

Where is the XANES photoelectron: Exploring wave function probability densities

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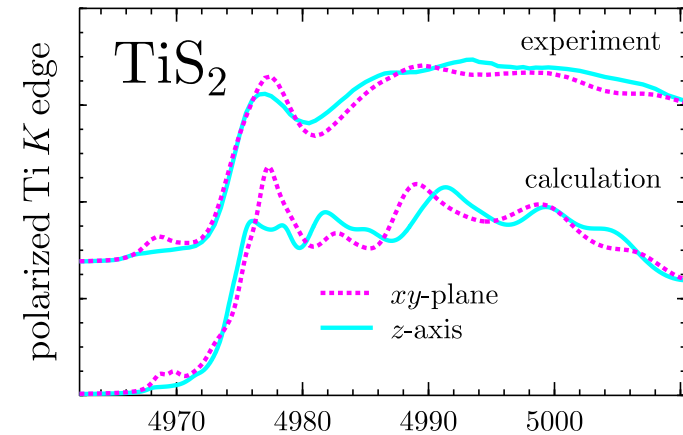
1. Motivation: Why to ask about it?
2. How to do it:
 - (a) Which question to ask?
 - (b) How to answer it?
3. (Hopefully) illustrative example: Ti *K*-edge XANES of TiS₂.

Further reading: O. Šipr, J. Synchrotron Rad. **8**, No. 3, pp. 232-234 (2001).

The situation: We have a XANES spectrum

The naive question we ask:

Where is the XANES photoelectron?



What is the probability density $|\psi(\mathbf{r})|^2$ for the wave function of a photoelectron with energy corresponding to a particular spectral peak.

Motivation: It may be helpful ...

- Use of XANES analysis for real structure determination
- Electron structure studies — translating from one language to another
- Is there any physics beyond maths? Making sense of the multiple-scattering expansion.
- It is nice to have an answer to a well-defined although maybe irrelevant question.

Motivation 1: **Use of XANES analysis for structural studies**

Connection between spectral peaks and real structure units. FAQ: Which atoms and/or which scattering paths contribute mostly to a specific peak?

Exploiting XANES fingerprints. Distinguished features are often put in relation to basic structural building blocks (especially pre-peak and its intensity are being studied as markers of ...).

How changing real structure affects XANES spectrum? Try and error method frequently employed: Move or remove an atom and see what's happening with the calculated spectrum.

Goal: To have a more quantitative measure of these aspects. Exact numbers instead of heuristics.

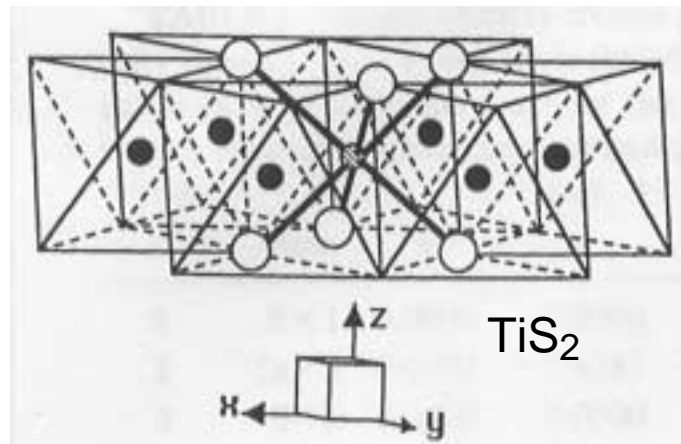
Motivation 2:

Use of XANES analysis for studying electron structure

Which electron states participate mostly in a creating particular peak?

Typical problem: Origin of pre-peak at Ti *K*-edge XANES of titanium compounds.

“Common framework”: Pre-peak is generated by dipole-allowed transitions of the photoelectron from $1s$ into $3d$ -derived states of Ti atoms in more distant coordination shells.



Examples:

- Ti *K*-edge XANES of TiS₂ [Wu, Ouvrard, Moreau & Natoli, Phys. Rev. B**55**, pp. 9508-9513 (1997)]
- Ti *K*-edge XANES of EuTiO₃ and PbTiO₃ [Vedrinskii, Kraizman, Novakovich, Demekhin, Urazhdin, Ravel & Stern, J. Phys. IV (Paris) **7**, Colloq. C2, pp. C2-107–C2-110 (1997)]
- Ni *K*-edge XANES of NiO [Vedrinskii, Kraizman, Novakovich, Elyafi, Bocharov, Kirchner & Dräger phys. stat. sol. (b) **226**, pp. 203-217 (2001)]

Motivation 3: Is there any physics beyond maths?

Searching for a possible “reality” behind the multiple-scattering expansion.

Effective calculation of XANES spectra relies on the **multiple-scattering expansion** [=perturbation series]

$$\tau_{LL'}^{ij} = t_\ell^i \delta^{ij} \delta_{LL'} + t_\ell^i G_{LL'}^{ij} t_{\ell'}^j (1 - \delta^{ij}) + \sum_{k,L''} t_\ell^i G_{LL''}^{ik} t_{\ell''}^k G_{L''L'}^{kj} t_{\ell'}^j + \dots ,$$

which allows to express XANES cross-section as a **sum of contributions of individual scattering paths**.

- Usually, terms associated with some scattering paths are more important than terms associated with other ones.
- The perturbation series written above does not require a physical interpretation by itself — smallness of t_ℓ^j is enough to guarantee convergency and thus justify its use.
- Interpreting individual terms of the sum as “scattering paths” may just be a convenient way of enumerating and ordering all the terms.
- Nevertheless, the scattering paths interpretation provides useful concepts such as focusing effect, which are helpful in assessing convergency of the multiple-scattering expansion.

Question:

Is the “concentration of excited photoelectrons” higher along significant scattering paths than along non-significant ones?

Motivation 4: To have an answer to a well-defined question.

Make your own choice of the beast!

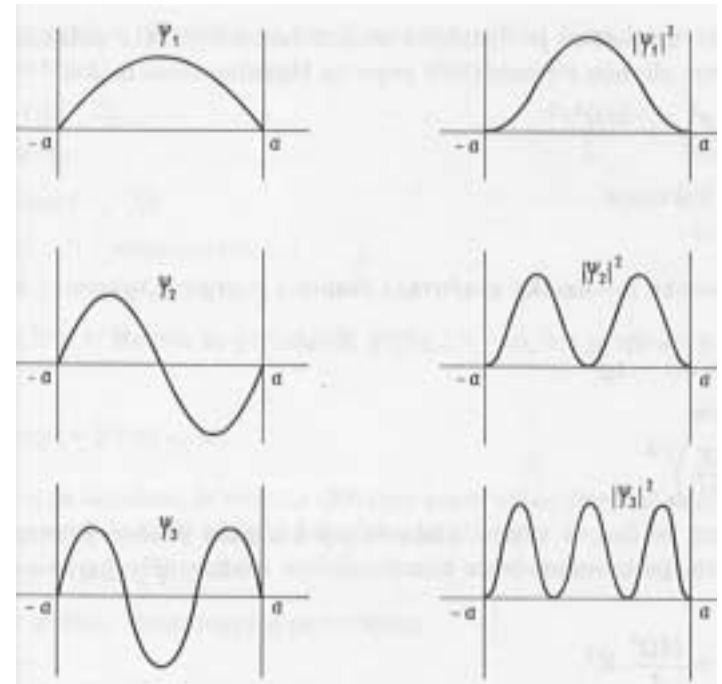
Scylla and Charybdis of XANES analysis:

1. Answering **useful** but **vague** questions.

Which scattering paths contribute to this peak?
What is the connection between pre-peak intensity and deviation from central symmetry?
How does shift of this atom affects position of that peak?

