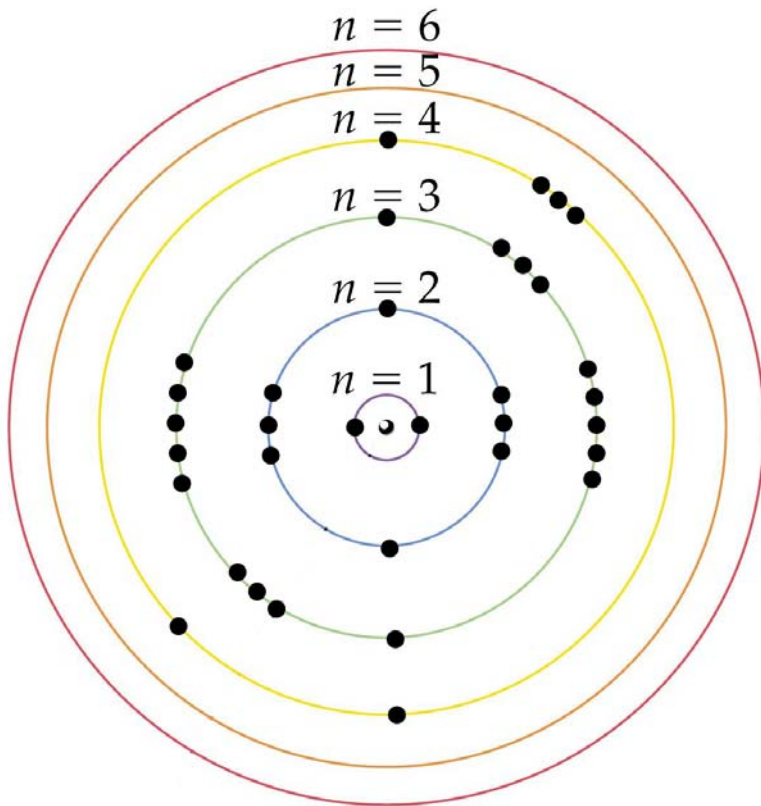


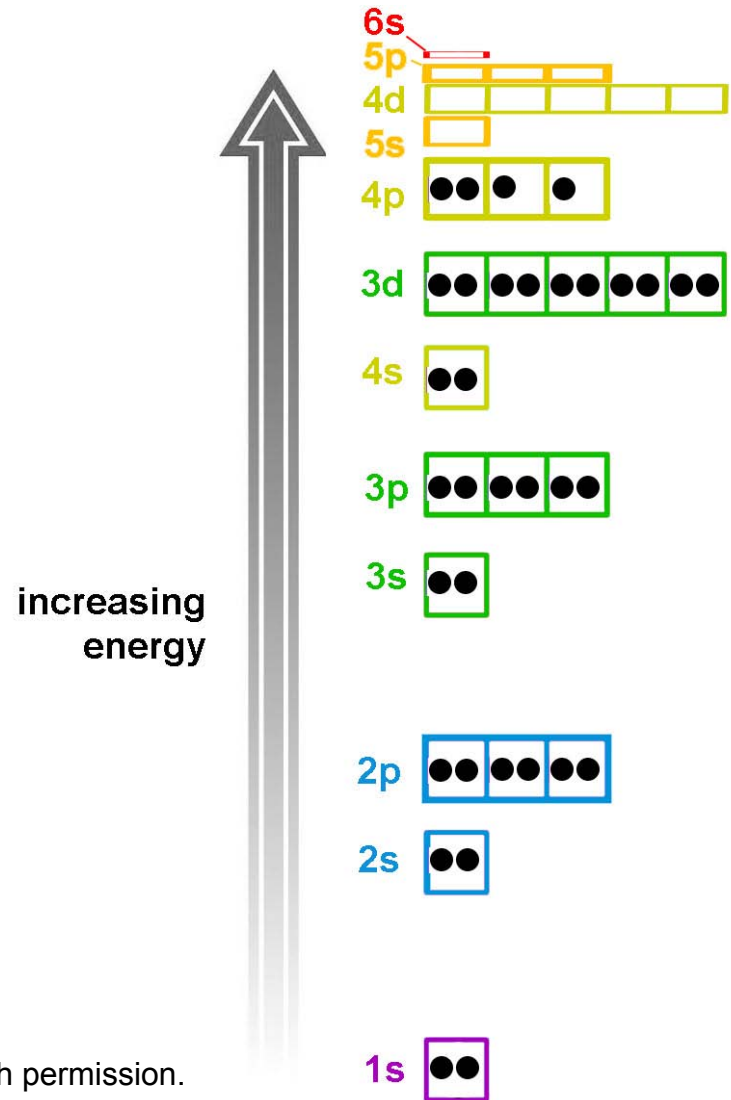
Anomalous Scattering

When the incident radiation has sufficient energy to promote an electronic transition in atoms contained in the crystal, we observe anomalous scattering in non-centrosymmetric crystals.



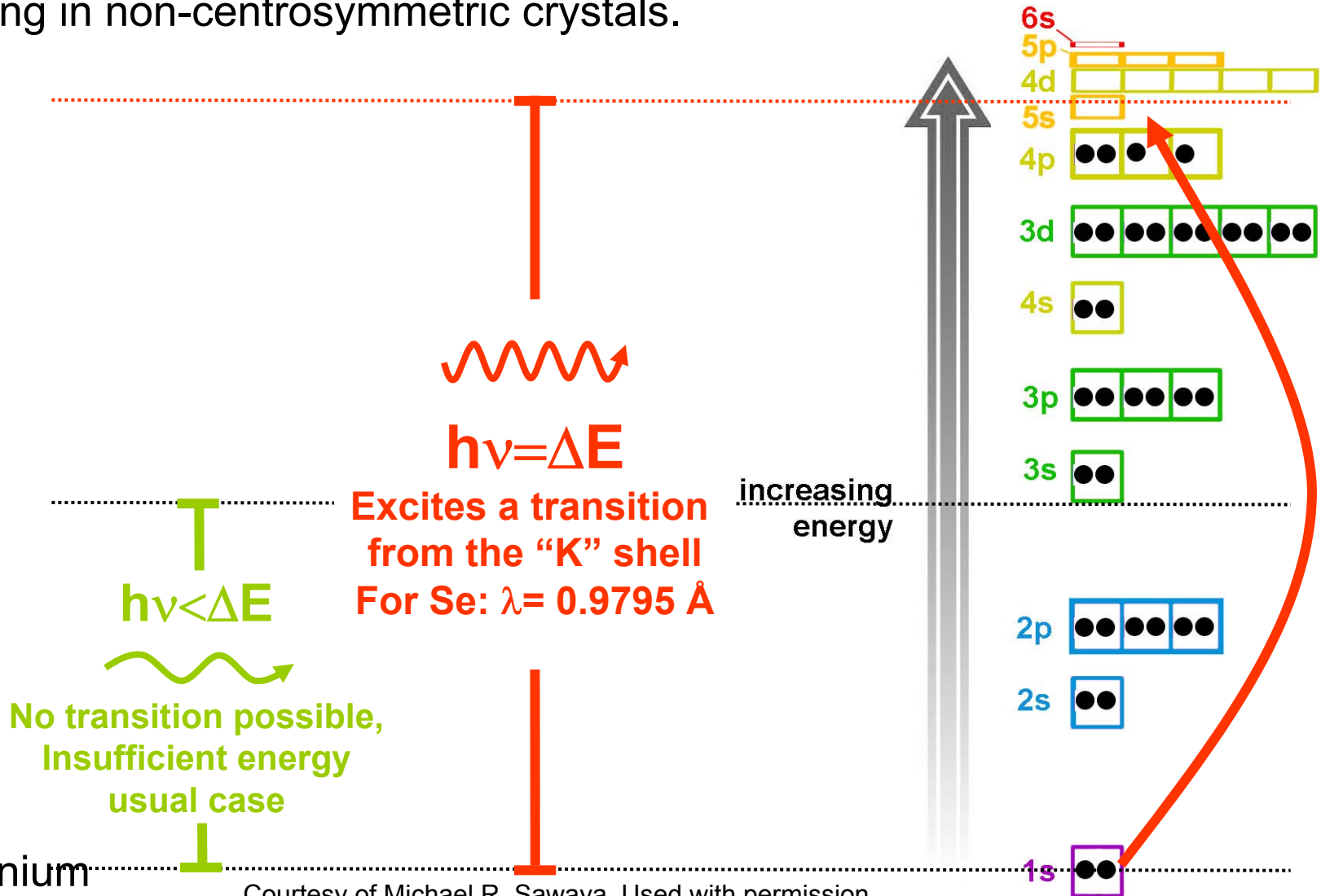
E.g. Selenium

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Anomalous Scattering

When the incident radiation has sufficient energy to promote an electronic transition in atoms contained in the crystal, we observe anomalous scattering in non-centrosymmetric crystals.



