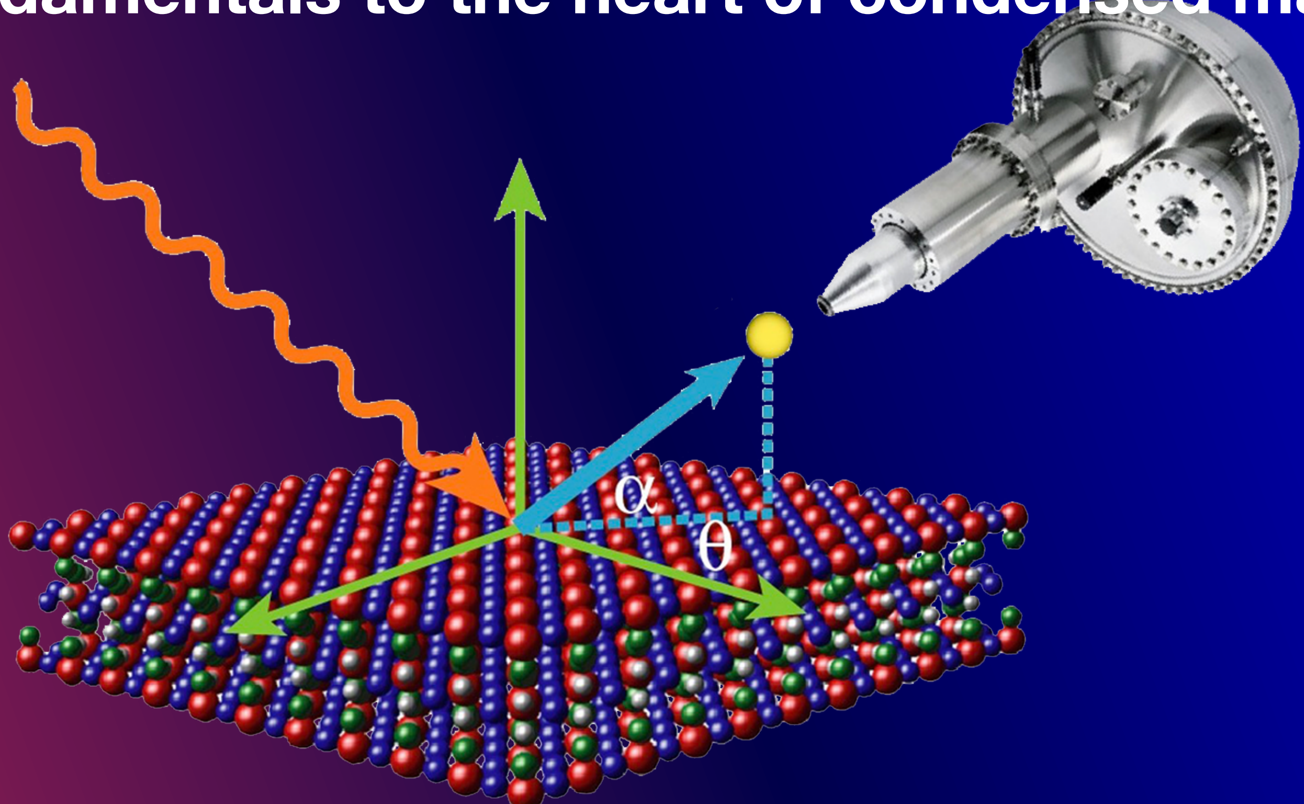
CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

SEVERO OCHOA SCHOOL

ICMAB EXCELENCIA SEVERO OCHOA
INSTITUT DE CIÈNCIA DE MATERIALS DE BARCELONA

Angle Resolved Photoemission Spectroscopy

From fundamentals to the heart of condensed matter



6-7 FEBRERO, 2023

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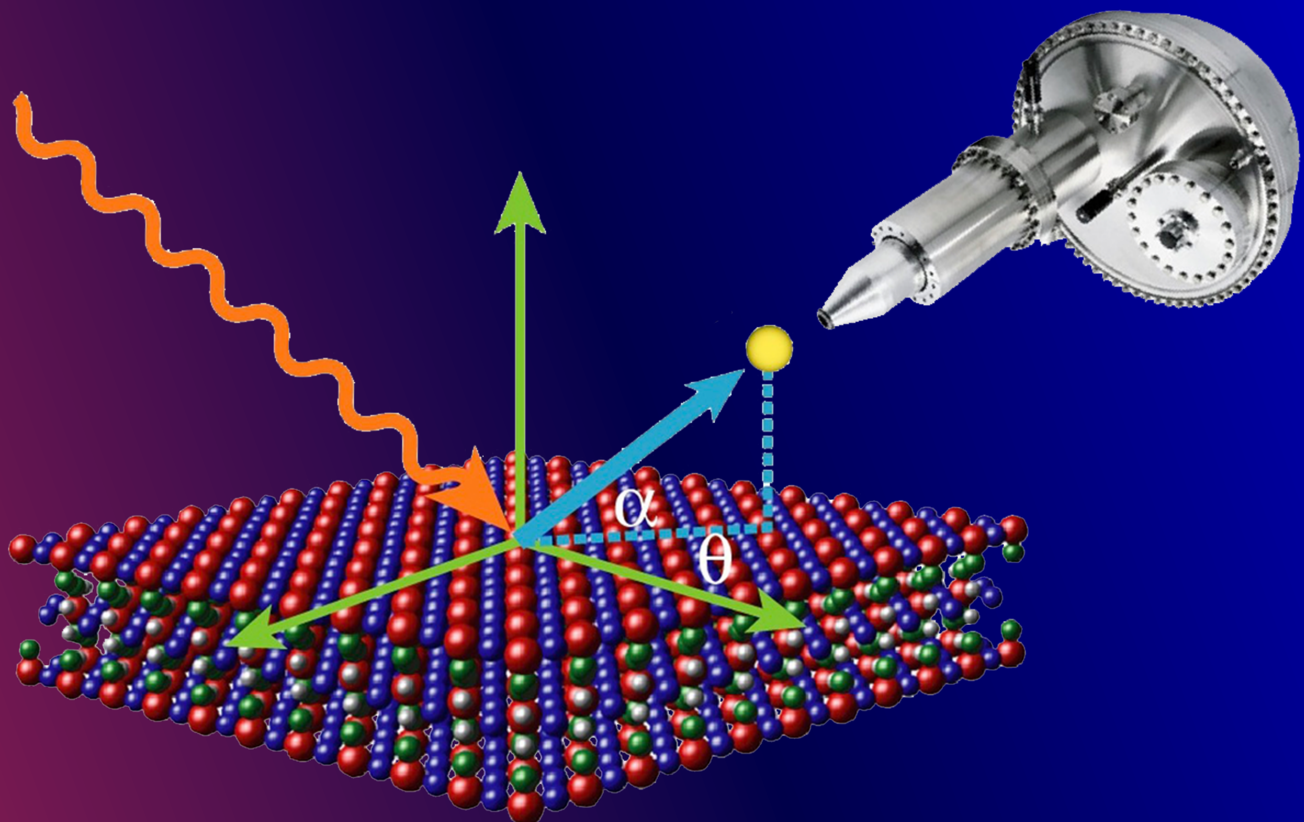
Lecture #1 : From Einstein to Band Mapping



6-7 FEBRERO, 2023

Overview of Lectures & Labs

Monday, February 6

- 9:30 - 11:00 Lecture #1 : From Einstein to Band Mapping
- 11:30 -13:00 Lecture #2 : From Particles to Quasiparticles

Tuesday, February 7

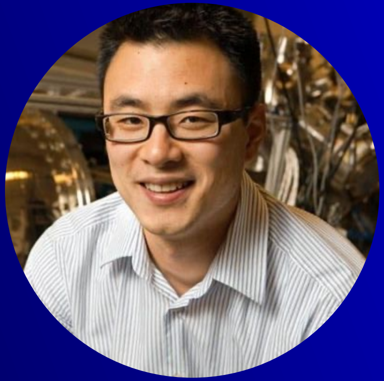
- 9:00 – 12:30 Visit to ALBA Synchrotron & ARPES demonstration at LOREA beamline
- 14:30 - 16:00 Lecture #3 : ARPES Studies of Quantum Materials
- 16:30 -18:00 Lecture #4 : Frontiers in ARPES – Time, Space, and Spin

Organizers

Gervasi Herranz
MULFOX, ICMAB

Josep Fontcuberta
MULFOX, ICMAB

Presenters



Kyle Shen
Cornell Univ. & ICMAB

Massimo Tallarida
ALBA Synchrotron

A few important points!

- Participation is *highly encouraged & important*! Please feel free to ask questions *any time*!

- A goal of our school is to encourage more local users at LOREA. *This means you!*

- Remember to bring your identification (DNI / TIE / Passport) tomorrow if you are registered for the ALBA visit

- If you have further questions, I am very happy to meet around ICMAB / UAB! My email is : kmshen@cornell.edu

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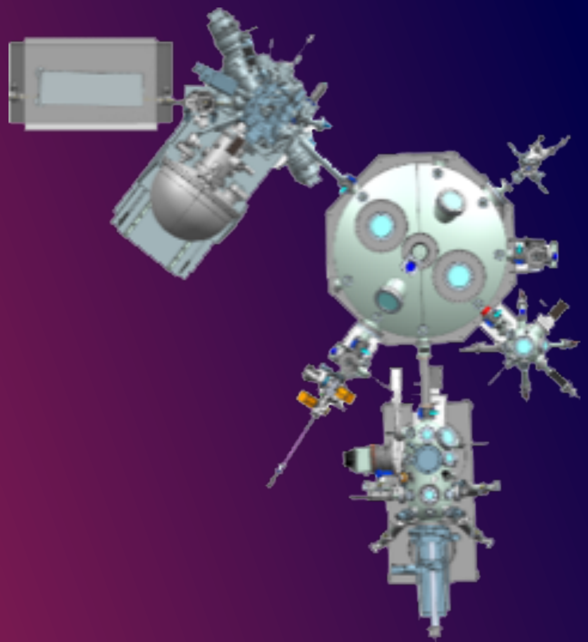
LOREA Beamline @ ALBA

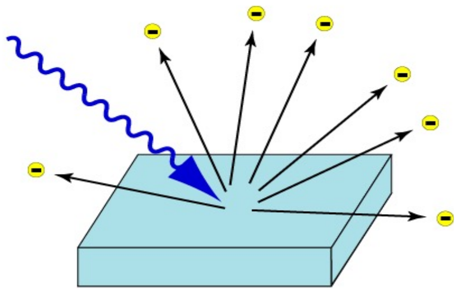


- High spatial resolution (~ 20 microns spot size with microscope)
- Advanced sample preparation capabilities (annealing, vacuum transfer)
- Spin-resolved detection (installed & coming online this spring)
- Wide photon energy range (20 – 500^{+} eV)

Your scientific background is best described as :

A. Materials Science & Engineering
B. Condensed Matter Physics
C. Electrical Engineering
D. Solid State Chemistry
E. Other

From Einstein's Photoelectric Effect to Band Mapping



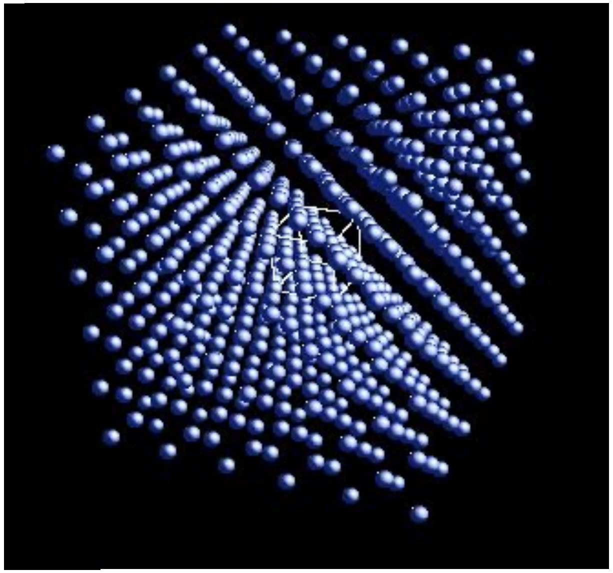
Angle Resolved PhotoElectron Spectroscopy

FIRST EVIDENCE FOR THE QUANTIZATION OF LIGHT!

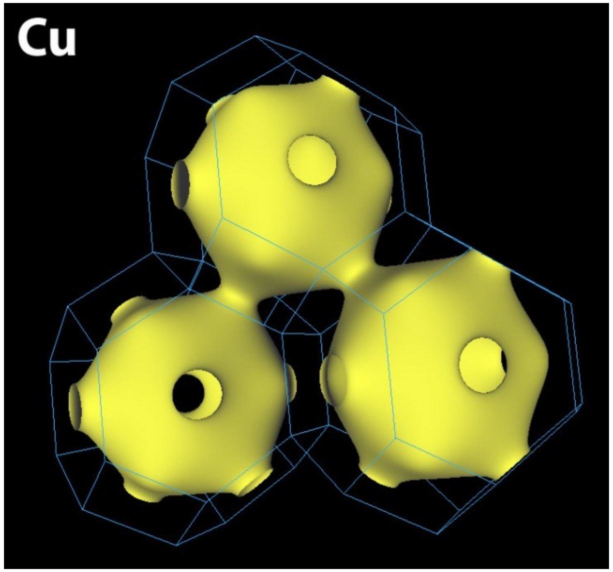
Velocity and direction of the electrons in the solid

Low-energy Electronic Structure → Macroscopic Physical Properties

Superconductivity, Magnetism, Density Waves, ….



X-ray diffraction

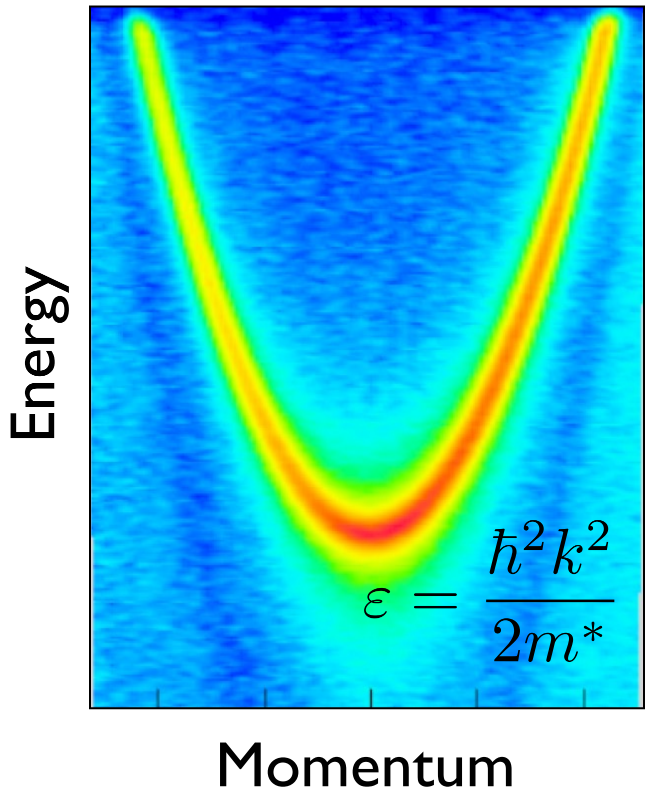


Photoemission

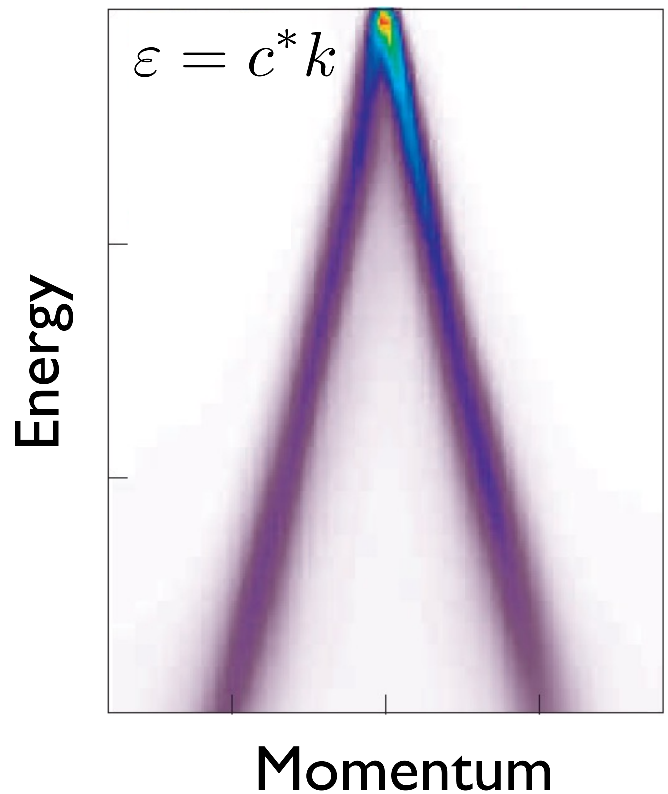
Measuring quasiparticle band velocities & band masses

$$\hbar v_k = \frac{\partial \varepsilon}{\partial k}$$

$$m_k^{-1} = \left(\hbar^{-2} \frac{\partial^2 \varepsilon}{\partial k^2} \right)$$