2. Answering **well-defined** but maybe **irrelevant** question.

What is the photoelectron wave function probability density here or there?



Particle in an infinitely deep potential well: Wave function probability density $|\psi(x)|^2$ is zero at the walls, yet those walls are pretty important for what's happening!

Defining the problem: **What is the probability of finding the XAS photoelectron here or there?**

Standart situation: I know the wave function $\psi(\mathbf{r})$ which describes the physical object, I can make square of its modulus $|\psi(\mathbf{r})|^2$ and that tells me what is the probability of finding that object at an arbitrary place \mathbf{r} .

The project: Find the photoelectron wave function $\psi_{\text{XAS}}(\mathbf{r})$ associated with XANES transition at a given energy, make of it $|\psi_{\text{XAS}}(\mathbf{r})|^2$ — and you have finished!

The problem: Which is the right photoelectron **wave function associated with XANES** process?

Finding wave function associated with XANES process

Formal procedure: Extract it from the expression for XANES transition probability per unit time w .

Within first order perturbation theory in Rydberg atomic units:

$$w = 2\pi \int d\nu |\langle \psi_\nu | H_I | \phi_c \rangle|^2 \delta(E_c + \omega - E_\nu),$$

where H_I is the interaction hamiltonian perturbing the initial core state $|\phi_c\rangle$ of the electron, ω is incoming photon energy and the sum/integration over ν spans *any* complete set of orthogonal electron wave functions $|\psi_\nu\rangle$.

⇒ XANES transition rate is given by an incoherent sum over many processes, hence there is **no unique photoelectron wave function** which would describe the whole process!

If there had been a unique electron wave function $\psi_{\text{XAS}}(\mathbf{r})$ to describe the XANES process, the transition probability would have been

$$w = 2\pi |\langle \psi_{\text{XAS}} | H_I | \phi_c \rangle|^2 \delta(E_c + \omega - E_{\text{XAS}})$$

instead.

Which question *can* be answered?

X-ray absorption spectrum arises as an incoherent sum of many participating processes (e.g., photoelectron can be ejected in *any* direction).

One can evaluate a **weighted sum of probability densities** of those wave functions which describe electrons in each of the participating processes,

$$P(\mathbf{r}) = \sum_f w_f |\psi_f(\mathbf{r})|^2 .$$

The weights w_f are partial probabilities that a core electron $|\phi_c\rangle$ is ejected into a particular state $|\psi_f\rangle$,

$$w_f \sim |\langle \phi_c | H_I | \psi_f \rangle|^2 ,$$

and ought to be normalized so that their sum yields w .

The quantity $P(\mathbf{r})$ is just the probability that at a given place \mathbf{r} , an electron created as a result of absorption of a photon of energy ω by a core electron $|\psi_c\rangle$, can be detected.

That problem has been reformulated: **What are the electron wave functions** associated with elementary participating processes?

Is choice of elementary wave functions $\psi_f(\mathbf{r})$ important?

Does the outcome of sum over states Σ_f depend on which complete set of wave functions do we take into account?

The expression for XANES transition probability w ,

$$w = 2\pi \int d\nu |\langle \psi_\nu | H_I | \phi_c \rangle|^2 \delta(E_c + \omega - E_\nu),$$

is independent on the choice of wave functions $|\psi_\nu\rangle$ — any complete set of orthogonal wave functions would do, provided that they are eigenstates of the unperturbed hamiltonian. [Therefore, one can get rid of $|\psi_\nu\rangle$ altogether in Green's functions formulation.]

However, the sum

$$P(\mathbf{r}) = \sum_f |\langle \phi_c | H_I | \psi_f \rangle|^2 |\langle \mathbf{r} | \psi_f \rangle|^2 \delta(E_c + \omega - E_f)$$

does depend on the choice of the set $|\psi_f\rangle$!

It is only a matter of physical intuition, not formal mathematical procedures, to establish which set of states $|\psi_f\rangle$ is **relevant to the physical process** in question.

Transitions to bound states

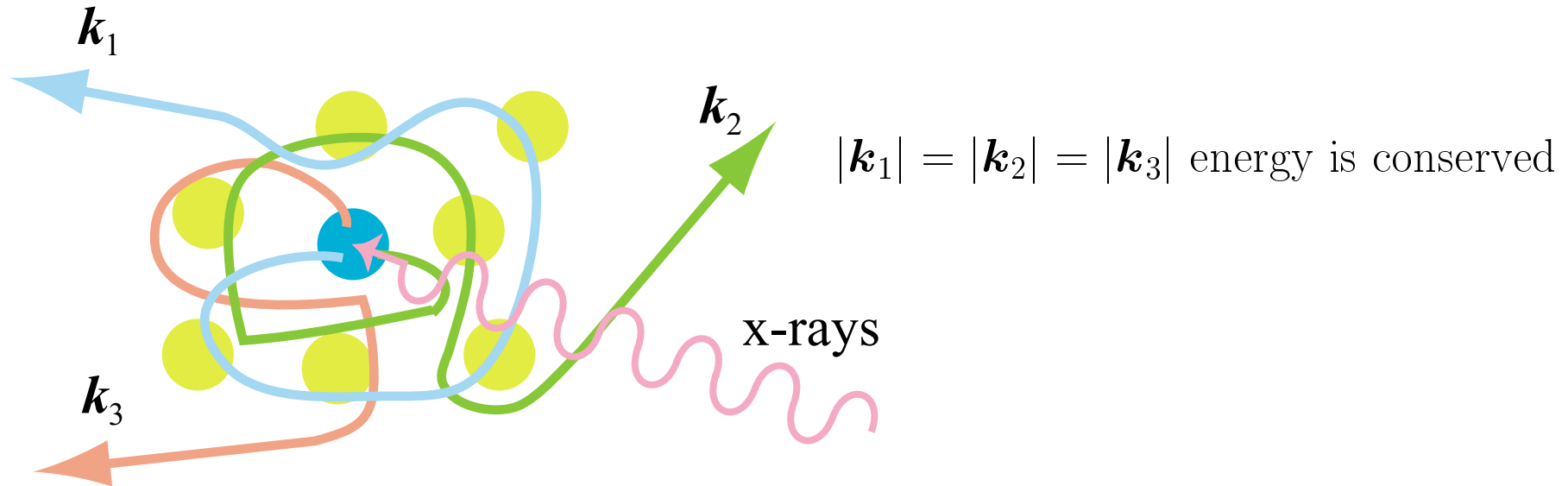
No problem for transitions to bound states (say, of molecules):

Proper final states $|\psi_f\rangle$ are just asymptotically decaying bound states $|\psi_b\rangle$, normalizable so that $\int d^3\mathbf{r} |\psi_b(\mathbf{r})|^2 = 1$.

Normalization to unity ensures that each **wave function** $|\psi_b\rangle$ corresponds just to **one electron** — so we have one electron in the beginning (in the core state) and one electron in the end (above the Fermi level/chemical potential).

Choice of proper $\psi_f(\mathbf{r})$ for transitions to continuum states

What kind of processes does the XANES calculation take into account?



Electron absorbs a photon, gets excited into continuum levels, then something complicated is happening and finally (after a long time) it **ends as a free electron** with wave function

$$\frac{1}{(2\pi)^{3/2}} \exp(i \mathbf{k} \mathbf{r}) .$$

Wave function normalized in this way (to δ -function of \mathbf{k}) corresponds to one electron; it is a direct and frequently employed “infinite-space” generalization of a particle in a box,

$$\frac{1}{V} \exp(i \mathbf{k}_n \mathbf{r}) \longrightarrow \frac{1}{(2\pi)^{3/2}} \exp(i \mathbf{k} \mathbf{r})$$

(employing periodic boundary conditions).

