Theory and computation of surface-sensitive spectroscopy: RAS and HREELS

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Yambo hands-on tutorial on electronic and optical excitations: from basic to advanced applications
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1. Apply external probe

2. Measure response of system

3. Deduce microscopic properties
“God made the bulk; surfaces were invented by the devil.”

Wolfgang Pauli
# Surfaces: the devil's playground

## Experimental challenges
- Variety of reconstructions
- Difficulty of preparation
- Difficulty of interpreting observations
- Variety of adsorbates (deposited...and accidental!)
- Capping/interfaces

## Theoretical challenges
- Computationally demanding:
  - Slab layers
  - Vacuum layers
  - k-points
- Theoretically demanding:
  - Semi infinite
  - Treatment of LFE/BSE/etc

Many early theoretical studies were over simplistic
Many early experimental studies were made on poorly prepared surfaces...
Electrons or photons?

Penetration depth of light is large: probe surfaces and buried interfaces

Surface/interface probes: light

Penetration depth of light is large: surfaces and buried interfaces, capped nanostructures.
Non destructive!

**How to extract surface response?**

**Second harmonic generation SHG** – exploit symmetry change normal to surface
**Surface differential reflectance SDR** – reflectance change after e.g. oxidation
**Spectroscopic ellipsometry SE** – change in light polarization on reflection from thin films
**Surface X-ray diffraction SXRD** – surface sensitivity to atomic positions at grazing incidence
**X-ray magnetic circular dichroism XMCD/Magneto-optical Kerr effect MOKE/Magnetic second harmonic generation MSHG**-related probes of magnetic nanostructures
Reflectance anisotropy spectroscopy

RAS measures the difference in reflectance ($\Delta r$) between two orthogonal directions ($x, y$) normalised to the mean reflectance ($r$), as a function of photon energy.

\[
\Delta r = \frac{r_x - r_y}{(r_x + r_y) / 2}
\]

$r = \text{complex Fresnel reflection coefficients}$
Reflectance anisotropy spectroscopy

Advantages

- Access to UHV, high pressure, ambient, liquid environments. (semiconductor growth environments)
- Sub-monolayer (~0.01 ML) sensitivity
- Monitor growth of thin films.
- Monitor at a fixed energy with millisecond time response.
- Sensitive to surface states.
- Surface morphology (roughness, reconstructions, steps)
- Molecular orientation, interface bonding

Restrictions

- Only surface sensitive for crystals having inversion symmetry
- The surface must have orthogonal directions (x, y) which are not symmetrically equivalent.
RAS setup

FCC(110) surface orientation

\[
\text{Re} \left( \frac{\Delta r}{r} \right) = \text{Re} \left( \frac{r_x - r_y}{(r_x + r_y)/2} \right)
\]

[Most common arrangement based on Aspnes design - JVST A6 1327 (1988)]

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Surface/interface probes: electrons

Huge array of techniques! STM, LEED, RHEED....

Transmission EELS: tunable over huge range
Reflection REELS/HREELS: surface sensitive variant
HREELS mostly used for probing meV range (vibrations) but can also probe optical regime like RAS
High-resolution EELS

\[
\frac{d^2 S}{d(q_\parallel) d(\hbar \omega)} = A(k, k') \times \text{Im } g(q_\parallel, \omega)
\]

= kinematic factor \times loss function

\[
q = (q_\parallel, \Delta k)
\]

\[
E' - E = \hbar \omega
\]

\[
k'_\parallel - k_\parallel = q_\parallel
\]
HREELS can also be used to measure **surface anisotropy**

Close correspondence with RAS, but with enhanced surface sensitivity


RAS and HREELS effectively probe the same surface response function
Ab-initio simulation

Three aspects to the problem:

1. **Modelling the system**
   (crystal termination; surface structure; one-electron wavefunctions)

2. **Modelling the dielectric susceptibility**
   (e-e and e-h interactions)
   = Previous days talks!

3. **Modelling the experimental process**
   (light or electron propagation)
Outline

Theory: RAS
- Reflection beyond Fresnel

Realistic calculations: RAS
- Surface-specific tips and tricks
- Technical approximations
- Physical approximations

Theory: HREELS
- Modeling experiment

Dipole regime - three-layer model

Realistic calculations: HREELS
- Modeling experiment
- Modeling system
- Modeling system
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Continuum approach

Bulk crystal

$$D(r, \omega) = \varepsilon(\omega) E(r, \omega)$$

- Local: $E$ is constant at short range
- Homogeneous: Ratio $D/E$ is independent of position
- Isotropic: In cubic crystals (symmetry)

Semi-infinite crystal (surface)

$$D_i(r, \omega) = \sum_j \int d^3 r' \varepsilon_{ij}(r, r', \omega) E_j(r', \omega)$$