ΔE is a function of the periodic table.

1	H 1																	He 2	
2	Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10	
3	Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	Ar 18	
4	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36	
5	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54	
6	Cs 55	Ba 56	La 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86	
7	Fr 87	Ra 88	Ac 89	Unq 104	Ha 105	Unh 106	Ns 107	Hs 108	Mt 109										
				Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71		
				Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103		

ΔE is near 8keV for most heavy and some light elements, so an anomalous signal can be measured on a home X-ray source with CuK α radiation (8keV $\lambda=1.54\text{\AA}$).

At a synchrotron, the energy of the incident radiation can be tuned to match ΔE (accurately).

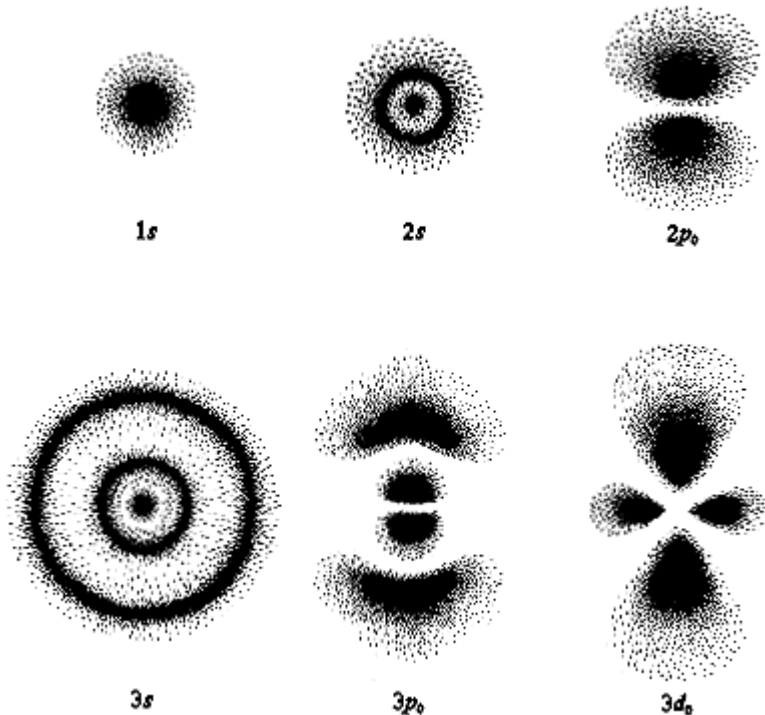
Importantly, ΔE s for C,N,O are out of the X-ray range.

K shell transitions L shell transitions

Anomalous Scattering

Anomalous scattering causes small but measurable differences in intensity between the reflections hkl and $-h-k-l$ not normally present. That means for non-centrosymmetric crystals in the presence of atoms heavier than sulfur, Friedel's law is not strictly true.

Under normal conditions, electron distributions within atoms are centrosymmetric:



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The centrosymmetry in the scattering atoms is reflected in the centrosymmetry in the pattern of scattered X-ray intensities.

The positions of the reflections hkl and $-h-k-l$ on the reciprocal lattice are related by a center of symmetry through the reciprocal lattice origin $(0,0,0)$.

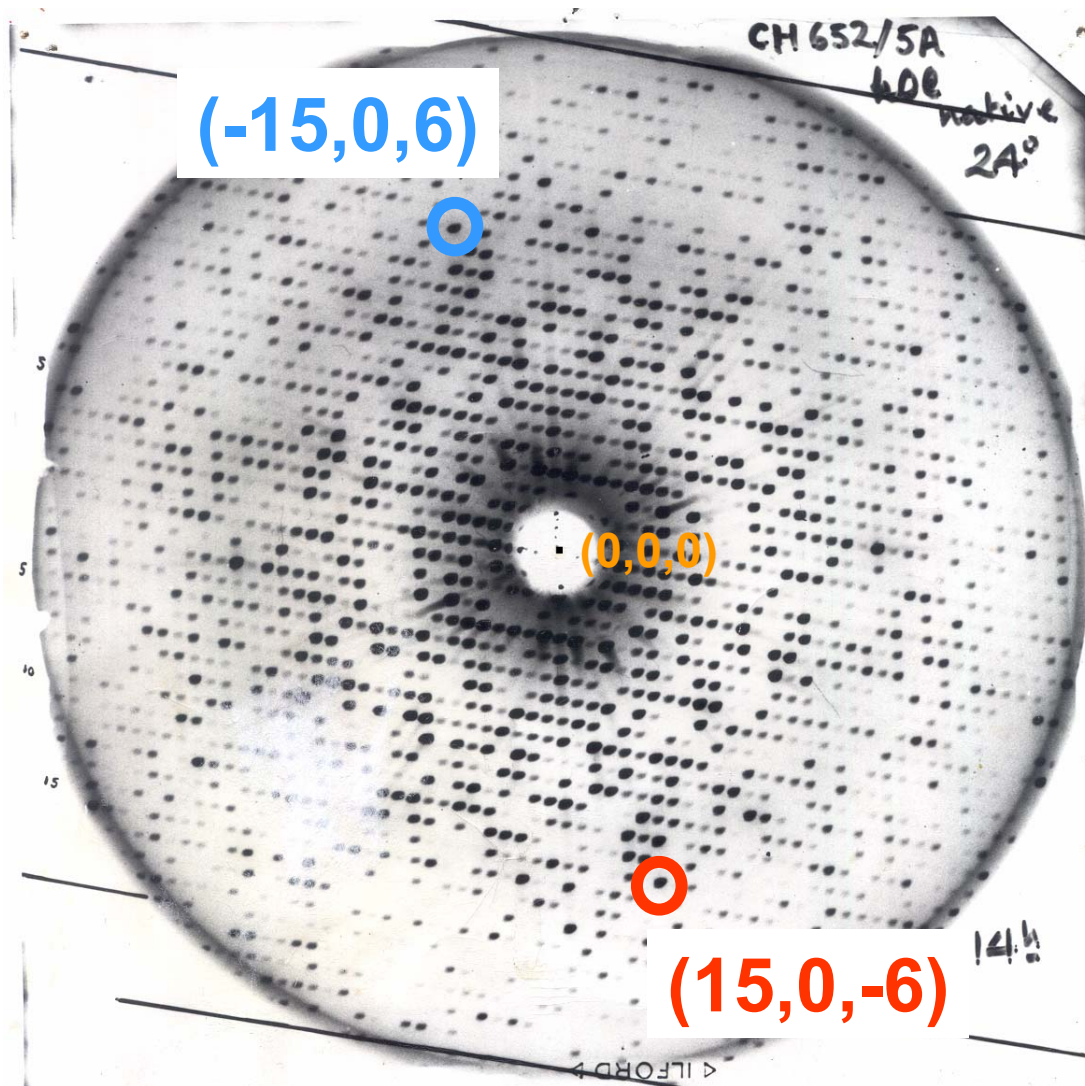
Pairs of reflections hkl and $-h-k-l$ are called Friedel pairs.

They share the same intensity by Friedel's law.

