A real space multiple scattering photoemission and valence

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method for angle resolved band photoelectron diffraction

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ABSTRACT

A computational method is presented for angle resolved photoemission spectra (ARPES) and photoelectron diffraction (PED) in the ultraviolet regime. The one-step model is emplyed and both initial valence and final continuum states are calculated using the finite clus ter real space multiple scattering method, which makes the method flexible and allows an easy link with core-level PED. The method is applied to the Cu(111) valence band and good agreement with experiment is found for both ARPES spectra and PED patterns. When the PED patterns are integrated over a filled band of a single orbital symmetry, such as Cu-3d, we show, both numerically and analytically, that the exact theory with delocalized initial states can be replaced by the much simpler, core-level-type PED theory where the initial states are taken as localized.

METHOD: REAL SPACE MULTIPLE SCATTERING

- real space multiple scattering (RSMS) is a method for solving the one electron Schrödinger (or Kohn-Sham) equation in the case of a cluster of atoms.

- It is very flexible and particularily suitable for continuum states, such as photoemission final states.

- The problem of scattering from a cluster of atoms is divided into two simpler sub-problems:
  a) resolution of the Schroedinger equation inside each atomic cells of the cluster
  b) matching of the local solutions at the boundaries between cells.

- Here both initial and final states are described by RSMS

Photoemission intensity

$$I(\omega, q, \mathbf{k}') \sim \sum_{\nu} |\langle \mathbf{k}' | D_q | \nu \rangle|^2 \delta(E_{\mathbf{k}'} - E_{\nu} - \hbar\omega)$$

both |i> and |f> wave functions are described in real space multiple scattering theory

$$\langle \mathbf{r} | \mathbf{k} \rangle = \sum_{iL} B_{iL}(\mathbf{k}) \phi_{iL}(\mathbf{r}, E_k)$$

$$B_{iL}(\mathbf{k}) = \sqrt{\frac{k}{\pi}} \sum_{jL'} \tau^{ij}_{LL'} i^{l'} Y_{L'}(\hat{\mathbf{k}}) e^{i\mathbf{k}\cdot R_{j0}}$$

sum over initial states

$$\sum_{\nu} \langle \mathbf{r} | \nu \rangle \langle \nu | \mathbf{r}' \rangle \delta(E - E_{\nu}) = \sum_{ijLL'} \phi_{iL}(\mathbf{r}, E_{\nu}) I^{ij}_{LL'} \phi^{*}_{jL'}(\mathbf{r}', E_{\nu})$$

→ optical theorem

τ = scattering path operator calculated by matrix inversion

$$I^{ij}_{LL'} \equiv -\frac{1}{2i\pi} (\tau - \tau^{\dagger})^{ij}_{LL'}$$

final expressions

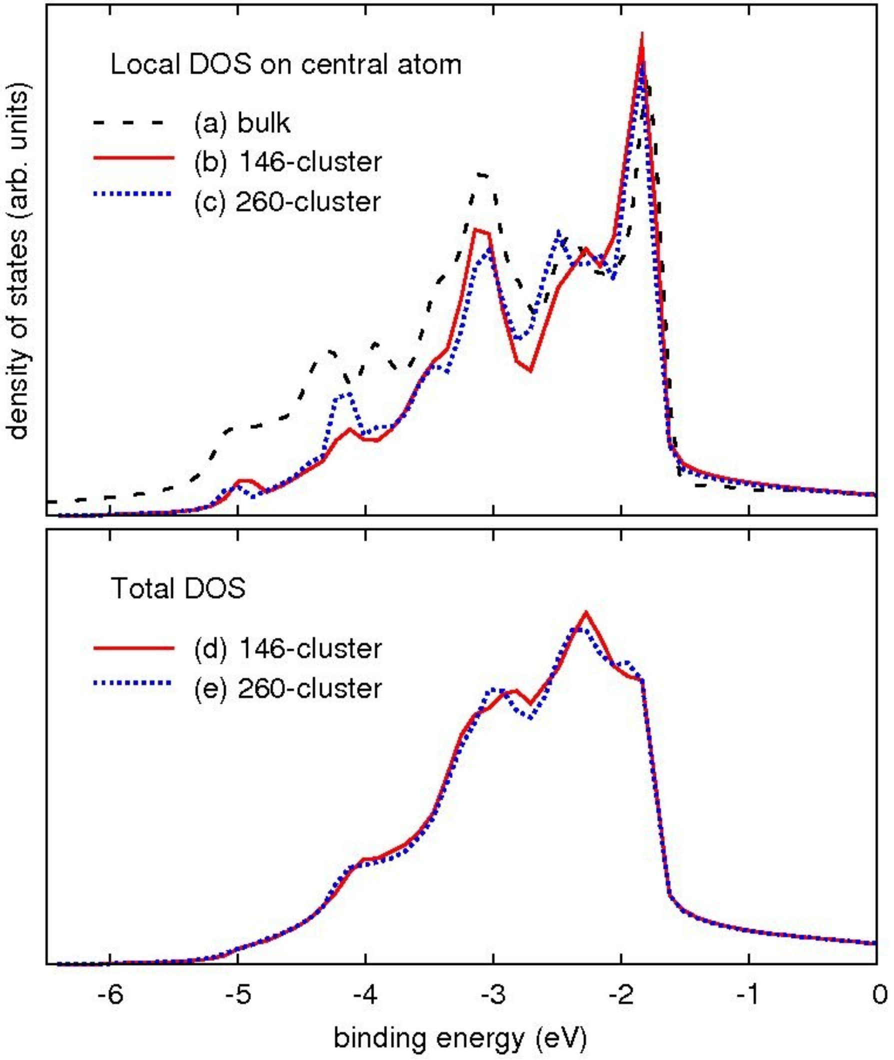
$$I(\omega, q, \mathbf{k}') \sim \sum_{ijLL'} M^{q}_{iL}(\mathbf{k}) I^{ij}_{LL'}(E_k - \hbar\omega) M^{q*}_{jL'}(\mathbf{k})$$

