X-ray Diffraction Crystallography

κρυσταλλος

krustallos "hard ice"

low quartz (α-SiO_2)

- plane *faces*
- straight line *edges*
- point *vertices*

- constant interfacial angles
- rational intercepts

- 3-D periodic internal lattice structure

κρυσταλλος
krustallos “clear ice”
low quartz (α-SiO_2)

A Chronology of Crystallography

Classical antiquity

Greco-Roman thinkers – Nature of matter, polyhedral geometry, κρυσταλλος

1611 Johannes Kepler – Hexagonal snow crystals, hcp and ccp spheres

1600s René Descartes, Robert Hooke, Christiaan Huygens –
Speculations on periodic spheroid packing in crystals

1669 Nicolaus Steno (Niels Stensen),

1688 Domenico Gugliemini, and

1772 Jean-Baptiste Louis Romé de l' Isle – Law of Constant Interfacial Angles

1783 Abbé René-Just Haüy –
Law of Rational Indices, "*molécules intégrantes*," unit cells

1839 William Hallowes Miller – stereographic projection, Miller indices

1849 Auguste Bravais – Lattice theory

1883 William J. Pope and William Barlow –
Speculations on atomic and ionic sphere-packing in crystals.

1890 Evgraf Stepanovich Federov,

1892 Arthur Moritz Schoenflies, and

1894 William Barlow (all three independently) – Space group theory

1883 Paul Heinrich Ritter von Groth – Chemical and optical crystallography

1895 Wilhelm Conrad Röntgen – X-rays

1912 Walther Friedrich, Paul Knipping, and Max von Laue – X-ray diffraction

1913 William Henry and William Lawrence Bragg – X-ray crystal structures

Discovery of X-Rays
1895

Wilhelm Konrad Röntgen
1845-1923

EINE NEUE ART

VON

STRAHLEN.

VON

DR. WILHELM KONRAD RÖNTGEN

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

2. Auflage.

WÜRZBURG.

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

1896.

Early X-ray photographs
Anna Bertha Ludwig Röntgen (above)
Albert von Kölliker (below)

http://en.wikipedia.org/wiki/Wilhelm_R%C3%B6ntgen

Founding Fathers of X-ray Crystallography

Röntgen

Discovery of X-rays 1895

Laue

Discovery of X-ray diffraction by crystals 1912

The Braggs

First X-ray crystal structures 1913

Nobel Laureates in Physics 1901, 1914, 1915

The Discovery of X-Ray Diffraction by Crystals

An der Ludwig-Maximilians-Universität München im Januar 1912:

Paul Peter Ewald, a Ph.D. candidate in Arnold Sommerfeld's Institute of Theoretical Physics working on a thesis concerned with visible light refraction by crystals:

If crystals consist of regular, periodic arrangements of atoms, the interatomic spacings and unit cell dimensions should be of the order of 10^{-8} cm.

$$a_{\text{cell}} = \sqrt[3]{\frac{M_{\text{r}}\, m_{\text{u}}}{N_{\text{A}}\, \rho_{\text{m}}}}$$

Max Von Laue, a professor in Sommerfeld's Institute:

If X-rays are waves they should have wavelengths of the order of 10^{-8} cm, as had been estimated in Wilhelm Röntgen's Institute of Experimental Physics, and they should manifest diffraction effects with crystals.

$$a\left(\cos \nu_1 - \cos \mu_1\right) = h\lambda$$
$$b\left(\cos \nu_2 - \cos \mu_2\right) = k\lambda$$
$$c\left(\cos \nu_3 - \cos \mu_3\right) = l\lambda$$

75 Years of X-Ray Diffraction and Crystal Structure Analysis (1987)

Fünfundsiebzig Jahre Röntgenstrahlbeugung und Kristallstrukturanalyse

Herbert A. Hauptman, Robert H. Blessing, Buffalo, New York/USA

Die Entdeckung der Beugung von Röntgenstrahlen in Kristallen durch Walther Friedrich, Paul Knipping und Max Laue im Jahre 1912 war ein Wendepunkt in der modernen Wissenschaft. Max von Laue erhielt für die Entdeckung 1914 den Nobelpreis für Physik. Als im Jahr 1901 der erste Nobelpreis verliehen wurde, bekam Wilhelm Röntgen diesen Preis für die Entdeckung der X-Strahlen, die nach ihm Röntgenstrahlen benannt wurden, und in den Jahren danach bis in die Gegenwart hinein gab es eine Aufeinanderfolge von Nobelpreisen, für die Arbeiten und Entdeckungen auf dem Gebiet der Röntgenstrahlung, Spektroskopie, Strahlenbeugung und Kristallographie. Im Folgenden wollen wir dem nichtspezialisierten Leser einen Einblick in die Geschichte dieser Methode vermitteln. Wir bedienen uns dazu einer

kursorisch abgefaßten Chronik, die sich auf jene Arbeiten bezieht, die die Kristallstrukturanalyse beinhalten und die durch Nobelpreise ausgezeichnet wurden. Wir möchten jedoch betonen, daß wir uns damit sehr selektiv mit dem Thema auseinandersetzen und unsere Darstellung außerdem sehr gekürzt ist. Interessierten Lesern empfehlen wir, die im Literaturverzeichnis angegebenen Arbeiten aufzugreifen, die sich durch ihre Gründlichkeit und Verständlichkeit auszeichnen und die auch anderen die nötige Aufmerksamkeit schenken, nämlich den vielen Mitwirkenden und ihren Beiträgen zur Entwicklung dieser Methode, die in diesem Übersichtsartikel notgedrungen leider unerwähnt bleiben.

Die Entdeckung der Röntgenstrahlbeugung und die ersten Kristallstrukturbestimmungen

Im Jahr 1910 begann Paul Ewald in Sommerfelds Institut für Theoretische Physik in München seine Doktorarbeit über das Problem, die optischen Eigenschaften einer anisotropen Anordnung von isotropen Resonatoren zu finden. Als Laue 1912 von Ewalds Berechnungen erfuhr, fragte er ihn, ob seine Arbeit auch für Wellenlängen, die kürzer sind als der Abstand zwischen benachbarten Resonatoren, gültig wäre. Als Ewald dies bejahte, kam Laue der Gedanke, daß ein Kristall, dessen Atome in einem regelmäßigen Gitter geordnet sind, in Übereinstimmung mit Ewalds Ergebnissen einen einfallenden Röntgenstrahl beugen würde, wenn dessen Wellenlänge mit den Abständen zwischen benachbarten Atomen des Kristalls vergleichbar wäre. Laue ermunterte daraufhin Walther Friedrich, einen Assistenten von Sommerfeld, sowie Paul Knipping, der gerade seine Doktorarbeit bei Röntgen abgeschlossen hatte, das Experiment auszuführen. Die Ergebnisse zeigten, daß Kristalle sich tatsächlich wie ein dreidimensionales Beugungsgitter für Röntgenstrahlen verhalten (Abb. 2, 3, 4). Innerhalb von wenigen Wochen hatte Laue dann die mathematische Beschreibung des Beugungsphänomens ausgearbeitet und die Grundzüge der Beugungsmuster fehlerfrei gedeutet (W. Friedrich, P. Knipping, M. Laue 1912).

Noch im selben Jahr vereinfachten Vater und Sohn Bragg von Laues mathematische Beschreibung der Beugungsbedingungen durch die Einführung des Gedankens der Spiegelung an Netzebenen im Kristall. Ihre Ableitung war die gefeierte Braggsche Gleichung

$$n\lambda = 2d \sin \theta,$$

hierbei ist n ein ganzzahliger Wert, den man die Ordnung des Reflexes nennt, λ ist die Wellenlänge der

Herbert A. Hauptman, Tagung der Nobelpreisträger, Lindau i. B. 1986. [Photo NR/Ro] ▶

Prof. Dr. Herbert Hauptman (geb. 14. Februar 1917) ist Präsident und Forschungsdirektor der Medical Foundation in Buffalo. 1985 erhielt er den Nobelpreis für Chemie, gemeinsam mit Jerome Karle, für die hervorragenden Leistungen in der Entwicklung von direkten Methoden zur Bestimmung von Kristallstrukturen.

Dr. Robert Blessing (geb. 7. April 1941) ist Senior Research Scientist in der Abteilung Molekulare Biophysik der Medical Foundation in Buffalo. Seine Forschungen befassen sich mit kristallographischen Daten sowie Elektronendichte-Verteilung und chemische Bindungen von Molekülen in Kristallen.

Der Beitrag basiert auf dem Vortrag von Herbert A. Hauptman "The Phase Problem of X-ray Crystallography" bei der Nobelpreisträgertagung in Lindau i. B. am 2. Juli 1986.

Medical Foundation of Buffalo, 73 High Street, Buffalo, NY 14203, USA.

Sitzungsberichte

der

mathematisch-physikalischen Klasse

der

K. B. Akademie der Wissenschaften

zu München

Jahrgang 1912

München 1912

Verlag der Königlich Bayerischen Akademie der Wissenschaften

Interferenz-Erscheinungen bei Röntgenstrahlen.

Von W. Friedrich, P. Knipping und M. Laue.

Vorgelegt von A. Sommerfeld in der Sitzung am 8. Juni 1912.

Theoretischer Teil

von M. Laue.

Einleitung. Barklas[1]) Untersuchungen in den letzten Jahren haben gezeigt, daß die Röntgenstrahlen in der Materie eine Zerstreuung erfahren, ganz entsprechend der Zerstreuung des Lichtes in trüben Medien, daß sie aber noch daneben im allgemeinen die Atome des Körpers zur Aussendung einer spektral homogenen Eigenstrahlung (Fluoreszenzstrahlung) anregen, welche ausschließlich für den Körper charakteristisch ist.

Andererseits ist schon seit 1850 durch Bravais in die Kristallographie die Theorie eingeführt, daß die Atome in den Kristallen nach Raumgittern angeordnet sind. Wenn die Röntgenstrahlen wirklich in elektromagnetischen Wellen bestehen, so war zu vermuten, daß die Raumgitterstruktur bei einer Anregung der Atome zu freien oder erzwungenen Schwingungen zu Interferenzerscheinungen Anlaß gibt; und zwar zu Interferenzerscheinungen derselben Natur wie die in der Optik bekannten Gitterspektren. Die Konstanten dieser Gitter lassen sich aus dem Molekulargewicht der kristallisierten Verbindung, ihrer Dichte und der Zahl der Moleküle pro Grammolekül,

[1]) C. G. Barkla, Phil. Mag., z. B. 22, 396, 1911.

sowie den kristallographischen Daten leicht berechnen. Man findet für sie stets die Größenordnung 10^{-8} cm, während die Wellenlänge der Röntgenstrahlen nach den Beugungsversuchen von Walter und Pohl[1]) und nach den Arbeiten von Sommerfeld und Koch[2]) von der Größenordnung 10^{-9} cm sind. Eine erhebliche Komplikation freilich bedeutet es, daß bei den Raumgittern eine dreifache Periodizität vorliegt, während man bei den optischen Gittern nur in einer Richtung, höchstens (bei den Kreuzgittern) in zwei Richtungen periodische Wiederholungen hat.

Die Herren Friedrich und Knipping haben auf meine Anregung diese Vermutung experimentell geprüft. Über die Versuche und ihr Ergebnis berichten sie selbst im zweiten Teil der Veröffentlichung.

[1]) B. Walter und R. Pohl, Ann. d. Phys. 25, 715, 1908; 29, 331, 1909.

[2]) A. Sommerfeld, Ann. d. Phys. 38, 473, 1912; P. P. Koch, Ann. d. Phys. 38, 507, 1912.

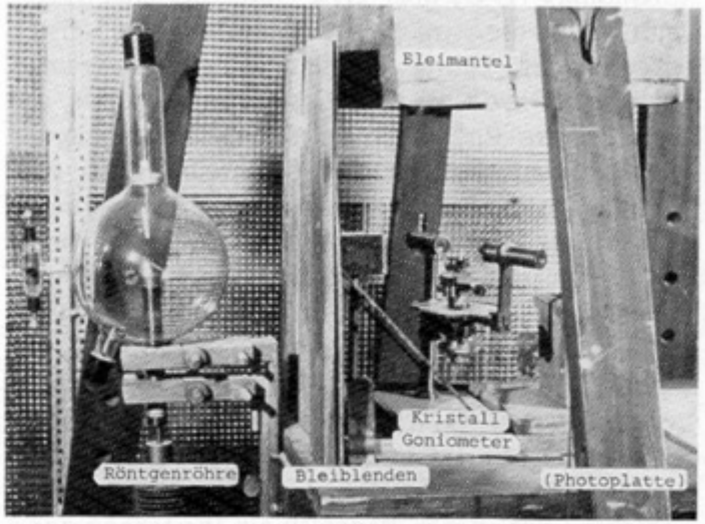


Abb. 3. Versuchsanordnung für die Beugung von Röntgenstrahlen nach Laue, Friedrich und Knipping (1912). — Ein durch Bleiblenden begrenztes Röntgenstrahlbündel durchdringt den auf einem Goniometer befestigten Einkristall und trifft auf die (hier durch das Stativ verdeckte) photographische Platte. Die Photoplatte samt Kristall und Blende ist von einem Bleimantel umgeben, der vor Streustrahlung schützt.

$CuSO_4 \cdot 5H_2O$
blue vitriol
chalcanthite

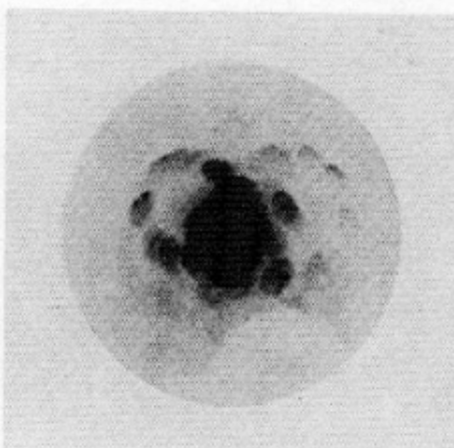


Abb. 2.
Das erste erfolgreiche Beugungsphotogramm von Friedrich und Knipping (1912).

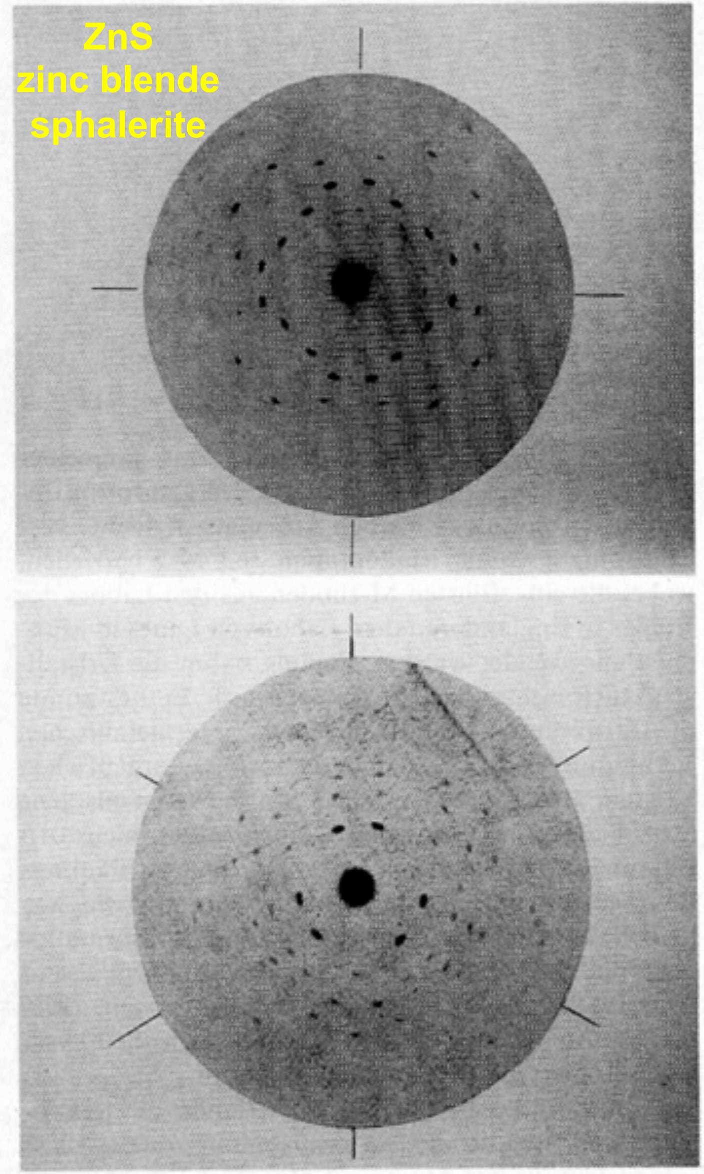
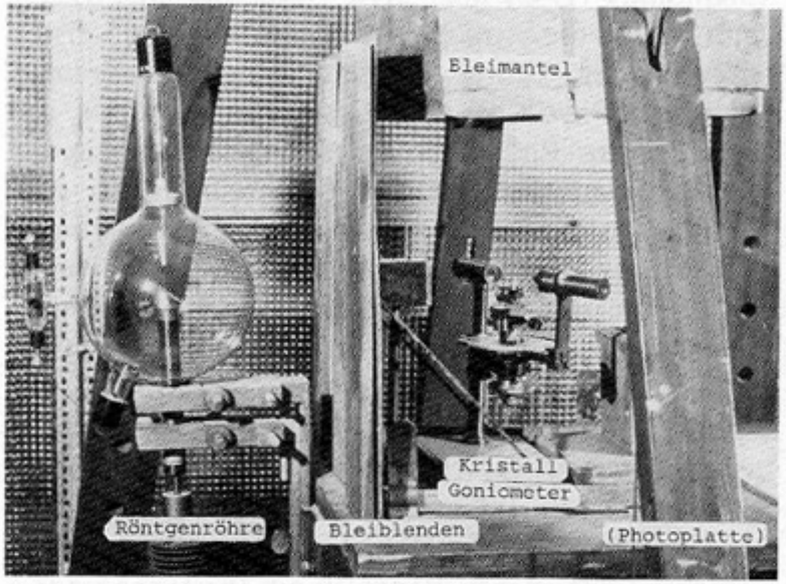


Abb. 4. Zinkblende-Laue-Photogramm längs einer vierzähligen (a) und dreizähligen (b) Achse (1912).



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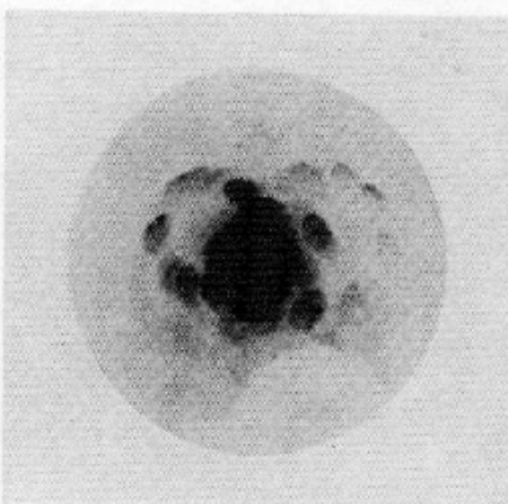

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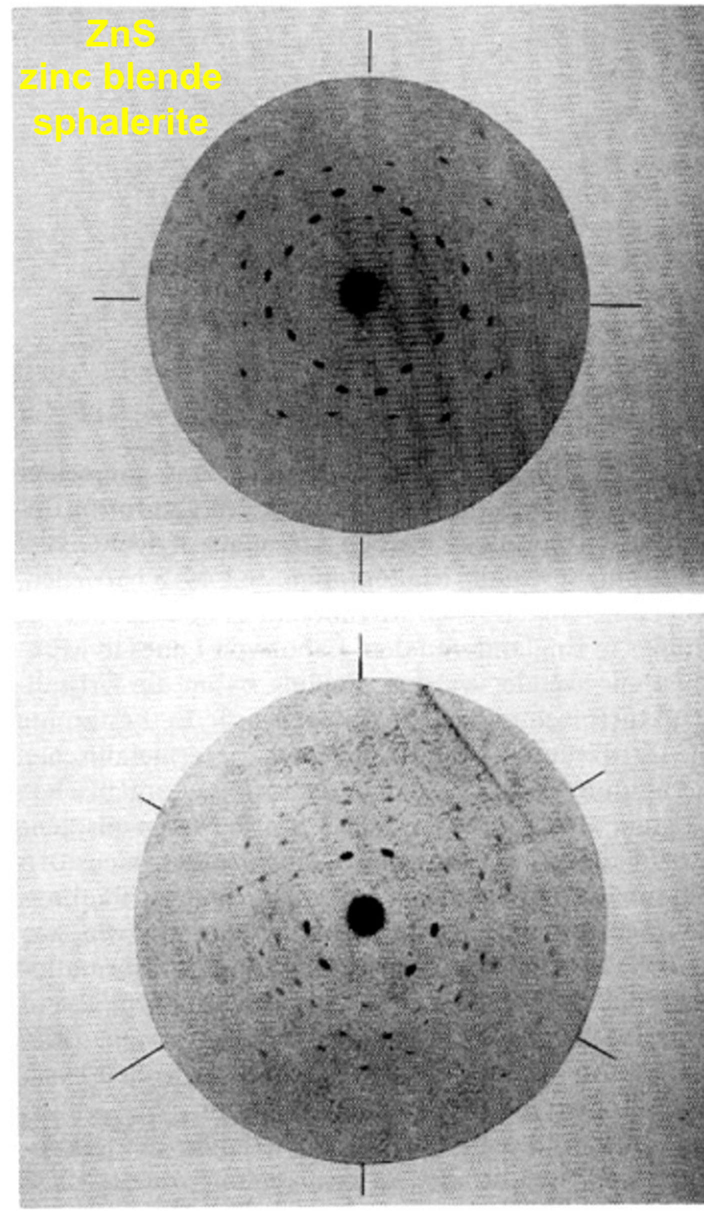

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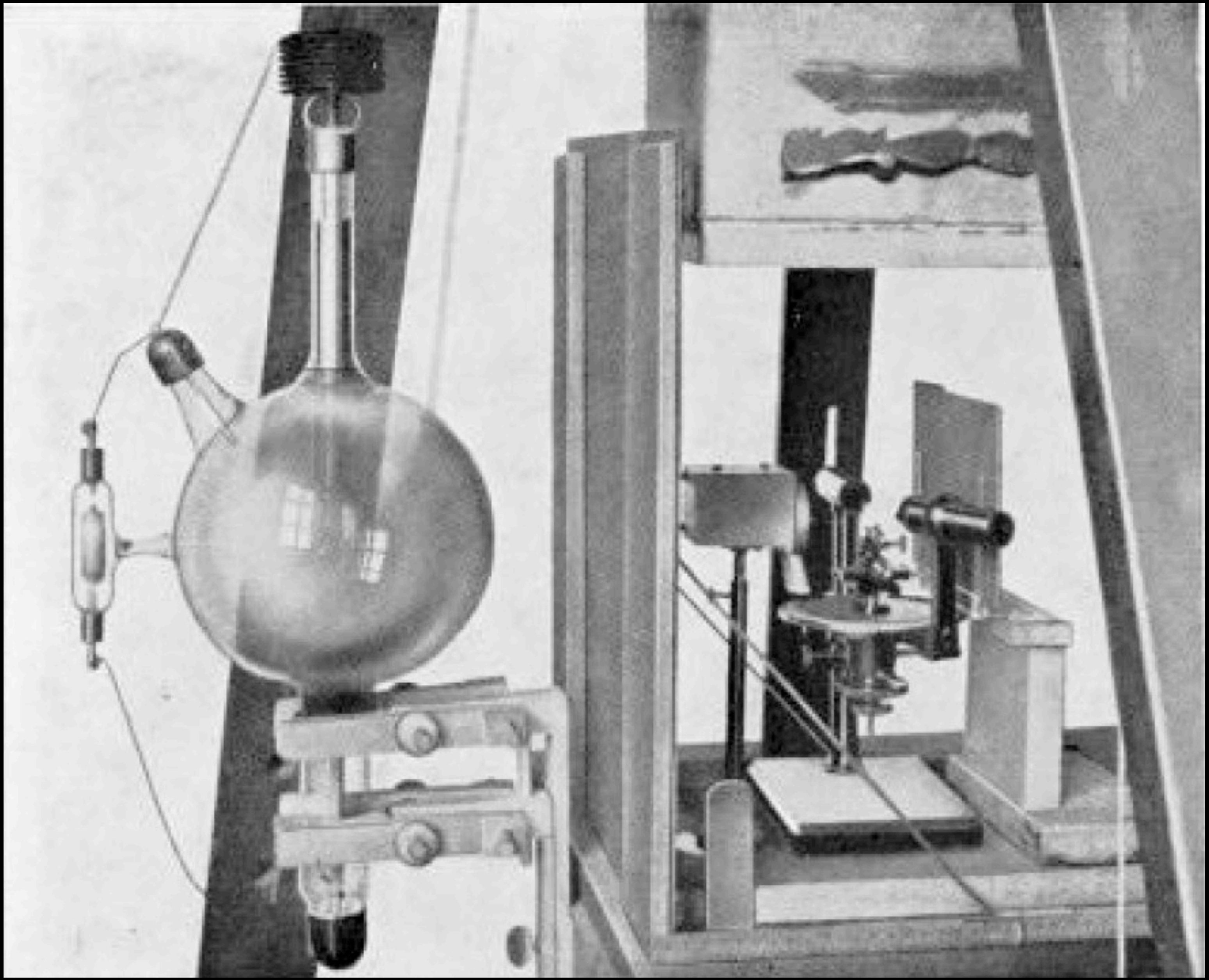
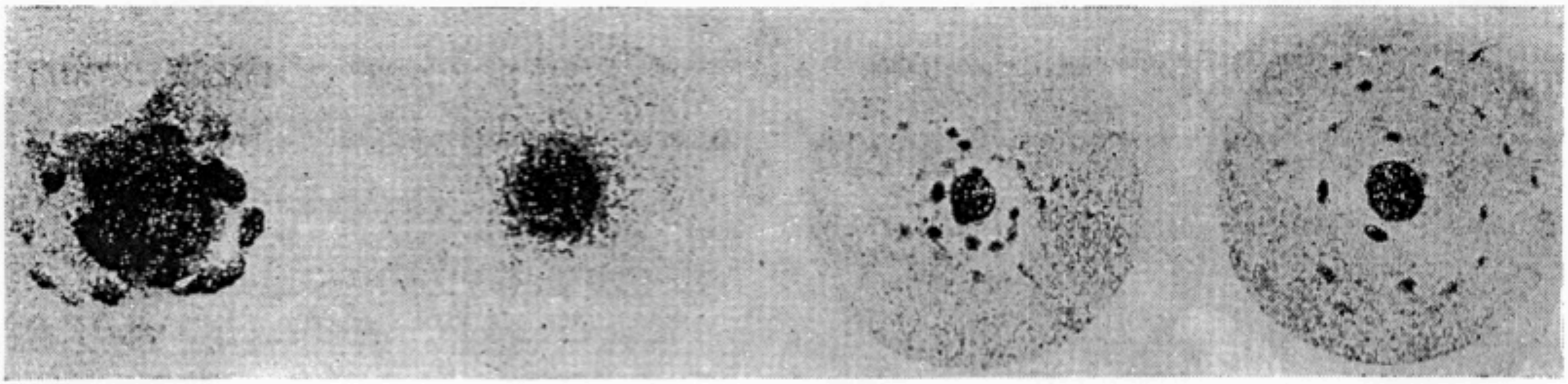


Walther Friedrich, Paul Knipping, and Max von Laue (1912)
X-ray diffraction from $CuSO_4 \cdot 5H_2O$ crystals

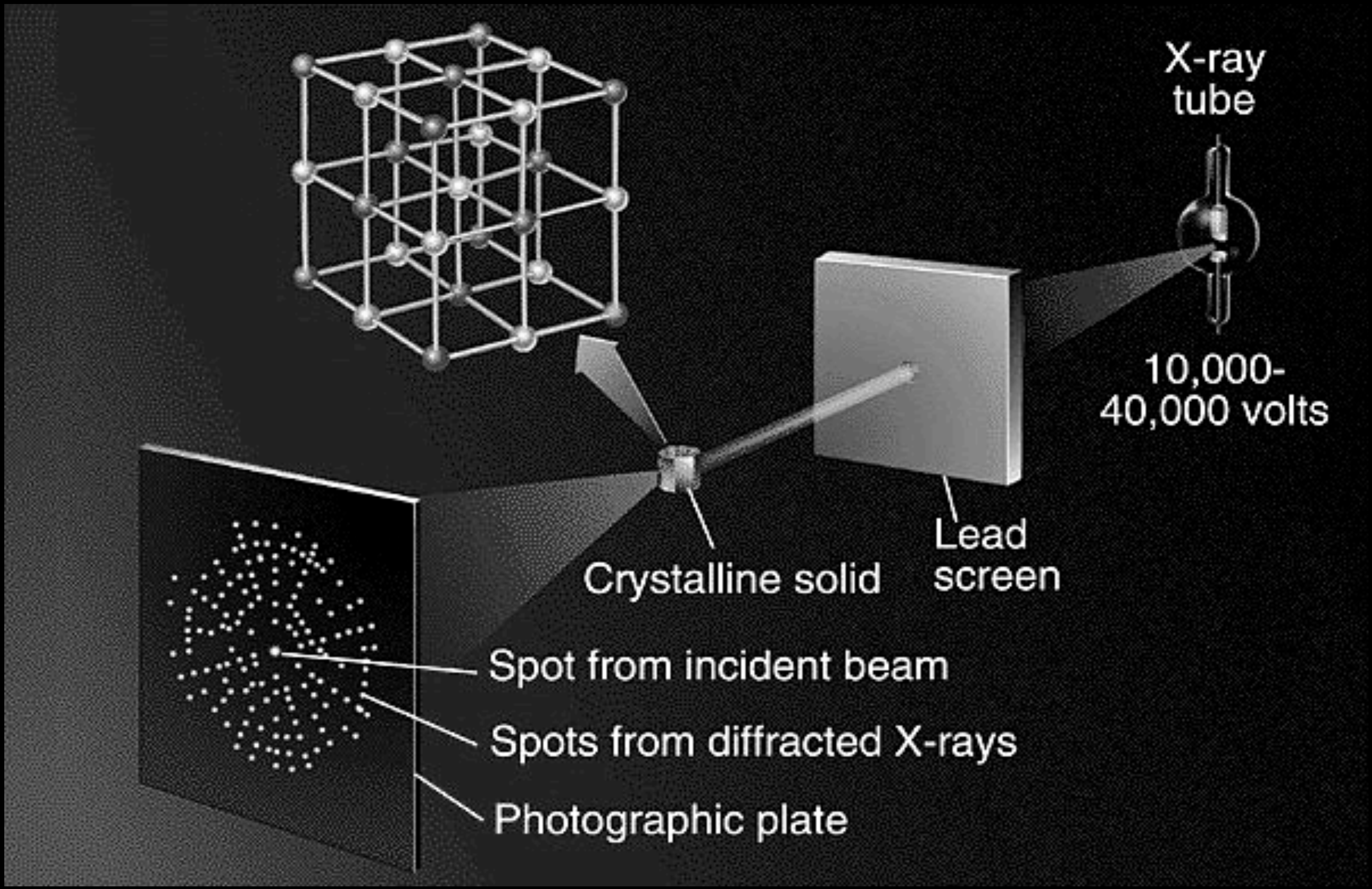


(a) (b) (c) (d)

(a) The first single-crystal X-ray diffraction pattern
(b) Pulverized sample crystal
(c) Longer crystal-to-film distance
(d) Shorter crystal-to-film distance

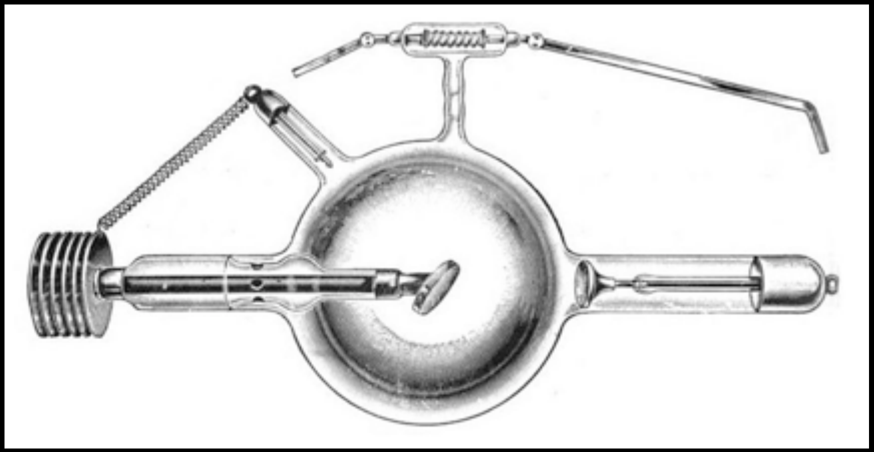
Figure copied from W.L. Bragg, *The Development of X-ray Analysis*, 1972.

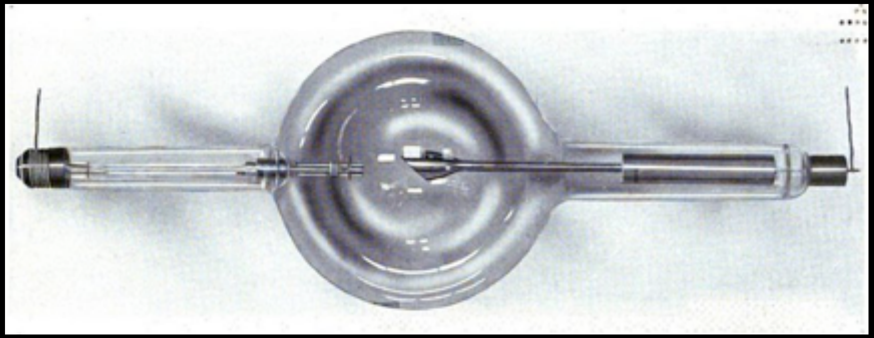
X-ray diffraction by a crystal

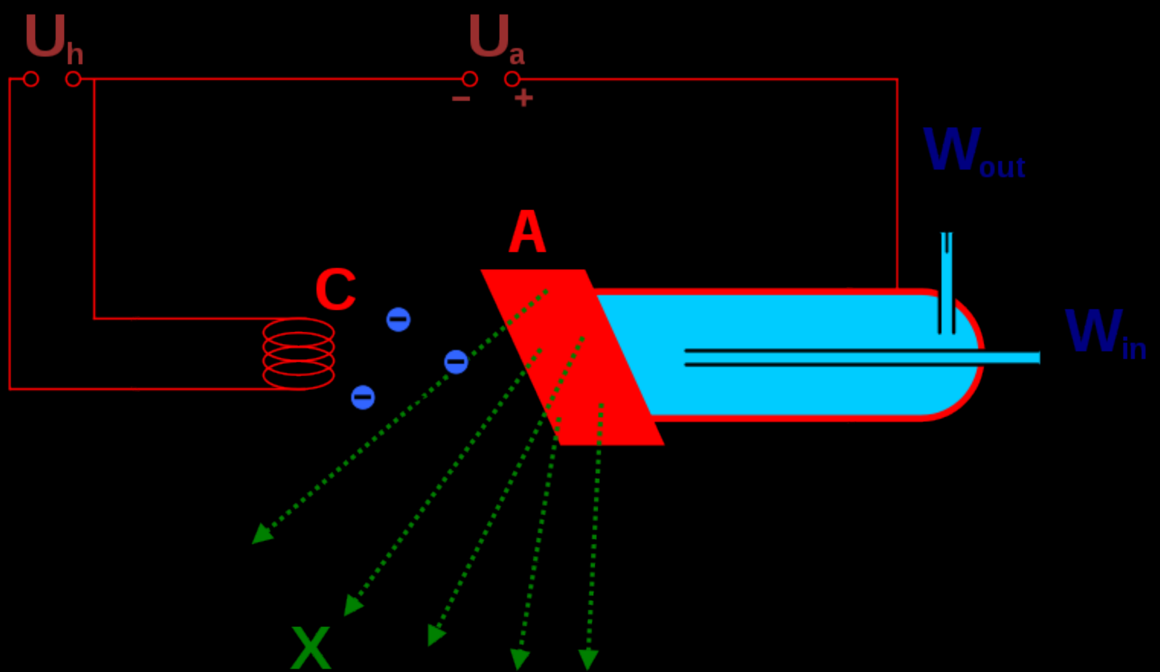


http://www.chem.ufl.edu/~itl/2045/matter/FG11_039.GIF

Crookes and Coolidge X-Ray Tubes

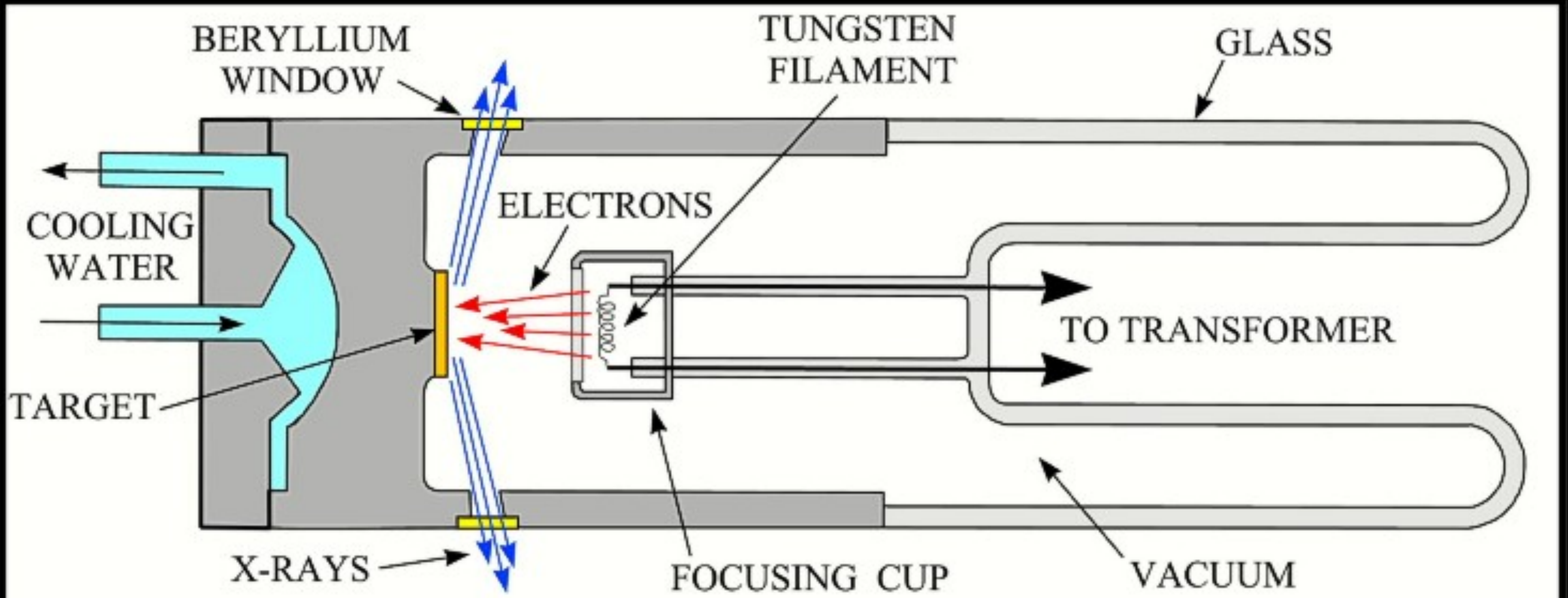






http://en.wikipedia.org/wiki/X-ray_tube

Generation of X-rays
kV acceleration, mA current



SCHEMATIC CROSS SECTION OF AN X-RAY TUBE

http://pubs.usgs.gov/of/2001/of01-041/htmldocs/images/xrdtube.jpg

Crystallographic Diffraction

Laue diffraction from a three-dimensional *abc* lattice grating

$$a\left(\cos\nu_1 - \cos\mu_1\right) = \mathbf{a}\bullet\left(\hat{\mathbf{s}} - \hat{\mathbf{s}}_0\right) = h\lambda$$
$$b\left(\cos\nu_2 - \cos\mu_2\right) = \mathbf{b}\bullet\left(\hat{\mathbf{s}} - \hat{\mathbf{s}}_0\right) = k\lambda$$
$$c\left(\cos\nu_3 - \cos\mu_3\right) = \mathbf{c}\bullet\left(\hat{\mathbf{s}} - \hat{\mathbf{s}}_0\right) = l\lambda$$

Max von Laue, Walther Friedrich, and Paul Knipping (1912).