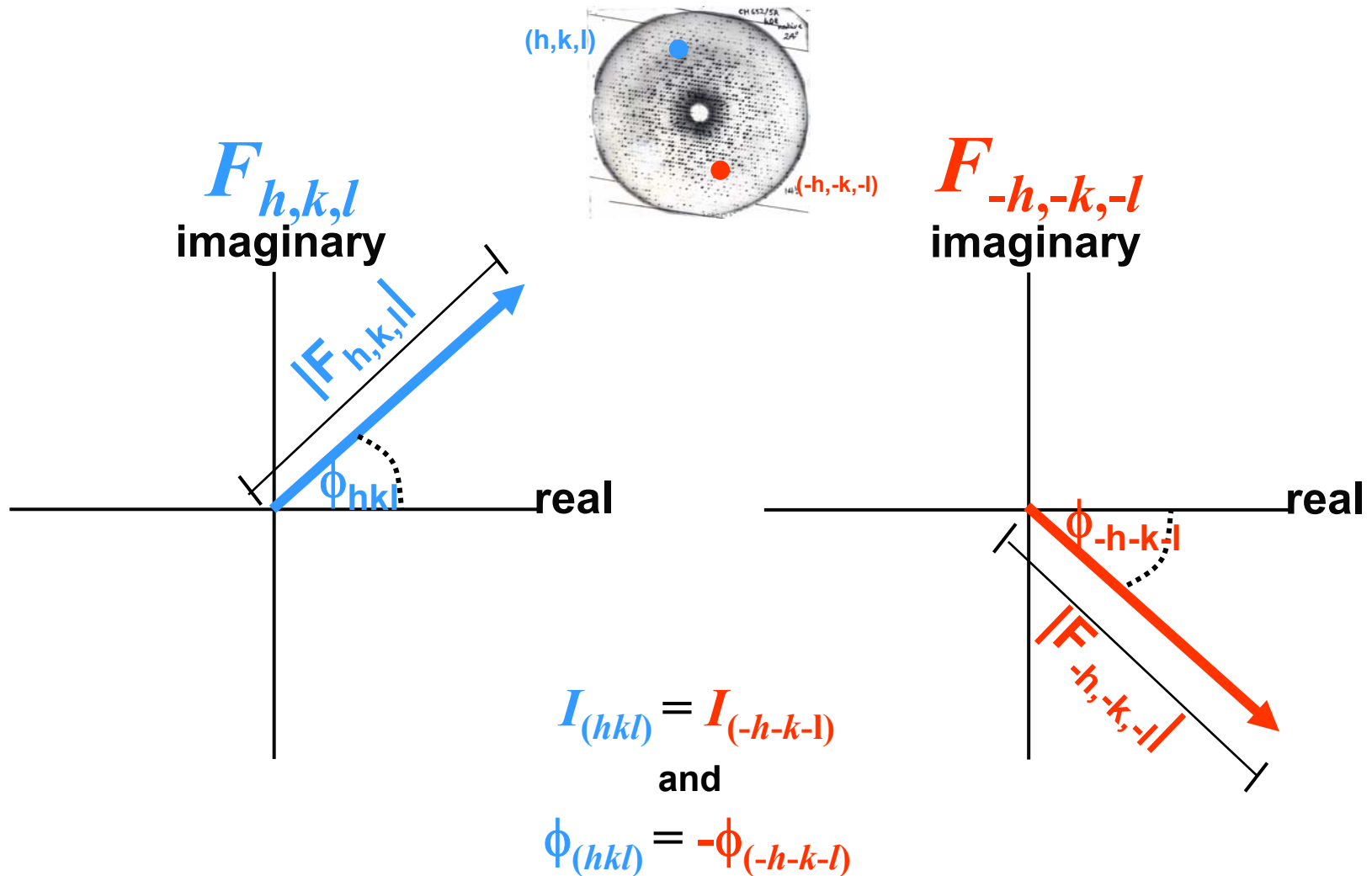
$$I_{(hkl)} = I_{(-h-k-l)}$$

and

$$\phi_{(hkl)} = -\phi_{(-h-k-l)}$$



On an Argand diagram, $F_{(hkl)}$ and $F_{(-h-k-l)}$ appear to be reflected across the real axis.

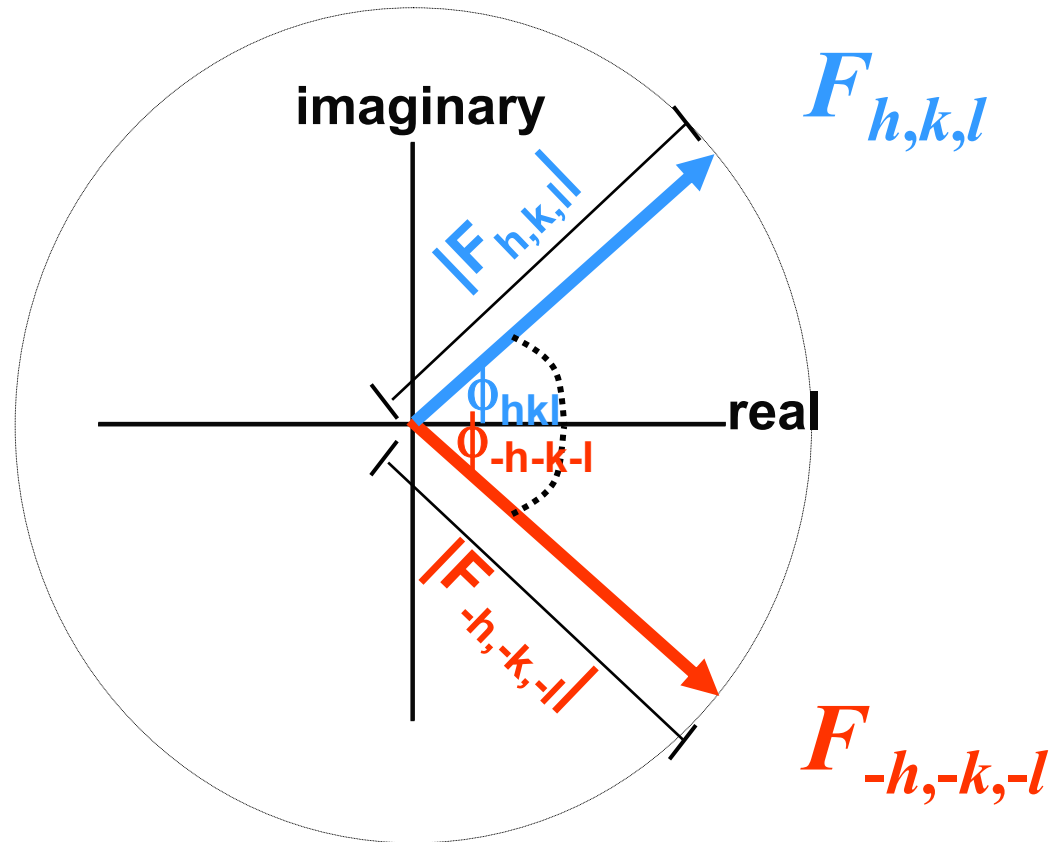


On an Argand diagram, $F_{(hkl)}$ and $F_{(-h-k-l)}$ appear to be reflected across the real axis.

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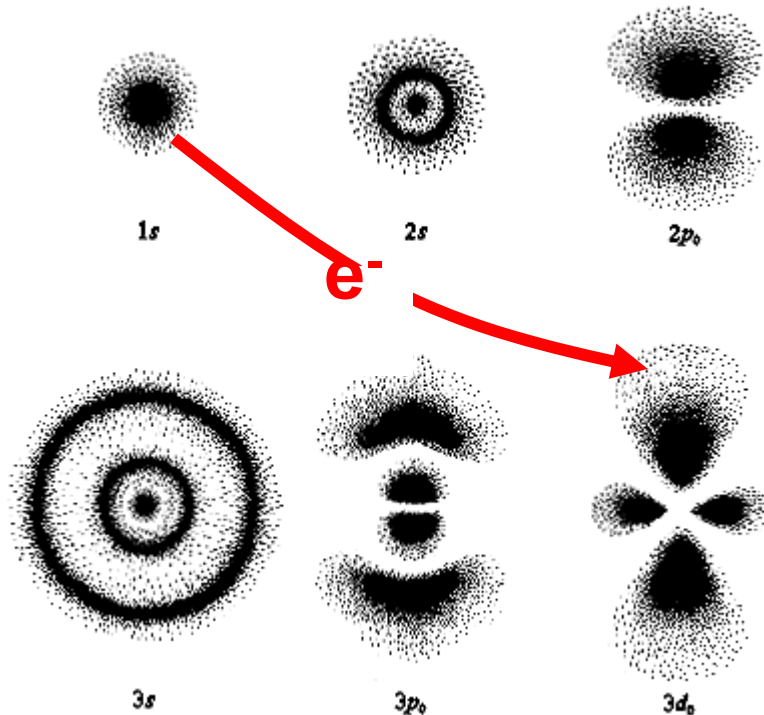
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True for any crystal in the absence of anomalous scattering. Normally, I_{hkl} and I_{-h-k-l} are averaged together.

Anomalous Scattering

Anomalous scattering causes small but measurable differences in intensity between the reflections hkl and $-h-k-l$ not normally present. That means for non-centrosymmetric crystals in the presence of atoms heavier than sulfur, Friedel's law is not strictly true.