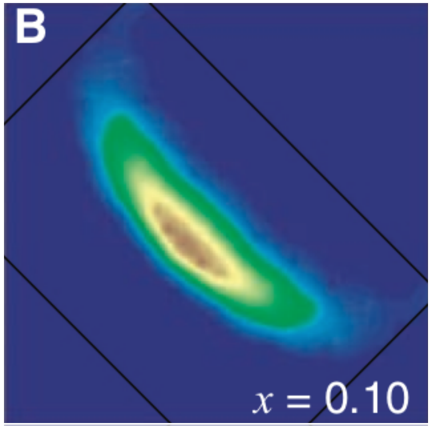
Reinert & Hufner NJP 2005



Zhou et al., Nature Physics 2006

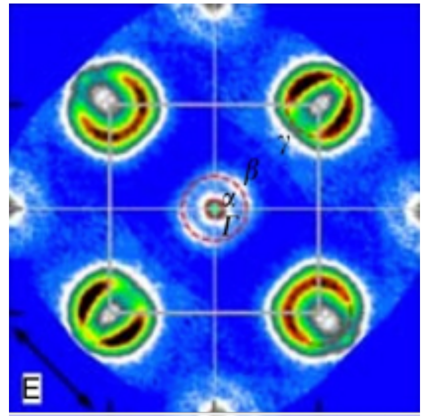
Quantum materials investigated by ARPES

Cuprate Superconductors



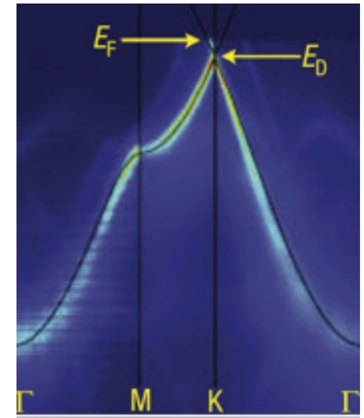
KMS et al, Science (2004)

Fe-based Superconductors



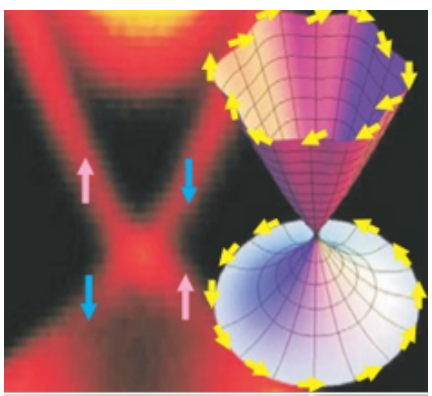
D. Liu et al, Nature Comm (2012)

2D Materials



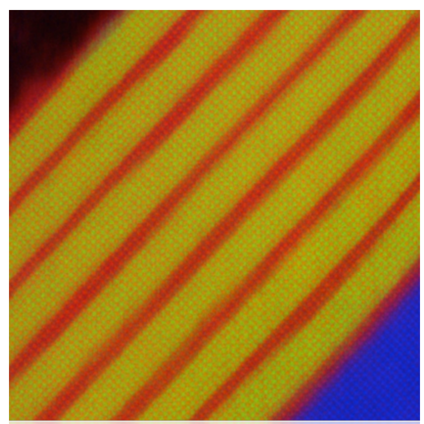
A. Bostwick et al. Nature Phys (2006)

Topological Materials



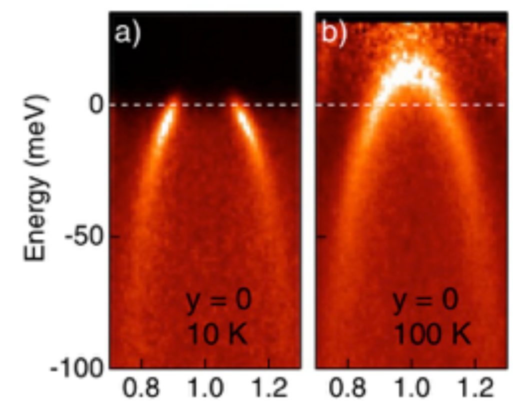
M.Z. Hasan, Annual Rev. (2010)

Superlattices & Interfaces



E. Monkman, Nature Matr. (2012)

Complex Oxides



KMS et al., Phys. Rev. Lett. (2007)

Einstein's Annus Mirabilis : 1905

- The Brownian motion

  "On the motion of small particles suspended in liquids atrest required by the molecular-kinetic theory of heat."
  Annalen der Physik, 17 (1905), pp. 549-560.

- **The photoelectric effect**

  "On a heuristic viewpoint concerning the production and transformation of light"
  Annalen der Physik, 17 (1905), pp. 132-148.

1921

- The special theory of relativity

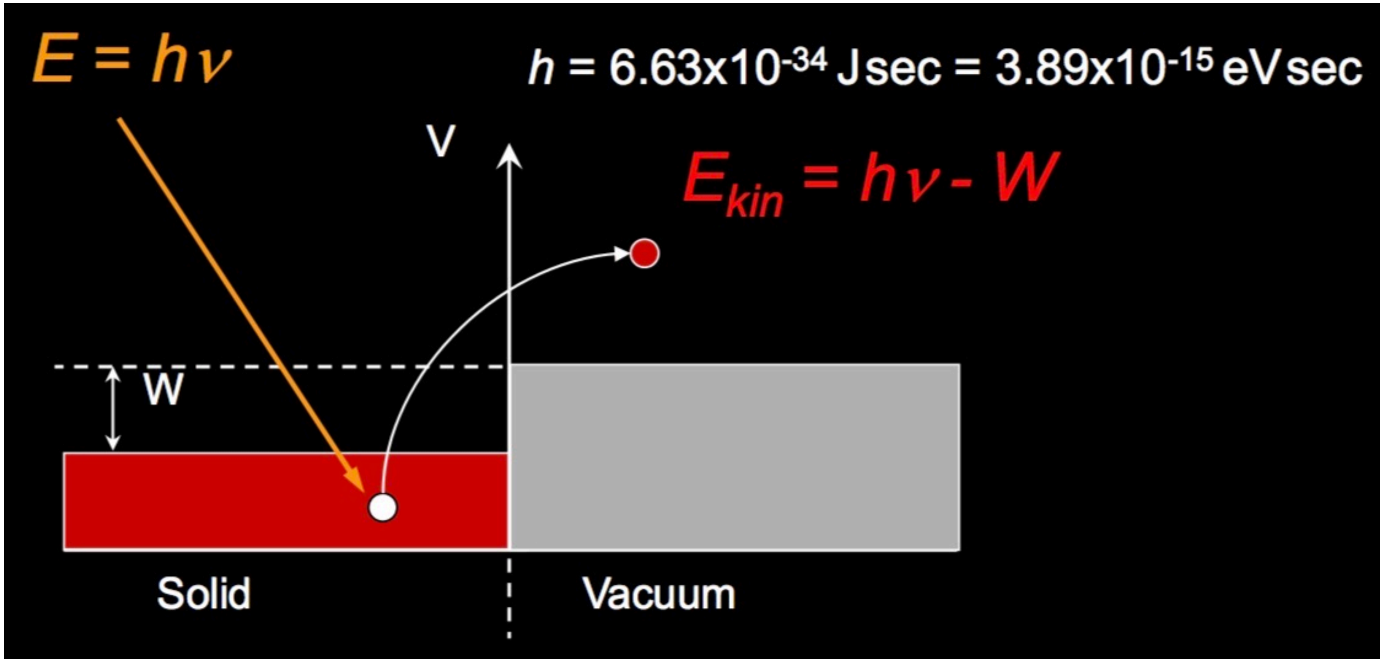
  "On the electrodynamics of moving bodies"
  Annalen der Physik, 17 (1905), pp. 891-921

- Mass-energy Equivalency $E=mc^2$

  "Does the inertia of a body depend on its energy?"
  Annalen der Physik, 18 (1905), pp. 639-41.

Principle of the Photoelectric Effect

1905 : Einstein' hypothesis: light quanta with $E = h\nu = hc / \lambda$



The maximum $E_{kin}=½mv^2$ is proportional to the FREQUENCY but depends also on the material work function W

The NUMBER of electrons is proportional only to the INTENSITY

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Einstein's hypothesis is too revolutionary

In 1913 Einstein was elected to the Prussian Academy of Sciences and appointed to a research position in Berlin. In his nomination speech to the Prussian Academy, Planck says:

"*Summing up, we may say that there is hardly one among the great problems in which modern physics is so rich, to which Einstein has not made an important contribution.* ***That he may sometimes have missed the target in his speculations, as for example, in his hypothesis of light quanta, cannot really be held too much against him****, for it is not possible to introduce fundamentally new ideas, even in the most exact sciences, without occasionally taking a risk*".

a brief history of photoemission spectroscopy

<u>1887</u> : discovery of photoelectric effect by Hertz

<u>1905</u> : quantization of light by Einstein : $E_{max} = h\nu - \phi$

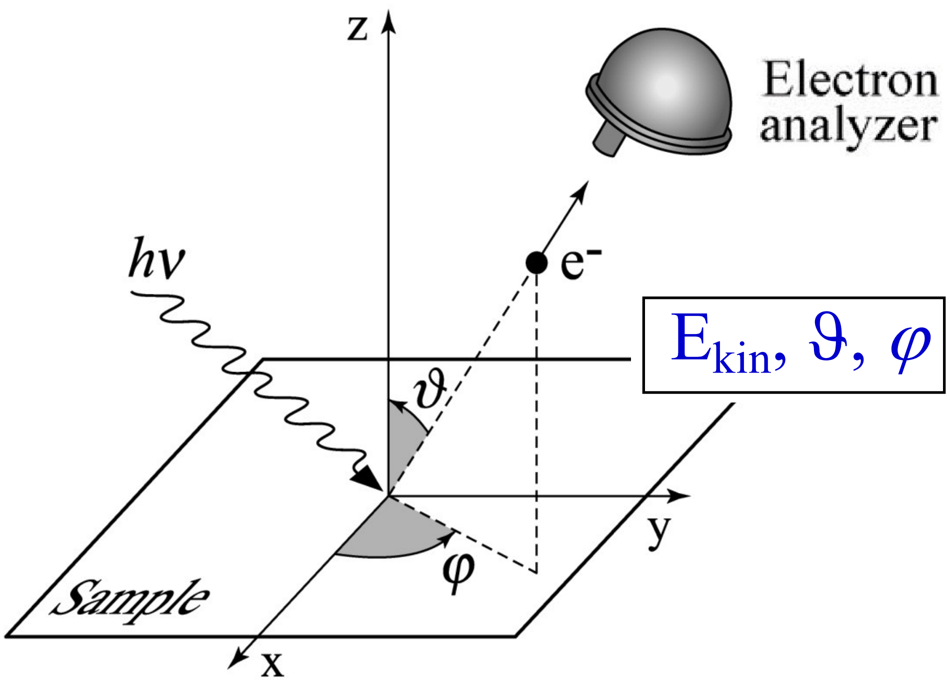
<u>1957</u> : x-ray photoelectron spectroscopy for chemical analysis (XPS or ESCA) by Siegbahn and others

<u>1960s</u> : ultraviolet photoemission spectroscopy (UPS) by Spicer, Turner, others

<u>1970s</u> : angle-resolved photoemission spectroscopy (ARPES) by Spicer, Smith, others

<u>1980s – present day</u> : widely used as materials characterization tool

Kinematics of the ARPES process



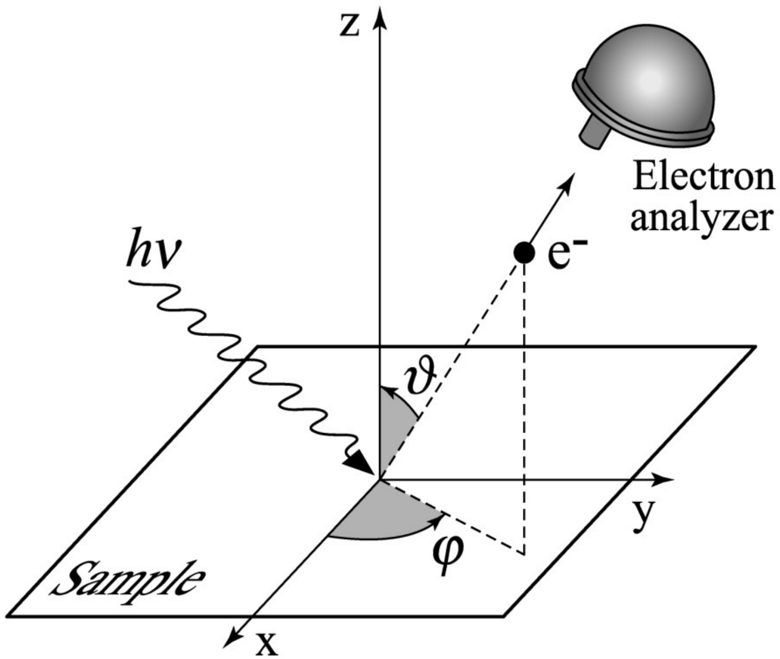
$$\mathbf{K} = \mathbf{p}/\hbar = \sqrt{2mE_{kin}}/\hbar$$

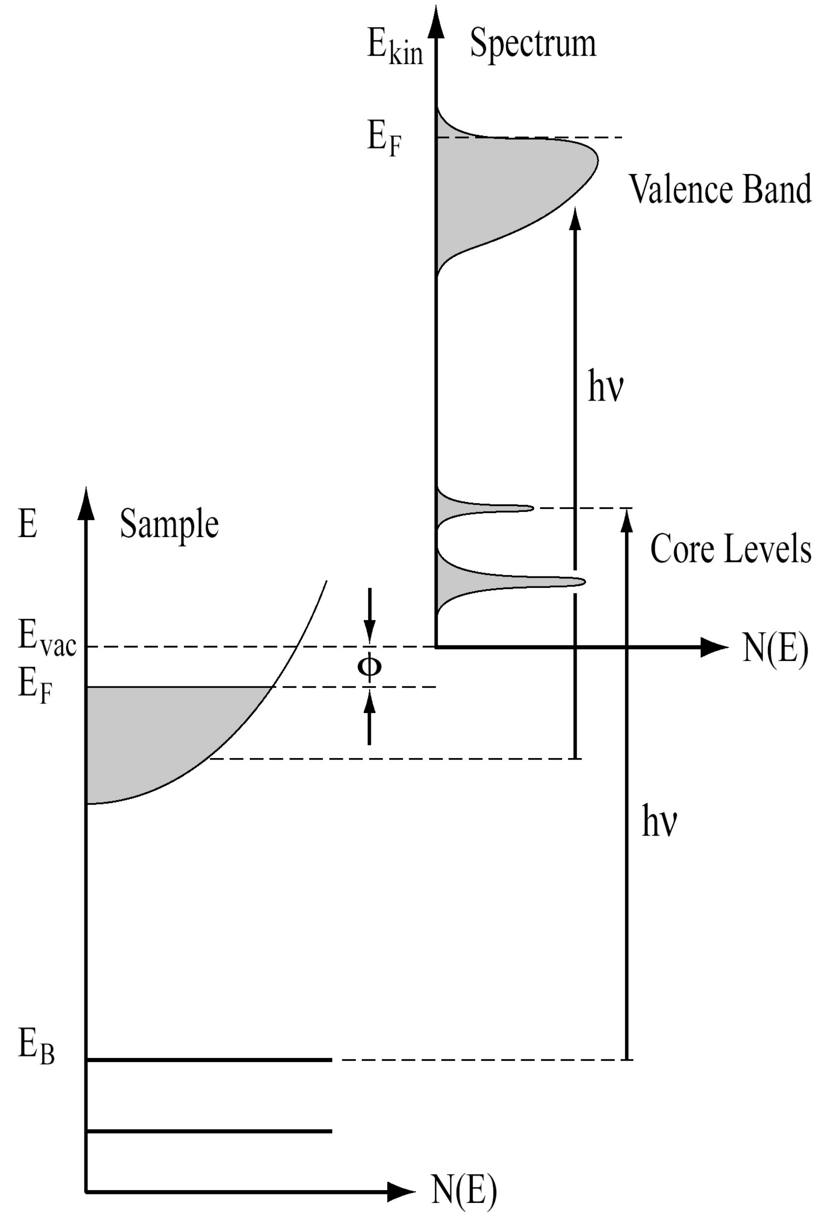
$$\begin{aligned} K_x &= \frac{1}{\hbar}\sqrt{2mE_{kin}}\sin\vartheta\cos\varphi \\ K_y &= \frac{1}{\hbar}\sqrt{2mE_{kin}}\sin\vartheta\sin\varphi \\ K_z &= \frac{1}{\hbar}\sqrt{2mE_{kin}}\cos\vartheta \end{aligned}$$