Bragg reflection from families of parallel *hkl* lattice planes

$$2d_{hkl}\sin\theta = n\lambda\,, \qquad 2\left(\frac{d_{hkl}}{n}\right)\sin\theta = \lambda\,, \qquad 2d_{nh\,nk\,nl}\sin\theta = \lambda$$

William Henry and William Lawrence Bragg (1913). (Father and son)

Integrated Bragg reflection intensities

$$\rho = \frac{E\omega}{I_0} = kALp\left|F_{hkl}\right|^2 = \left(\frac{e^2}{mc^2}\right)^2 \lambda^3 \left(\frac{v_{\mathrm{xtal}}}{V_{\mathrm{cell}}}\right)^2 \left[\int_{v_{\mathrm{xtal}}} \mathrm{e}^{-\mu(t_0+t_1)}\,\mathrm{d}v\right] \frac{1}{\sin 2\theta}\left(\frac{1}{2} + \frac{1}{2}\cos^2 2\theta\right)\left|F_{hkl}\right|^2$$

Charles G. Darwin (1914). (Grandson of the author of the theory of evolution)

X-Rays

Electromagnetic radiation beam

Ultra-short wavelength light $$E = h\nu = \frac{hc}{\lambda}, \qquad \begin{cases} \lambda = 1\,\text{Å} \\ E = 12.4\,\text{keV} \end{cases}$$

Scattered by atomic electron densities

$$f_a^{\text{X}}(\mathbf{h}) = \mathcal{F}^{-1}\left[\rho_a(\mathbf{r})\right], \qquad |\mathbf{h}| = \frac{1}{d_{hkl}} = 2\left(\frac{\sin\theta_{hkl}}{\lambda}\right), \qquad \begin{cases} 0 \le |\mathbf{h}| < \infty \\ Z_a \ge f_a^{\text{X}} > 0 \end{cases}$$

Electrons

Negative particle beam

deBroglie matter-waves $$\lambda = \frac{h}{p} = \frac{h}{m_e v}, \qquad E = \frac{1}{2} m_e v^2, \qquad \begin{cases} E \sim 100\,\text{keV} \\ \lambda \sim 0.1\,\text{Å} \end{cases}$$

Scattered by atomic electrostatic potentials

$$f_a^{\text{e}}(\mathbf{h}) = \mathcal{F}^{-1}\left[\phi_a(\mathbf{r})\right] \approx \frac{1}{4\pi\varepsilon_0}\left(\frac{2m_e e^2}{h^2}\right)\frac{Z_a - f_a^{\text{X}}(\mathbf{h})}{|\mathbf{h}|^2}$$

Neutrons

Neutral particle beam

deBroglie matter-waves $$\lambda = \frac{h}{p} = \frac{h}{m_n v}, \qquad E = \tfrac{1}{2} m_n v^2 = \tfrac{3}{2} k_B T, \qquad \begin{cases} T \sim 300\,\text{K} \\ \lambda \sim 1.5\,\text{Å} \end{cases}$$

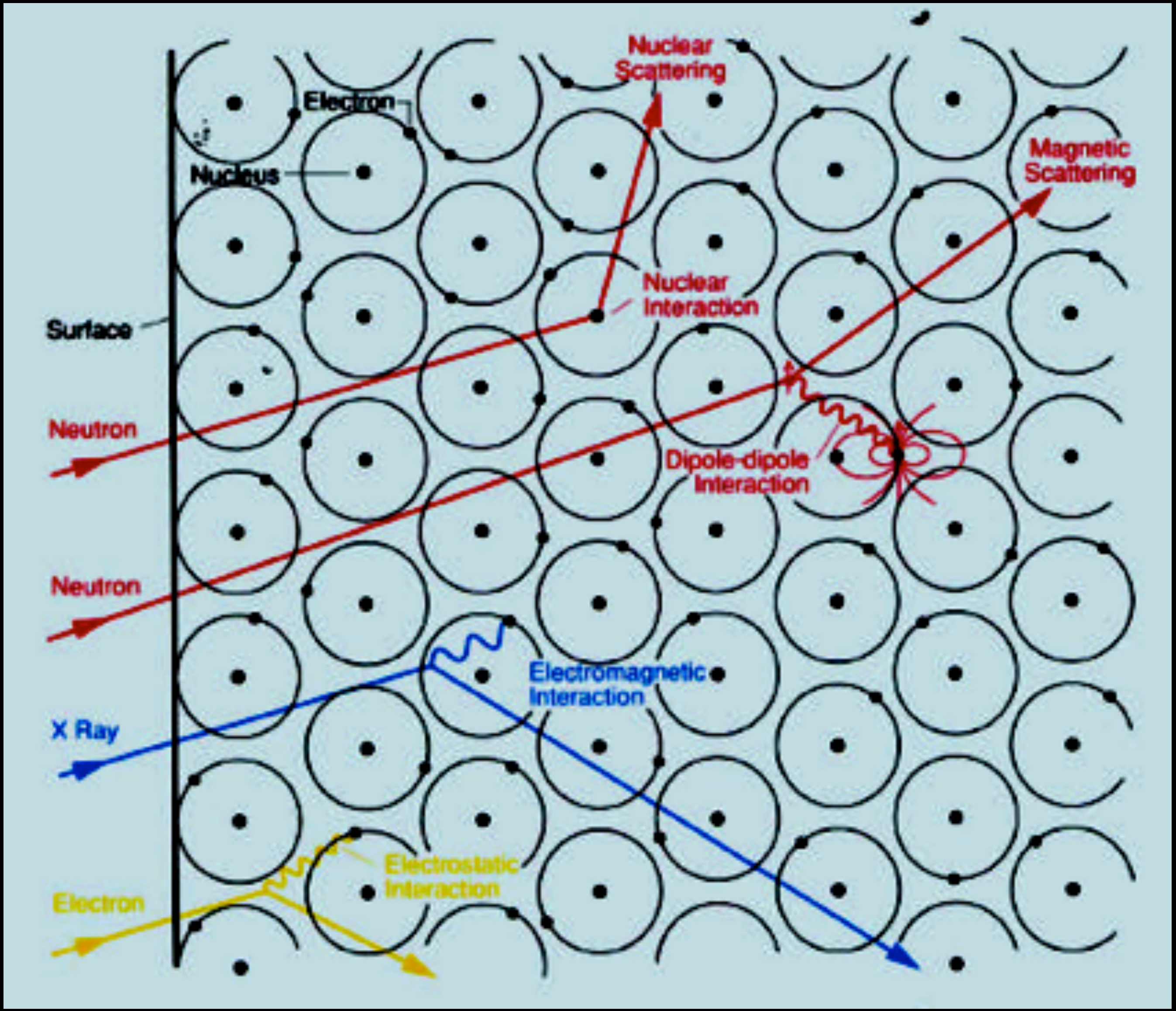
Scattered by atomic nuclei

(point scatterers $\Leftrightarrow$ θ-independent scattering lengths)

$$b_{c,a} = \mathcal{F}^{-1}\left[\rho_a(\mathbf{r})\right] \qquad \langle b_c \rangle \approx 5\,\text{fm} \qquad b_{c,\text{H}} = -3.74\,\text{fm} \qquad b_{c,\text{D}} = +6.67\,\text{fm}$$

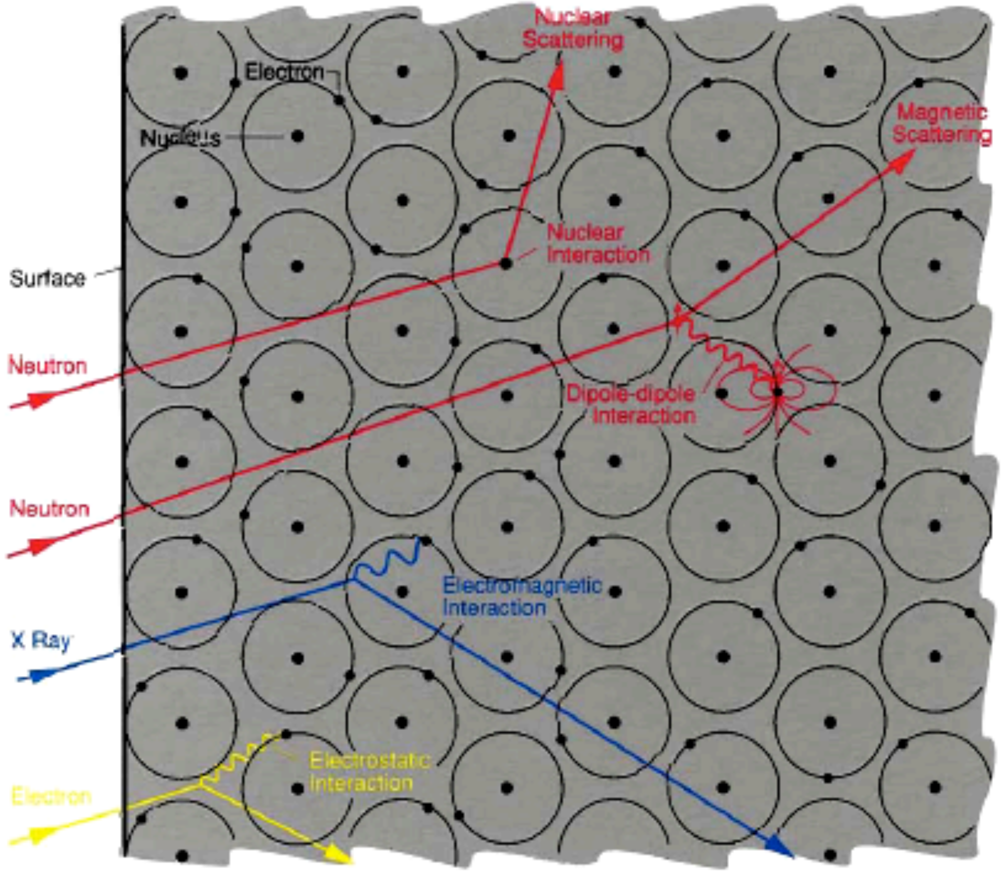
$$b_{i,\text{H}} = 25.3 \qquad b_{i,\text{D}} = 4.04$$

Neutron, X-ray, and electron scattering in a crystal



Roger Pynn, Neutron Scattering: A Primer. *Physics Today*, Special Supplement, Jan. 1985.
http://la-science.lanl.gov/lascience19.shtml

Neutron, X-ray, and electron scattering



SCATTERING INTERACTIONS

Fig. 2. Beams of neutrons, x rays, and electrons interact with material by different mechanisms. X rays (blue) and electron beams (yellow) both interact with electrons in the material; with x rays the interaction is electromagnetic, whereas with an electron beam it is electrostatic. Both of these interactions are strong, and neither type of beam penetrates matter very deeply. Neutrons (red) interact with atomic nuclei via the very short-range strong nuclear force and thus penetrate matter much more deeply than x rays or electrons. If there are unpaired electrons in the material, neutrons may also interact by a second mechanism: a dipole-dipole interaction between the magnetic moment of the neutron and the magnetic moment of the unpaired electron.

Roger Pynn, Neutron Scattering: A Primer. *Physics Today*, Special Supplement, Jan. 1985.
http://la-science.lanl.gov/lascience19.shtml

Some Elementary Optics Principles

Wave Interference and Diffraction

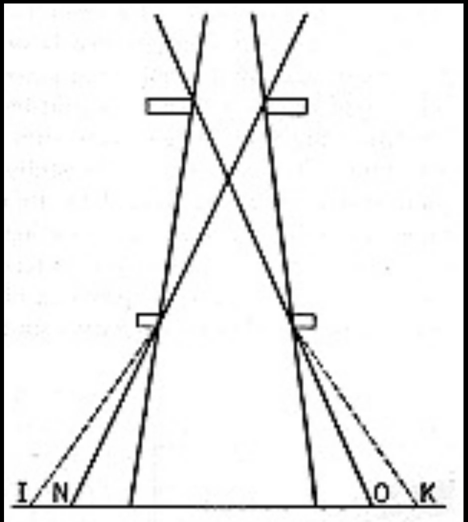
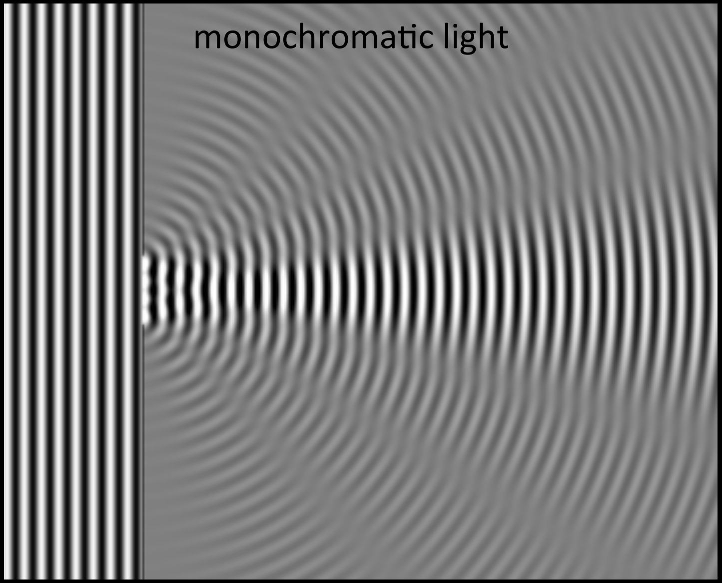


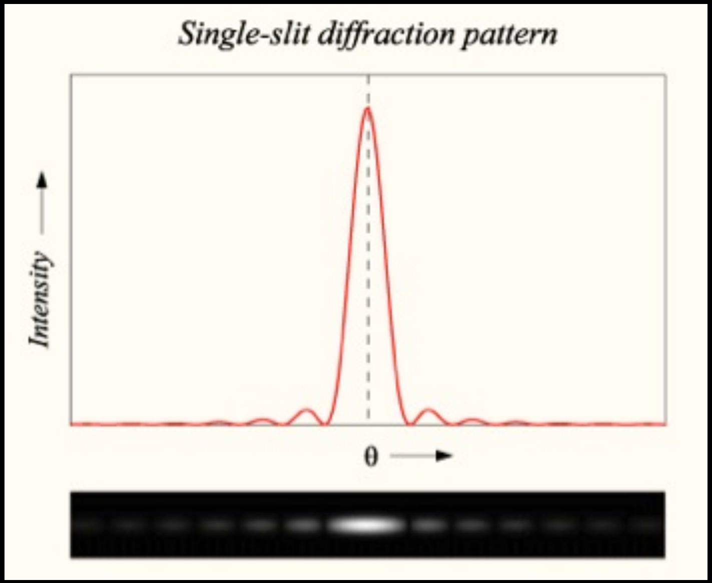
FIG. 315. GRIMALDI'S OBSERVATION OF DIFFRACTION

"When the light is incident on a smooth white surface it will show an illuminated base *IK* notably greater than the rays would make which are transmitted in straight lines through the two holes. This is proved as often as the experiment is tried by observing how great the base *IK* is in fact and deducing by calculation how great the base *NO* ought to be which is formed by the direct rays. Further it should not be omitted that the illuminated base *IK* appears in the middle suffused with pure light, and at either extremity its light is colored."

Francesco Maria Grimaldi, S.J. (1613-1665)

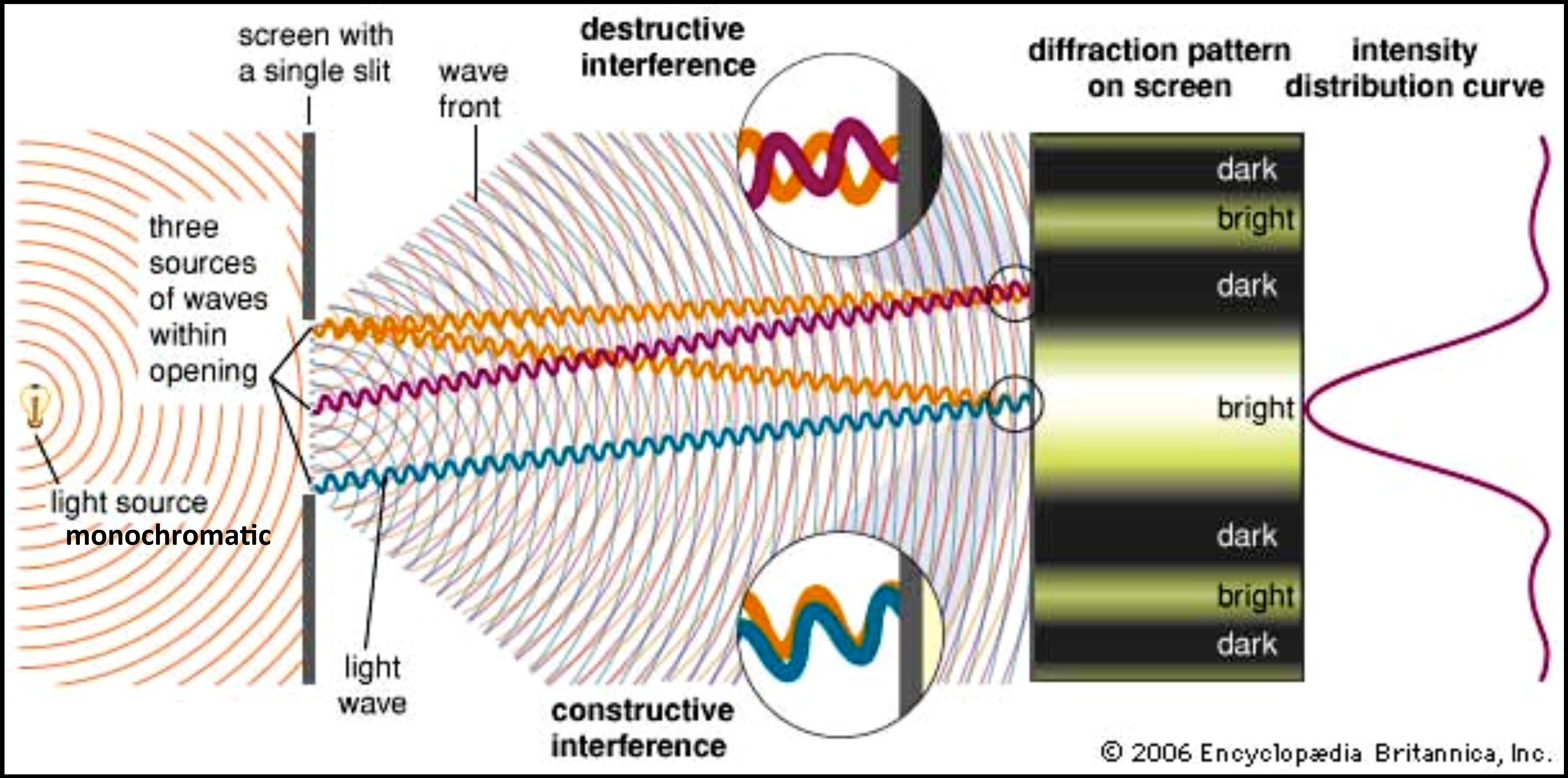
"diffraction" from Latin *diffringere* "to break into pieces"





http://www.faculty.fairfield.edu/jmac/sj/scientists/grimaldi.htm http://en.wikipedia.org/wiki/Diffraction

Single Slit Diffraction



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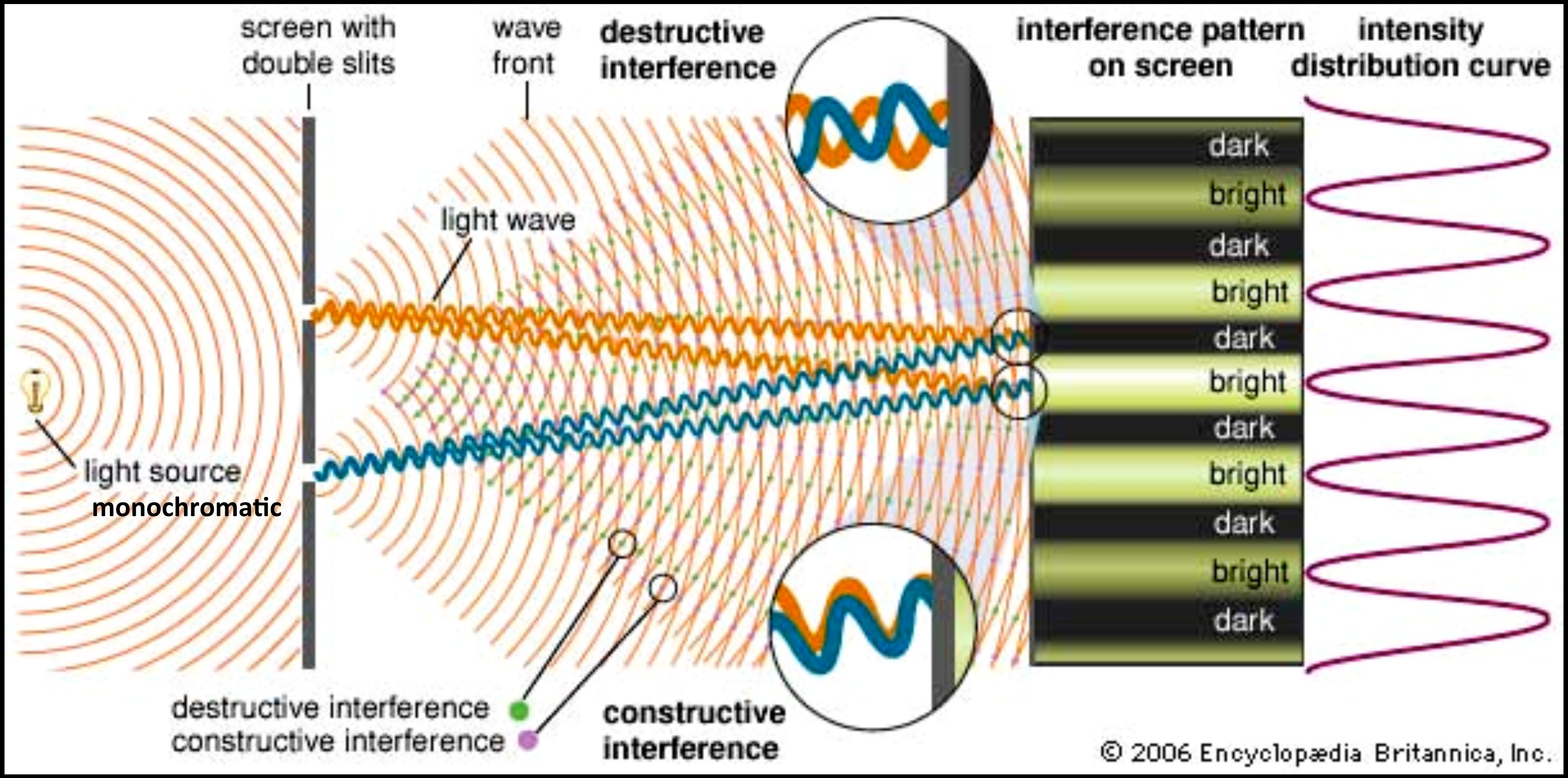
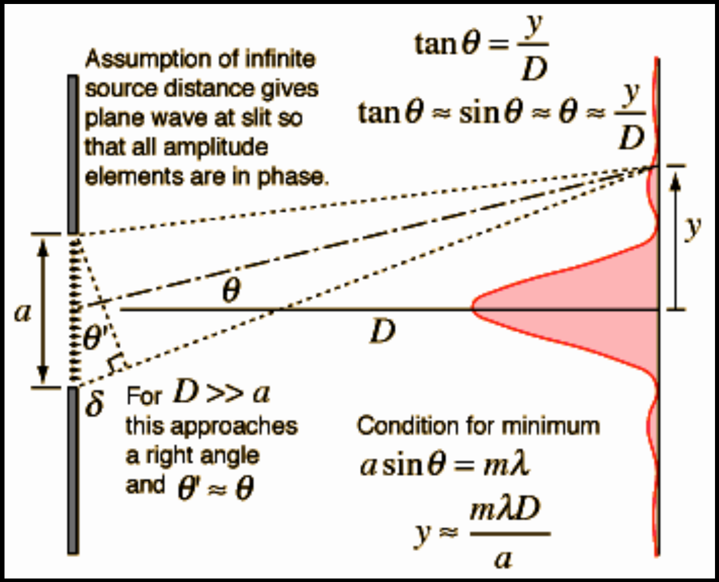
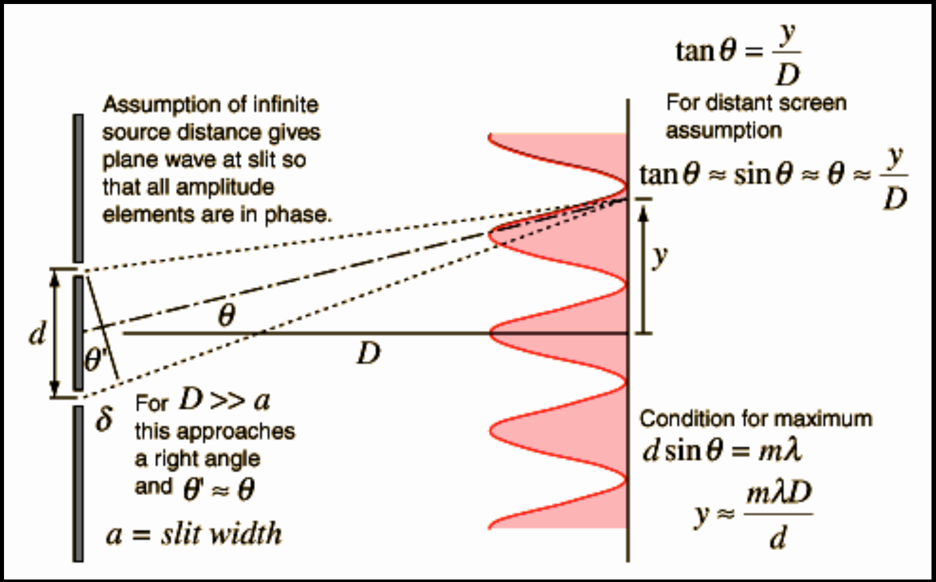
Double Slit Diffraction

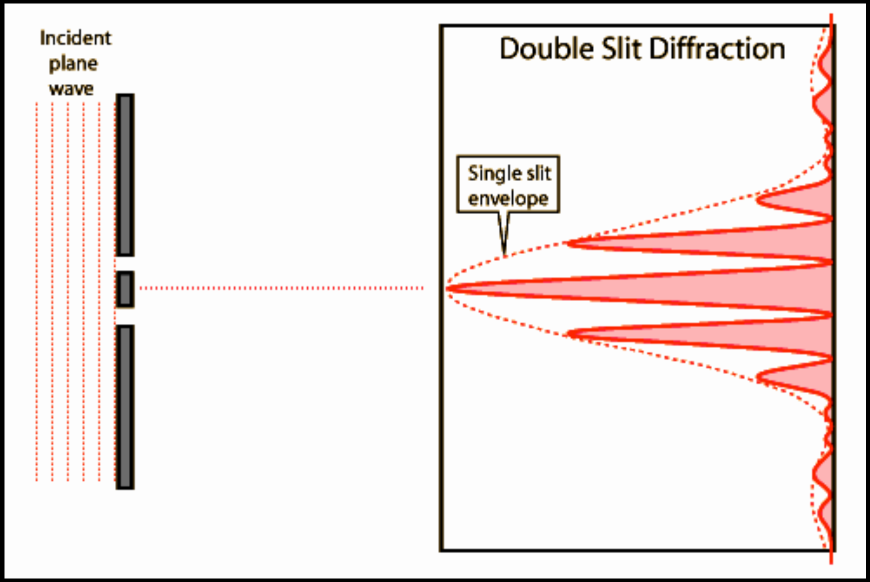


http://media-2.web.britannica.com/eb-media/96/96596-004-1D8E9F0F.jpg

Fraunhofer single and double slit diffraction

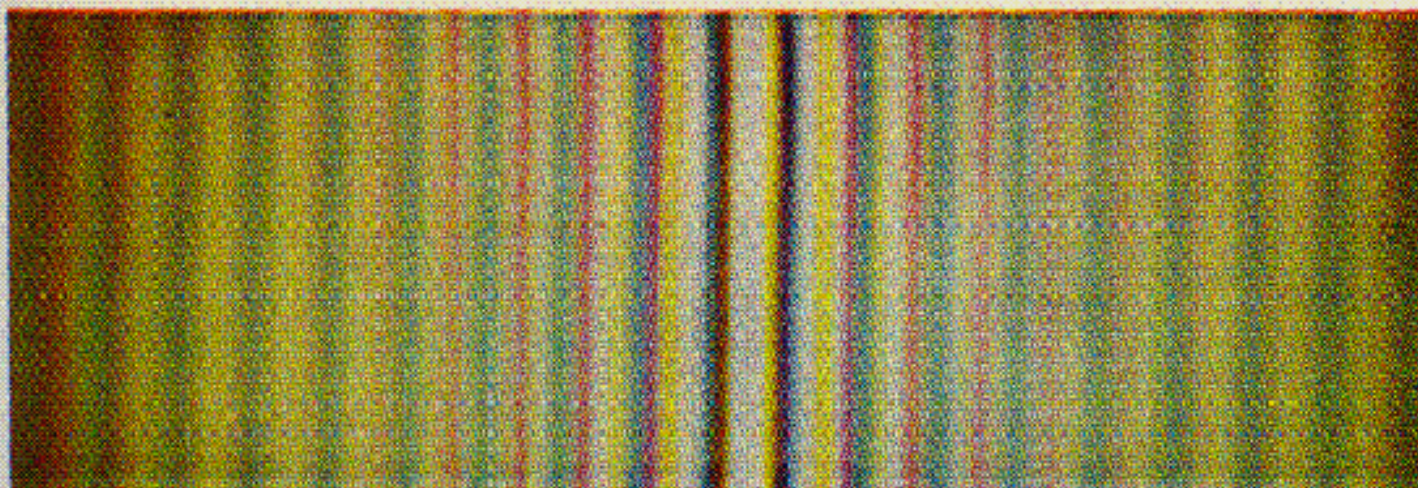






http://hyperphysics.phy-astr.gsu.edu/hbase/phyopt/imgpho/doubsli.gif

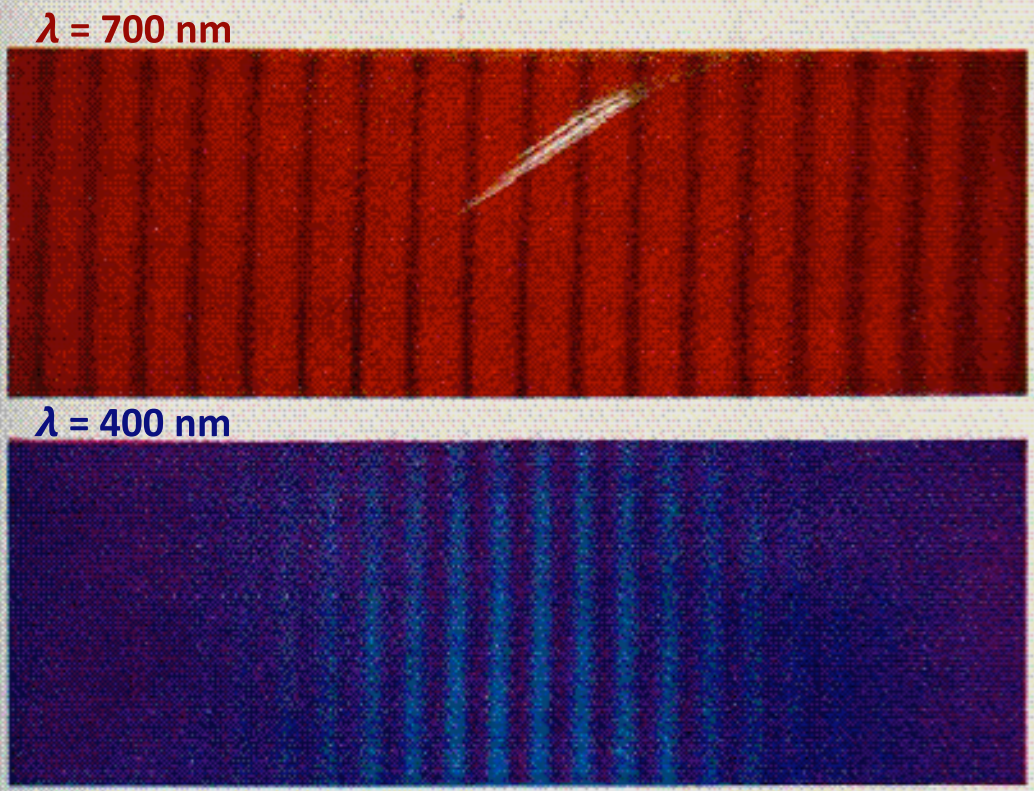
Optical Diffraction



Interference pattern produced by white light passing through two narrow slits.

