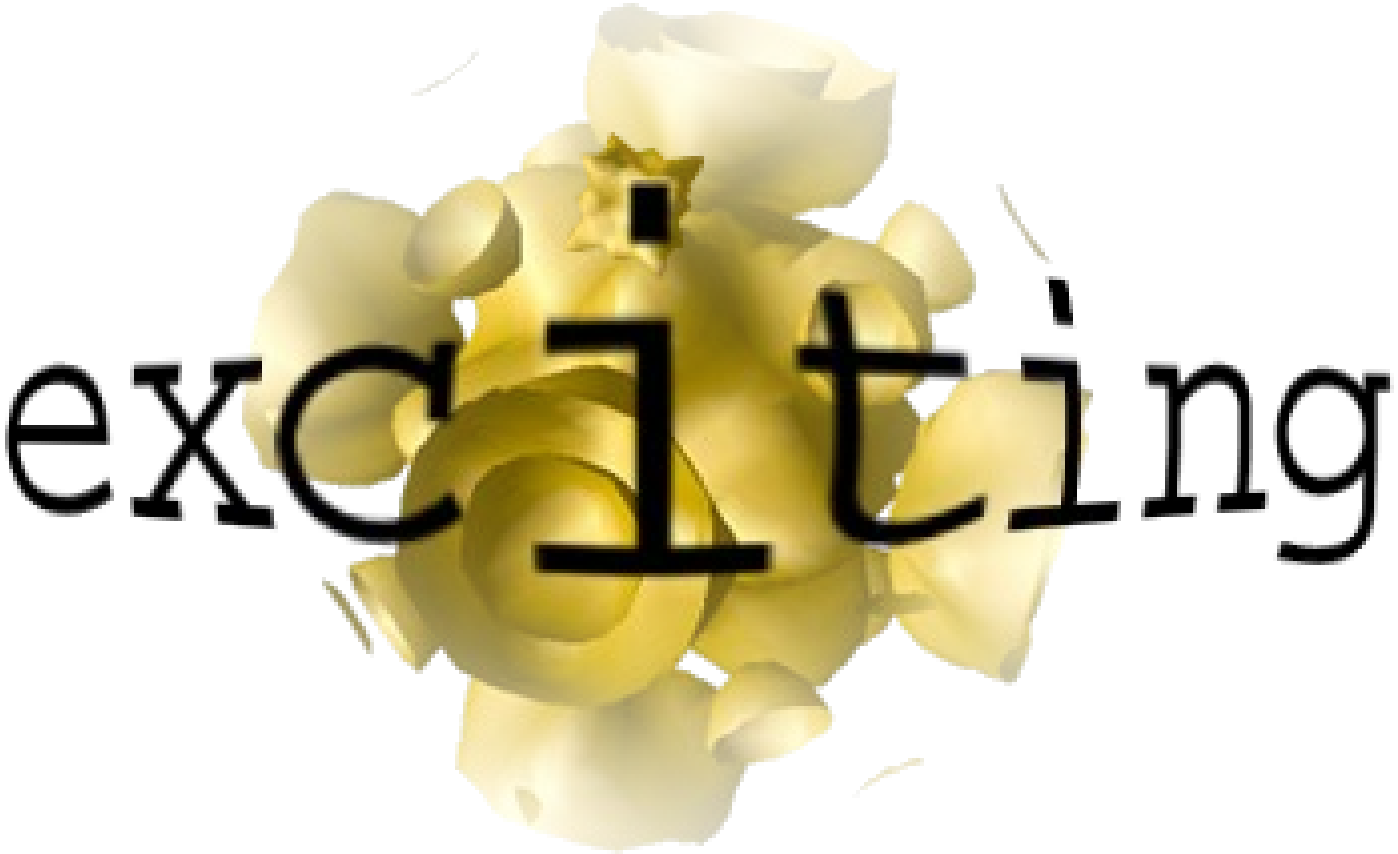
http://exciting-code.org



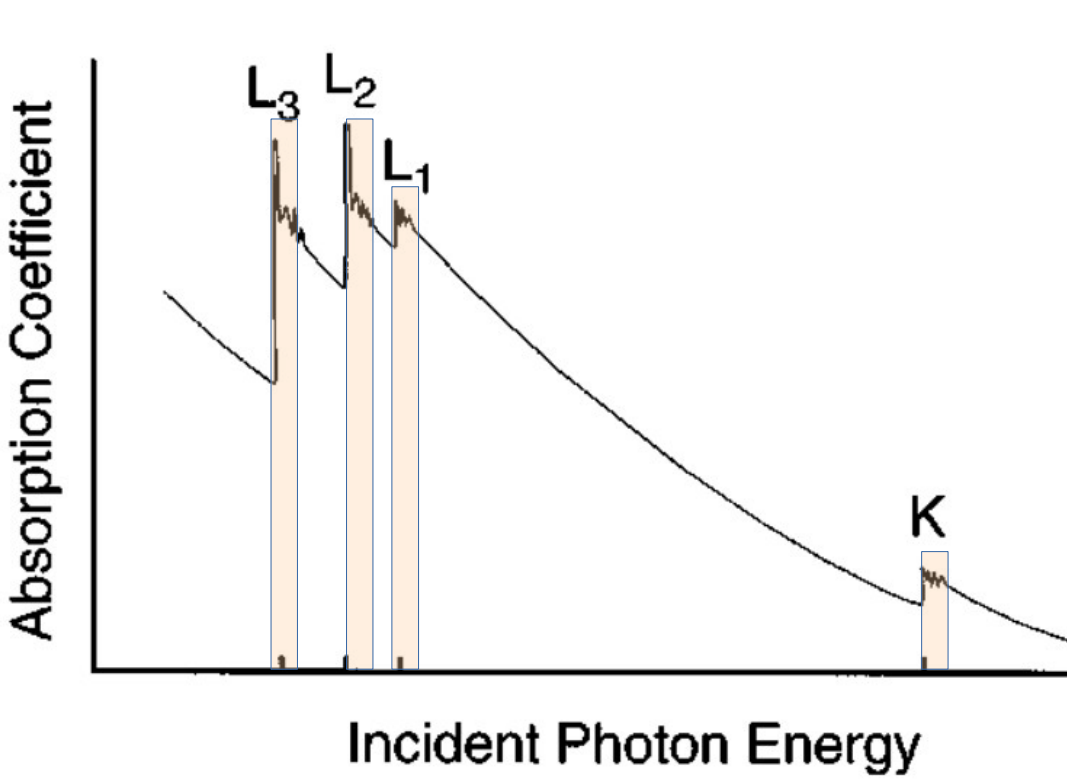
Core-Level Excitations in exciting

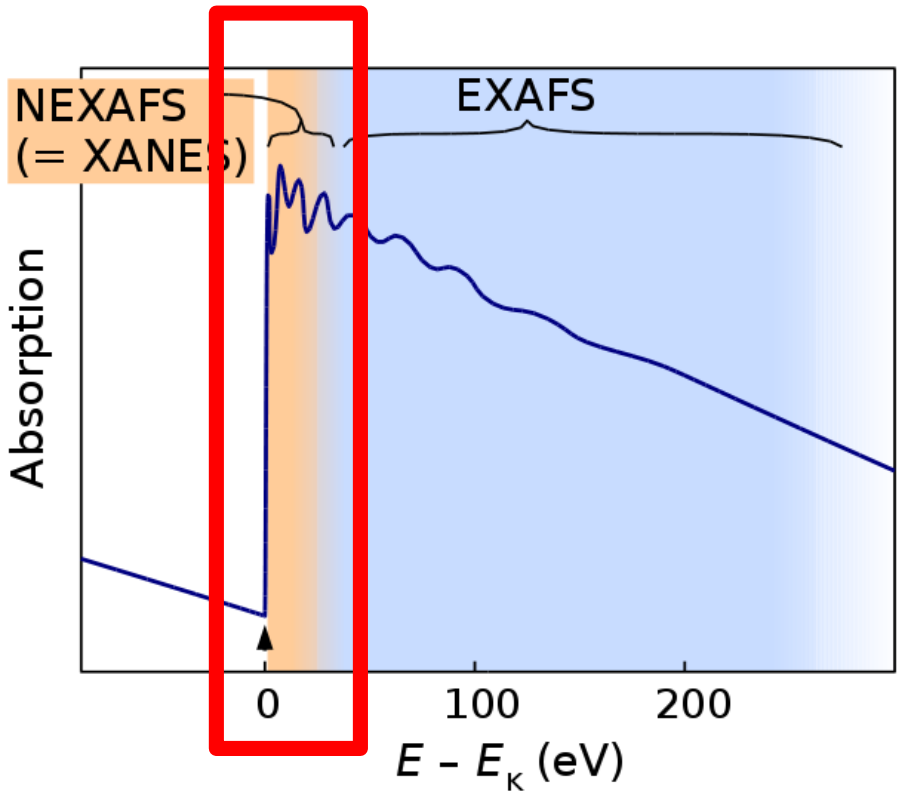
Christian Vorwerk
Humboldt Universität zu Berlin

Outline

- X-ray absorption spectroscopy
- Core-excitations in BSE formalism
- Implementation & Usage
- Selected Examples

X-Ray Absorption Spectroscopy