- Non-local: $E(z)$ strongly varies at interface
- Inhomogeneous: Surface - vacuum
- Anisotropic: Reduced symmetry of surface, also in-plane (RAS!)
Light propagation: solutions

3-layer model

McIntyre & Aspnes, Surf. Sci. 24, 417 (1971)

\[ \frac{\Delta R_\alpha}{R} = \frac{4 \omega d}{c} \cos \theta \ \text{Im} \left[ \frac{\varepsilon_s - \varepsilon_b}{\varepsilon_b - 1} \right] \]
Light propagation: solutions

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Perturbative solution

Bagchi, Barrera, Rajagopal, Phys. Rev. B 20, 4824 (1979)


Jellium

Real surfaces

\[
\frac{\Delta R_\alpha(\omega)}{R_0(\omega)} = \frac{4\omega}{c} \Im \left[ \frac{\Delta \varepsilon_{\alpha\alpha}(\omega)}{\varepsilon_b(\omega) - 1} \right]
\]

\[
\Delta \varepsilon_{\alpha\alpha}(\omega) = \int dz \int dz' \left[ \varepsilon_{\alpha\alpha}(\omega, z, z') - \delta(z - z')\varepsilon_0(\omega, z) \right] - \int dz \int dz' \int dz'' \int dz''' \varepsilon_{az}(\omega, z, z'')\varepsilon_{z\alpha}^{-1}(\omega, z'', z''')\varepsilon_{z\alpha}(\omega, z''', z')
\]
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\[
\Delta \varepsilon_{\alpha\alpha}(\omega) = \int dz \int dz' \left[ \varepsilon_{\alpha\alpha}(\omega, z, z') - \delta(z - z')\varepsilon_0(\omega, z) \right]
- \int dz \int dz' \int dz'' \int dz''' \varepsilon_{\alpha z}(\omega, z, z'') \varepsilon_{z z''}^{-1}(\omega, z'', z''' \varepsilon_{z\alpha}(\omega, z'''', z')
\]

Note: MA model correct if
\[
\langle \Delta \varepsilon_{\alpha\alpha} \rangle = d (\varepsilon_s - \varepsilon_b)
\]
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\]

\[
\Delta \varepsilon_{\alpha\alpha}(\omega) = \int dz \int dz' [\varepsilon_{\alpha\alpha}(\omega,z,z') - \delta(z - z')\varepsilon_0(\omega,z)]
\]

\[
- \int dz \int dz' \int dz'' \int dz''' \varepsilon_{\alpha z}(\omega,z,z'')\varepsilon_{zz''}^{-1}(\omega,z'',z''')\varepsilon_{z\alpha}(\omega,z''',z')
\]

Off diagonal elements non-zero for semi-infinite crystal
Reported to be negligible in III-V(110) case

Light propagation: solutions

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\frac{\Delta R_\alpha}{R} = \frac{4\omega d}{c} \cos \theta \quad \text{Im} \left[ \frac{\varepsilon_s - \varepsilon_b}{\varepsilon_b - 1} \right]
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\[
\frac{\Delta R_\alpha(\omega)}{R_0(\omega)} = \frac{4\omega}{c} \text{Im} \left[ \frac{\Delta \varepsilon_{\alpha\alpha}(\omega)}{\varepsilon_b(\omega) - 1} \right]
\]

\[
\frac{\Delta R_\alpha(\omega)}{R_0(\omega)} = \frac{4\omega}{c} \text{Im} \left[ \frac{4\pi \alpha^\text{hs}_{\alpha\alpha}(\omega)}{\varepsilon_b(\omega) - 1} \right]
\]

Slab approximation to surface:
Main quantity to be computed is half-slab polarizability

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Realistic calculations: HREELS

– Modelling experimental setup

- Modeling experiment
- Modeling system
- Modeling experiment
- Modeling system
Surface-specific approach

Supercell scheme easiest: repeated slabs + vacuum

Not all DFT codes created equal for surface structure optimizations!

Always check the electrostatic potential! (dipole correction?)

Vacuum: ~10Å if IP; much more if GW!