Under normal conditions, electron distributions within atoms are centrosymmetric:



Under conditions of anomalous scattering, electrons are perturbed from their centrosymmetric distributions; electrons are jumping between orbitals.

The breakdown of centrosymmetry in the scattering atoms is reflected in a loss of centrosymmetry in the pattern of scattered X-ray intensities.

Thus $I_{(hkl)} = I_{(-h-k-l)}$ is no longer true.

The differences between I_{hkl} and I_{-h-k-l} are small; typically between 1-3%.

Anomalous Scattering

In the presence of anomalous scattering, $F_{(hkl)}$ and $F_{(-h-k-l)}$ obey neither of the two relationships of Friedel's Law and we are able to measure the differences between $F_{(hkl)}$ and $F_{(-h-k-l)}$.

$$I_{(hkl)} \neq I_{(-h-k-l)}$$

and

$$\phi_{(hkl)} \neq -\phi_{(-h-k-l)}$$

How to calculate F for an anomalous scatterer?

The correction to the atomic scattering factor is derived from classical physics and is based on an analogy of the atom to a forced oscillator under resonance conditions.

Examples of forced oscillation:

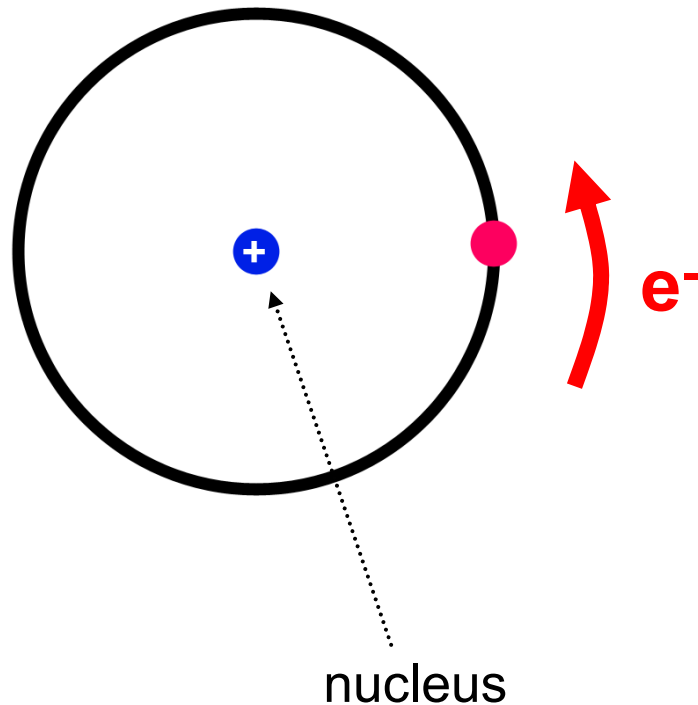
Figures removed due to copyright restrictions.

A tuning fork vibrating when exposed to periodic force of a sound wave.

The housing of a motor vibrating due to periodic impulses from an irregularity in the shaft.

A bridge swaying under the influence of marching soldiers or gusts of wind.

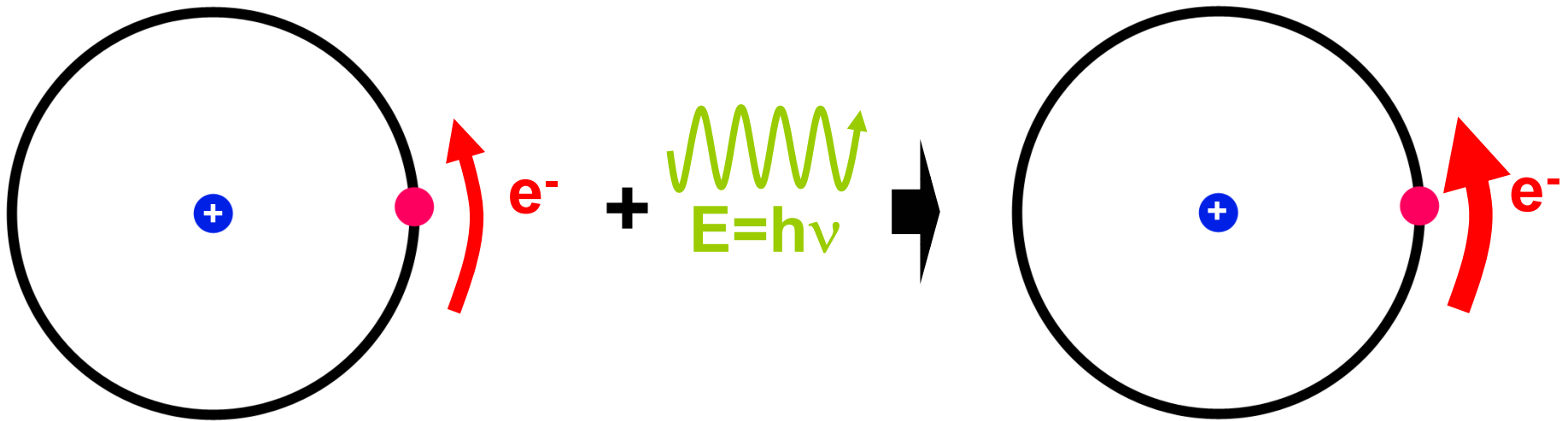
An atom can be viewed as a dipole oscillator where the electron oscillates around the nucleus.



The oscillator is characterized by

- Mass = m
- Position = x, y
- Natural circular frequency = ν_B
Characteristic of the atom.
Bohr frequency from Bohr's representation of the atom

An incident photon's electric field can exert a force on the e^- , affecting its oscillation frequency.



Courtesy of Michael R. Sawaya. Used with permission.

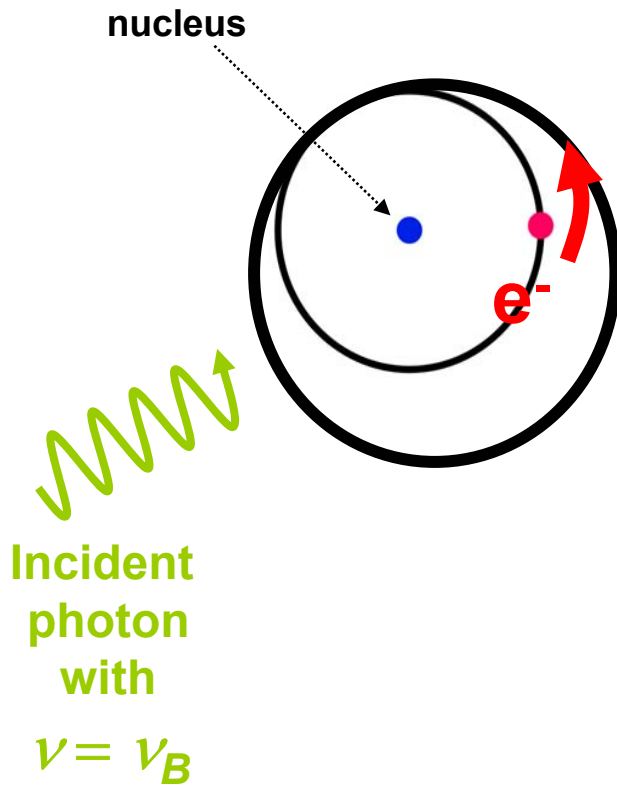
What happens when the external force matches the natural frequency of the oscillator (a.k.a resonance condition)?

If the external force is a periodic gust of wind and the oscillator is the Tacoma Narrows bridge, then disaster occurs.

Photograph removed due to copyright restrictions.

Tacoma Narrows bridge, 1940

In the case of an atom, resonance ($n = n_B$) leads to electronic transition analogous to the condition $h\nu = \Delta E$ discussed earlier.