XANES

X-ray Absorption Near-Edge Structure

Rehr, J.J.; Albers, R.C.: Rev. Mod. Phys. 72 (2000), 621-654.

https://commons.wikimedia.org/w/index.php?curid=832879

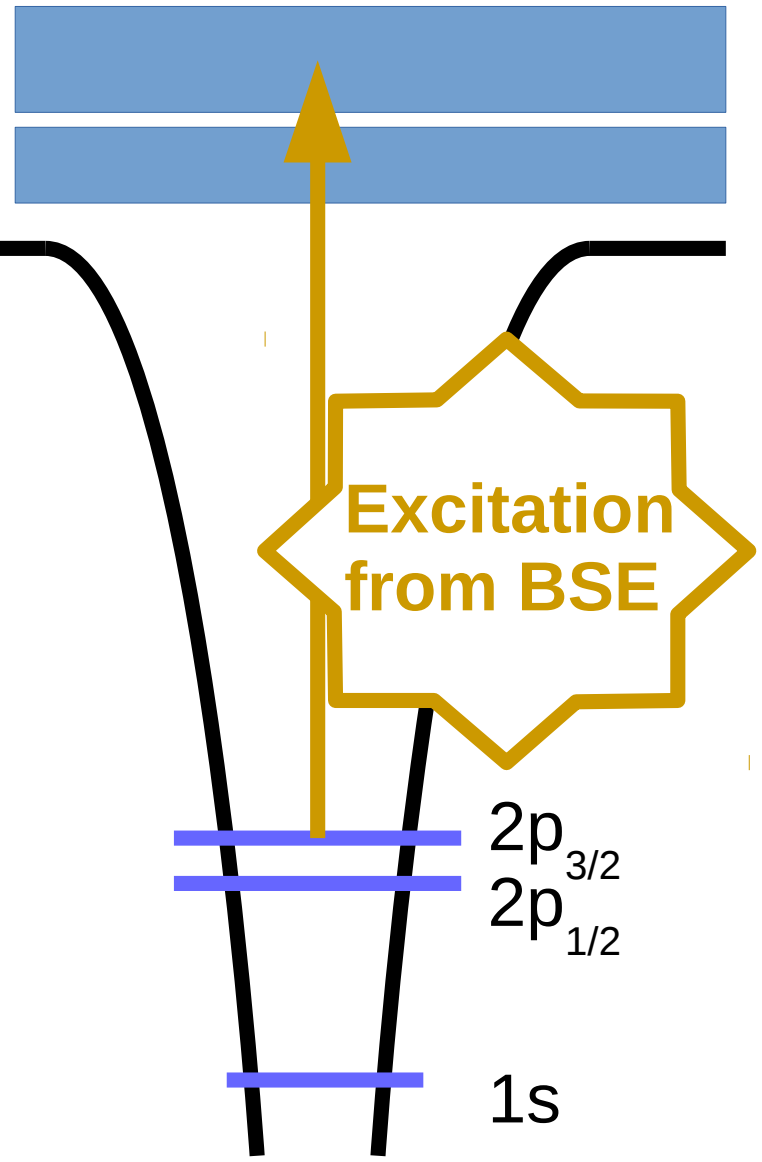
XANES: What makes it interesting?

- Probes unoccupied states
- Obeys strict selection rules
- Sensitive to local electronic structure, local symmetry and bonding

XANES: Why BSE?

