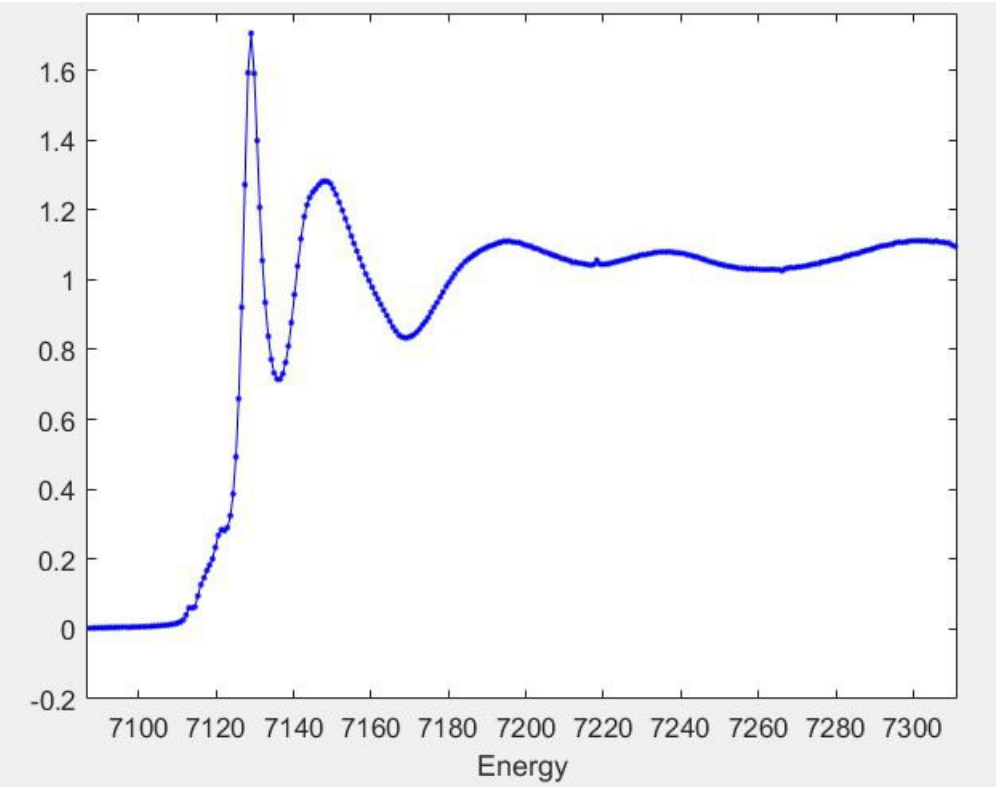


Part III – Examples

XANES spectroscopy on iron complexes

3.1. Example: $[Fe(CN)_6]^{4-}$

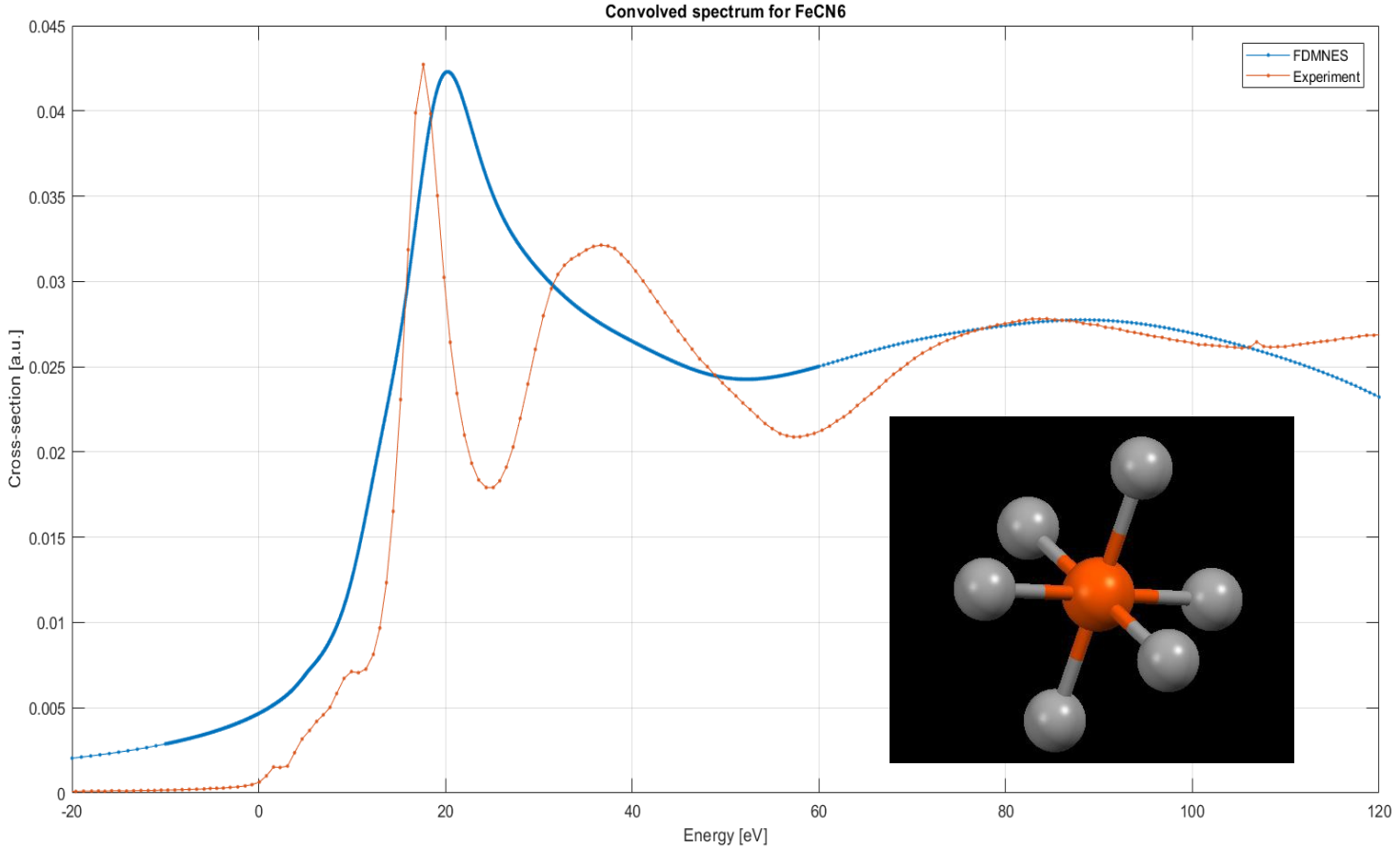




Experimental spectrum of iron hexacyanide $[Fe(CN)_6]^{4-}$

