Lasers Emerge as a Tool for the Direct Study of Electrons in Solids

Lasers offer many advantages over their synchrotron-based counterparts as sources of high-energy photons for angle-resolved photoemission spectroscopy.

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Angle-resolved photoemission spectroscopy is the most direct way to observe the quantum-mechanical structure of electrons in solids and one of the key tools used to understand the complex electronic interactions that lead to high-temperature superconductivity.¹

In these experiments, high-energy photons eject electrons from the material of interest. Because the electron momentum is conserved in this process, the angular distribution of the ejected electrons — or photoelectrons — is representative of the initial quantum-mechanical distribution of electronic states in the solid. Using an electron spectrometer that measures this photoelectron distribution with very high energy and momentum resolution, physicists can study the intricate details of the electronic interactions in the solid.

High-resolution angle-resolved photoemission spectroscopy experiments typically require a synchrotron source to obtain the necessary photon energy, photon flux and resolution. These are large, multiseer facilities, costing on the order of $100 million, of which there are four in the US regularly used for these experiments. However, UV lasers have emerged as an excellent photon source, offering some clear advantages over their synchrotron counterparts. This development also is expected to open up the field to researchers who may not be able to get adequate access to the limited amount of available synchrotron time.

**Photoelectric effect**

Angle-resolved photoemission spectroscopy is based on the photoelectric effect, for which Albert Einstein won the 1921 Nobel Prize.

![Figure 1. In the photoelectric effect, a photon of energy $h\nu$ is absorbed by an electron of kinetic energy $E_{\text{initial}}$ inside the solid. If the photon has sufficient energy to overcome the work function $\Phi$, the electron will be ejected from the solid above the vacuum level with a kinetic energy of $E_{\text{final}}$ equal to $h\nu - E_{\text{initial}} - \Phi$. In this way, the spectrum of ejected electrons represents the spectrum of occupied states in the solid.](image-url)
in physics. Einstein said that, when an electron in a solid absorbs a photon with enough energy to overcome the work function (a constant, typically 4 to 5 eV for most materials), that electron can escape from the surface of the solid with a kinetic energy equal to the photon’s energy less the electron’s initial kinetic energy and the work function. This simple relation means that counting the total number of electrons that are ejected from the solid as a function of their kinetic energy tells us the electron density of states in the solid (Figure 1). The electronic density of states is an important property of the solid and is sufficient to understand most aspects of a material’s physical properties.

We also must consider that the electrons primarily responsible for the properties of a material are not localized in real space. This is a counterintuitive idea because the objects with which we directly interact have a well-defined structure in real space. The magazine before you, for example, has pages of a specific shape and size, in a clear order. Electrons in a solid, on the other hand, are characterized by their momenta, having only a well-defined velocity and direction of travel relative to the crystal lattice.

This is because, quantum mechanically speaking, an electron cannot simultaneously have a well-defined momentum and real-space position, as a result of Heisenberg’s uncertainty principle. The electrons in a solid literally are smeared out, or “delocalized,” in real space. Accurate pictures of electrons in solids therefore must be taken in momentum space. This is what angle-resolved photoemission spectroscopy can do.

As the electrons escape from the face of a single-crystal sample, the components of their momenta that are parallel to the crystal face are conserved. Because the photon momentum is essentially zero, the electrons fly away from the sample surface at an angle governed only by their initial momentum in the crystal. If we count the number of photoelectrons as a function of energy and emission angle, we are directly observing their distribution in momentum space (Figure 2a).

Modern electron spectrometers can analyze electrons from many angles at once, using a CCD camera to image the electron distribution in a
1-D slice of momentum space (Figure 2b). In materials with complicated electron interactions, such as high-temperature superconductors, angle-resolved photoemission spectroscopy can be used to observe how their electronic structure deviates from the simple predictions of band theory, possibly identifying the cause of their bizarre properties.

(Band theory predicts the momentum-dependent quantum states for a periodic solid using an effective single-electron approximation, in which the interactions with other electrons and degrees of freedom are included in an average way. Going beyond this to include explicit many-body corrections is believed to be critical for understanding complex solids such as the high-temperature superconductors.)

Typical angle-resolved photoemission spectroscopy experiments are carried out using photons in the 20-to 100-eV range (i.e., with wavelengths of around 10 to 60 nm), where synchrotron sources offer a good combination of resolution and flux. Unfortunately, the bulk sensitivity of the spectroscopy technique, limited by the photoelectron mean free path while escaping the solid, is minimal in this energy range, with the photoelectrons coming from only the top few monolayers of the sample. Because of this, the technique must be performed on samples with extremely high-quality surfaces, requiring sample preparation such as cleaving or annealing and measurement under ultrahigh-vacuum conditions at pressures of less than $10^{-11}$ atmos.

Furthermore, this complicates the interpretation of angle-resolved photoemission spectroscopy data because the electronic structure near the surface of a solid may differ from the structure in the bulk. The bulk sensitivity can be greatly increased by moving to a lower photon energy, but because the low-energy photoelectrons are more susceptible to deflection by stray magnetic fields —and as a result of concerns regarding possible impacts from a breakdown of the sudden approximation— this energy range largely went unexplored.

**Laser sources**

Several research groups have begun using UV lasers to explore this low-photon-energy regime. These...
photon sources not only increase the 
bulk sensitivity of angle-resolved 
photoemission spectroscopy by roughly 
an order of magnitude, but also offer 
improved resolution, increased pho-
ton flux and reduced noise compared 
with the high-energy sources.

