X-ray Characterization of Nanomaterials

Michael Bedzyk (Northwestern University)

3 hour Tutorial for
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Northwestern University
Horacio Espinosa (Organizer)

Micro and Nano Devices with Applications to Biology and Nanoelectronics

Acknowledgements:

Some figures borrowed from

[ANM]: J. Als-Nielson & D. McMorrow, Elements of Modern X-ray Physics, Wiley (2001)

[EI]: Eric Isaacs (ANL/CNM), Class Notes for Diffraction Course

[LL]: S.G. Lipson & H. Lipson, Optical Physics, 2nd Ed. Cambridge Univ. Press (1981)

[BW]: M. Born & E. Wolf, Principles of Optic 6th Ed. Pergamon Press (1980).

Outline:

I. Fundamental principles for the interaction of x-rays with matter

II. X-ray Sources X-ray Tubes & Synchrotrons

III. X-ray Optics monochromators & mirrors

IV. X-ray Scattering fudamentals

V. Key Examples to illustrate x-ray characterization of nanomaterials

- Self-Assembled Monolayer / Si(111)
- Nanocomposite film self-assembly
- nano- and micro- crystal growth
- Biomolecular adsorption to charged surface

VI. X-ray **scattering techniques and application** to nanomaterials

- X-ray relectivity (XRR) ⇒ e- density profile of thin-film / interface structure
- Grazing-incidence x-ray scattering (GIXS) to study molecular self-assembly on surfaces
- Crystal-Truncation-Rod (CTR) technique applied to coherent epitaxial film grown on single crystal substrate.

VII. X-ray **spectroscopy** techniques and **application** to nanomaterials

- X-ray fluorescence (XRF) ⇒ elemental composition (RBS caibrated)
- X-ray photoelectron spectroscopy (XPS) (chemical state)
- X-ray absorption fine-structure spectroscopy (XAFS) ⇒ local atomic bonding geometry
- X-ray absorption near-edge spectroscopy (XANES) ⇒(chemical state)

VIII. Combined X-ray scattering + spectroscopy techniques and applications to nanomaterials

- X-ray resonance scattering = X-ray scattering + XANES
- X-ray standing wave (XSW) technique = X-ray scattering + (XRF or XPS)

Wilhelm Conrad Röntgen 1845-1923

EINE NEUE ART

VON

STRAHLEN.

VON

DR. W. RÖNTGEN,

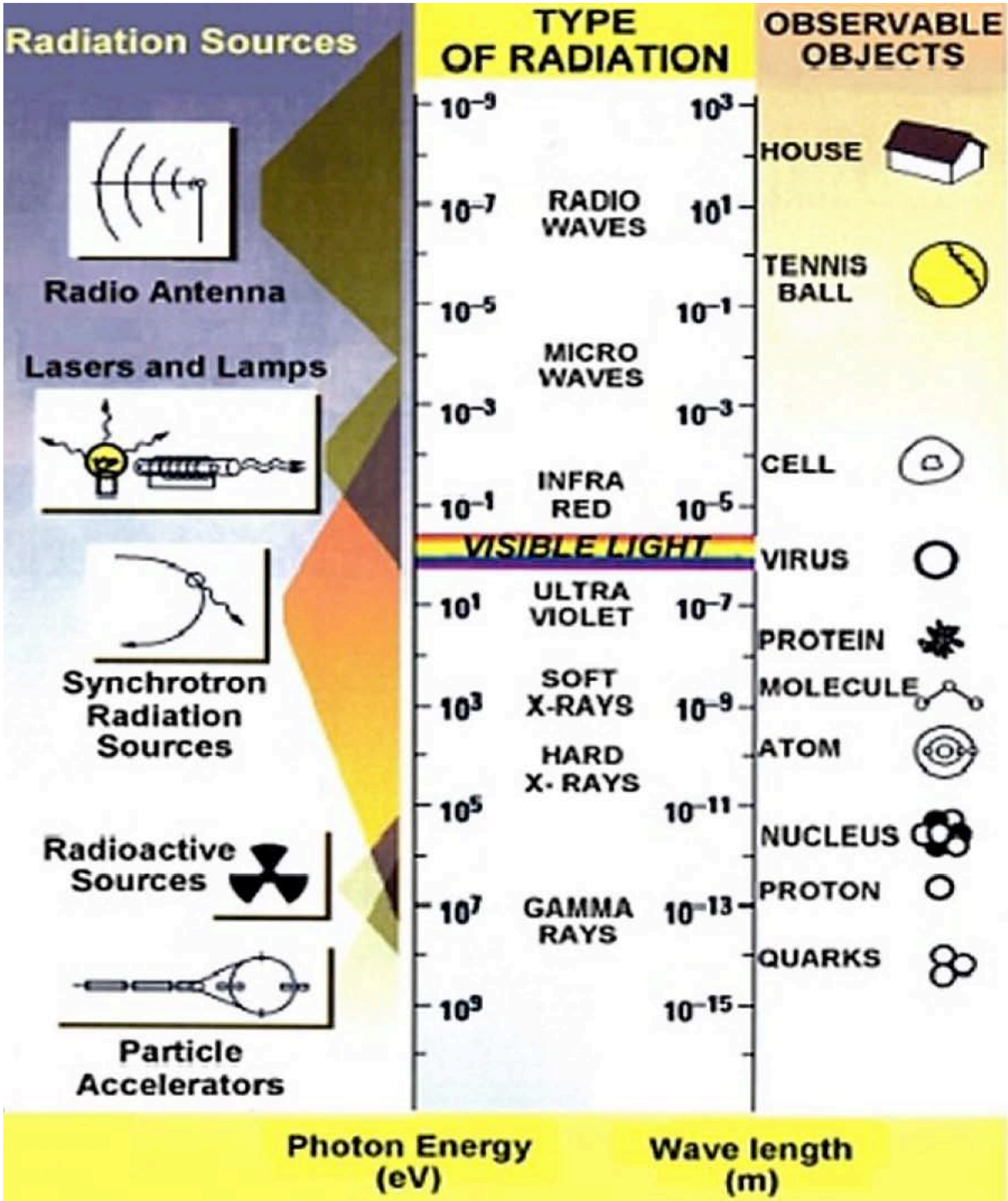
Ö. O. PROFESSOR AN DER K. UNIVERSITÄT WÜRZBURG.

WÜRZBURG.

VERLAG UND DRUCK DER STAHEL'SCHEN K. HOF- UND UNIVERSITÄTS-
BUCH- UND KUNSTHANDLUNG.
Ende 1895.

60 ₰.

1895: Discovery of X-Rays



Wavelength

≈

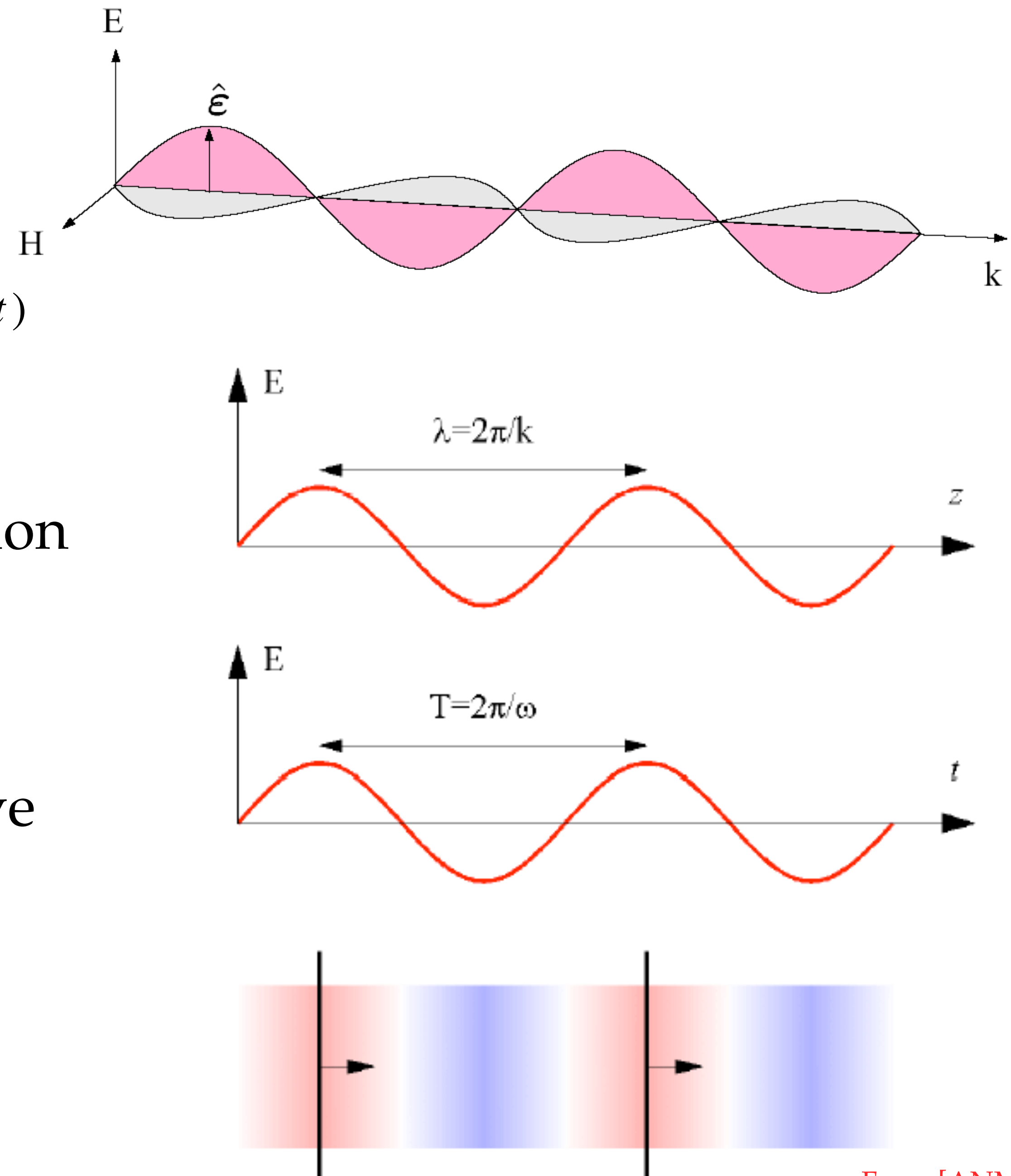
Object Size

≈

Angstroms for Condensed Matter Research

$$\lambda[\text{Å}] = \frac{12.398}{E_{\mathrm{ph}}[\mathrm{keV}]}$$

X-rays are Electro-Magnetic traveling waves



From [ANM]

$$\overline{E}(\overline{r},t) = \hat{\varepsilon}E_0\, e^{i(\overline{k}\bullet\overline{r}-\omega t)}$$