XANES spectroscopy on iron complexes

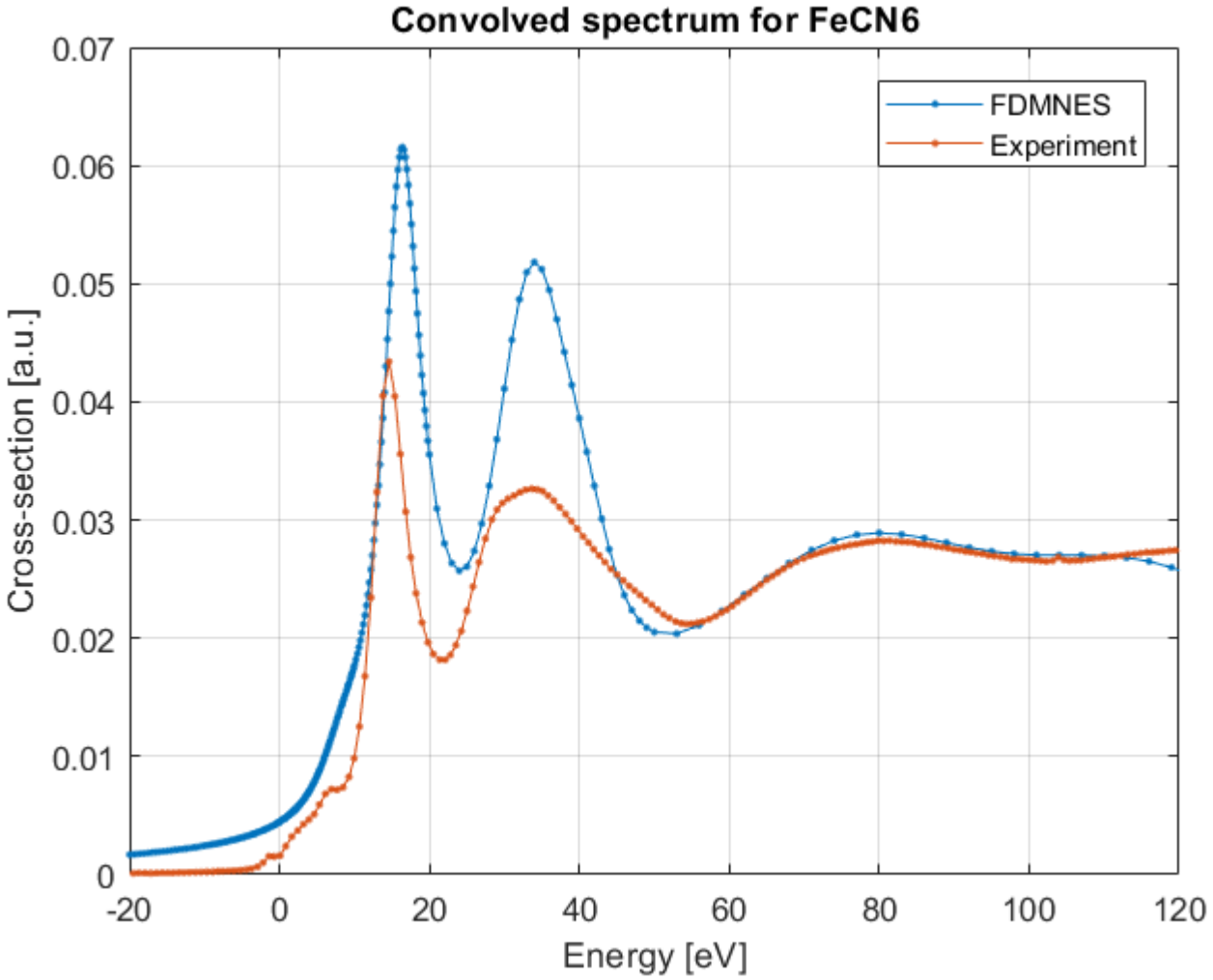
3.1. Example: $[Fe(CN)_6]^{4-}$

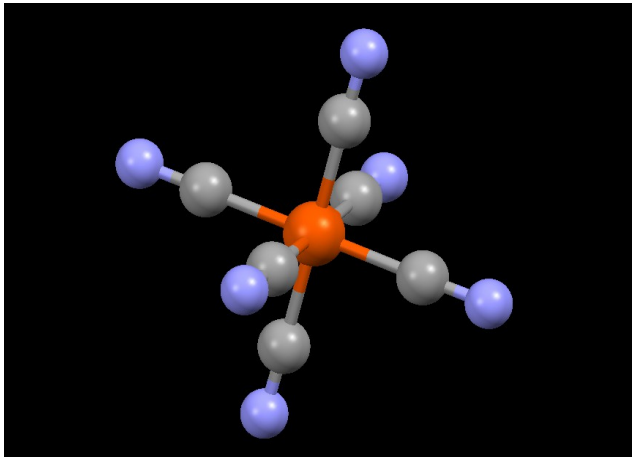


With only the first shell of C atoms, there is a single peak.

