# Homework

Chen Zhaoxu

November 2, 2019

1 Synchrotron Radiation

Question 1.1 Describe the operation and emission characteristics from an undulator and a wiggler. Make comparisons of the spectrum. Draw images of the devices and indicate electron trajectories and emission angles.

Answer 1.1 Both undulator and wiggler belong to insertion devices, of which the use defines the third-generation synchrotron . They are operated by forcing the electrons to execute an oscillatory path in the plane of the storage ring, employing a set of dipoles that produce magnetic fields that point alternately up and down. The difference between undulators and wigglers is the size of angular excursions from a straight path that they force electrons to execute.

For undulators, the magnetic field is not strong and has a short space period length. The emission angle of the beam is quite small, so the light cones emitted by electrons overlap adequately. Only the light which can satisfy some special conditions can produce optical interference. Generally speaking, there are enough sapce periods of magnetic fields to make sure the effect that spectral flux is concentrated in evenly separated, narrow bands of radiation.

For wigglers, the magnetic fields is quite strong, which make the emission angle is large. The light cone emitted by electrons won't produce the light interference. The spectral line is continuous and smooth. Because of the strong magnetic fields, the characteristic photon energy is high and the flux is directly proportional to the numbers of effective dipoles.
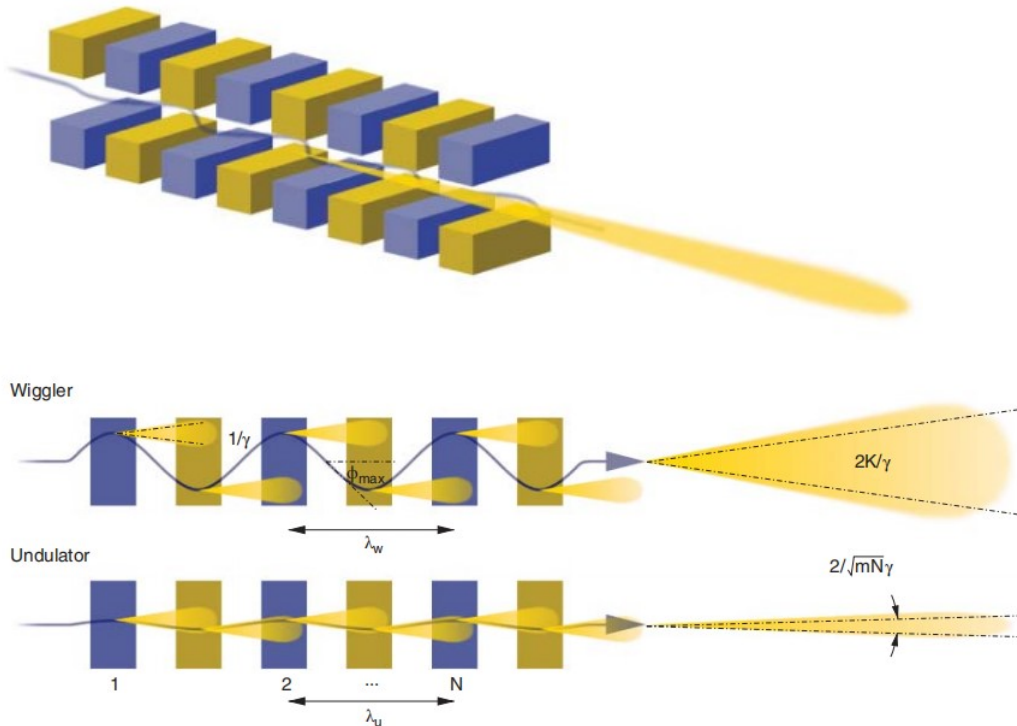
2 Neutron Source

Question 2.1 What is the advantages and disadvantages with a Neutron Reactor and a Neutron Spallation Source respectively.

Answer 2.1 Generally speaking, a neutron reactor source is continuous, while a neutron spallation source is usually a pulsed source. For a neutron reactor source, advantages:

1. Optimized for average flux;
2. Good enough for most applications;
3. Fission neutrons easier to shield;
4. easy to build compact and simple instruments.

disadvantage:

1. Tried and tested.

For a neutron spallation source, advantages:

1. Optimized for peak flux and pulase shaping;
2. Better for most applications;
3. Fast electronics and huge data sets.
4. Instruments are advanced.

disadvantages:

1. Cascade neutrons hard ti shield;
2. Instruments are long and expensive;
3. Still developing.

Question 2.2 Indicate flux profiles for both sources.

Answer 2.2 Steady state nuclear reactor generates neutron flux, which is constant in time. A neutron spallation source have a periodic structure of neutron pulses.

3 Photo Electron Spectroscopy

Question 3.1 Explain the photoemission process.

Answer 3.1 Photoemission in solid is a complicated process. There are many models to explain the process. The following is about two of the models: one-step model and three-step model.