PSSC Physics, Figure 18-A, p. 202-203 (1965)

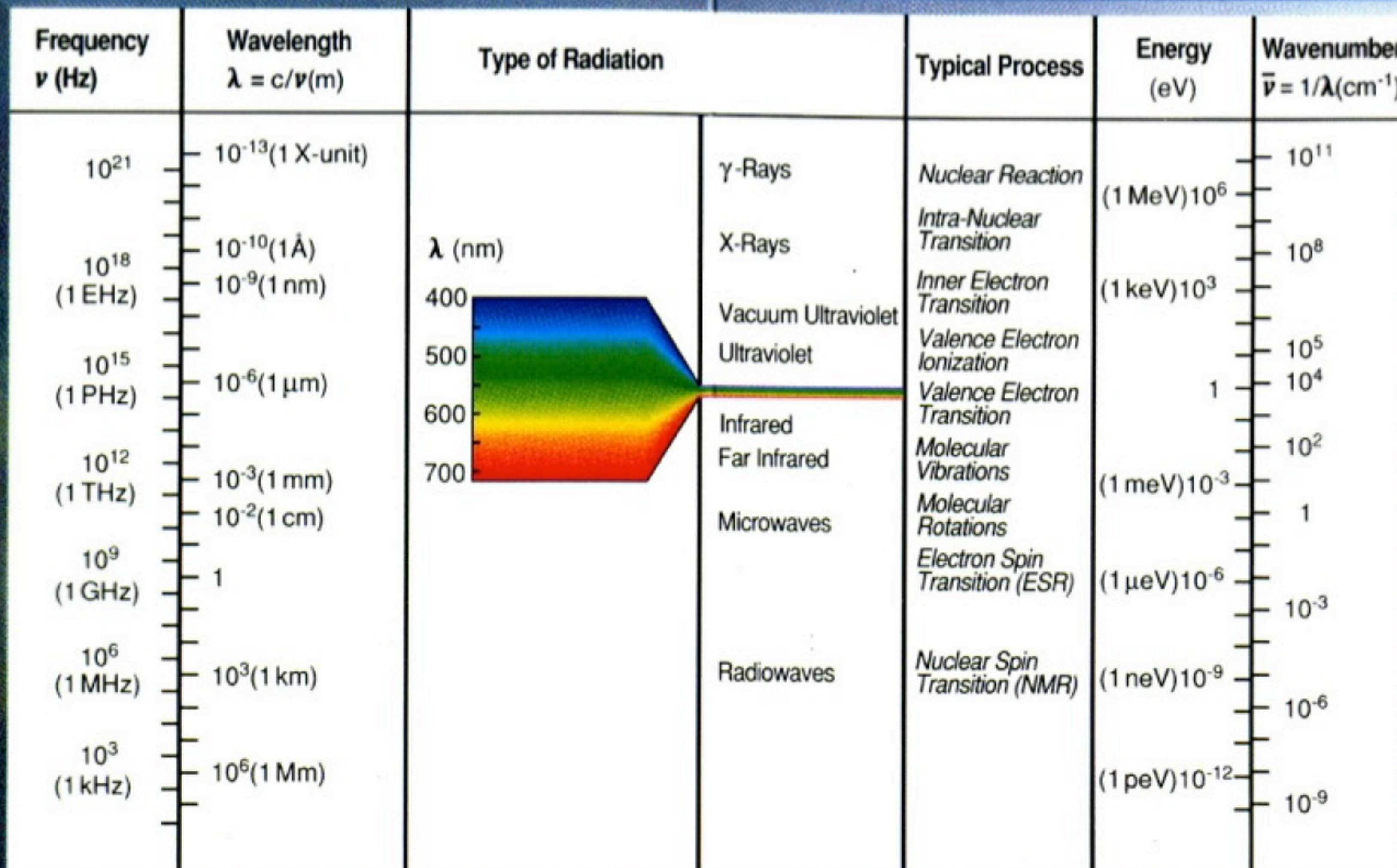
Optical Diffraction



18-B Interference patterns of red light and blue-violet light made with exactly the same setup used to make the white light interference pattern in Fig. 18-A.

PSSC Physics, Figure 18-B, p. 202-203 (1965)

THE ELECTROMAGNETIC SPECTRUM



1 eV = 1.602177×10^{-19} J; h = 6.626075×10^{-34} J·s (Planck Constant); c = 2.997925×10^{8} $m \cdot s^{-1}$ (light velocity)

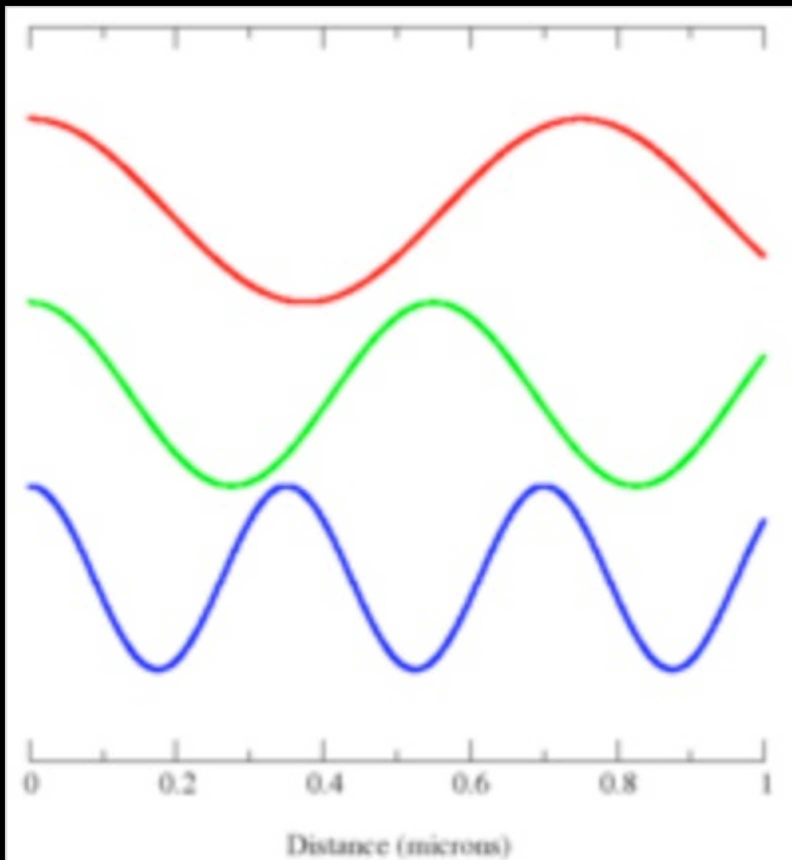
1Å = 10^{-10}m = 10^{-8}cm~2.997925×10^{18} s^{-1} (light frequency)~1.239852×10^{4} eV (energy of light quantum)

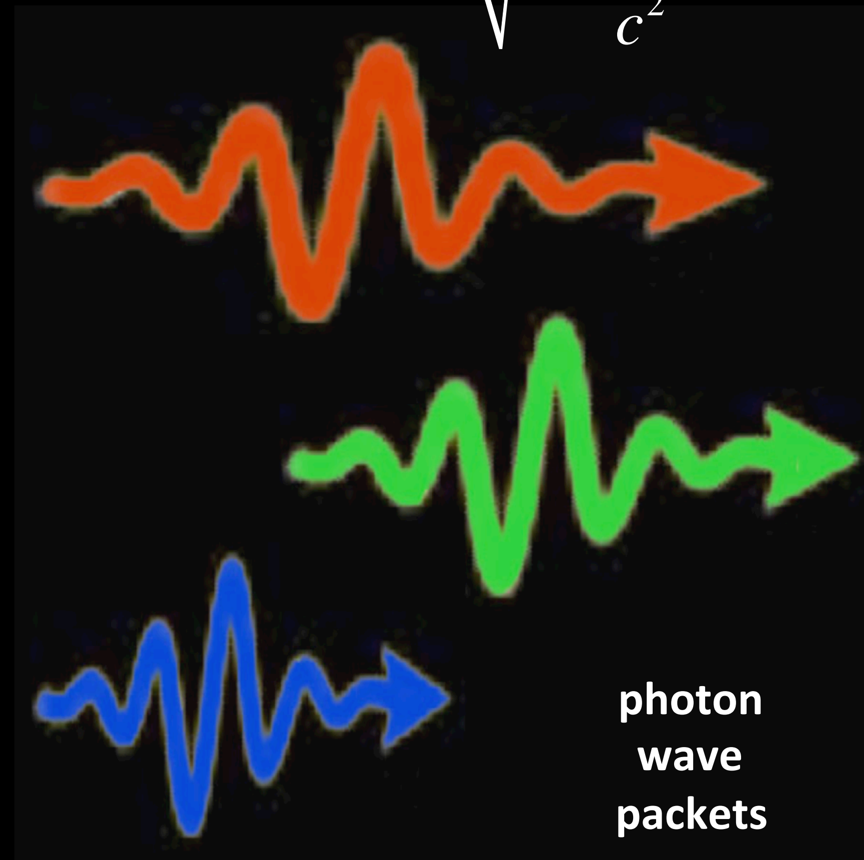
Wave/Particle Duality

light wave energies ↔ **photon momenta**

$$E = \hbar\omega = h\nu = \frac{hc}{\lambda}$$

$$p = \hbar k = \frac{h}{\lambda} = \frac{m_0 v}{\sqrt{1 - \frac{v^2}{c^2}}}$$





http://www.answers.com/topic/photon-2
http://www.windows2universe.org/physical_science/magnetism/photon.html

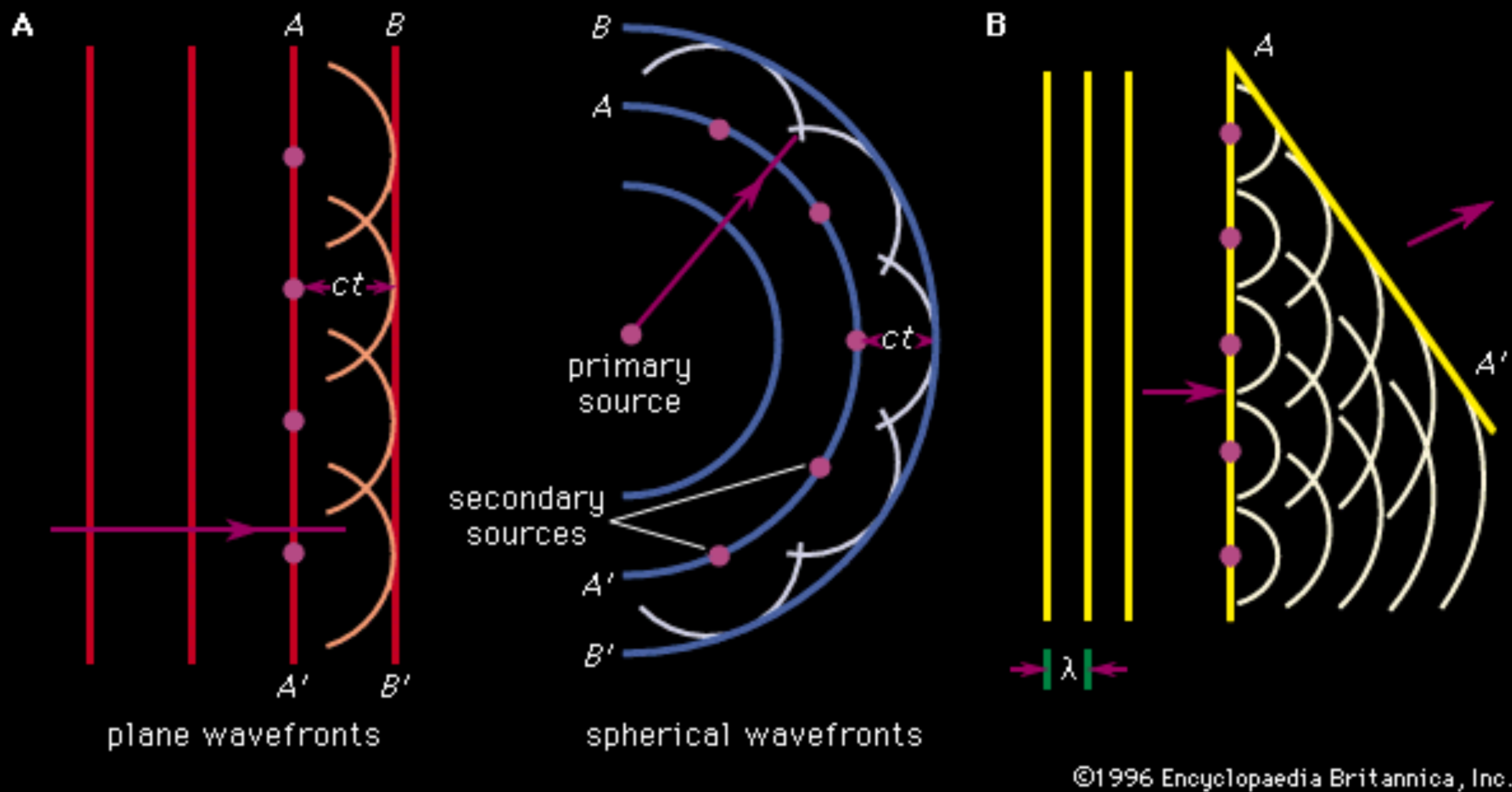
Huygens' wavelets principle

Huygens (1678). *Traité de la Lumière*.

Every point on a propagating wavefront acts as the source of a spherical secondary wavelet that has the same wavelength and speed of propagation as the primary wavefront, such that at some later time the propagating wavefront is the envelope surface tangent to the secondary wavelets.

Diffraction according to Huygens' wavelets principle

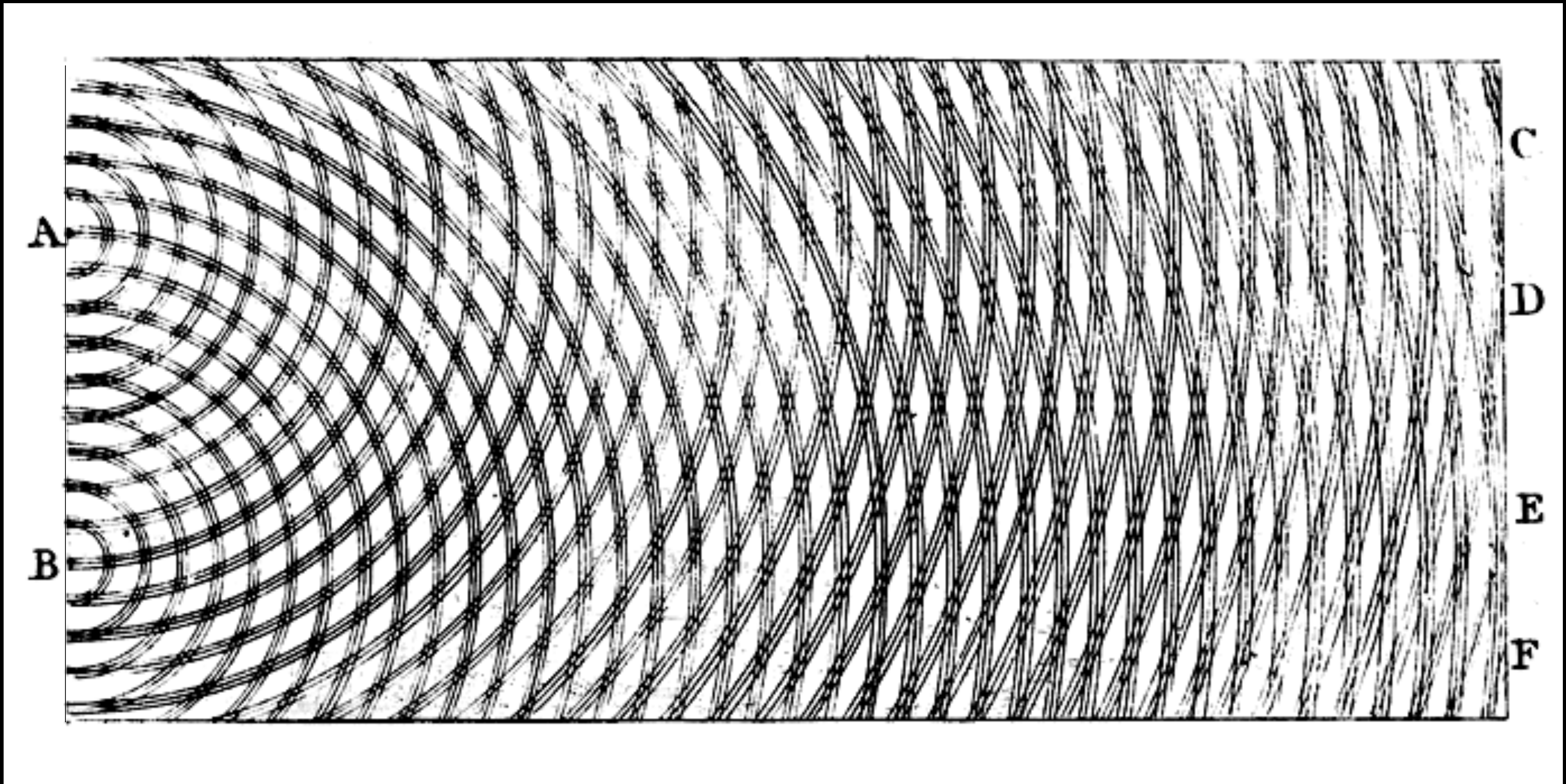
1st order diffraction



AA' is tangent to wavefronts of secondary wavelets from adjacent sources that differ by one wavelength.

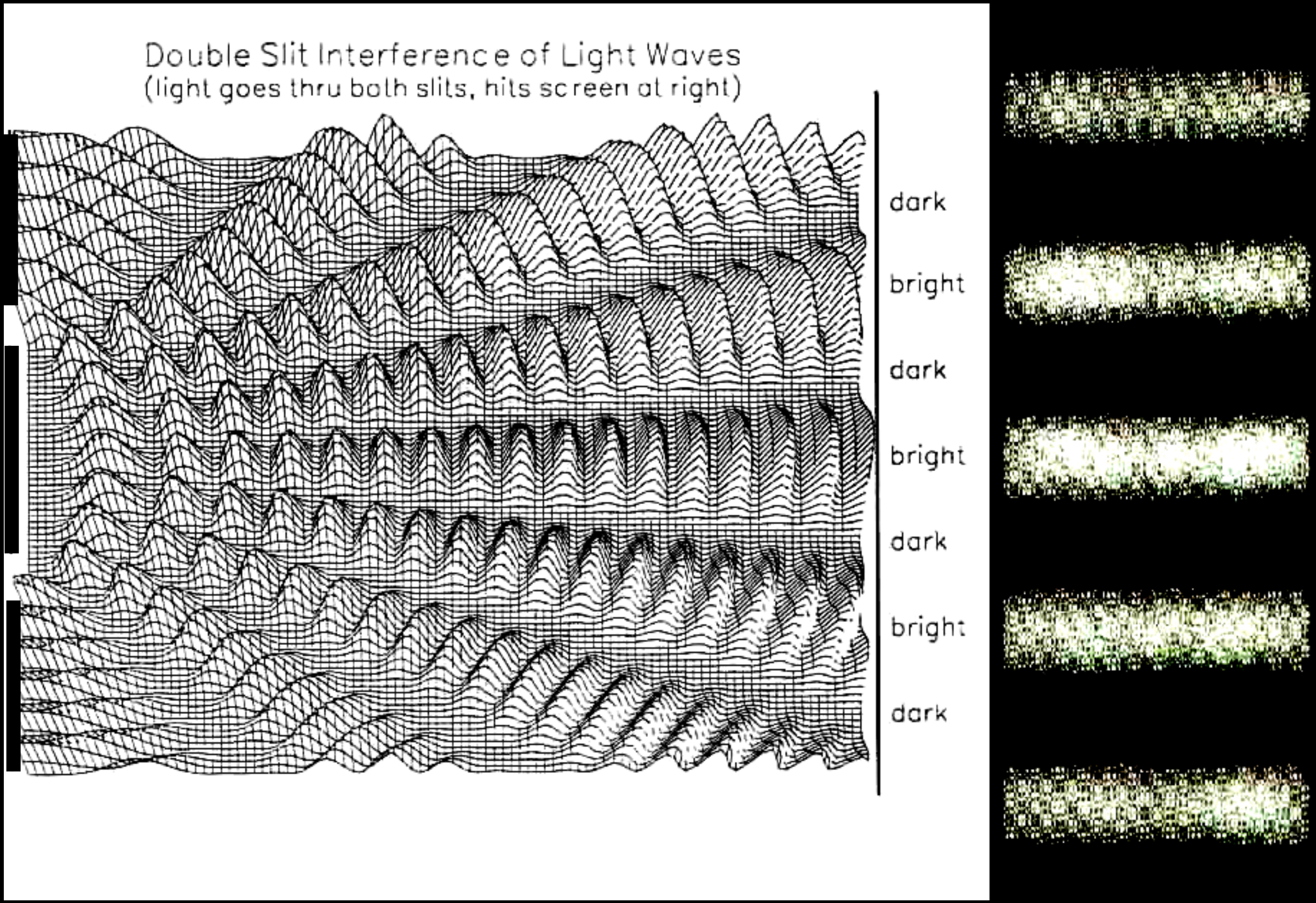
http://www.britannica.com/ebc/art-3156

Thomas Young's drawing to explain the results of his two-slit interference experiment in 1803



http://en.wikipedia.org/wiki/Diffraction

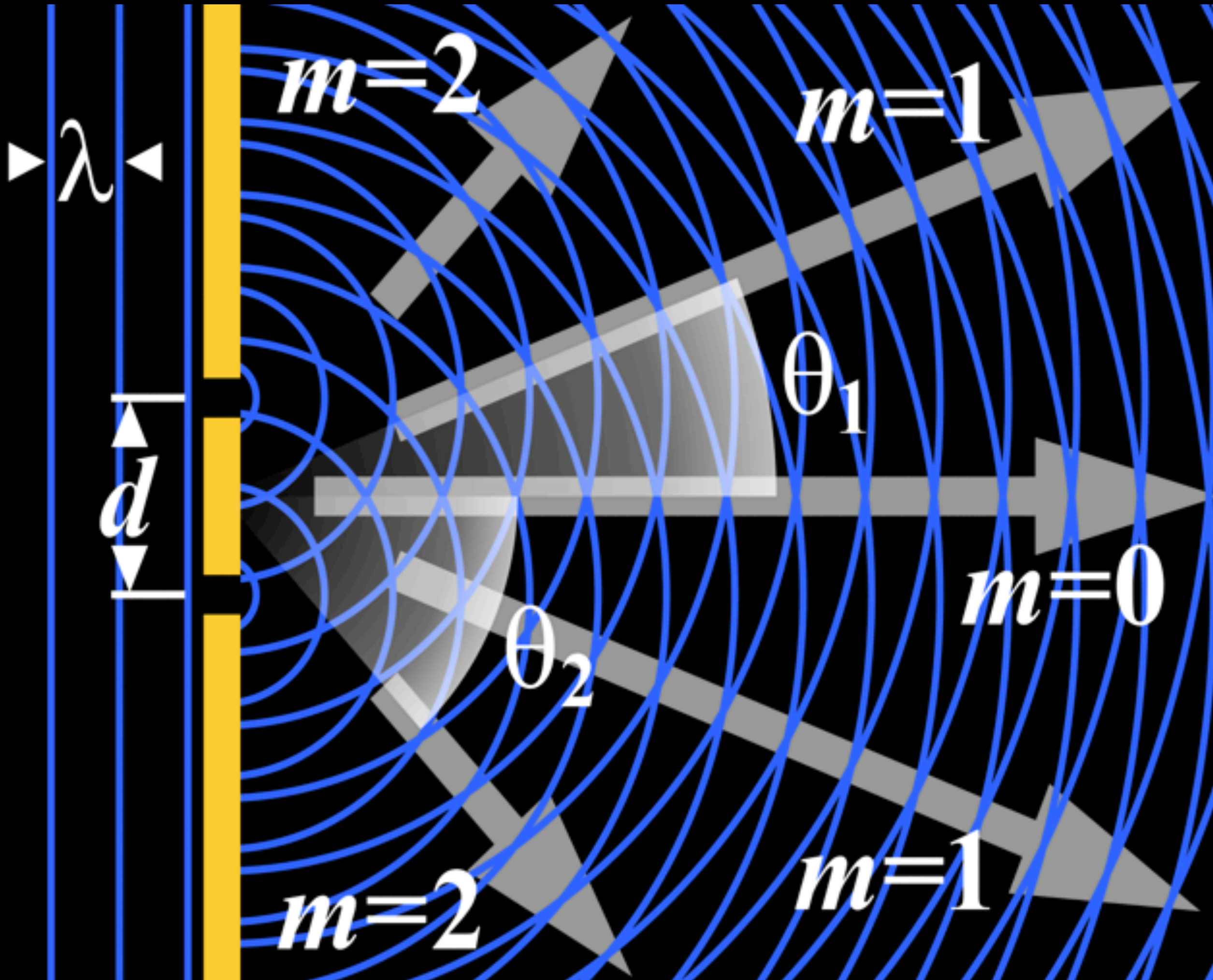
Double Slit Interference of Light Waves



http://physics.weber.edu/carroll/honors-time/doubleslit.htm

Huygens-Fresnel construction for Young's two-slit experiment

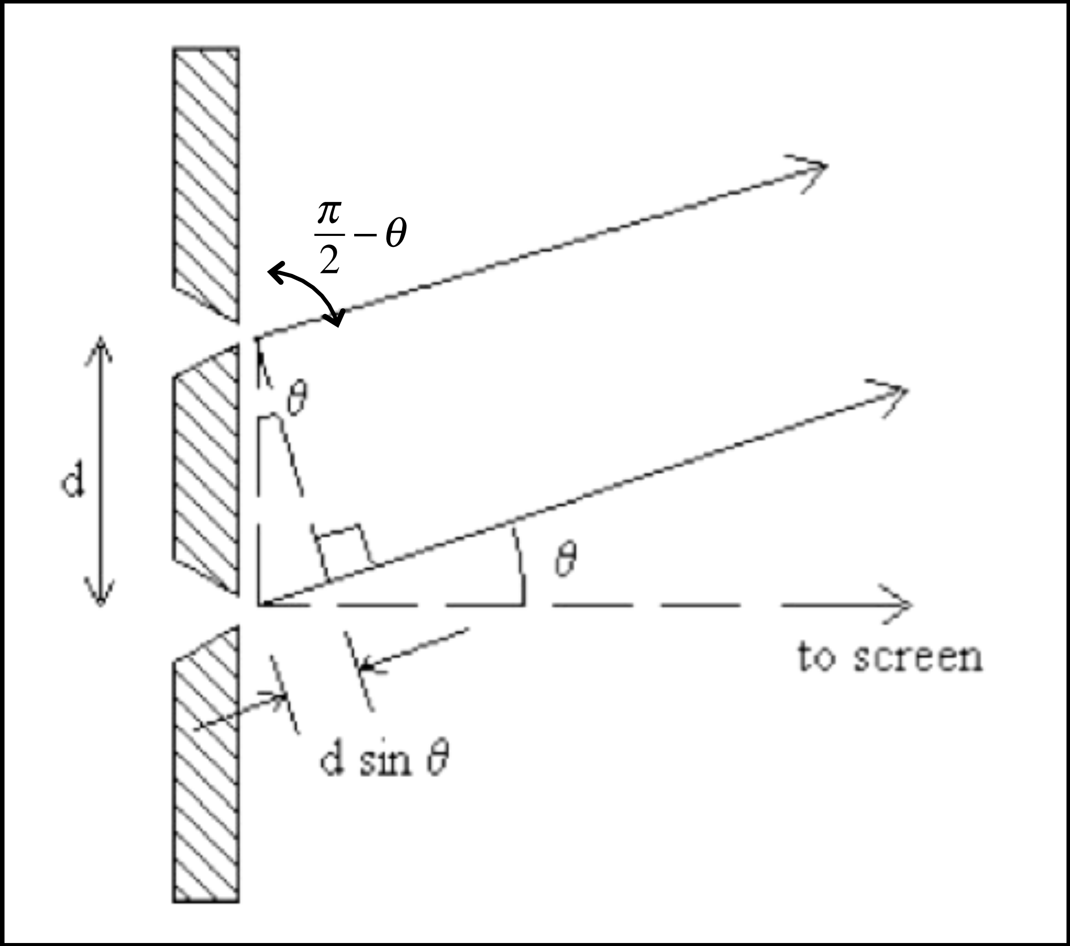
$d \approx 2.5\,\lambda$



Constructive interference in the directions with $\sin\theta_m = m\lambda/d$

http://commons.wikimedia.org/wiki/Image:Two-Slit_Diffraction.png

Fraunhofer (far field) diffraction condition

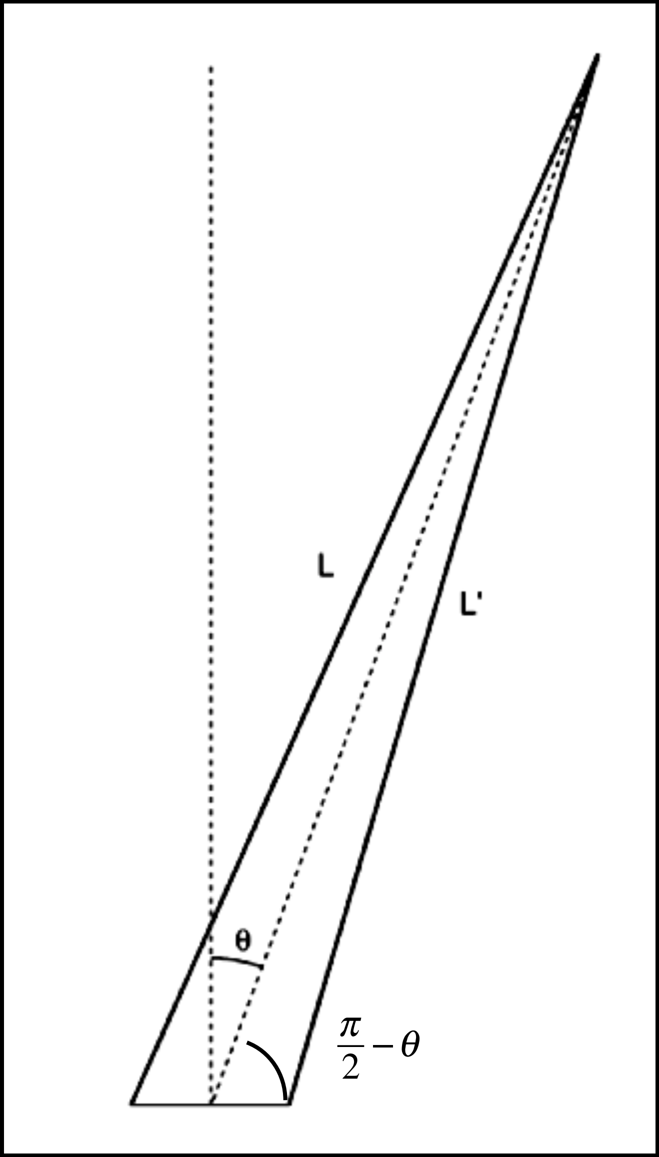


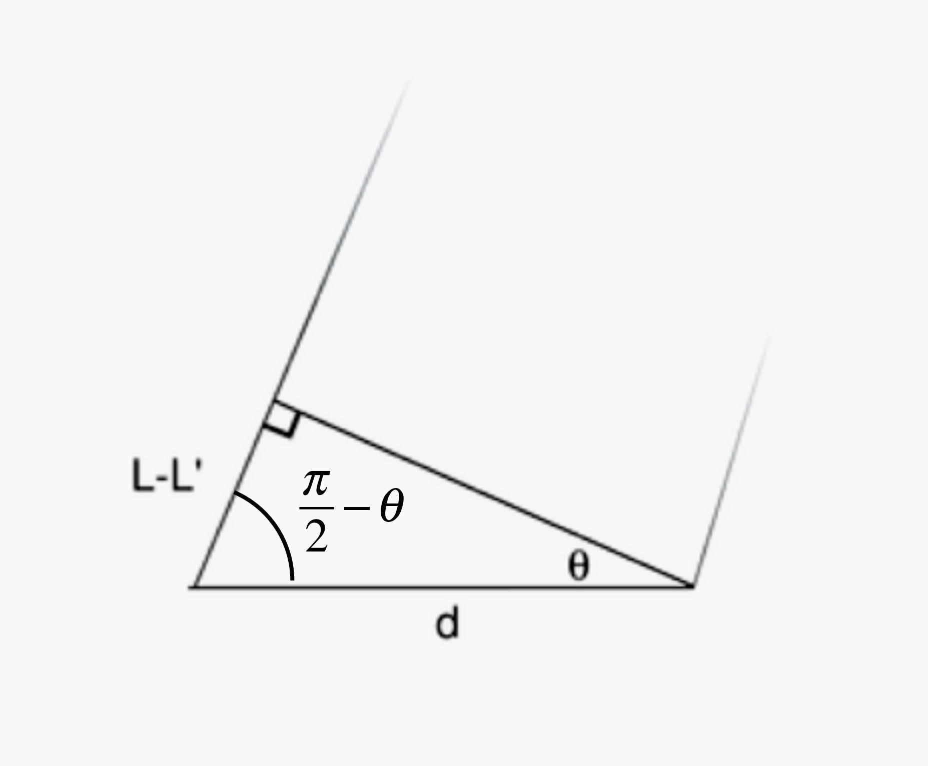
bright $\quad d\sin\theta = m\lambda$

dark $\quad d\sin\theta = \left(m+\frac{1}{2}\right)\lambda$

$m = 0, \pm 1, \pm 2, ...$

Path length difference ΔL at scattering angle θ





$$\Delta L = L - L' = d\sin\theta$$

$$\Delta L = \begin{cases} n\lambda & \Rightarrow \quad \textbf{constructive interference} \\ \left(n+\frac{1}{2}\right)\lambda & \Rightarrow \quad \textbf{destructive interference} \end{cases}$$

Some Elementary Principles of Wave Motion

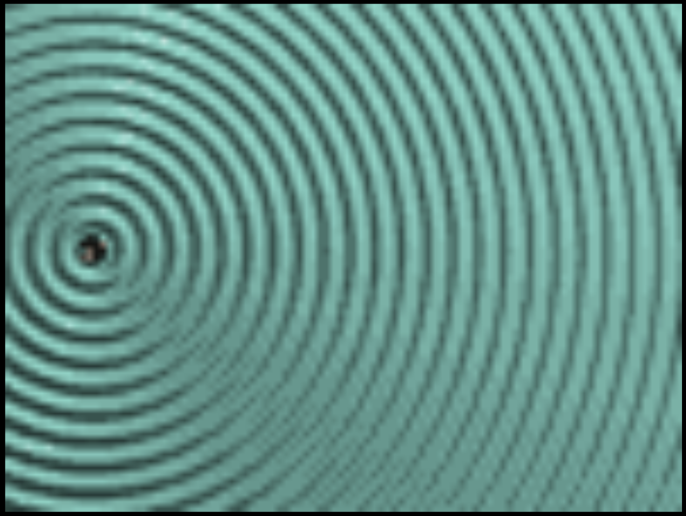
Sinusoidal surface wave

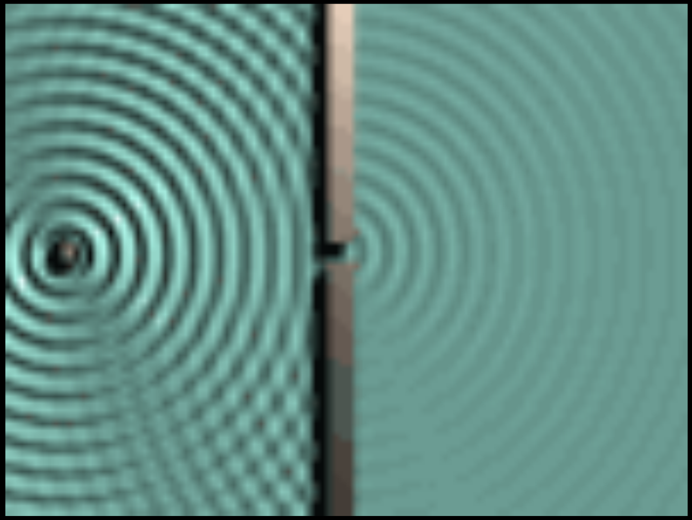
Ripples from a pebble dropped into a still pond

