

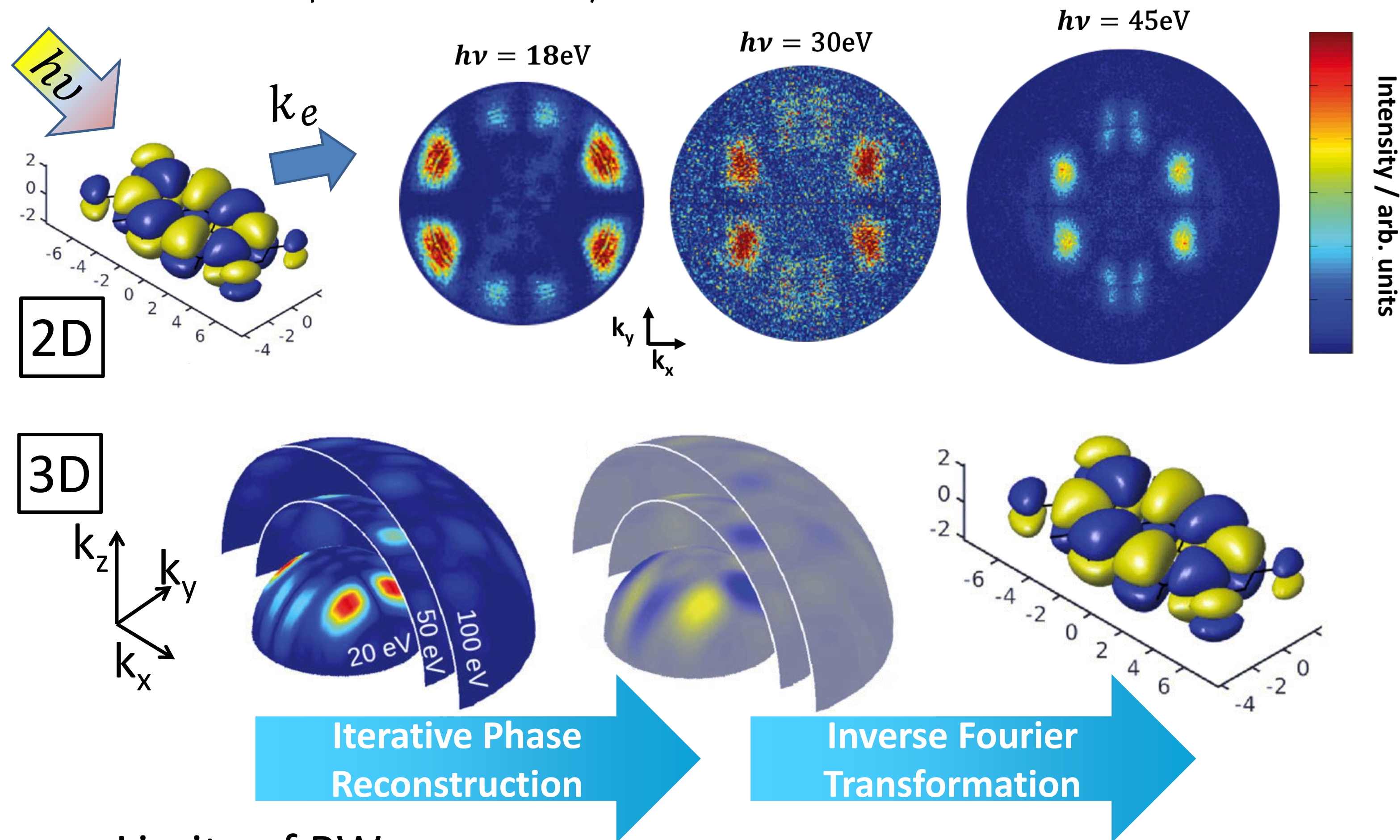
Advancing Photoemission Orbital Tomography Towards Absolute Electron Density Reconstruction

Hans Kirschner, Hendrik Kaser, Alexander Gottwald and Mathias Richter

Physikalisch-Technische Bundesanstalt (PTB), Abbestr. 2-12, 10587 Berlin Germany

Motivation: Photoemission Orbital Tomography (POT)