One-step model From the perspective of quantum mechanics, photoemission is a quite complicated process and can be regarded as a one-step quantum-mechanical event. It is a whole and intercorrelative process that electrons in solid are emitted from the occupied state to the detector. In this situation, we need to deal the photoemission process as a coherence process of the whole system.

Three-step model In three-step model, photoemission can be regarded as three processes in turn. Firstly, the electron is excited from the initial state to the final state. Then, the excited electron will be transferred to the surface of solid. In this process, inelastic scattering of electrons may occur. Finally, the excited electrons that has enough energy are emitted to vacuum through potential barrier at surface.

Question 3.2 Discuss the implications of cross sections and the limited mean free path of photo-electrons. Especially for quantification.

Answer 3.2 Photoionization cross section implicates the probility that an electron is excited by a photon and ionizes.

"Photoelectric cross sections decrease dramatically as photon energy, or equivalenty kinetic energy E_{kin} is increased, varying in a high-energy asymptotic limit roughly as $\sigma_{Qnlj}(E_{kin}) \propto (E_{kin})^{-7/2} = (E_{kin})^{-3.5}$ for s subshells and $\propto (E_{kin})^{-9/2} = (E_{kin})^{-4.5}$ for p, d , and f subshells."

The limited mean free path of photoelectrons implicates the distance an electron travels between collisions.

Question 3.3 Describe why you sometimes need synchrotron radiation.

Answer 3.3 Synchrotron radiation has many advantages that other technique can not achieve:

1. Spectrum: Spectrum of synchrotron radiation has a wide wavelength coverage from infrared radiation to hard x-rays. The spectrum is both continuous and smooth. Using monochromator, we can select light with specific wavelength and bandwidth.

2. Collimation: The power of synchrotron radiation is mainly concentrated near the tangent of the electron bending orbit. The synchrotron radiation emitted by a single electron at a point in the orbit is like a narrow cone of light extending in this direction. For monochromatic light, the higher the photon energy is, the smaller the emission angle is.

3. High radiation power

4. High brilliance: It causes the higher brilliance than normal light source with the combination of collimation that the synchrotron radiation system uses magnet to constrain the cross section and divergence angle of the beam.

5. Polarization: For monochromatic light, the polarization is related to the photon energy and the porportion of the parallel component of synchrotron radiation vector. The polarization is crucial to the experiment of anisotropic samples.

6. Temporal structure: Suitable for the study of some dynamic processes.

7. High vacuum: It is quite important to ultraviolet rays which is easy to be absorbed by air.

8. Calculability: Don't need to take consideration of some factors that are difficult to measure, such as medium density fluctuation, temperature distribution and so on.

Question 3.4 Describe chemical shifts and how you may use core levels to obtain chemical information.

Answer 3.4 The binding energy of a atom is not constant. It may change because of the change of the chemical environment around the atom, i.e. change of the distribution of valance electrons. The electrons on core levels are repelled by valence electrons, while attracted by the nucleus. Therefore, different distributions will make core electrons feel different potentials. Then, the spectrum positions of some core levels differ from those of elementary substance or other componds. The shift can be from a few tenths of eV to more than 10eV. The change of core levels' binding energy resulting from chemical environment is defined as chemical shift.

Using core levels, there are many ways to obtain chemical information. First of all, we can obtain the elemental compsition. Futhermore, Koopmans's theorem make it possible for us to calculate binding energy and chemical shifts. More accurately, we need to take consideration of electron relaxation, relativisic effects of electrons and electronic correlation. What's more, we can also obtain the chemical information about the shaking up/down of electrons, plasmon, compoment, etc.

Question 3.5 What are the drawbacks and benefits with HAXPES.

Answer 3.5 Benefits:

1. The probing depth is controlled by the inelastic mean free path (IMFP), which also means electron escape depth." The conclusions from this and other recent experimental work are that the only reliable way to increase bulk or buried layer and interface sensitivity for all material types is to go to higher photon energies in the soft X-ray (ca. 0.5–2 keV) or hard X-ray (ca. 2–10 keV) regime. Going to very low photon energies with laser excitation is also often discussed as a method for enhancing bulk sensitivity, but it seems clear that this will not be a universal benefit for all materials, and may only be true for those with a significant bandgap."

2. Sometimes, spectral analysis is simpler at high photon energies. For example, " the inelastic backgrounds under spectra are significantly reduced, thus making the allowance for them in

fitting to derive various peak intensities easier".

3. More bulk sensitive. Avoid the interference of surface factor effectively.

4. There is no high requirement as SXPES or VUVPES.

5. By changing the geometry configuration between incident light and sample surface and changing the escape depth of emitted electrons, we can study the interfacial effects between surface components and substrates.

Drawbacks:

1. It is a clear challenge that photoelectric cross sections decrease dramatically as photon energy, or equivalenty kinetic energy E_{kin} is increased. It means that a better electron energy analyzer is needed.

2. For many researches, surface sencitivity is quite necessary.

Question 3.6 Describe how ARPES is being performed and how band structure information can be extracted. What is the free electron final state approximation? When is it valid?

