Spectroscopies for “Unoccupied States” = Electrons

<table>
<thead>
<tr>
<th>Method</th>
<th>1 Hole</th>
<th>1 Electron</th>
<th>1 Electron/Hole</th>
<th>2 Electrons + 1 Hole</th>
<th>2 Holes</th>
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<tbody>
<tr>
<td>Photoemission</td>
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<td>Inverse Photoemission</td>
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<td>Tunneling Spectroscopy Emission</td>
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<td>Absorption</td>
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<td>Electron Energy Loss</td>
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<td>Resonant Inelastic X-ray Scattering (RIXS)</td>
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<td>Auger</td>
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<td>Appearance Potential</td>
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Two-Photon Photoemission

While photoemission is the technique of choice for occupied states, there is no such “silver bullet” for unoccupied states.
Inverse Photoemission (BIS, IPES, KRIPE)

- Measures an "unoccupied state" by filling it with an electron
- Determines the complete set of quantum numbers
- Probes about 5 atomic layers (surface + bulk)
- Complements photoemission (time-reversed process)
- But very low cross section (down by $\alpha^2$ from photoemission)
(Scanning) Tunneling Spectroscopy

(STS)

• An electron tunnels across a barrier into an unoccupied state
• Spatially resolved with atomic resolution
• Probes only states outside the surface (need $\psi$ overlap with tip)
Resonant Tunneling into Empty States

The energy width of the “electron beam” is about $\frac{1}{4} \text{ eV}$ (due to the energy-dependent tunneling barrier).

For positive sample voltage electrons tunnel resonantly into empty states of the sample.

For negative sample voltage electrons tunnel resonantly into empty states of the tip.

Caveat for STS: Sample and Tip both Contribute

Contrast reversal between Cu and Mo by changing the tunnel voltage.

An atom jumping onto the STM tip and back reverses the contrast between Cu and Mo.
Mapping the Density of States by Tunneling Spectroscopy

The DOS is approximately proportional to the differential conductance:

$$\text{DOS} \propto \frac{dI}{dV}$$

Explanation: For a simple metal tip the density of occupied tip states is approximated by a step function. An I(V) spectrum sweeps the tip DOS ($D_{\text{tip}}$) past the sample DOS ($D_{\text{spl}}$), i.e. one has the convolution:

$$I \propto \int D_{\text{tip}}(E-E') \cdot D_{\text{spl}}(E') \, dE' \quad E = e \cdot V$$

The derivative of the convolution is the convolution by the derivative, and the derivative of the Fermi cutoff in $D_{\text{tip}}$ approximates a $\delta$-function.

The derivative $\Delta I/\Delta V$ is obtained experimentally by modulating the sample voltage sinusoidally and picking up the oscillating part of the current. Electronic noise at all other frequencies is filtered out.
The Si(111)7x7 surface (the most stable surface of silicon) has two types of broken surface bonds:

- **Adatoms** trade three broken bonds for one.
- **Rest atoms** are part of the truncated silicon surface.
- One electron is transferred from two adatoms to a rest atom, thereby converting its broken bond orbital into a stable lone pair.
Quantum Wires: Carbon Nanotubes

$\pi$-bands quantized along the circumference of a nanotube

Calculated Density of States

Scanning Tunneling Spectroscopy (STS)

Magnetic Tunneling via Spin-Polarized Surface States (due to Spin Conservation)

Wave function of the spin-polarized $d_{z^2}$ surface state on Fe(100), Cr(100)
Two-Photon Photoemission (2PPE)

- Measures “unoccupied” intermediate states by filling them with the 1\textsuperscript{st} photon and then probing them with a 2\textsuperscript{nd} photon
- Determines the complete set of quantum numbers
- Allows <100 fs time resolution, but selects long-lived states
Relaxation Observed by Two-Photon Photoemission

Rügheimer et al., PRB 75, 121401(R) (2007)
Quantum Beats from a Superposition of Several Image States

Höfer et al., Science 277, 1480 (1997)
The uncertainty relation does not allow simultaneous measurement of position and momentum with an accuracy smaller than the unit cells in real and reciprocal space. One needs to choose a basis set either in a real space or in reciprocal space.

Photoemission operates in reciprocal space, and STS in real space. Is it possible to perform the transformation from reciprocal space to real space and vice versa?

At the simplest level, this is a Fourier transform. Since both photoemission and STS measure intensities (not amplitudes), the phase information is lost. This is the age-old phase problem in diffraction. It has been overcome by a variety of tricks, for example by a cycle of iterative Fourier transforms incorporating information about a sample with compact support in real space (e.g. inside an aperture).

At a more sophisticated level one would need to take multiple scattering of the photoelectrons into account (like in LEED calculations).
From Reciprocal Space to Real Space in 1D

Angular Pattern in Photoemission

1D Quantum Well States on a Terrace

Phase from iterated Fourier transform cycle

Mugarza et al., PR B 67, 0814014 (2003)
Standing Waves in ARPES and STS

Standing waves are seen by STS in confined systems (quantum corrals).
STS and photoemission complement each other:
STS works best at large distance (compared to the size of an orbital), ARPES works best at small distances (k is large compared to the BZ).

Mugarza et al. (2003)
How is STS of Standing Waves Connected with Photoemission?

• Photoemission measures the imaginary part of the Greens function $G$.

• STS involves $G$ and $T$, the reflectivity of the barrier that creates a standing wave.
Imaging Molecular Orbitals in 2D by Photoemission

Photoemission momentum map (square root of the intensity) for sexiphenyl on Cu (110) at a binding energy of 1.9 eV which corresponds to the HOMO.

(A) HOMO of sexiphenyl reconstructed from the photoemission momentum map in 2D.
(B) HOMO of an isolated sexiphenyl molecule from density functional theory (DFT).

Puschnig et al., Science 326, 702 (2009)
Extras
Find Isolated Nano-Objects for Wave Function Reconstruction

The previous examples provide proof of principle that photoemission data can be transformed into real space to provide wave functions, something that experimental chemists and theoretical physicists alike are interested in.

For iterative phase retrieval it is important to have an isolated object, or at least an array of decoupled identical objects (such as molecules adsorbed with a well-defined orientation at a surface).

Nanocrystals or nanowires usually have a certain size distribution. It would be very useful to focus the light beam onto a single nano-object and take a valence photoelectron diffraction pattern from that.

The following examples from focused laser spectroscopy show that a sub-micron focus significantly improves the sharpness of the spectral features. They should be $\delta$-functions for a quantum dot confined in all directions.

Projects in micro- and nano-focused ARPES are under way, such as the MAESTRO project at the ALS.
Micro-Spectroscopy with Lasers

Overcoming the size distribution of quantum dots

Free-Standing Nanotubes between Pillars

Lefebvre et al., PRL 90, 217401 (2003)
Need to isolate nanotubes from the substrate and from each other to obtain a sharp spectrum. (c) is from free-standing nanotubes (2 μm spot).
Isolating Nanotubes inside Micelles

Separate the Optical Spectra from Nanotubes with Different Diameter and Chirality

Bachilo, ... ... , Weisman, Science 298, 2361 (2002)
Photoemission from Carbon Nanotubes

See critical points, but need to select individual types of nanotubes to resolve the fine structure.