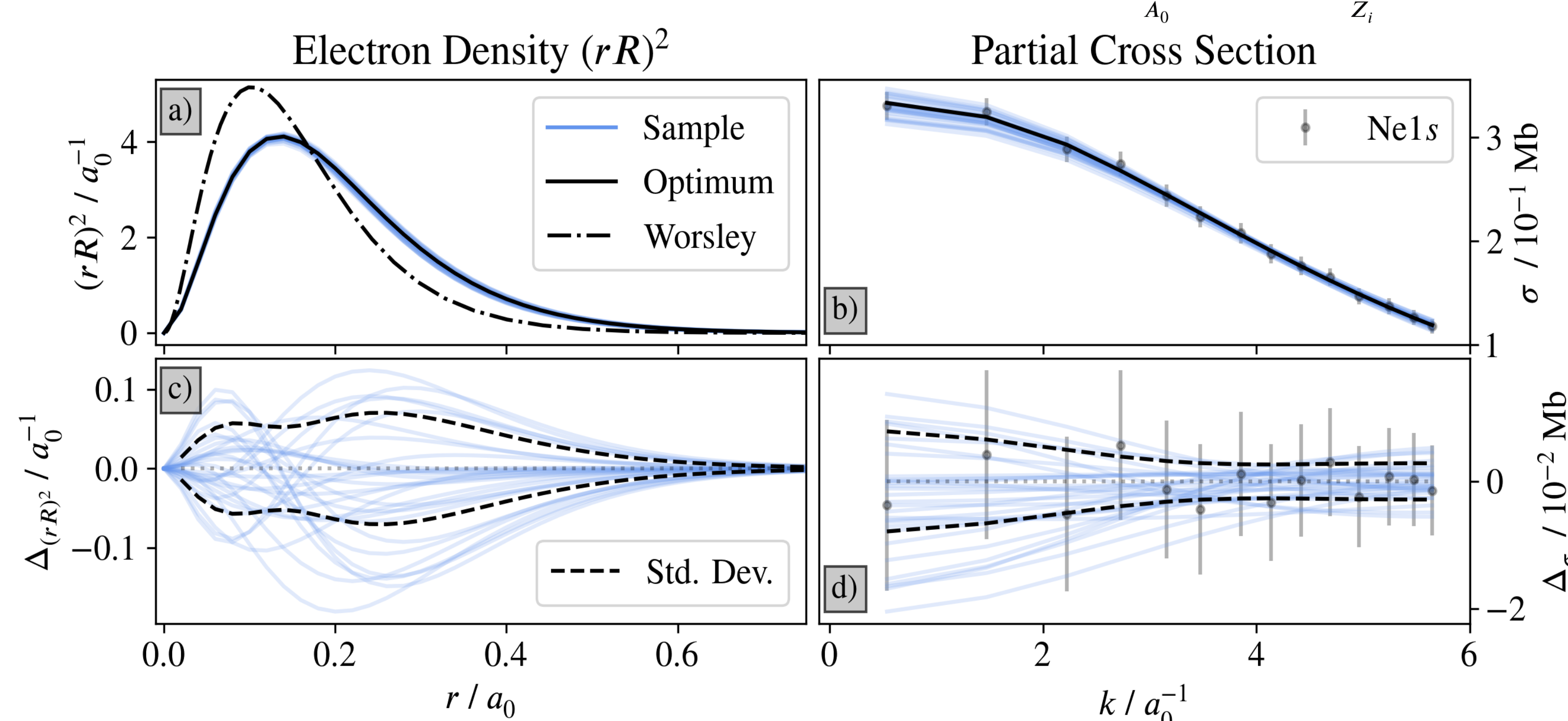
- Reconstruct molecular orbitals $\Psi_i(\vec{r})$ from ARPES data
- Direct access to molecular orbital by plane wave (PW)
- $I(\vec{k}) \propto \left| \langle \Psi_i | \vec{\epsilon} \cdot \vec{\nabla} | e^{i\vec{k}\vec{r}} \rangle \right|^2 \propto \left| (\vec{k}\vec{\epsilon}) \int \Psi_i(r) e^{i\vec{k}\vec{r}} d\vec{r} \right|^2$