Finding the wave function of the proper final state

Looking for such states $|\psi_f\rangle$ which, after a sufficiently long time, will turn into plane waves.

Time-inversed scattering states $|\psi_{\mathbf{k}}^{(-)}\rangle$ — solutions of the Lippman-Schwinger equation

$$\psi_{\mathbf{k}}^{(-)}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} + \int d^3\mathbf{r}' G_0^{(-)}(\mathbf{r}, \mathbf{r}') V(\mathbf{r}') \psi_{\mathbf{k}}^{(-)}(\mathbf{r}')$$

($G_0^{(-)}(\mathbf{r}, \mathbf{r}')$ is the advanced free electron Green function, $V(\mathbf{r}')$ describes the potential of the cluster).

Normalization: States $|\psi_{\mathbf{k}}^{(-)}\rangle$ are normalizable to the delta function $\delta(\mathbf{k})$ and are thus pegged to free-electron wave function $\exp(i\mathbf{k}\mathbf{r})$. Thus one keeps a universal definition of probability density $P(\mathbf{r})$, related to one electron in the whole space.

Physical interpretation of final states $|\psi_{\mathbf{k}}^{(-)}\rangle$

- Wave function, from which a plane wave evolves within a sufficiently long time.
- State into which the core electron “jumps” as a result of the electromagnetic perturbation H_I [One-step photoemission model.]
- $P(\mathbf{r})$ is then the probability, that the **electron ejected from a core level can be found at position \mathbf{r}** , “just after” having absorbed an x-ray photon.

Elementary incoherent processes involved in the sum Σ_f must be *photoelectron diffraction* events.

X-ray absorption is conceptually nothing else but angularly integrated photoelectron diffraction.

Basic equations: How to proceed in practice

Probability of finding a XANES photoelectron at a position \mathbf{r}

$$P(\mathbf{r}) = \sum_f w_f |\psi_f(\mathbf{r})|^2 \quad \longrightarrow$$

$$P(\mathbf{r}) = \frac{1}{\sigma_{\text{XAS}}} \int d^2 \hat{\mathbf{k}} \frac{d\sigma}{d\Omega_{\mathbf{k}}} |\psi_{\mathbf{k}}^{(-)}(\mathbf{r})|^2$$

Photoelectron diffraction cross section:
$$\frac{d\sigma}{d\Omega_{\mathbf{k}}} = \frac{1}{4\pi} \alpha \omega k |\langle \psi_{\mathbf{k}}^{(-)} | \hat{\mathbf{e}}_{\mathbf{r}} | \phi_c \rangle|^2$$

Normalizing XA(NE)S cross section:
$$\sigma_{\text{XAS}} = \int d^2 \hat{\mathbf{k}} \frac{d\sigma}{d\Omega_{\mathbf{k}}}$$

Employing the *muffin-tin approximation*, the wave functions $\psi_{\mathbf{k}}^{(-)}(\mathbf{r})$ can then be **expanded inside the j -th muffin-tin sphere** as

$$\psi_{\mathbf{k}}^{(-)}(\mathbf{r}) = \sum_L \beta_L^{(j)}(\mathbf{k}) R_\ell^{(j)}(kr) Y_L(\hat{\mathbf{r}}) ,$$

where single-sphere solutions of the radial Schrödinger equation $R_\ell^{(j)}(kr)$ are normalized so that they smoothly match a free-space solution,

$$R_\ell^{(j)}(kr) = \cot \delta_\ell^{(j)} j_\ell(kr) - n_\ell(kr) ,$$

outside the muffin-tin sphere.

Further equations needed during $P(\mathbf{r})$ evaluation

- Relevant equations can be in that or other form be found in that or other form in, e.g.,
 H. A. Bethe and E. E. Salpeter: Quantum mechanics of one- and two-electron atoms, p. 295.
 (Berlin, Springer, 1957)
 D. Dill and J. L. Dehmer, J. Chem. Phys. **61**, 692 (1974)
 P. A. Lee, Phys. Rev. B**13**, 5261 (1976)
 C. R. Natoli, M. Benfatto and S. Doniach, Phys. Rev. B**34**, 4682 (1986)
 C. R. Natoli, M. Benfatto, C. Brouder, M. F. Ruiz López and D. L. Foulis, Phys. Rev. B**42**,
 1944 (1990)

Expansion of the PED final state: $\psi_{\mathbf{k}}^{(-)}(\mathbf{r}) = \sum_L \beta_L^{(j)}(\mathbf{k}) R_\ell^{(j)}(kr) Y_L(\hat{\mathbf{r}})$

Amplitudes: $\beta_L^{(j)}(\mathbf{k}) = 4\pi \sum_{L''} i^{\ell''} \beta_{L''}^{(j)}(L'') Y_{L''}^*(\hat{\mathbf{k}})$, $\beta_{L''}^{(j)}(L'') = \sum_{pL'} W_{LL'}^{jp} J_{L'L''}^{p0}$

The scattering matrix W is an inverse matrix of

$$[W^{-1}]_{LL'}^{ij} = \left(\sin \delta_\ell^{(j)} e^{-i\delta_\ell^{(j)}} \right)^{-1} \delta_{ij} \delta_{LL'} + 4\pi(1-\delta_{ij}) \sum_{L_1} i^{\ell-\ell'+\ell_1} i h_{\ell_1}^{(-)}(k|\mathbf{R}^{ij}|) Y_{L_1}(\mathbf{R}^{ij}) C_{LL_1}^{L'}$$

Gaunt symbol: $C_{LL_1}^{L'} = \int d^2\hat{\mathbf{n}} Y_L(\hat{\mathbf{n}}) Y_{L'}^*(\hat{\mathbf{n}}) Y_{L_1}(\hat{\mathbf{n}})$

Propagator: $J_{LL'}^{pq} = 4\pi \sum_{L_1} i^{\ell-\ell'+\ell_1} j_{\ell_1}(k|\mathbf{R}^{pq}|) Y_{L_1}(\mathbf{R}^{pq}) C_{LL_1}^{L'}$, $\mathbf{R}^{pq} \equiv \mathbf{R}^p - \mathbf{R}^q$

Practical aspects of calculating and analyzing photoelectron WFPD

Probability density $P(\mathbf{r})$ is **dominated by DOS and/or single-atom effects**.

DOS-like probability density: $\hat{\mathbf{k}}$ -independent, “unidirectional” cross section $d\sigma/d\Omega$

$$P_{\text{DOS}}(\mathbf{r}) \equiv \frac{1}{\sigma_{\text{XAS}}} \frac{d\sigma}{d\Omega} \int d^2\hat{\mathbf{k}} |\psi_{\mathbf{k}}^{(-)}(\mathbf{r})|^2 = \frac{1}{4\pi} \int d^2\hat{\mathbf{k}} |\psi_{\mathbf{k}}^{(-)}(\mathbf{r})|^2 = \frac{4\pi^2}{k} \left(-\frac{1}{\pi} \text{Im}G(\mathbf{r}, \mathbf{r}; E) \right)$$

AXAFS analogy — case of an isolated atom: **Single-atom probability density** $P_{\text{ato}}(\mathbf{r})$
(cluster PED wave function $\psi_{\mathbf{k}}^{(-)}(\mathbf{r})$ is substituted with corresponding isolated-atom-case wave function).

Quantities of interest: *Differential wave function probability densities*

$$P(\mathbf{r}) - P_{\text{DOS}}(\mathbf{r}) \quad , \quad P(\mathbf{r}) - P_{\text{ato}}(\mathbf{r})$$

Original motivation: To compare the importance of particular atoms for generating x-ray absorption fine structure.