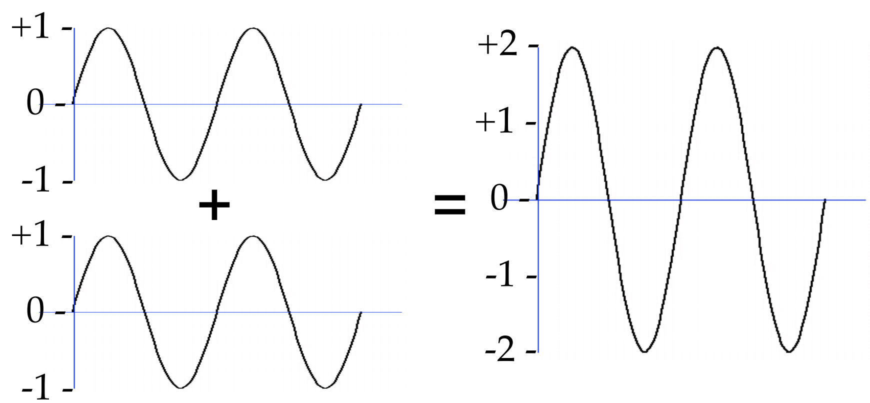
k: wavevector
direction of propagation

ε: Polarization direction

k•ε = 0 : transverse wave

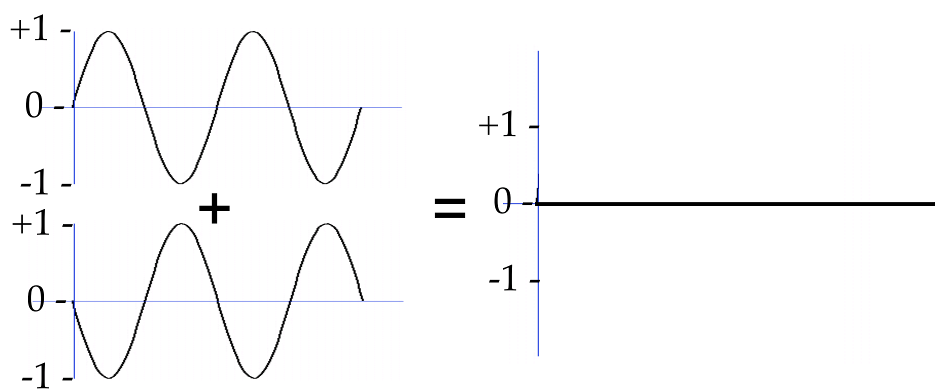
Interference of Waves:
The superposition of 2 or more coherent (same wavelength) waves.

2 waves in-phase ⇒ constructive interference:



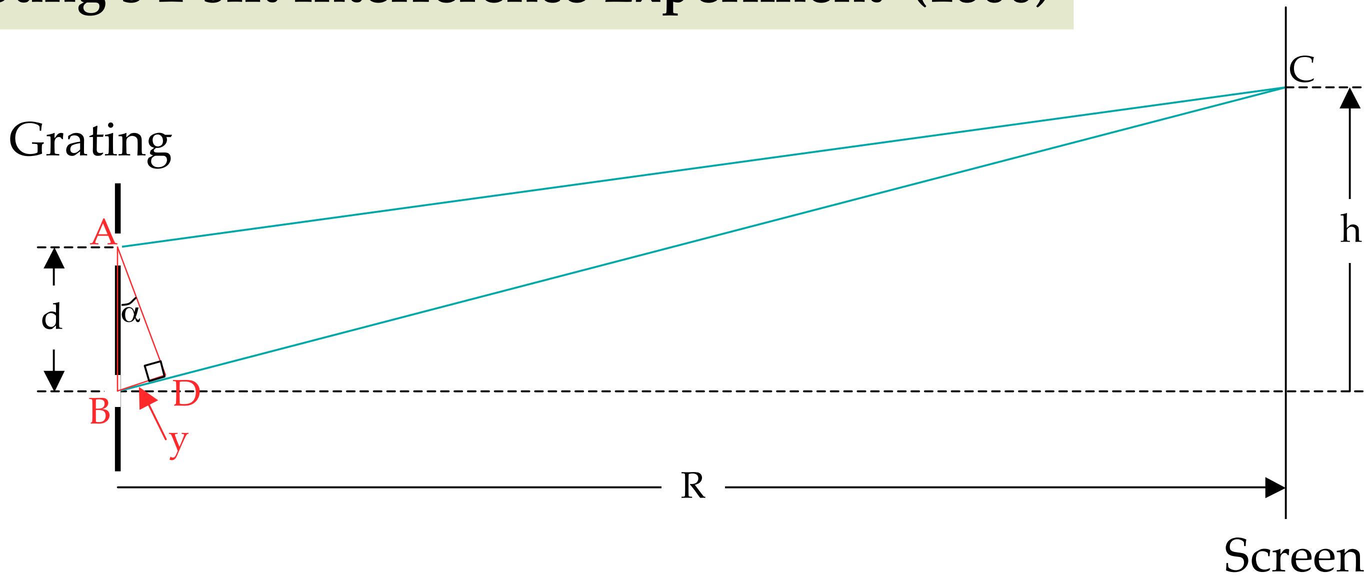
An electron driven by 2 in-phase oscillating E-fields will be subject to twice the force.

2 waves out-of-phase ⇒ destructive interference:



An electron driven by 2 180°out-of-phase oscillating E-fields will be subject to zero force.

Young's 2-slit Interference Experiment (1800)



A plane light wave of wavelength λ traveling to the right with in-phase wave-fronts parallel to the grating produces two coherent circular waves emanating from slits *A* and *B*.

The 2 waves will add-up in-phase at point *C* on the screen,
if the path-length difference $y = BD$ is an integer multiple of the wavelength λ.

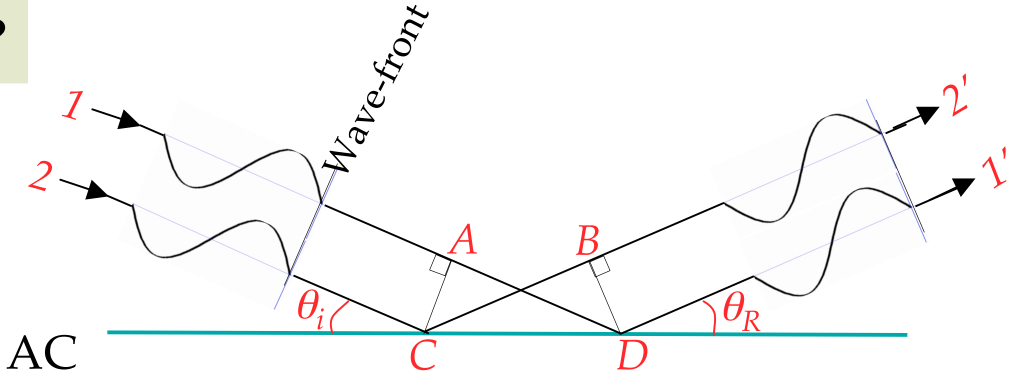
$$y = d\,sin\alpha = n\lambda \implies \text{interference maxima at } h$$

To produce inference fringe pattern: $d \sim \lambda$.

If $d < \lambda$, $sin\alpha = n\lambda/d > 1$, not possible, since $sin\alpha < 1$

If $d >> \lambda$, $sin\alpha = \lambda/d$ *too small to separate n=1 max from direct beam.*

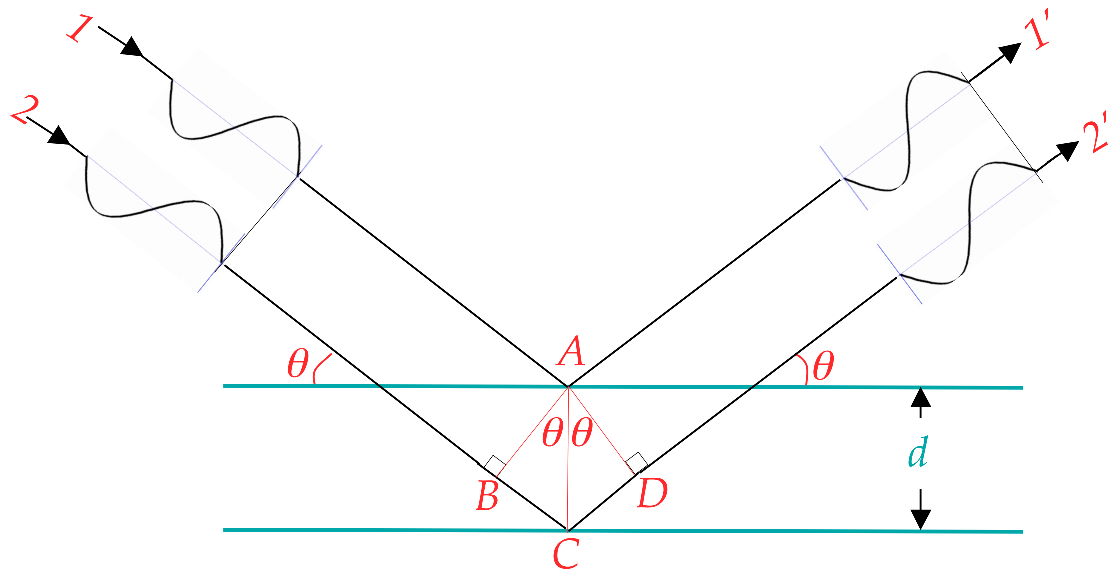
How does X-ray Diffraction work?