- Limits of PW:
 - Erroneous energy dependence (along k_z)
 - Neglects spherical wave nature
 - Arbitrary scale \rightarrow Reconstruction only in arbitrary units
- **Goal:**
 - Final state description beyond the PW to
 - Provide absolute scale reconstruction + uncertainties

POT on gas-phase atoms/molecules

- POT in gas-phase: Photoionization cross section (PCS)
- $\sigma_{nl}(k) \propto |\langle \Psi_{i,nl} | \vec{r} | \Psi_f \rangle|^2 \propto \int_0^\infty R_{nl}(r) r F_l(kr) r^2 dr$
- $F_l(kr)$: Spherical wave + Coulomb potential (central-field)
- Absolute scale data for neon well-known and available
- Optimization algorithm: Probability distribution for parameters

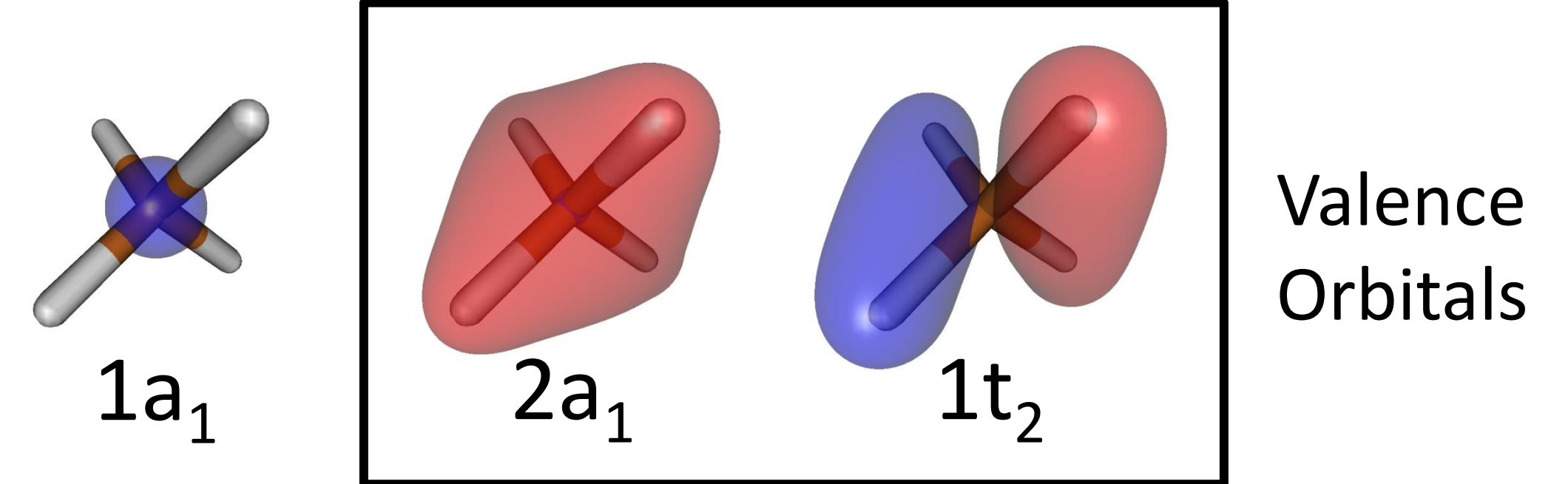


- Reconstruction of **1s**, **2s** and **2p** electron densities
- However: neon is difficult to handle, as it is a noble gas
- Methane (CH4) as a bridge between single atoms and complex molecules on surfaces, as used in POT