Thick slabs needed (>20Å) – delocalized states/resonances

Symmetric slab or H-terminated

The MOST important thing, by far, is having the correct surface structure
Extracting surface from slab

Symmetric slab: just halve the full slab polarizability

\[
\text{Im}[4 \pi \alpha_{ii}^{\text{cut}}(\omega)] = \frac{4 \pi^2 e^2}{m^2 \omega^2 A} \sum_k \sum_{v,c} [P_{vk,ck}^i]^* P_{vk,ck}^i \\
\times \delta(E_{ck} - E_{vk} - \hbar \omega)
\]

Not always possible:

- Forbidden by symmetry
- Symmetric slab may have zero RAS...e.g III-V(001)
- Reconstruction too large
Extracting surface from slab

Non-symmetric slab: Passivating back surface with H?
- Removes the surface states in the gap
- Still contributions from resonances/surface-perturbed states

\[ \text{Im}[4\pi \alpha_{ii}^{\text{cut}}(\omega)] = \]

\[ \frac{8\pi^2 e^2}{m^2 \omega^2 A} \sum_k \sum_{v,c} \left[ P_{v,k,c,k}^i \right]^* \tilde{P}_{v,k,c,k}^i \delta(E_{c,k} - E_{v,k} - \hbar \omega) \]

\[ \tilde{P}_{v,k,c,k}^i = -i\hbar \int dr \psi_{v,k,c,k}^* \theta(z) \frac{\partial}{\partial r_i} \psi_{c,k}(r) \]

Simple “boxcar” function
Extracting surface from slab

Solution: Passivation of back surface + real-space cutoff technique

Can extend to layer by layer analysis


Mendoza, Nastos, Arzate, and Sipe, PRB 74, 075318 (2006)
Symmetry issues

RAS of bulk layers = zero: care with wavefunctions and BZ integration

Si(111) ideal (isotropic)
Symmetry issues

RAS of bulk layers = zero: care with wavefunctions and BZ integration

Si(111) ideal (isotropic)
Spin-orbit coupling on RAS

Si(557)-(5x1):Au
- a stepped, vicinal Si(111) surface reconstruction

DFT-LDA bandstructure:
Clear relationship between bands and surface motifs
Si(557)-(5x1):Au
- a stepped, vicinal Si(111) surface reconstruction

**DFT-LDA bandstructure:**
Clear relationship between bands and surface motifs

**Spin orbit coupling:**
Clear splitting of Au bands near Fermi level (0.2 eV)

Spin-orbit coupling on RAS
Spin-orbit coupling on RAS

Si(557)-(5x1):Au
- a stepped, vicinal Si(111) surface reconstruction

DFT-LDA bandstructure:
Clear relationship between bands and surface motifs

Spin orbit coupling:
Clear splitting of Au bands near Fermi level

RAS:
Negligible effect!

Spin-orbit coupling on RAS

GaSb(001)

- bulk GaSb: strong SO splitting of 0.8eV

Influence on the RAS: mostly broadening

Quite independent of surface motifs

Nonlocal terms in matrix elements

\[ \langle c_{\mathbf{k}} \mid e^{i\mathbf{q} \cdot \mathbf{r}}, H \mid v_{\mathbf{k}'} \rangle = (E_{v_{\mathbf{k}'}} - E_{c_{\mathbf{k}}}) \langle c_{\mathbf{k}} \mid e^{i\mathbf{q} \cdot \mathbf{r}} \mid v_{\mathbf{k}'} \rangle \]

\[ \langle c_{\mathbf{k}} \mid \frac{\mathbf{p}}{m} + \frac{i}{\hbar} [V_{NL}, \mathbf{r}] \mid v_{\mathbf{k}'} \rangle = (E_{v_{\mathbf{k}'}} - E_{c_{\mathbf{k}}}) \langle c_{\mathbf{k}} \mid e^{i\mathbf{q} \cdot \mathbf{r}} \mid v_{\mathbf{k}'} \rangle \]
Si(557)-Au: RAS & nonlocal term

\[
\Delta R/R
\]

\[|P|^2 \text{ only} \]
\[|P|^2 + V_{nl} \]

Energy (eV)

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Gap correction

“Scissors” shift to conduction band

Works well in most cases

Better: hybrid functional

Patterson, Banerjee and McGilp, Phys. Rev. B 84 155314 (2011)

Include MB effects only when other factors resolved!
GW+BSE: bulk excitons

Si(110):H slab calculation
=> No surface states

Excitonic effects:
- Enhanced E1, dip
- 0.1-0.2eV redshift

Local-field effects:
- Generally small

GW correction:
- 0.6-0.7eV blueshift
- Moderate lineshape changes

DFT-LDA:
- Features at E1 and E1

What do you learn?
GW+BSE: surface excitons

C(100)-(2x1) slab

GW spectrum:
Features at A and B:
dimer pi-\pi* transitions
GW+BSE: surface excitons

C(100)-(2x1) slab

Excitonic effects:
Enhanced A, B peaks
0.9eV redshift (strongly bound)

GW spectrum:
Features at A and B:
dimer pi-pi* transitions
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HREELS: slow e- scattering

Small angular deflection: dipole regime
  – scattering from excitations far from surface