The amplitude of the oscillator (electron) is given by classical physics:

$$A = \frac{e}{mc^2} \frac{\nu^2 E_o}{\nu_B^2 - \nu^2 + ik\nu}$$

m = mass of oscillator

e = charge of the oscillator

c = speed of light

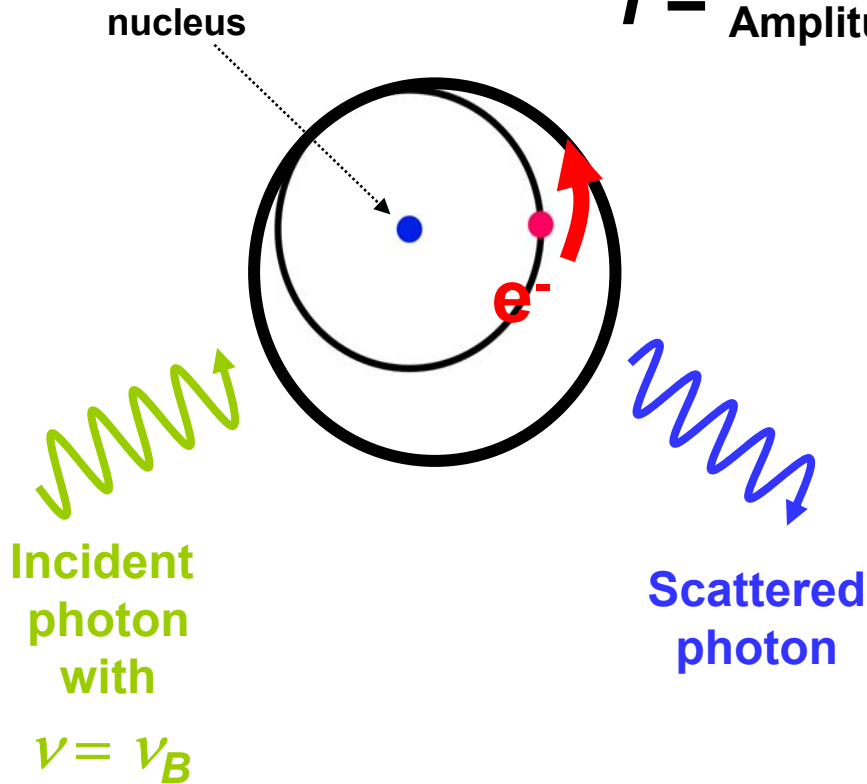
E_o = max value of electric vector of incident photon

ν = frequency of external force (photon)

ν_B = natural resonance frequency of oscillator (e^-)

Knowing the amplitude of the e^- leads to a definition of the scattering factor, f .

$$f = \frac{\text{Amplitude of scattered radiation from the forced } e^-}{\text{Amplitude of scattered radiation by a free } e^-}$$



The amplitude of the scattered radiation is defined by the oscillating electron.

The oscillating electron is the source of the scattered electromagnetic wave which will have the same frequency and amplitude as the e^- .

Keep in mind, the frequency and amplitude of the e^- is itself strongly affected by the frequency and amplitude of the incident photon as indicated on the previous slide.

The scattering factor is a complex number,
with value dependent on ν .

$$f = \underline{f_0} + \underline{\Delta f'} + i \underline{\Delta f''}$$

ν = frequency incident photon

ν_B = Bohr frequency of oscillator (e^-)

(corresponding to electronic transition)

$$f_0$$

$$\Delta f' = g \left(\frac{\nu_B}{\nu} \right)^2 \log_e \left| \left(\frac{\nu}{\nu_B} \right)^2 - 1 \right|$$

$$\Delta f'' = g \frac{\pi \nu_B^2}{\nu^2}$$

**Normal
scattering
factor
REAL**

**correction
factor
REAL**

**correction
factor
IMAGINARY**

Correction factors are largest near $\nu = \nu_B$.

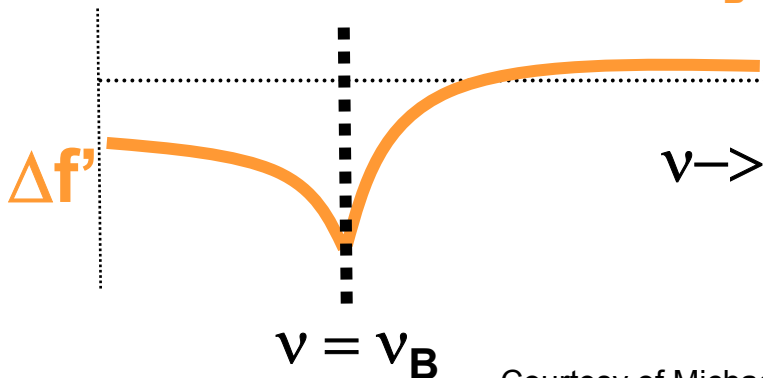
$$f = f_0 + \Delta f' + i\Delta f''$$

$$\Delta f' = g \left(\frac{\nu_B}{\nu} \right)^2 \log_e \left| \left(\frac{\nu}{\nu_B} \right)^2 - 1 \right|$$

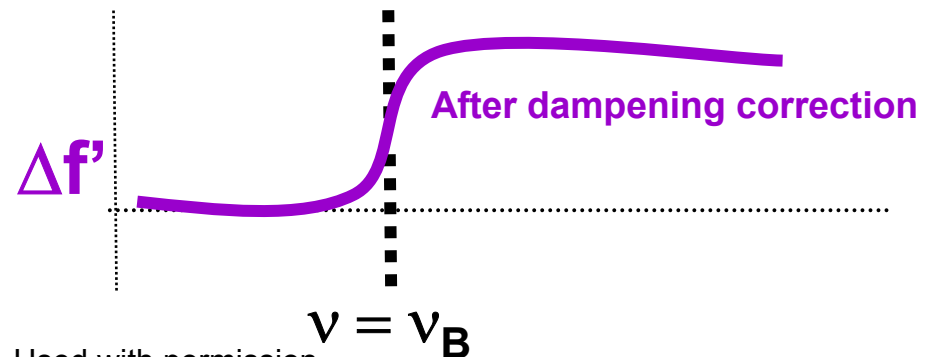
$$\Delta f'' = g \frac{\pi \nu_B^2}{\nu^2} \quad \begin{array}{l} \text{when } \nu > \nu_B \\ \text{Else, } 0 \end{array}$$

ν = frequency of external force (incident photon)
 ν_B = natural frequency of oscillator (e^-)

The **REAL COMPONENT**
 becomes negative near $\nu = \nu_B$.

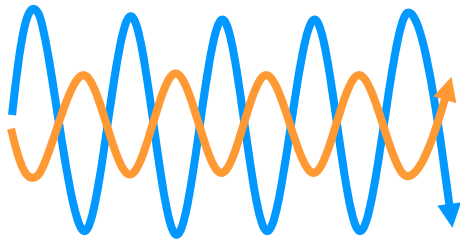


The **IMAGINARY COMPONENT**
 becomes large and positive near $\nu = \nu_B$.



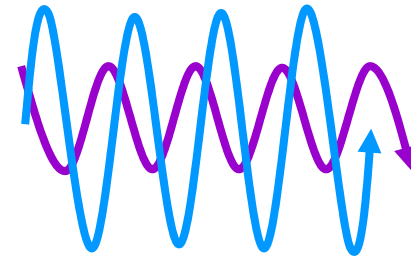
Physical interpretation of the real and imaginary correction factors of f .

$$f = f_0 + \Delta f' + i\Delta f''$$



real component, $\Delta f'$

A small component of the scattered radiation is 180° out of phase with the normally scattered radiation given by f_0 .