PCS of Methane

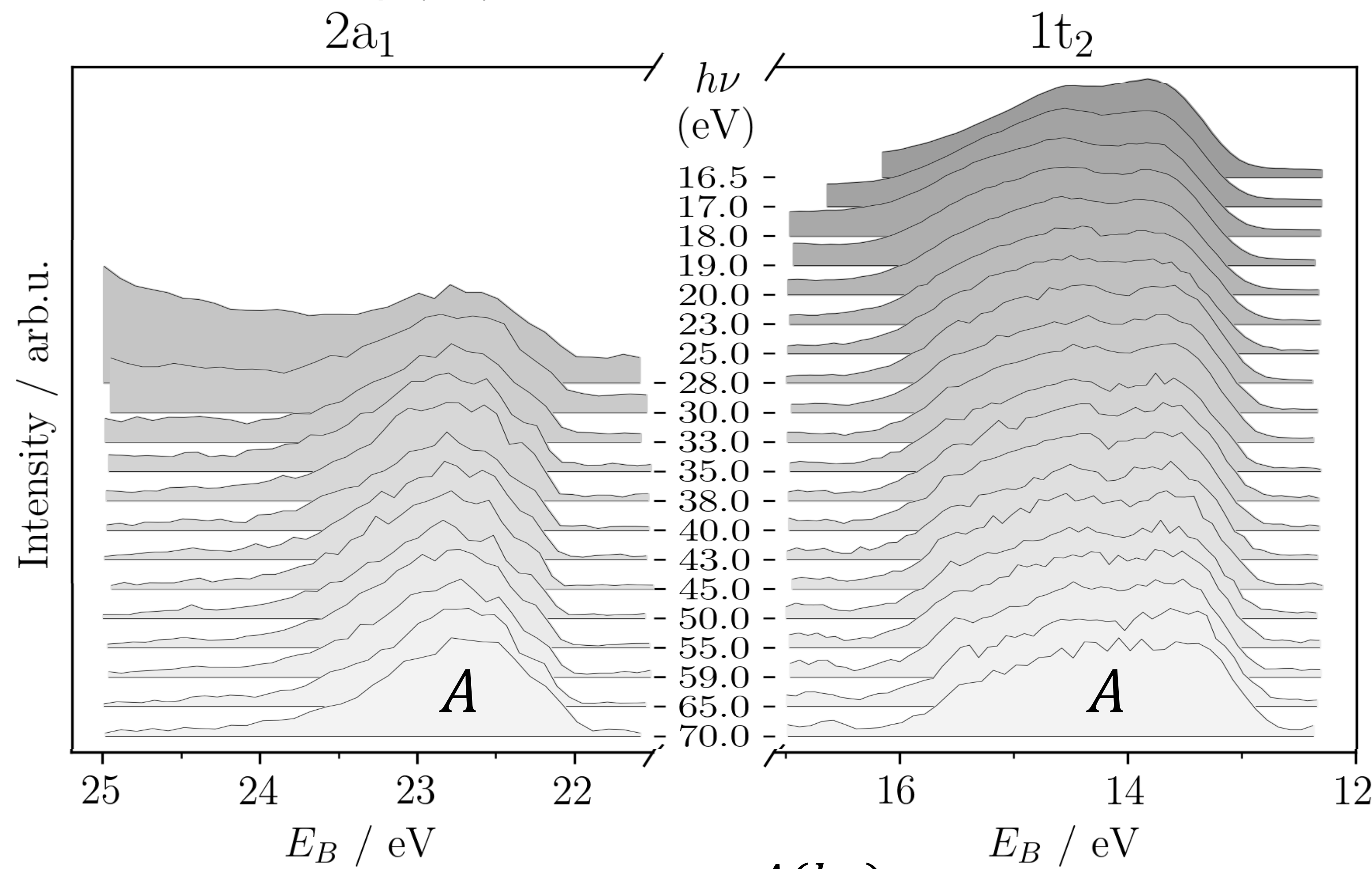
- Similar to neon: 10 electrons + el. Configuration $1a_1^2 2a_1^2 1t_2^6$