XANES spectroscopy on iron complexes

3.1. Example: $[Fe(CN)_6]^{4-}$

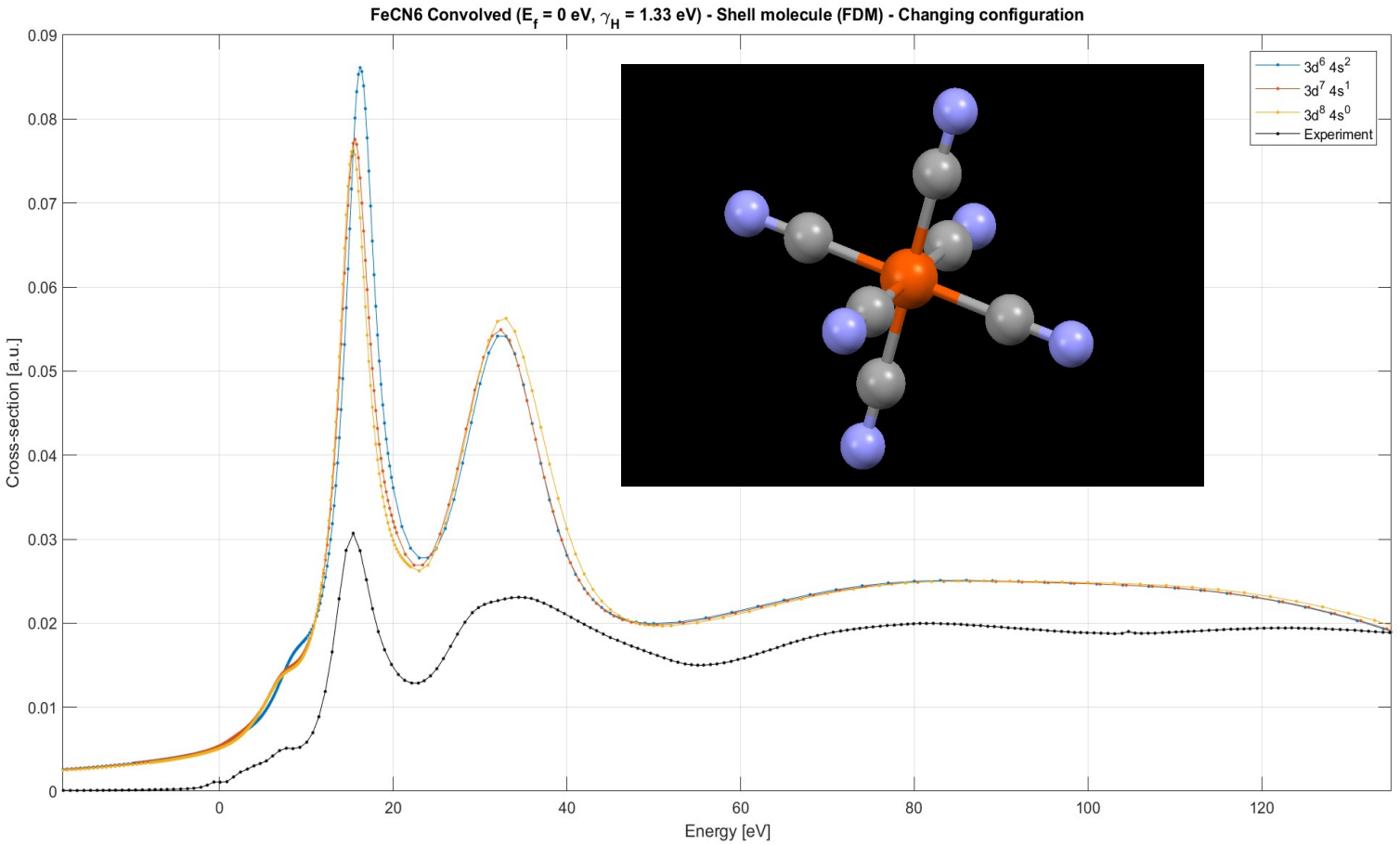




Look promising, but the amplitudes are too big

XANES spectroscopy on iron complexes

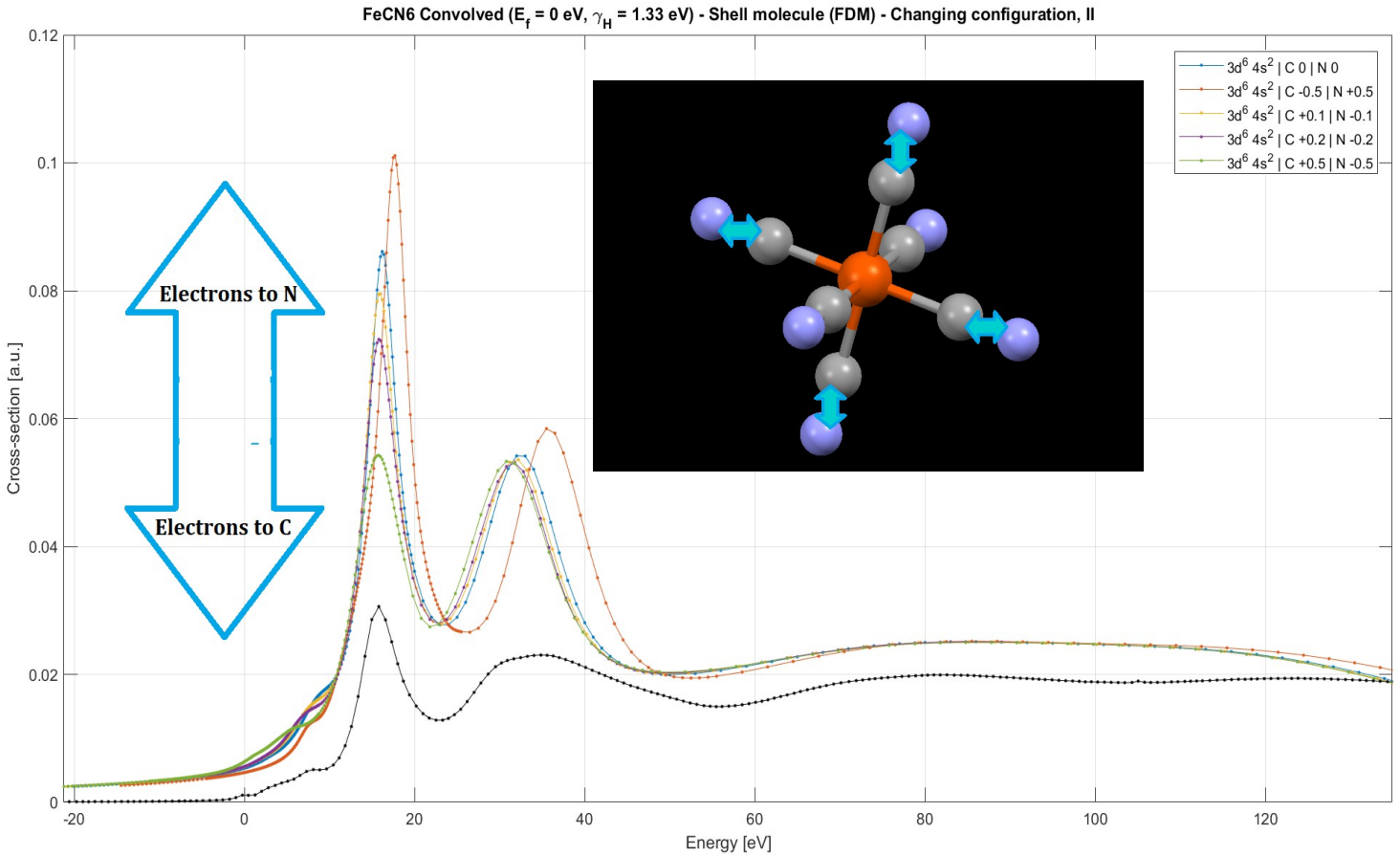
3.1. Example: $[Fe(CN)_6]^{4-}$



Changing the internal configuration of the Fe atom is not very effective