Sufficient and less “junky” is to compare not $P(\mathbf{r})$ but rather its integral inside suitably chosen spheres.

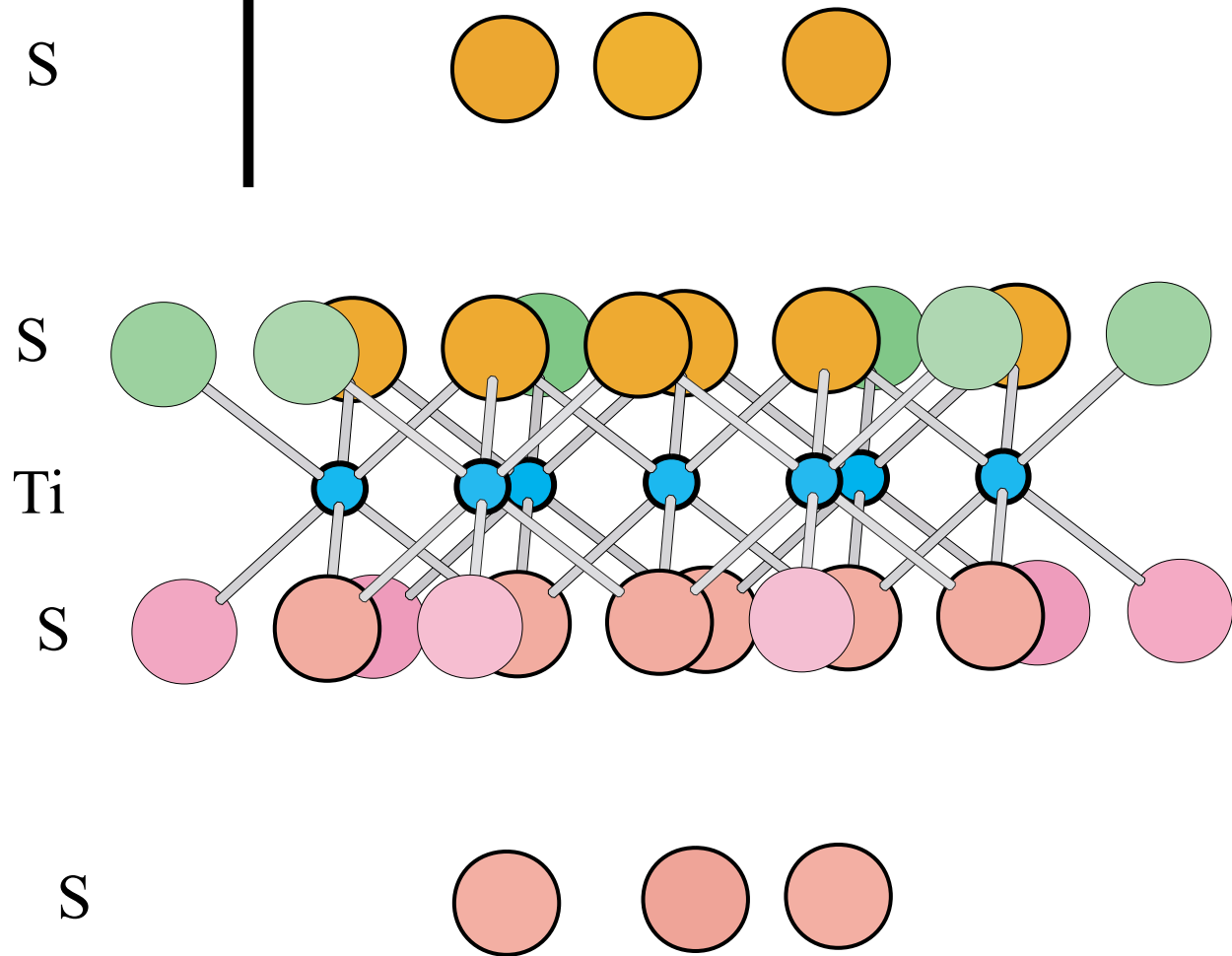
Atomic site related quantities $P^{(j)}$ etc.:

$$P^{(j)} \equiv \frac{1}{V^{(j)}} \int_0^{R_N^{(j)}} dr r^2 \int d^2\hat{\mathbf{r}} P(\mathbf{r})$$

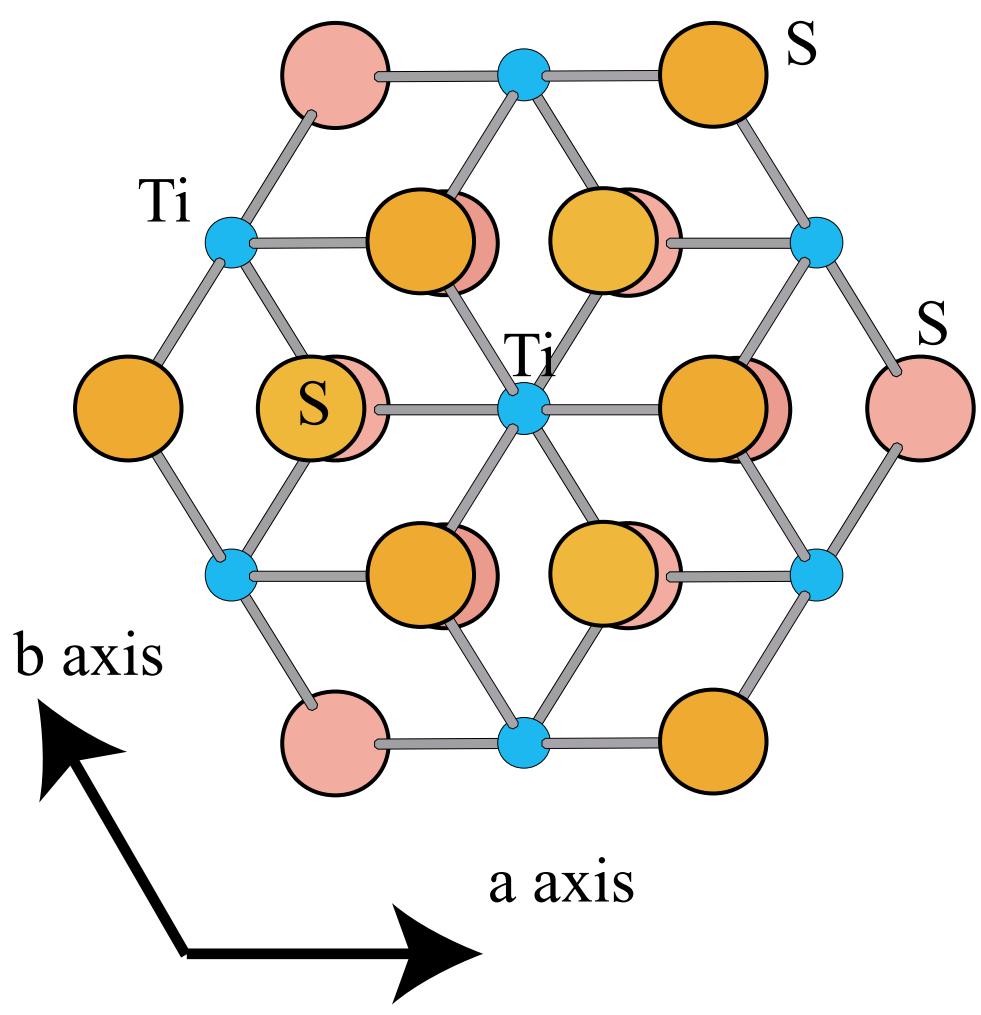
c axis



TiS₂ structure



TiS₂ structure

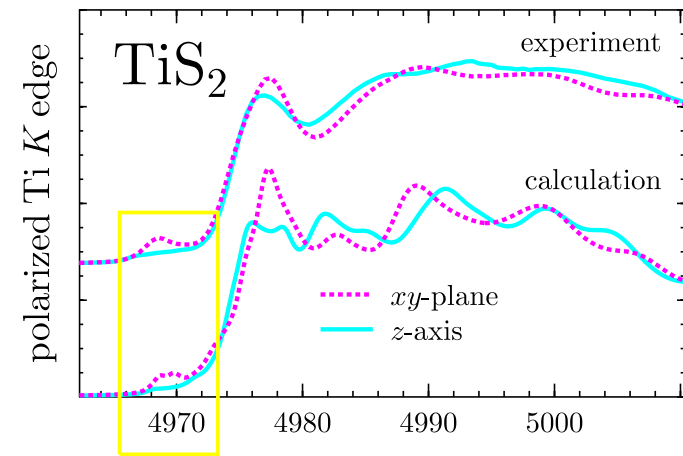


Application of WFPD analysis:

Polarized Ti K -edge XANES of TiS_2

The model question:

What is the mechanism behind pre-break at xy polarization?



Few papers were dealing with Ti K -edge absorption spectrum of TiS_2 , e.g.,

F. Antonangeli, M. Piacentini, R. Girlanda, G. Martino and E. S. Giuliano, Phys. Rev. B **32**, 6644 (1983),

Z. Y. Wu, G. Ouvrard, P. Moreau and C. R. Natoli, Phys. Rev. B **55**, 9508 (1997),

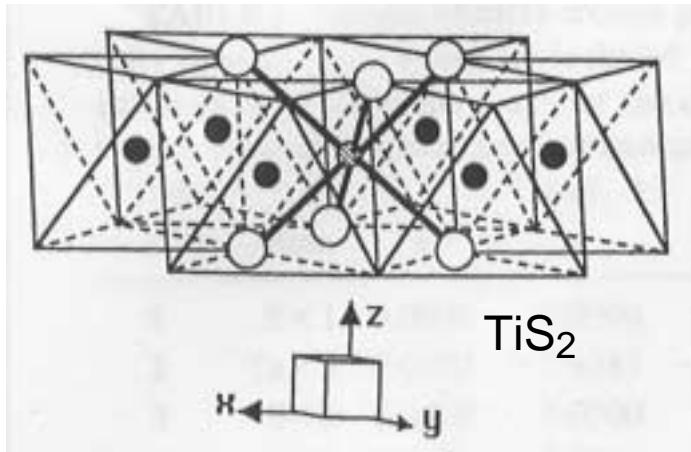
A. Šimůnek, O. Šipr, S. Bocharov, D. Heumann and G. Dräger, Phys. Rev. B **56**, 12232 (1998),

S. Sharma, T. Nautiyal, G. S. Singh, S. Auluck, P. Blaha and C. Ambrosch-Draxl, Phys. Rev. B **59**, 14833 (1999).

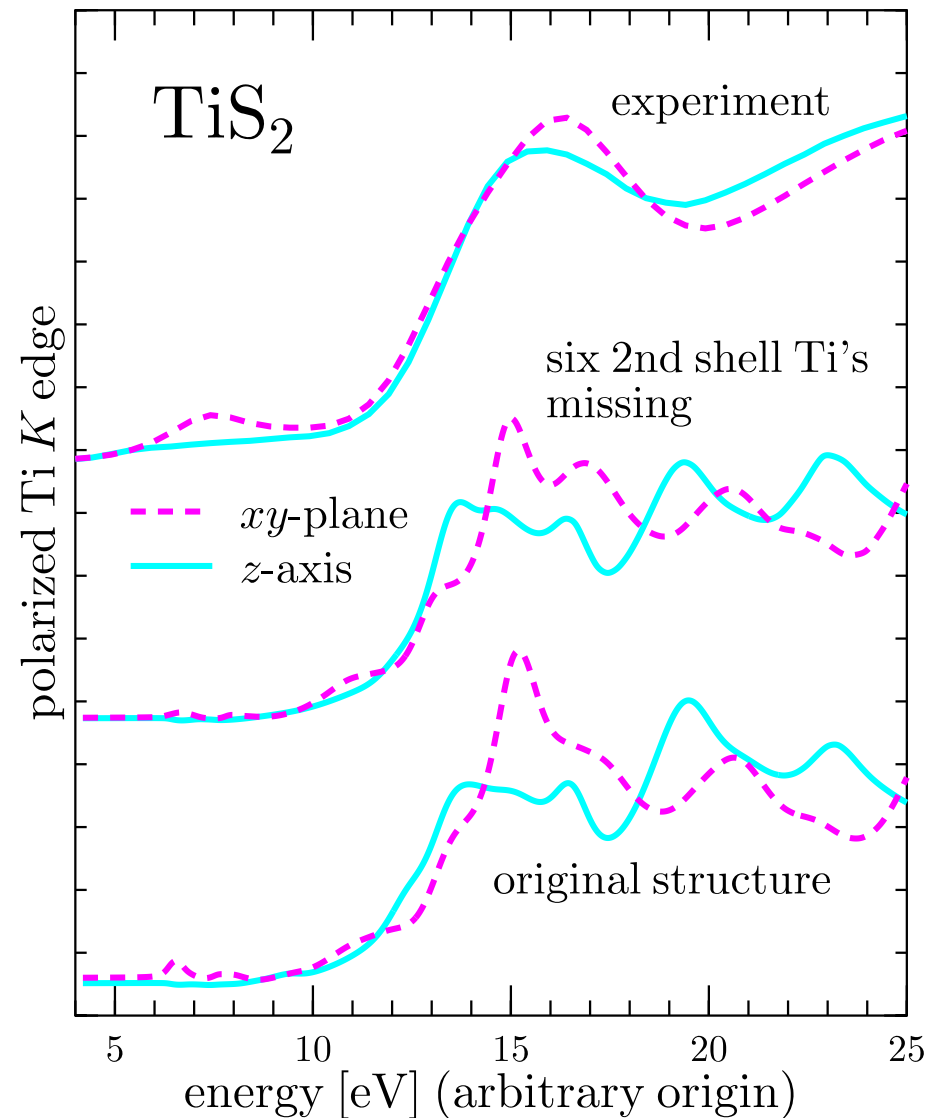
Interpretation of the pre-peak proposed by Wu *et al.*: Generated by dipole-allowed transitions to Ti t_{2g} and e_g bands which arise from hybridization of $4p$ orbitals of the **central Ti atom** and of $3d$ orbitals of **Ti atoms belonging the next-nearest coordination shell**.

Role of six 2nd-shell titanium atoms in Ti *K*-edge XANES

What happens to the calculated spectrum if six Ti atoms of the second nearest coordination shell are omitted?



Significant changes in spectrum can be observed only at the pre-edge structure [Z. Y. Wu, G. Ouvrard, P. Moreau and C. R. Natoli, Phys. Rev. B **55**, 9508 (1997)].



Role of Ti atoms from the second coordination shell seems to be crucial.