1st consider reflection from a plane of atoms.

Plane-Wave ⇒ Rays 1 & 2 in-phase at AC
Reflected rays 1′ & 2′ will be in-phase at BD if $\theta_R = \theta_i$.
Since path-lengths will be equal. i.e., $\theta_R = \theta_i \Rightarrow AD = CB$
Note: Atoms do not need to be evenly spaced within the plane.
This is the **<u>Law of Reflection</u>**.

2nd consider reflecting from a set of equally spaced atomic planes.



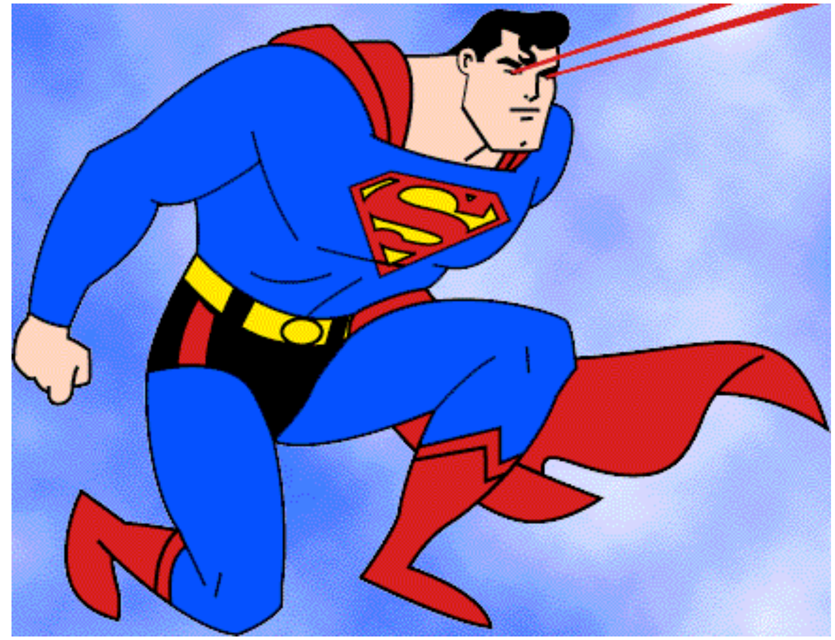
If path diff. $\delta = BCD = n\lambda$
⇒ scattered rays 1′ & 2′ in-phase

$BC = CD = d\,sin\theta$

Bragg's Law: $\boldsymbol{n\lambda = 2d\,sin\theta}$

This simple adhoc theory explains direction, but not intensity of diffracted beams.

X-ray Vision



Pros:

Weak interaction with matter

High penetrating power

→In situ analysis

→ Buried structures

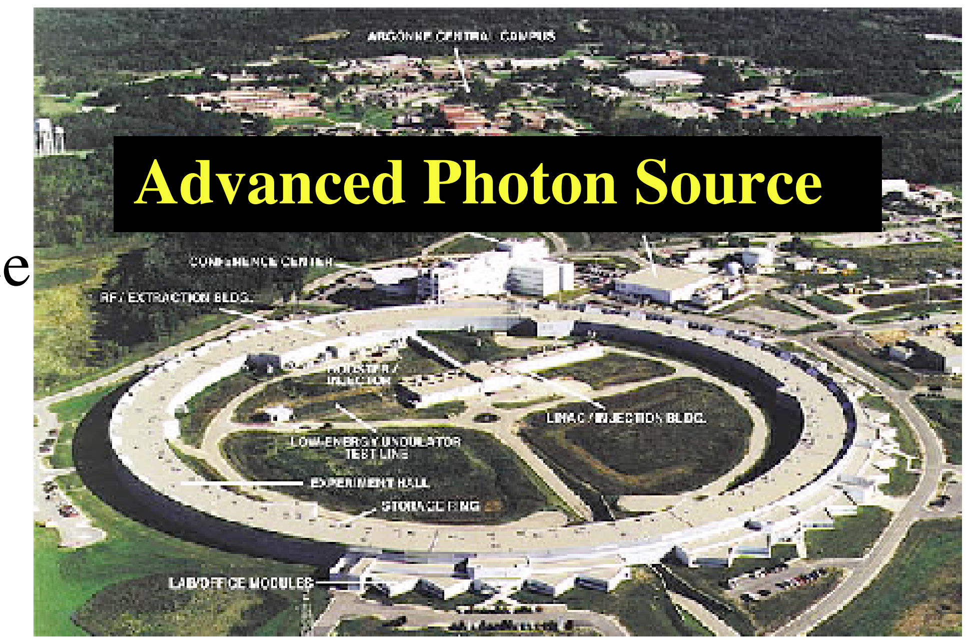
Atomic-scale resolution

Cons:

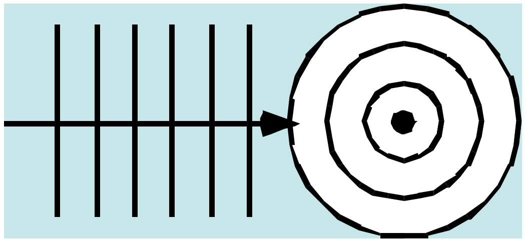
Weak interaction with matter

Need very intense X-ray source

→ Synchrotron X-ray Source



Some X-ray Basics:



Wave Property → Structural Info

λ = 0.1 to 10 Å wavelength

X-rays scatter coherently from electrons

From de Broglie:

$$\lambda \bullet p = h$$

For Photons:

E_γ[keV]= 12.4 / λ[Å]

Particle Property → Compositional Info

E_γ= 1 to 100 keV energy

<u>Photo effect:</u> Inner shell (K, L) ionization

X-ray Absorption Spectroscopy (XAS)

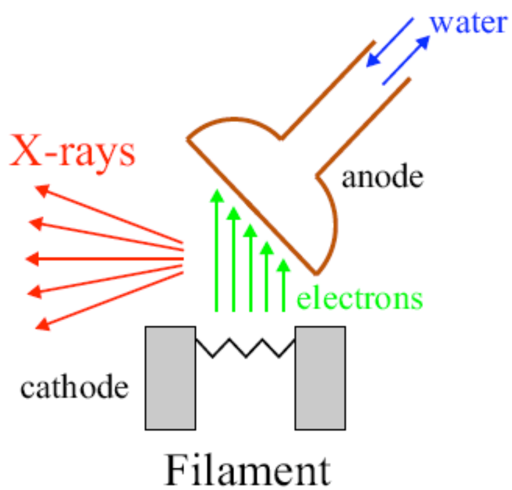
XRF Spectroscopy: Decay of excited ion to ground state

X-ray Sources:

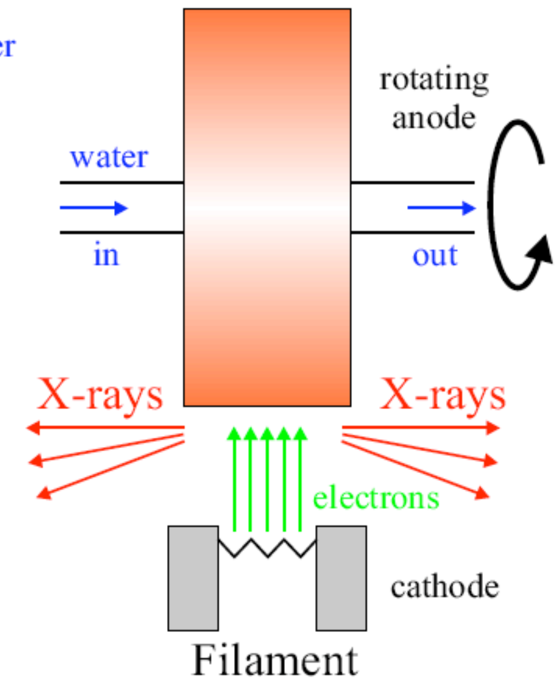
- X-ray Tube: e.g. Cu rotating anode
- Radioactive Source: e.g.: Fe^{55}
- Synchrotron: e.g. e- storage ring