Answer 3.6 The performance of ARPES can be seen in the following figure.
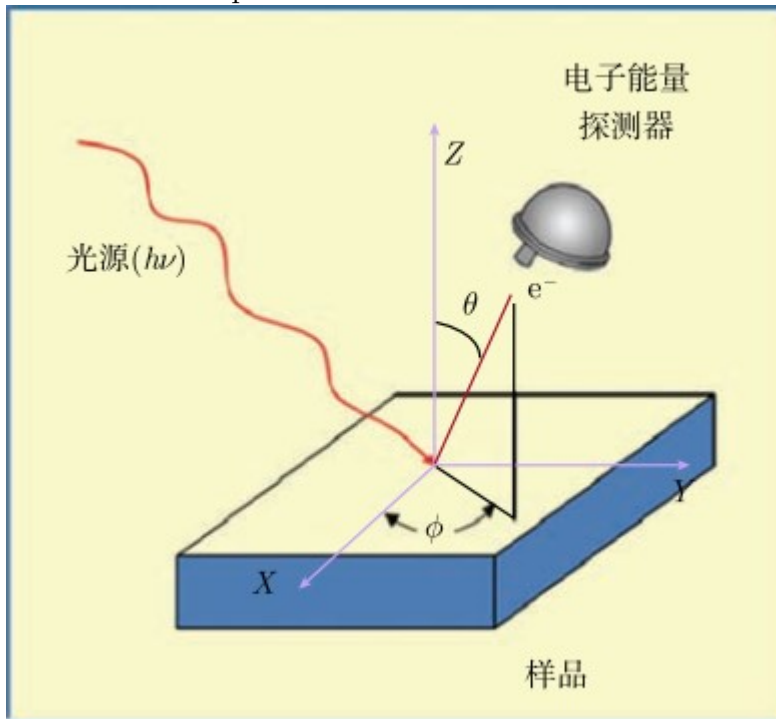
Band structure is the relation between energy and wave vector. Dispersion relation is about ω and wave vector. So, band structure information can be extracted, if we obtain the information about dispersion relation. Generally speaking, there are two experimental ways to extract dispersion relation from the original data: energy distribution curve fitting and momentum distribution curve fitting. There are also other ways, such as a full two-dimensional analysis.

The momentum of photoelectron is not conservative in the direction of perpendicular to the surface of the sample, so it is a little complicated to determine the wave vector in the vertical direction. The free electron final state approximation is one of ways to determine that. In the situation of free electron final state approximation, $\hbar(k + G) = \sqrt{2m\left(E_{\text{kin}} + V_0\right)}$, where V_0 represents inner potential. The inner potential can be obtained by comparing the band structure calculated from theory to that measured by experiment, or measuring the inherent symmetry in the band, etc. With the determined inner potential, the wave vector in the vertical direction can be obtained.

In a system with anisotropic electron structure, usually unascertainable dispersion in the z direction can be ignored in general.

Question 3.7 Describe ambient pressure XPS and complications with the technique.

Answer 3.7   Generally speaking, ambient-pressure XPS is XPS at ambient pressure.

An exception to the rule of thumb that XPS at synchrotrons is not in general used for high-resolution chemical analysis is the case of high-pressure XPS or ambient-pressure XPS. Although photoemission is a highly powerful tool for investigating clean surfaces under ultra-high-vacuum conditions, many interesting processes occur on surfaces under reaction conditions, which can be at several orders of magnitude higher pressure than those typically used for traditional XPS experiments.Such systems are excluded from investigation using standard PES spectrometers, and have been the spur to develop the ambient-pressure XPS technique.

There are two basic problems that need to be overcome in XPS experiments under non-vacuum conditions. The fundamental problem is the scattering of photoelectrons by gas molecules, which limits the distance that electrons can travel through the gas atmosphere. The other issue is of technical nature and concerns discharging through the gas where high voltage differences are present, as in the electrostatic lens system or the electron detectors.

4   Reference

Actually, the homework may be a little difficult, so a lot of books are cited. To be honest, I did not read many of those in detail.

[1]P. Willmott, An Introduction to Synchrotron Radiation: Techniques and Applications, Second edition (John Wiley & Sons, Inc, Hoboken, New Jersey, 2019)

[2]J. C. Woicik, editor , Hard X-Ray Photoelectron Spectroscopy (HAXPES) (Springer, Cham Heidelberg New York Dordrecht London, 2016)

[3]Operando Studies in Heterogeneous Catalysis (Springer Berlin Heidelberg, New York, NY, 2016)

[4]麦振洪等著, 同步辐射光源及其应用, 下册[M] (北京：科学出版社, 2013)

[5]麦振洪等著, 同步辐射光源及其应用, 上册[M] (北京：科学出版社, 2013)

[6]徐彭寿，潘国强编, 同步辐射应用基础 (合肥：中国科学技术大学出版社, 2009)

[7]姜传海，杨传铮编著, 中子衍射技术及其应用[M] (北京：科学出版社, 2012)