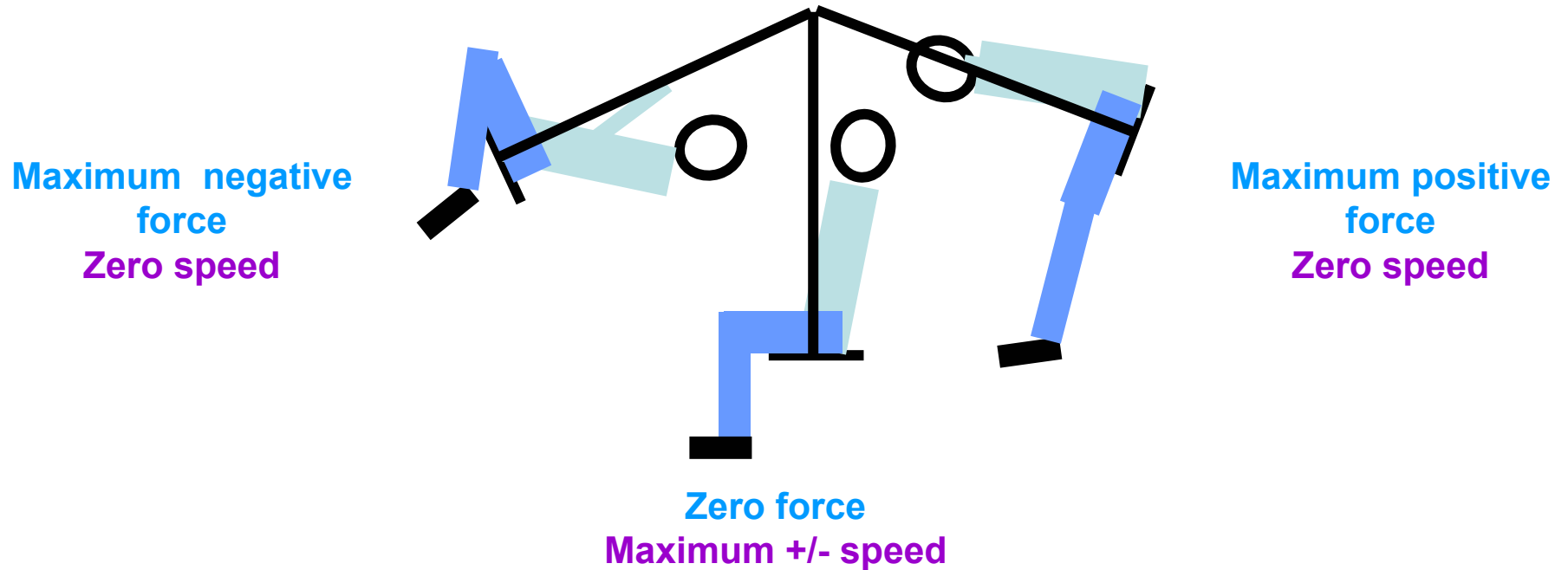


imaginary component, $\Delta f''$

A small component of the scattered radiation is 90° out of phase with the normally scattered radiation given by f_0 .

Always diminishes f_0 .
Absorption of X-rays

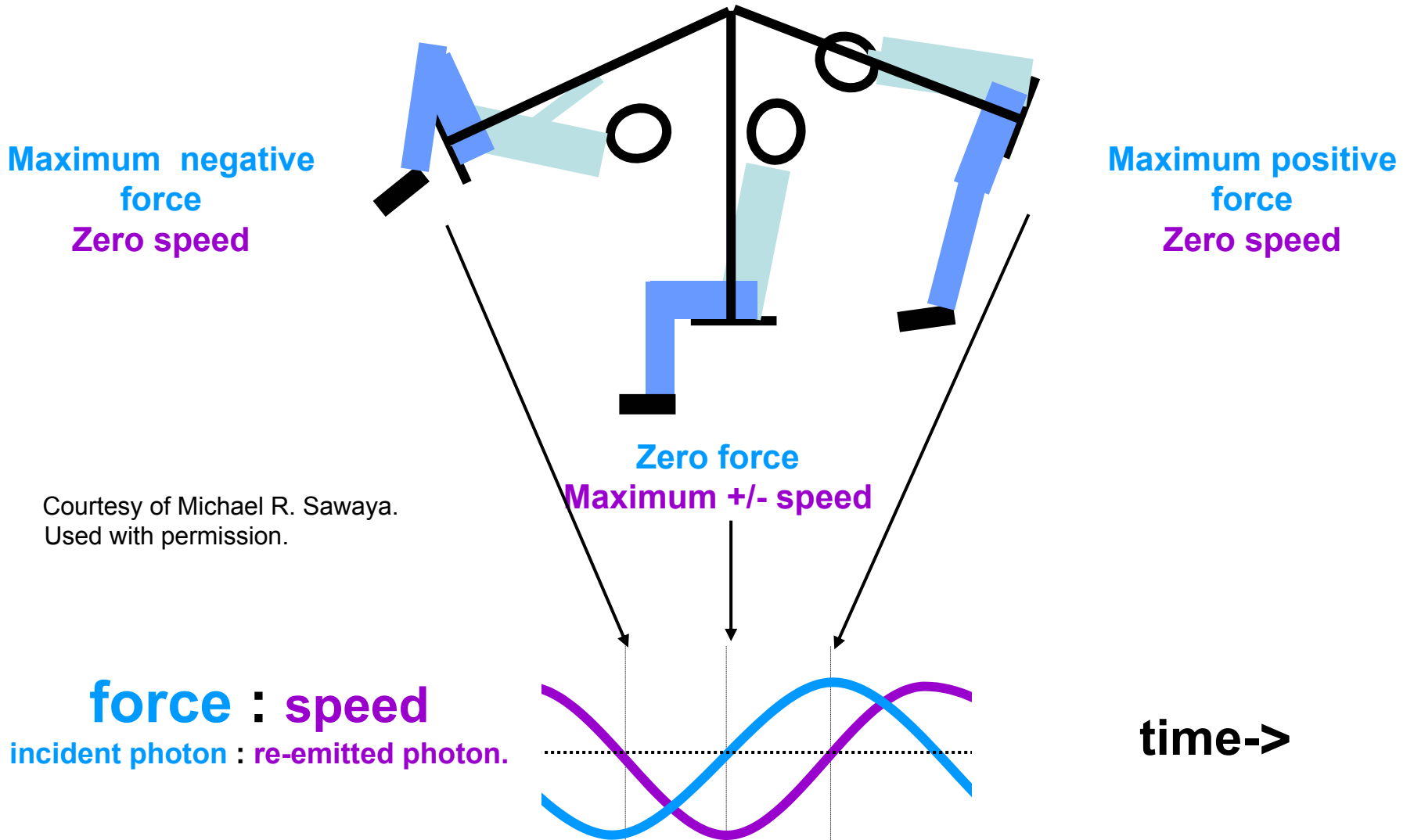
90° phase shift analogy to a child on a swing Forced Oscillator Analogy



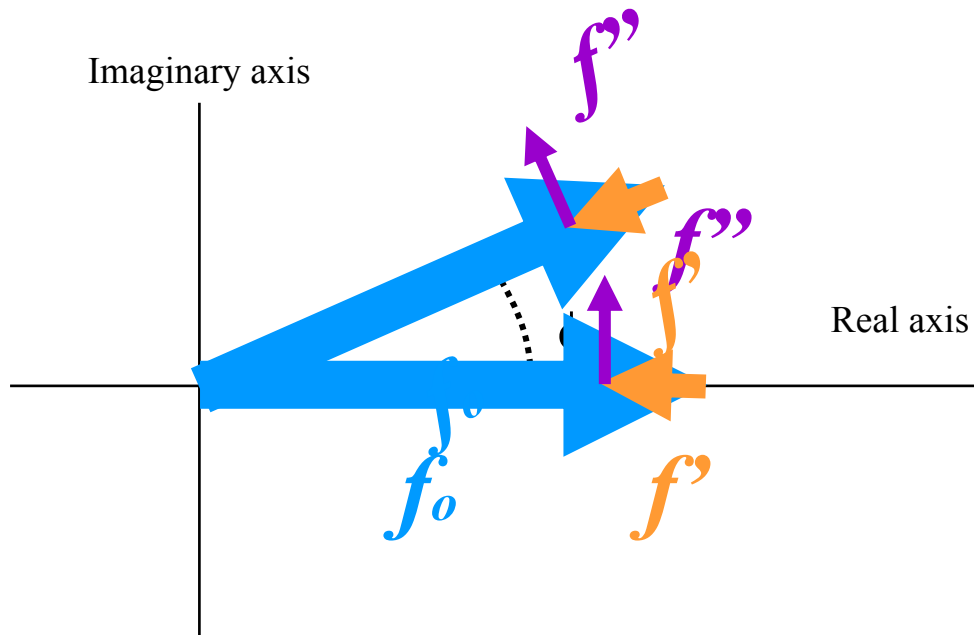
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Swing speed is 90° out of phase with the **applied force**.