- State-of-the-art approach for many-body effects
- Calculations from 2p, 3d, ... initial states possible
- Insight into character of spectral features
- Open source

BSE formalism: Ingredients



- Extended unoccupied states
- Spin-unpolarized system

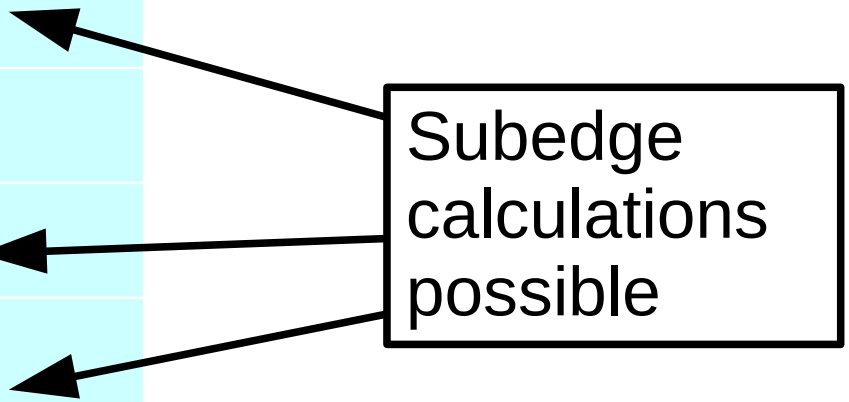
→ All-electron, full-potential DFT calculation

- Strongly bound states
- Spherical symmetric potential
- Strong spin-orbit coupling

→ Radial Dirac equation in spherical potential

Core State Notation

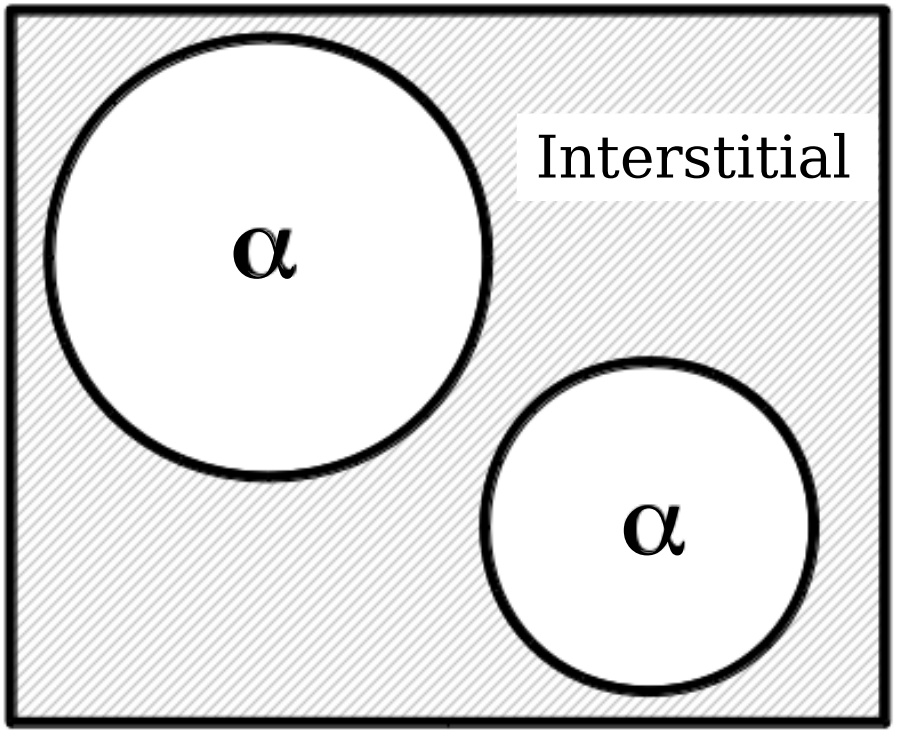
Edge	Initial core states
K	1s
L_1	2s
$L_{2,3}$	$2p_{1/2}$, $2p_{3/2}$
M_1	3s
$M_{2,3}$	$3p_{1/2}$, $3p_{3/2}$
$M_{4,5}$	$3d_{3/2}$, $3d_{5/2}$



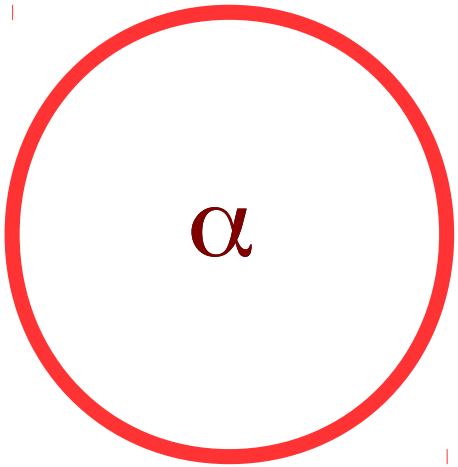
Unoccupied states have same counting as in optical BSE

Spectra of equivalent atoms are identical!

BSE formalism: Ingredients



BSE formalism: Ingredients



Only integrals over the atomic spheres are needed

$$\psi_{\kappa,M}(\mathbf{r}) = \begin{cases} u_\kappa(r)\Omega_{\kappa,M}(\hat{\mathbf{r}}) & \text{for } r_\alpha \leq R_{MT} \\ 0 & \text{else} \end{cases}$$

Spin spherical harmonics

$$\psi^{i\mathbf{k}}_{spinor}(\mathbf{r}) = \begin{pmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{pmatrix} \sum_{lm} u^{i\mathbf{k}}_{lm}(r_\alpha) Y_{lm}(\hat{\mathbf{r}}_\alpha)$$

Spinor approximation

Spherical harmonics

BSE formalism: results

Diagonalization of

$$H^{BSE} = H^{diag} + H^{x} + H^{c}$$

yields

$$\underbrace{\mathrm{Im}\ \epsilon_M(\omega)}_{\text{Absorption spectrum}} = \frac{8\pi^2}{\Omega} \sum_{\lambda} \underbrace{|t_\lambda|^2}_{\text{Oscillator strength}} \delta(w - \underbrace{E^\lambda}_{\text{Excitonic energy}})$$