XANES spectroscopy on iron complexes

3.1. Example: $[Fe(CN)_6]^{4-}$



Moving electrons from N to C lowers the first peak...

XANES spectroscopy on iron complexes

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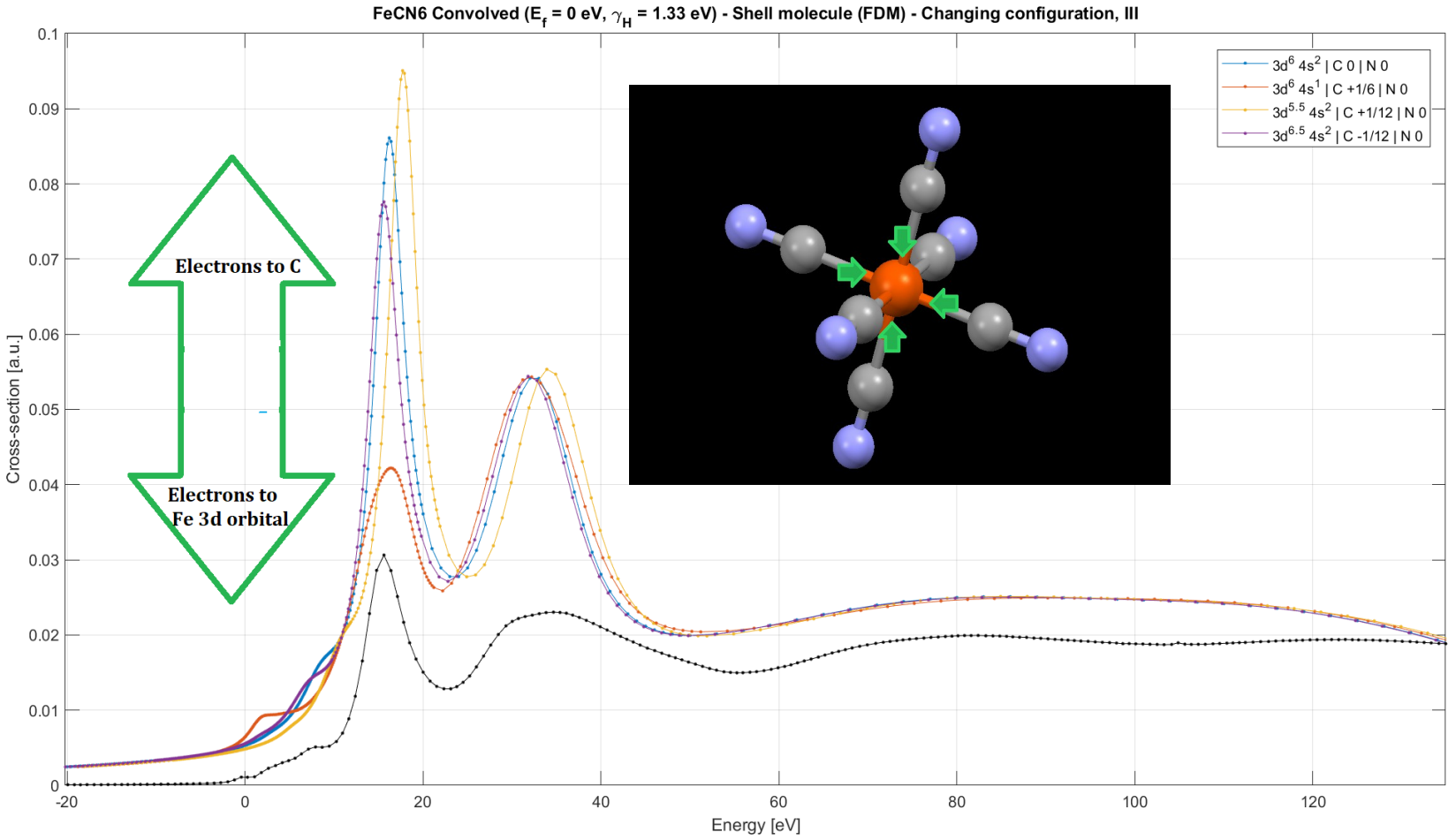
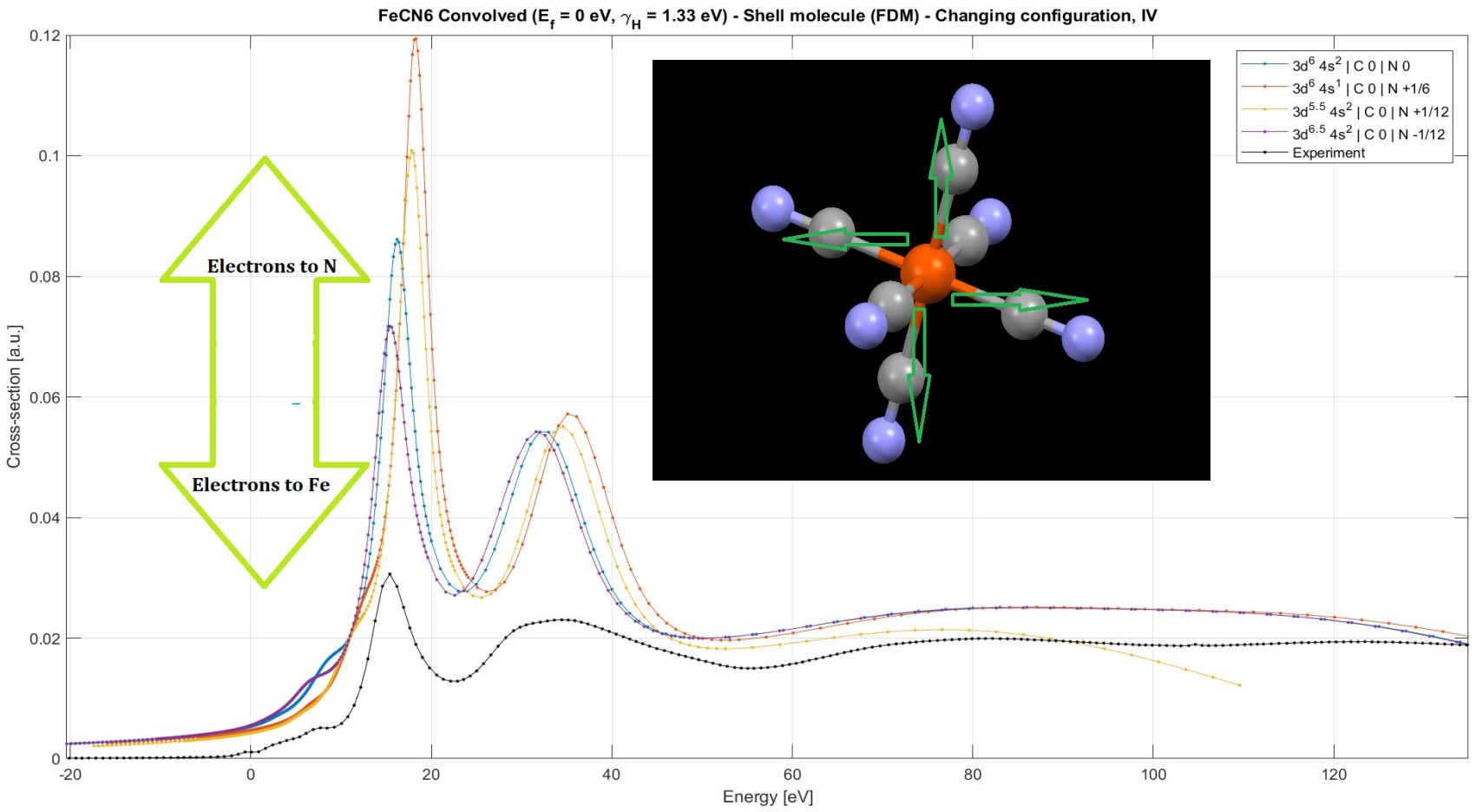