90° phase shift analogy to a child on a swing Forced Oscillator Analogy



Argand diagram for $F_{H(hkl)}$ under conditions of anomalous scattering



$$F_H = [f_0 + \Delta f'(\lambda) + i\Delta f''(\lambda)] e^{2\pi i(hx_H + ky_H + lz_H)}$$

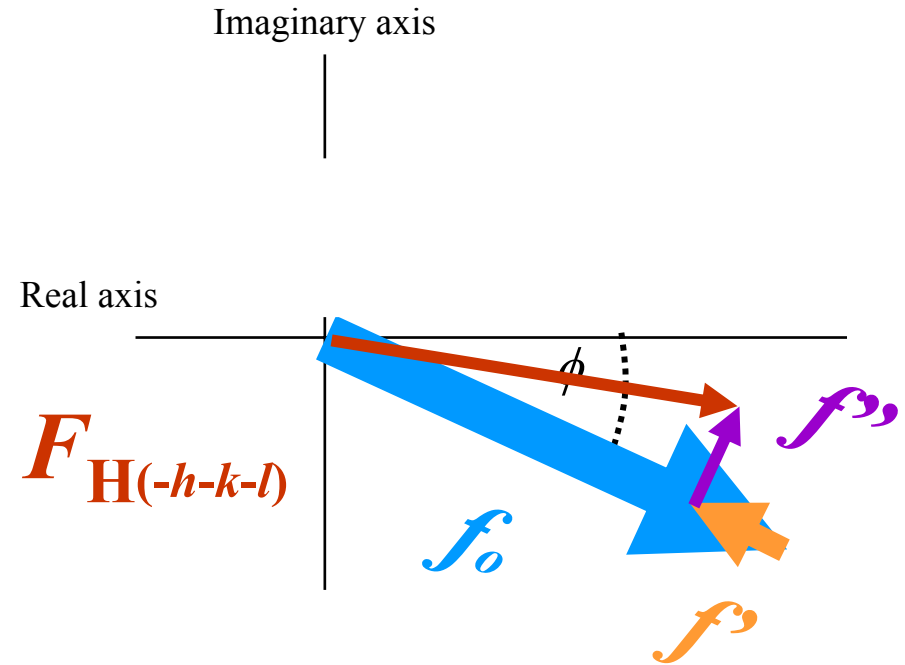
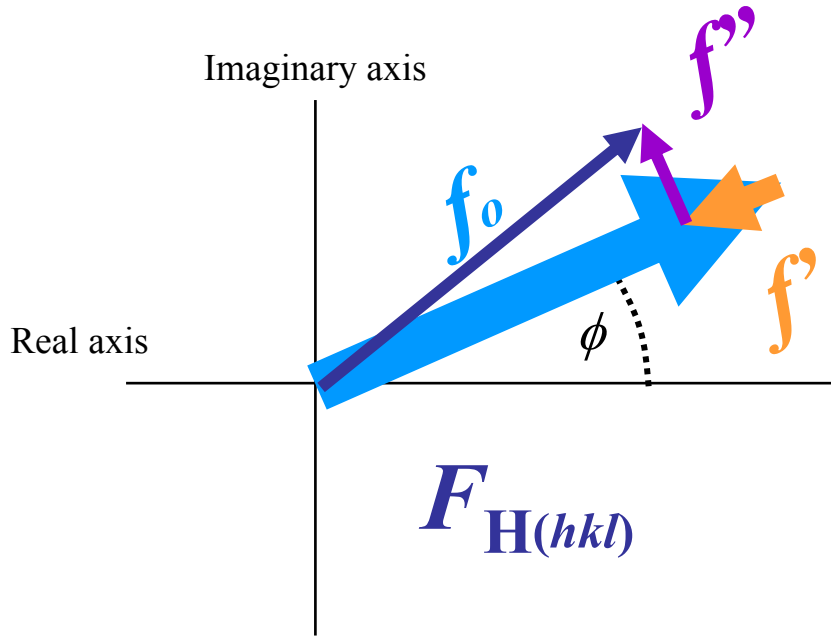
..... scattering factor for H

real
Positive
number

real
180° out of phase

imaginary
90° out of phase

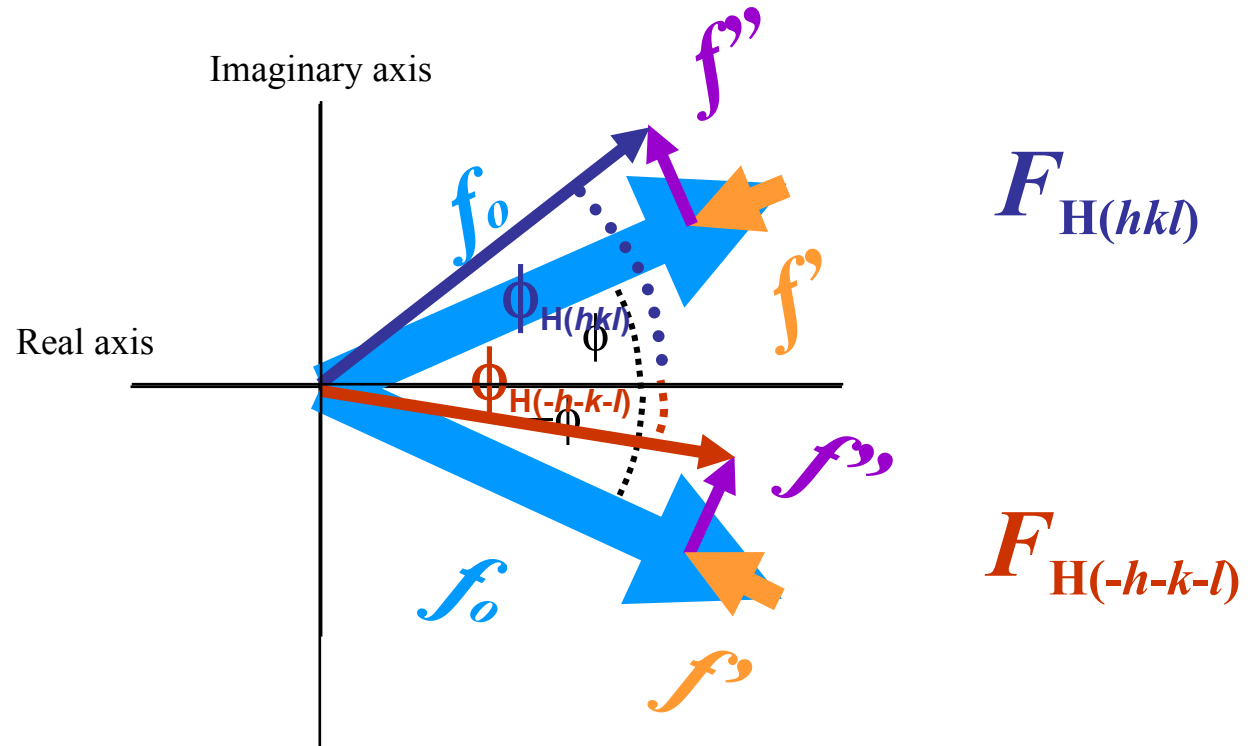
Argand diagram for $F_{H(-h-k-l)}$ is constructed in a similar way as $F_{H(hkl)}$ except ϕ is negative.



$$F_{H(hkl)} = [f_0 + \Delta f'(\lambda) + i\Delta f''(\lambda)] e^{2\pi i(hx + ky + lz)}$$

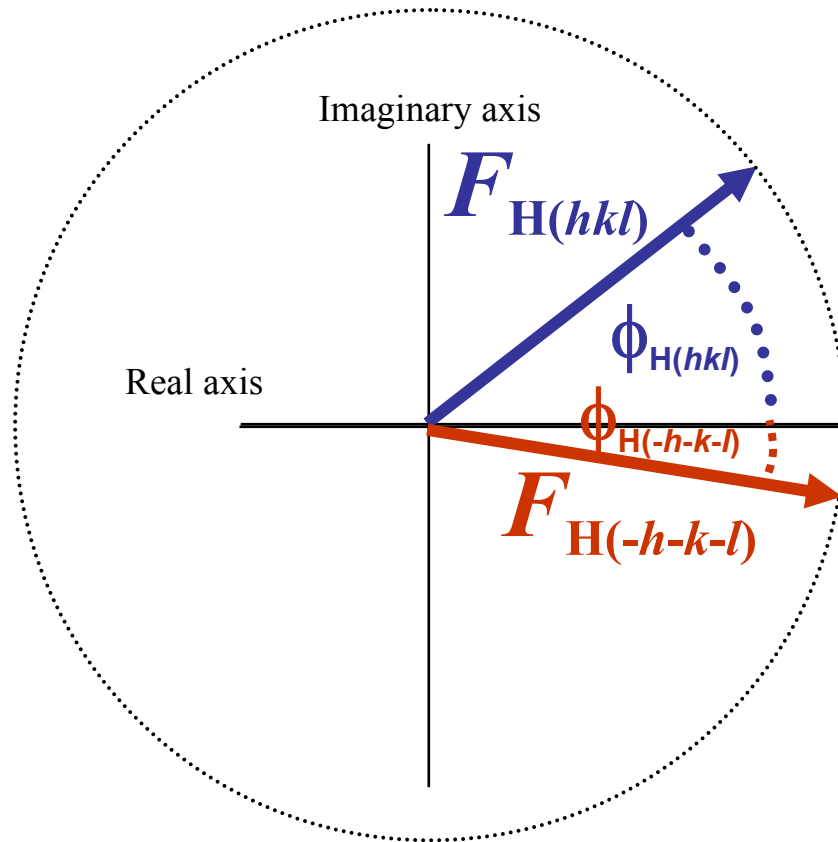
$$F_{H(-h-k-l)} = [f_0 + \Delta f'(\lambda) + i\Delta f''(\lambda)] e^{2\pi i(-hx - ky - lz)}$$