The research group of Shik Shin 
at the University of Tokyo and at 
Riken in Japan has focused its 
efforts on achieving the highest pos-
sible energy resolution for perform-
ing nonangle-resolved photoemis-
sion, or density of states measure-
ments, as in Figure 1. The scientists 
use the rare nonlinear crystal 
KBe$_2$BO$_3$F$_2$, sandwiched between a 
pair of UV prisms, to frequency-dou-
ble the output of a commercially 
available 355-nm quasi-CW laser 
source.$^6$ The resulting 7-eV (177 nm) 
photons have a bandwidth of only a 
few hundred microelectron volts. 
(Synchrotron sources typically re-
quire at least a few millielectron volts 
of bandwidth to achieve reasonable 
flux.) Combined with an ultralow 
sample temperature of roughly 2 K, 
this has enabled the group to obtain 
beautiful data, uncovering fine struc-
ture in the density of states never 
before seen by photoemission.

Our research group at the Uni-
versity of Colorado at Boulder has 
taken a different path, developing an 
angle-resolved photoemission spec-
troscopy apparatus specifically de-
signed for high angular resolution 
when measuring very low energy 
electrons. The magnetic fields in our 
chamber have been shielded to a level 
below 1 mG, enabling us to perform 
true angle-resolved measurements 
using 6-eV (~210 nm) photons.

Angle-resolved measurements per-
formed at such a low photon energy 
have the advantage of greatly im-
proved momentum resolution com-
pared with those that use higher-en-
ergy photons. This is simply because, 
at low energy, the photoelectron mo-
mentum distribution is more widely 
dispersed in angle, resulting in an 
improved momentum resolution for 
a given angular resolution.

The 6-eV laser angle-resolved 
photoemission spectroscopy system 
(Figure 3) is based on a Ti:sapphire 
oscillator that produces 6-nJ pulses 
centered at a wavelength of approx-
imately 840 nm. The 100-fs pulses 
are focused into a BBO crystal, gen-
erating a few hundred milliwatts of 
420-nm light through Type I non-
linear second-harmonic generation.

Figure 4. Raw angle-resolved photoemission spectroscopy data is presented for a high-temperature superconductor. The data was collected using 6-eV laser photons at the University of Colorado (left), 28-eV synchrotron photons from beam-line 12.0.1 at the Advanced Light Source in Berkeley, Calif., (middle) and 52-eV syn-
chrotron photons from beam-line 10.0.1 at the Advanced Light Source (right). The increased sharpness of the laser data indicates that quasiparticles may exist in this unusual material.
The second harmonic is separated from the fundamental wavelength, and the light is focused into another Type I BBO crystal, resulting in a few hundred microwatts of the fourth harmonic (6 eV) in a bandwidth of less than 5 meV. This corresponds to more than $10^{14}$ photons per second, approximately two orders of magnitude higher than what is available from the best synchrotron beam lines at this bandwidth.

Finally, the 6-eV photons pass through a wave plate to select the desired linear or circular polarization, and they are focused onto the sample. This ease of polarization control, often not available at synchrotron beam lines, is important because the angle-resolved photoemission spectroscopy signal-to-noise can depend heavily on polarization.

**Probing superconductivity**

One class of materials most studied using angle-resolved photoemission spectroscopy is that of the high-temperature superconductors, ceramic materials that gain infinite electrical conductivity at relatively high temperatures—in certain cases, up to almost 170 K. Even after two decades of intense research, the mechanism responsible for superconductivity in these materials remains one of the biggest mysteries in physics.

Figure 4 compares raw data from the high-temperature superconductor Bi$_{2}$Sr$_{2}$CaCu$_{2}$O$_{8+\delta}$ taken using different photon energies. The images are almost exactly what the CCD camera sees while viewing a slice of the electronic structure in momentum space, aside from the scaling of the axes and the addition of the false-color scale normalized to the peak for each image, which represents the number of electrons detected as a function of their energy (vertical axis) and momentum (bottom axis).

Not immediately obvious from the figure is the fact that the photoelectron count rate is much higher for the laser spectroscopy data as a result of the higher photon flux, enabling better counting statistics in a shorter amount of time than was possible for the synchrotron data. The laser data display the same overall structure as in the higher-energy synchrotron data, which is important because it indicates that the measured electronic structure does not change significantly as we probe deeper into the sample using lower-energy photons.

Perhaps the most noticeable difference in the spectra is the fact that the laser data are much sharper, primarily as a result of the improved momentum resolution. This is of great significance because it brings angle-resolved photoemission spectroscopy spectra into a new regime where the spectral peaks are sharper than their energy positions, a property that was not previously observed in a high-temperature superconductor. This may simplify the understanding of high-temperature superconductivity because it opens up the possibility of using relatively simple theoretical techniques, such as the concept of Landau quasiparticles, to describe the electrons and their interactions.

With laser sources offering the state of the art in both energy and momentum resolution, they will become more common in angle-resolved photoemission spectroscopy studies of high-temperature superconductors and other materials. Perhaps most exciting is the possibility of performing pump-probe time-resolved measurements of electronic structure using the pulsed nature of many laser sources.

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**References**

5. J.D. Koralek et al (Jan. 13, 2006). Laser based angle-resolved photoemission, the sudden approximation, and quasiparticle-like spectral peaks in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$. PHYS REV LETT. 017005.

**RUNNING HED: Angle-Resolved Photoemission Spectroscopy**

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