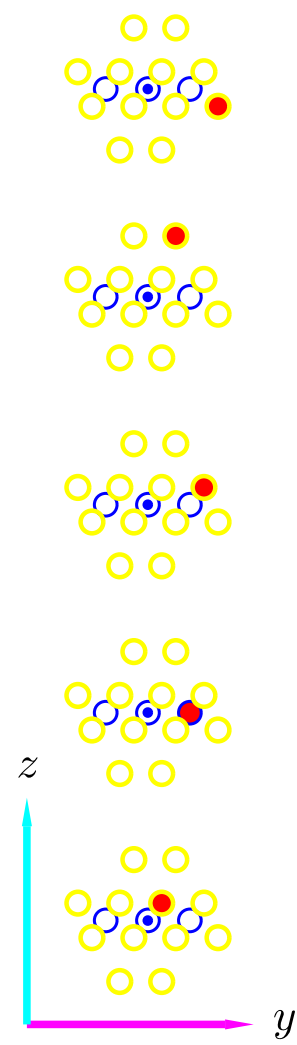
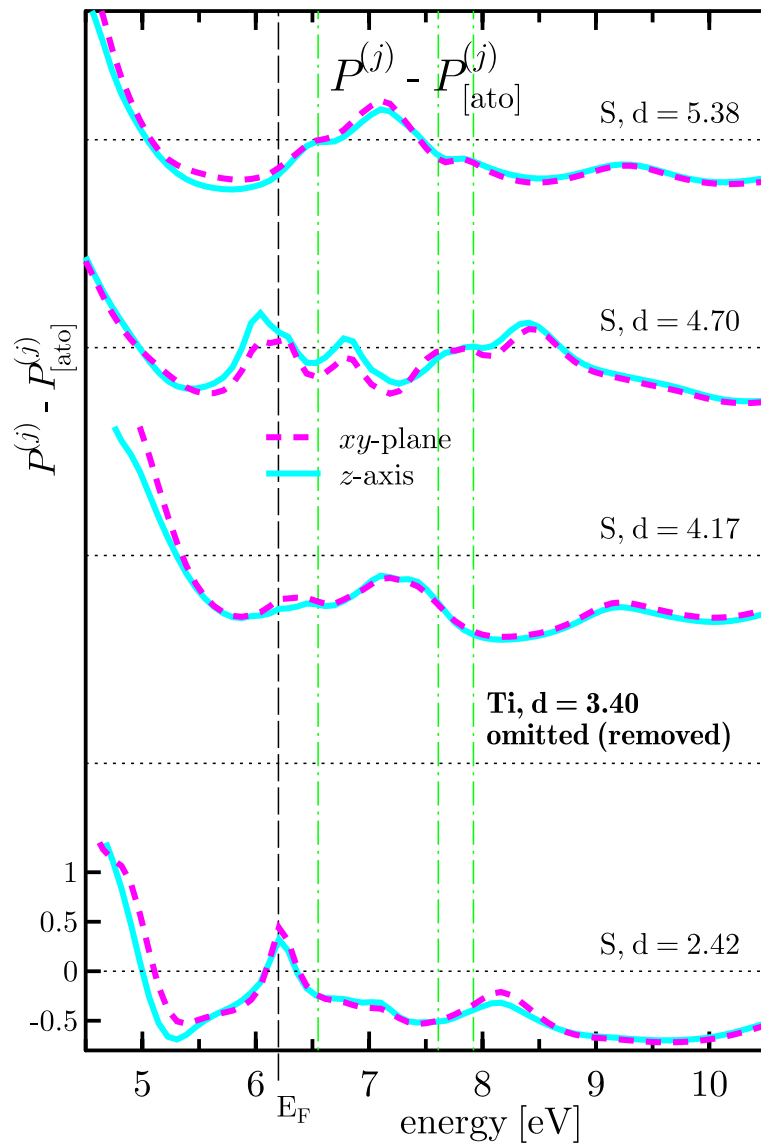
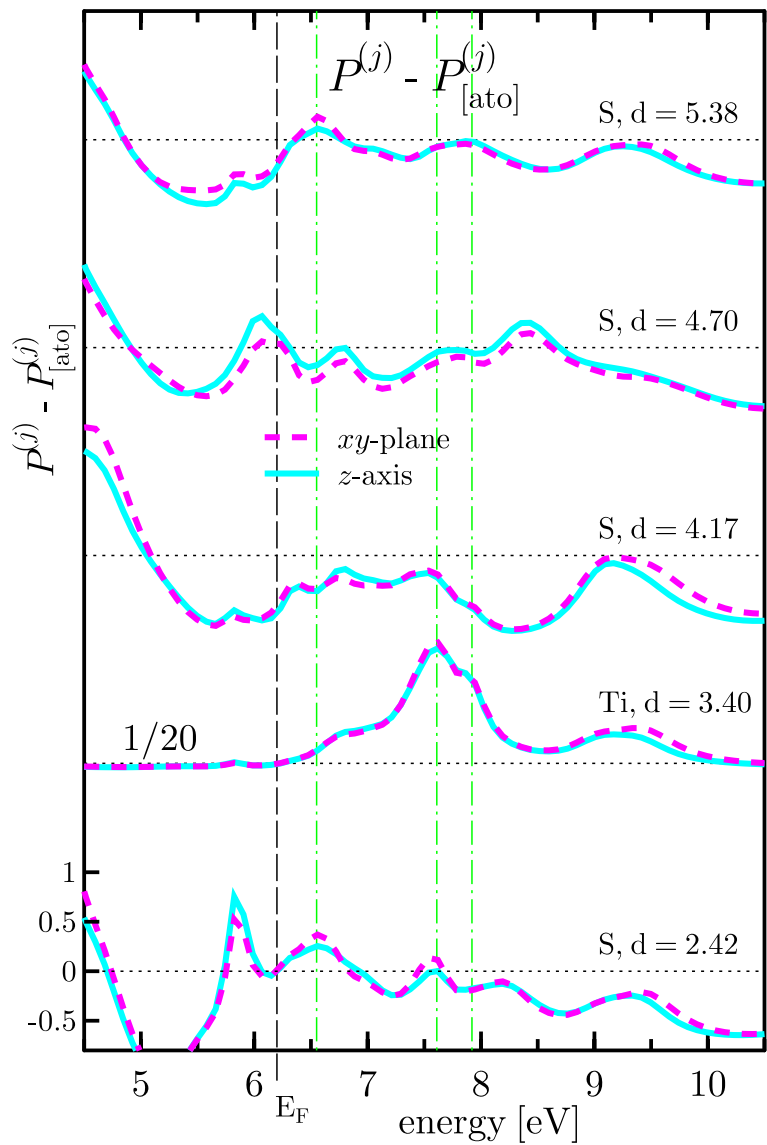
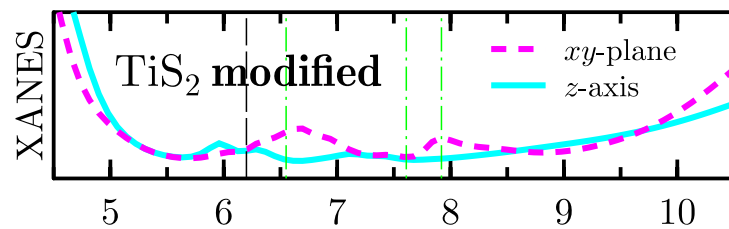
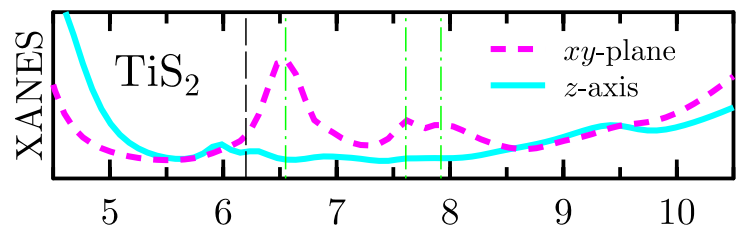
Assessing roles of 2nd-shell Ti atoms (and other neighbours) in creating the pre-edge structure