$$M^{q}_{iL}(\mathbf{k}) = \sum_{L''} B^{*}_{iL''}(\mathbf{k}) \langle \phi_{iL''}(E_k) | D_q | \phi_{iL}(E_k - \hbar\omega) \rangle$$

Application to Cu(111)

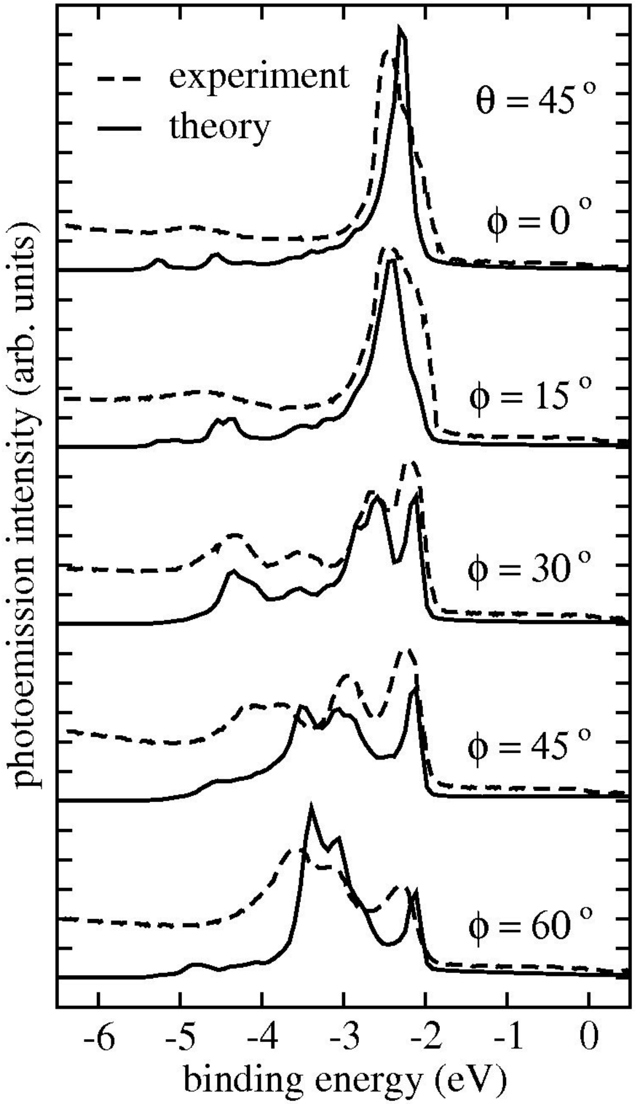
density of states

bulk vs cluster DOS

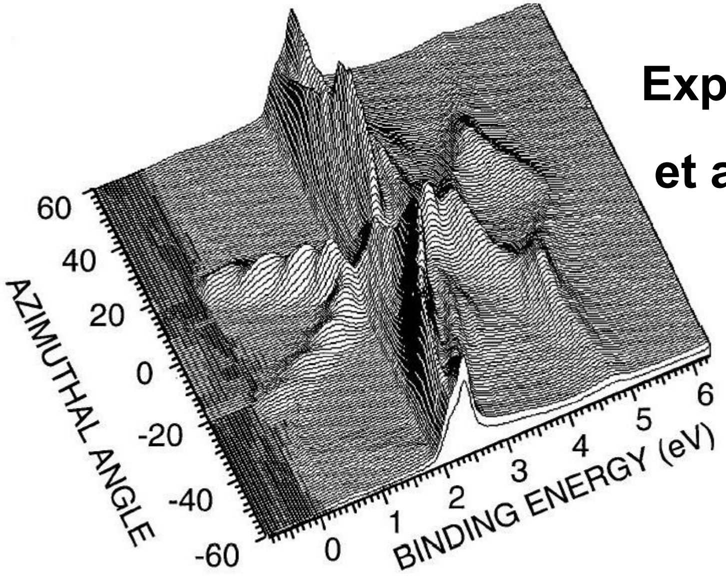


ARPES

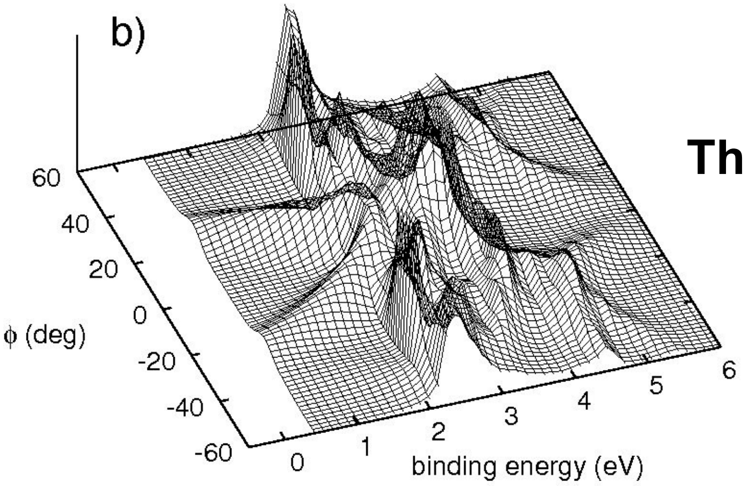
θ= 60°



Exp: L. Ilver et al. SSC 18 ('76) 677



Exp: Osterwalder et al PRB 1996.