...and also moving electrons from C to N

XANES spectroscopy on iron complexes

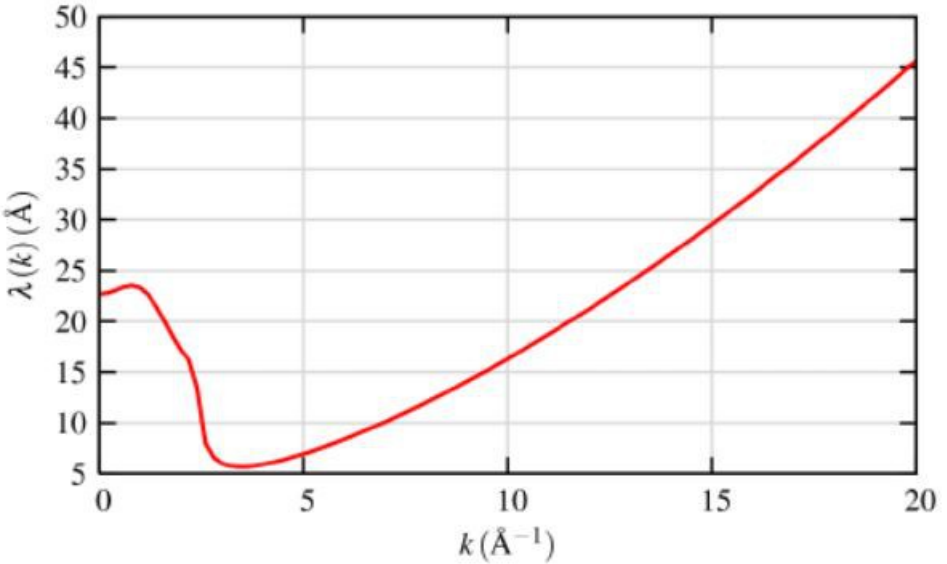
3.1. Example: $[Fe(CN)_6]^{4-}$



Electron transfer from N to Fe shows the same trend

3.1. Example: $[Fe(CN)_6]^{4-}$

The second peak is inamovable; the only way to vary it is to change the convolution.