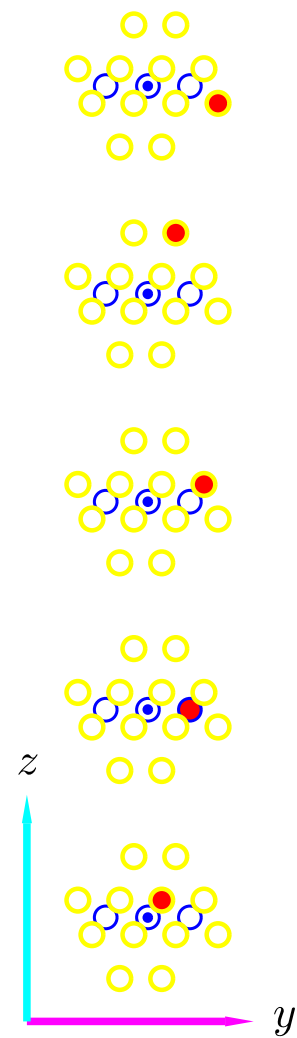
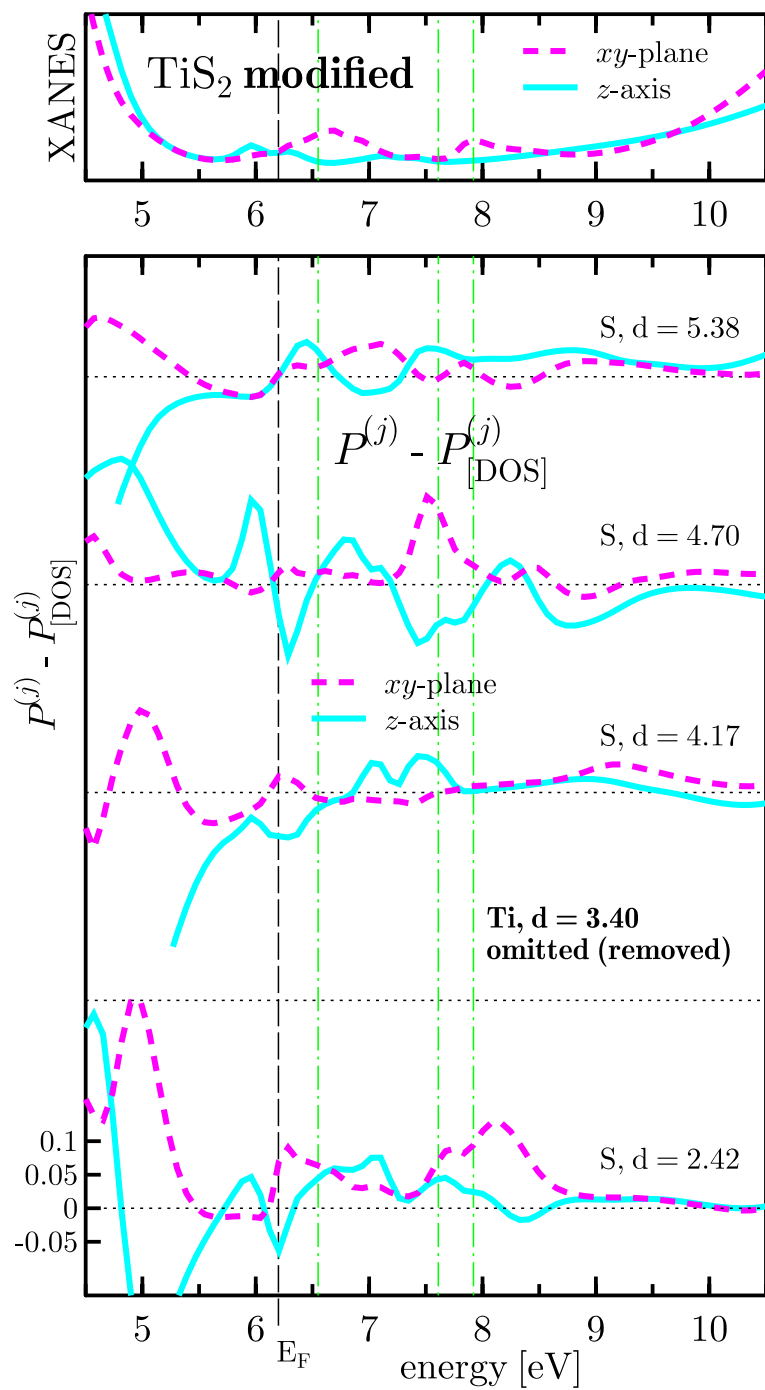
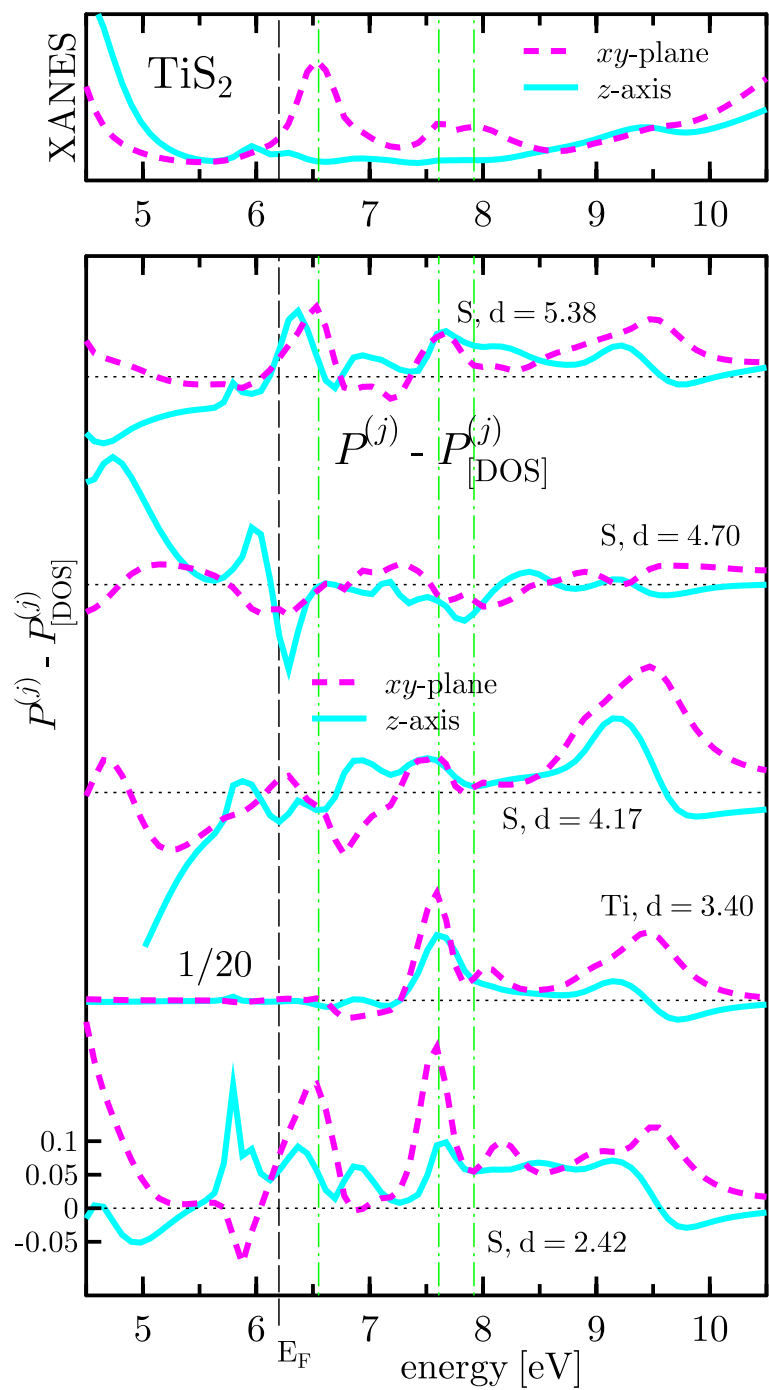
Question we ask: What is the probability that an excited photoelectron can be found in the vicinity of various atoms for an original TiS_2 structure and for a modified TiS_2 structure — with six Ti atoms of the second coordination shell removed.