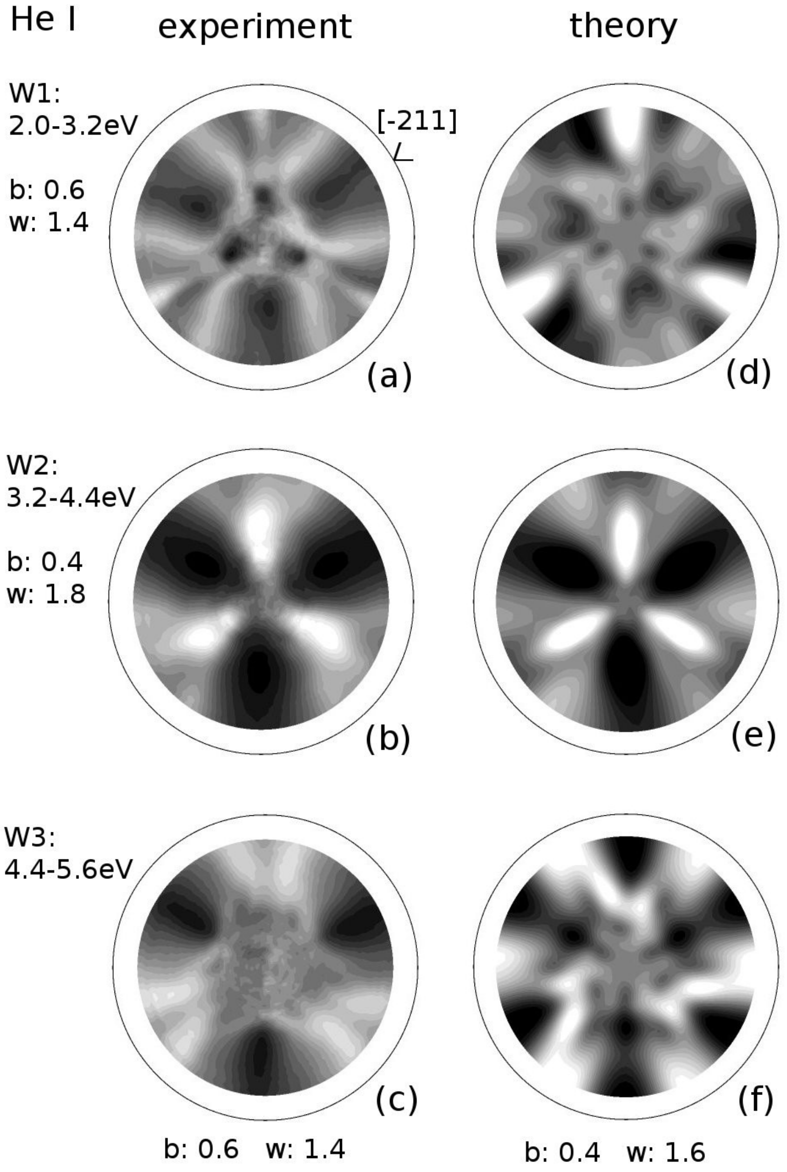


Theory

UPD

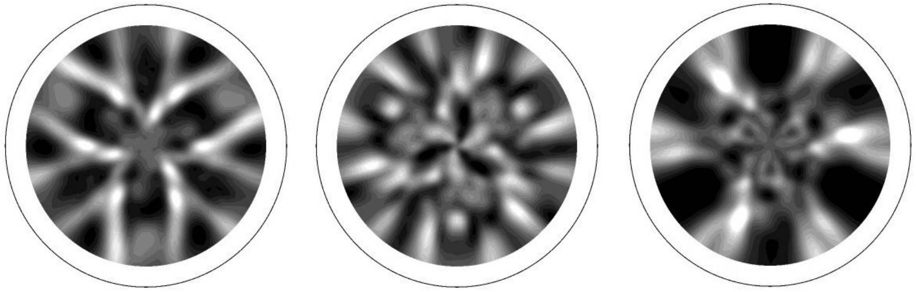
3 energy windows

E = 21.2 eV (He I)



E = 40.8 eV (He II)