Friedel's Law is broken



$$\phi_{H(hkl)} \neq \phi_{H(-h-k-l)}$$

Friedel's Law is broken



For only the contribution of one type of heavy atom:

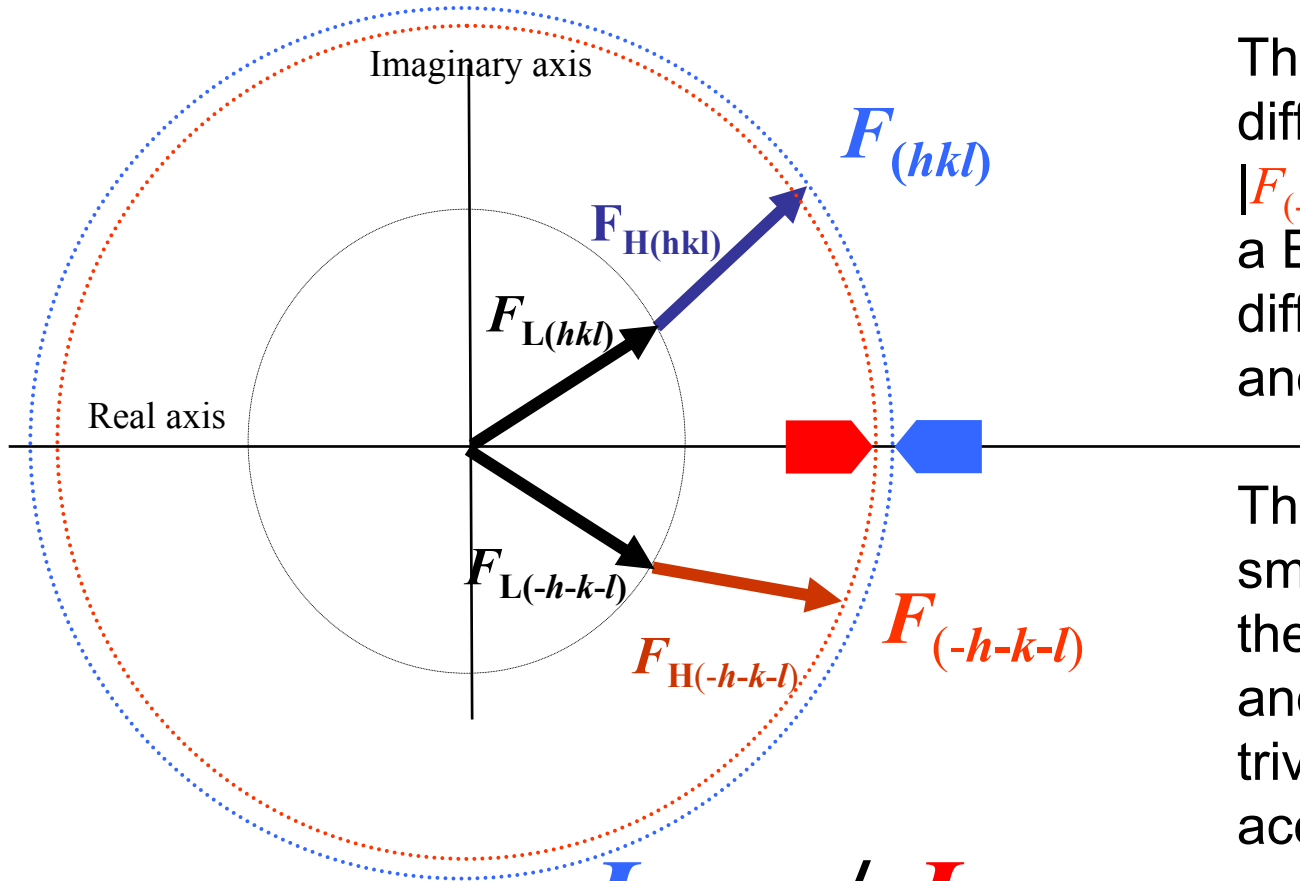
$$I_{\text{H}(hkl)} = I_{\text{H}(-h-k-l)}$$

This situation changes in the presence of other atoms. *E.g.* lighter atoms that do not show anomalous scattering.

$$I_{\text{H}(hkl)} = I_{\text{H}(-h-k-l)}$$

$$\phi_{\text{H}(hkl)} \neq \phi_{\text{H}(-h-k-l)}$$

Friedel's Law is broken



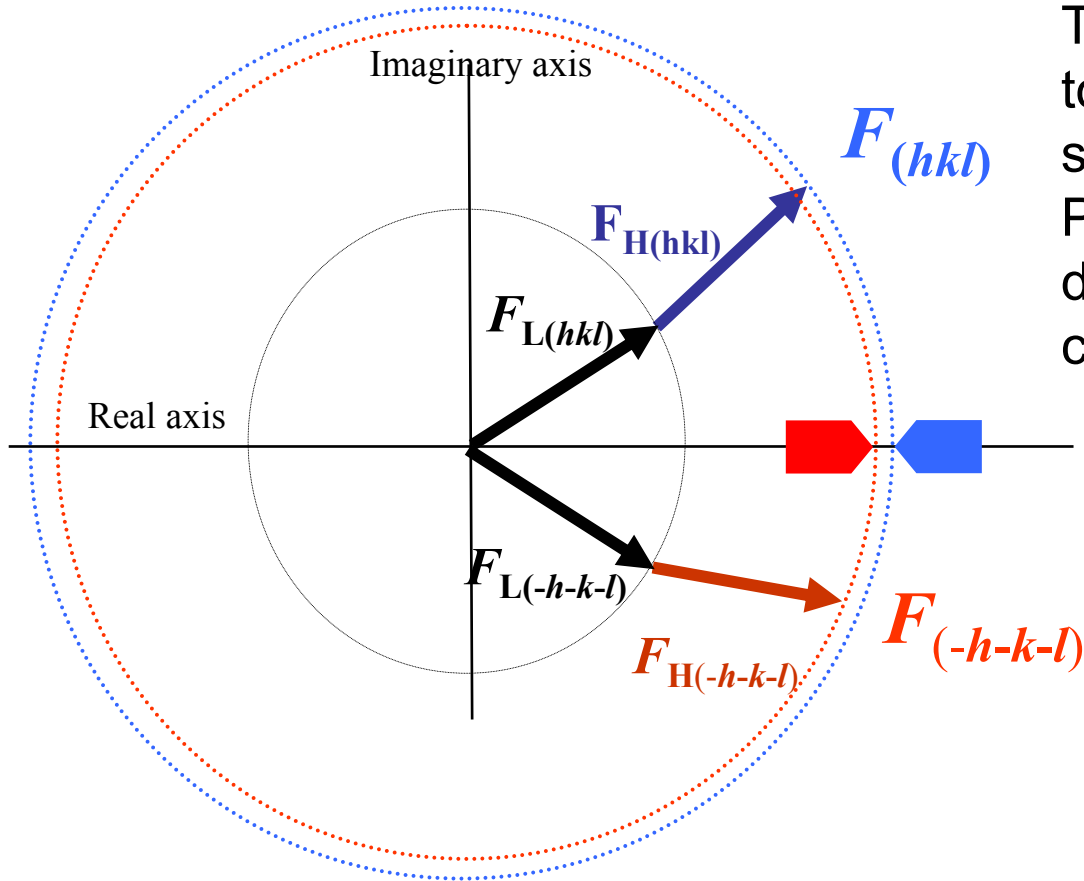
There is an observable difference between $|F_{(-h-k-l)}|$ and $|F_{(hkl)}|$ called a Bijvoet or Friedel difference or an anomalous difference.

This difference is only small (typically 1-3% of the measured intensity) and it is not always trivial to determine it accurately.

$$I_{(hkl)} \neq I_{(-h-k-l)}$$

$$\phi_{(hkl)} \neq \phi_{(-h-k-l)}$$

Anomalous Signal



This weak signal can be used to solve the phase problem in several ways (anomalous Patterson, MAD), and also to determine the absolute configuration of a molecule.

$$F_{(hkl)} \neq F_{(-h-k-l)}$$

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5.069 Crystal Structure Analysis
Spring 2008

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