Vacuum		Conservation laws		Solid
E_{kin} $\mathbf{K}$	→	$E_f - E_i = h\nu$ $\mathbf{k}_f - \mathbf{k}_i = \mathbf{k}_{h\nu}$	→	E_B $\mathbf{k}$

Courtesy of Andrea Damascelli

Kinematics of the ARPES process : Energy Conservation





Energy Conservation

$$E_{kin} = h\nu - \phi - |E_B|$$

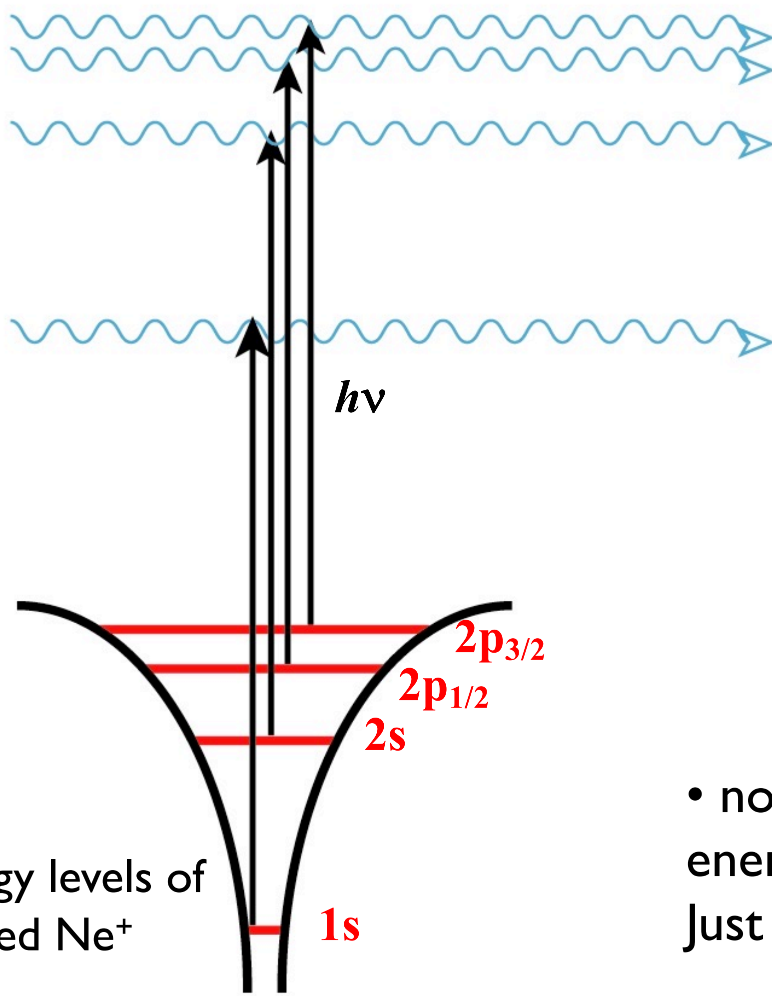
Momentum Conservation

$$\hbar k_{||} = \hbar K_{||} = \sqrt{2mE_{kin}} \cdot \sin\vartheta$$

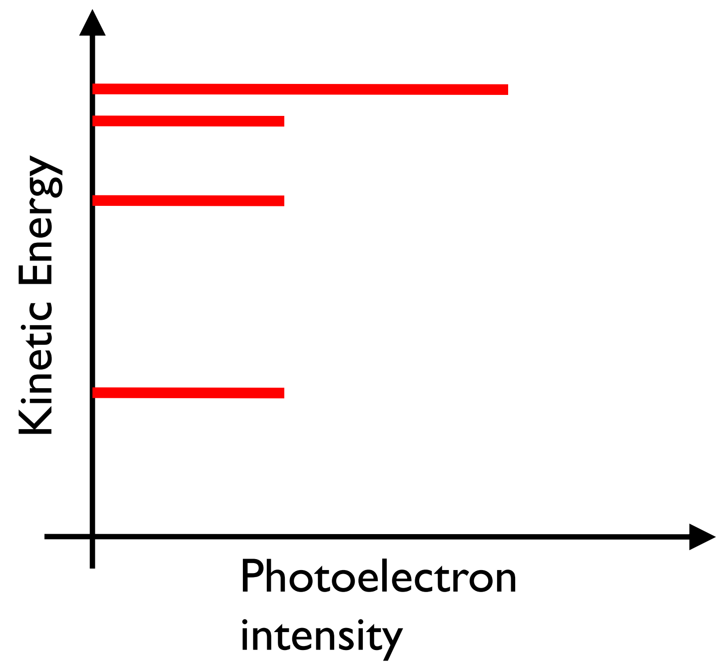
Courtesy of Andrea Damascelli

Electron ionization levels are formed from *discrete levels* in an atom

Energy conservation : $h\nu - E_I = KE$



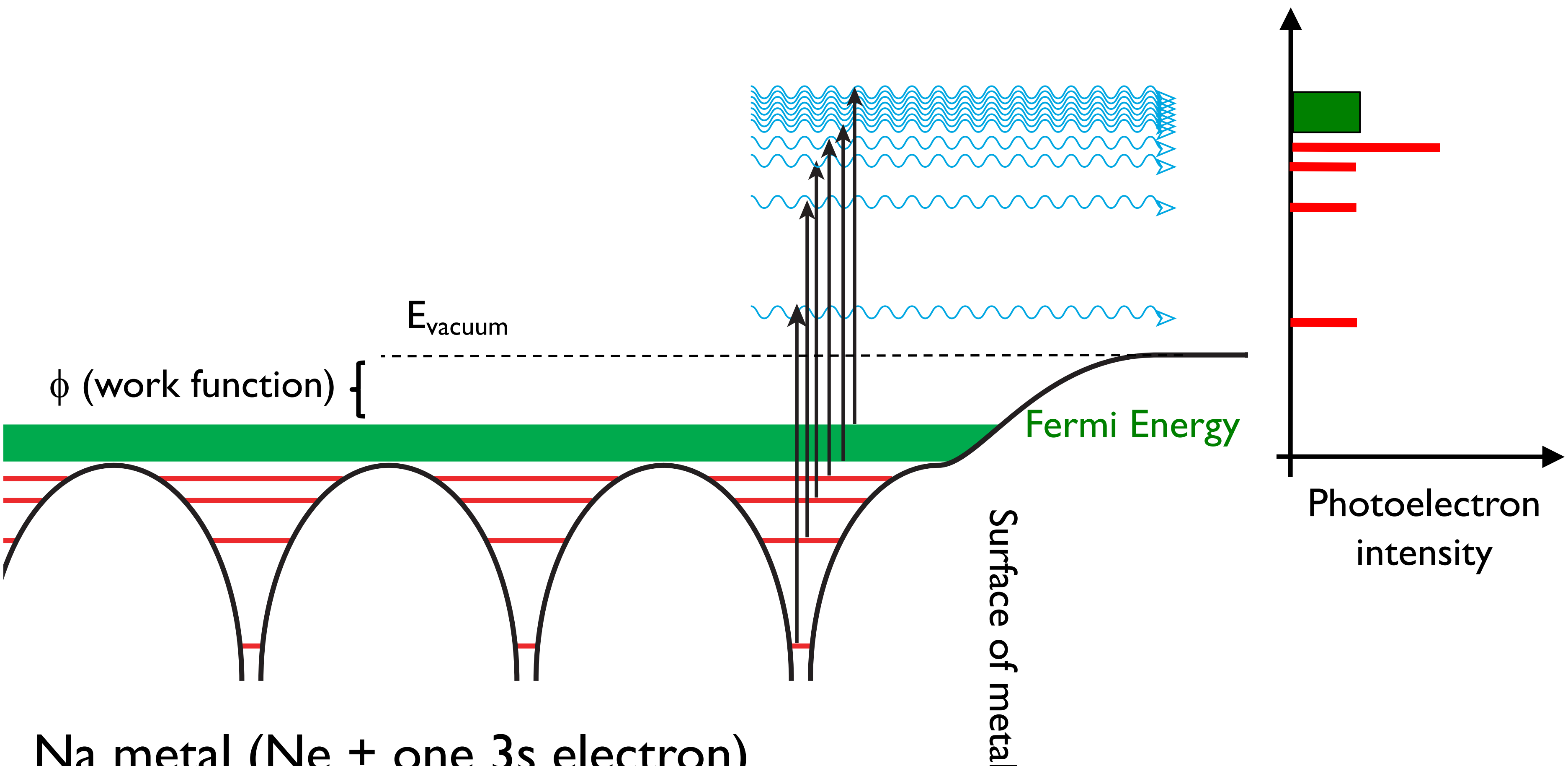
Energy levels of ionized Ne^+



• no need to be on resonance or scan photon energies (e.g. NMR, optical measurements). Just need photons to have high enough energy!

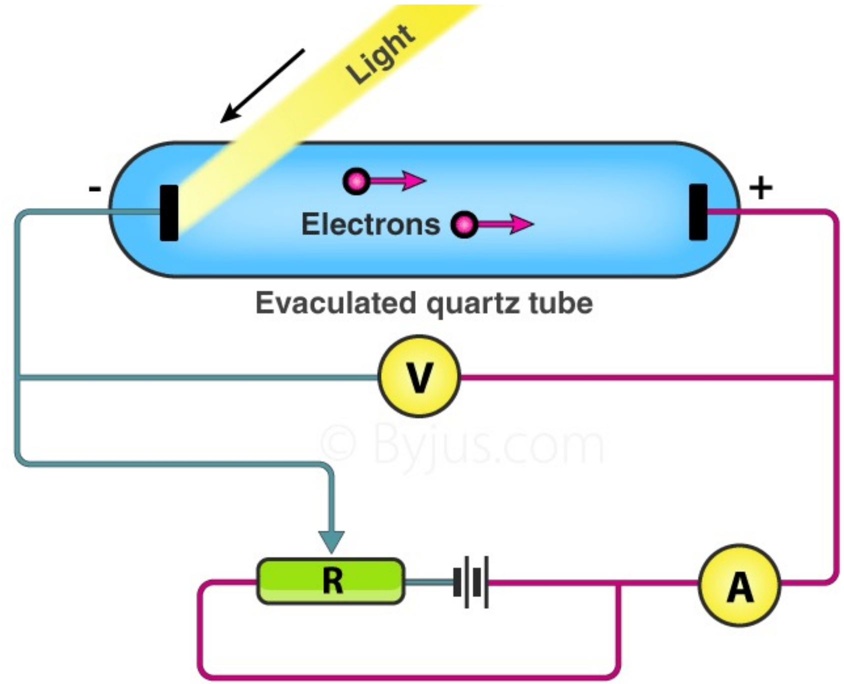
photoemission from solids : an array of atoms

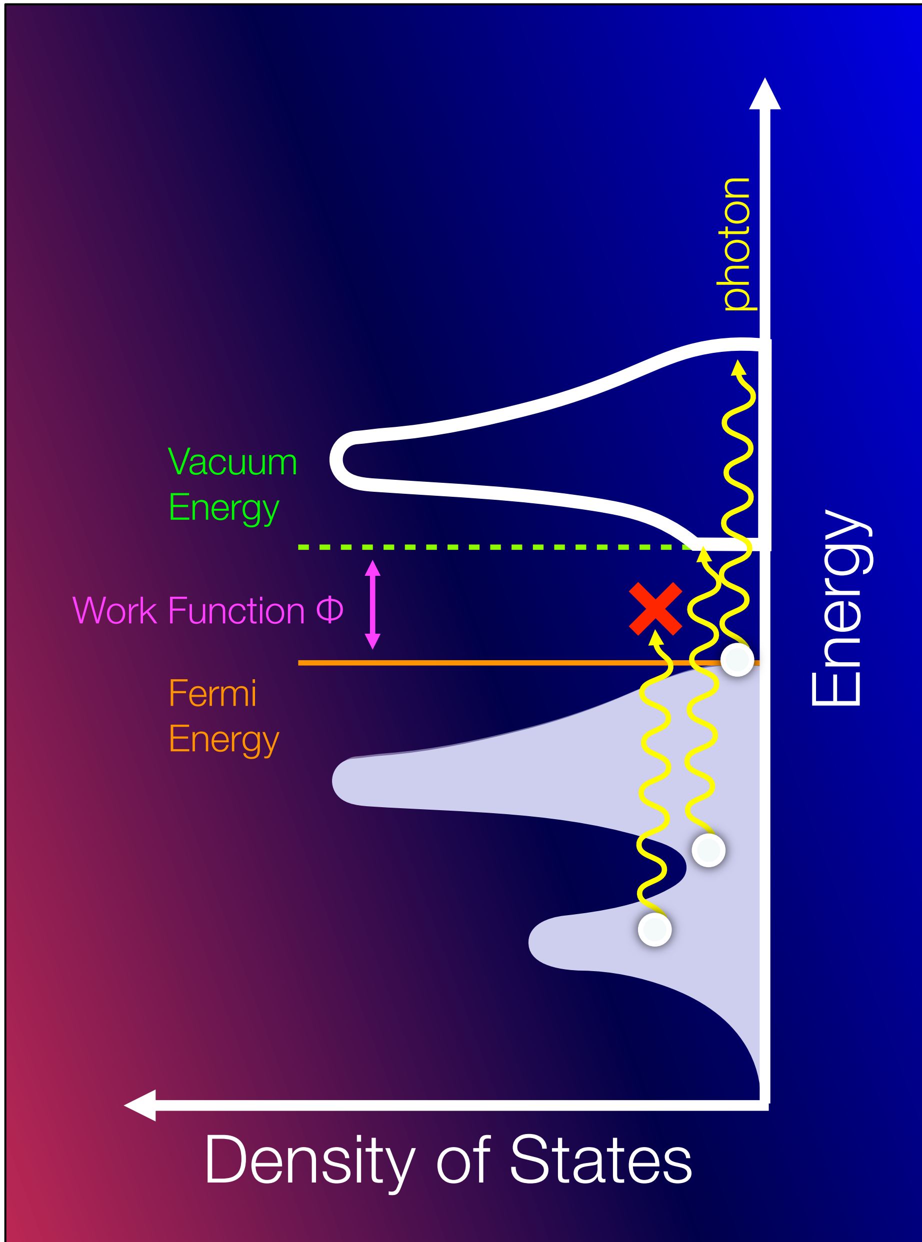
- Deeply bound "*core*" electrons remain basically unchanged
- Outermost "*valence*" electrons hybridize forming continuous "*energy bands*"