Constructive and destructive interference of water surface waves

https://www.flickr.com/photos/brewbooks/309494512/in/photostream/

Wave Interference and Diffraction

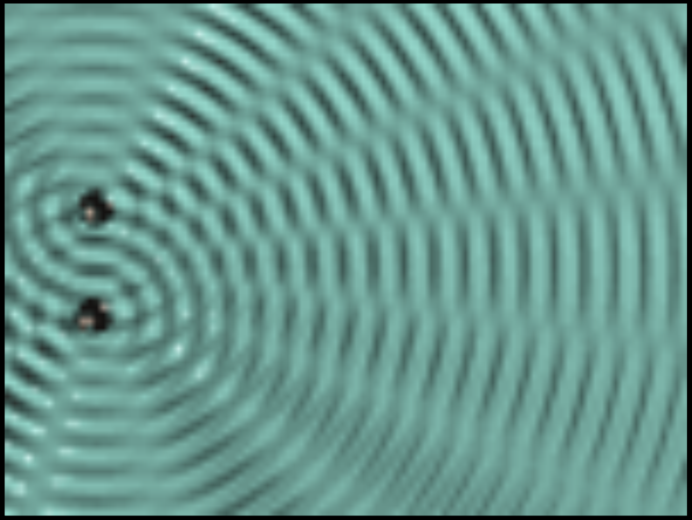




$$\theta_2 = \sin^{-1}(2\lambda/d)$$

$$\sin\theta_n = n\lambda/d$$

$$d \approx 3.5\lambda$$



$$\theta_1 = \sin^{-1}(\lambda/d)$$

$$\sin\theta_1 \approx 0.29$$

$$\theta_1 \approx 16°$$

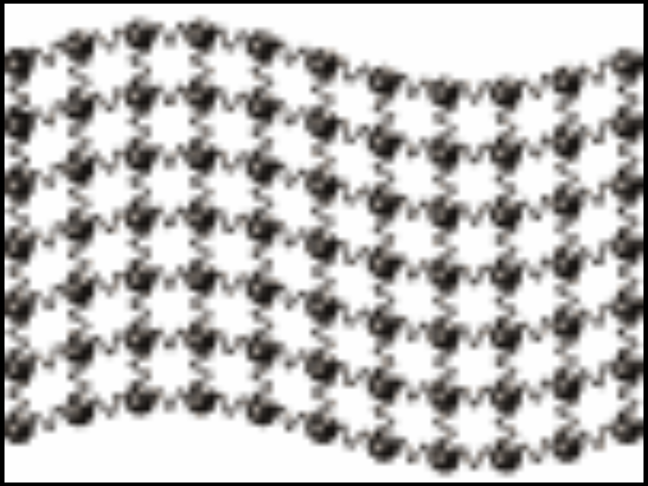
$$\theta_0 = 0$$

$$\sin\theta_2 \approx 0.57$$

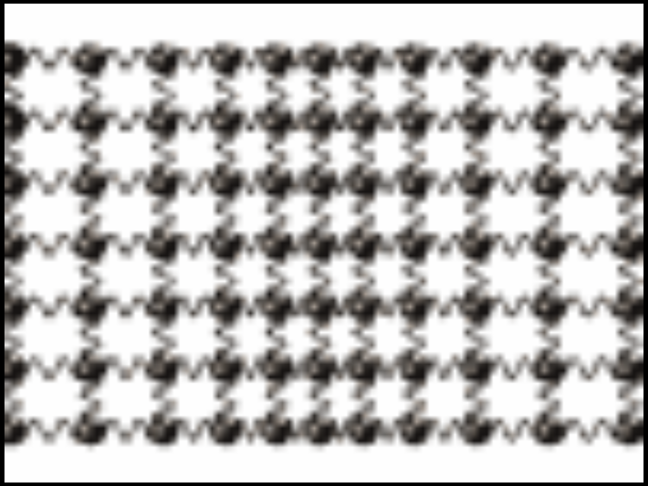
$$\theta_2 \approx 35°$$

http://physics-animations.com/Physics/English/waves.htm

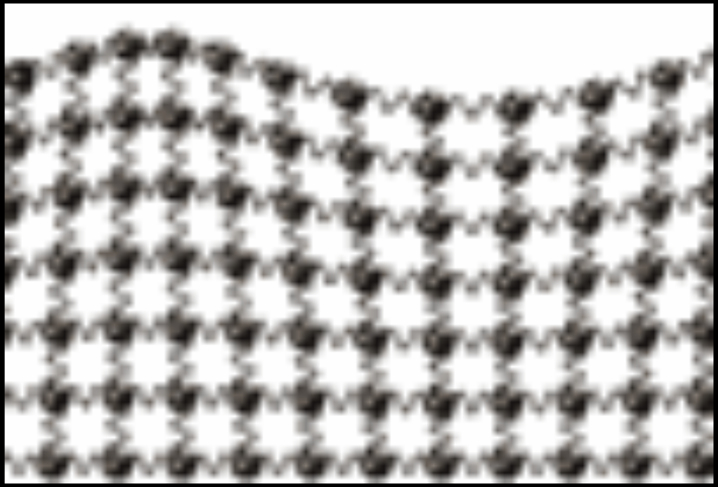
Sinusoidal traveling waves



Transverse wave



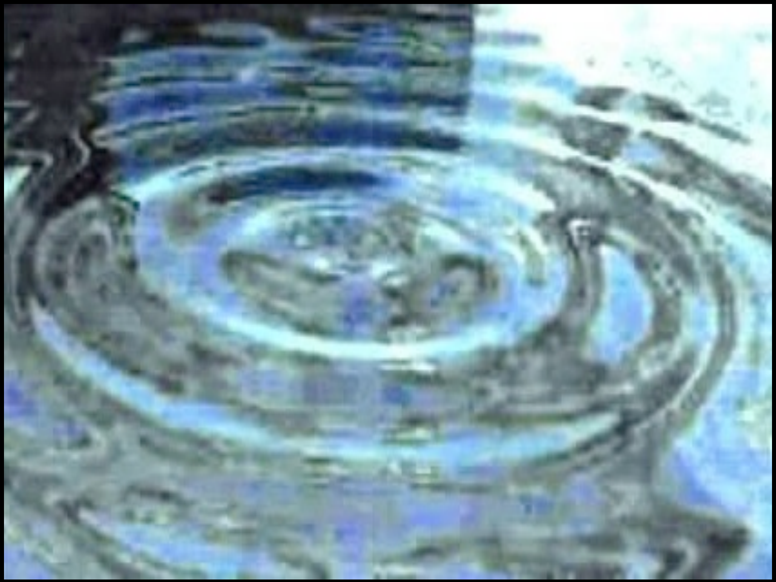
Longitudinal wave

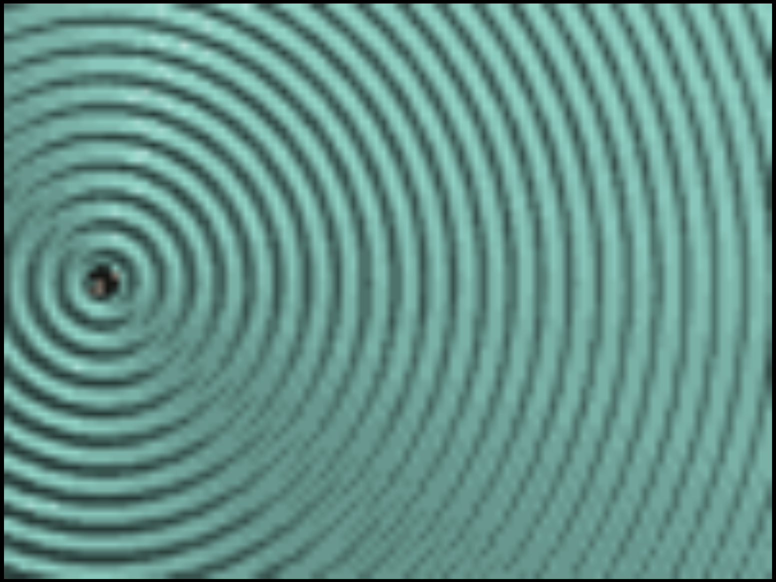


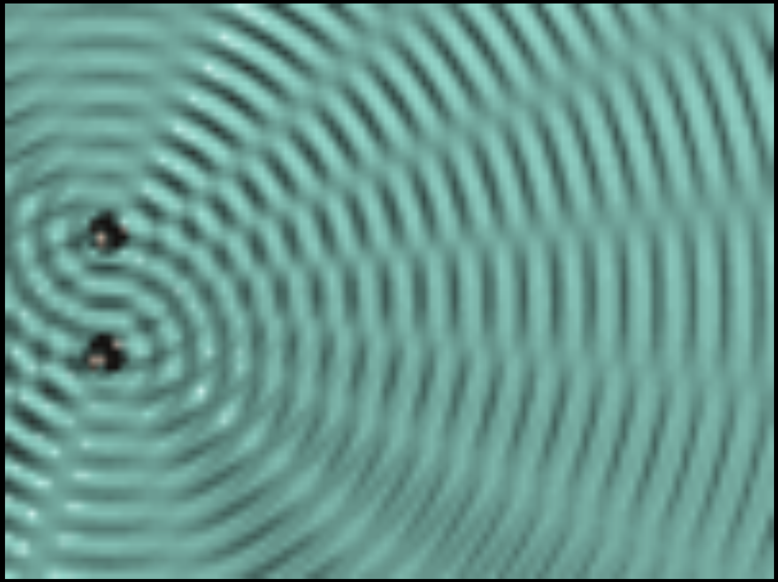
Water wave

http://physics-animations.com/Physics/English/waves.htm

Sinusoidal surface waves and wave interference



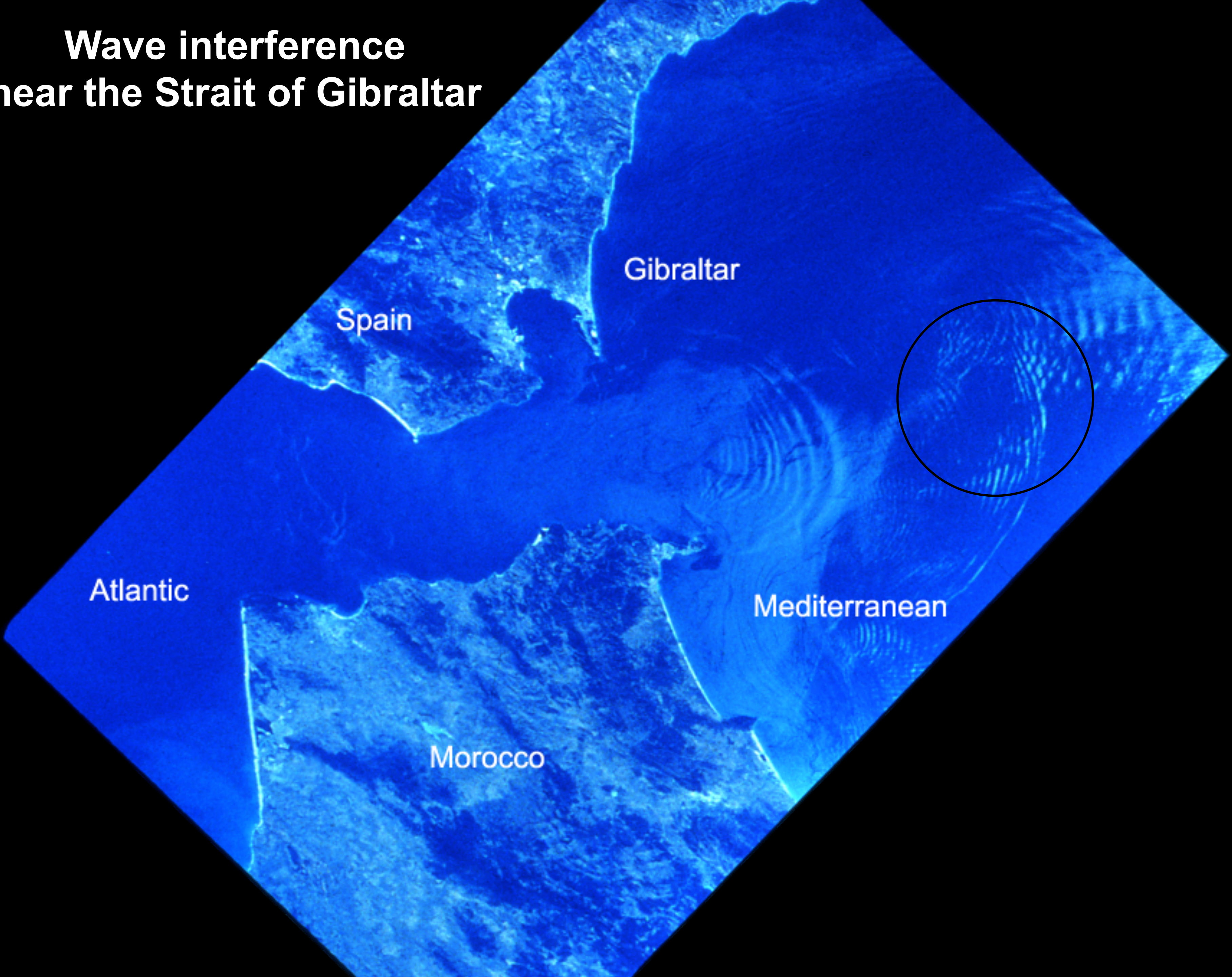




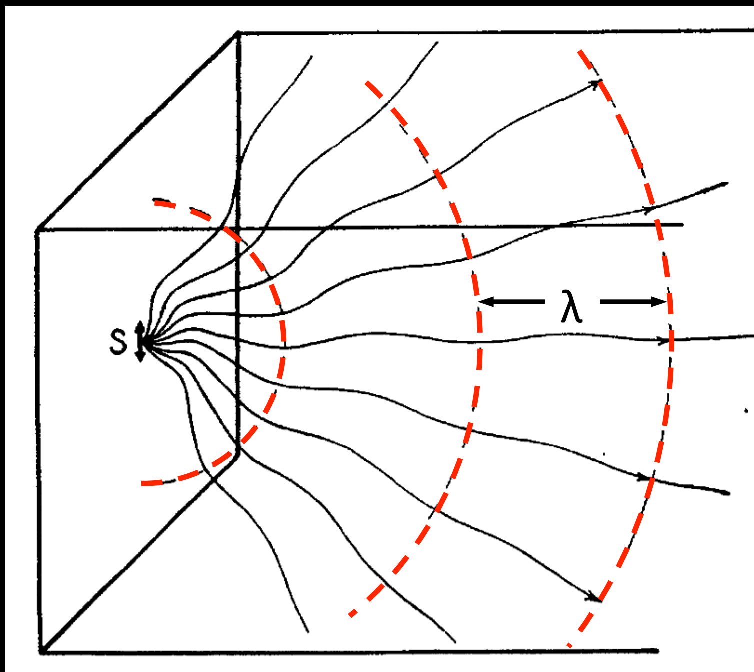
Plane waves passing through slits

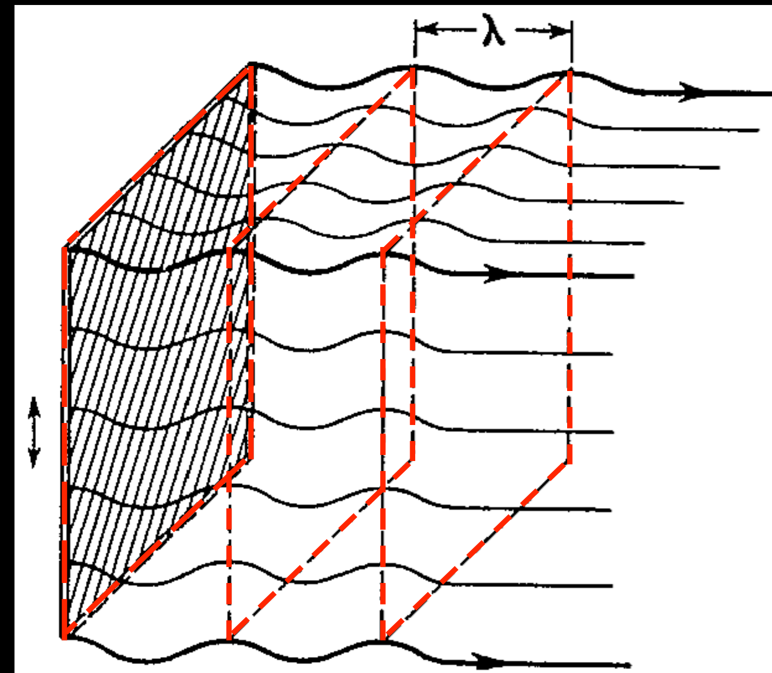
http://www.physics.gatech.edu/gcuoUltrafastOptics/OpticsI/lectures/OpticsI-20-Diffraction-I.ppt

Wave interference near the Strait of Gibraltar



Transverse wave in a homogeneous medium





Spherical wave

near field

amplitude $1/R$

$\propto$

intensity amplitude ^{2}

intensity $1/R^2$

$\propto$

$\propto$

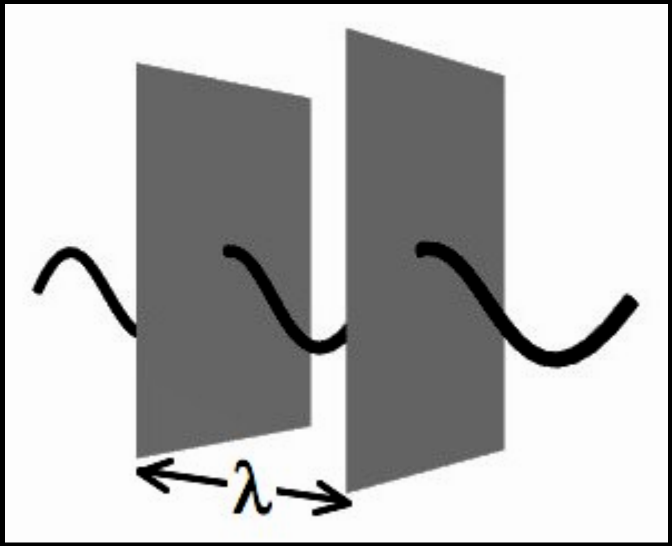
Plane wave

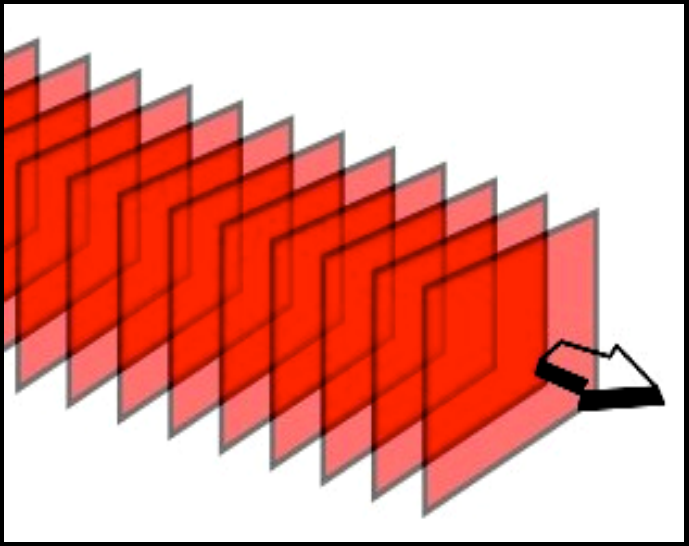
constant amplitude

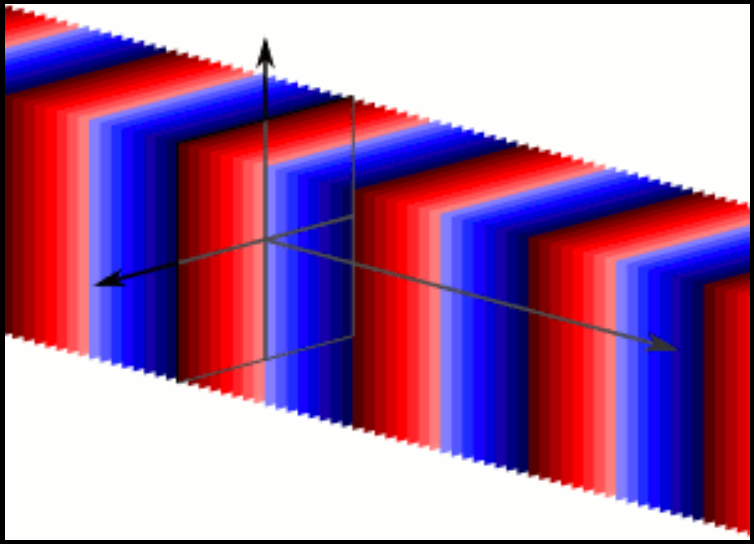
intensity = energy area^{-1} time^{-1}

F.A. Jenkins and H.E. White (1957). ***Fundamentals of Optics.*** **3rd ed. New York: McGraw-Hill Book Co., Inc.**

Plane-wave wavefronts
Wavefronts are surfaces of constant phase.

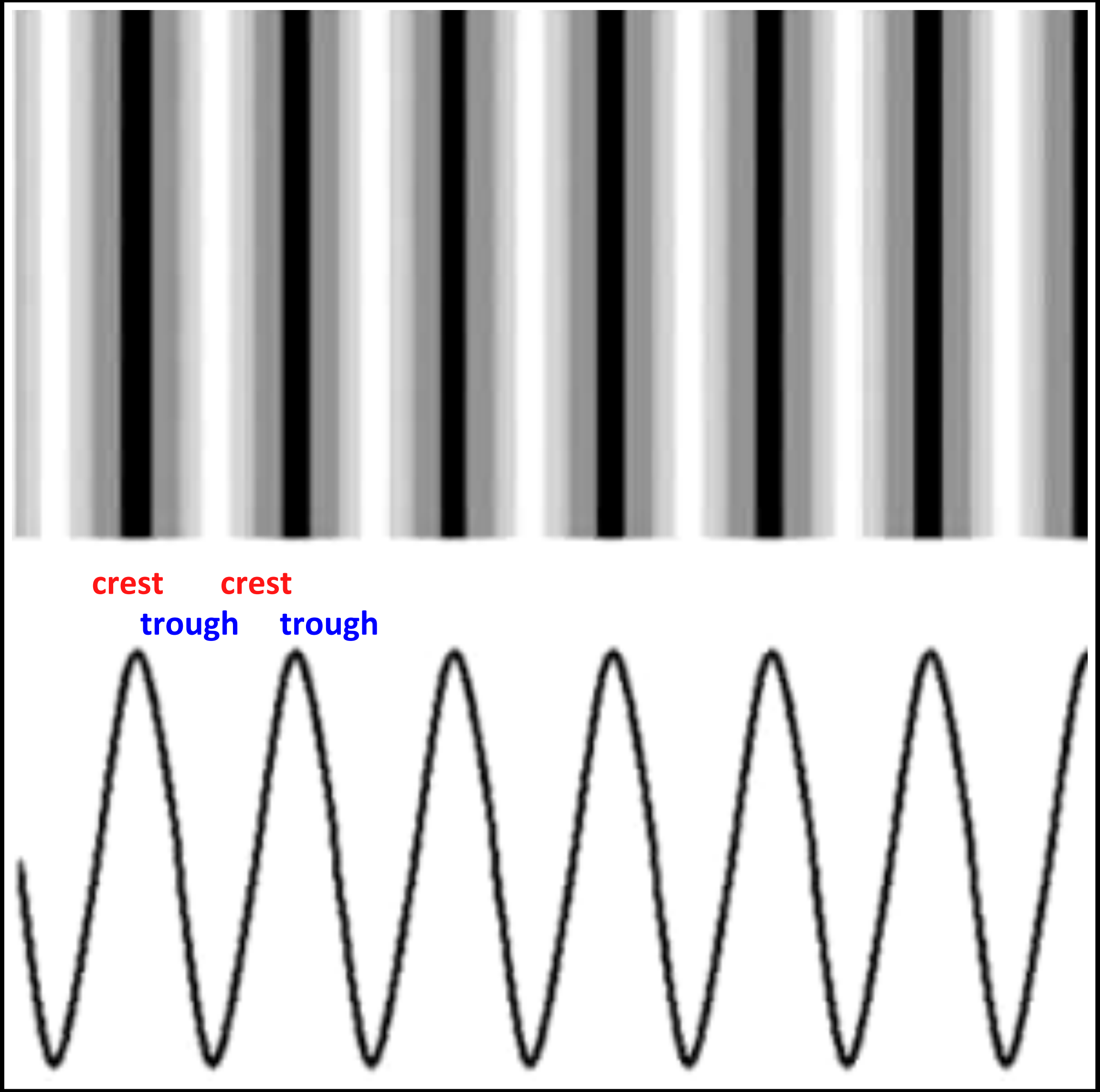






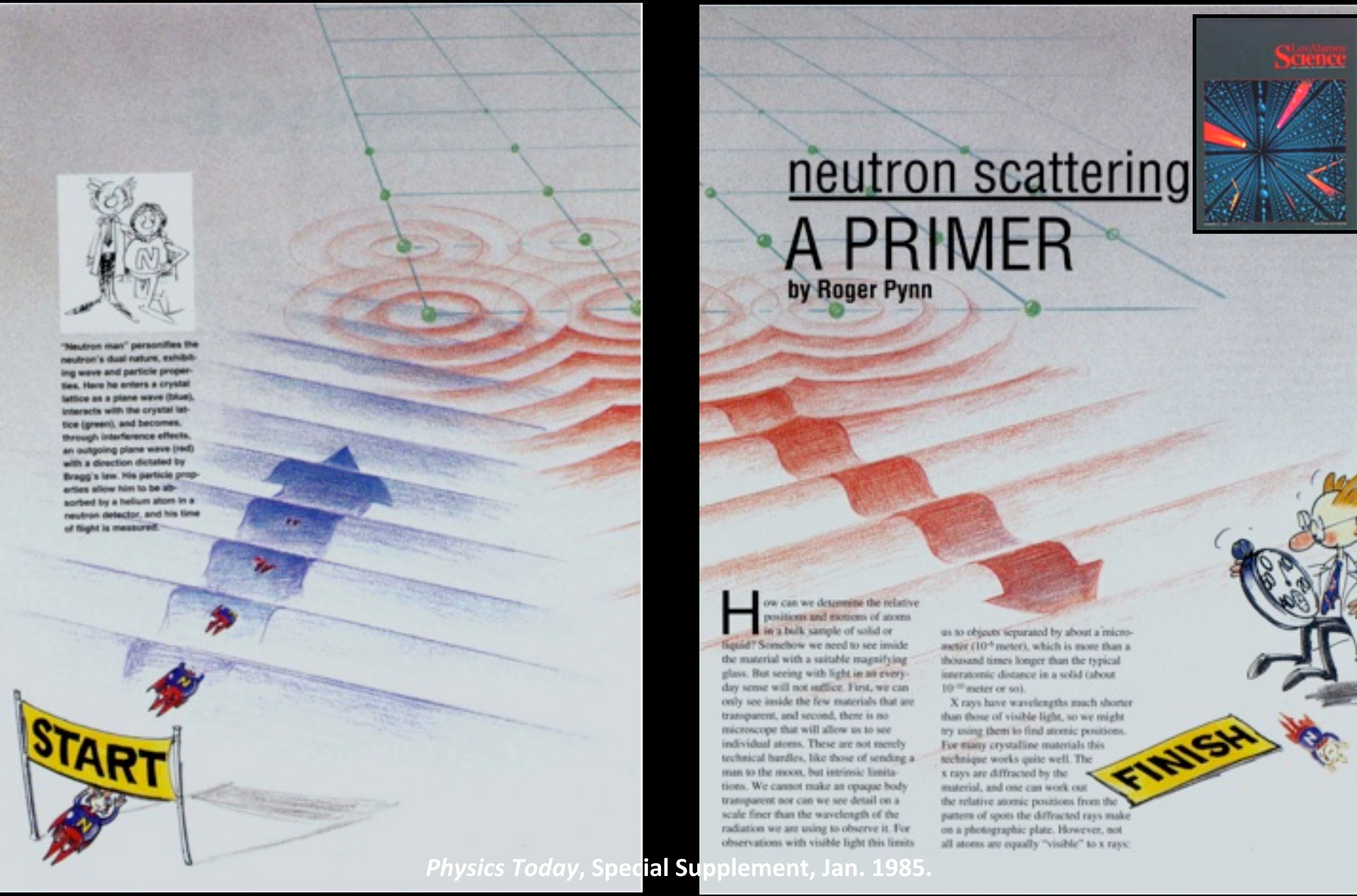
http://en.wikipedia.org/wiki/Plane_wave http://gemologyproject.com/wiki/index.php?title=Image:Wavefront.png

Projection and cross-section views of a sinusoidal plane wave



http://www.school-for-champions.com/science/waves.htm

Incident plane wave **Scattered spherical waves**


"Neutron man" personifies the neutron's dual nature, exhibiting wave and particle properties. Here he enters a crystal lattice as a plane wave (blue), interacts with the crystal lattice (green), and becomes, through interference effects, an outgoing plane wave (red) with a direction dictated by Bragg's law. His particle properties allow him to be absorbed by a helium atom in a neutron detector, and his time of flight is measured.

neutron scattering
A PRIMER
by Roger Pynn

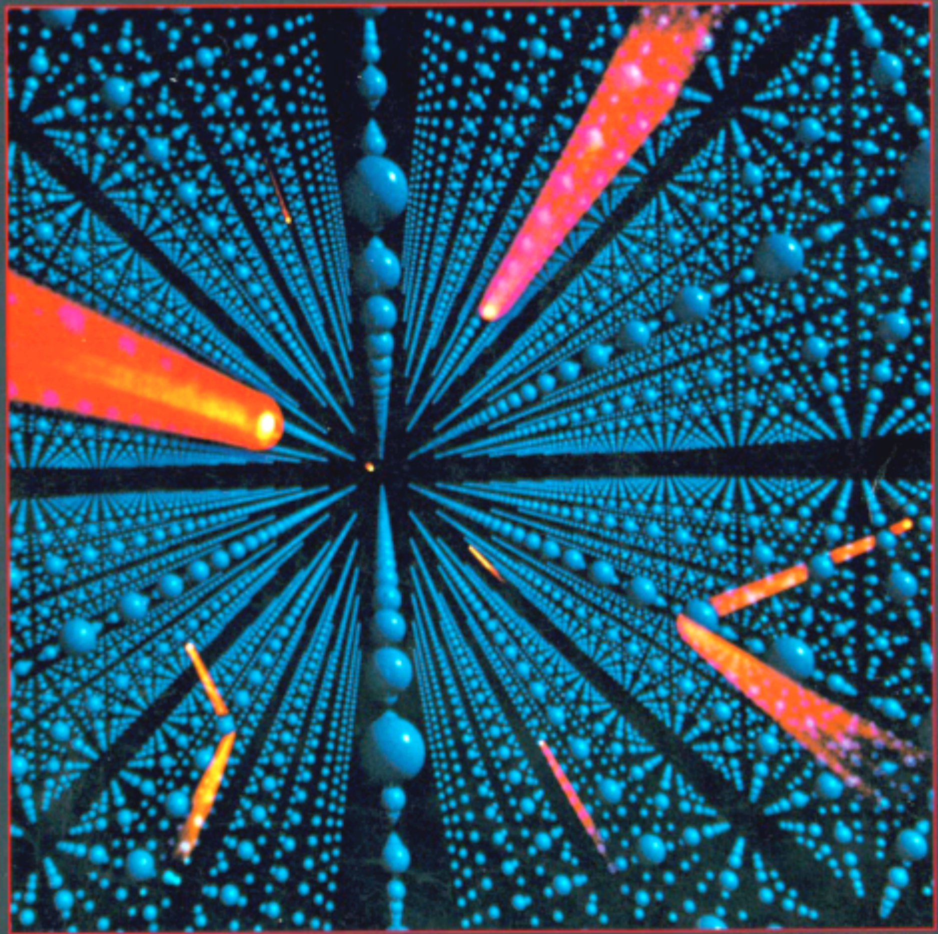
How can we determine the relative positions and motions of atoms in a bulk sample of solid or liquid? Somehow we need to see inside the material with a suitable magnifying glass. But seeing with light in an everyday sense will not suffice. First, we can only see inside the few materials that are transparent, and second, there is no microscope that will allow us to see individual atoms. These are not merely technical hurdles, like those of sending a man to the moon, but intrinsic limitations. We cannot make an opaque body transparent nor can we see detail on a scale finer than the wavelength of the radiation we are using to observe it. For observations with visible light this limits us to objects separated by about a micrometer (10^{-6} meter), which is more than a thousand times longer than the typical interatomic distance in a solid (about 10^{-10} meter or so).

X rays have wavelengths much shorter than those of visible light, so we might try using them to find atomic positions. For many crystalline materials this technique works quite well. The x rays are diffracted by the material, and one can work out the relative atomic positions from the pattern of spots the diffracted rays make on a photographic plate. However, not all atoms are equally "visible" to x rays:

Physics Today, Special Supplement, Jan. 1985.

http://la-science.lanl.gov/lascience19.shtml

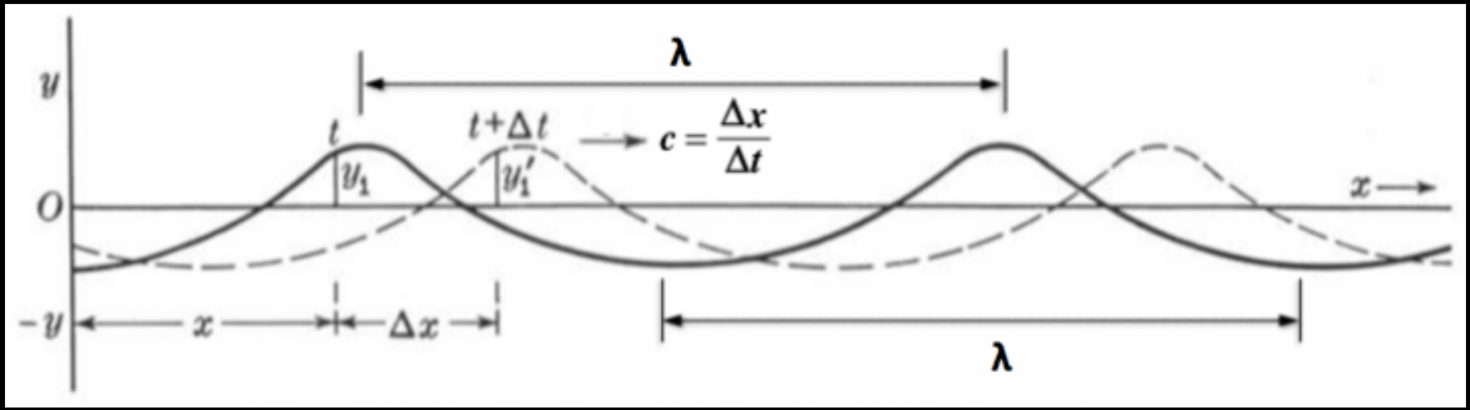
Los Alamos Science
LOS ALAMOS NATIONAL LABORATORY



NUMBER 19 1990

NEUTRON SCATTERING

Propagation of a water surface wave



$$y_1 = f(x - ct)$$
$$y_1' = f[(x + \Delta x) - c(t + \Delta t)] = f[(x - ct) + (\Delta x - c\Delta t)] = y_1$$
$$c = \frac{\Delta x}{\Delta t} \quad \Rightarrow \quad \Delta x = c\,\Delta t$$

The composite function chain rule: $y = f(u(x)) \quad \Rightarrow \quad \frac{\partial y}{\partial x} = \frac{\partial f}{\partial u}\frac{\partial u}{\partial x} = f'(u)\frac{\partial u}{\partial x}$

$$\underbrace{\frac{\partial y}{\partial x} = f'(x - ct)}_{\text{Slope at } x}, \qquad \underbrace{\frac{\partial y}{\partial t} = -c\, f'(x - ct)}_{\text{Velocity at } t}$$

$$\underbrace{\frac{\partial^2 y}{\partial x^2} = f''(x - ct)}_{\text{Curvature at } x}, \qquad \underbrace{\frac{\partial^2 y}{\partial t^2} = c^2 f''(x - ct)}_{\text{Acceleration at } t}$$

$$\underbrace{\frac{\partial^2 y}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2 y}{\partial t^2}}_{\text{The wave equation}}$$

F.A. Jenkins and H.E. White (1957). *Fundamentals of Optics.* 3rd ed. New York: McGraw-Hill Book Co., Inc.