Input file

```
<BSE
   xas="true"
   xasspecies="1"
   xasatom="2"
   xasedge="L23"
   bsetype="singlet"
   nstlxas="1 20" />
```

triggers XAS calculation

Specify absorbing atom

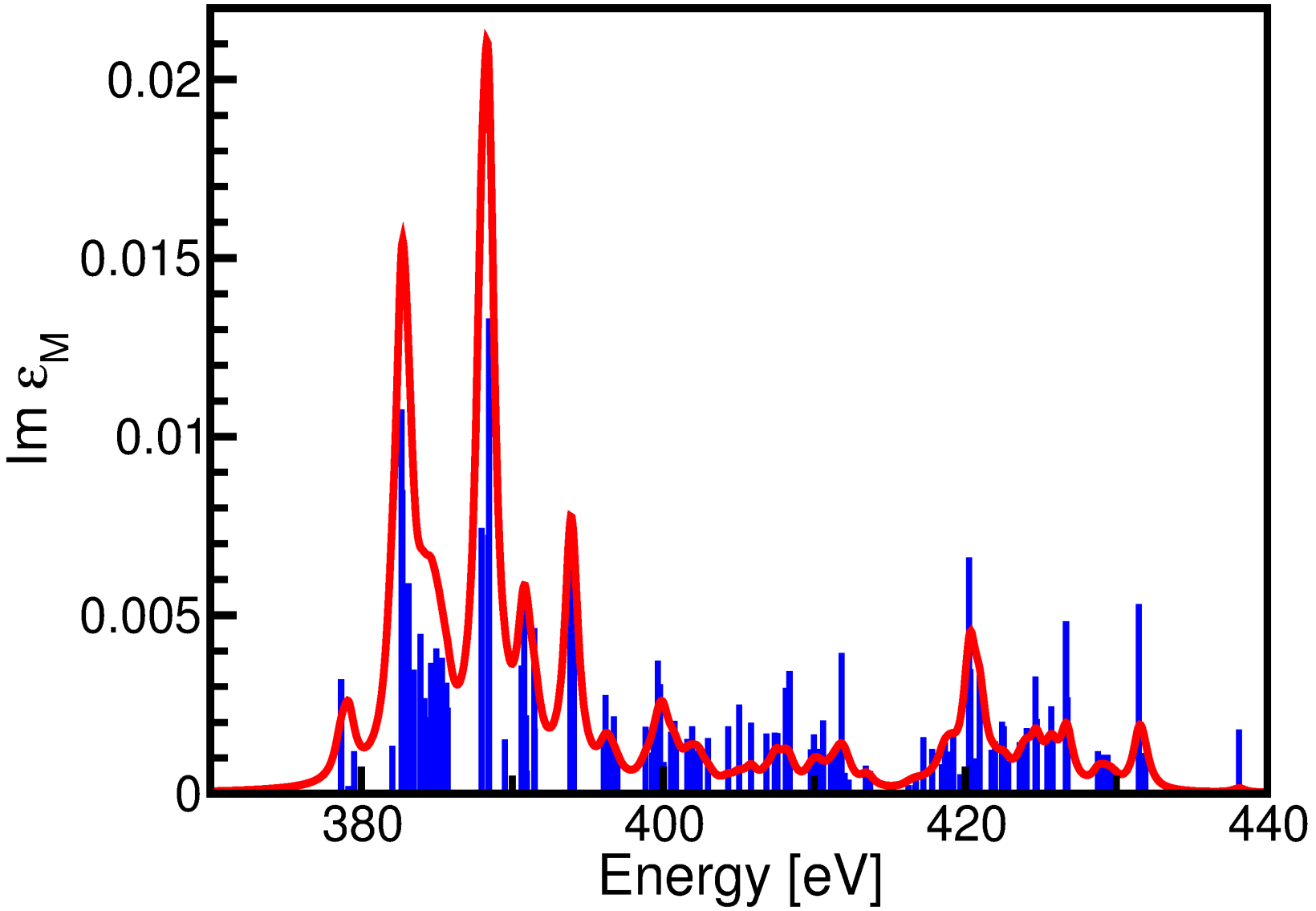
Initial states

Final states

```
<species speciesfile="Ti.xml" rmt="1.8000">
   <atom coord="0.0000000000      0.0000000000      0.0000000000"/>
   <atom coord="0.5000000000      0.5000000000      0.5000000000"/>
</species>
<species speciesfile="O.xml" rmt="1.8000">
   <atom coord="0.3050853616      0.3050853616      0.0000000000"/>
   <atom coord="0.6949146384      0.6949146384      0.0000000000"/>
   <atom coord="0.1949146384      0.8050853616      0.5000000000"/>
   <atom coord="0.8050853616      0.1949146384      0.5000000000"/>
</species>
```