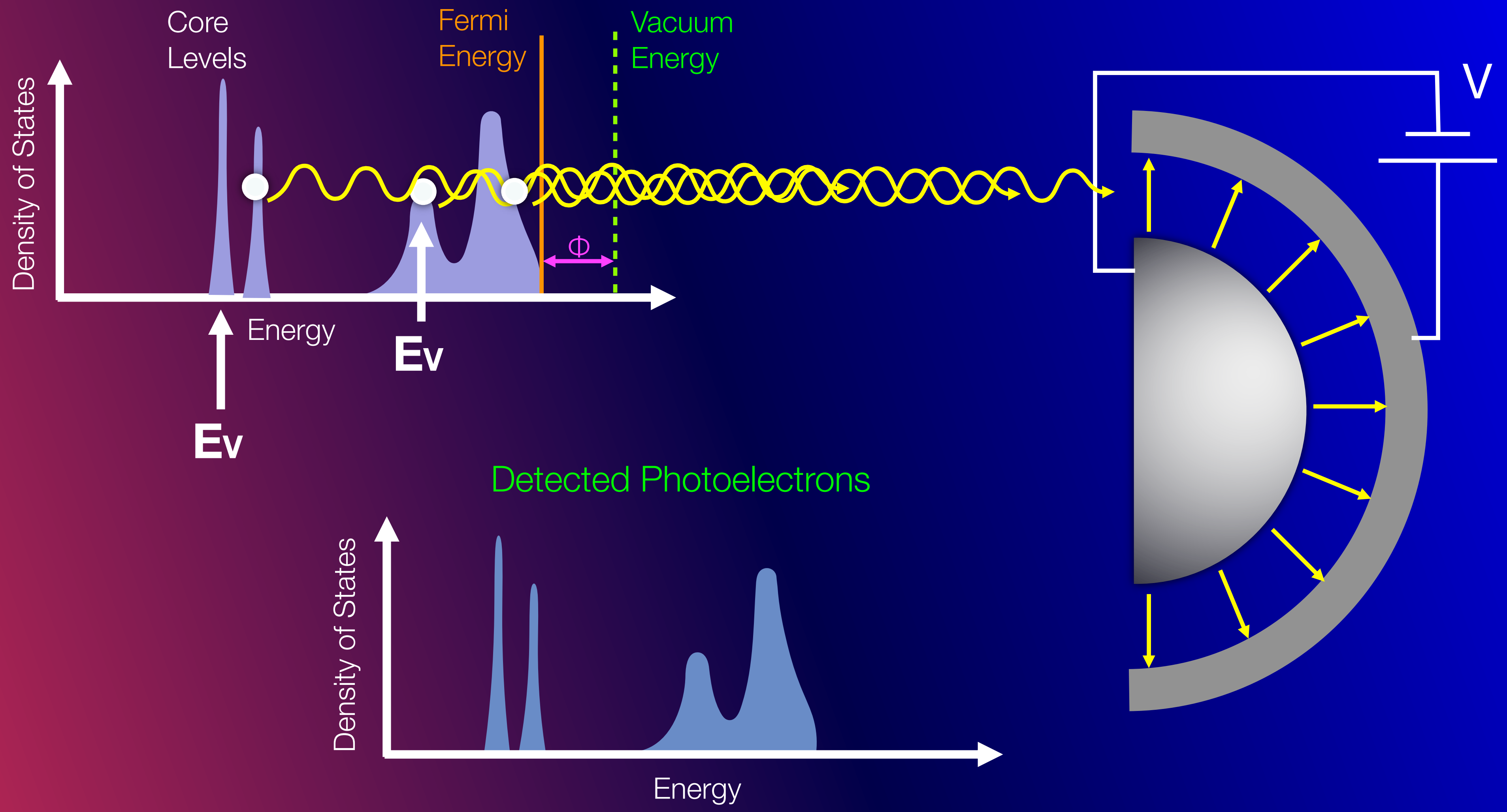
Na metal (Ne + one 3s electron)

Using the photoelectric effect to learn about materials

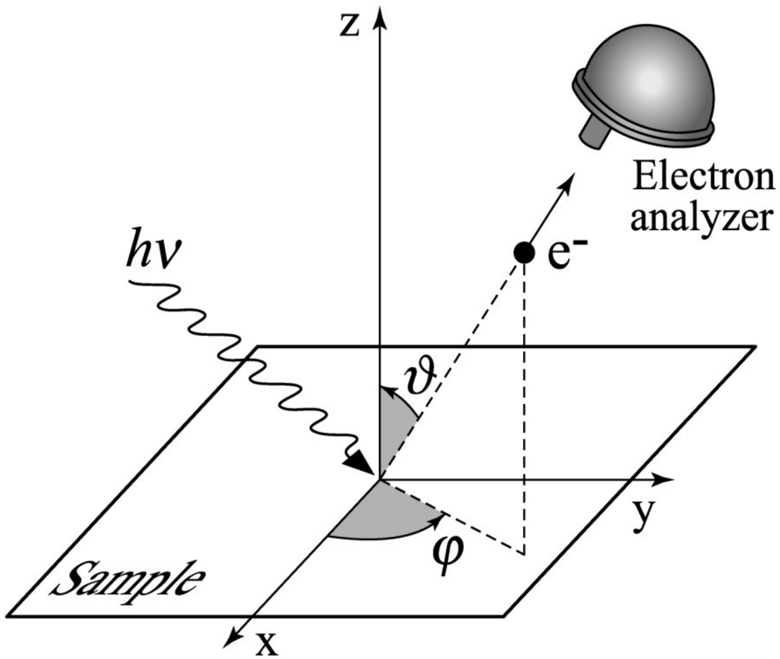




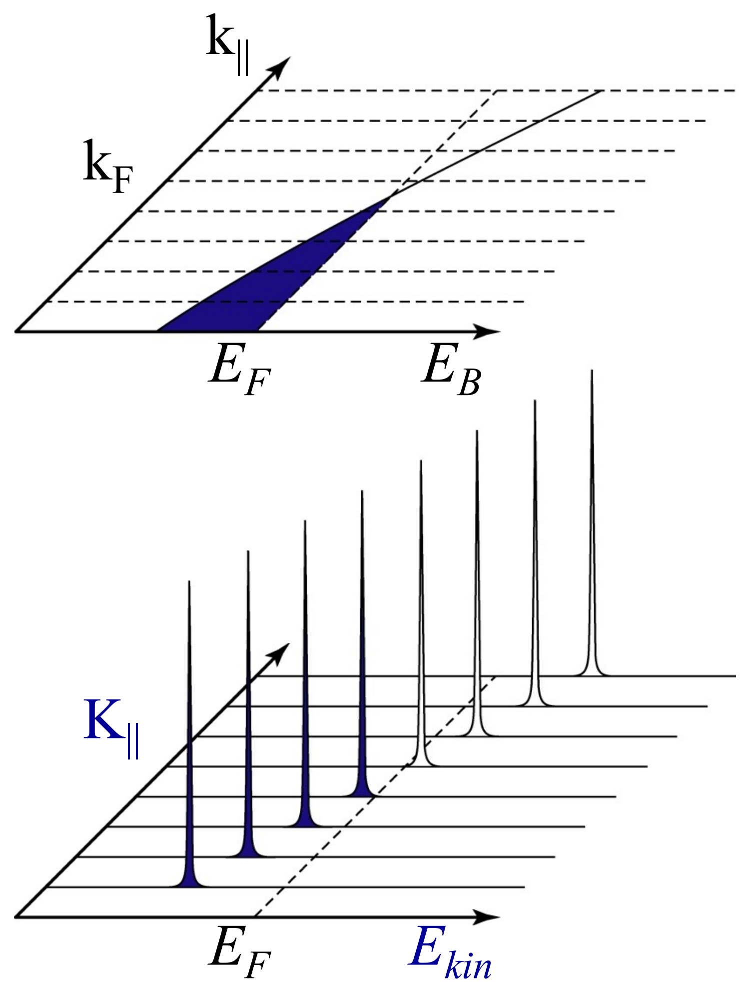
Energy analysis of photoelectrons gives density of states



Kinematics of the ARPES process : Momentum Conservation



Electrons in Reciprocal Space



Energy Conservation

$$E_{kin} = h\nu - \phi - |E_B|$$

Momentum Conservation

$$\hbar k_{||} = \hbar K_{||} = \sqrt{2mE_{kin}} \cdot \sin\vartheta$$

Courtesy of Andrea Damascelli

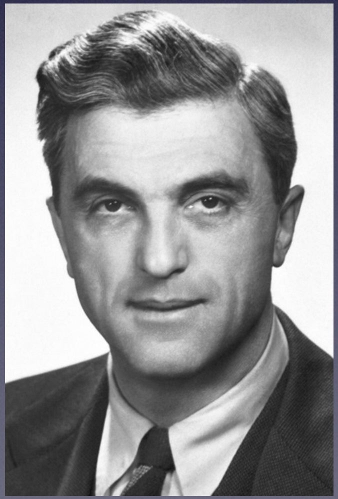
towards a quantum theory of solids

Erwin Schrodinger

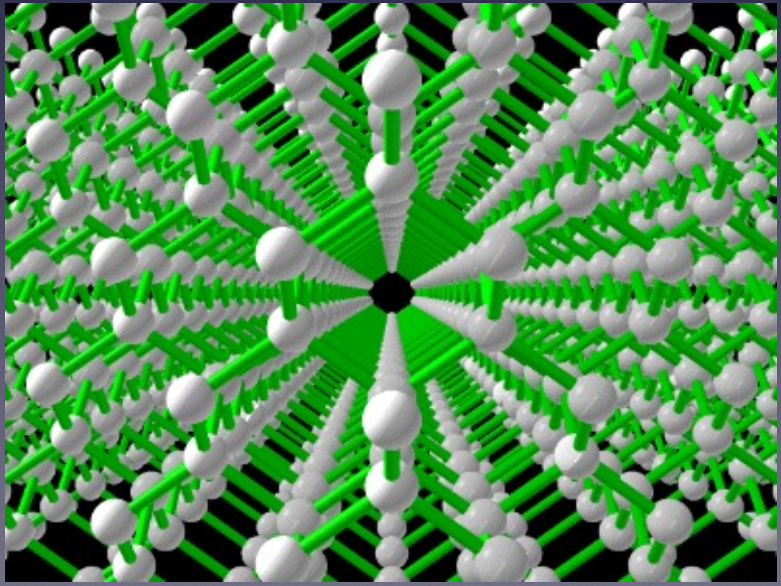
Schrodinger Equation

$$\frac{-\hbar^2}{2m}\frac{\partial^2 \psi(x)}{\partial x^2} + U(x)\psi(x) = E\psi(x)$$

time-independent in 1D



Felix Bloch



"When I started to think about it, I felt that the main problem was to explain how the electrons could sneak by all the ions in a metal ... By straight Fourier analysis I found to my delight that the wave differed from the plane wave of free electrons only by a periodic modulation"

- Felix Bloch

towards a quantum theory of solids

Erwin Schrodinger

Schrodinger Equation

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + U(x)\psi(x) = E\psi(x)$$

time-independent in 1D

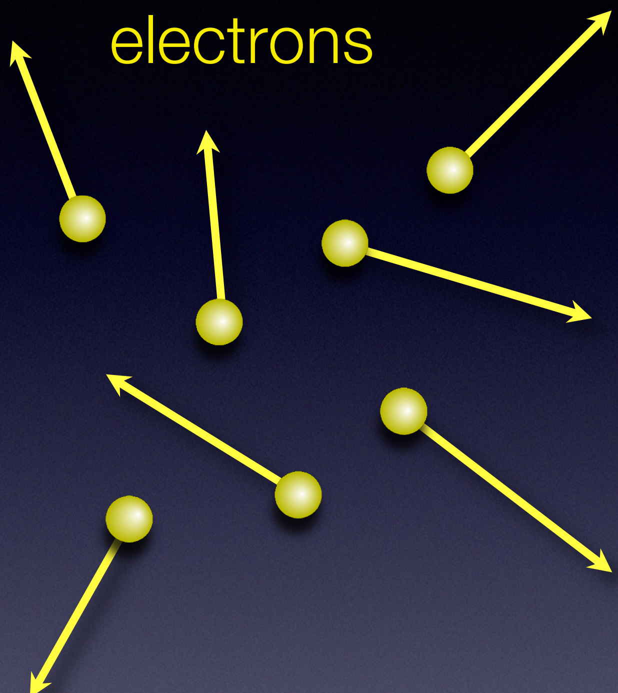
the Hamiltonian for interacting electrons & nuclei is basically unsolvable!

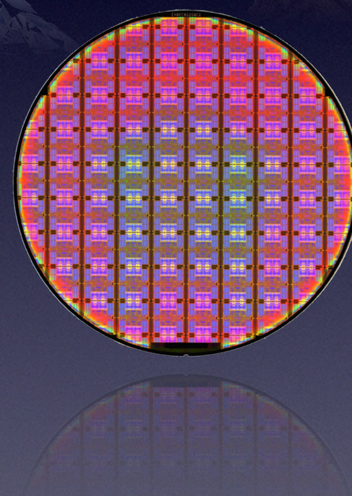
electron KE	electron-electron interactions	nuclei KE	electron-nuclei interactions	nuclei-nuclei interactions

$$-\sum_{j}^{N_e}\frac{\hbar^2}{2m}\nabla_j^2 + \sum_{j\ll k}^{N_e}\frac{e^2}{|\vec{r}_j - \vec{r}_k|} - \sum_{\alpha}^{N_i}\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2 - \sum_{j}^{N_e}\sum_{\alpha}^{N_i}\frac{Z_\alpha e^2}{|\vec{r}_j - \vec{R}_\alpha|} + \sum_{\alpha\ll\beta}^{N_j}\frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha - \vec{R}_\beta|}$$

the “independent electron” approximation

independent
electrons



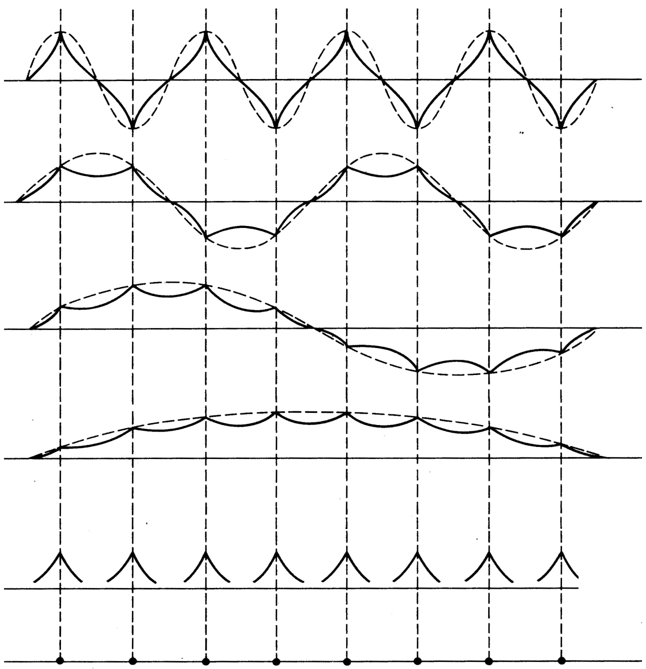


electron KE	electron-electron interactions	nuclei KE	electron-nuclei interactions	nuclei-nuclei interactions

$$-\sum_{j}^{N_e} \frac{\hbar^2}{2m}\nabla_j^2 + \sum_{j \ll k}^{N_e} \frac{e^2}{|\vec{r}_j - \vec{r}_k|} - \sum_{\alpha}^{N_i} \frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2 - \sum_{j}^{N_e}\sum_{\alpha}^{N_i} \frac{Z_\alpha e^2}{|\vec{r}_j - \vec{R}_\alpha|} + \sum_{\alpha \ll \beta}^{N_j} \frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha - \vec{R}_\beta|}$$