From *a wave function* to *the wave equation*

Given a general form for the ***wave function*** for a traveling wave,

$$y = f\big(u(x,t)\big), \qquad u = (x - ct),$$

application of the chain rule for differentiation gives

$$\begin{cases} \dfrac{\partial y}{\partial x} = \dfrac{\mathrm{d}f}{\mathrm{d}u}\dfrac{\partial u}{\partial x} = f'(u)\dfrac{\partial u}{\partial x} = f'(x-ct) \\[2ex] \dfrac{\partial y}{\partial t} = \dfrac{\mathrm{d}f}{\mathrm{d}u}\dfrac{\partial u}{\partial t} = f'(u)\dfrac{\partial u}{\partial t} = -c\,f'(x-ct) \end{cases}$$

$$\begin{cases} \dfrac{\partial^2 y}{\partial x^2} = f''(u)\dfrac{\partial u}{\partial x} = f''(x-ct) \\ \\ \end{cases}$$

and thence ***the wave equation***,

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2 y}{\partial t^2}.$$

The *dispersion relations* for a wave function

Dispersion relations describe the interrelationship of the wave properties: wavelength $\boldsymbol{\lambda}$, period $\boldsymbol{\tau}$, speed of propagation ***c***, frequency $\boldsymbol{\omega}$, and wavenumber ***k***.

$$y = f(x, t) = f(x - ct)$$

$$c = \lambda / \tau$$

$$\omega = 2\pi\nu = 2\pi/\tau = 2\pi c/\lambda$$

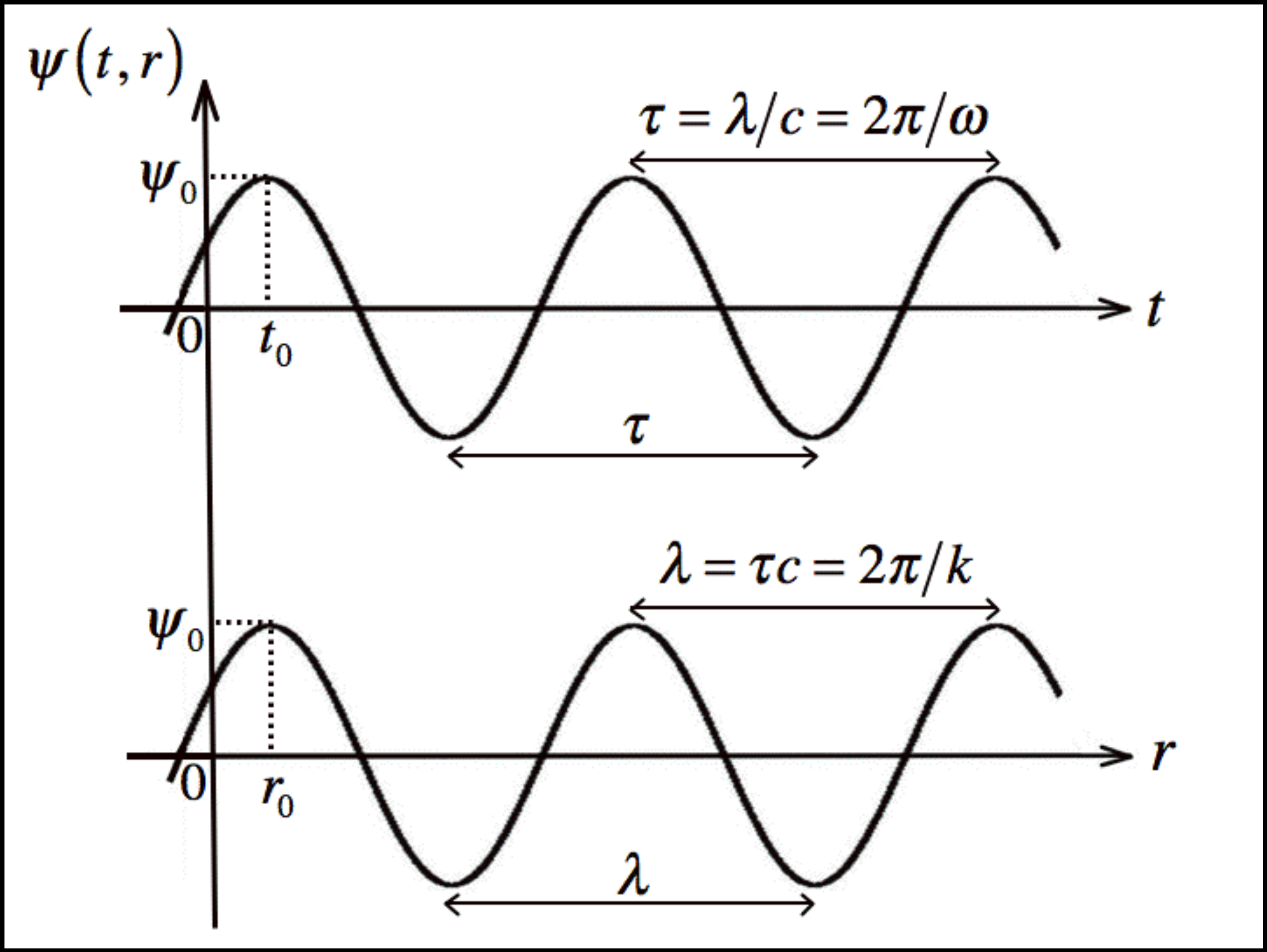
$$k = 2\pi\sigma = 2\pi/\lambda = 2\pi c/\tau$$

$$c = \frac{\lambda}{\tau} = \lambda\nu = \left(\frac{2\pi}{k}\right)\left(\frac{\omega}{2\pi}\right) = \frac{\omega}{k}$$

$$y = f(x - ct) = f\left[x - (\omega/k)t\right] = f\left[(kx - \omega t)/k\right]$$

Sinusoidal wave function

$$\psi = \psi\left(t, r\right)$$



$$\psi = \mathrm{Re}\left[\psi_0 e^{i(\omega t - \mathbf{k}\bullet\mathbf{r} - \varphi_0)}\right] = \psi_0 \cos\left(\omega t - \mathbf{k}\bullet\mathbf{r} - \varphi_0\right), \qquad \varphi_0 = \begin{cases} 2\pi t_0/\tau = \omega t_0 \\ 2\pi r_0/\lambda = k r_0 \end{cases}$$

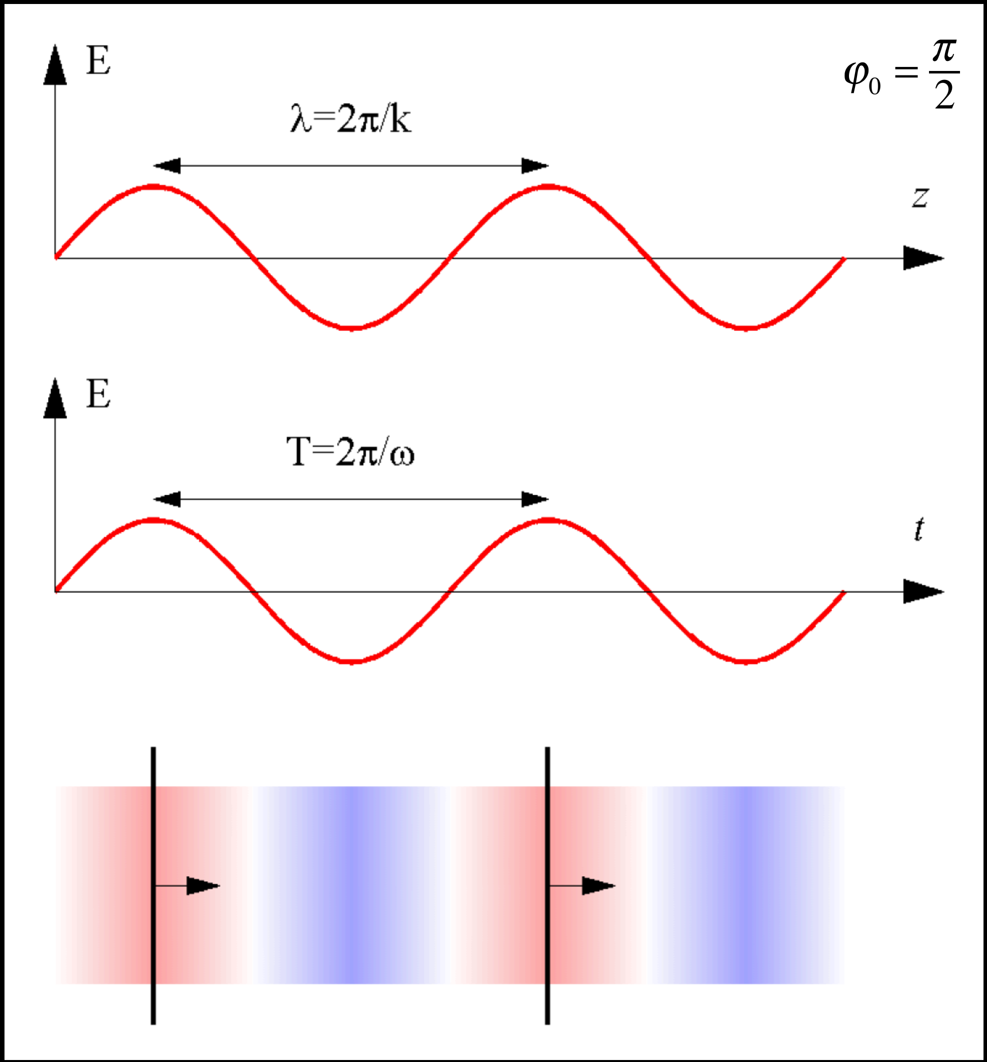
Wave properties

$$\psi = \mathrm{Re}\left[\psi_0\, \mathrm{e}^{i(\omega t - \mathbf{k}\bullet\mathbf{r} - \varphi_0)}\right] = \psi_0 \cos\left(\omega t - \mathbf{k}\bullet\mathbf{r} - \varphi_0\right), \qquad \varphi_0 = \begin{cases} 2\pi\, t_0/\tau = \omega t_0 \\ 2\pi\, r_0/\lambda = k r_0 \end{cases}$$

amplitude	$\psi_0 = \psi_{\max}(t, r)$		maximum wave displacement
phase	$\varphi = \varphi(t, r)$	(rad)	argument of the 2π-periodic sinusoidal wave function $\psi = \psi_0 \cos\varphi = \psi_0 \sin\left(\frac{\pi}{2} - \varphi\right)$
wavelength	$\lambda = c\tau$	L	distance crest-to-crest and trough-to-trough
period	$\tau = \lambda/c$	T	time per wave cycle
speed	$c = \lambda/\tau = \lambda\nu$	$L\,T^{-1}$	speed of wave propagation
frequency	$\nu = 1/\tau = c/\lambda$	T^{-1}	wave cycles per unit time
wavenumber	$\sigma = 1/\lambda$	L^{-1}	wave cycles per unit distance
angular frequency	$\omega = 2\pi/\tau = 2\pi\nu$	(rad) T^{-1}	phase angle cycles per unit time
angular wavenumber	$k = 2\pi/\lambda = 2\pi\sigma$	(rad) L^{-1}	phase angle cycles per unit distance

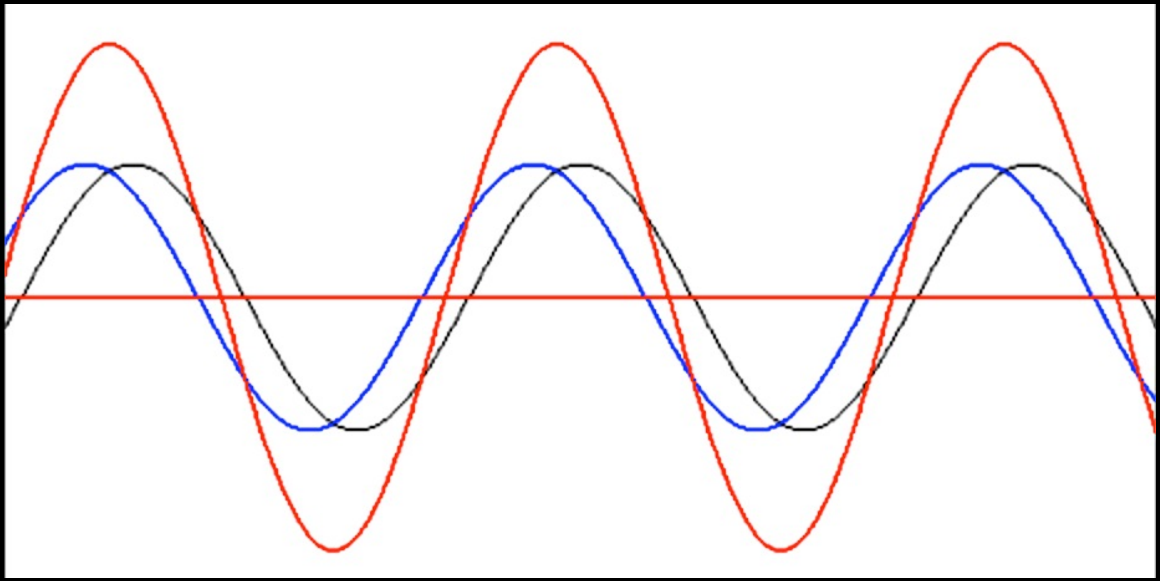
Electromagnetic wave in space-time

$$\mathbf{E} = \mathrm{Re}\left[\mathbf{E}_0\, e^{i(\omega t - \mathbf{k}\cdot\mathbf{r} - \varphi_0)}\right] = \mathbf{E}_0 \cos(\omega t - \mathbf{k}\bullet\mathbf{r} - \varphi_0)$$

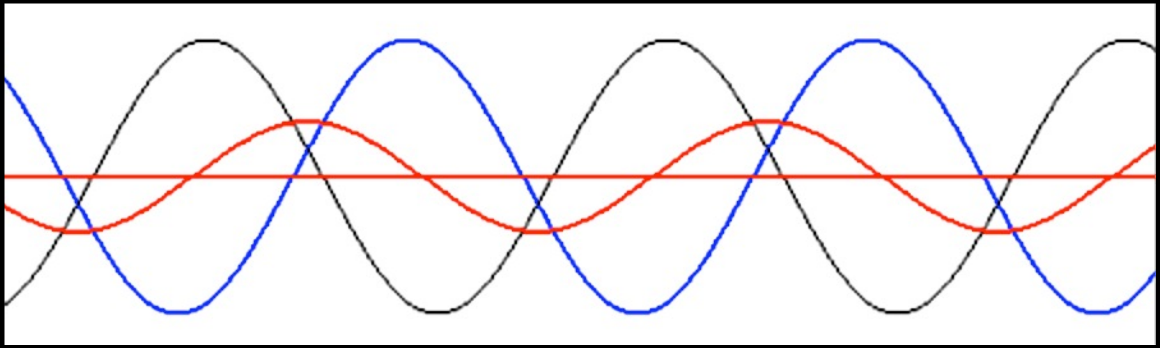


Jens-Als Nielsen & Des McMorrow (2001). *Elements of Modern X-Ray Physics*. New York: John Wiley & Sons.

Superposition of two equal-frequency, equal-amplitude waves



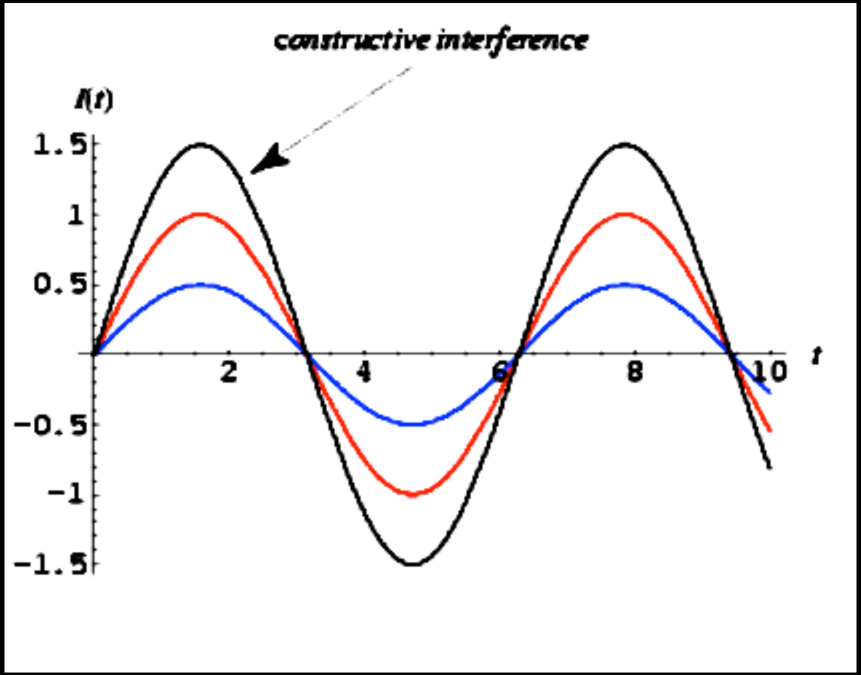
Constructive interference of waves almost in phase

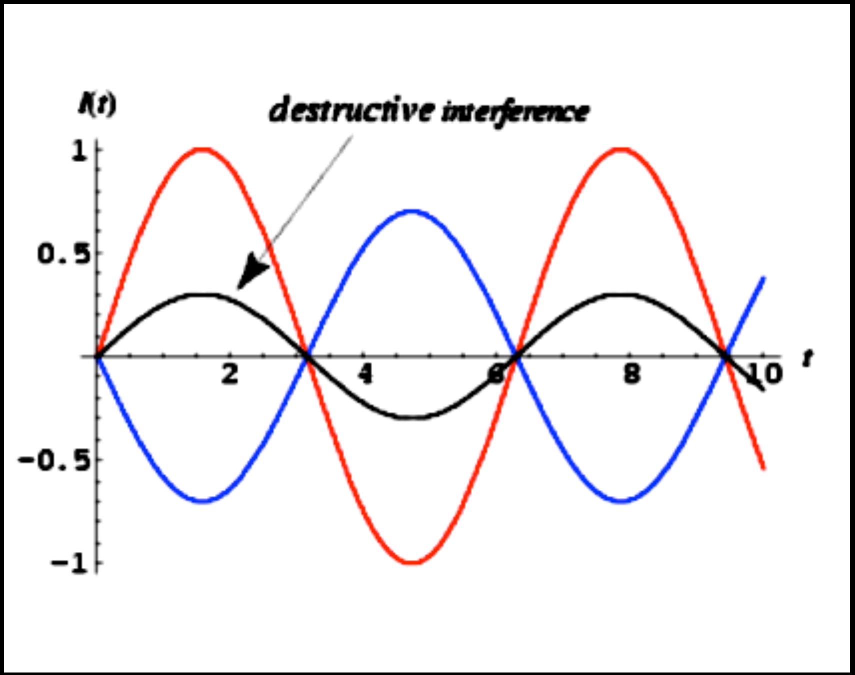


Destructive interference of waves almost 180° out of phase

http://www.phy.ntnu.edu.tw/ntnujava/index.php

Superposition of two equal-frequency, unequal-amplitude waves





in phase

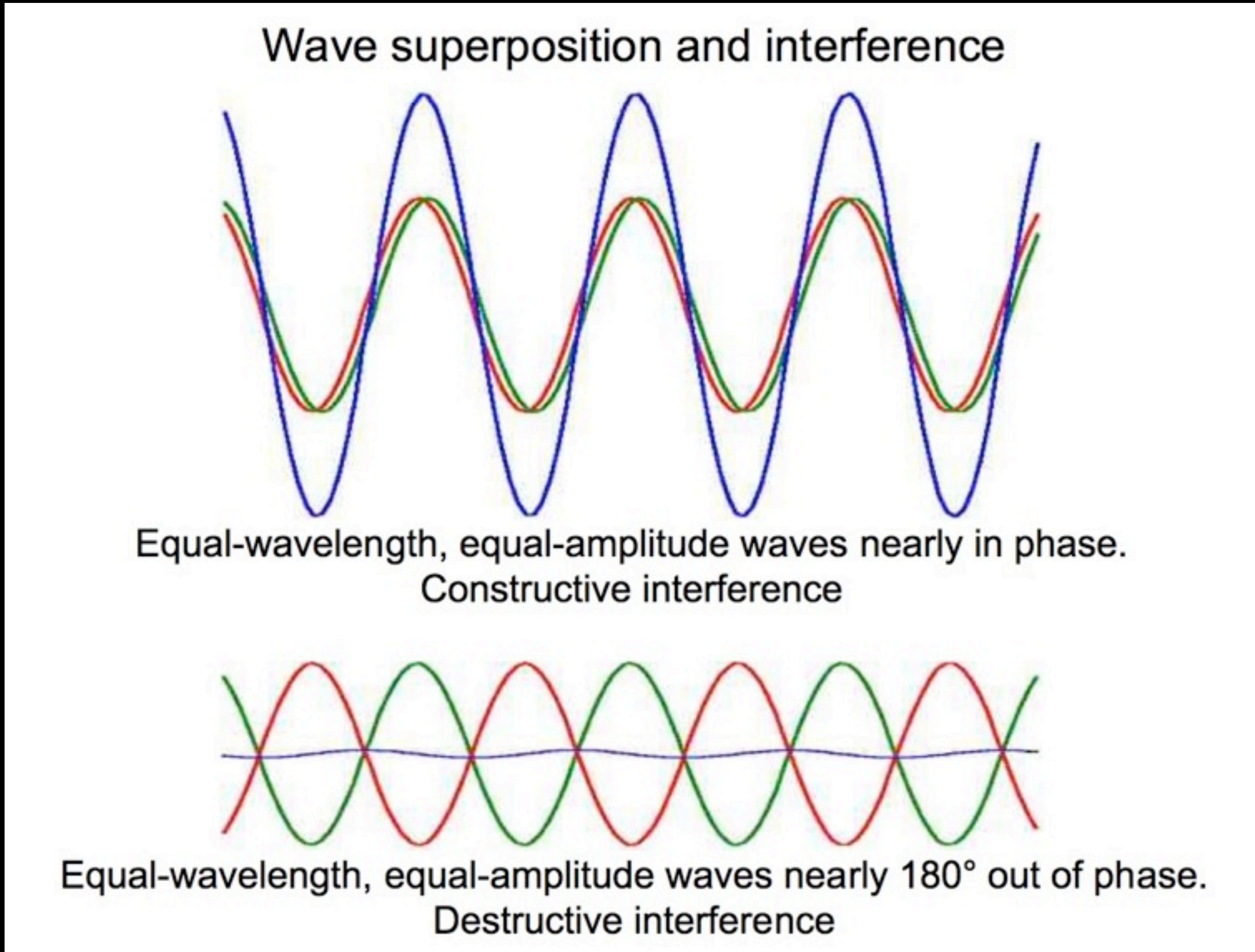
crest on crest
and
trough on trough

180º out of phase

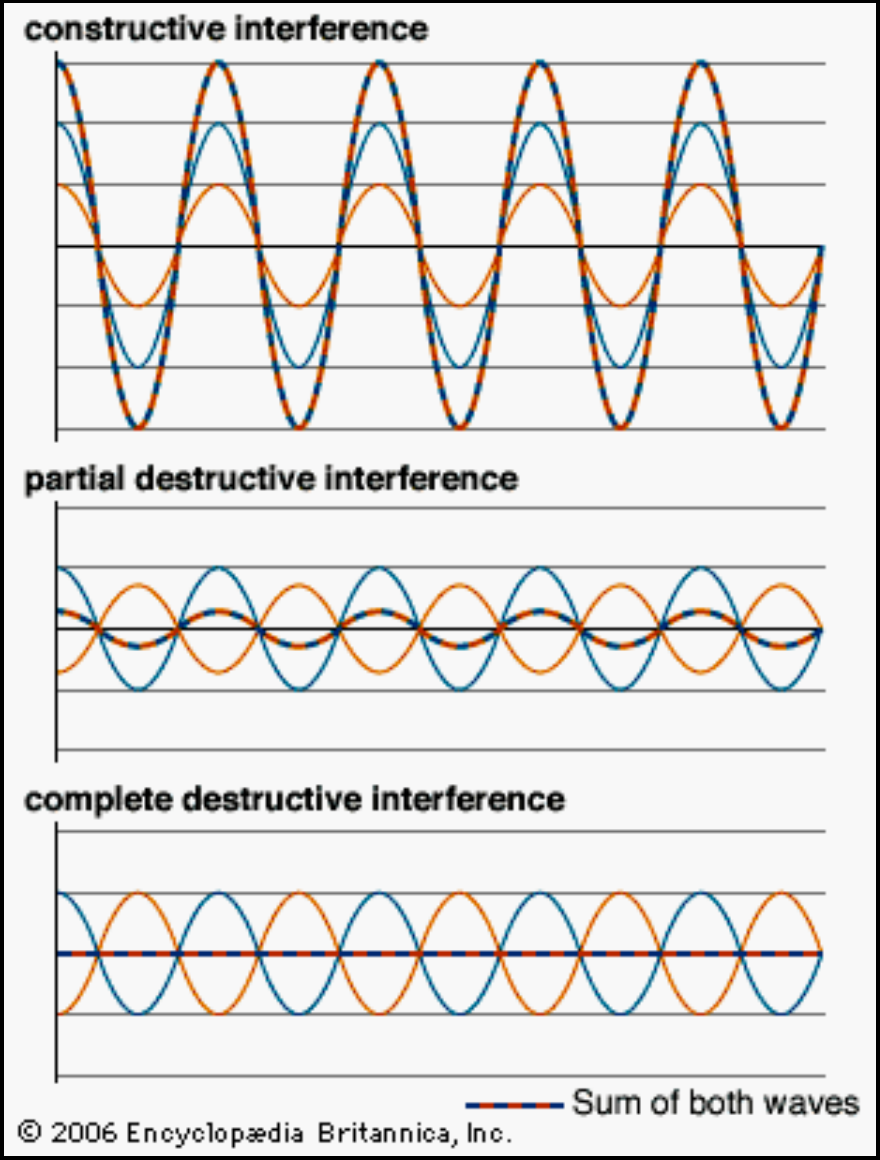
crest on trough
and
trough on crest

http://scienceworld.wolfram.com/physics/ConstructiveInterference.html

Superposition of two equal-frequency, equal-amplitude waves



Superposition and interference of sinusoidal transverse waves of equal wavelength



http://media-2.web.britannica.com/eb-media/95/96595-004-16C2DCAD.gif

Superposition of any number of equal-wavelength sinusoidal (sine and/or cosine) waves gives a sinusoidal resultant wave

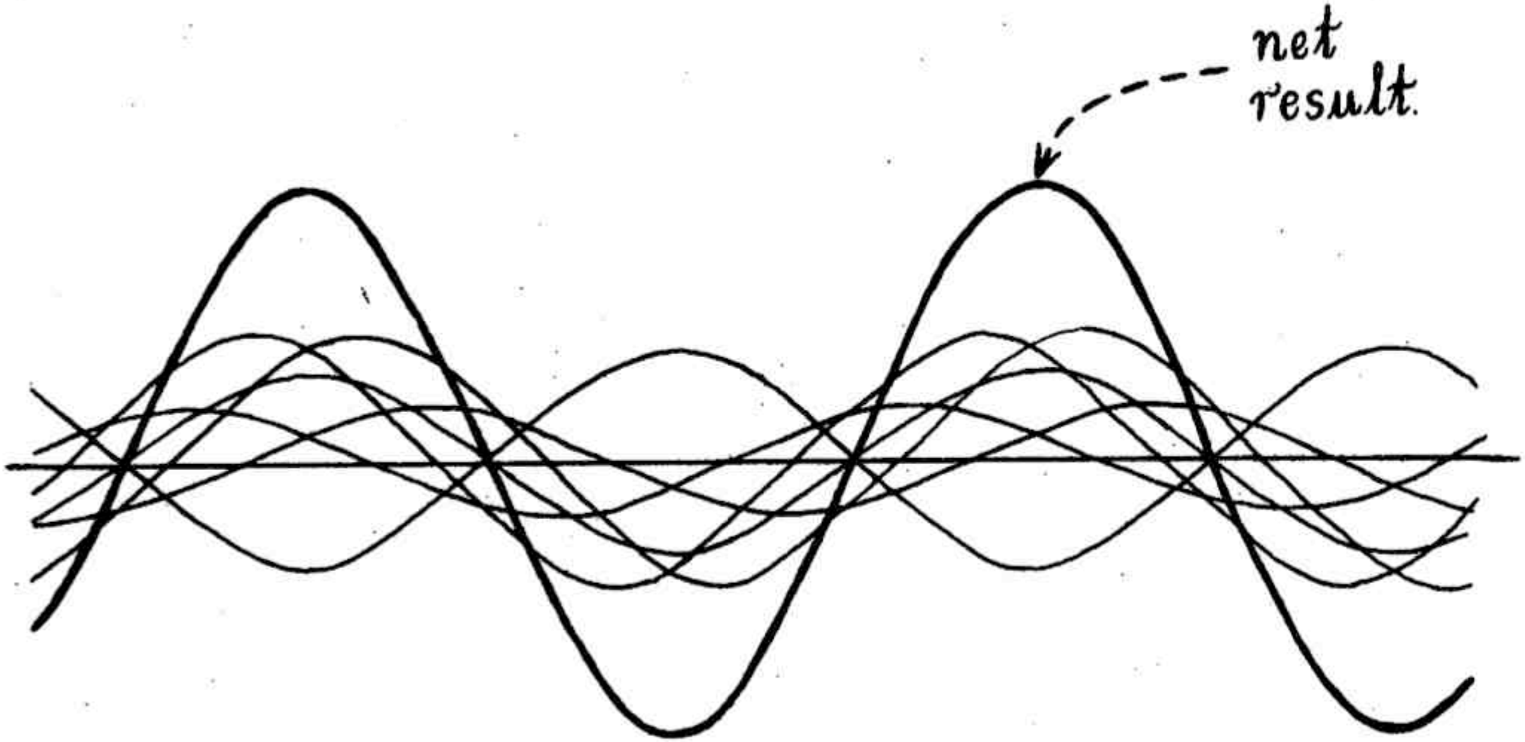


FIG. 115. For complex crystals, the net wave for any particular reflection is the result of a combination of a number of waves out of step by different amounts.

Charles W. Bunn (1964). *Crystals: Their Role in Nature and in Science*. New York: Academic Press

A superposition of three equal-wavelength, equal-amplitude sinusoidal waves with different phases

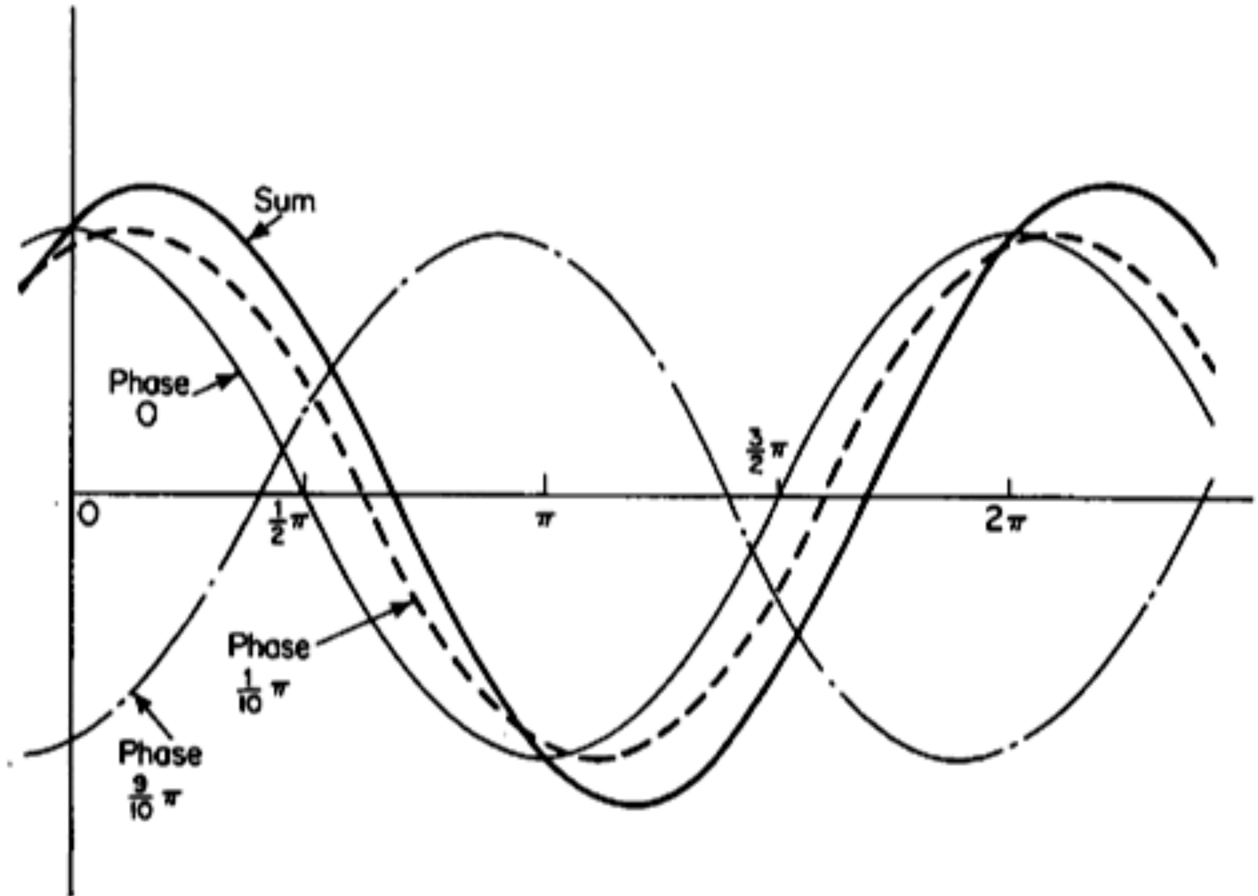
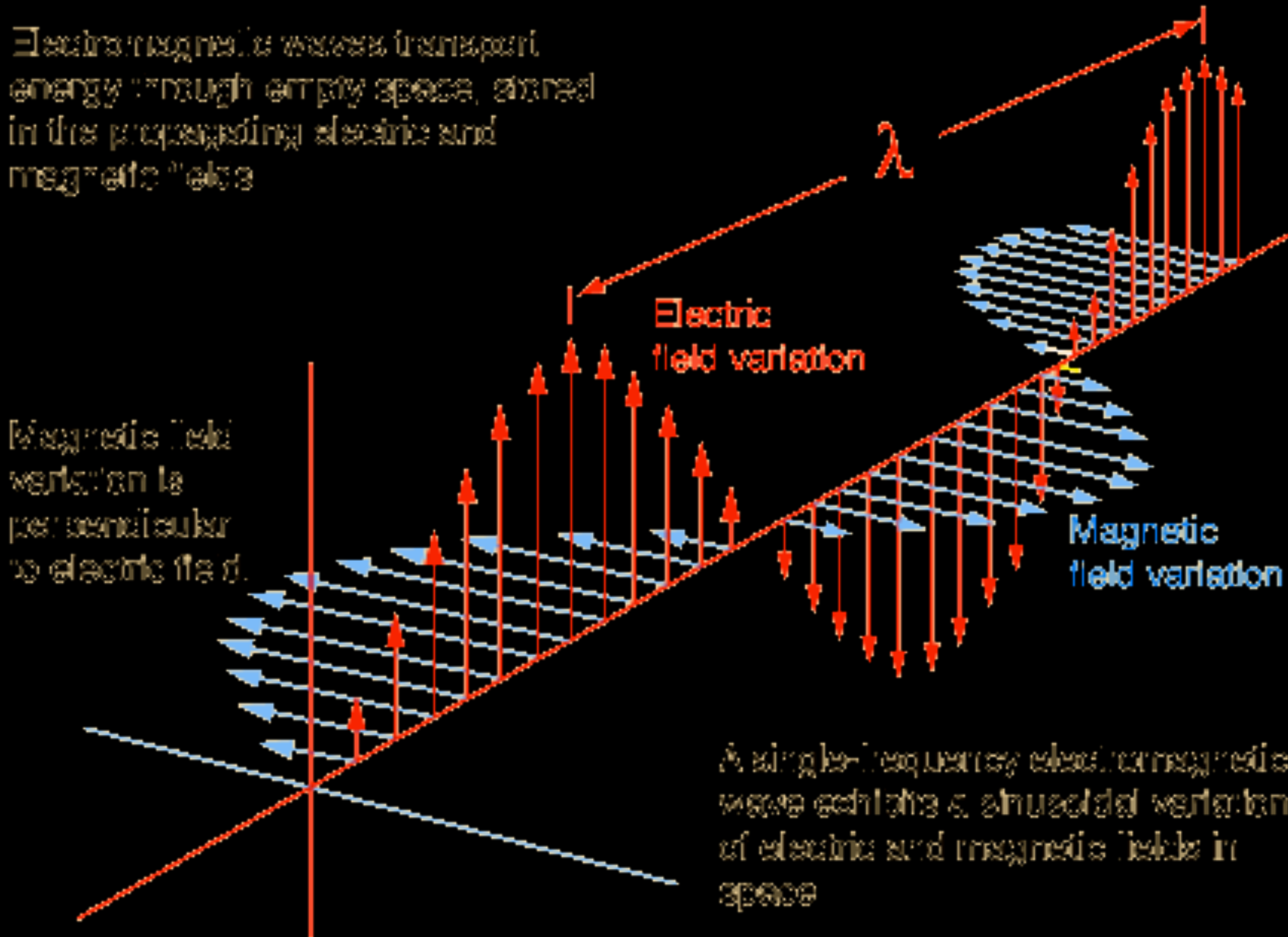


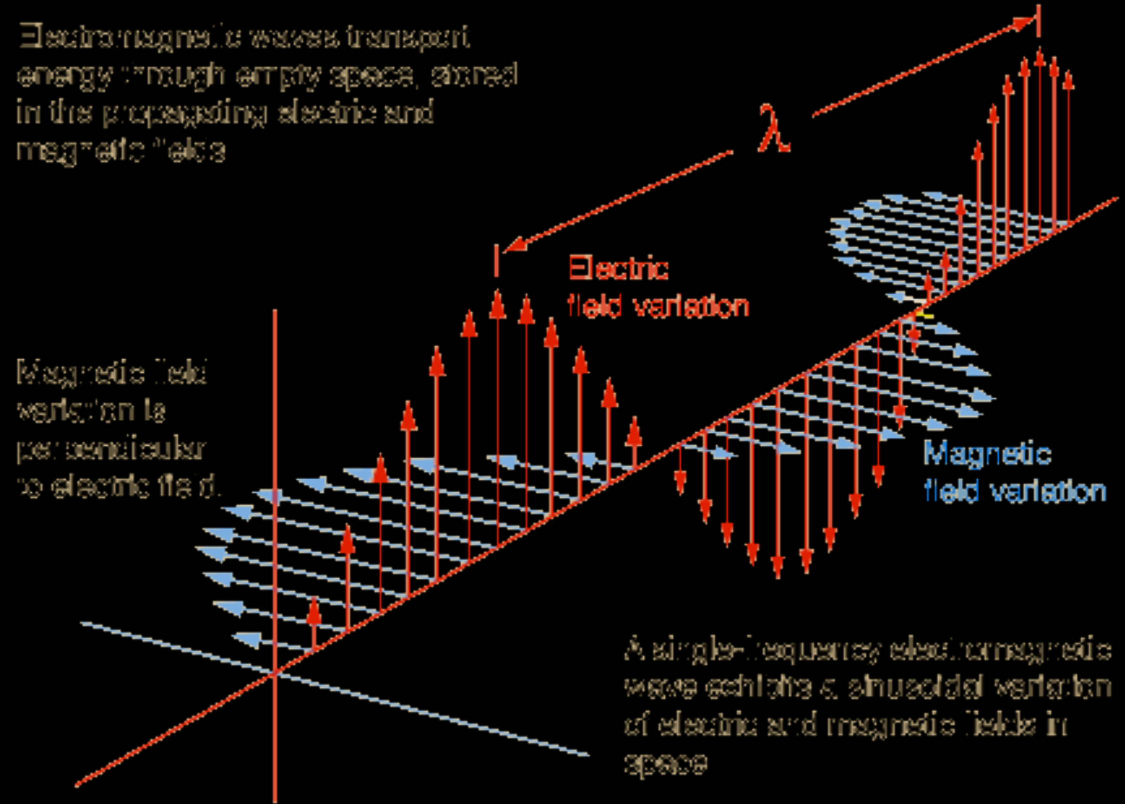
Fig. 4.12. Addition of three sinusoidal waves with different phase angles, showing ~~that~~ a case in which the sum is not greatly different from the contribution of one atom.

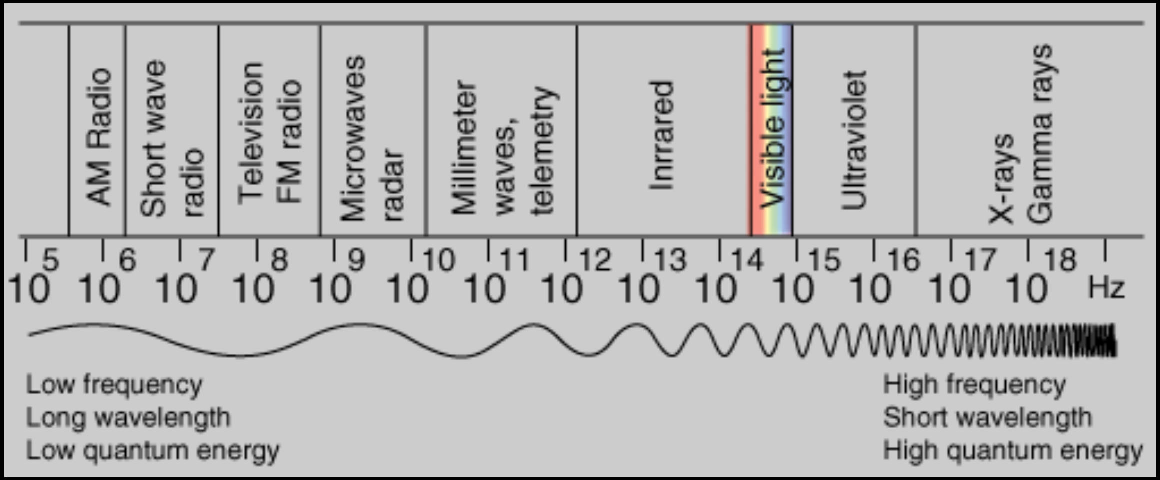
Henry S. Lipson (1970). *Crystals and X-Rays*. London: Wykeham Publications.