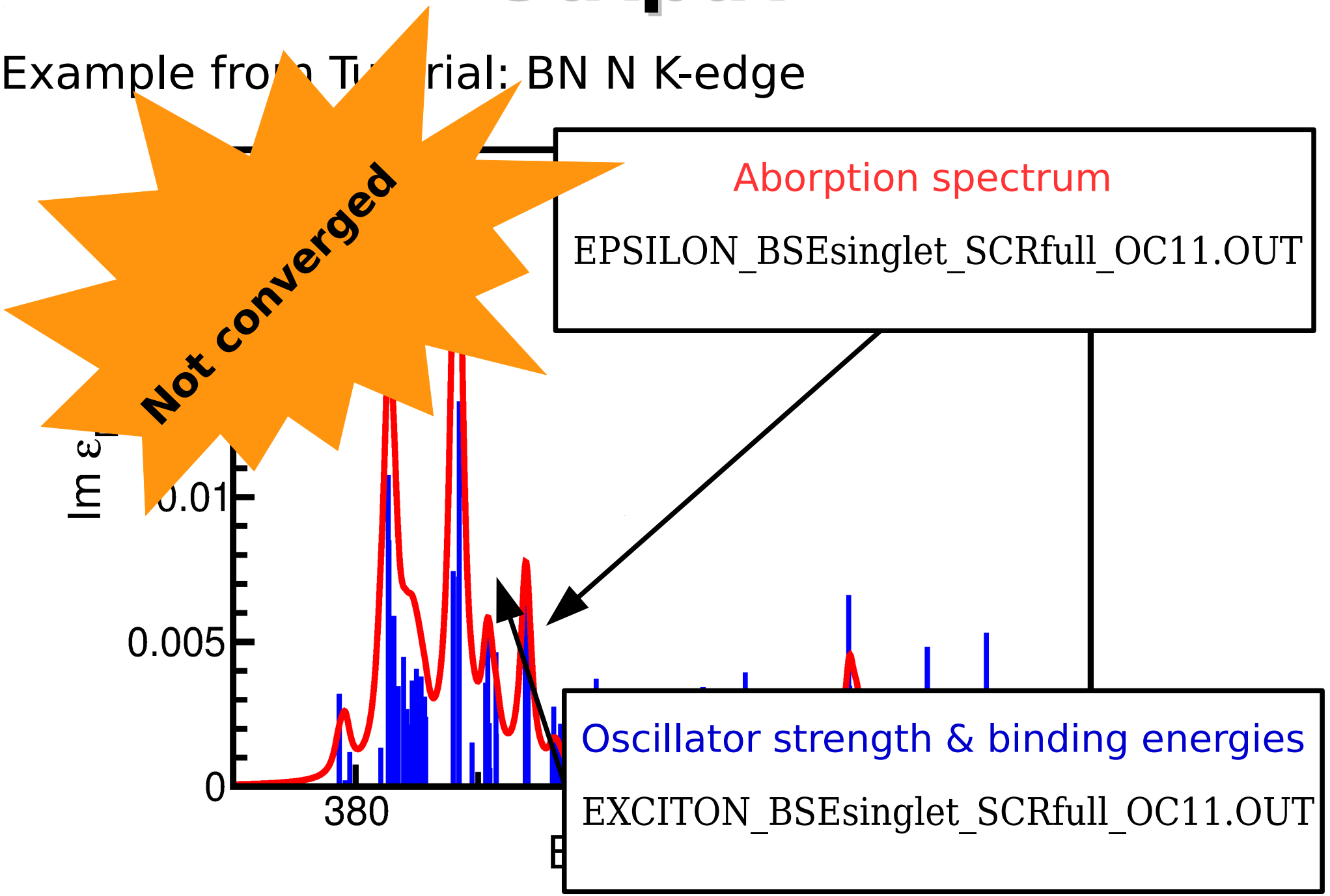
Output

Example from Tutorial: BN N K-edge

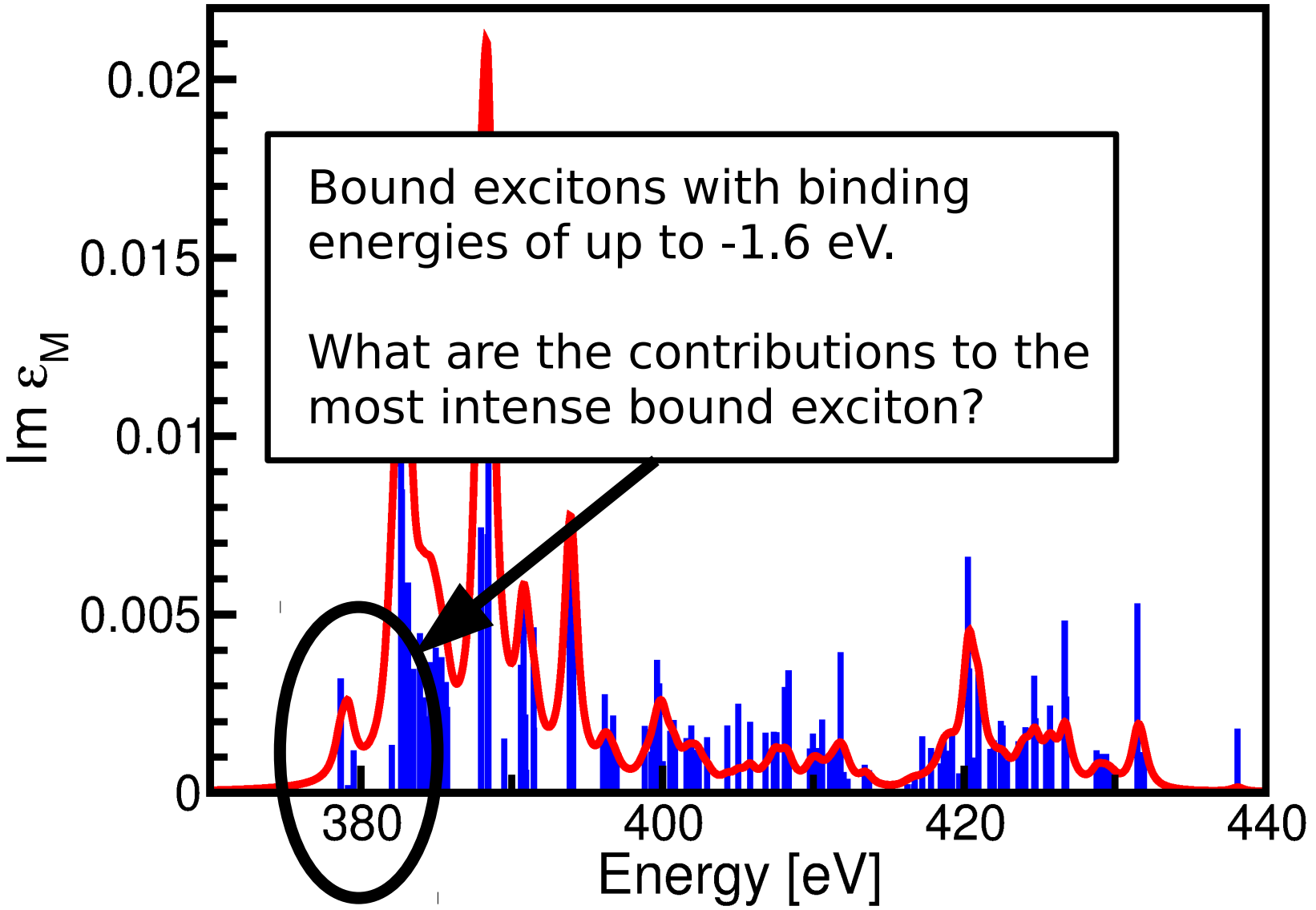


Output

Example from Tutorial: BN N K-edge



Output

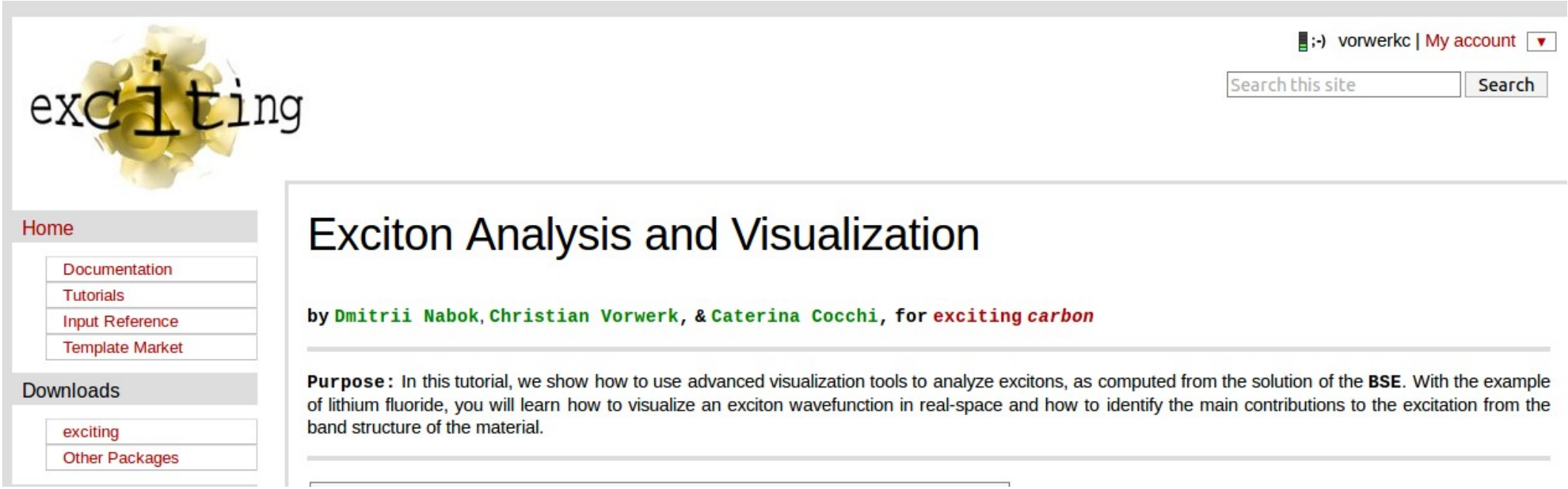

Bound excitons with binding energies of up to -1.6 eV.
What are the contributions to the most intense bound exciton?
Im ε_M
0.02
0.015
0.01
0.005
0
380
400
420
440
Energy [eV]

Output

```
...
<plan>
   <doonly task="bse"/>
   <doonly task="writebevec"/>
</plan>