Conventional X-ray Lab Source

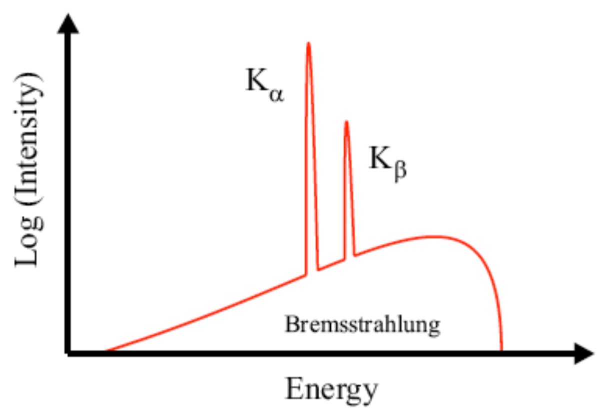
Coolidge Tube

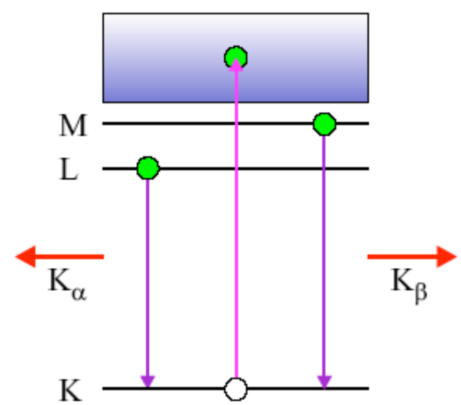


Rotating Anode



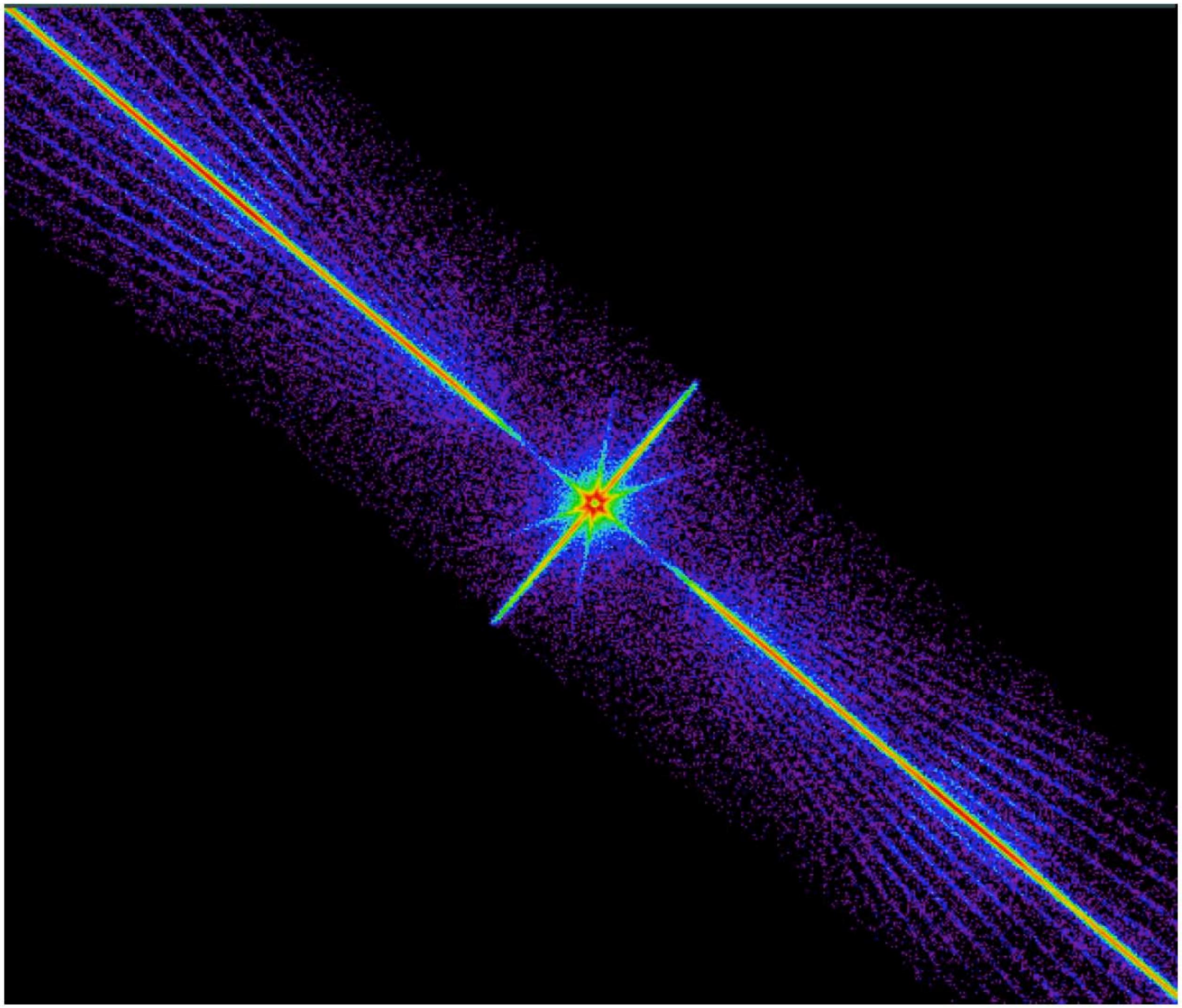
X-ray Spectrum





From [ANM]

Galactic Synchrotron Radiation Sources



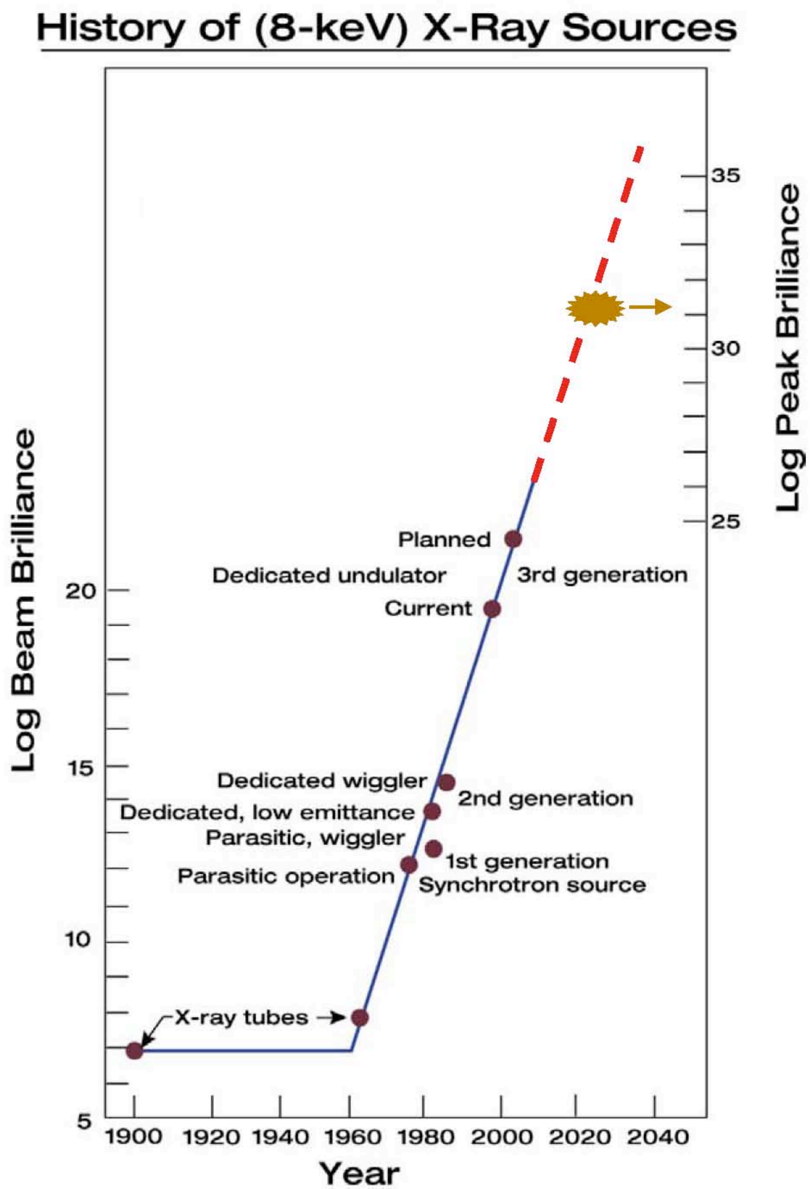
This Chandra X-ray Observatory image is a spectrum of a black hole, which is similar to the colorful spectrum of sunlight produced by a prism. These data reveal that a flaring black hole source has an accretion disk that stops much farther out than some theories predict. Scientists theorize that the accretion disk is truncated there as the material erupts into a hot bubble of gas before taking its final plunge into the black hole. This provides a better understanding of how energy is released when matter spirals into a black hole.

http://chandra.harvard.edu/photo/cycle1/xtej1118/index.html

The Evolution of Synchrotron Radiation Sources

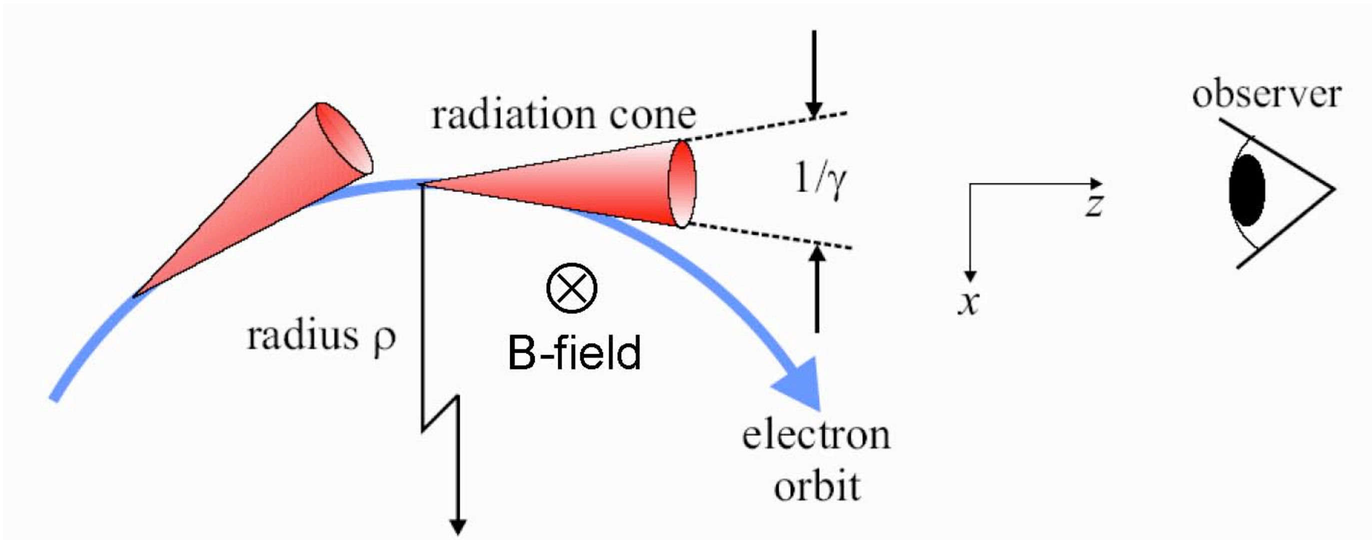
Synchrotron radiation (from VUV to X-ray and now even IR) has been used a research tool for nearly 50 years.