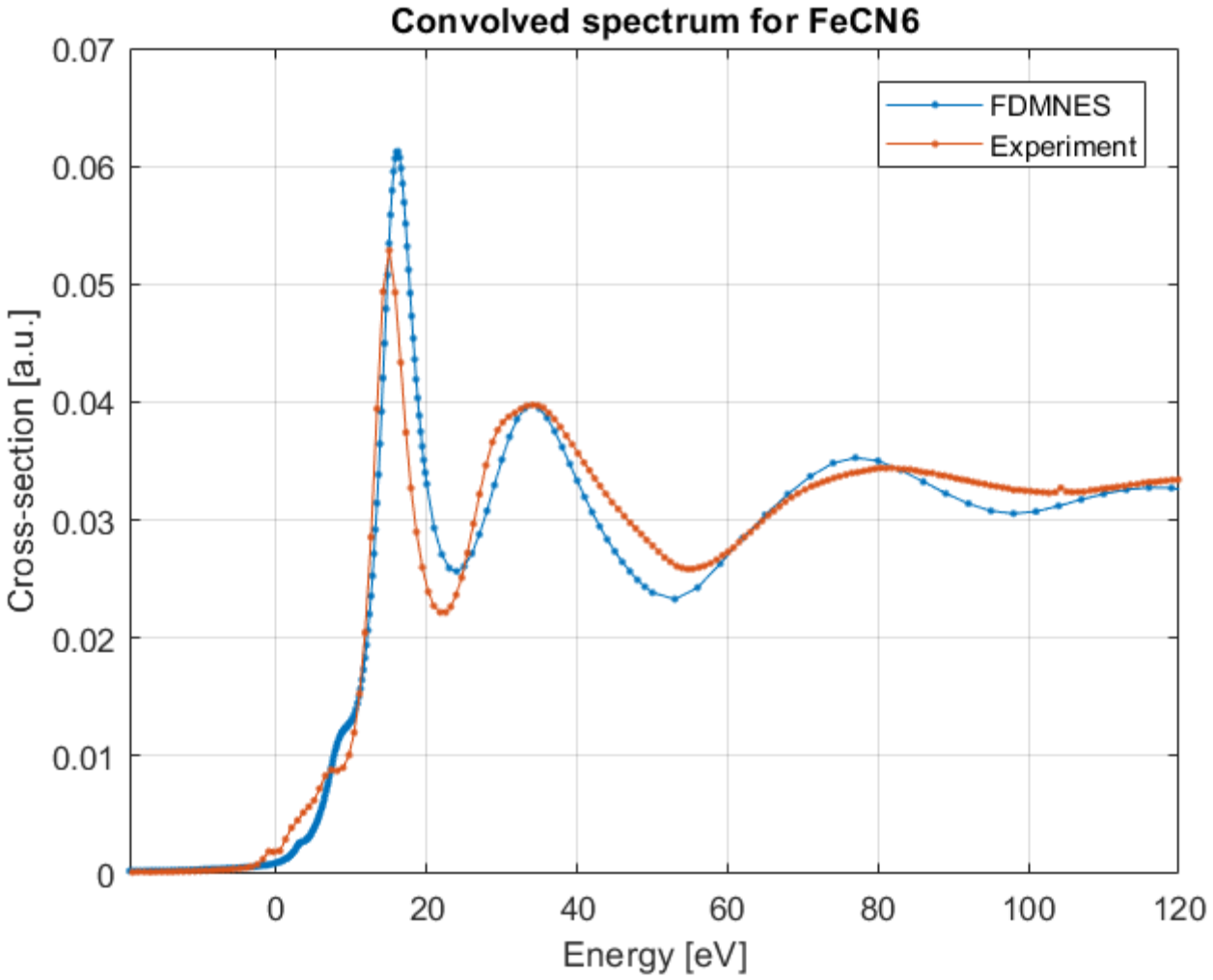


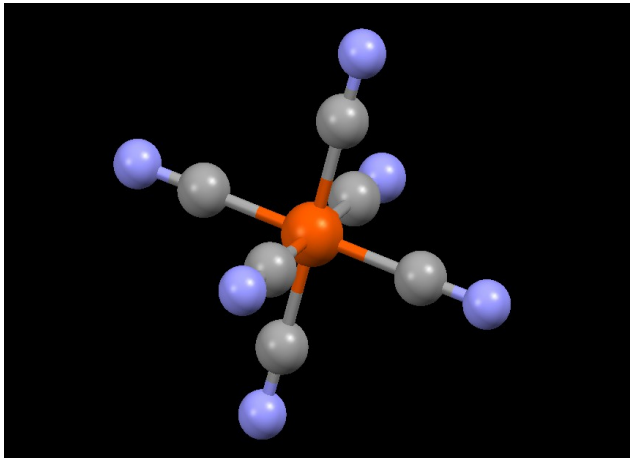
Mean free path of photoelectrons (from Newville)