Large deflection angle: impact regime
  – scattering from ion cores

Specific angular deflection: resonant regime
  – temporary ion mechanism

Approach of Mills: electron does not enter surface!
HREELS: dipole regime

\[
\frac{d^2 S}{d(\hbar\omega)d\Omega} = \text{Im} \int_0^0 \rho^{\text{ext}}(q_\parallel, z; \omega) dz \int_{-\infty}^{\infty} \left[ \varepsilon^{-1}(q_\parallel, z, z'; \omega) - \delta(z - z') \right] \phi^{\text{ext}}(q_\parallel, z'; \omega) dz'
\]

Simplest approach: Two phase model
truncated bulk (isotropic)

\[\varepsilon_0(q \to 0, z, \omega) = \varepsilon_b(\omega)\theta(z) + \theta(-z)\]

\[
\frac{d^2 S}{d\Omega(k)d(\hbar\omega)} = A(k, k') \text{Im} g(q_\parallel, \omega)
\]
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Surface loss function

\[
\frac{d^2 S}{d(q_\parallel)d(\hbar\omega)} = A(k, k') \times \text{Im } g(q_\parallel, \omega) = \text{kinematic factor} \times \text{loss function}
\]

One phase (transmission)

Bulk loss function:

\[
-\text{Im}\left\{\frac{1}{\varepsilon_b(\omega)}\right\}
\]

Quasi-continuum picture:

- Surface scattering:

\[
-\text{Im}\left\{\frac{2}{1 + \varepsilon_b(\omega)}\right\} = 2\frac{\varepsilon_2}{(1 + \varepsilon_1)^2 + \varepsilon_2^2}
\]

Thin surface layer:

- Effective, \(q\)-dependent dielectric function:

\[
-\text{Im}\left\{\frac{2}{1 + \varepsilon_{\text{eff}}(q_\parallel, \omega)}\right\}
\]

- Extended to account for anisotropy
HREELS: practical calculation

Real surfaces: anisotropic 3-phase model

\[ A(k, k') = 2 \left( \frac{m e}{\hbar^2 \pi} \right)^2 \frac{1}{\cos \theta_0} \frac{|k'|}{|k|} \frac{|q_{||}|}{|q_{||}^2 + q_z^2|} \]

Kinematic factor

\[ \varepsilon_{\text{eff}}(q_{||}, \omega) = \varepsilon_{s \text{ av}}^s(\omega) \left\{ \frac{[\varepsilon_{s \text{ av}}^s(\omega) + \varepsilon^b(\omega)]^+ q_{s d} - [\varepsilon_{s \text{ av}}^s(\omega) - \varepsilon^b(\omega)]^- q_{s d}}{[\varepsilon_{s \text{ av}}^s(\omega) + \varepsilon^b(\omega)]^+ q_{s d} + [\varepsilon_{s \text{ av}}^s(\omega) - \varepsilon^b(\omega)]^- q_{s d}} \right\} \]

Effective dielectric function

\[ \varepsilon_{s \text{ av}}^s(\omega) = \sqrt{\varepsilon_z^s(\omega) \left[ \varepsilon_x^s(\omega) \cos^2(\theta) + \varepsilon_y^s(\omega) \sin^2(\theta) \right]} \]

Geometric mean surface dielectric function

In practice: use the optical dielectric function

\[ \Rightarrow \varepsilon_{x}(q_{||}, \omega) := \lim_{q_{||} \to 0} \varepsilon_{x}^s(q_{||}, \omega) \]

HREELS: other factors

Finite detector size/shape

Integrate loss function

\[ \int A(k, k') \text{Img} (q_{||}, \omega) d\Omega \]

Surface Bulk layers Surface

Extract DF of surface layer: subtraction/cutoff
HREELS: example

Note this is the HREELS anisotropy signal
Concluding remarks

Accurate simulations of RAS from first principles, are now reasonably straightforward

*Often can neglect: SOC/Vnl/LFE/GW/BSE*

HREELS can be reasonably well modeled

*But: Care with LFE etc!*

Collaboration between theory and experiment is therefore very fruitful

Many tricks included in Yambo, *but ...*

Much scope for implementing other experimental techniques (SE, MOKE, nonlinear optics .... )
References

Theoretical foundations: RAS

McIntyre & Aspnes, Surf. Sci. 24, 417 (1971)
Bagchi, Barrera, Rajagopal, Phys. Rev. B 20, 4824 (1979)

RAS/HREELS fundamentals & reviews


Practical methods

Patterson, Banerjee and McGilp, Phys. Rev. B 84 155314 (2011)
Mendoza, Nastos, Arzate, and Sipe, PRB 74, 075318 (2006)

Realistic (slab) calculations


Many body effects