- 1st Generation Sources
  Ran parasitically on accelerations for high energy physics (CHESS)
- 2nd Generation Sources
  Built to optimize synchrotron radiation from the bending magnets (NSLS)
- 3rd Generation Sources
  Built to optimize synchrotron radiation from insertion devices (APS)
- 4th Generation Sources
  X-ray Free Electron Lasers (X-FELs)



From: [EI]

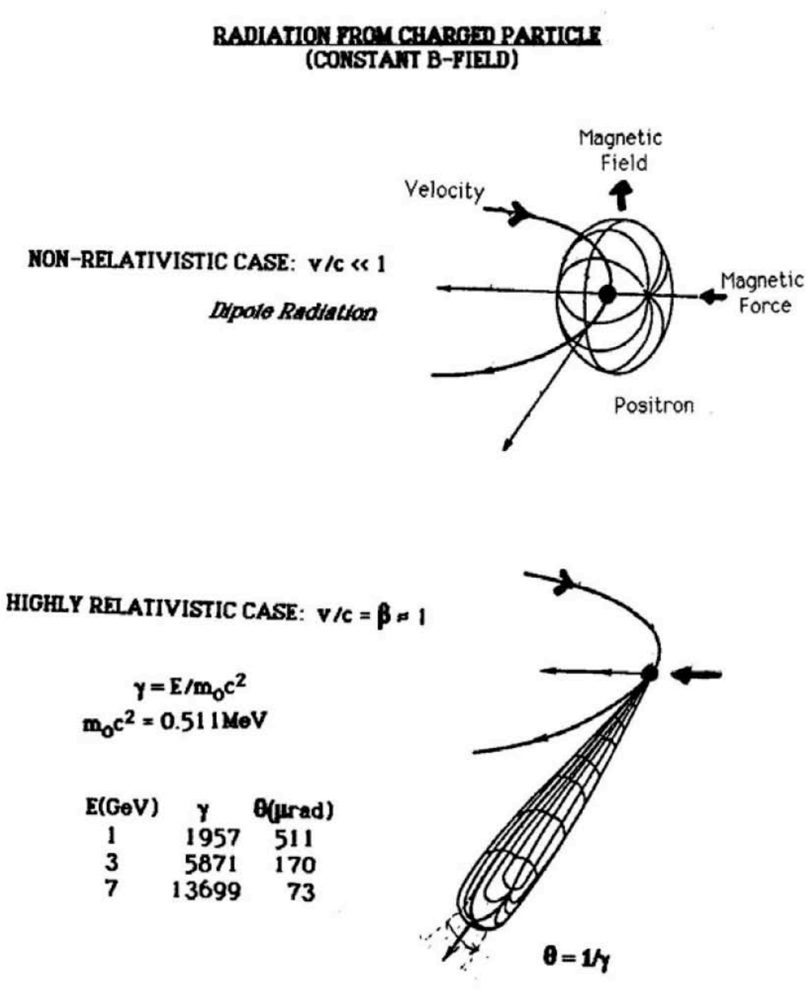
Synchrotron radiation



An electron is kept in a circular orbit with a magnetic field B. An observer in the direction of the tangent point will see the electron as having a large acceleration and hence synchrotron radiation confined to a narrow cone, $1/\gamma$.

From [ANM]

Radiation from Highly-Relativistic Particles



When v/c~1, the opening angle in both the horizontal and vertical directions, is given approximately by:

$$\theta = 1/\gamma,$$

where $$\gamma \equiv \frac{1}{\sqrt{1-\left(\frac{v}{c}\right)^2}}$$

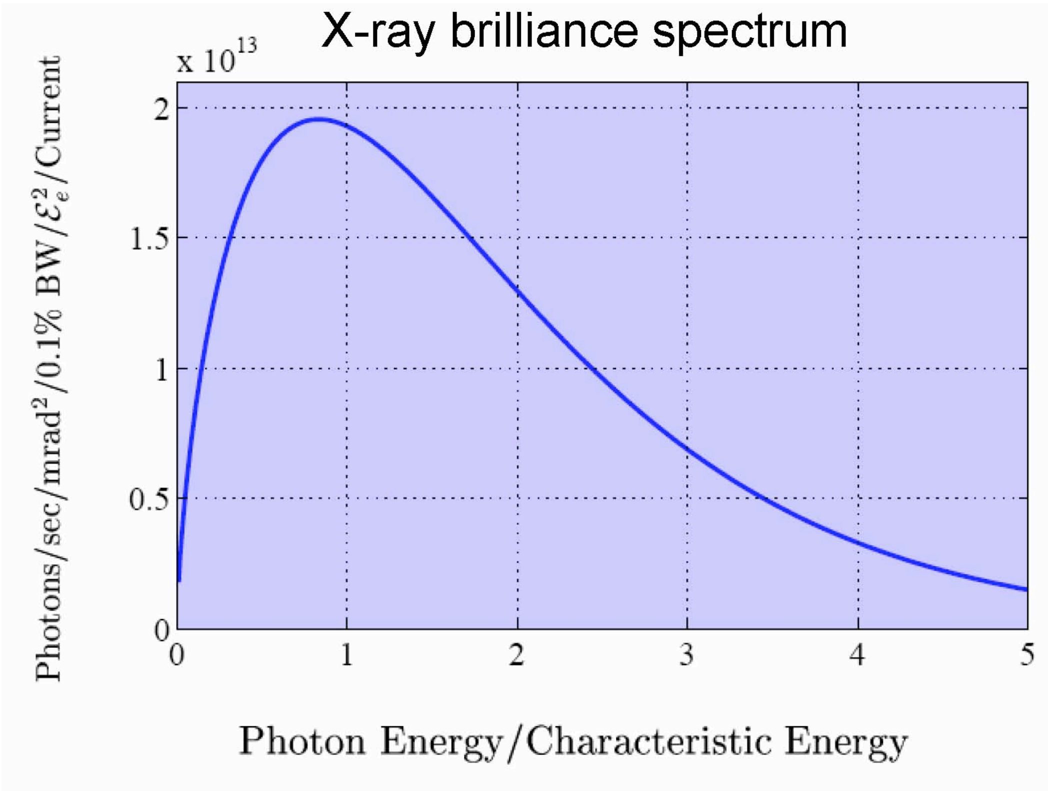
From: [EI]

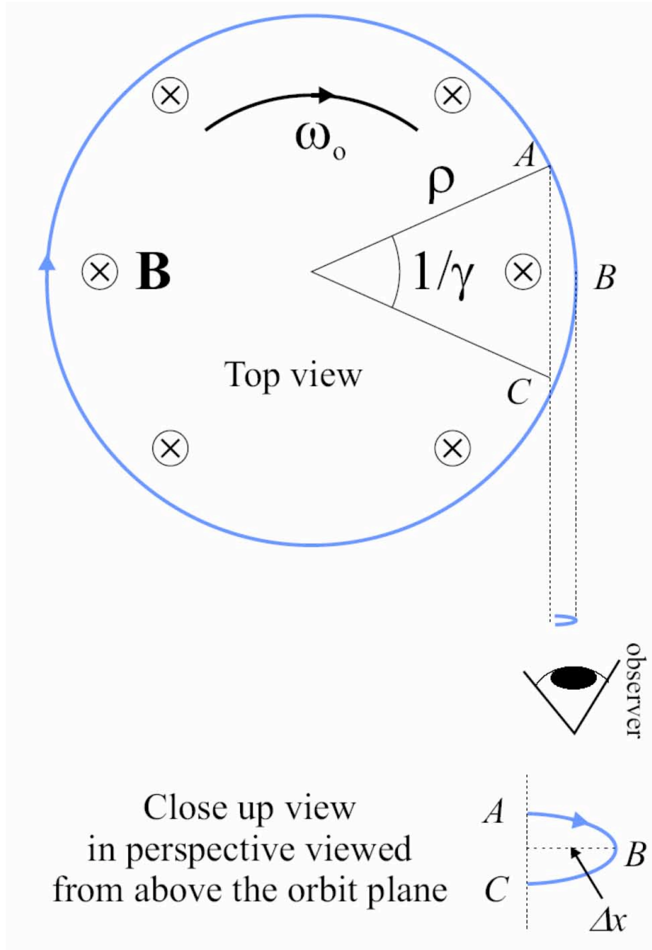
Synchrotron radiation formulae

$$\rho[m] = 3.3\frac{E_e(GeV)}{B[Tesla]} \quad \text{where} \quad E_e = \gamma mc^2$$