Picturing the Electromagnetic Wave Nature of X-Rays



http://hyperphysics.phy-astr.gsu.edu/hbase/HFrame.html





http://hyperphysics.phy-astr.gsu.edu/hbase/HFrame.html

z

$\mathbf{a}$ $\mathbf{r}$

$$\mathbf{a}_\perp = (\hat{\mathbf{r}} \times \mathbf{a}) \times \hat{\mathbf{r}}$$

$\mathbf{E}$

α

q

y

x

$$\mathbf{E} = -\frac{q}{c^2 r}(\hat{\mathbf{r}} \times \mathbf{a}) \times \hat{\mathbf{r}}\,, \qquad \hat{\mathbf{r}} = \frac{\mathbf{r}}{|\mathbf{r}|}\,, \qquad |\mathbf{r}| = r$$

$$E = -\frac{q}{c^2 r} a \sin\alpha\,, \qquad E = |\mathbf{E}|\,, \qquad a = |\mathbf{a}|$$

em radiation from an accelerated charge

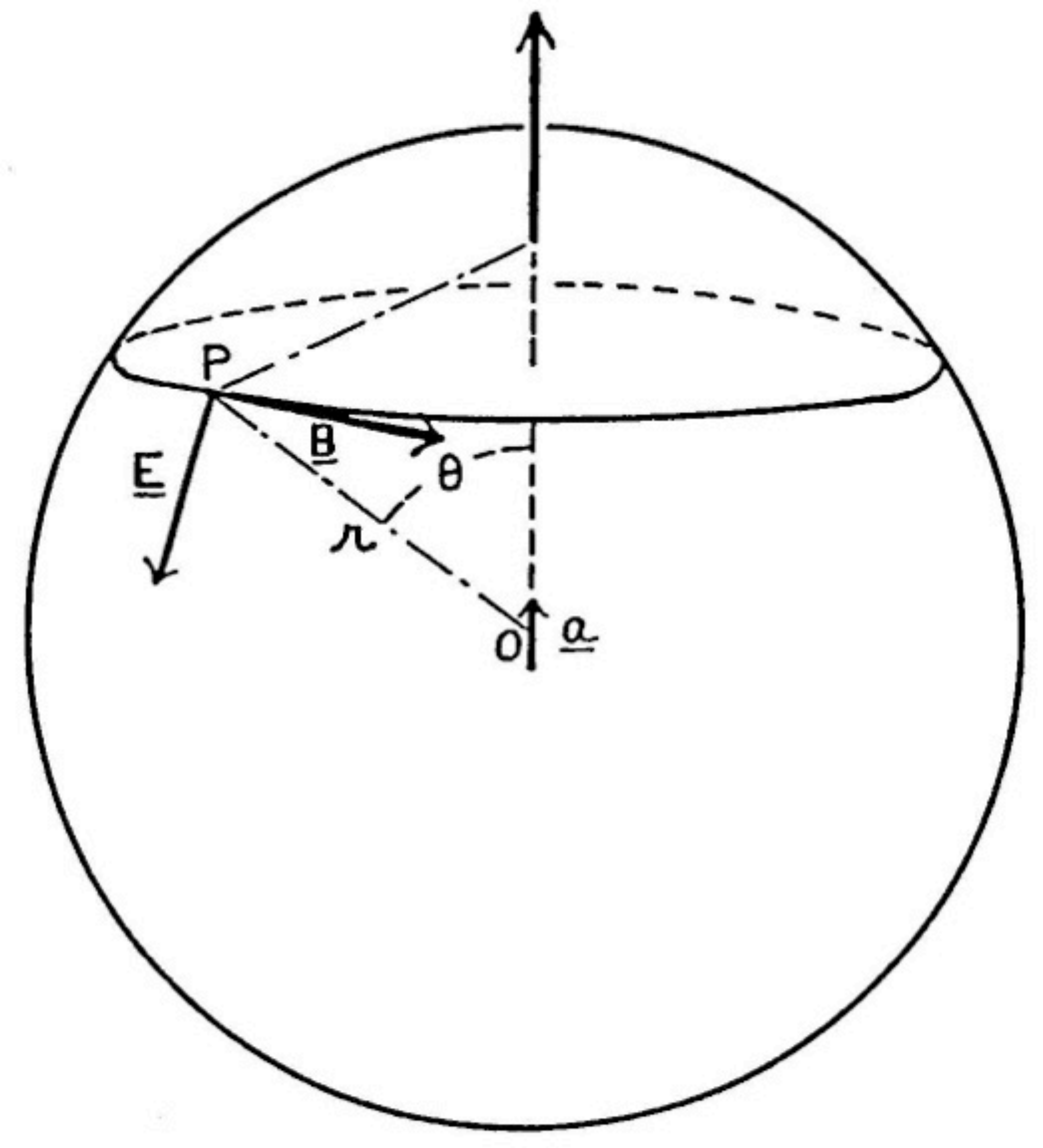
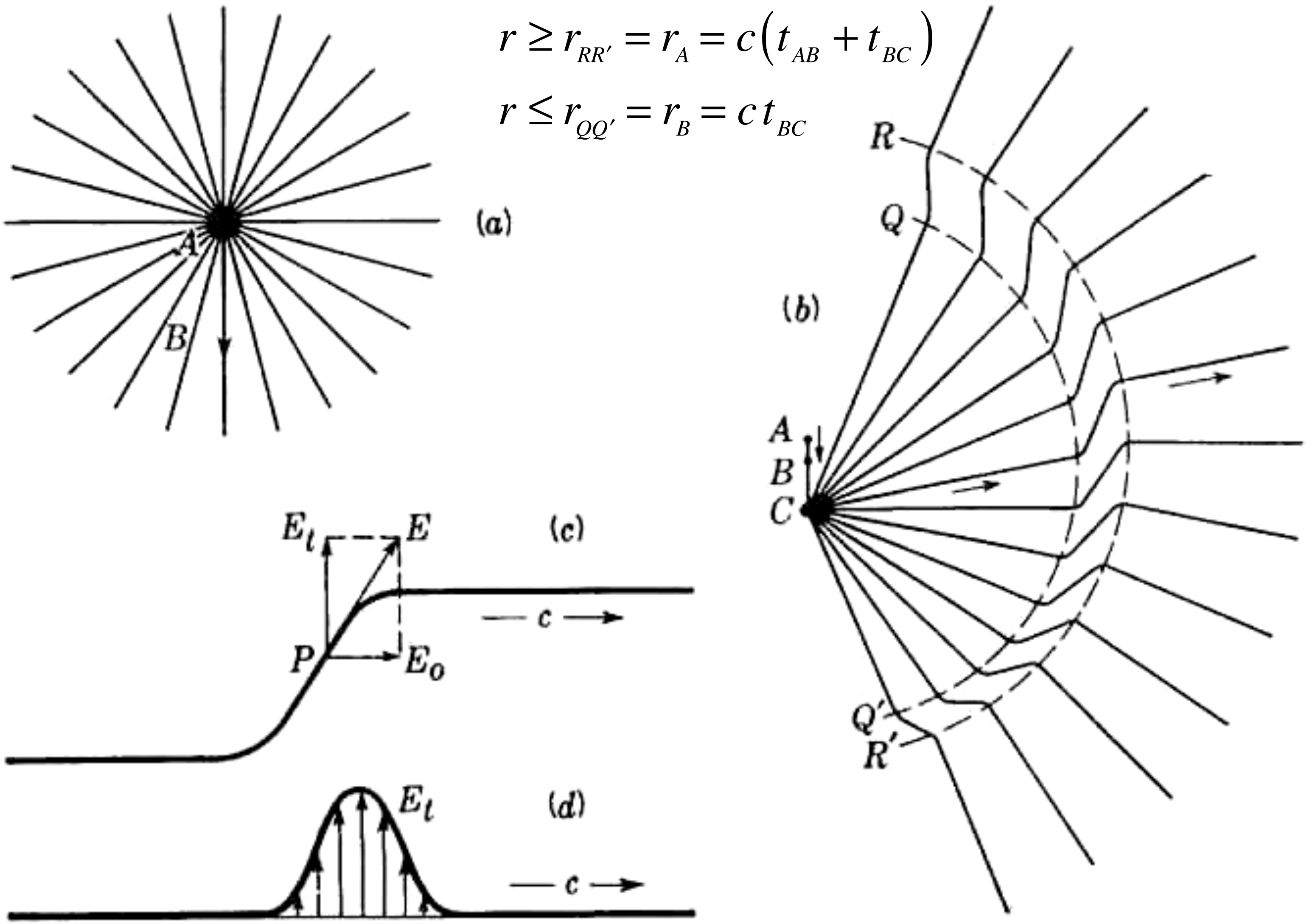


Figure copied from Compton and Allison (1935). *X-Rays in Theory and Experiment*.

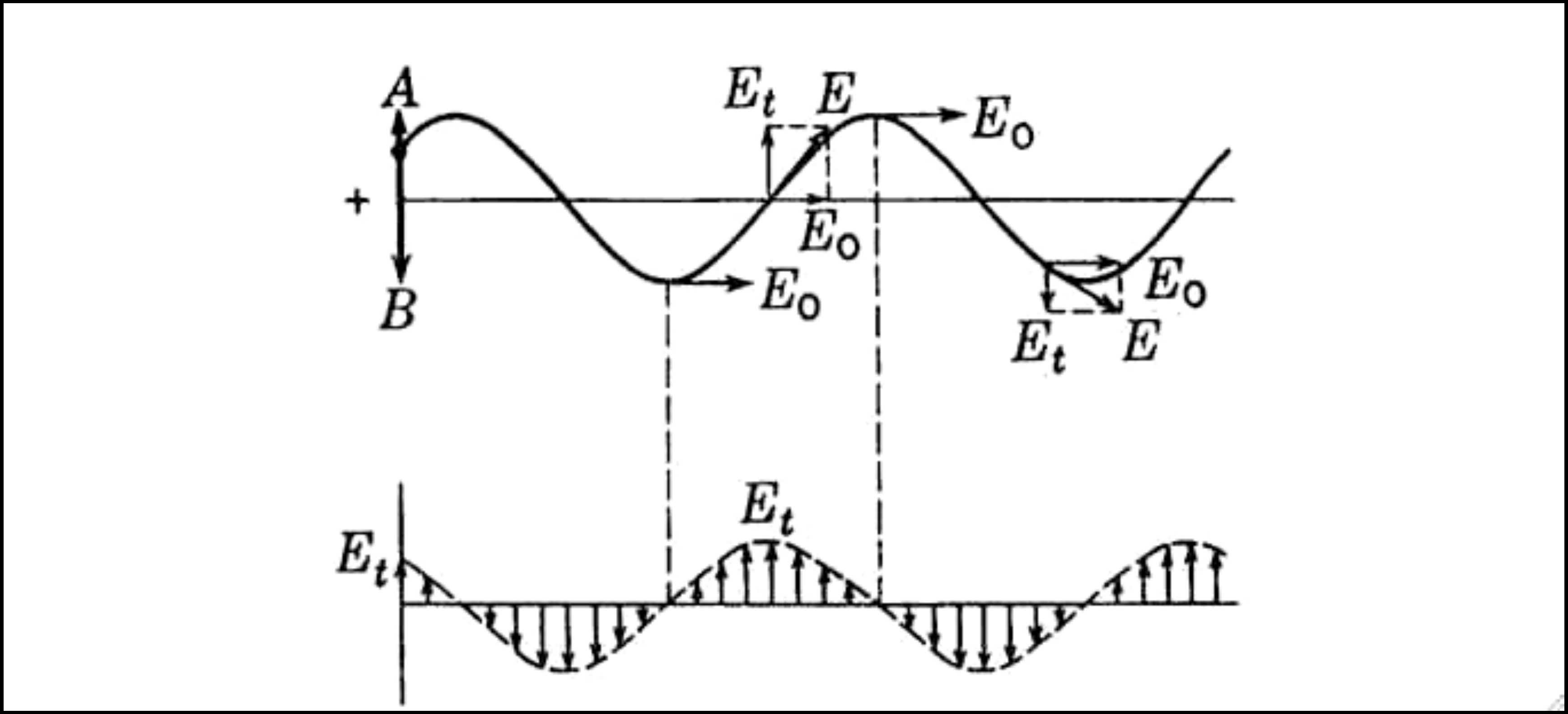
em radiation pulse from a momentarily accelerated charge

$$r \geq r_{RR'} = r_A = c\left(t_{AB} + t_{BC}\right)$$

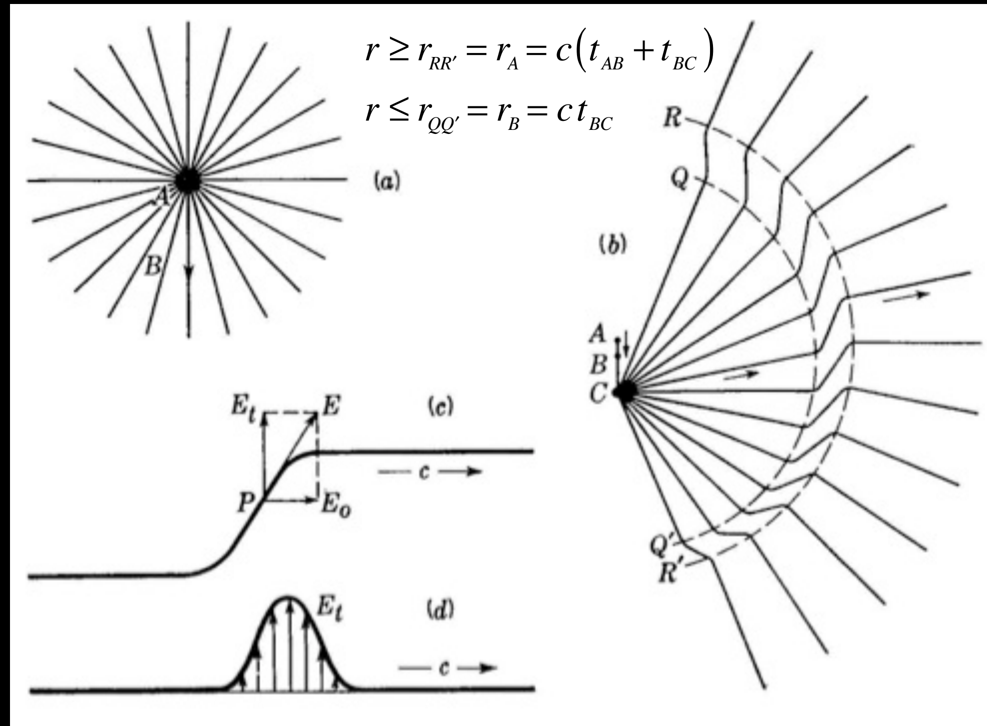
$$r \leq r_{QQ'} = r_B = c\,t_{BC}$$



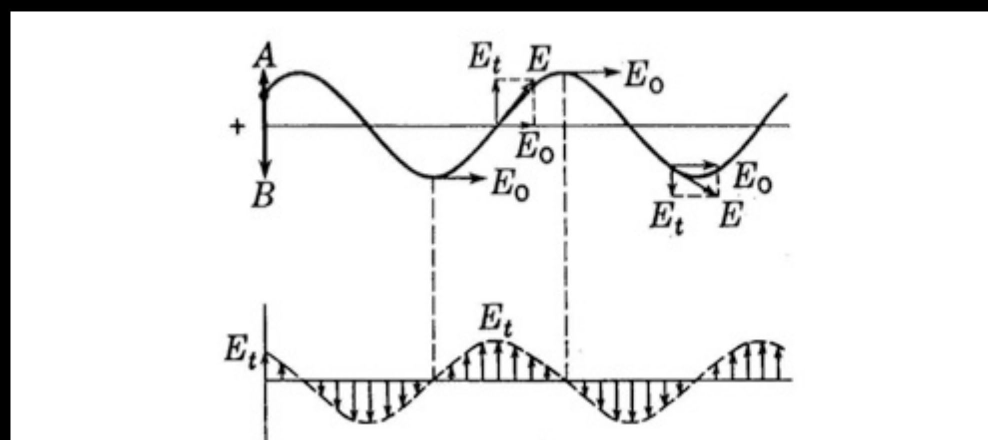
em radiation wave from a harmonically oscillating charge



em pulse from a momentary charge acceleration

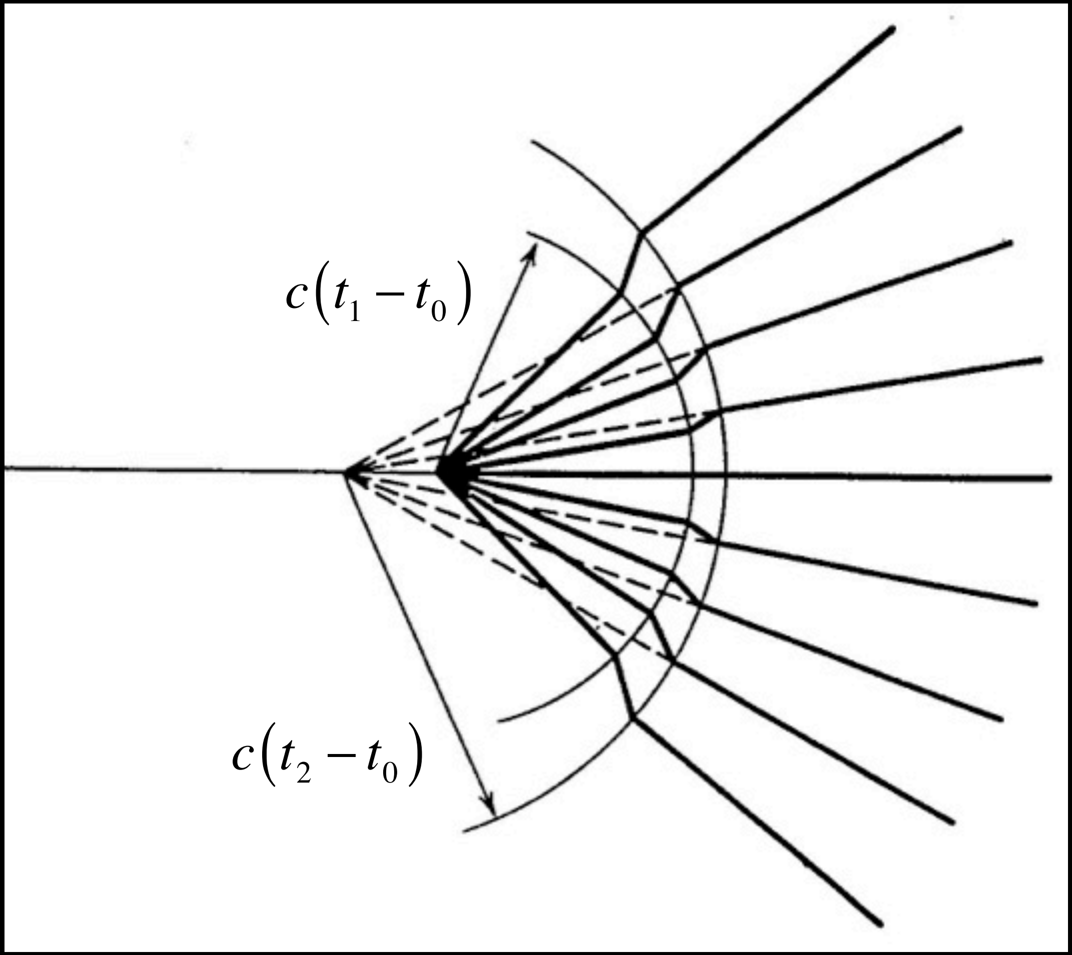


em wave from a sinusoidal charge oscillation



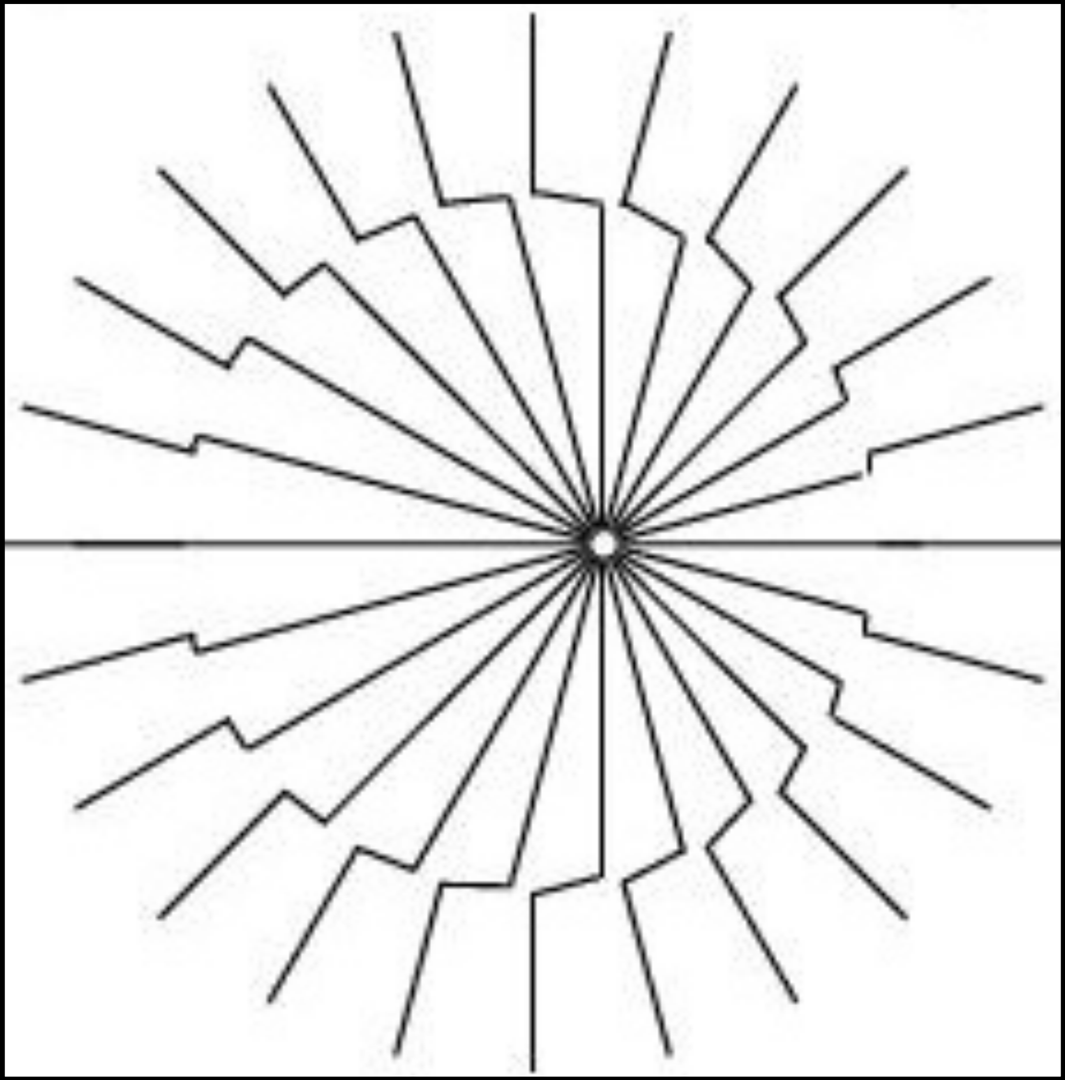
em radiation pulse from an accelerated charge

- At rest at t_0
- Accelerated from t_0 to t_1
- Constant velocity from t_1 to t_2



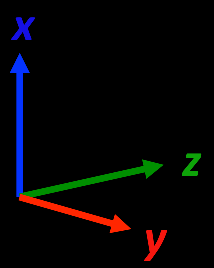
R.M. Eisberg (1963). *Fundamentals of Modern Physics*. New York: John Wiley and Sons, Inc.

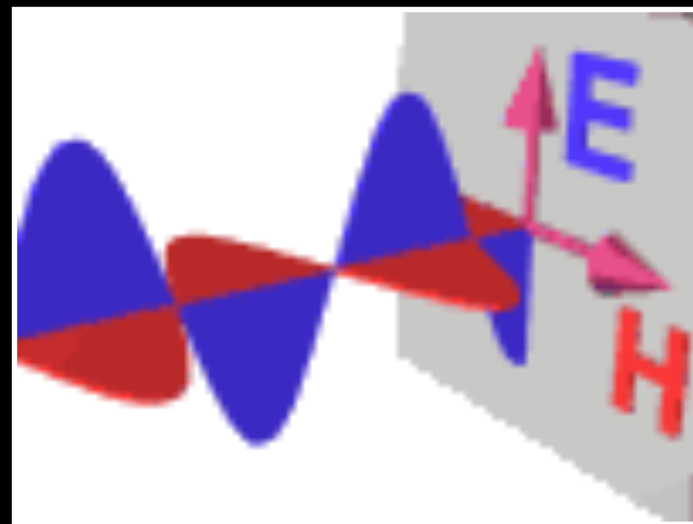
em radiation from an accelerated charge



Maximum radiation perpendicular to the acceleration direction.
Zero radiation in the acceleration direction

Electromagnetic Waves





$$|\mathbf{E}_0| \quad c|\mathbf{H}_0|$$

$$E_x = E_0 \cos(\omega t - kz) \qquad E_y = 0 \qquad E_z = 0$$

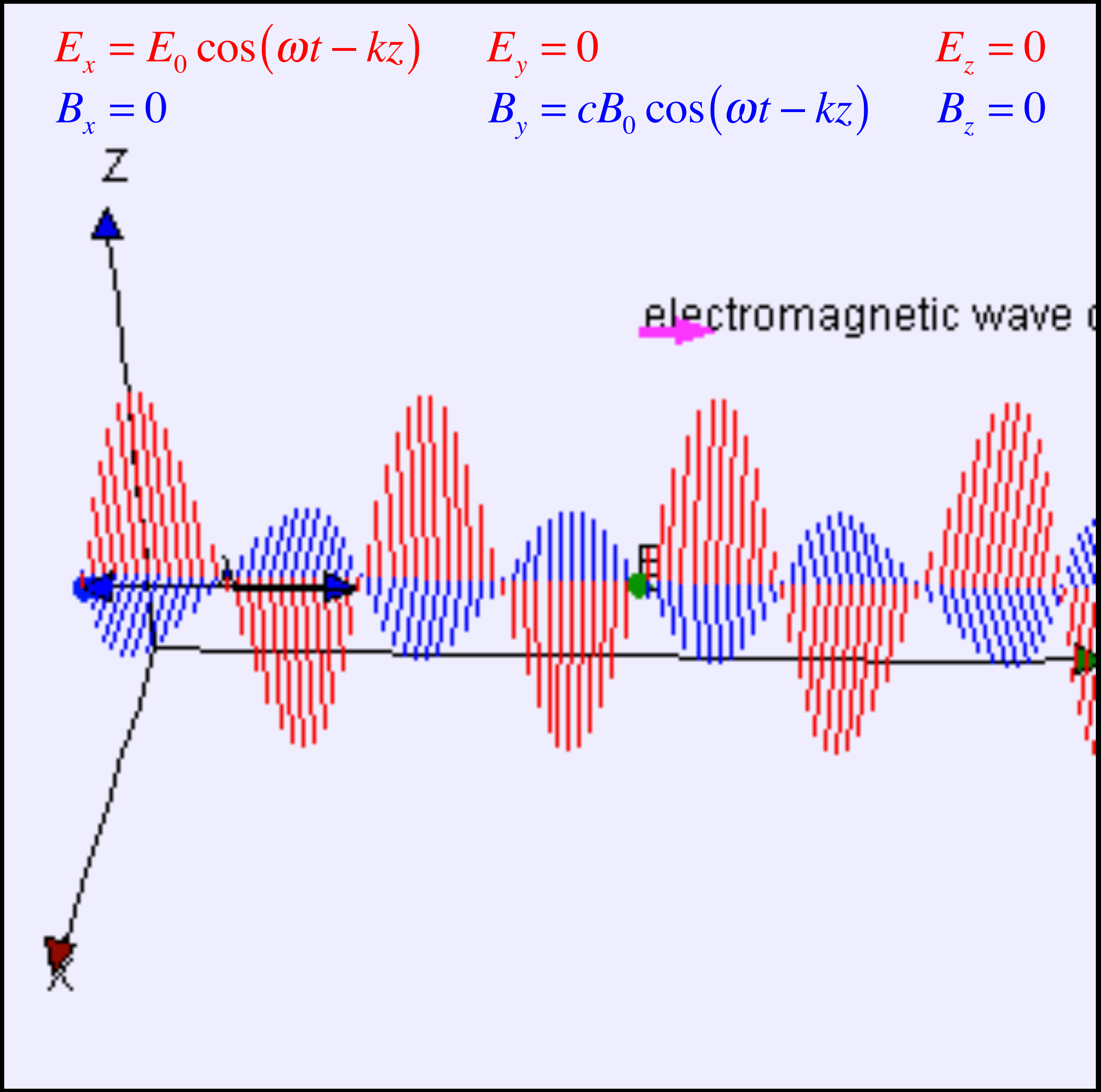
$$H_x = 0 \qquad H_y = cH_0 \cos(\omega t - kz) \qquad H_z = 0$$

$$\underbrace{E_\gamma = \hbar\omega = h\nu = \frac{hc}{\lambda}, \quad p_\gamma = \hbar k = \frac{h}{\lambda}}_{\text{Plank-Einstein-deBroglie wave-particle properties}}$$

Plank-Einstein-deBroglie
wave-particle properties

http://physics-animations.com/Physics/English/down.htm http://www.youtube.com/watch?v=4CtnUETLIFs

Electromagnetic wave - side view

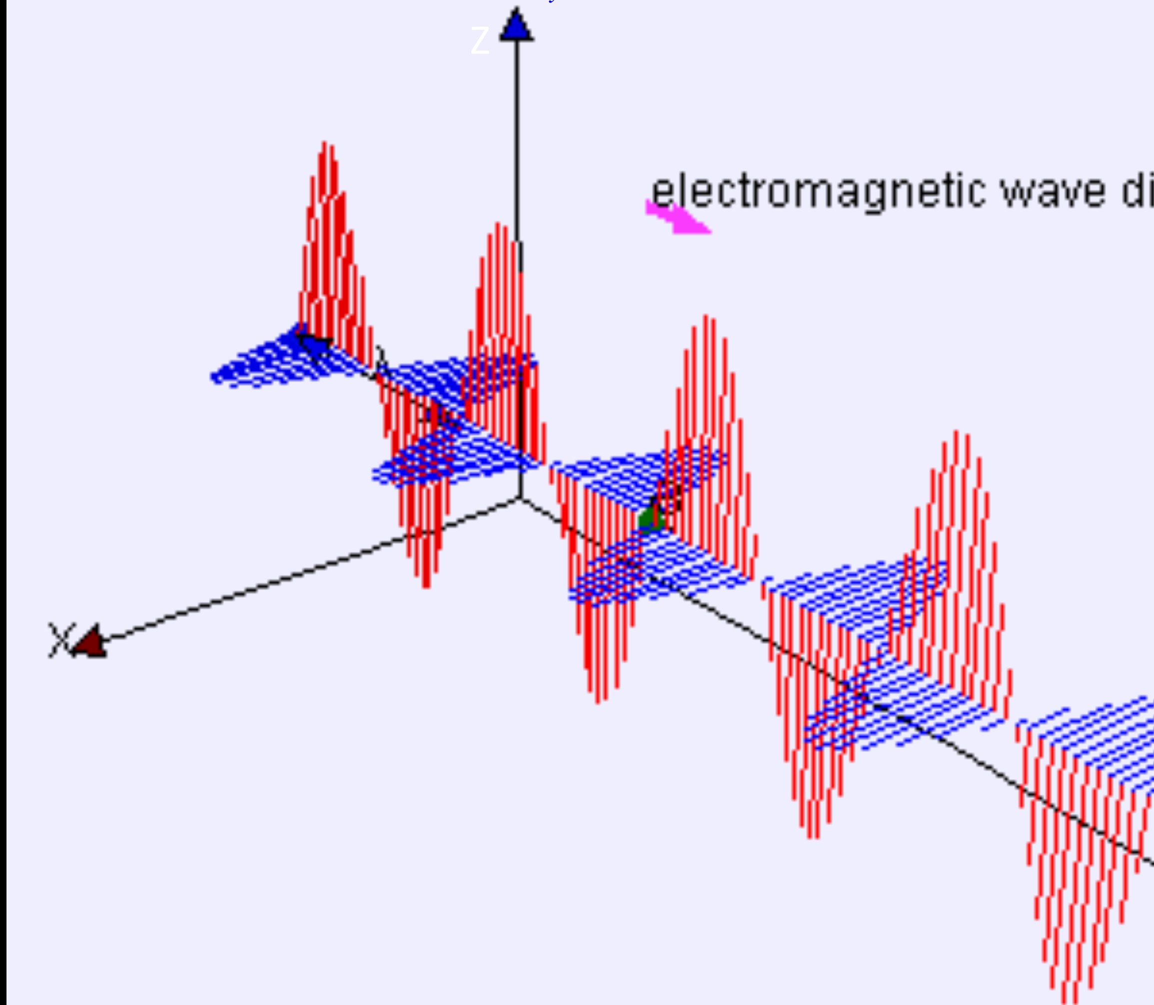


http://en.wikipedia.org/w/index.php?title=File%3AElectromagneticwave3Dfromside.gif

Electromagnetic wave - 3D view

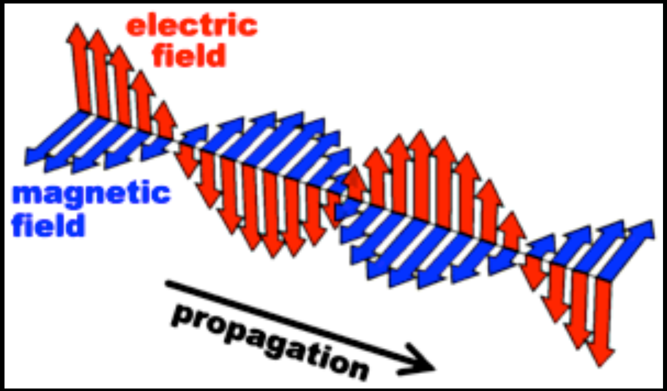
$E_x = E_0 \cos(\omega t - kz)$ $\quad E_y = 0$ $\quad E_z = 0$

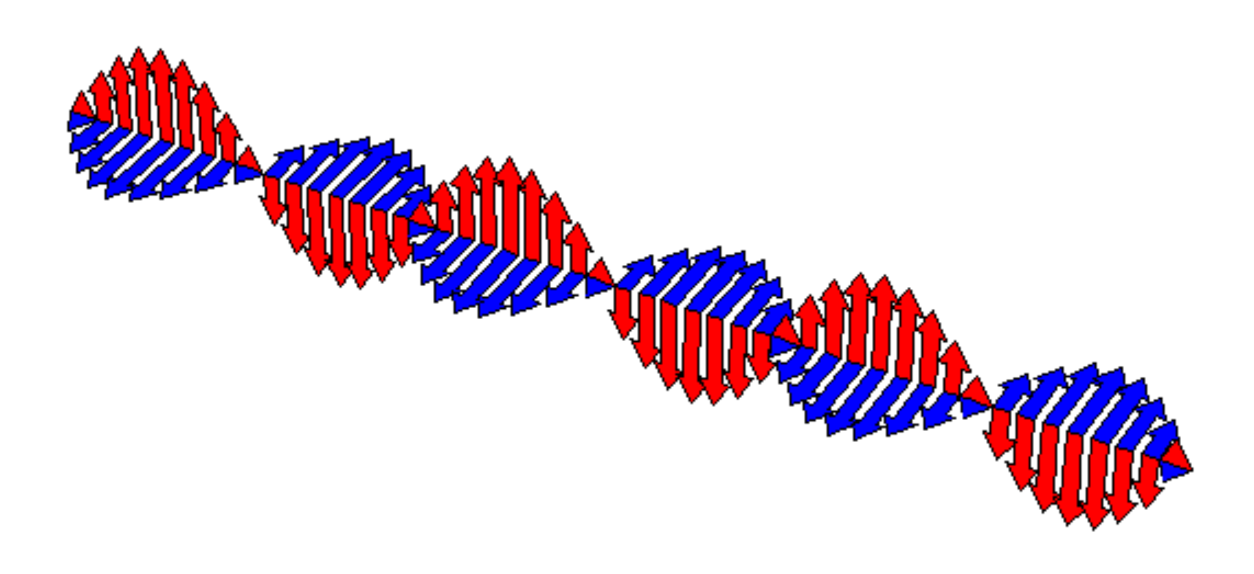
$B_x = 0$ $\quad B_y = cB_0 \cos(\omega t - kz)$ $\quad B_z = 0$



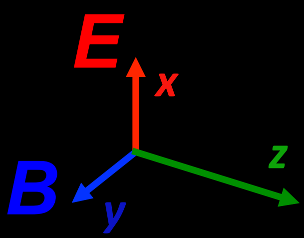
http://en.wikipedia.org/w/index.php?title=File%3AElectromagneticwave3D.gif