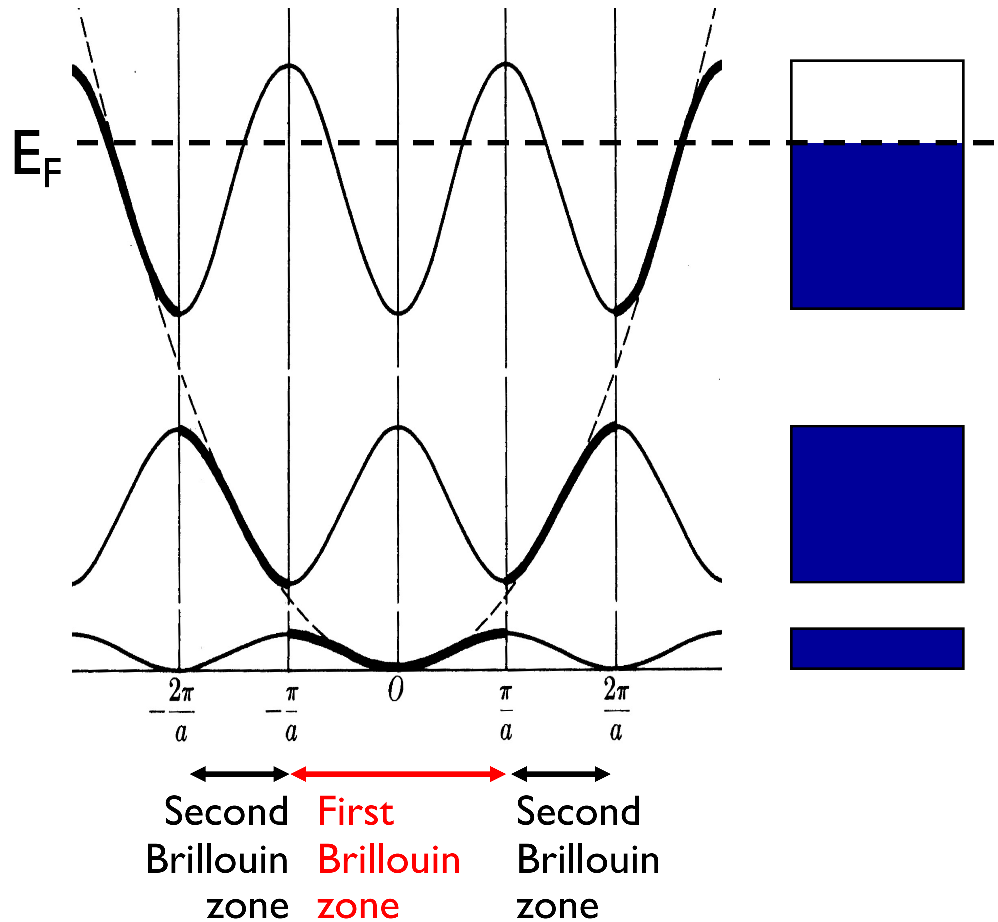
Electrons in reciprocal space : momentum states

Wave functions
in a 1D lattice



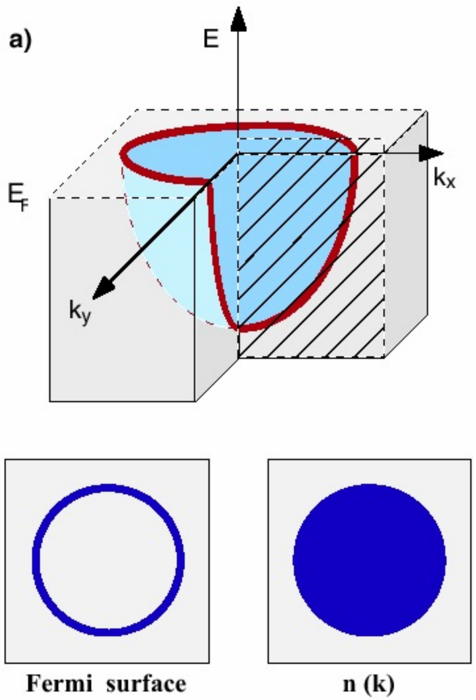
1D chain of atoms

Allowed electronic states
Repeated-zone scheme



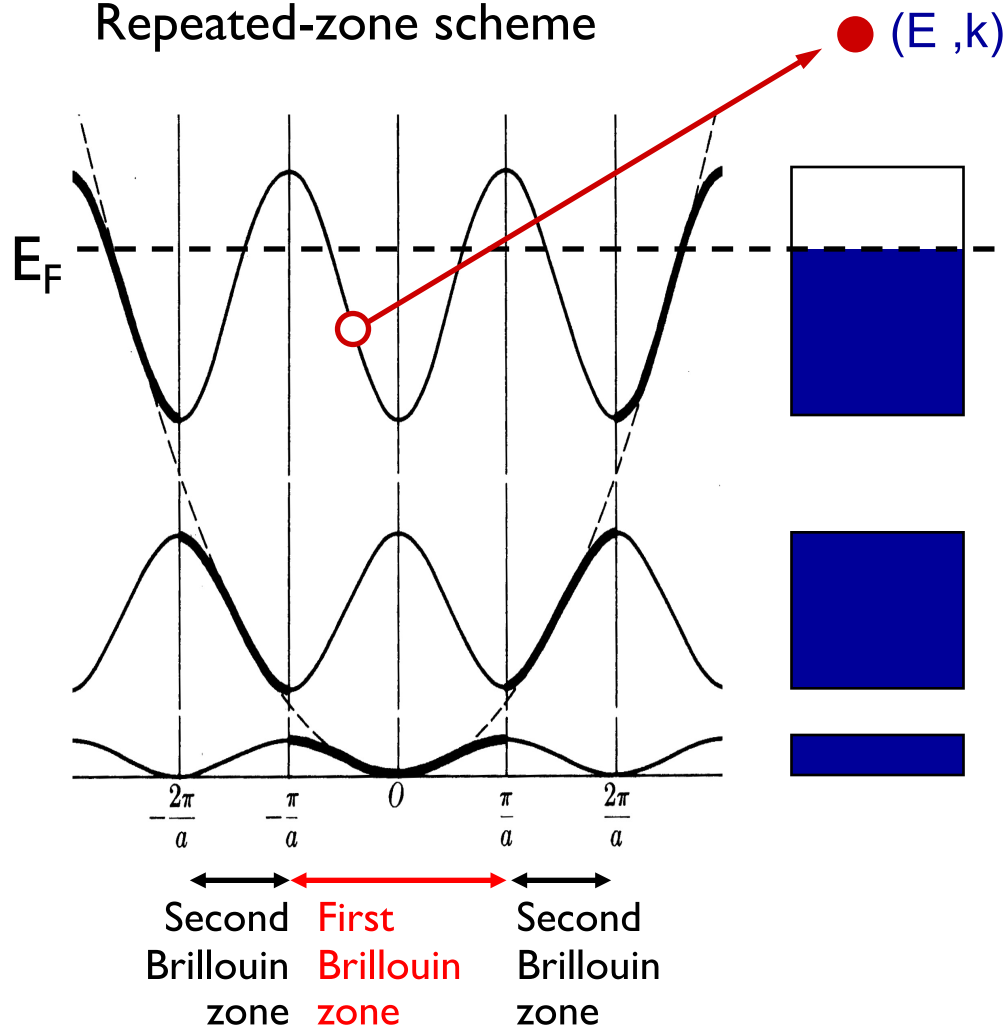
Electrons in reciprocal space : momentum states

Many properties of a solids are determined by electrons near E_F (conductivity, magnetoresistance, superconductivity, magnetism)



Only a narrow energy slice around E_F is relevant for these properties (kT=25 meV at room temperature)

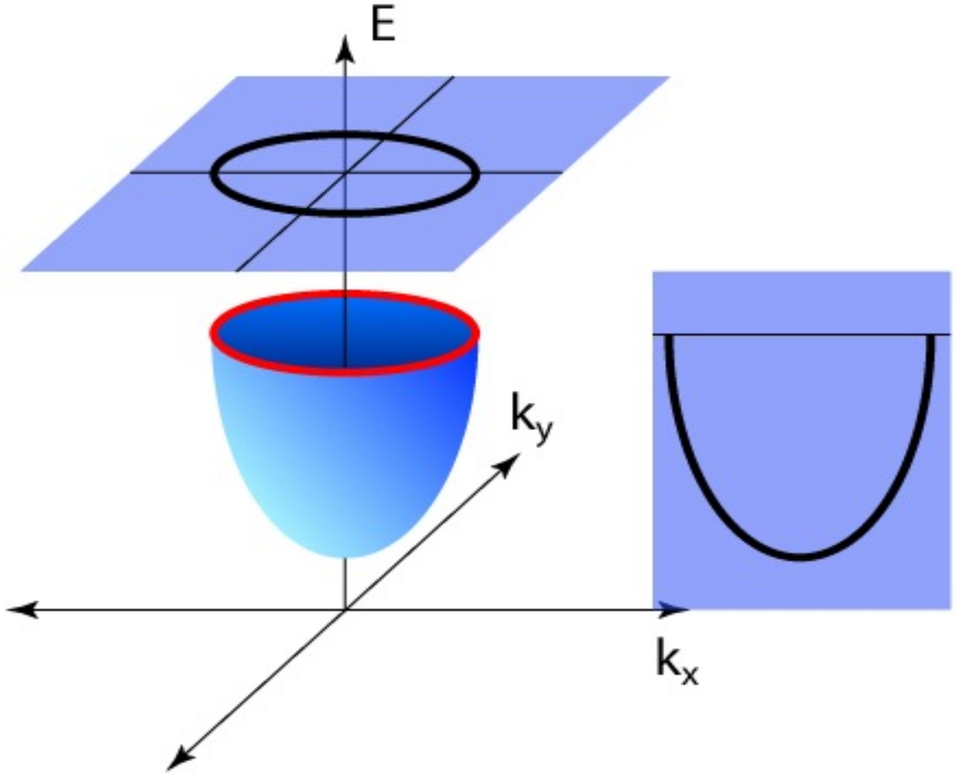
Allowed electronic states
Repeated-zone scheme

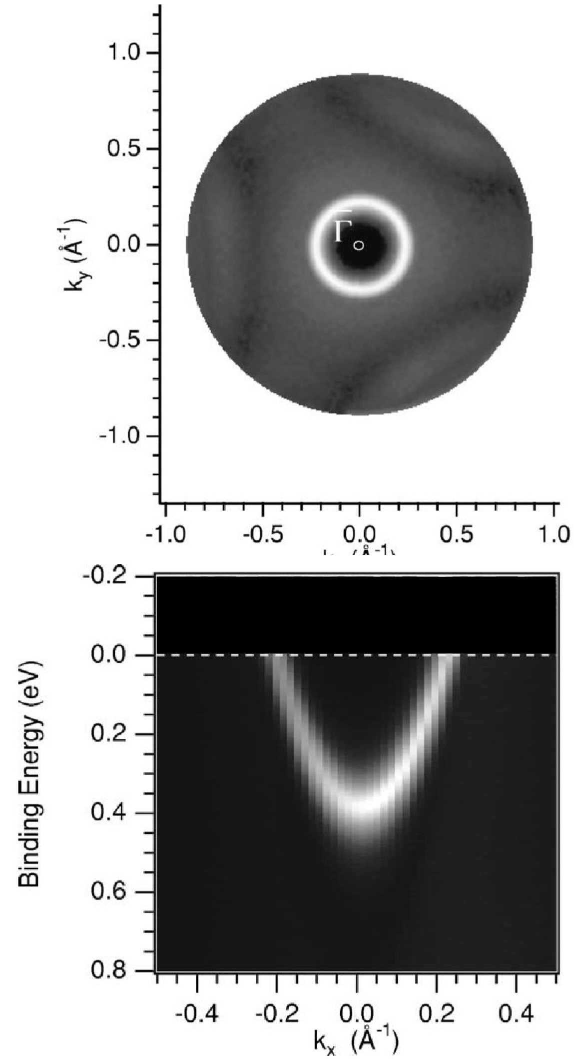


a simple example of ARPES : 2D free electron gas on Cu (111)

ARPES2023

Cu (111)





$$E = \hbar^2 \mathbf{k}^2 / 2m^*$$

F. Baumberger et al., PRB 64, 195411 (2001)

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Concept Question #1

In the photoemission process, energy conservation allows us to relate the energy of the exiting photoelectron to the initial state energy of the electron by considering the energy of the incident photon.

When considering momentum conservation in the photoemission process, which statement is **true**?

A. In a photon-in, electron-out experiment, the momentum of the incident photon never needs to be considered (in contrast, to photon-in, photon-out, like x-ray scattering)

B. The photon's momentum does not need to be considered because translational symmetry is broken in the perpendicular direction

C. Due to its relativistic nature, the photon's momentum is typically negligibly small when compared to the electron's momentum, and can therefore be ignored in an ARPES experiment

D. The photon's momentum affects the ARPES spectra in the form of momentum broadening, Δk

E. None of the above statements are true

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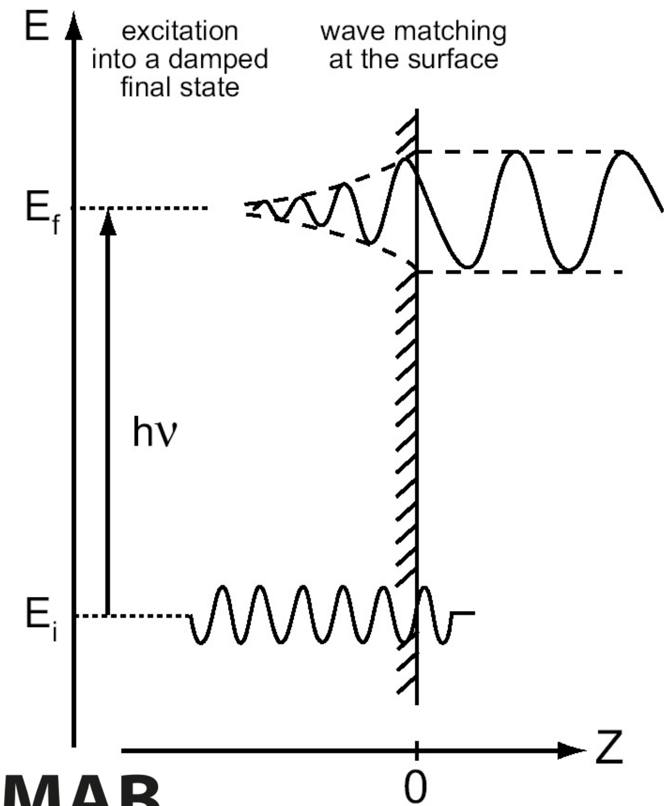
One-step vs. Three-step model of photoemission

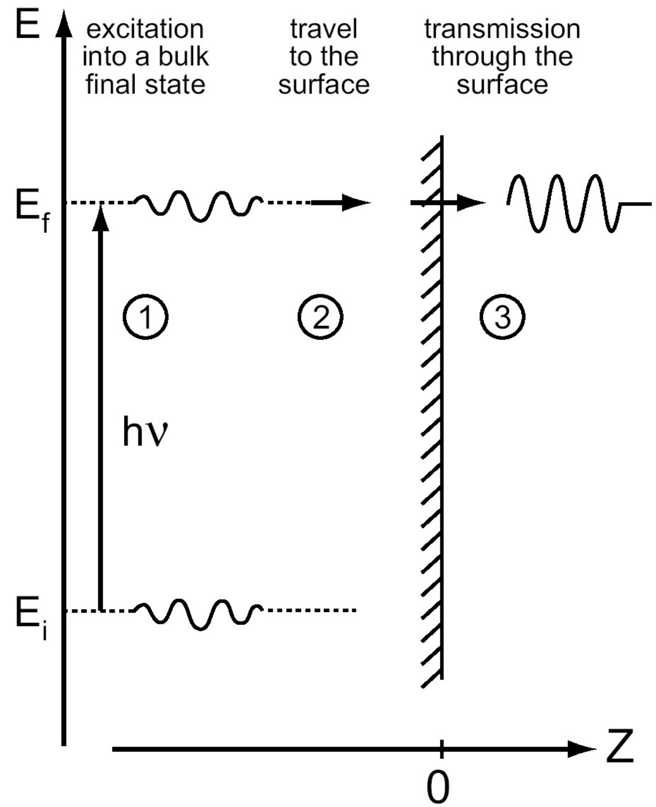
Photoemission
Intensity $I(k,\omega)$

$$w_{fi} \propto |\langle \Psi_f^N | \mathbf{A}\cdot\mathbf{p} | \Psi_i^N \rangle|^2 \delta(E_f^N - E_i^N - h\nu)$$