<storeexcitons MinNumberExcitons="1" MaxNumberExcitons="5"/>
<writeexcitons MinNumberExcitons="1" MaxNumberExcitons="5"/>
...
```

```
$ bandstructure_exciton.py bandstructure.dat exciton_evec_0002.dat xas > plot_exciton_0002.dat
```



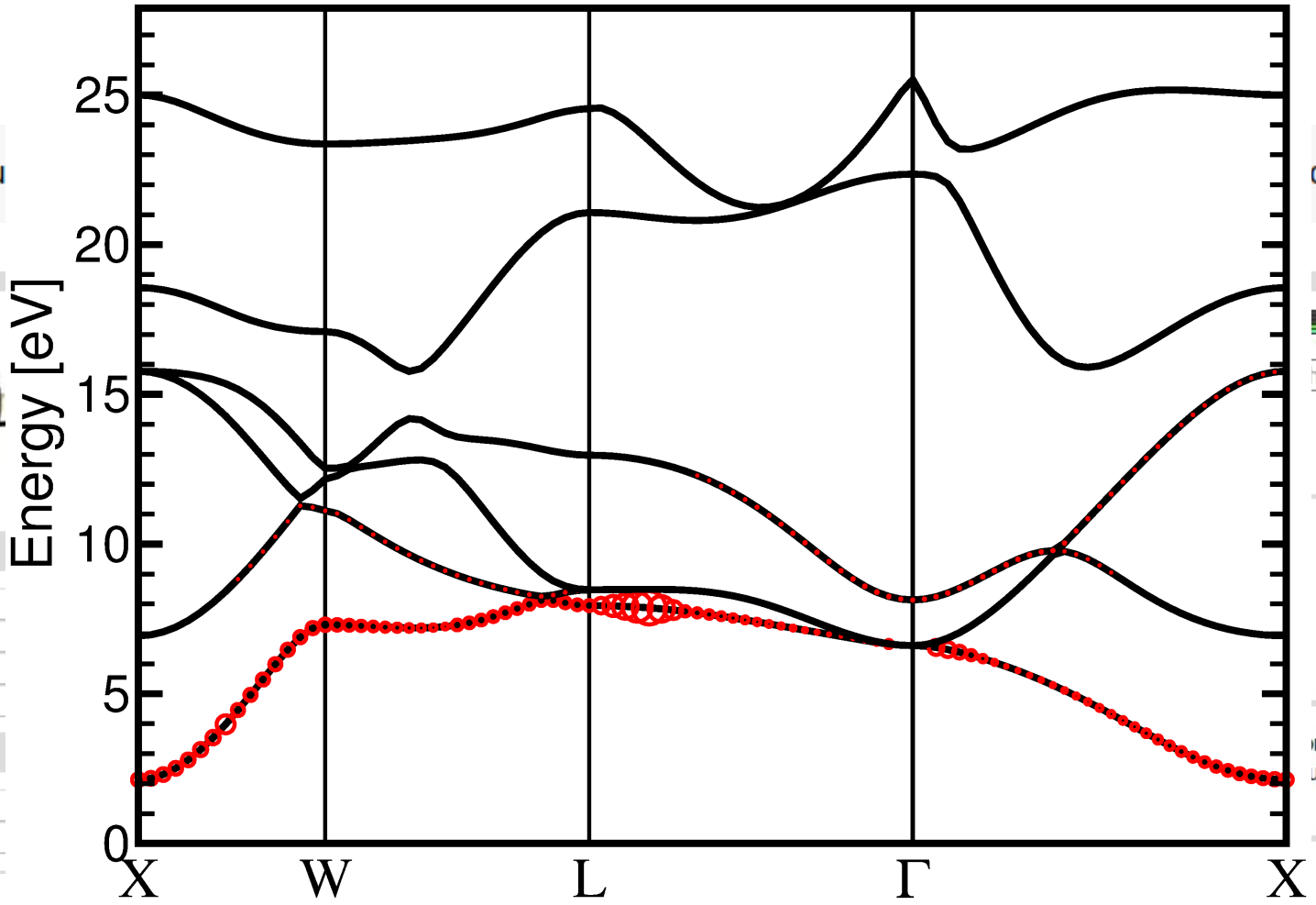
Output

```
...
<plan>
   <doonly task="bse"/>
   <doonly task="writebevec"/>
</plan>

<storeexcitons MinNumberExcitons="1" MaxNumberExcitons="5"/>
<writeexcitons MinNumberExcitons="1" MaxNumberExcitons="5"/>
```