Inelastic processes absorb emitted electrons
→ Additional broadening

XANES spectroscopy on iron complexes

3.1. Example: $[Fe(CN)_6]^{4-}$

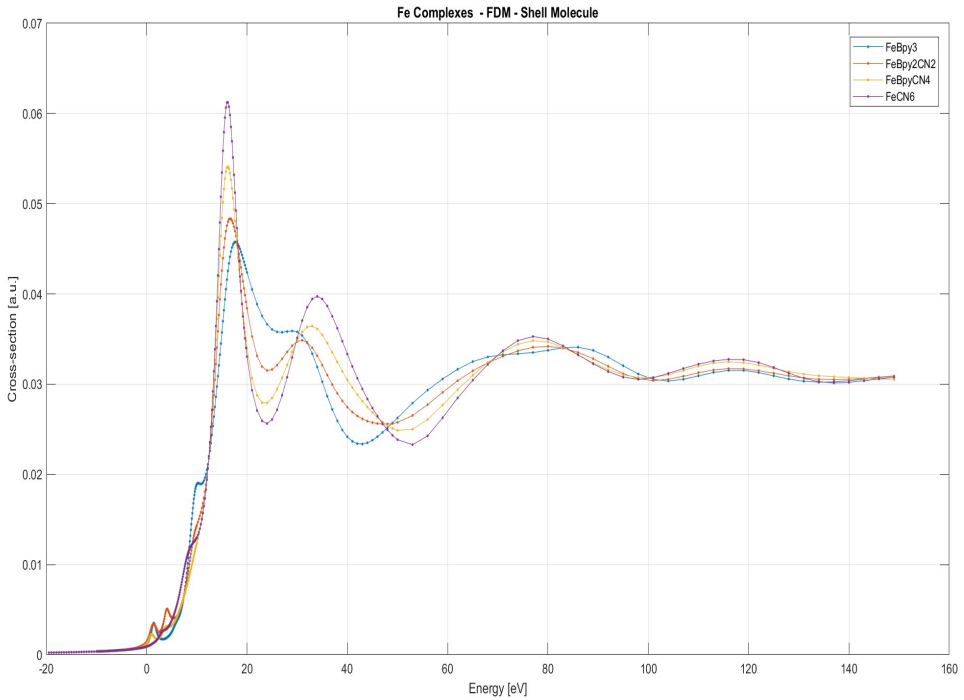


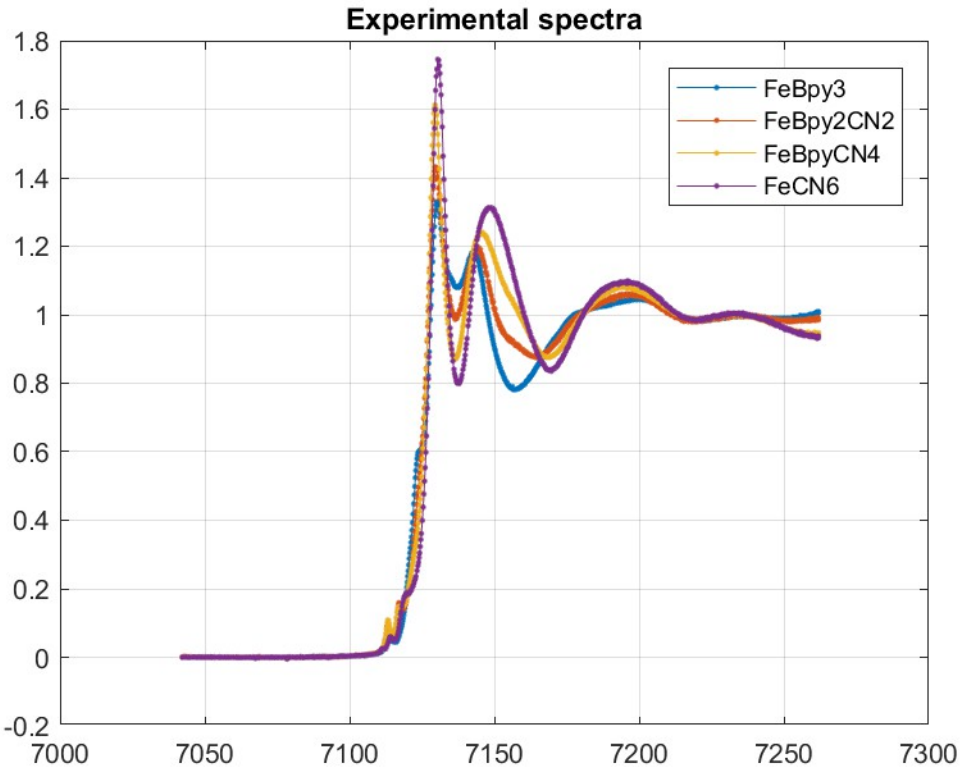


Result with the correct convolution (no charge transfer)