One-step model

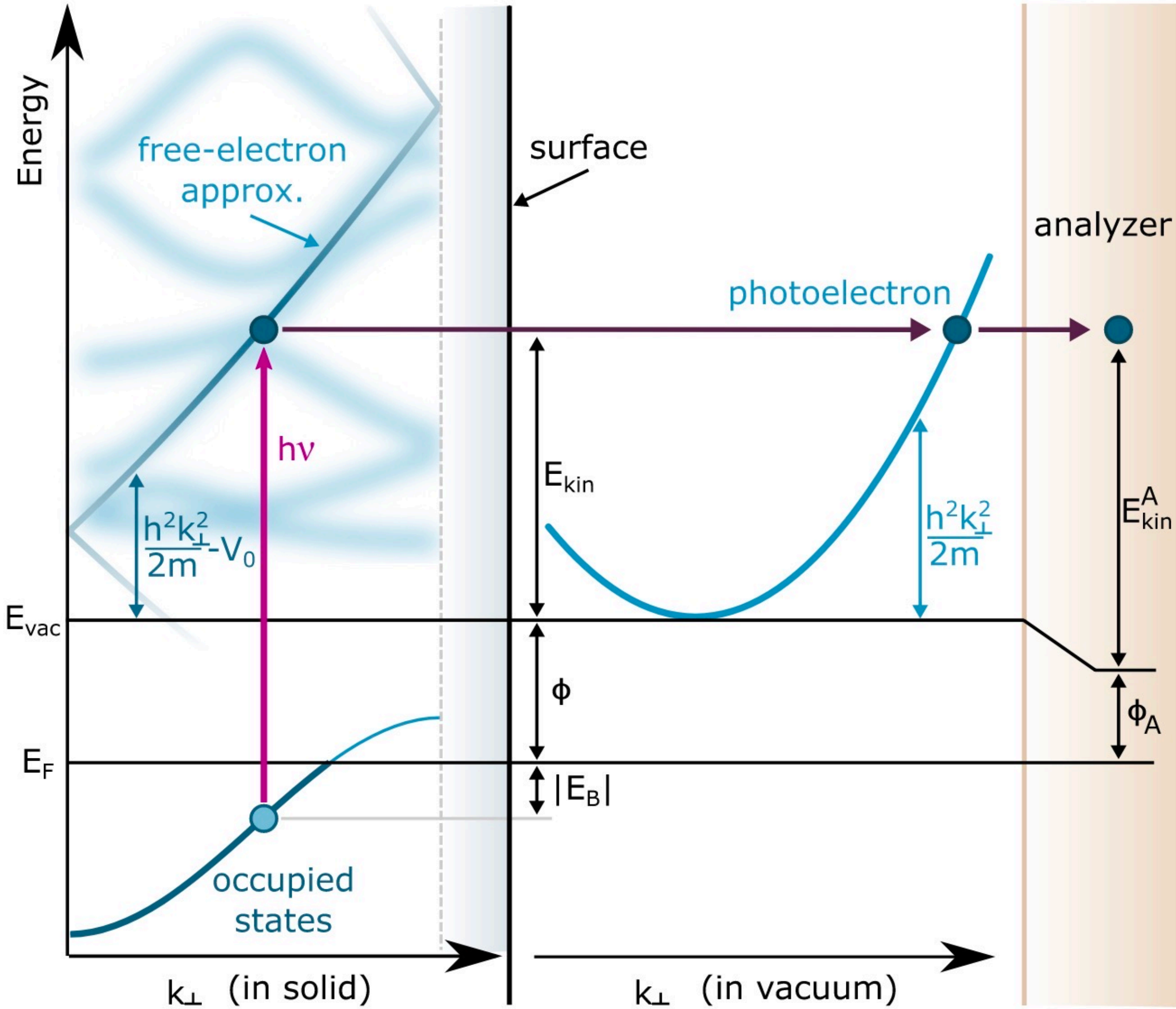


Three-step model



Courtesy of Andrea Damascelli

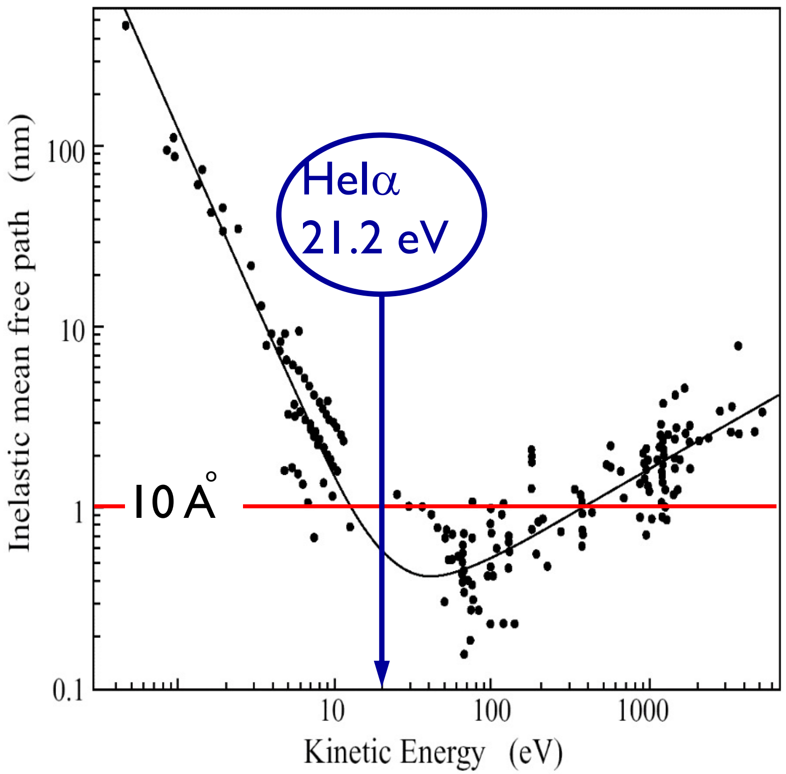
Kinematics of the ARPES process : Transition to the Vacuum



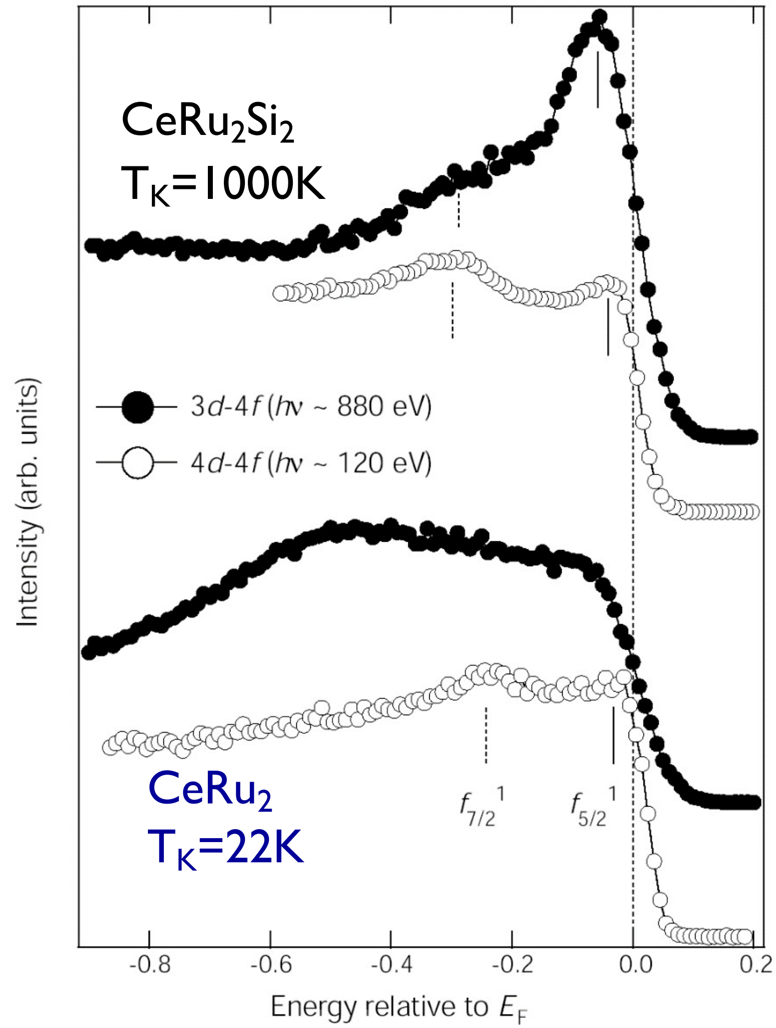
From Sobota, He, and Shen, RMP 93, 025006 (2021)

Surface sensitivity of ARPES

"Universal Curve" of Mean-free path for excited electrons



Seah, Dench *et al.*, SIA 1, 2 (1979)



Sekiyama *et al.*, Nature 403, 396 (2000)

Courtesy of Andrea Damascelli

Concept Question #2

Photoemission is a highly surface sensitive measurement (typically < 1 nm probing depth). What are the main factor(s) determining the probing depth (inelastic mean free path) in the photoemission process?

1. Adsorbed molecules on the surface of the sample
2. The absorption length (skin depth) of photons in the VUV
3. The kinetic energy of the photoelectrons
4. The plasma frequency of the measured sample
5. The polarization of the photons being used to measure the sample

A. 1, 3, 5 & 6

B. 3 & 4

C. 2, 3, 4 & 5

D. 2, 3 & 5

E. All of the above

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2. The absorption length (skin depth) of photons in the VUV
3. The kinetic energy of the photoelectrons
4. The plasma frequency of the measured sample
5. The polarization of the photons being used to measure the sample

A. 1, 3, 5 & 6

B. 3 & 4

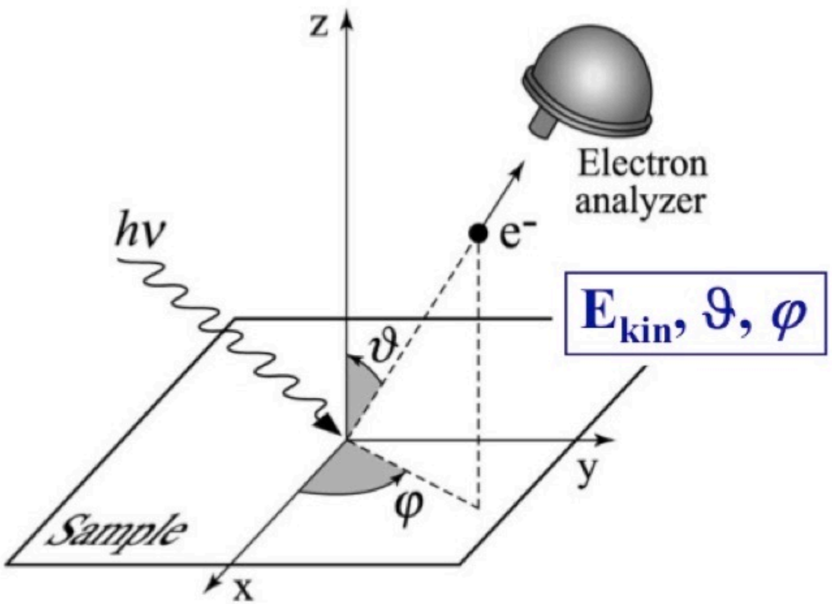
C. 2, 3, 4 & 5

D. 2, 3 & 5

E. All of the above

Concept Question #3

In the photoemission process, the in-plane (longitudinal) momentum of the photoelectron can be directly related to the in-plane momentum of the electron when it was inside the solid, due to translational symmetry. For the out-of-plane (perpendicular) component of the photoelectron's momentum :



A. The out-of-plane momentum of the electron in the solid is equal to the out-of-plane momentum of the outgoing photoelectron

B. The perpendicular component of the electron's momentum cannot be experimentally determined

C. The perpendicular momentum of the electron inside the crystal is not a good quantum number

D. The out-of-plane photoelectron momentum can be related to the out-of-plane momentum of the electron when it was in the solid, but they are not precisely equal

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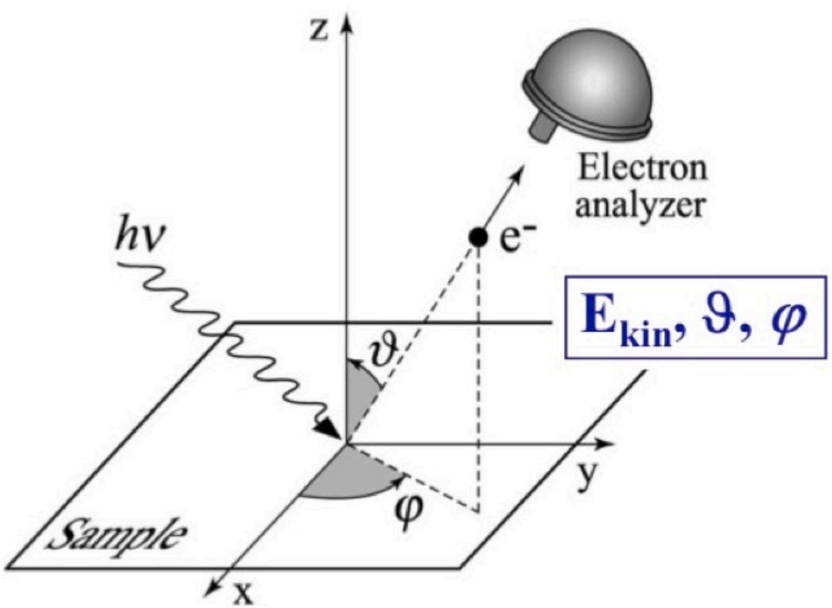

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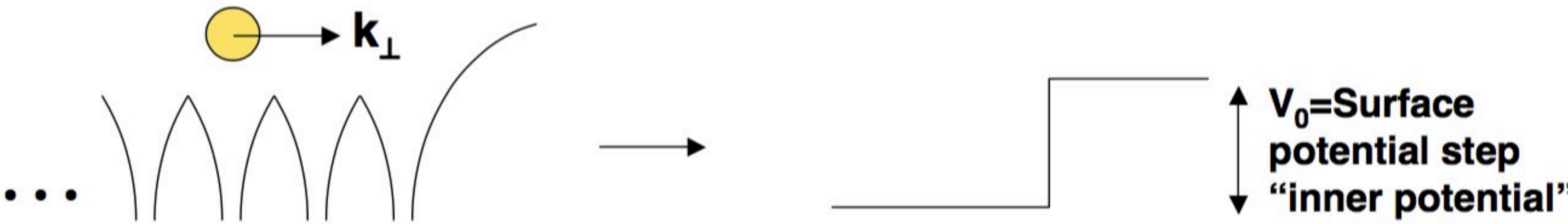
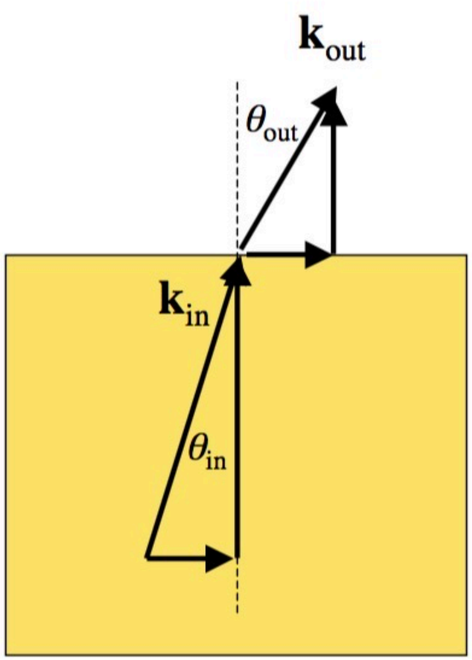
We approximate the surface as a square potential barrier.