$$\hbar\omega_c[keV] = 0.665 E_e^2[GeV]B[Tesla]$$

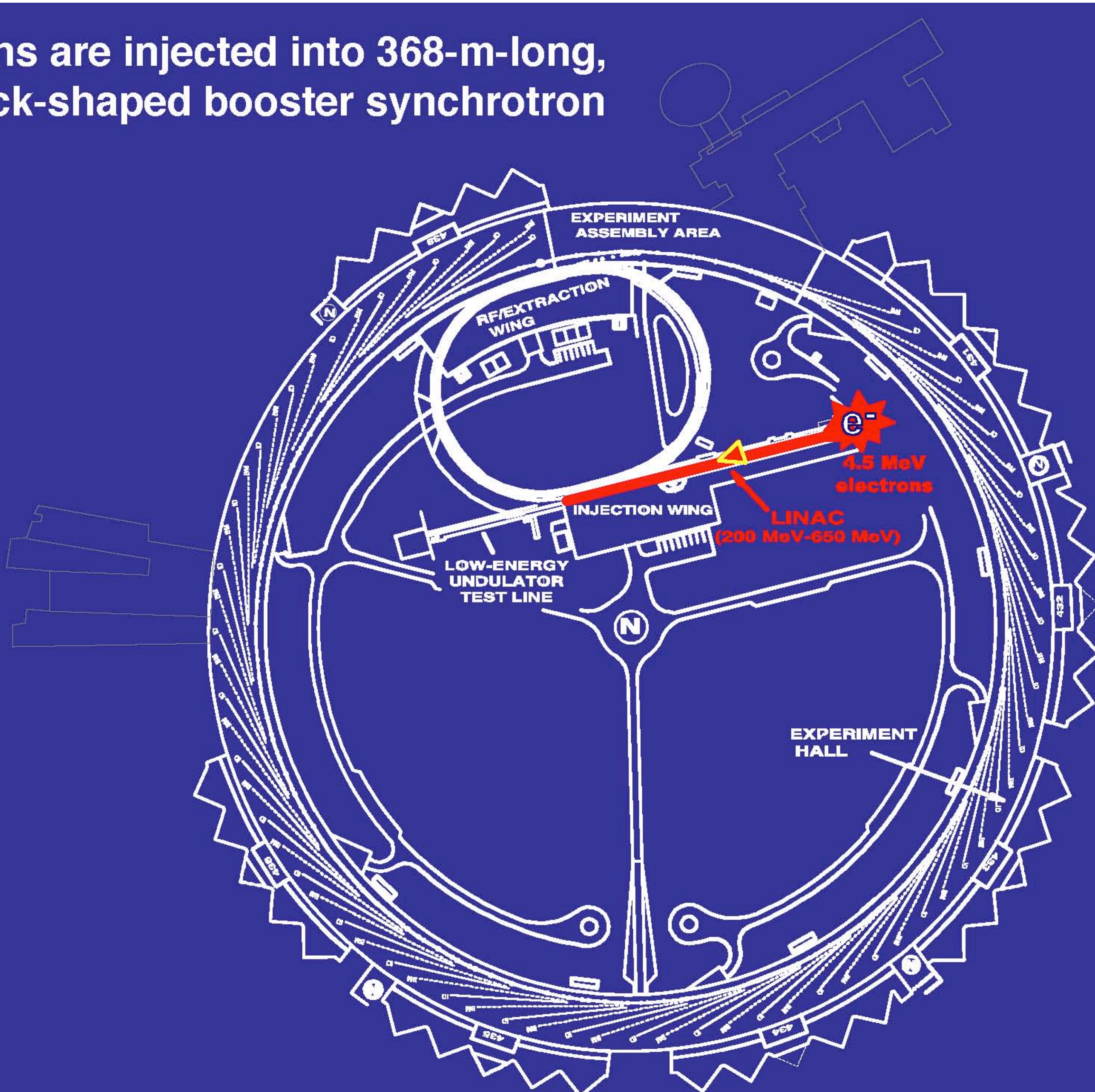
$$p[kW] = 1.266 E_e^2[GeV]B^2[Tesla]L[m]I[Amps]$$



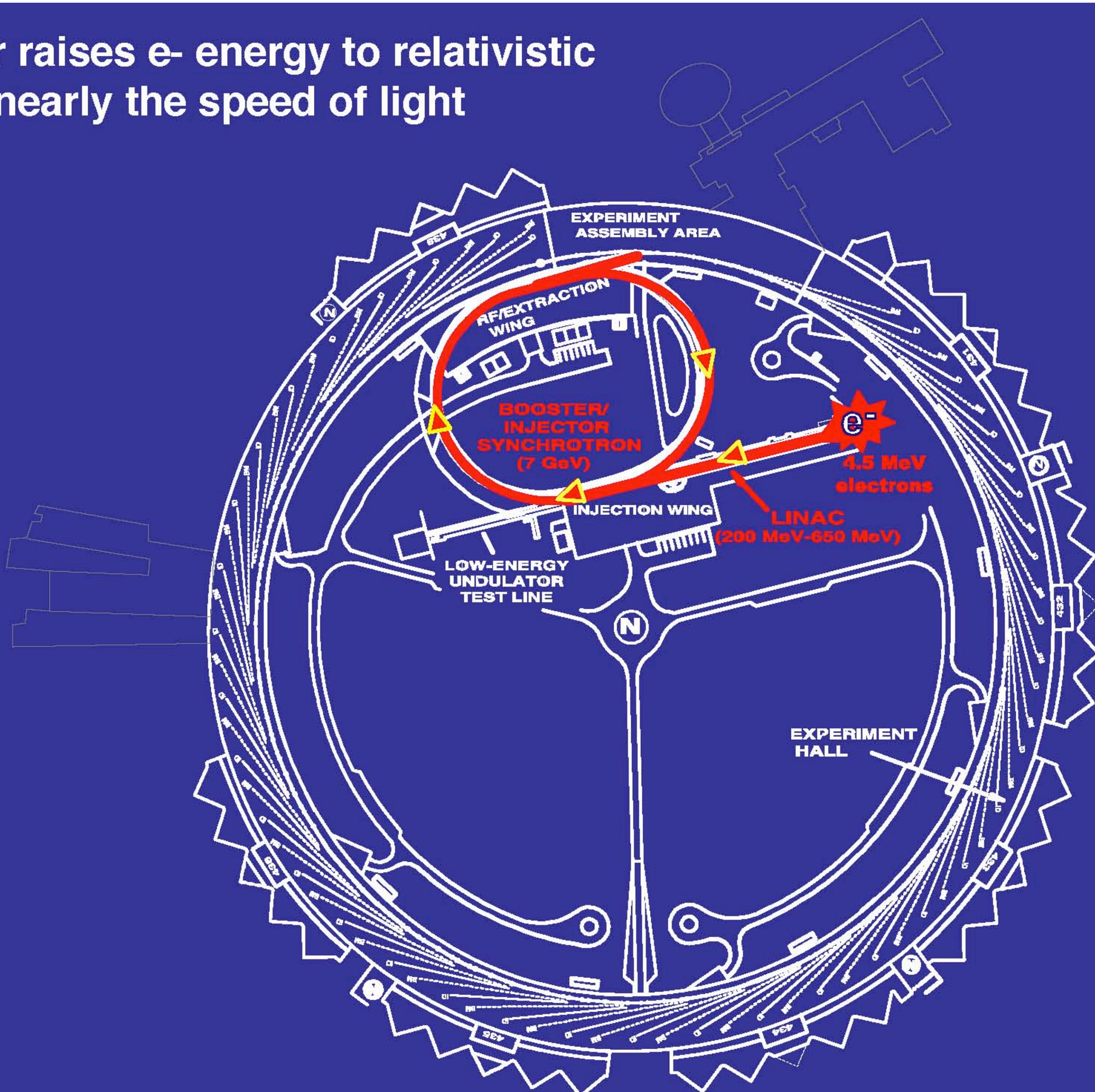


From [ANM]