- Experimental PCS data necessary

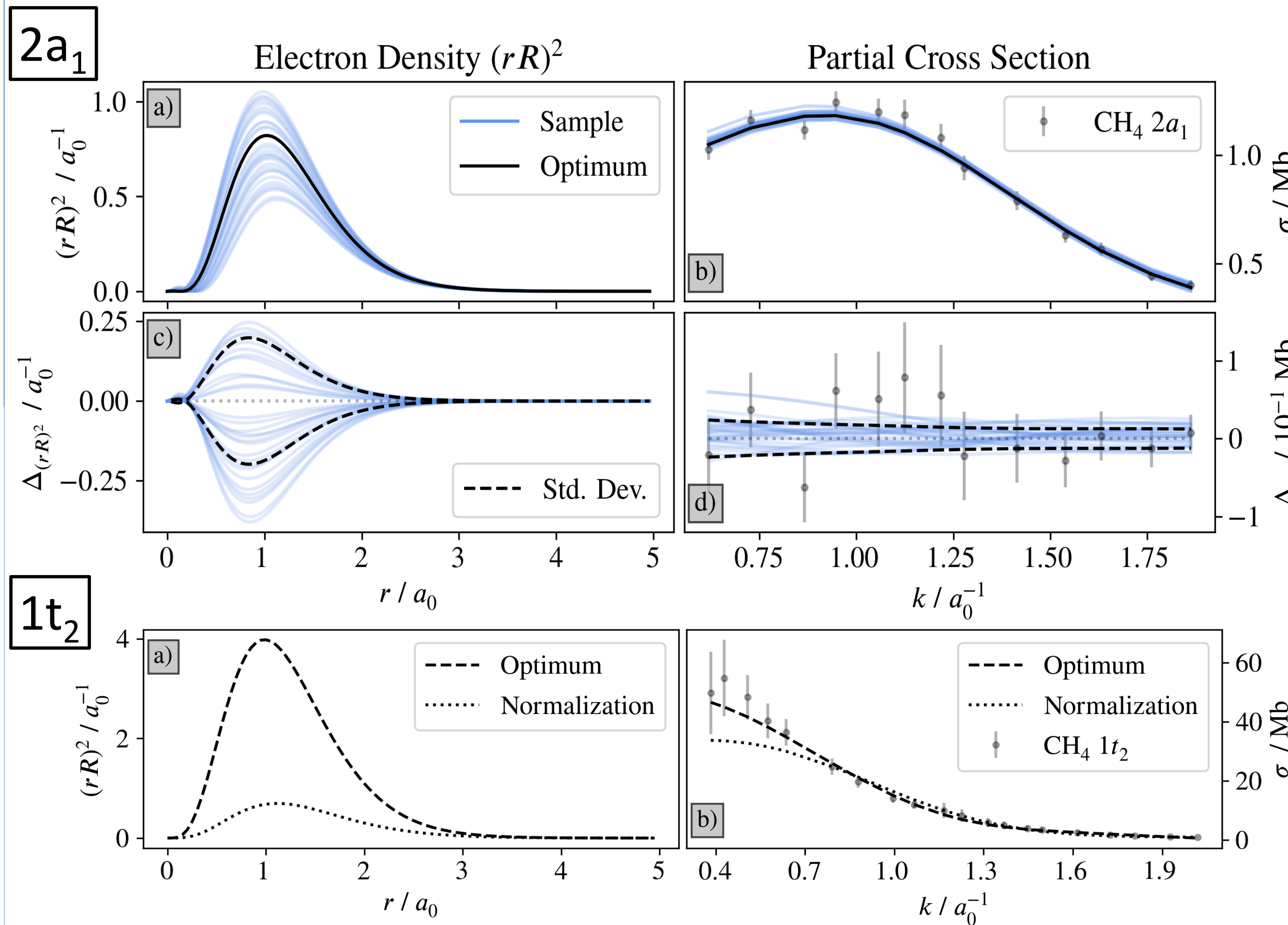
Photoemission Spectra (PES)

- Gas phase PES of CH4 measured with known absolute photon flux $\phi(h\nu)$ at the undulator beamline of PTB's



Results

- PCS + uncertainties $\sigma(h\nu) \propto \frac{A(h\nu)}{\phi(h\nu)}$
- Test central-field based reconstruction method



Summary

- Final state beyond the PW approximation
- Reconstruction of absolute radial electron densities + uncertainties
- PES + PCS of methane $1t_2$ and $2a_1$ with uncertainties
- Test central-field reconstruction method on methane
 - $2a_1$ ok
 - $1t_2$ shows limits of the central-field method