We assume the electrons outside the sample have energy $E = p^2/2m = \hbar^2 k^2/2m$



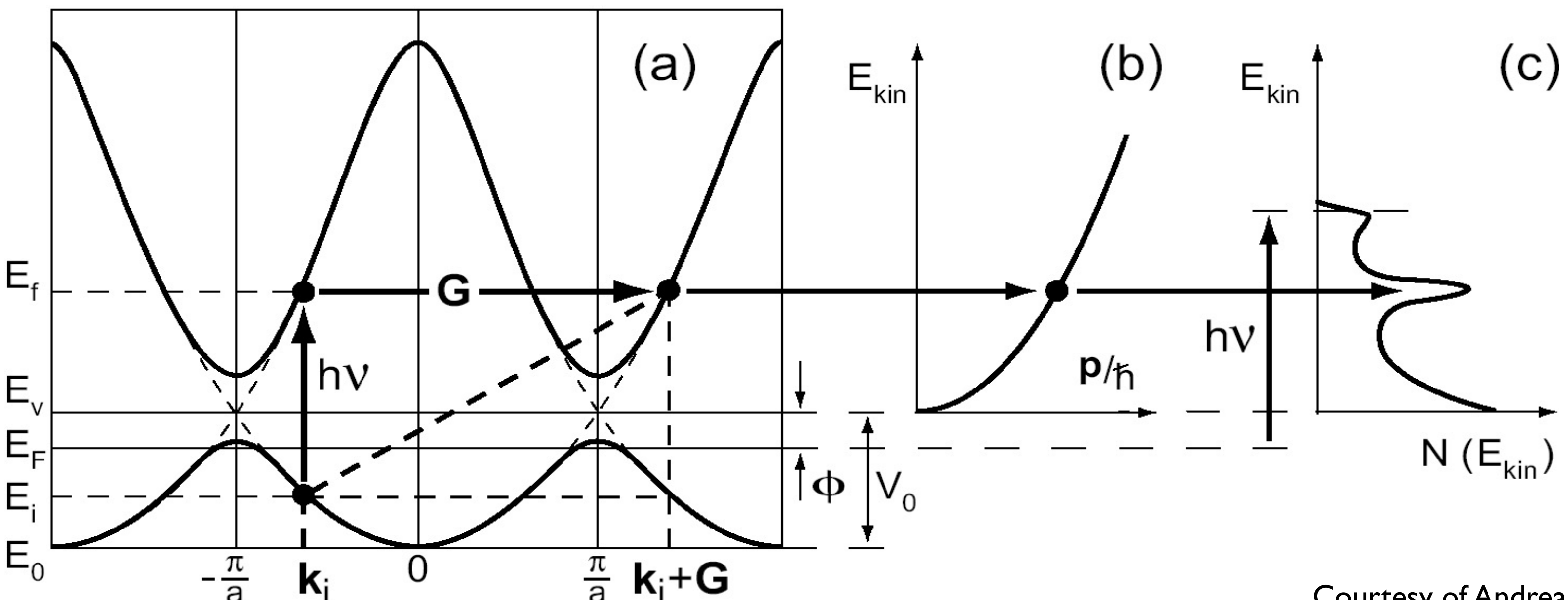
Can think of a analogous "Snell's Law" for photoemission, where the in-plane momentum is conserved and the out-of-plane momentum changes due to scattering off the potential barrier (work function)

Courtesy of Eli Rotenberg

Free-electron final state
$$E_f(\mathbf{k}) = \frac{\hbar^2\mathbf{k}^2}{2m} - |E_0| = \frac{\hbar^2({\mathbf{k}_\parallel}^2 + {\mathbf{k}_\perp}^2)}{2m} - |E_0|$$

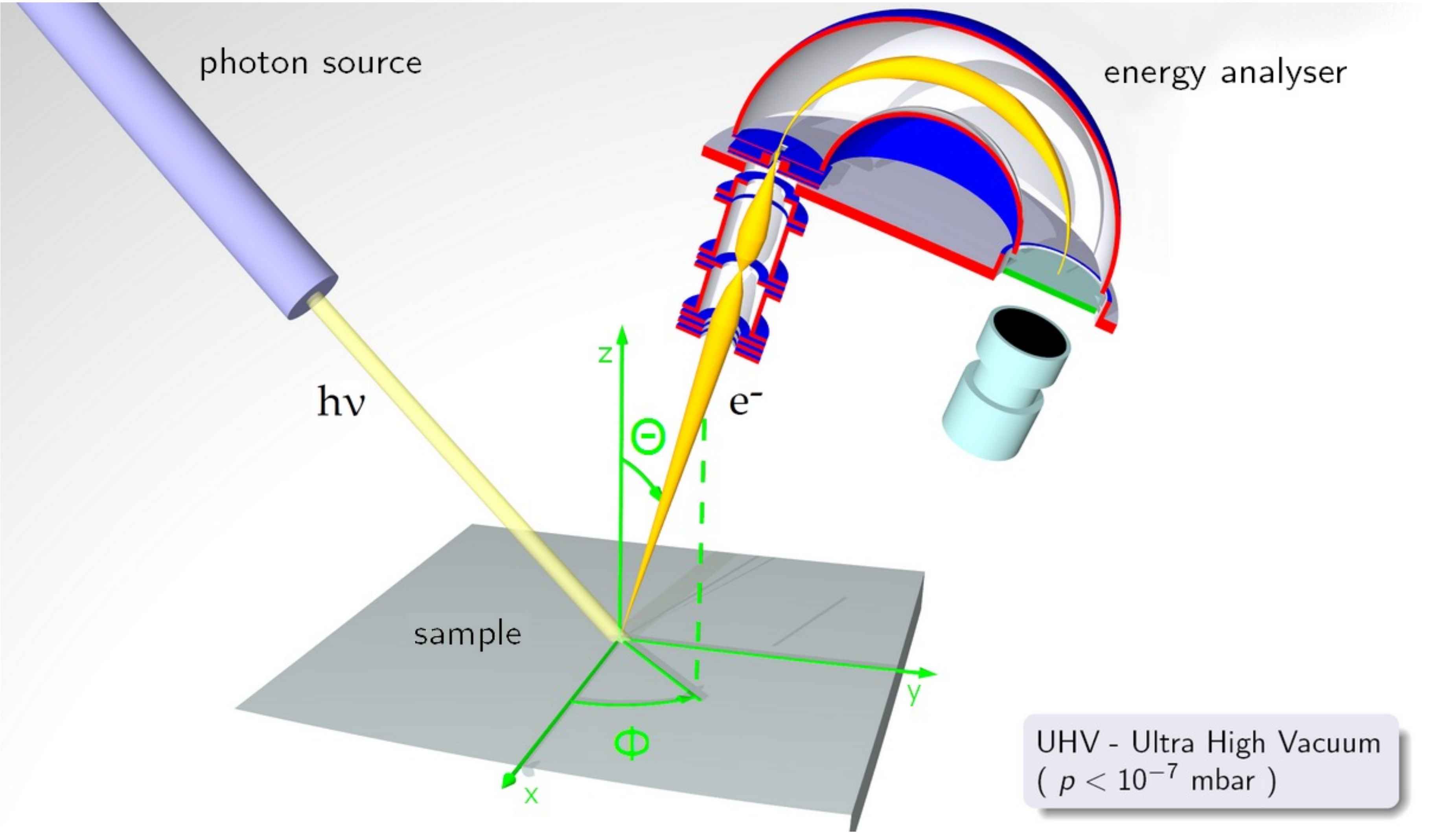
because $\hbar^2\mathbf{k}_\parallel^2/2m = E_{kin}\sin^2\vartheta$ $\quad E_f = E_{kin} + \phi \quad V_0 = |E_0| + \phi$

$$\boxed{\mathbf{k}_\perp = \frac{1}{\hbar}\sqrt{2m(E_{kin}\cos^2\vartheta + V_0)}}$$

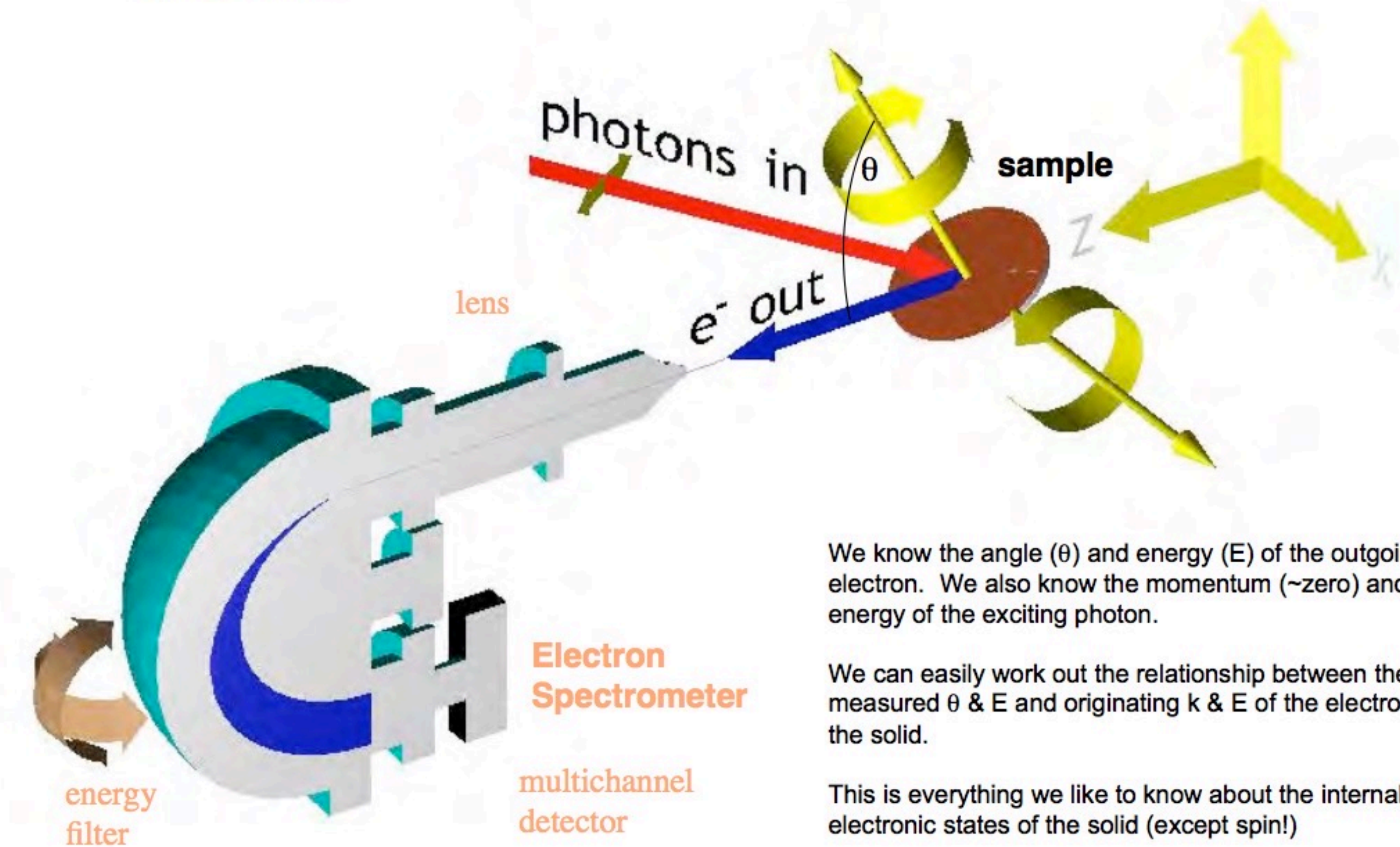


Courtesy of Andrea Damascelli

Schematic of the ARPES process



Schematic of the ARPES process



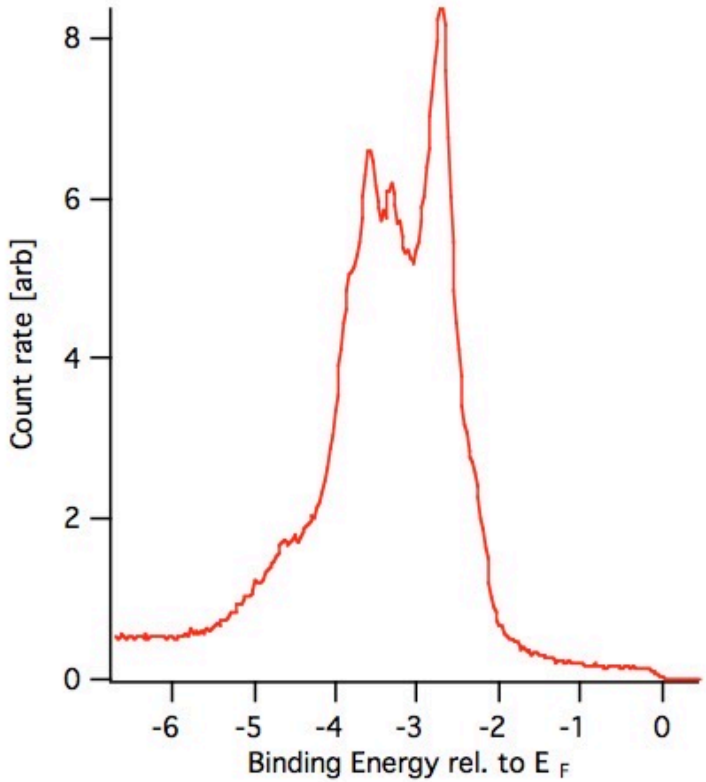
We know the angle (θ) and energy (E) of the outgoing electron. We also know the momentum (~zero) and the energy of the exciting photon.

We can easily work out the relationship between the measured θ & E and originating k & E of the electrons in the solid.

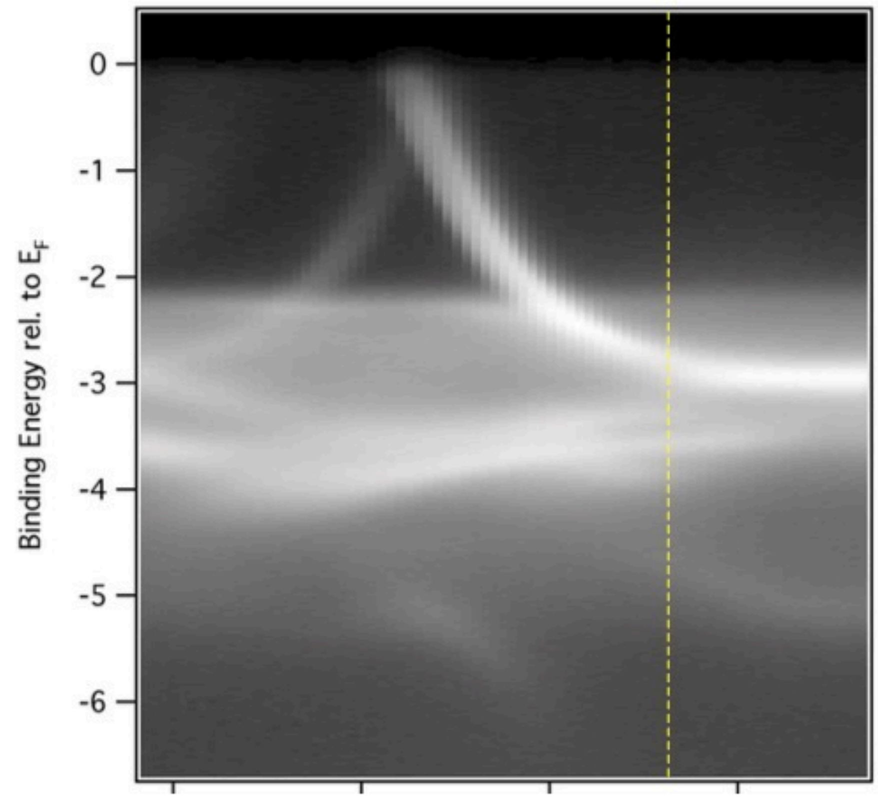
This is everything we like to know about the internal electronic states of the solid (except spin!)