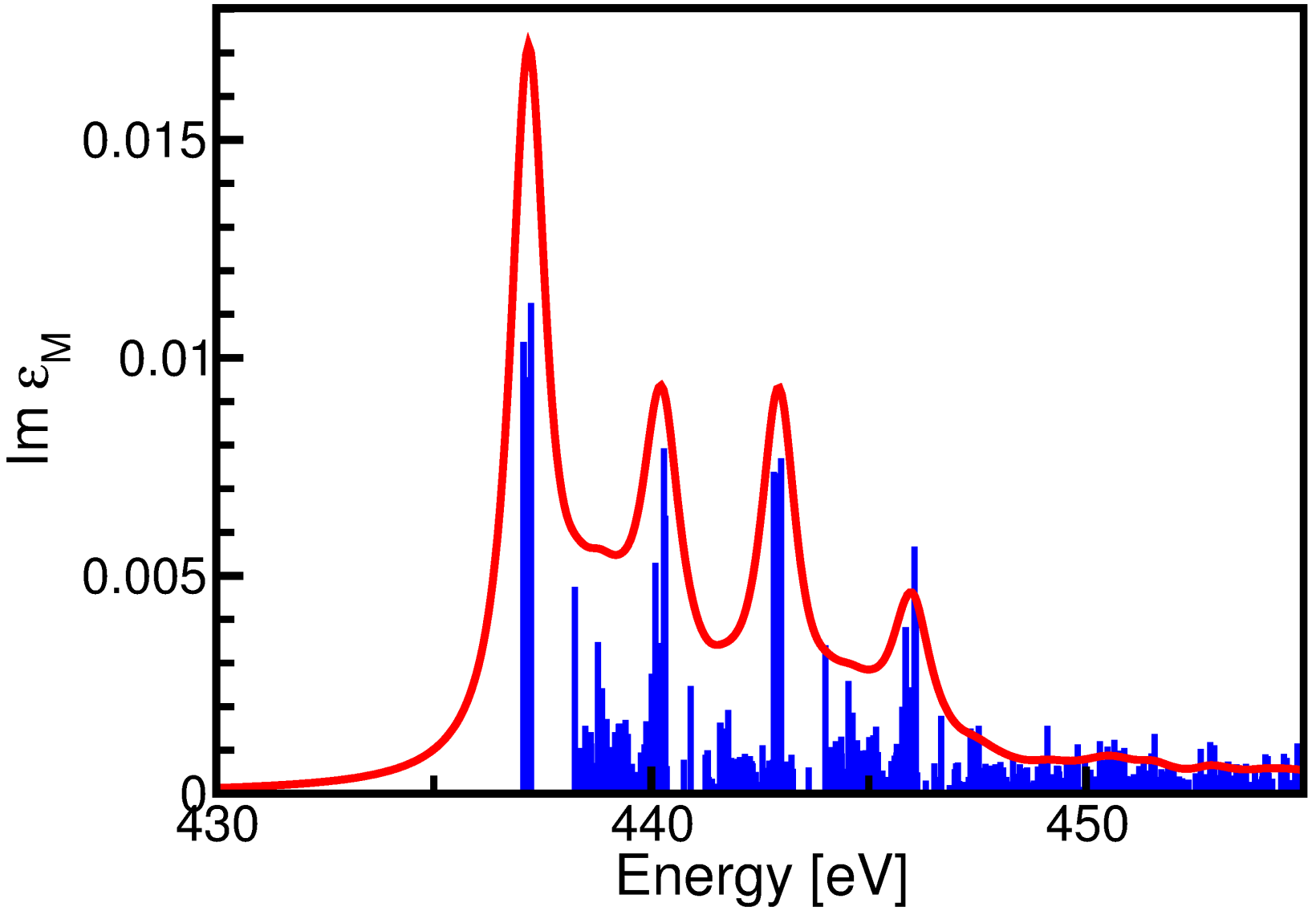
```
$ bandstructu
```

```
citon_0002.dat
```