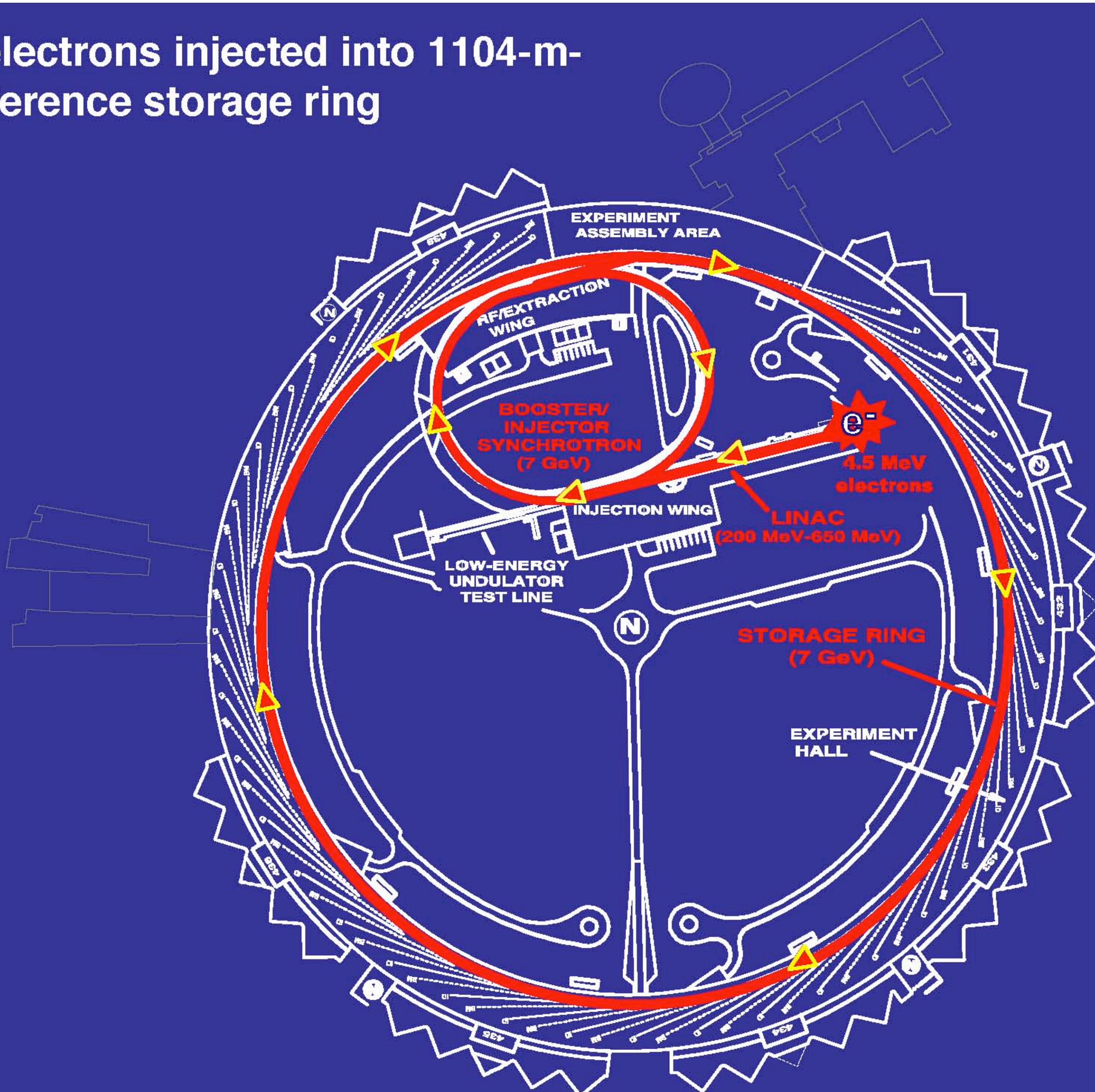
Electrons are injected into 368-m-long, racetrack-shaped booster synchrotron



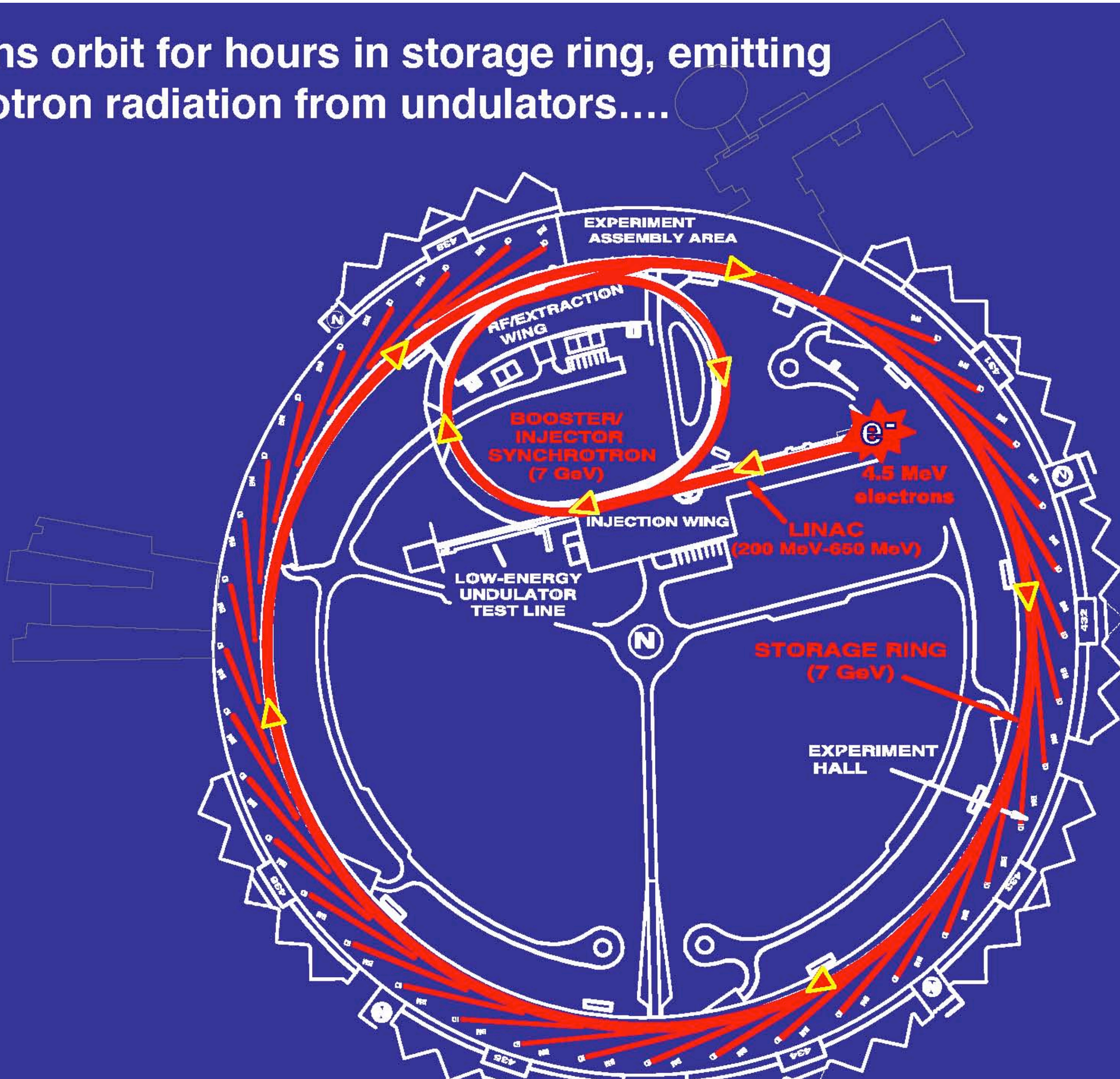
Booster raises e- energy to relativistic 7 GeV -nearly the speed of light



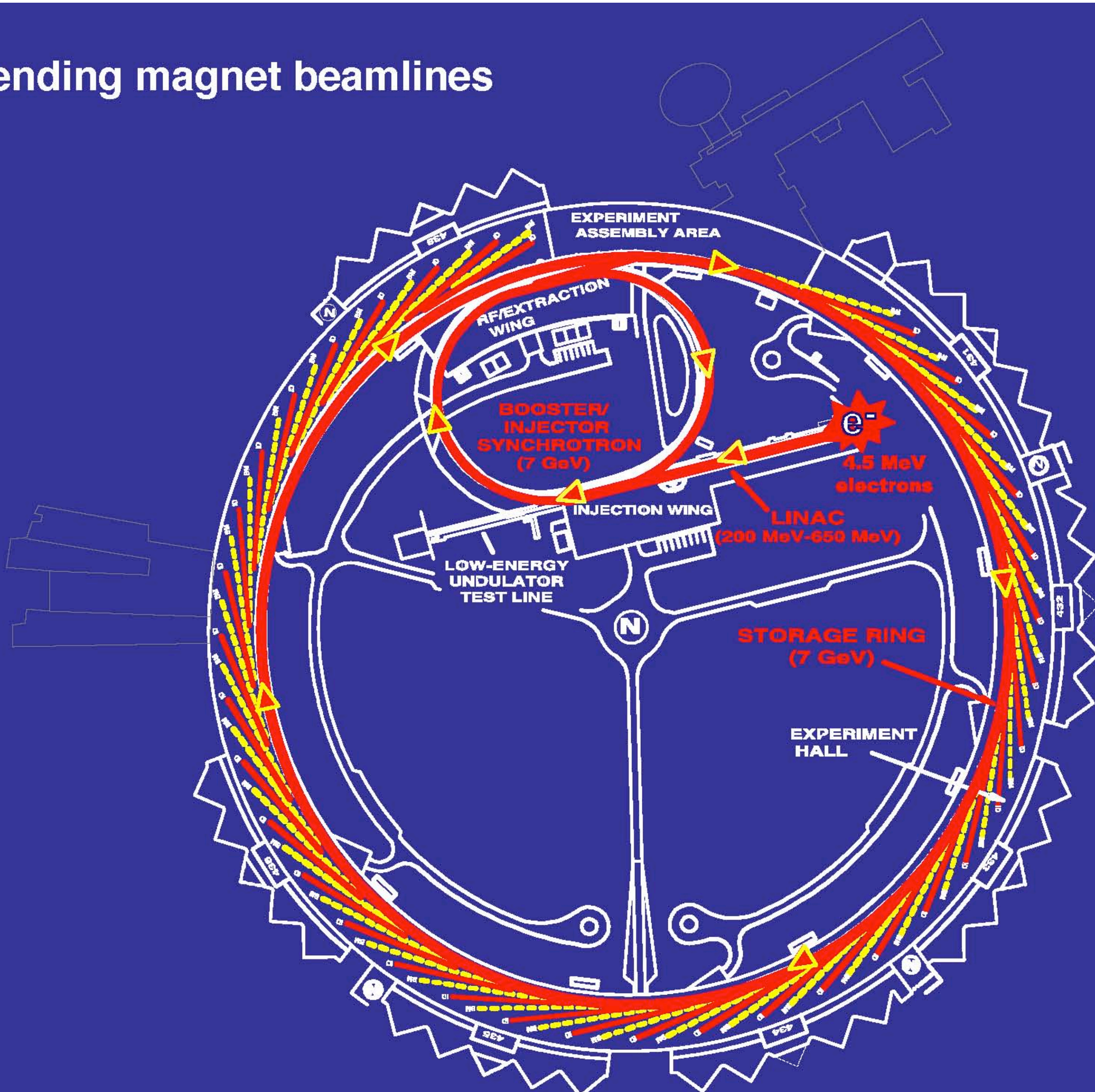
7 GeV electrons injected into 1104-m-circumference storage ring