Courtesy of Eli Rotenberg

ARPES data acquisition



A spectrum at a single momentum k_x

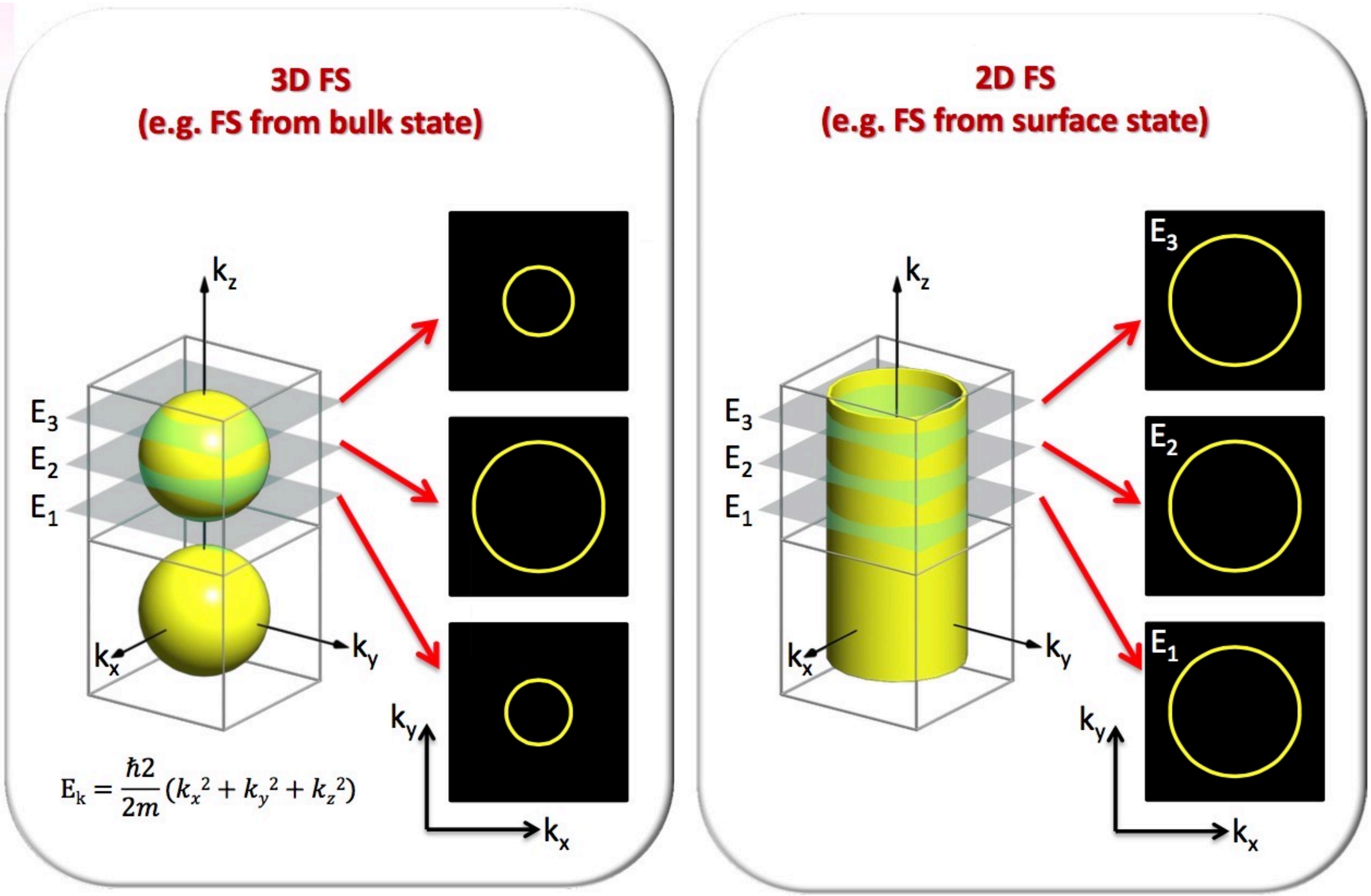


Accumulate spectra as the momentum k_x is scanned

Courtesy of Eli Rotenberg

Three-dimensional electronic structure mapping

$$\boxed{\mathbf{k}_\perp = \frac{1}{\hbar}\sqrt{2m(E_{kin}\cos^2\vartheta + V_0)}}$$



Courtesy of Eli Rotenberg

photoemission at different photon energy ranges

$h\nu$ (eV)	ΔE & Δk	Cross Section	Primarily Used For / Special Capabilities
10 – 100 eV synchrotrons, plasma lamps, lasers	**10^{-3} eV** **10^{-3} A^{-1}**	**10 - 1** (Mb / atom)	High-resolution studies of electronic structure & surfaces, Fermi surface & band mapping, low-energy physics
100 – 1000 eV synchrotrons	**10^{-2} eV** **10^{-2} A^{-1}**	**10 - 0.01** (Mb / atom)	Resonant photoemission X-ray absorption / magnetic dichroism XPS (elemental chemical analysis)
1000 – 10,000 eV X-ray tubes, synchrotrons	**10^{-1} eV** **10^{-1} A^{-1}**	**10^{-2} – 10^{-4}** (Mb / atom)	Bulk sensitivity Elemental & chemical analysis Changing orbital cross-sections

photon sources for photoemission can be…

X-ray tubes — Most common sources for XPS (Al, Mg anodes), can be used with grating for better energy resolution (1000-10,000 eV, $\Delta E \sim 0.1$-1 eV)

Plasma Discharge — Narrow bandwidth, high intensity lamps in VUV (10-100 eV, $\Delta E \sim 0.001$ eV); used for ARPES

Synchrotrons — Complete control over photon beam (energy, polarization, resolution); user facilities

Lasers — Higher harmonic generation; low energy (> 10 eV). Pump-probe, or high resolution

Photon source must be :

1. Monochromatic
2. High intensity ($> 10^9\ s^{-1}$)
3. Energetic ($h\nu > \phi \sim 5$ eV)

X-ray photoemission measurements of core electrons

- elemental & chemical analysis of sample surfaces
- determination of oxidation states, contaminants, surface composition
- simple, user-friendly technique
- widespread use in physics, materials science, chemistry, engineering, as well as the "real world"

Photon Energy (eV)	Energy Resolution (eV)	Spatial Resolution	Found in
10^3 – 10^4 eV (X-Ray tubes, Synchrotrons)	**0.1 – 1 eV**	**0.01 – 1 mm**	Many universities National labs Synchrotrons Some companies

UV photoemission measurements of valence electrons

• studies of electronic band structure & density of states

• low temperature (> 10 K), high resolution (0.001 eV) measurements

• commonly studied materials : superconductors, novel electronic materials, topological materials, surfaces, nanostructures on surfaces

• a specialized technique used in solid state physics & materials science to study electronic structure & interactions (accessible at synchrotrons)

Photon Energy (eV)	Energy Resolution (eV)	Angular Resolution	Found in
10 – 100 eV (Synchrotrons, Lasers, Plasma lamps)	**0.01 – 0.001 eV**	**0.1 – 1°**	Some academic groups; Synchrotrons

Concept Question #4

Which of the following is strongly dependent on the value of the photon energy used to perform the experiments? Assume the photon energy is always large enough to eject electrons from the sample.

1. The work function of the sample
2. The number of (occupied) states that we can access below E_F
3. The number of (unoccupied) states that we can access above E_F
4. The intensity of the measured photoemission signal

A. 2 only

B. 2, 3 & 4

C. 1, 2, & 4

D. 2 & 4

E. All of the above

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A. 2 only

B. 2, 3 & 4

C. 1, 2, & 4

D. 2 & 4

E. All of the above

Concept Question #5

Which of the following is strongly dependent on the value of the photon energy used to perform the experiments? Assume the photon energy is always large enough to eject electrons from the sample.

1. The momentum resolution of our measurement (i.e. how fine a feature Δk we can resolve)
2. The range in momentum space (span of the Brillouin zone) that we can access
3. The out-of-plane momentum, k_z, that is being accessed

A. None of the above

B. 2 only

C. 2 & 3

D. 3 only

E. All of the above

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Which of the following is strongly dependent on the value of the photon energy used to perform the experiments? Assume the photon energy is always large enough to eject electrons from the sample.

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A. None of the above

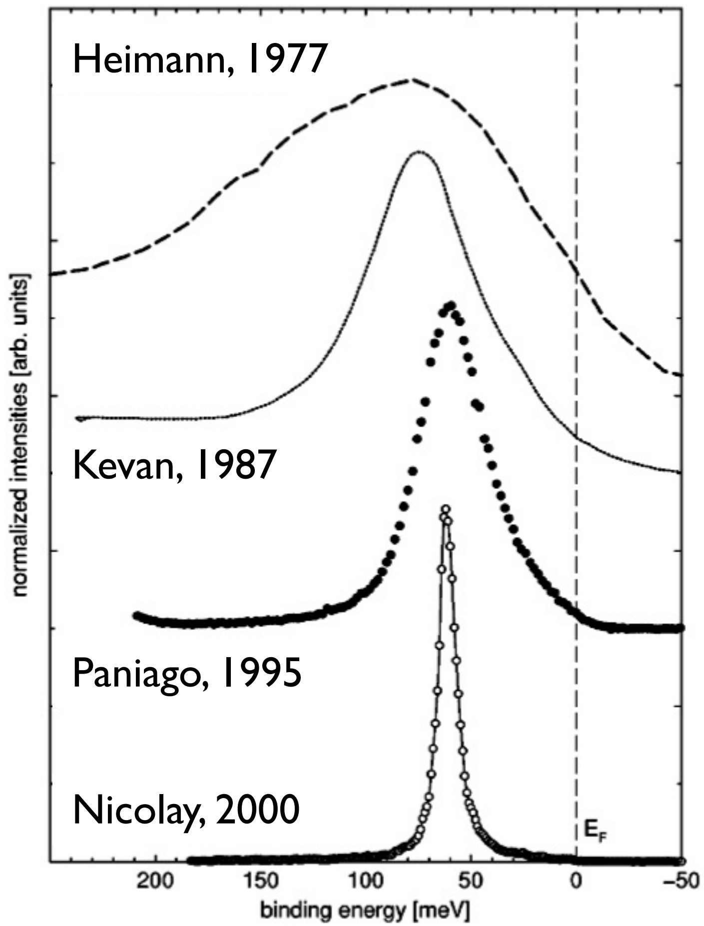
B. 2 only

C. 2 & 3

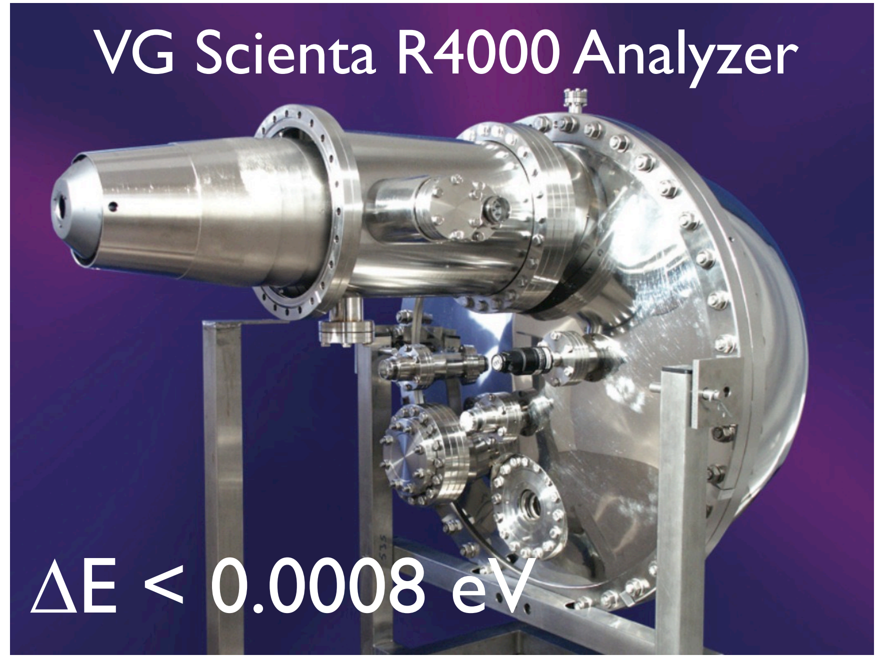
D. 3 only

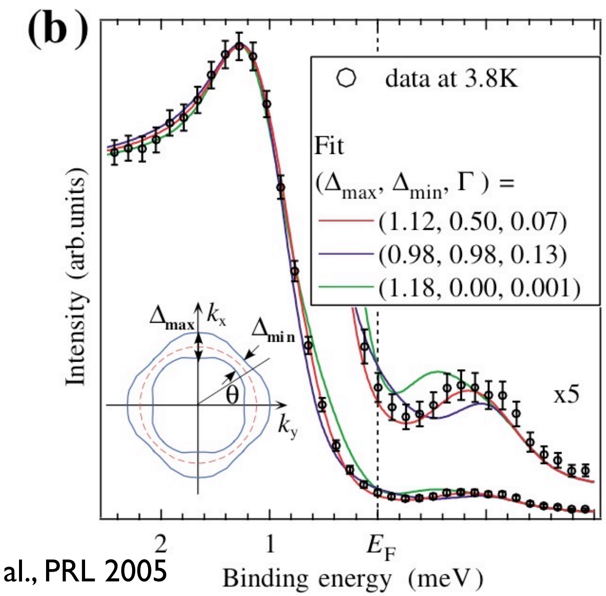
E. All of the above

Evolution of instrumental resolution over time



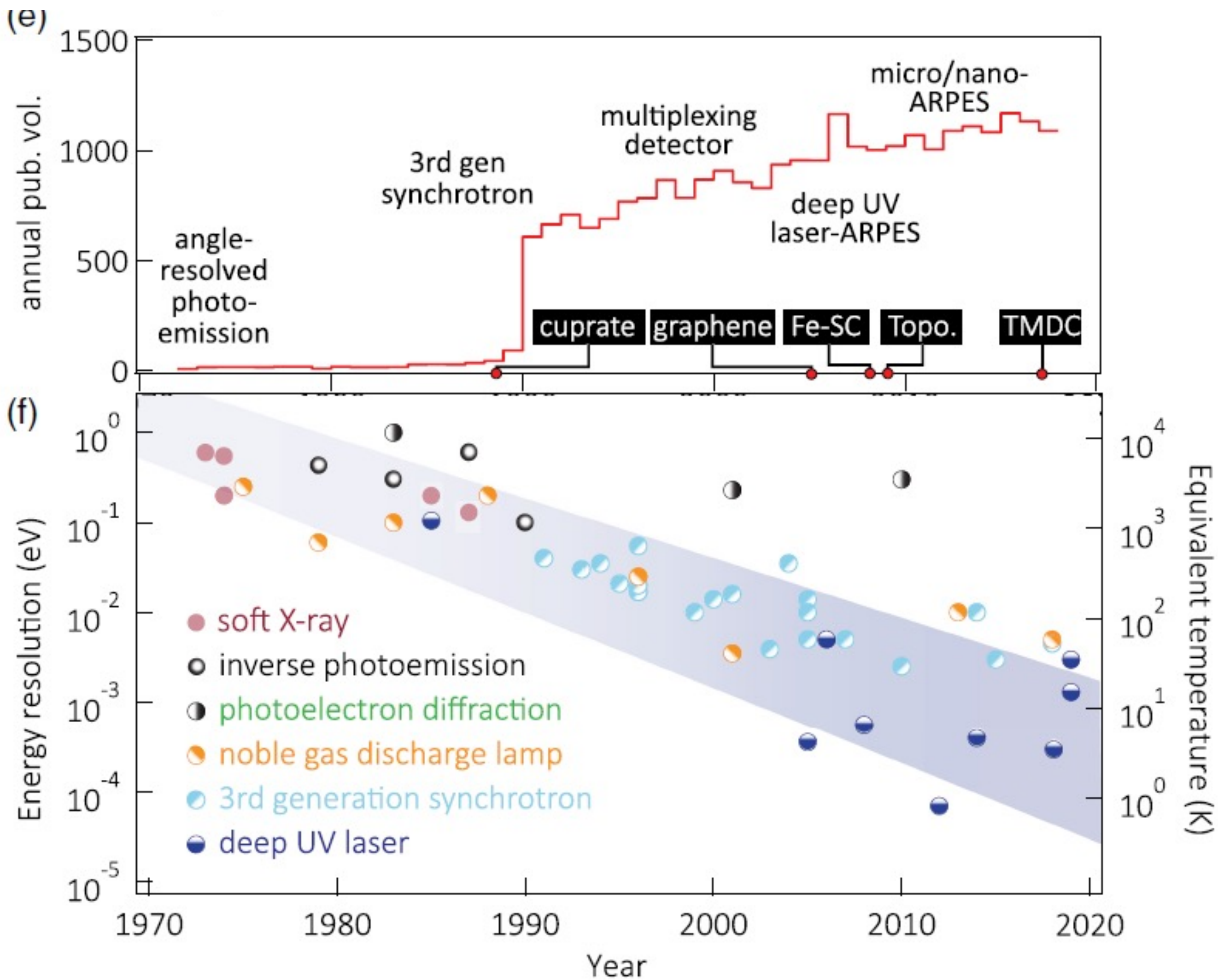
F. Reinert *et al.*, PRB (2001)





T. Kiss et al., PRL 2005

Evolution of ARPES over time



J.A. Sobota, Y. He, and Z.-X. Shen. Reviews of Modern Physics 93, 025006 (2021)

• mean free path (mfp) of photoelectrons in solids is ~ **1 nanometer**. Measurements are sensitive to top unit cells & monolayers

• short mfp means sample surfaces must be kept pristine (no adsorbed gases) in ultrahigh vacuum (UHV - 10^{-10} torr)

• need to reduce stray electromagnetic fields (deflection)

• infeasible to measure samples *in vivo* or in solution