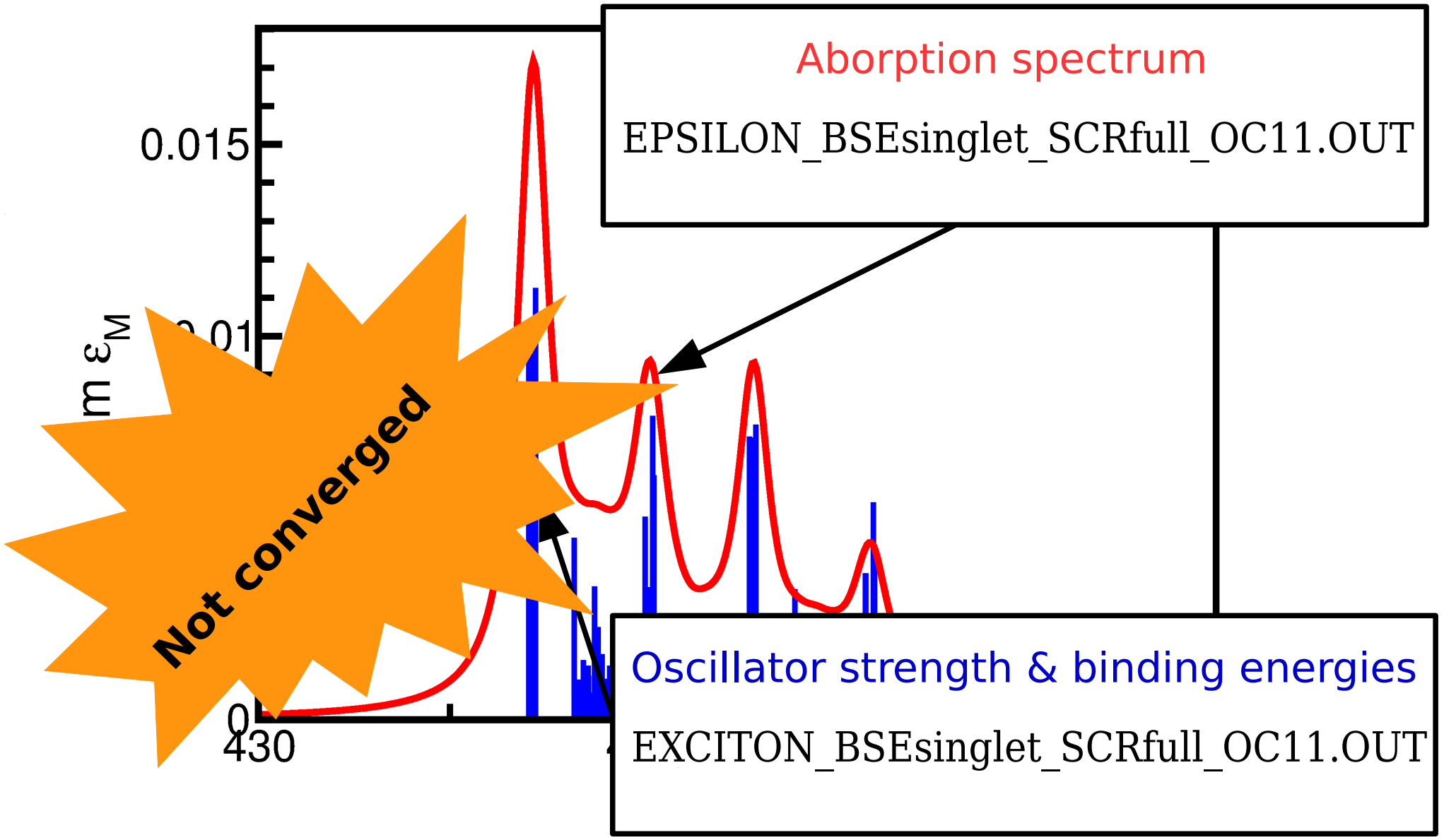
Output

Example from Tutorial: TiO_2 Ti $L_{2,3}$-edge

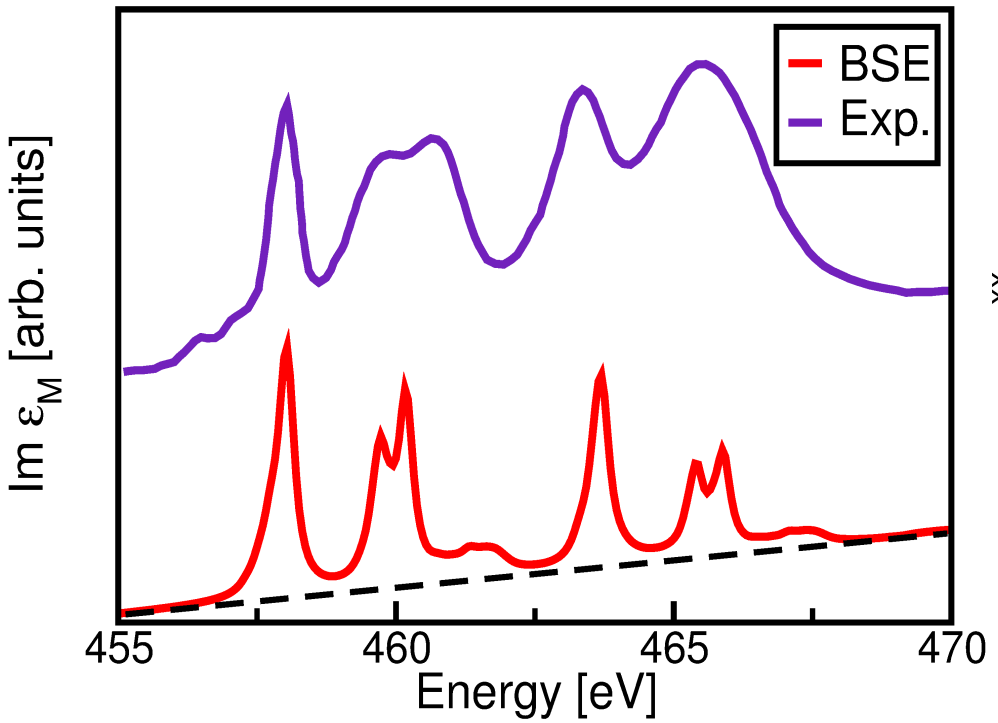


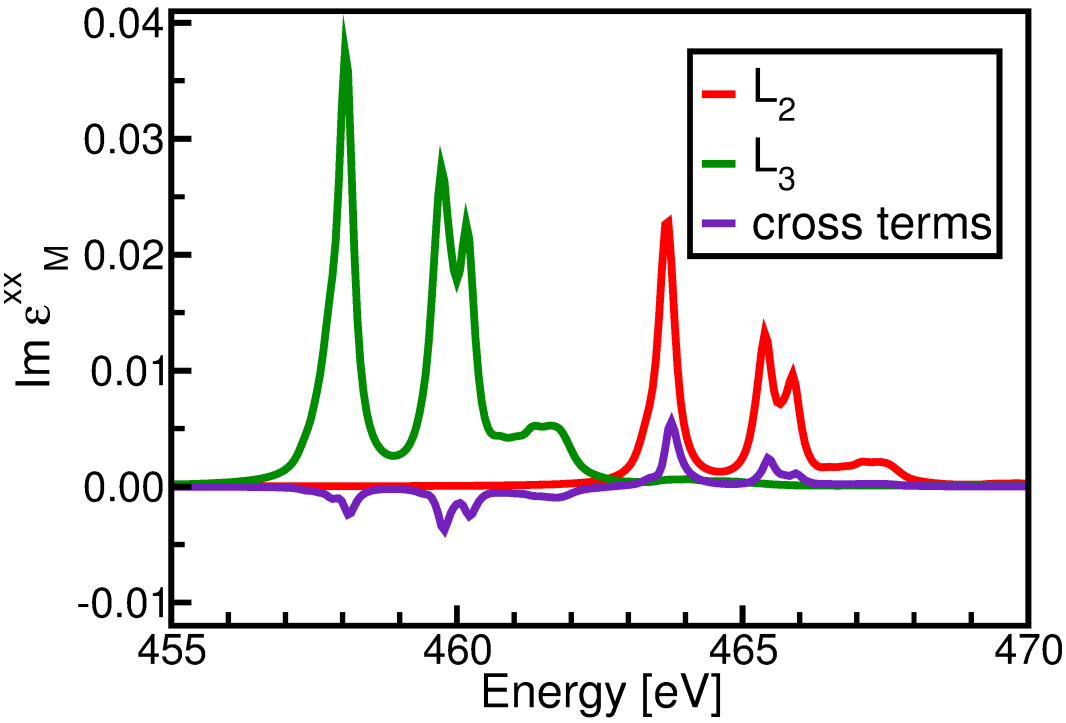
Output

Example from Tutorial: TiO_2 Ti $L_{2,3}$-edge



Converged Results





Cross terms= $L_{2,3}$-(L_2+L_3)

From Master Thesis “All-Electron Many-Body Approac to X-ray Absorption Spectroscopy“ by Christian Vorwerk

Work in Progress...

- Spin-polarized calculations
- X-ray magnetic circular dichroism (XMCD)
- Core spectra of metals

Tutorial: Examples of N K-Edge in BN and Ti $L_{2,3}$ Edge in TiO_2

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X-ray absorption spectra using BSE

by Christian Vorwerk and Caterina Cocchi for exciting *carbon*

Purpose: In this tutorial, we present an example of the calculation of the X-ray absorption near-edge structure (**XANES**) spectra of core-states by solving the Bethe-Salpeter equation (**BSE**). The general way to set up **BSE** computations for **XANES** in **exciting** is shown, together with examples of the N **K**-edge in cubic boron-nitride, as well as of the Ti $L_{2,3}$-edge in rutile titanium dioxide.

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