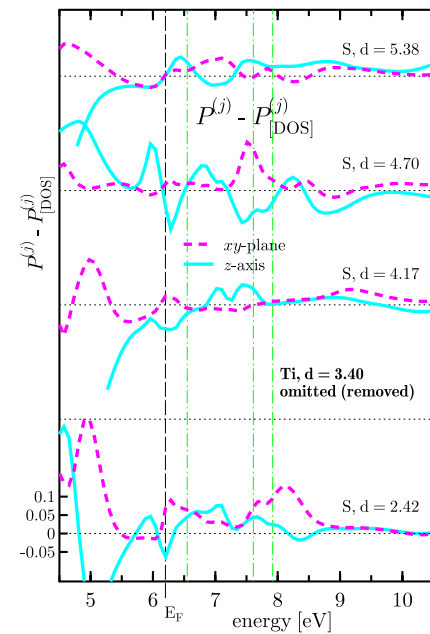
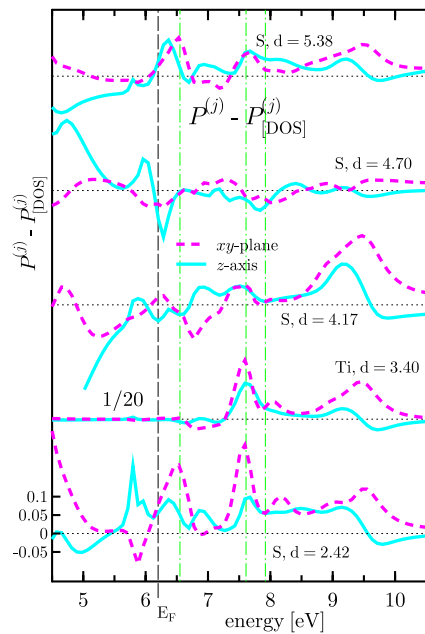
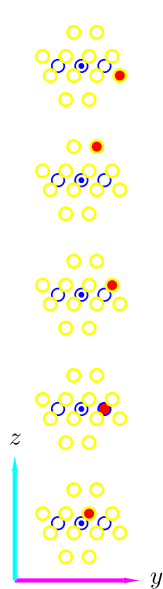
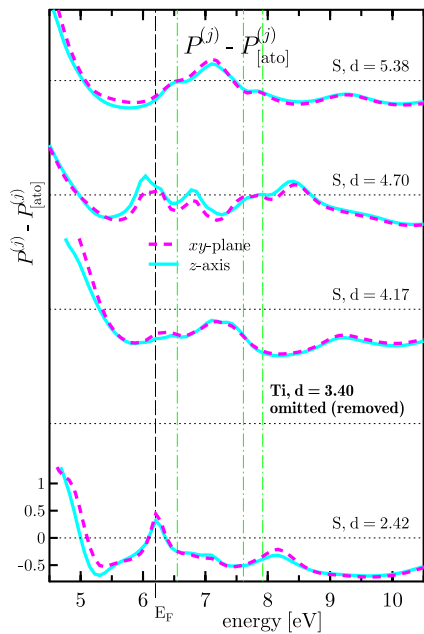
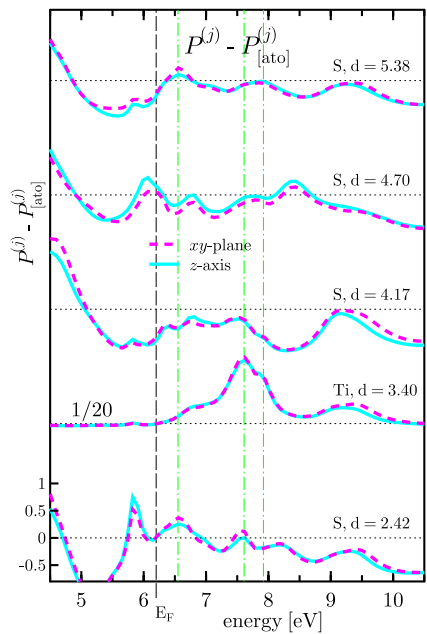
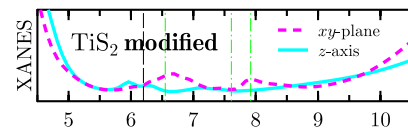
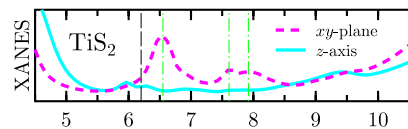
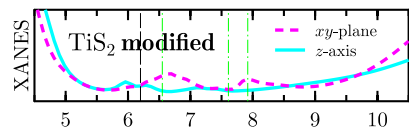
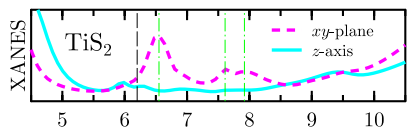
Tools we use: Evaluate differential photoelectron wave function probability density integrated within spheres around respective atoms,

$$P^j = P_{\text{DOS}}^j, \quad P^j = P_{\text{ato}}^j$$

Few technical details: (In fact they do not matter as we try to understand the calculated spectrum, not the experimental one.) Cluster of 135 atoms employed, non self-consistent muffin-tin potential constructed via Mattheiss prescription (self-consistency it not important in this case), damping of photoelectron accounted for via constant imaginary potential (corresponds to a half of $1s$ core hole lifetime smearing), relaxed and screen core hole included (roughly equivalent to $Z + 1$ model).







Photoelectron probability density at Ti K (pre-)edge of TiS_2

Discussion

1. Exhibits **resonance-like structure** and depends on particular choice of atom around which it is evaluated.
2. The bulk of $P^{(j)}$ is **dominated by DOS**-like effects — hardly any polarization dependence can be found in $P^{(j)}$ unless $P_{\text{DOS}}^{(j)}$ is subtracted.
3. For some atoms and/or peaks, a visual **connection between XANES and $P^{(j)}$** can be established, for other features such a discernible connection is clearly absent.
4. *Electron states contributing to the pre-peak:*
 - Although a lot of wave function rests on 2nd-shell titanium atoms, most of it is just DOS-like stuff, i.e., not specifically connected with XAS process.
 - Nearest **sulphur atom participates significantly** in constituting the XANES photoelectron wave function at both pre-peaks.
 - XANES-related enhancement of wave function on 2nd-shell Ti's occurs only at the second, less important, peak of the pre-edge structure.
 - The physical process responsible for the $\epsilon_{\parallel xy}$ pre-peak is thus a more **complicated one that mere mixing of central Ti 4p and next-neighboring Ti 3d orbitals**.

Current state of the photoelectron wave function business

Tentative conclusions:

- **Yes, it makes a physical sense** to explore the probability that the photoelectron participating in a XANES process can be found at a specific place. [And it can be done in practice.]
- The fine structure of such a probability density, taken as a function of photoelectron energy, **does not copy the corresponding XANES:**
Is this a consequence of the interference nature of x-ray absorption fine structure?
- Nothing can be really said about relation between photoelectron probability density and importance of various scattering paths (as **different terms occur** in multiple-scattering expansion of the scattering matrix and of the photoelectron wave function).
- The spatial dependence of this probability density provides **information complementary to analyzing theoretical spectra** for various trial structures (“move and calculate”).