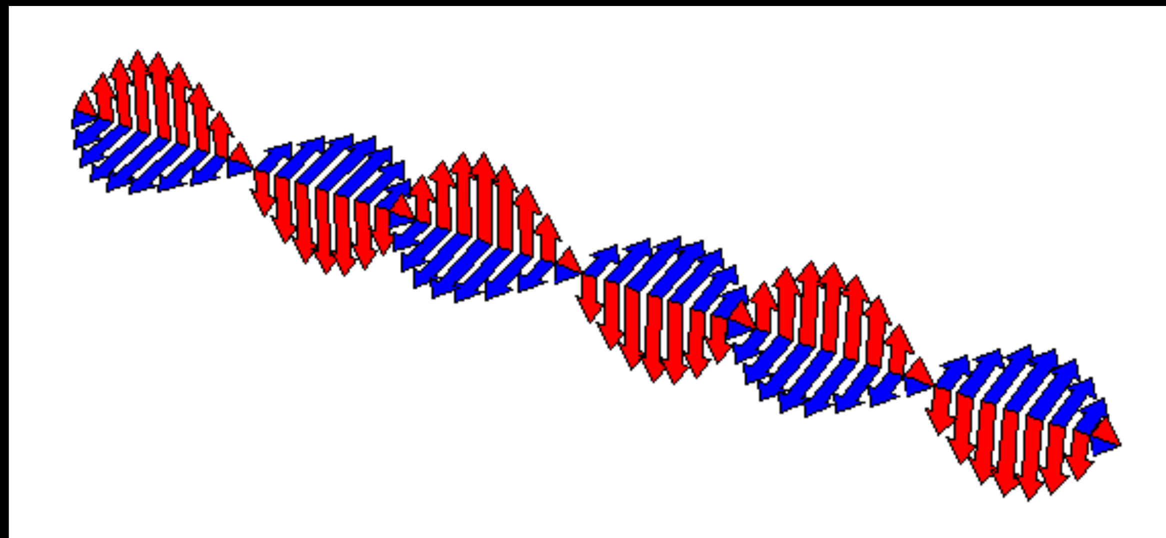
electric field
magnetic field





http://www.monos.leidenuniv.nl/smo/basics/images/wave.gif
http://www.optics.arizona.edu/Wright/images/wave_anim.gif





$$|\mathbf{E}_0| \qquad c|\mathbf{B}_0|$$

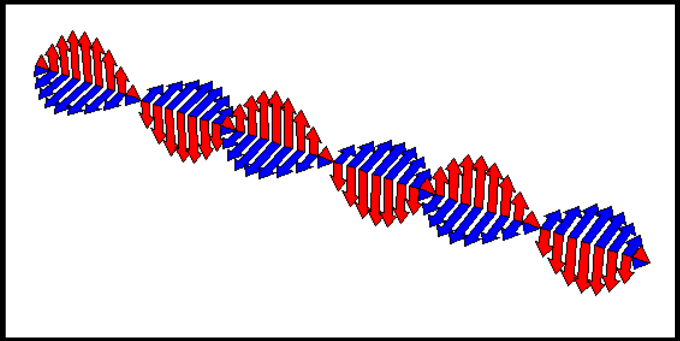
$$E_x = E_0 \cos(\omega t - kz) \qquad E_y = 0 \qquad E_z = 0$$

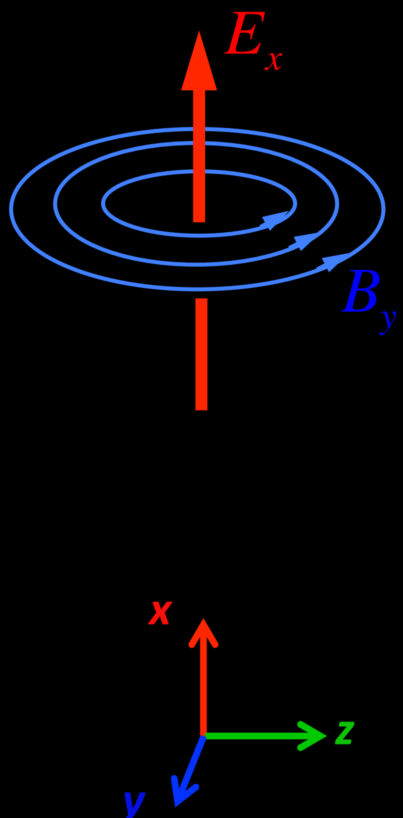
$$B_x = 0 \qquad B_y = cB_0 \cos(\omega t - kz) \qquad B_z = 0$$

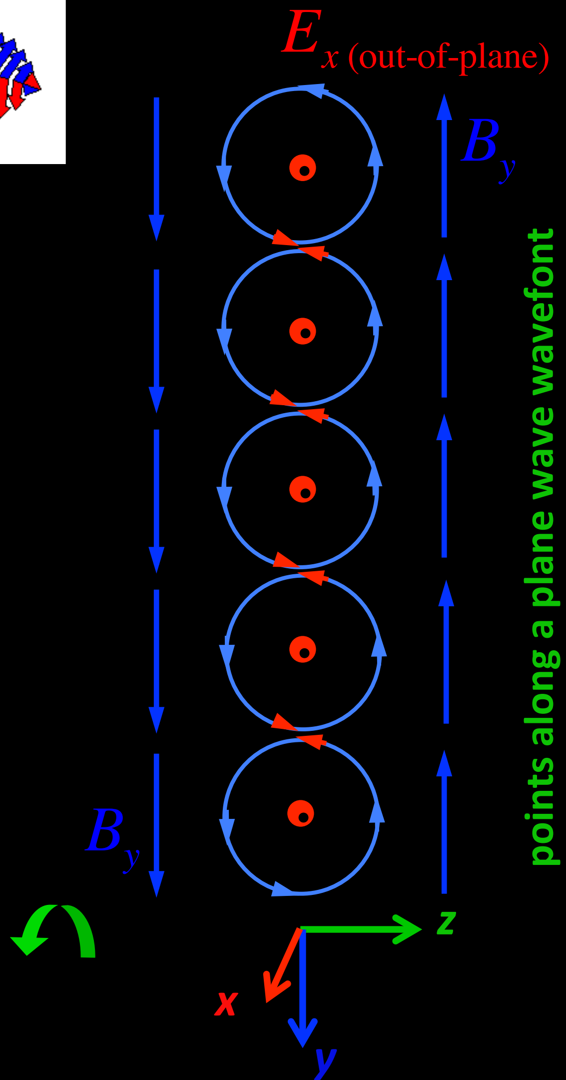
$$\underbrace{E_\gamma = \hbar\omega = h\nu = \frac{hc}{\lambda}, \quad p_\gamma = \hbar k = \frac{h}{\lambda}}$$

Plank-Einstein-deBroglie
wave-particle properties

http://www.optics.arizona.edu/Wright/images/wave_anim.gif







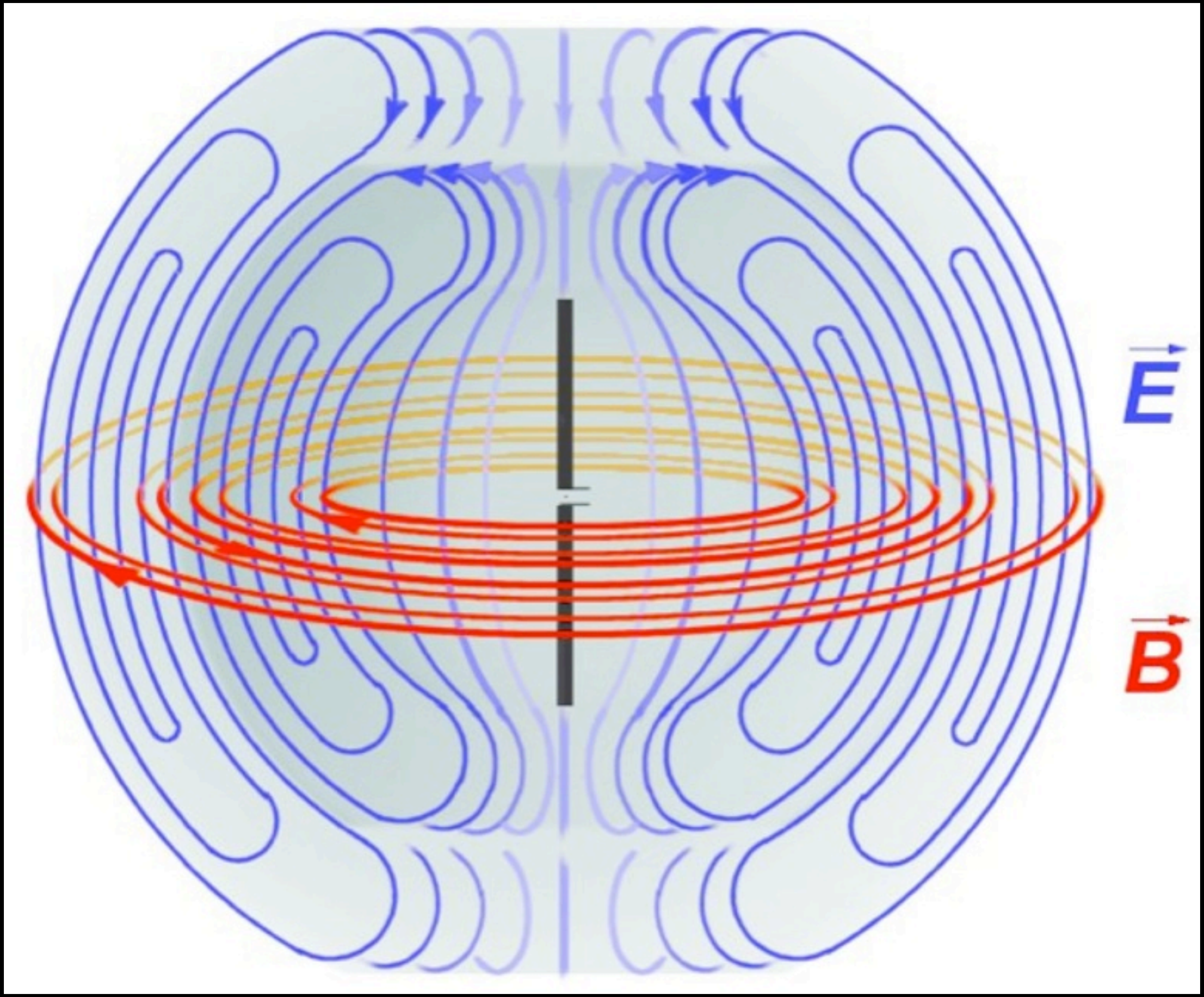
$$
\begin{cases}
E_x = E_0 \cos(\omega t - kz) \\
E_y = 0 \\
E_z = 0
\end{cases}
$$

$$
\begin{cases}
B_x = 0 \\
B_y = cB_0 \cos(\omega t - kz) \\
B_z = 0
\end{cases}
$$

$$
\begin{cases}
E_\gamma = \hbar\omega = h\nu = hc/\lambda \\
p_\gamma = \hbar k = h/\lambda
\end{cases}
$$

http://www.optics.arizona.edu/Wright/images/wave_anim.gif

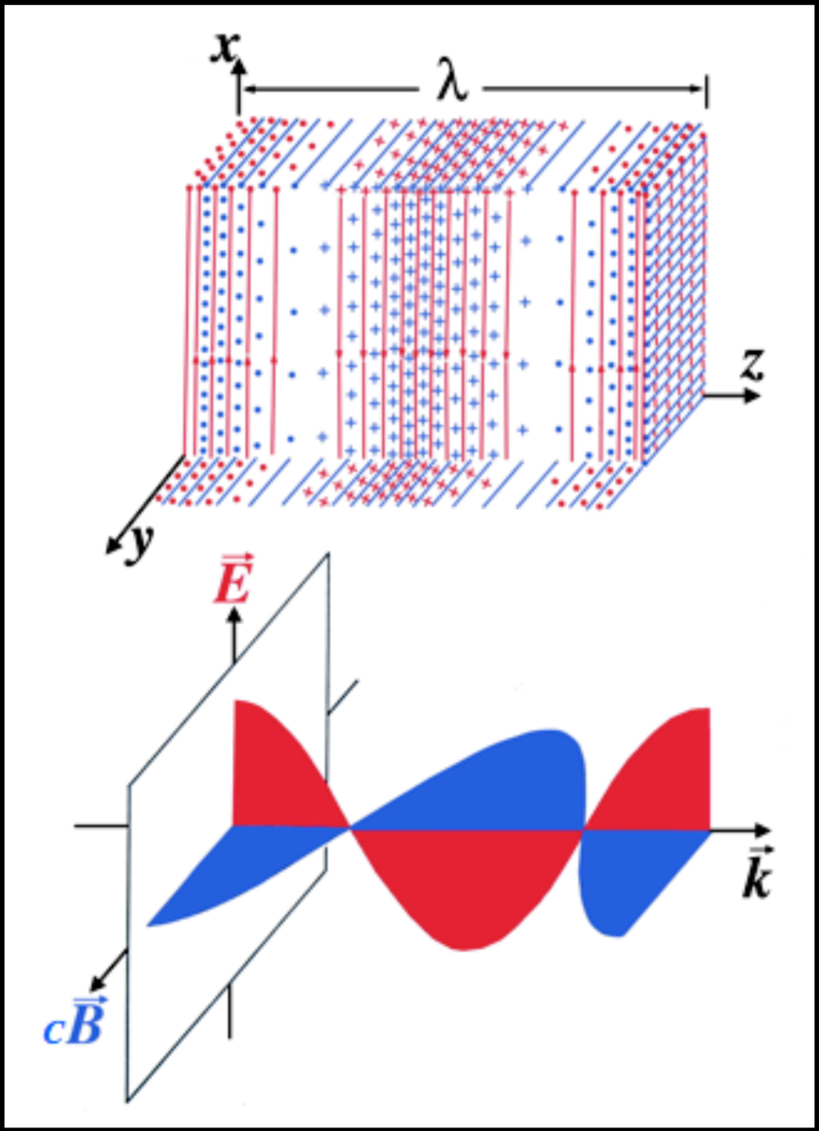
e and m wave fields from an electric dipole oscillator



For a vertical oscillation, horizontal radiation is maximal.

http://physics.stackexchange.com/questions/20331/understanding-the-diagrams-of-electromagnetic-waves em

em

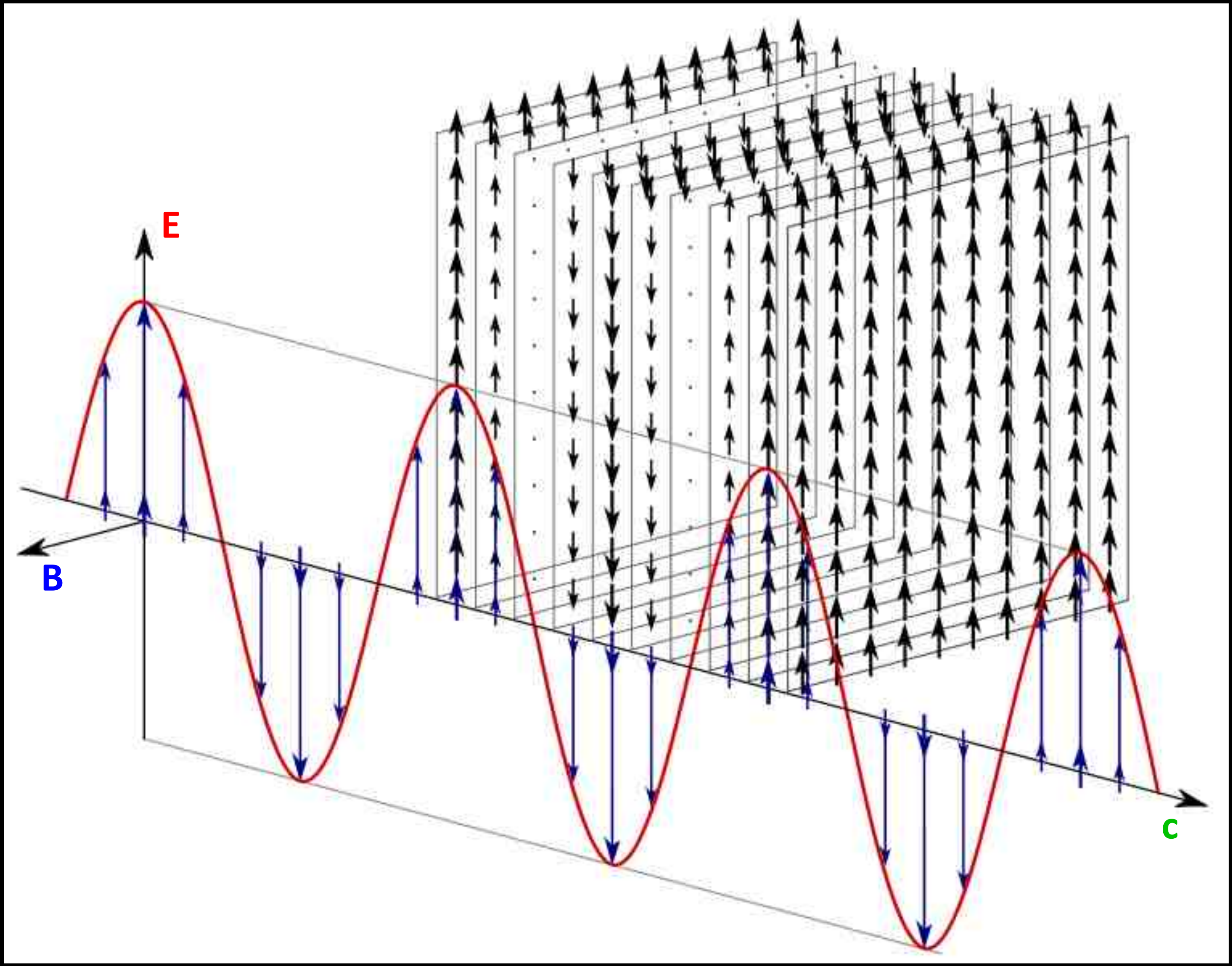


$$\begin{cases} E_x = E_0 \cos(\omega t - kz) \\ E_y = 0 \\ E_z = 0 \end{cases}$$

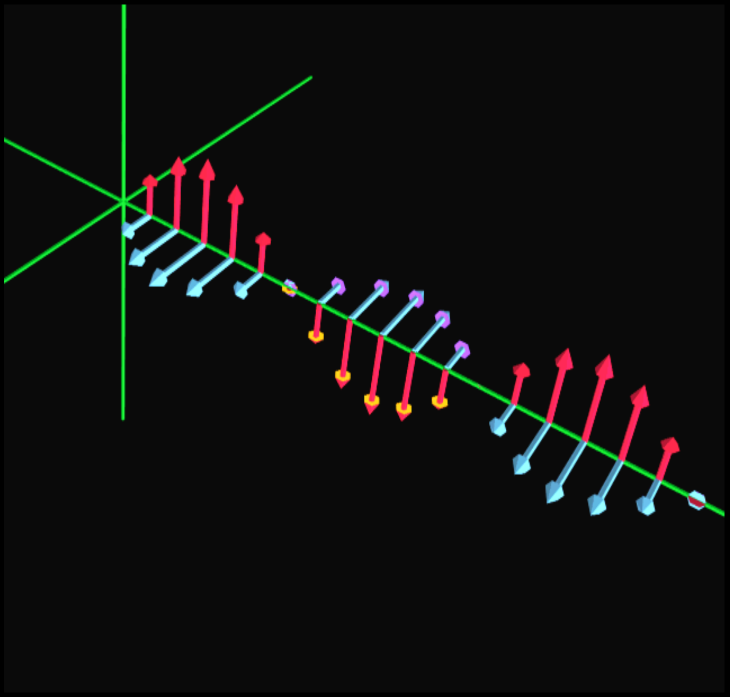
$$\begin{cases} B_x = 0 \\ B_y = cB_0 \cos(\omega t - kz) \\ B_z = 0 \end{cases}$$

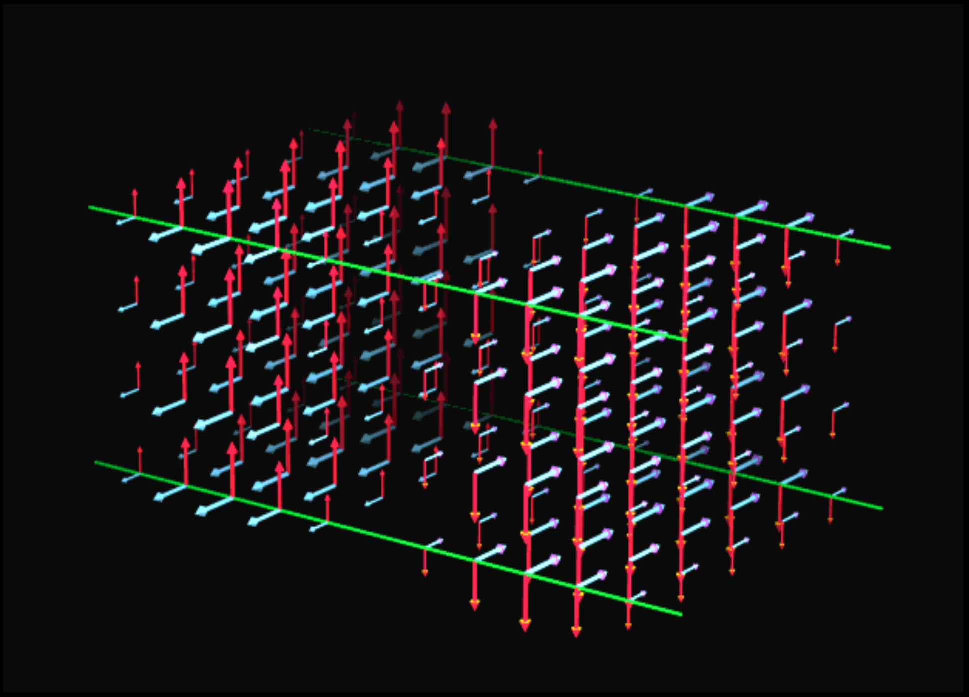
$$\begin{cases} E_\gamma = \hbar\omega = h\nu = hc/\lambda \\ p_\gamma = \hbar k = h/\lambda \end{cases}$$

An illustration of the electric component of a monochromatic, linearly polarized, em plane wave



http://en.wikipedia.org/wiki/Plane_wave



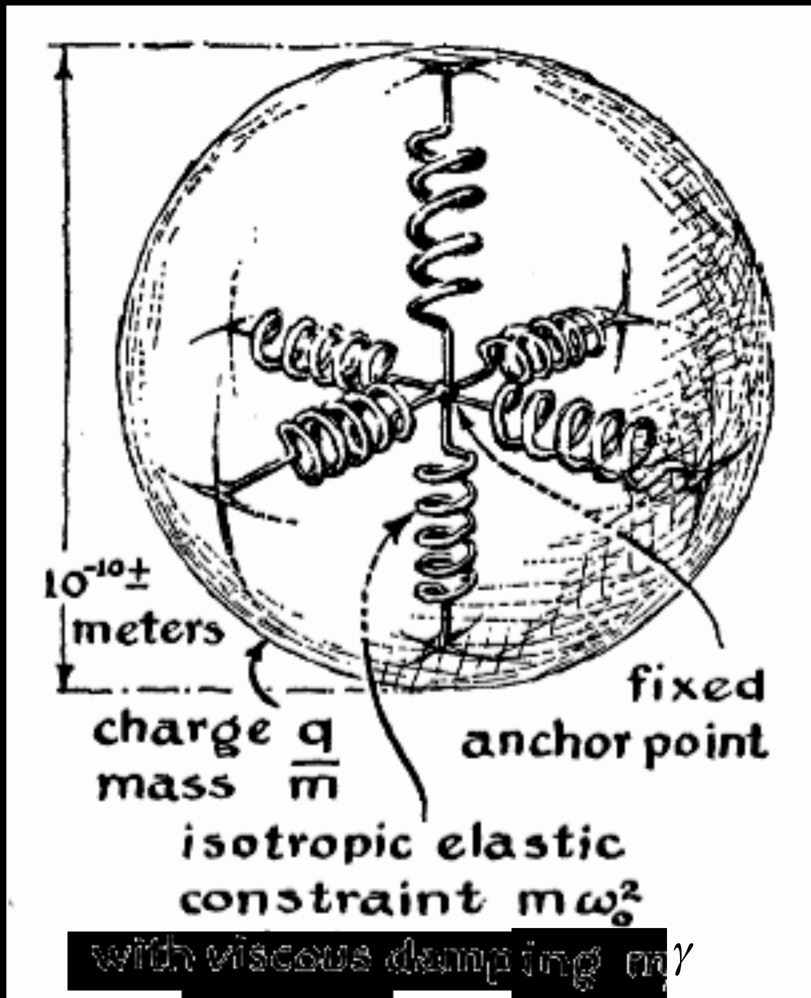


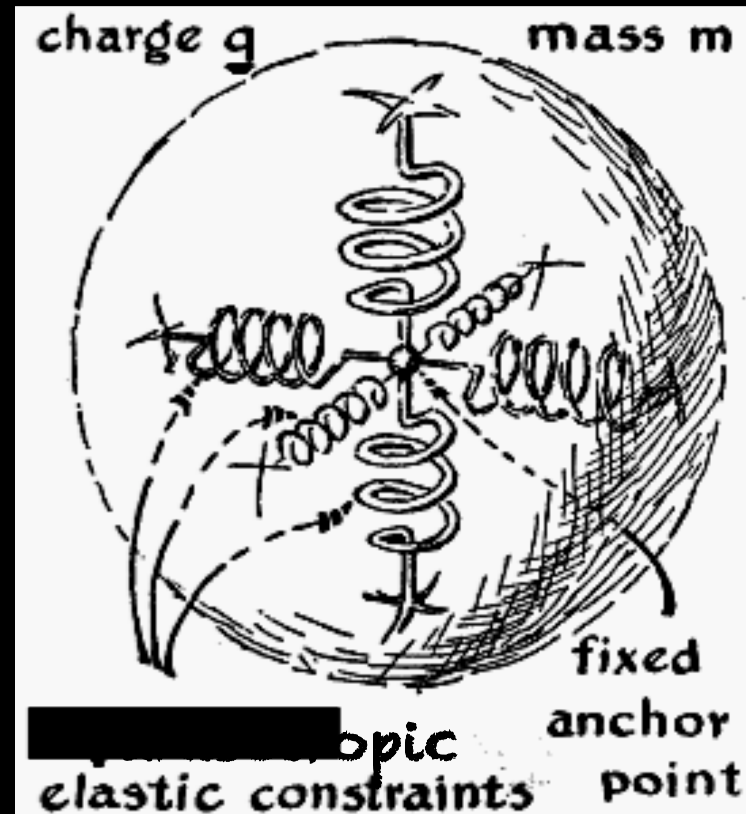
electric magnetic

http://www.cs.brown.edu/stc/outrea/greenhouse/nursery/physics/emwave.html

Mechanical models for 3-D electron oscillators

Spheres of uniform charge density with total charge *q* and mass *m*





Classical electron radius

Electrostatic potential energy

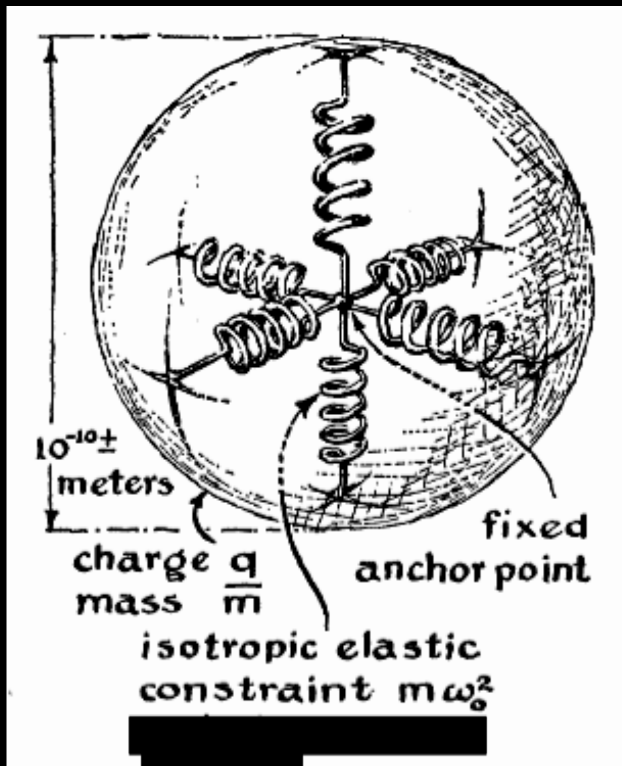
$$E = q\phi(r) = q(q/r) = e^2/r_e$$

Relativistic mass - energy

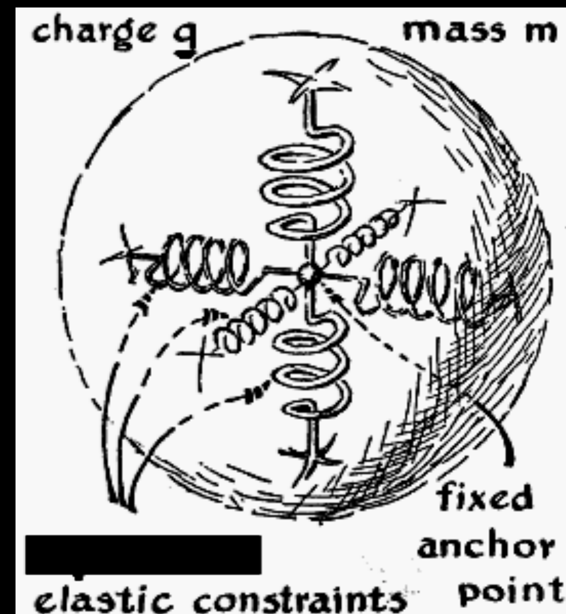
$$E = m_e c^2$$

$$r_e = \frac{e^2}{m_e c^2}$$

John Strong (1958). *Concepts of Classical Optics*. San Francisco: W.H. Freeman & Co.

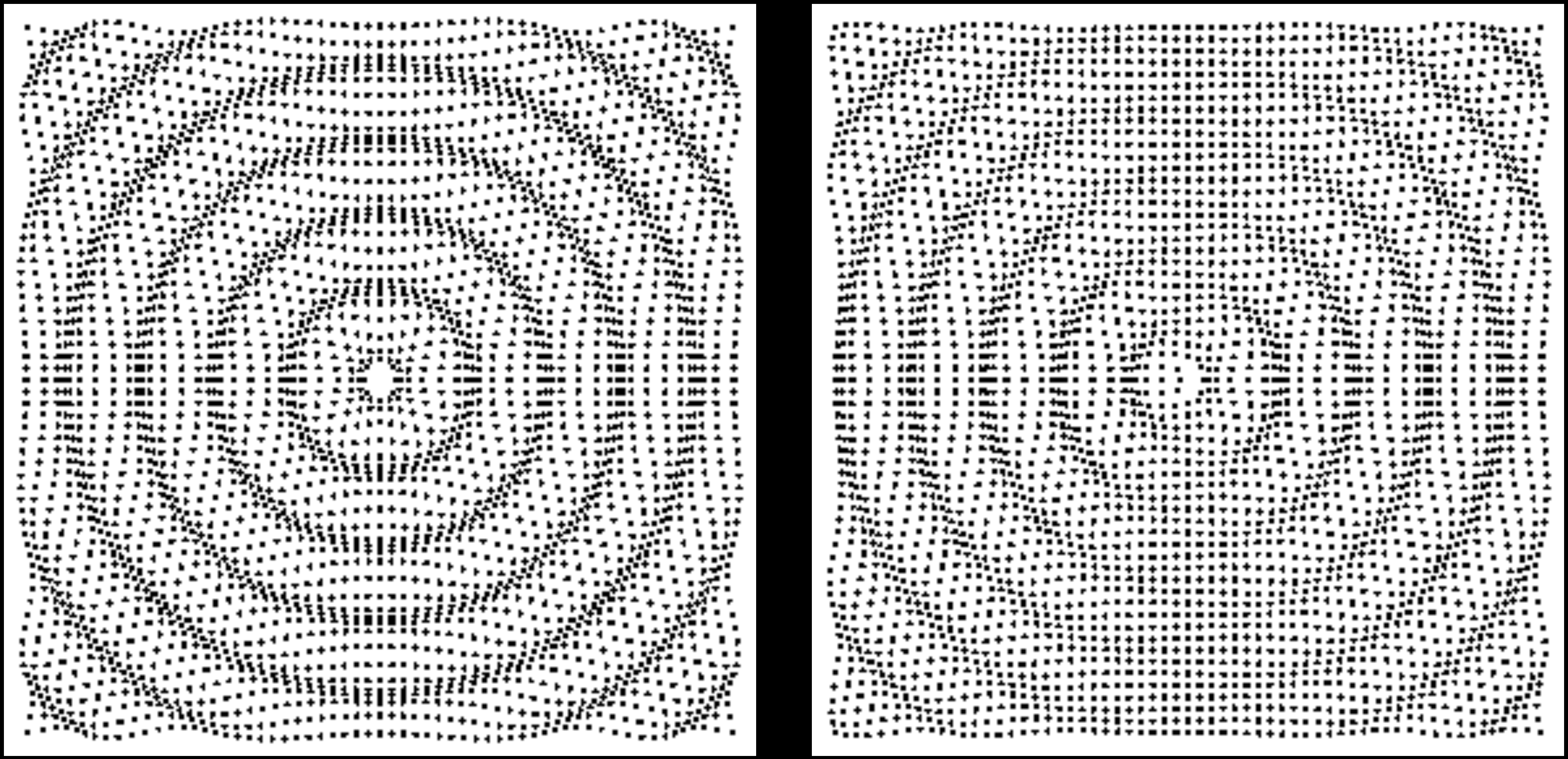


$10^{-10}\pm$ meters
charge q
mass $\overline{m}$
fixed anchor point
isotropic elastic constraint $m\omega_0^2$
[redacted]



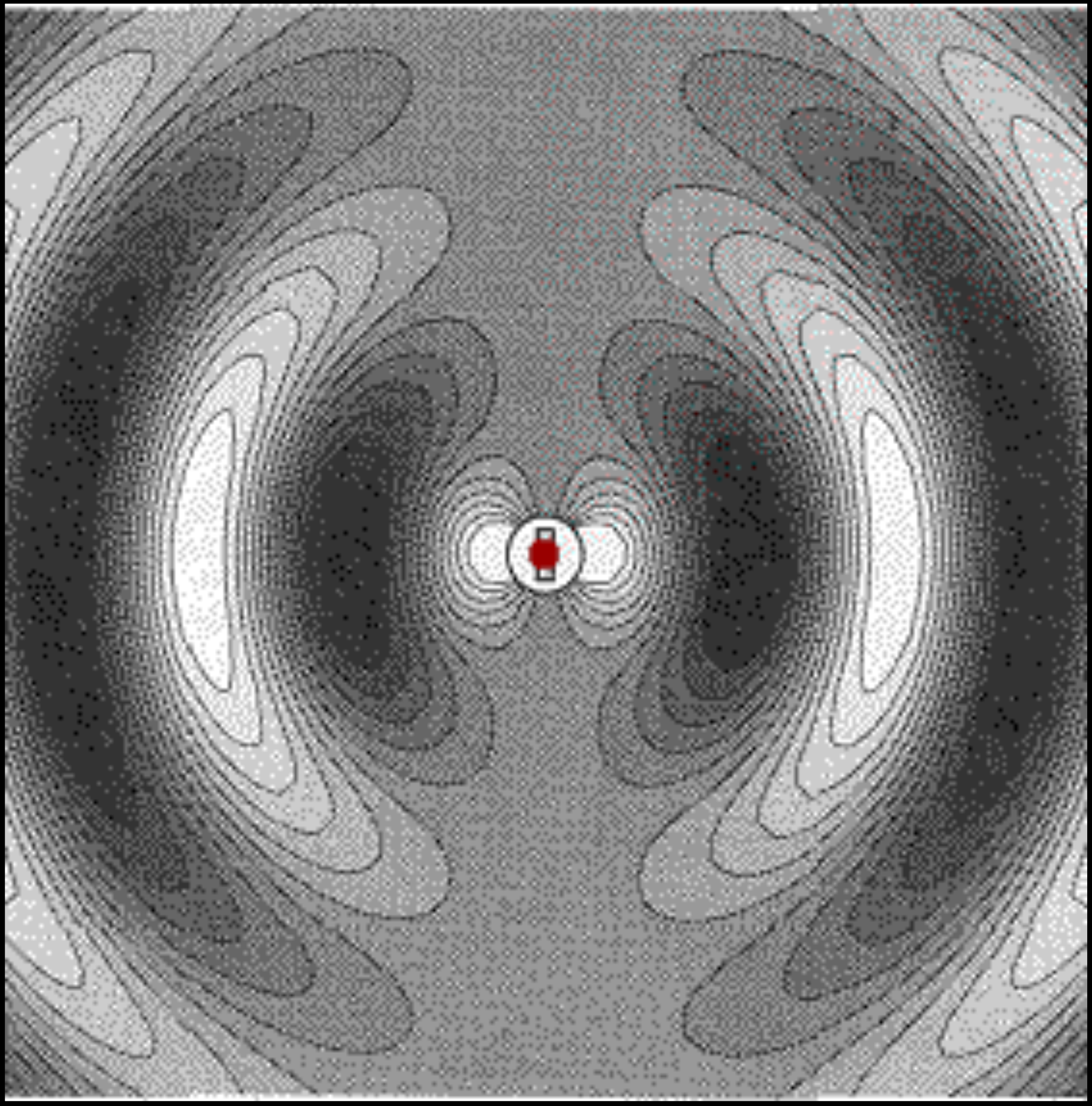
charge q
mass m
fixed anchor point
[redacted]
elastic constraints

em



http://www.acs.psu.edu/drussell/demos/rad2/mdq.html

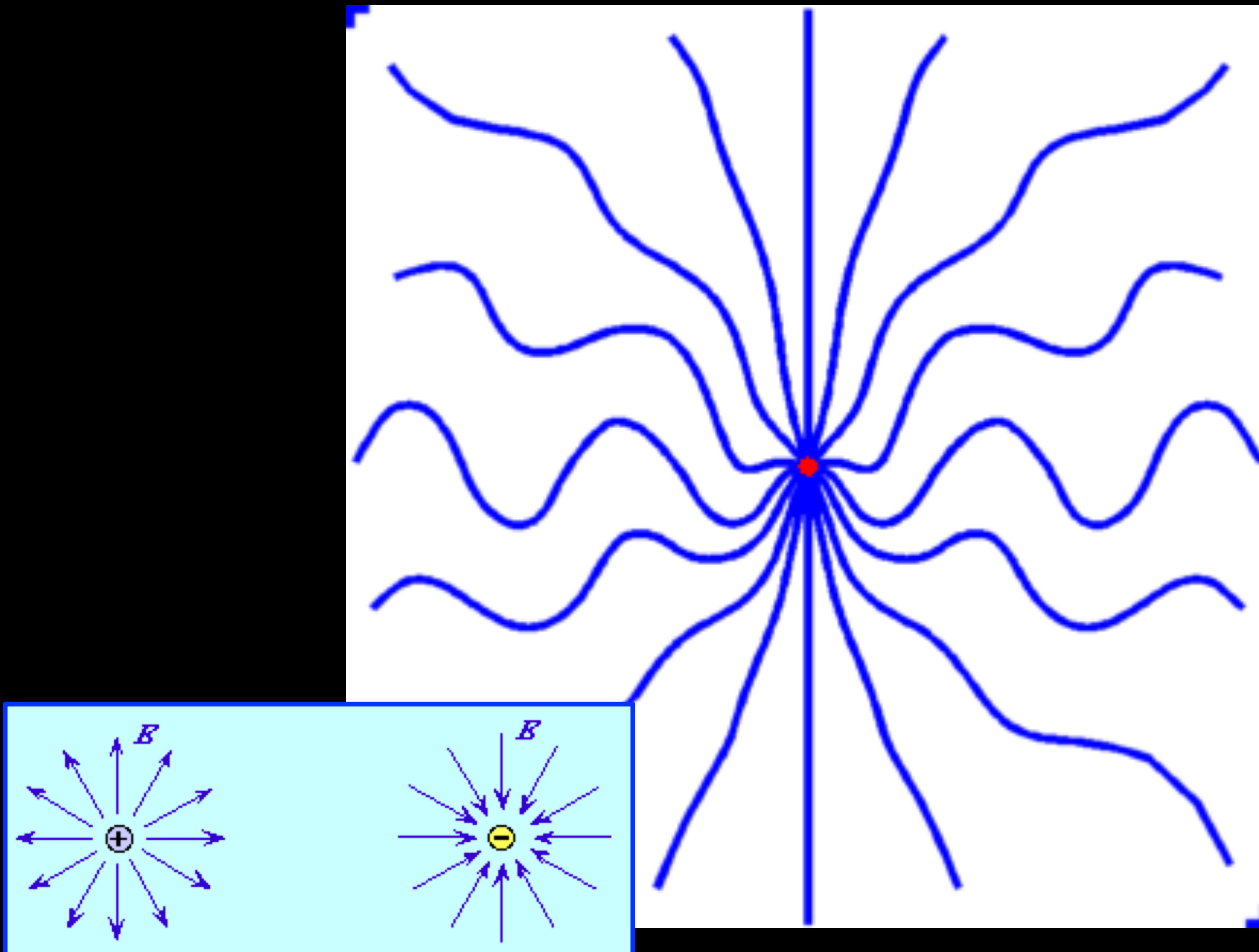
em waves from an electric dipole oscillator



For a vertical oscillation, horizontal radiation is maximal.