XANES spectroscopy on iron complexes

3.2. Iron bipyridine-cyanide series

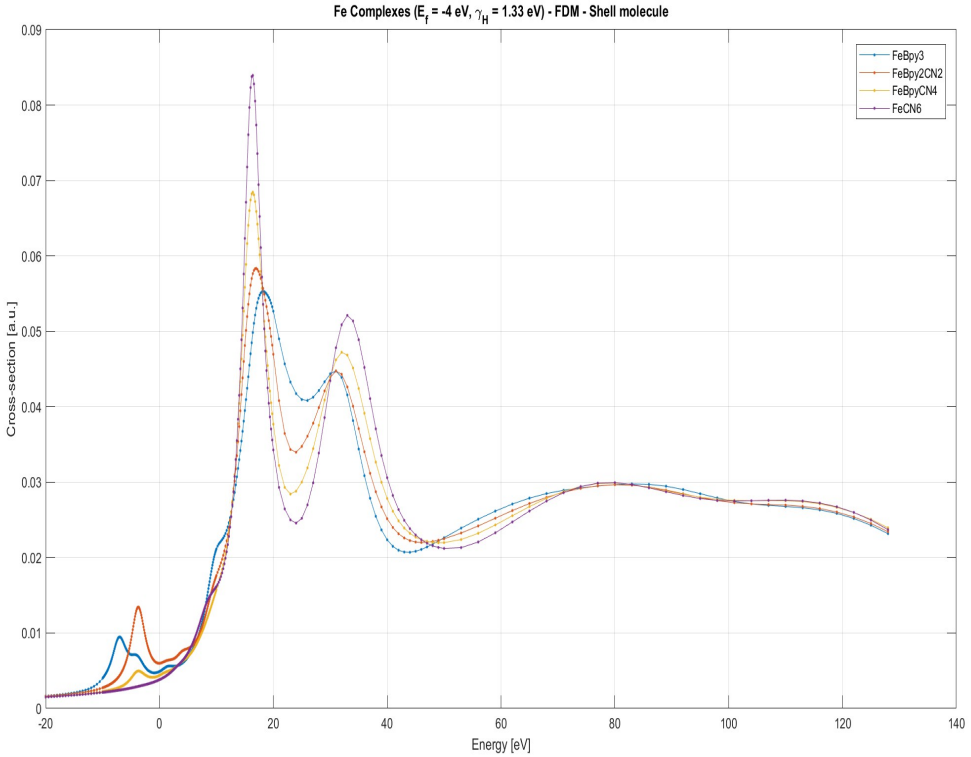


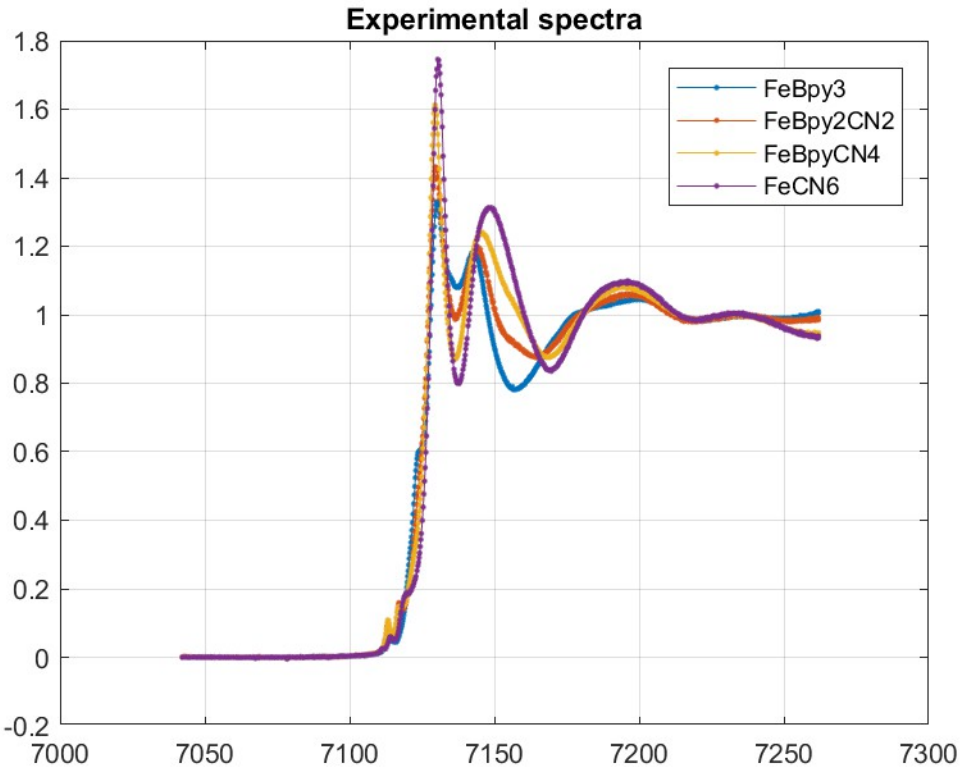


Convolution with default parameters for inelastic processes

XANES spectroscopy on iron complexes

3.2. Iron bipyridine-cyanide series

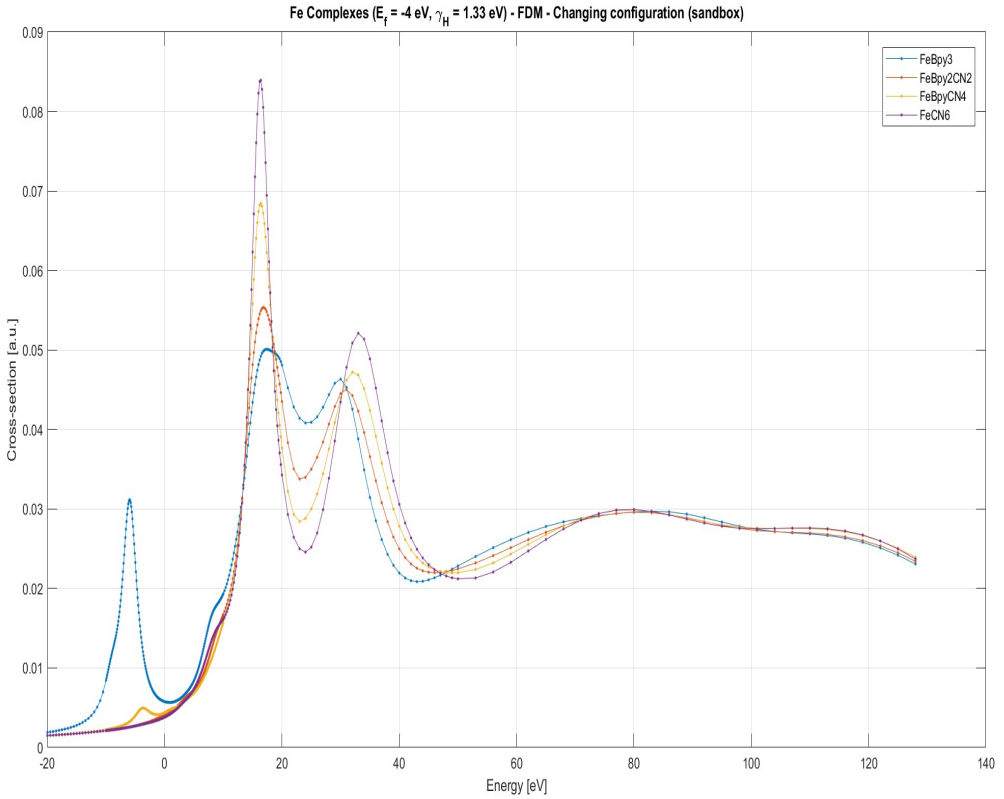


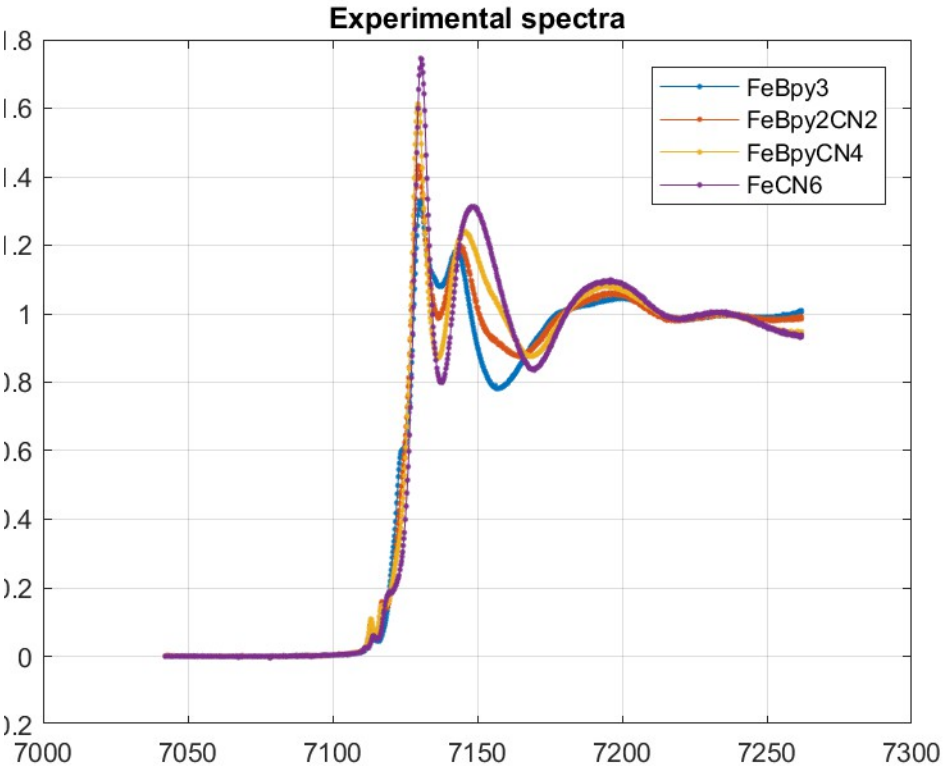


Convolution with core hole broadening (Γ = 1.33 eV) in the XANES region

XANES spectroscopy on iron complexes

3.2. Iron bipyridine-cyanide series





The same, with some electron transfer