theory



W1: 2.0-3.2eV
b: 0.4 w: 2.0

W2: 3.2-4.4eV
b: 0.6 w: 1.6

W3: 4.4-5.6eV
b: 0.3 w: 2.4

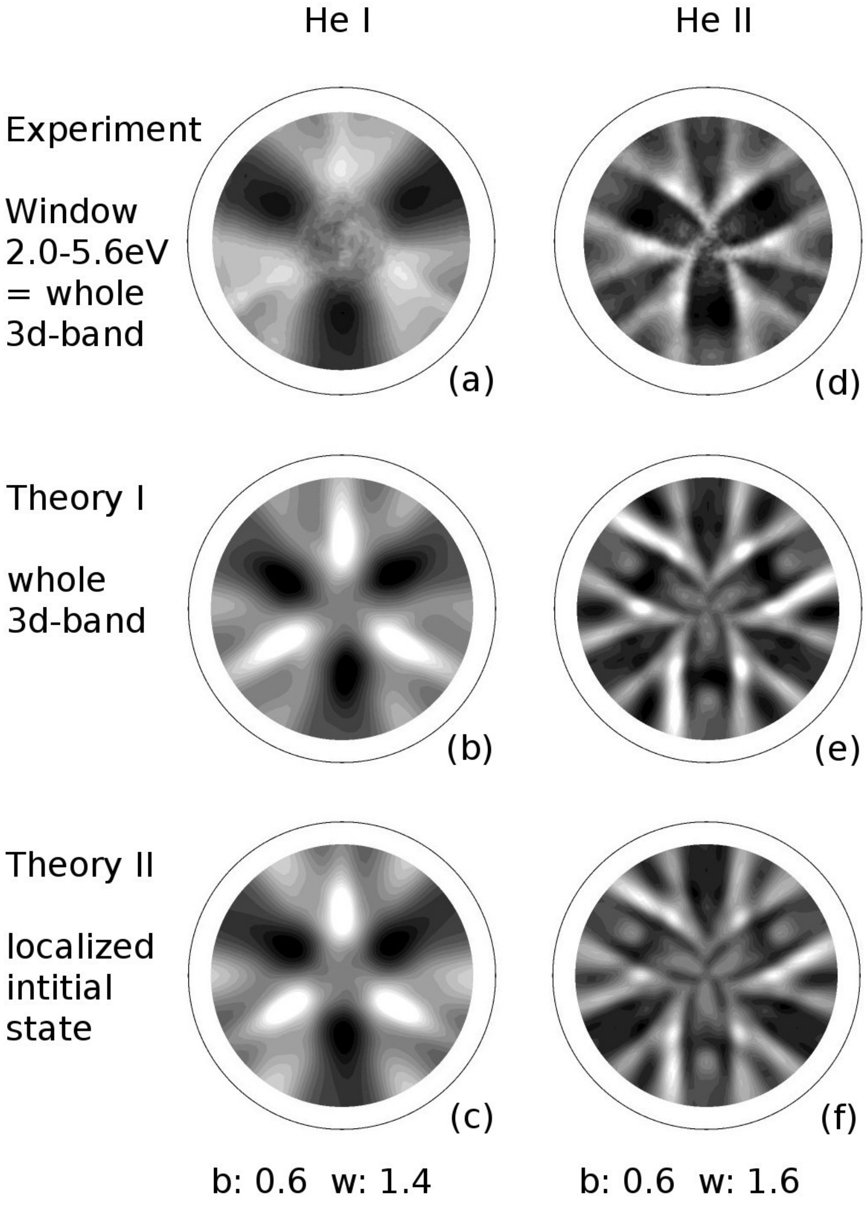
UPD

whole Cu-3d band

excellent agreement

both with exact theory I (delocalized Initial states)

and with simplified theory II (localized Initial states)



equivalence between exact theory (I) and simplified theory (II) for integration over filled band of single l-character

$$I(\mathbf{k}') = \sum_{\nu} |\langle \mathbf{k}'|D_q|\nu\rangle|^2 \delta(E_{\mathbf{k}'} - E_\nu - \hbar\omega)$$

$$|\nu\rangle = \sum_{im} C^{\nu}_{ilm} |ilm\rangle \qquad\qquad \sum_{\nu} C^{\nu}_{ilm} C^{\nu *}_{jlm'} = \delta_{ij}\delta_{mm'} \ .$$

$$I(\mathbf{k}') = \sum_{ijmm'} \langle \mathbf{k}'|D_q|ilm\rangle\langle jlm'|D^{\dagger}_q|\mathbf{k}'\rangle \times \sum_{\nu} C^{\nu}_{ilm} C^{\nu *}_{jlm'} \delta(E_{\mathbf{k}'} - E_\nu - \hbar\omega)$$

$$I_{\text{int}}(\hat{\mathbf{k}}') \equiv \int_{E_1+\hbar\omega}^{E_2+\hbar\omega} I(\mathbf{k}')dE_{k'} = \sum_{ijmm'} \sum_{\nu} C^{\nu}_{ilm} C^{\nu *}_{jlm'} \times \int_{E_1+\hbar\omega}^{E_2+\hbar\omega} \langle \mathbf{k}'|D_q|ilm\rangle\langle jlm'|D^{\dagger}_q|\mathbf{k}'\rangle \delta(E_{\mathbf{k}'} - E_\nu - \hbar\omega) dE_{\mathbf{k}'}$$

$$\langle \mathbf{k}'|D_q|ilm\rangle \approx \langle \bar{E}_f, \hat{\mathbf{k}}'|D_q|ilm\rangle$$

$$I_{\text{int}}(\hat{\mathbf{k}}') \approx \sum_{im} |\langle \bar{E}_f, \hat{\mathbf{k}}'|D_q|ilm\rangle|^2 \ .$$

Conclusions

- real-space multiple scattering method is able to reproduce the essential features of valence band spectra both in angle and energy resolved modes

- supported by our theoretical method, UPD can become a promising probe for surface structure

- ARPES (E(k) dispersion) and energy resolved UPD are well described

- localized d-orbitals as initial states give very similar patterns as energy integrated UPD with delocalized initial states. Thus the much simpler (XPD-like) theory with localized orbitals is sufficient for describing UPD data integrated over the full d-band.
- this was conjectured by J. Osterwalder et al. [PRB 53 ('96) 10209]

- conjecture is proven here analytically and numerically:
integration over a filled an pure l-band is equivalent to summing over localized l-orbitals