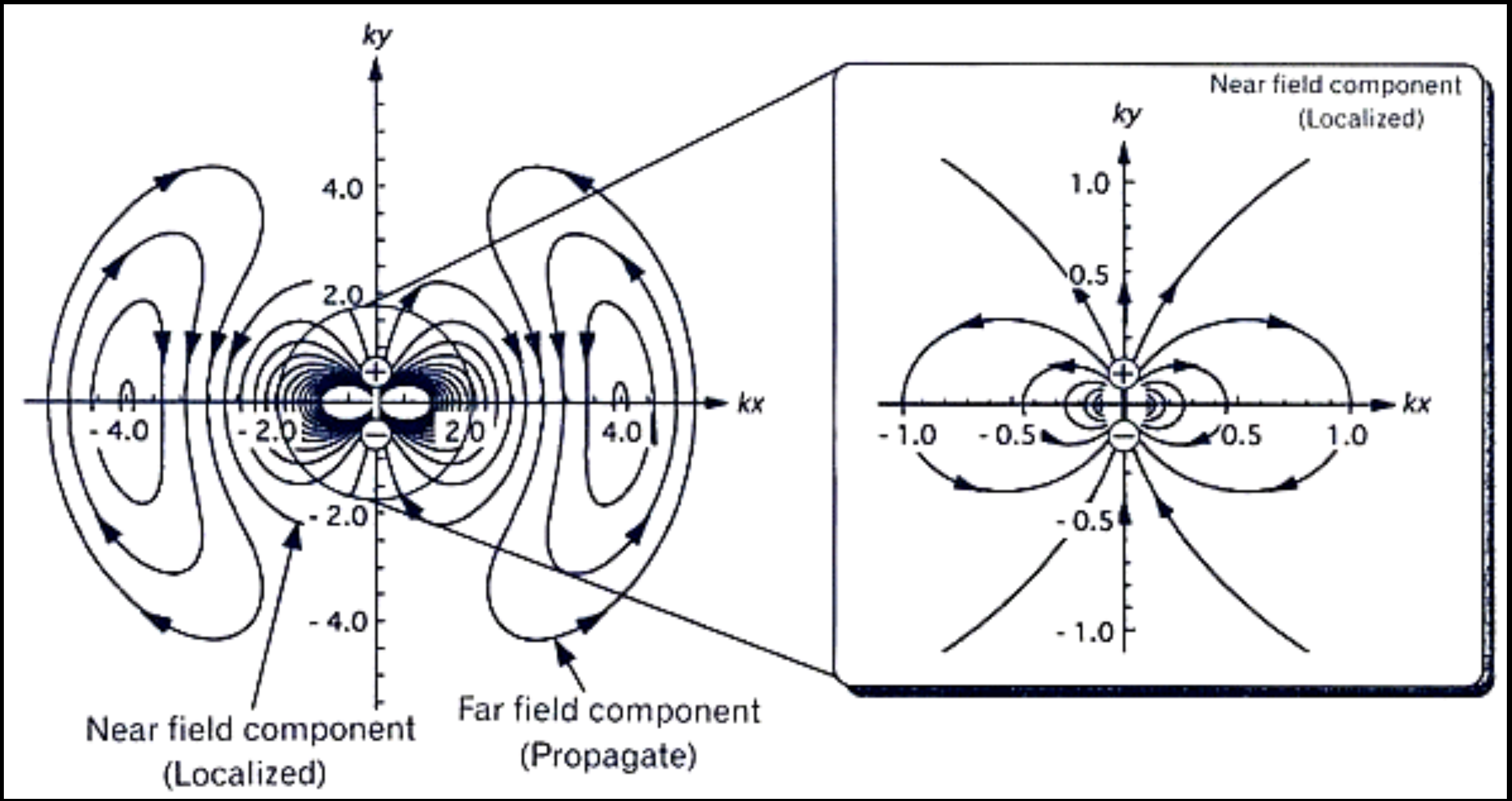
http://www.ryerson.ca/~kantorek/ELE884/EMdipole.gif

Sinusoidally oscillating lines of force in the electric field of an oscillating electric charge



For vertical oscillation, horizontal radiation is maximal.

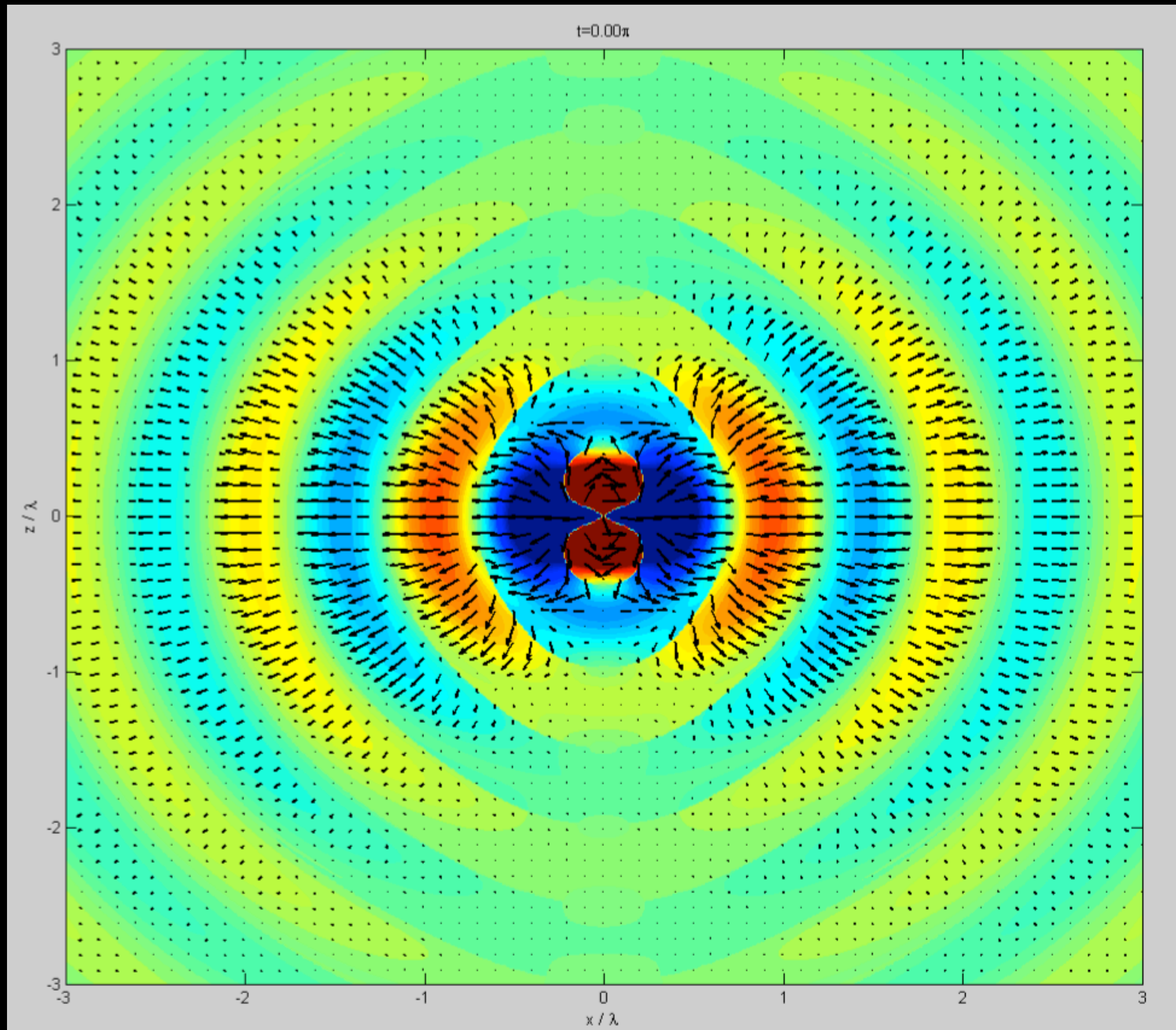
Oscillating electric field around an oscillating electric dipole



http://www.physics.upenn.edu/courses/gladney/phys151/lectures/lecture_apr_07_2003.shtml

em waves from an electric dipole oscillator

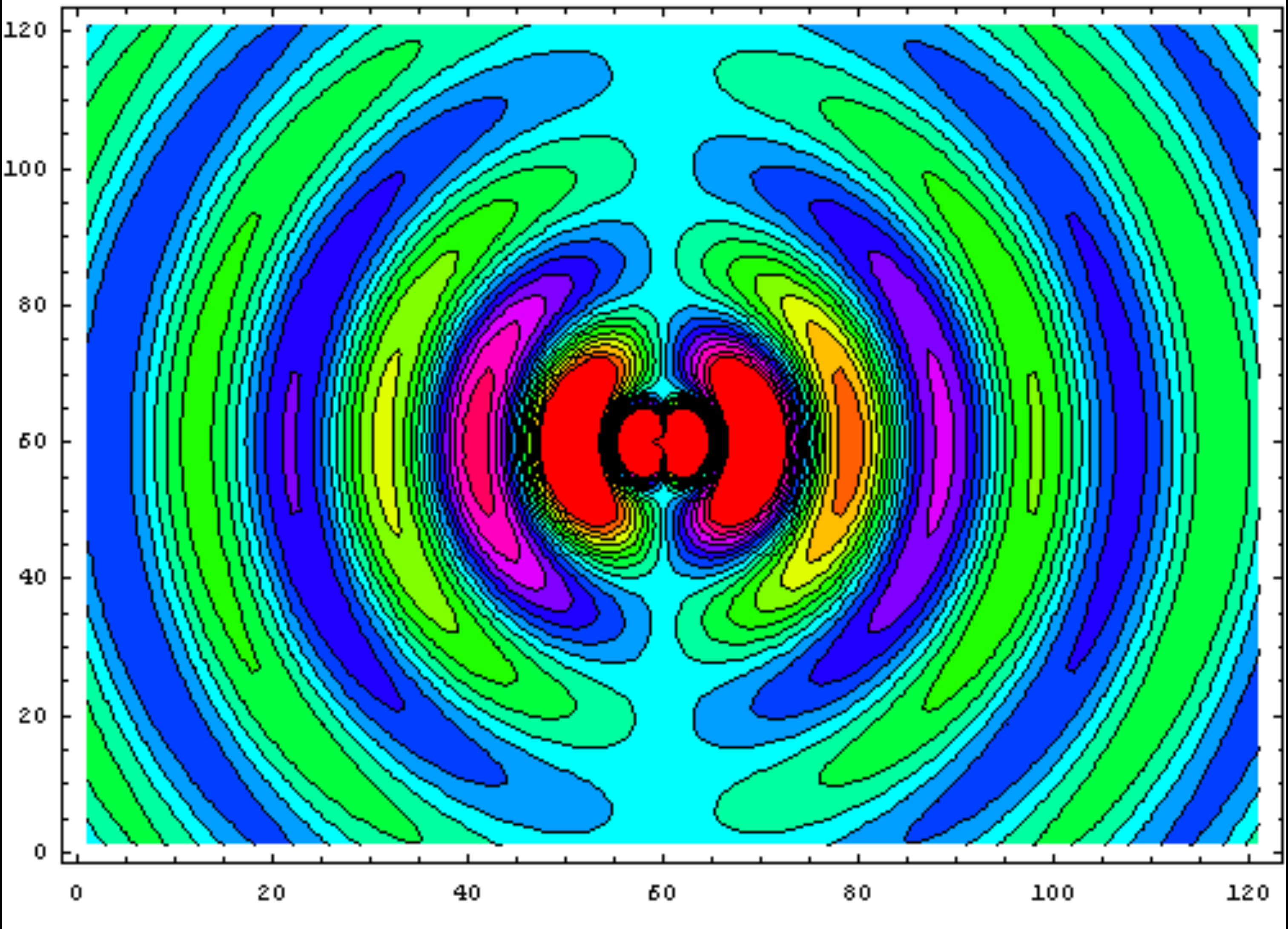
Oscillating electric dipole radiator



For a vertical oscillation, horizontal radiation is maximal.

http://en.wikipedia.org/wiki/File:DipoleRadiation.gif

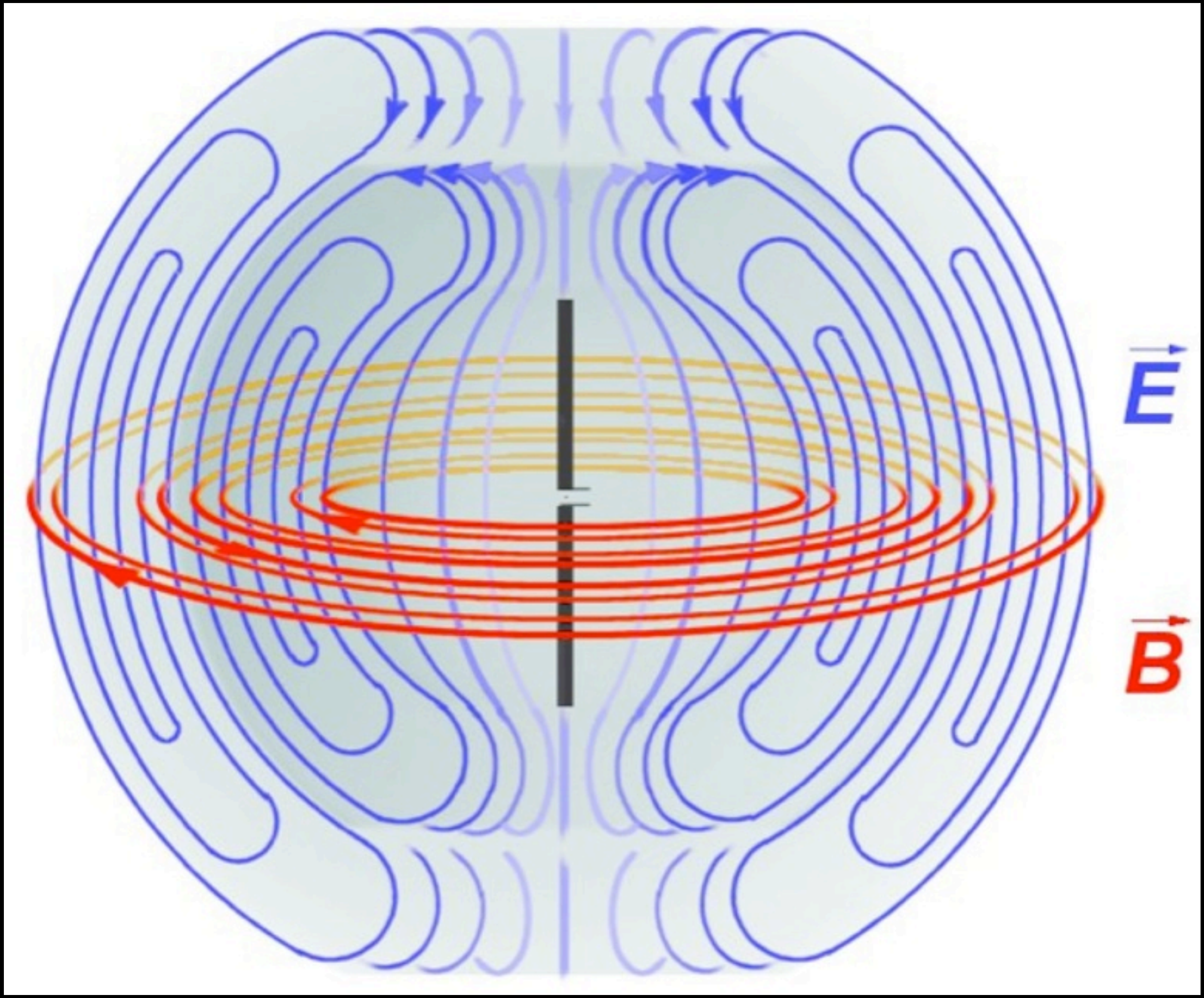
em waves from an electric dipole oscillator



For a vertical oscillation, horizontal radiation is maximal.

http://commons.wikimedia.org/wiki/File:Dipole.gif

e and m wave fields from an electric dipole oscillator



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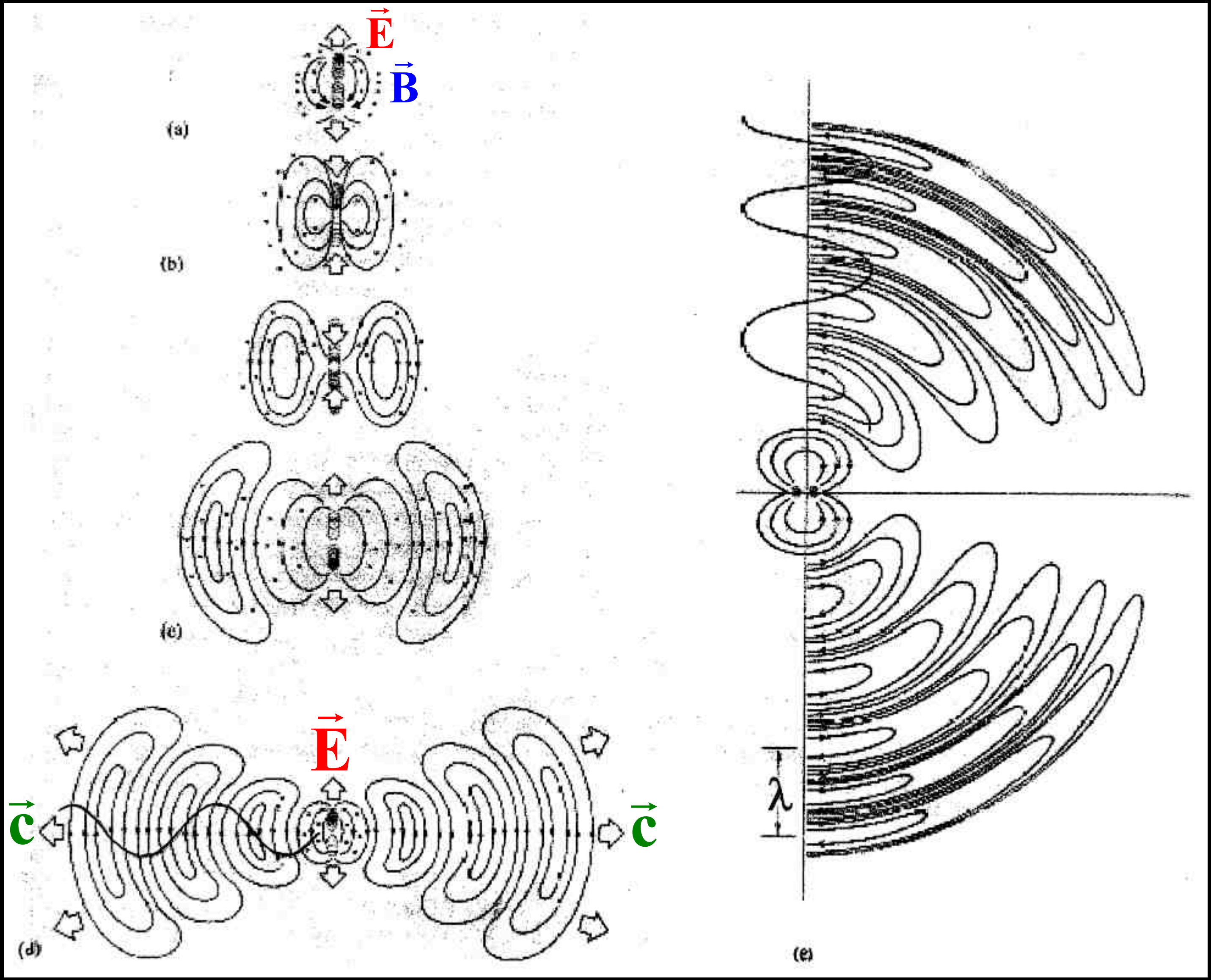
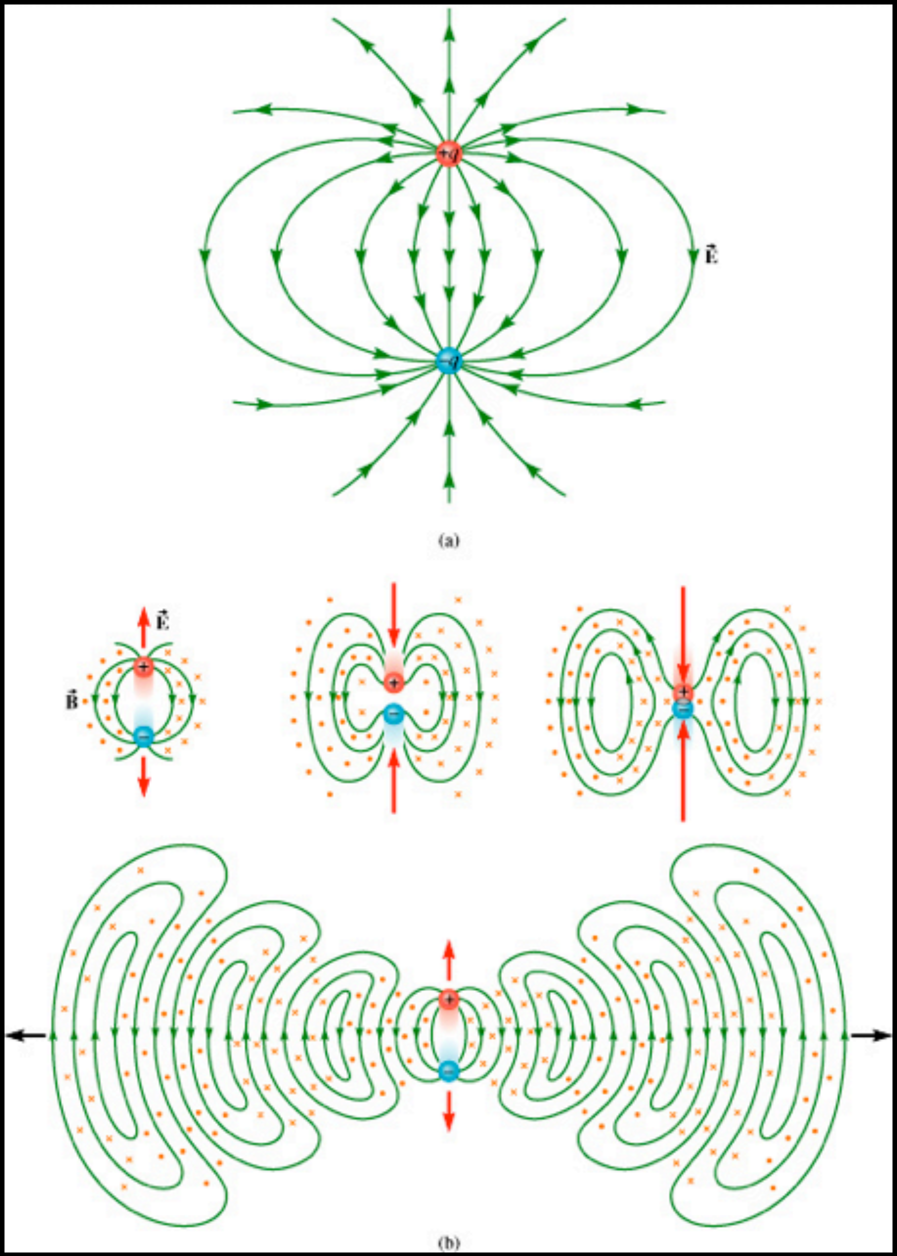
Electromagnetic radiation from an electric dipole oscillator



Oscillating em fields **E** and **B** propagating with velocity **c**

http://www.physics.upenn.edu/courses/gladney/phys151/lectures/lecture_apr_07_2003.shtml

e and m waves from an electric dipole oscillator



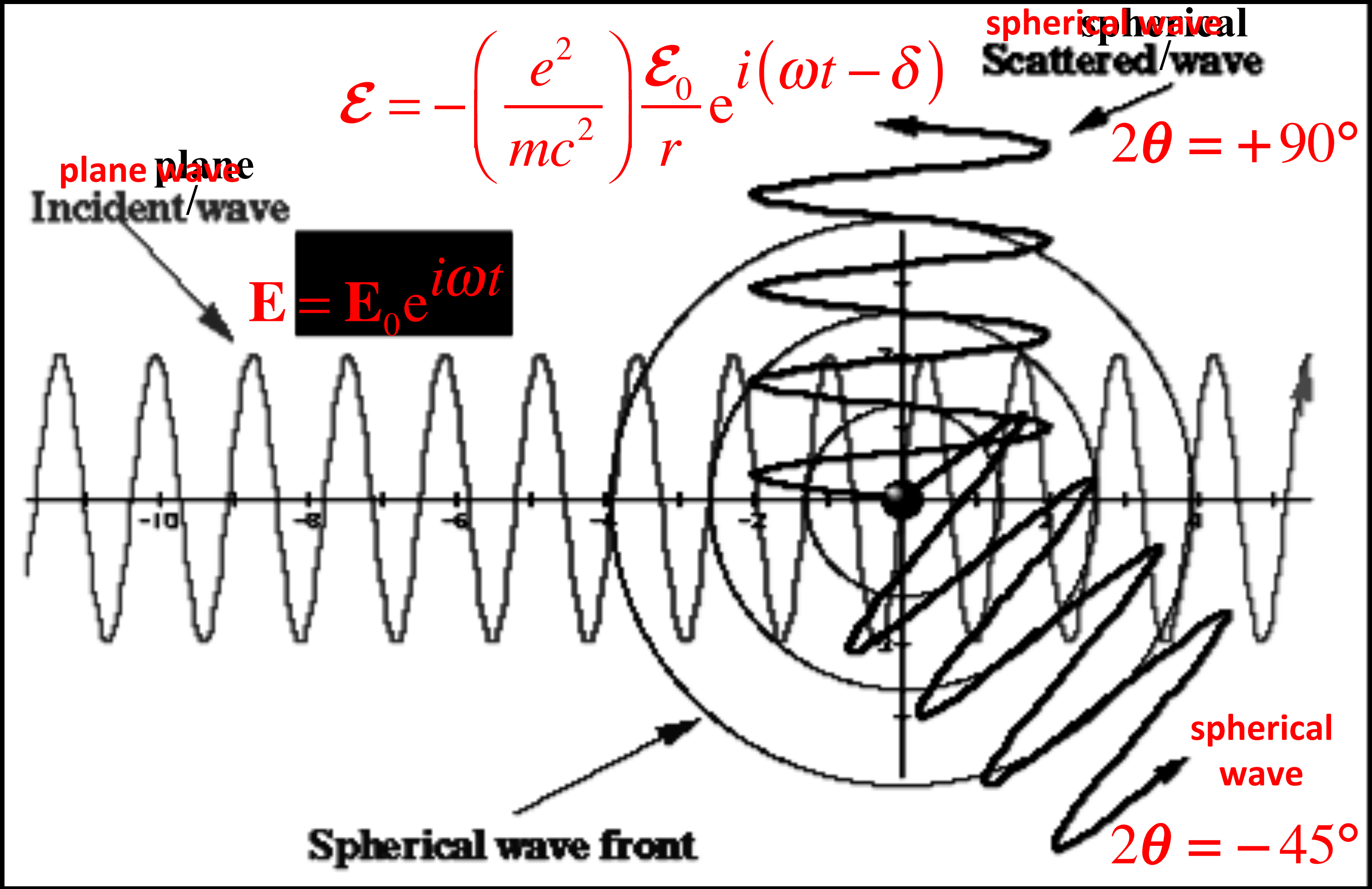
http://it.stlawu.edu/~jahncke/clj/cls/104/104Links.html

X-Ray Scattering, Interference, and Diffraction

Electromagnetic radiation scattering

em radiation scattering		IR - vis - UV wavelengths	X-ray wavelengths
	coherent, elastic	Rayleigh scattering	Thomson scattering
	incoherent, inelastic	Raman scattering	Compton scattering

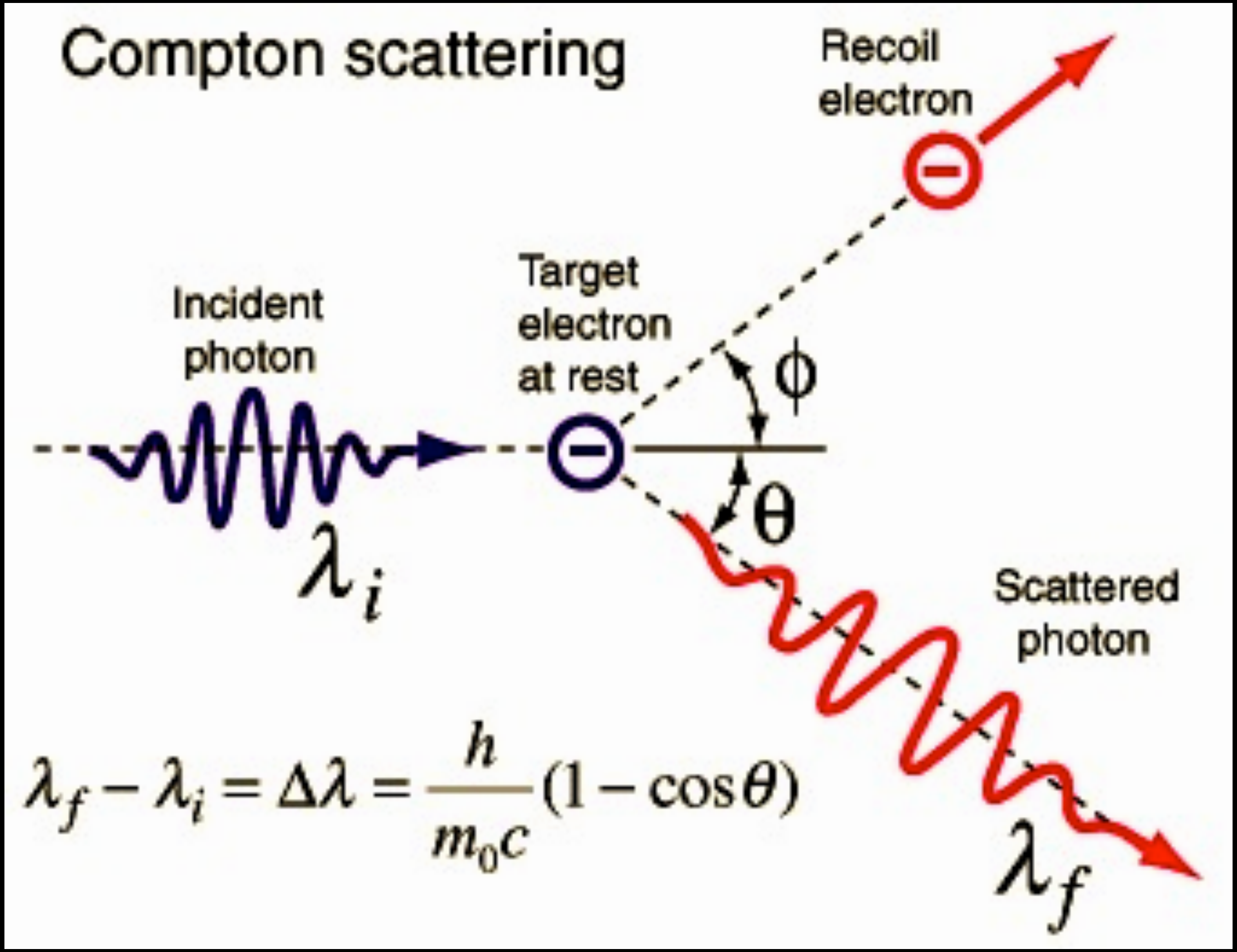
Thomson scattering of an X-ray wave *via* driven oscillation of an electron



Elastic scattering of an electromagnetic wave

http://www.gly.uga.edu/schroeder/geol3010/3010lecture09.html

Compton scattering of an X-ray photon by an electron



Inelastic photon-electron particle collision

http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/imgqua/compton.gif

Interactions of $\lambda \approx 1$ Å X-rays within a typical 100 µm protein crystal

~98%	transmission
~1.7%	photoelectric absorption
~0.15%	inelastic, Compton scattering
~0.15%	elastic, Laue-Bragg scattering

Murray,…, & Garman (2005). "… the X-ray dose absorbed by macromolecular crystals." *J. Synchrotron Rad.* 12, 268.

Crystallographic Diffraction

Laue diffraction from a three-dimensional *abc* lattice grating

$$a\left(\cos\nu_1 - \cos\mu_1\right) = \mathbf{a}\bullet\left(\hat{\mathbf{s}} - \hat{\mathbf{s}}_0\right) = h\lambda$$
$$b\left(\cos\nu_2 - \cos\mu_2\right) = \mathbf{b}\bullet\left(\hat{\mathbf{s}} - \hat{\mathbf{s}}_0\right) = k\lambda$$
$$c\left(\cos\nu_3 - \cos\mu_3\right) = \mathbf{c}\bullet\left(\hat{\mathbf{s}} - \hat{\mathbf{s}}_0\right) = l\,\lambda$$

Max Laue, Walther Friedrich, and Paul Knipping (1912).

Bragg reflection from families of parallel *hkl* lattice planes

$$2d_{hkl}\sin\theta = n\lambda\,, \qquad 2\left(\frac{d_{hkl}}{n}\right)\sin\theta = \lambda\,, \qquad 2d_{nh\,nk\,nl}\sin\theta = \lambda$$

William Henry and William Lawrence Bragg (1913). (Father and son)

Integrated Bragg reflection intensities

$$\rho = \frac{E\omega}{I_0} = kALp\left|F_{hkl}\right|^2 = \left(\frac{e^2}{mc^2}\right)^2 \lambda^3 \left(\frac{v_{\text{xtal}}}{V_{\text{cell}}}\right)^2 \left[\int_{v_{\text{xtal}}} \mathrm{e}^{-\mu(t_0+t_1)}\,\mathrm{d}v\right] \frac{1}{\sin 2\theta}\left(\frac{1}{2}+\frac{1}{2}\cos^2 2\theta\right)\left|F_{hkl}\right|^2$$

Charles G. Darwin (1914). (Grandson of the author of the theory of evolution)