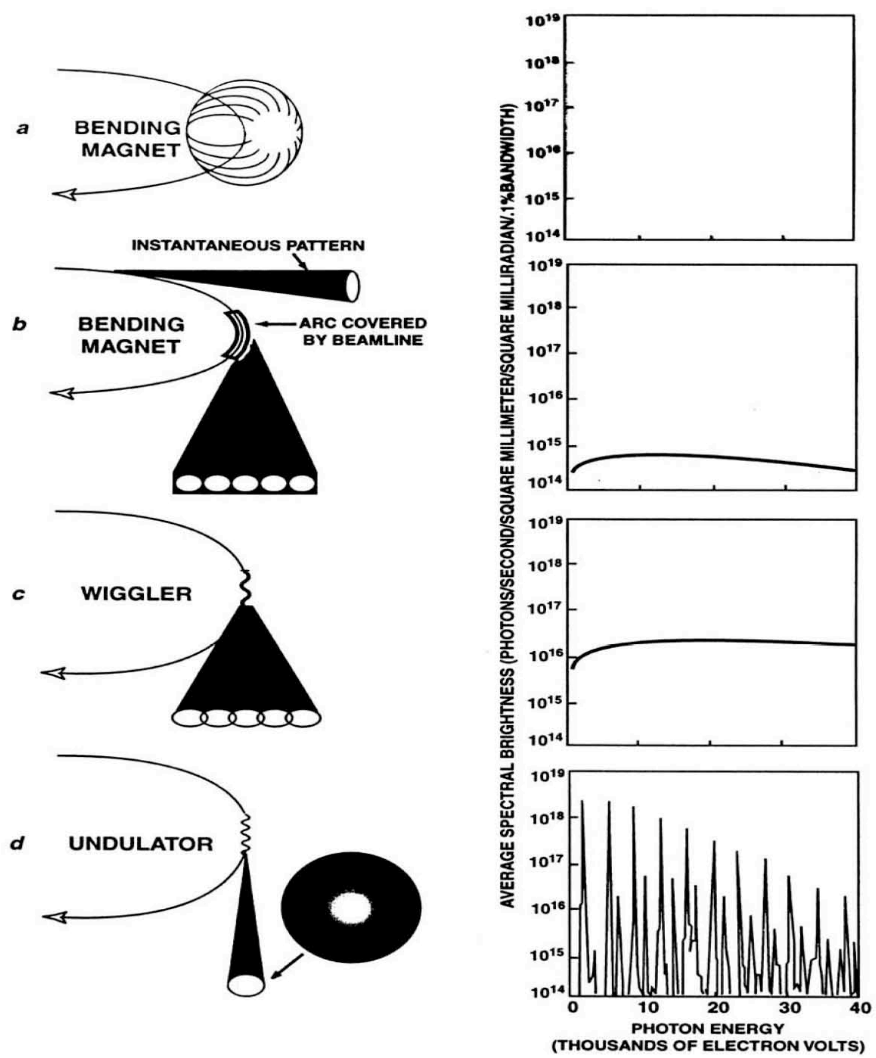
Electrons orbit for hours in storage ring, emitting synchrotron radiation from undulators….



… and bending magnet beamlines



Radiation Sources at 3rd Generation Facilities



There are two different sources of radiation at 3rd generation sources:

- bending magnets (BMs)

- insertion devices (IDs); periodic arrays of magnets inserted between the BMs (wigglers or undulators)

The important parameters to know about each one is:

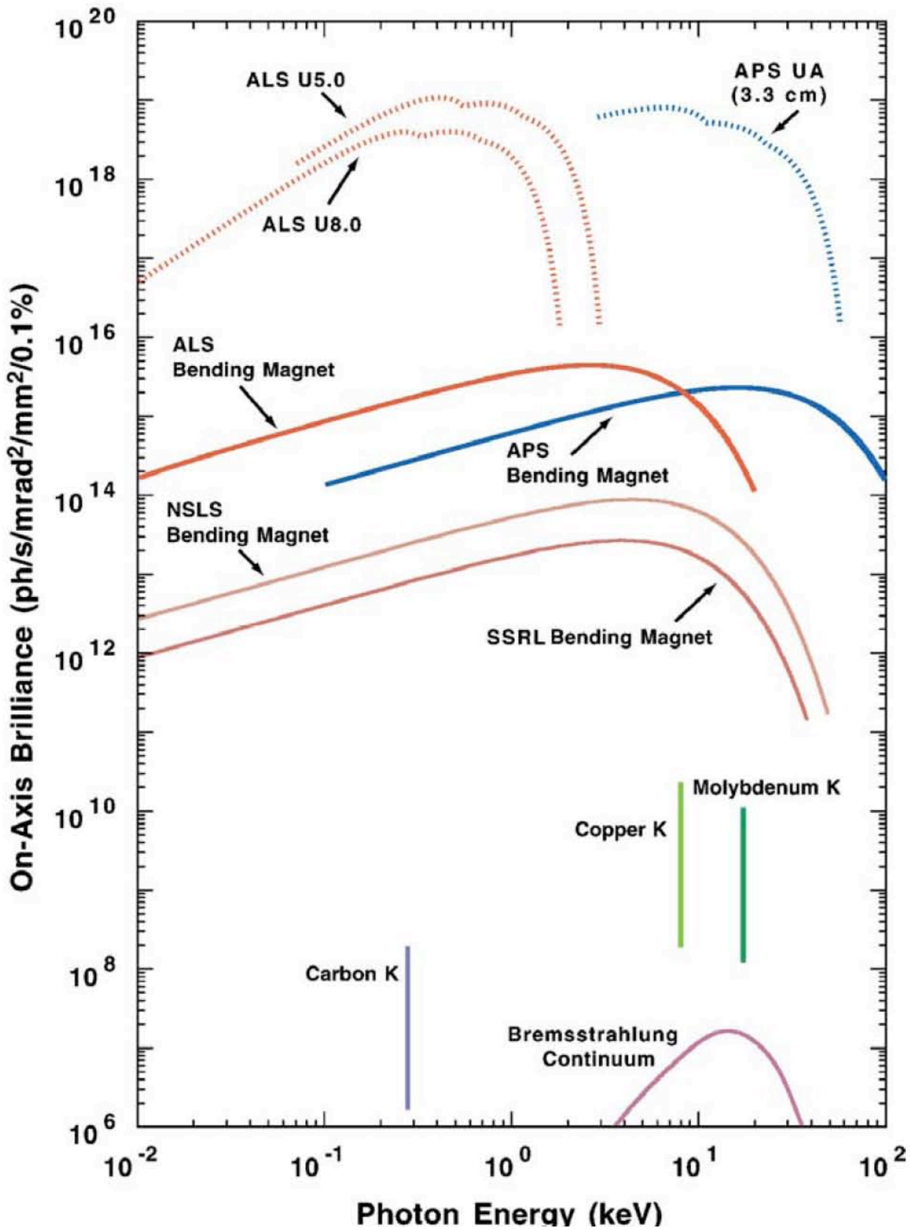
Spectral distribution
- energy range
- continuous/quasi-monochromatic

Flux (number of x-rays/sec - 0.1%bw)

Brightness (flux/source size-source div)

Polarization (highly linear or circular)

Brightness vs. Photon Energy for Various SR Facilities



X-ray Optics:

Energy Tunable Monochromators

Bragg Diffraction Optic

Si Single Crystal (Small Band-Pass) 0.01%

Si/W periodic multilayer (Wide BP) 1%

High-E Cut-off Filter →Mirror: e.g. Glass, Si, Rh, Pt

Low-E Cut-off Filter →Low-Z Vac. Windows (Be) and Foils:

X-ray Mirrors are based on Total External Reflection (TER)

Index of Refraction: n ~< 1 for x-ray frequencies

→ Snell's Law → TER w/ critical angle $\theta_C < 1°$

X-ray Focusing Optics:

Reflection from Curved Mirrors and Crystals

Refraction from Fresnel Zone Plates

X-ray Optics:

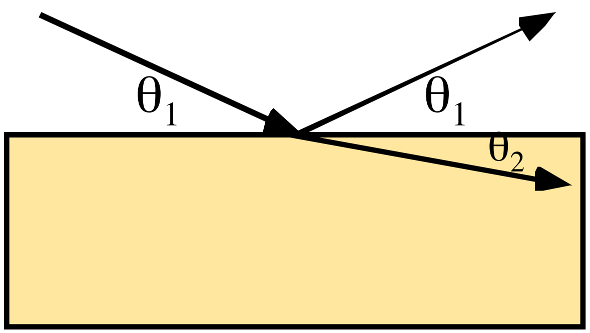
Total External Reflection of X-rays from a Mirror Surface

Index of refraction: $n < 1$ for x-ray frequencies

$n = 1 - \delta - i\beta$, $\quad \delta = N'_e r_e \lambda^2 / 2\pi \qquad \beta = \lambda\mu / 4\pi$

Snell's Law: $n_1 \cos\theta_1 = n_2 \cos\theta_2 \rightarrow$ TER when $\theta_2 \leq 0$

at $\theta_2 = 0$, $\theta_1 = \theta_C$ (critical angle)



$\theta_C = (2\delta)^{1/2}$, where $n = 1 - \delta$, $\delta \propto N_e$

Eg. Si at $\lambda = 1.54$ Å, $\delta = 7.4 \times 10^{-6}$,
$\theta_C = 3.9$ mrad $= 0.22°$

X-Ray Experimental Setup

Undulator beamline Advanced Photon Source, Argonne National Lab