Physical Principles of Solid State Characterization

Selected lecture notes for MtSE 719

Dr. Vitaly A. Shneidman

Department of Physics, New Jersey Institute of Technology, Newark, NJ 07102 (Dated: December 9, 2004)

Abstract

These notes will contain only some cumbersome equations and graphics. All other material will be presented on the board in class

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I. MAXWELL EQUATIONS AND ELECTROMAGNETIC WAVES

A. The Maxwell equations

$$\oint \vec{E} \cdot \vec{A} = q_{enc}/\epsilon_0 \tag{1}$$

$$\oint \vec{B} \cdot d\vec{A} = 0 \tag{2}$$

$$\oint \vec{E} \cdot d\vec{s} = -\frac{d\Phi_B}{dt} \tag{3}$$

$$\oint \vec{B} \cdot d\vec{s} = \mu_0 i_{enc} + \frac{1}{c^2} \frac{d\Phi_E}{dt} \tag{4}$$

with $c = 1/\sqrt{\mu_0\epsilon_0} \simeq 3 \cdot 10^8 \ m/s$, the speed of light.



FIG. 1: Structure of an electromagnetic wave. The electric field (red) is in the $\pm z$ -direction, the magnetic field (blue) is in the $\pm x$ -direction and the wave propagates in the *y*-direction. (This is known as a plane, polarized wave). The distance in the *y*-direction in which the oscillations start to repeat themselves is the *wavelength*.

B. Light!

Maxwell's equations in empty space

$$\oint \vec{E} \cdot d\vec{A} = 0$$

$$\oint \vec{B} \cdot d\vec{A} = 0$$

$$\oint \vec{E} \cdot d\vec{s} = -\frac{d\Phi_B}{dt}$$

$$\oint \vec{B} \cdot d\vec{s} = \frac{1}{c^2} \frac{d\Phi_E}{dt}$$

For example, the wave in Fig. 2 is described by

$$\vec{E} = \vec{E}_0 \sin\left\{2\pi\left(\frac{y}{\lambda} - ft\right)\right\}$$
$$\vec{B} = \vec{B}_0 \sin\left\{2\pi\left(\frac{y}{\lambda} - ft\right)\right\}$$

with

$$\left|\vec{E}_{0}\right| = c \left|\vec{B}_{0}\right|$$

f is known as frequency and λ as wavelength. One has

$$f = \frac{c}{\lambda}$$

for any wavelength in empty space.

 $\omega=2\pi f$ - angular frequency

 $k=2\pi/\lambda$ - wavevector (or wavenumber, but often in optics the "wavenumber" is without $2\pi)$ Now

$$\vec{E} = \vec{E}_0 \sin\left\{ky - \omega t\right\}$$

Circular polarization:

$$\vec{E} = E_0 \vec{i} \sin \left(ky - \omega t \right) + E_0 \vec{j} \cos \left(ky - \omega t \right)$$

Now $\left| \vec{E} \right| = const$

C. Diffractional grating

Consider narrow slits $b \ll a$. Then intensity

$$I = I_0 \left(\frac{\sin\beta}{\beta}\right)^2 \left(\frac{\sin(N\alpha)}{\sin\alpha}\right)^2$$

with

$$\alpha = \frac{ka}{2}\sin\Theta = \pi m$$
$$\beta = \frac{kb}{2}\sin\Theta = \pi mb/a$$



FIG. 2:

II. QUANTUM PROPERTIES OF LIGHT

A. Photon

Energy

$$E = h\nu = \hbar\omega$$

 $\hbar\simeq 1.055\cdot 10^{-34}\;J\cdot s,\,h=2\pi\hbar$

Momentum:

or

 $p = h/\lambda$

E = cp

 $\vec{p} = \hbar \vec{k}$

Note:

as classical.

B. Compton Effect

$$\lambda' = \lambda + \frac{h}{m_e c} \left(1 - \cos\phi\right)$$

 h/m_ec - Compton wavelength (Calculate!)

Problem. A beam of X-rays with $\nu = 2 \cdot 10^{18} Hz$ hits a block of carbon. Plot $\lambda(\phi)$. The Mathematica program can be helpful - see file 719_2.pdf

C. Planck distribution

Intersting - in combination with (a) T and (b) interactions

Planck = Boltzmann + discrete energies

$$P_n \propto e^{-E_n/k_B T}$$
, $E_n = n\hbar\omega$

Proportionality from

$$\sum_{n=0}^{\infty} P_n = 1$$

thus

$$P_n = e^{-n\hbar\omega/k_BT} \left(1 - e^{-\hbar\omega/k_BT}\right)$$

(HW: check this)

Average number of quanta in a single state:

$$\bar{n} = \sum_{n} nP_n = \frac{1}{e^{\hbar\omega/k_B T} - 1}$$

(HW: check this)

The above formula is THE ONLY quantum part of the Plank's law (below). The rest is classical. We need to calculate the total number of classical states with frequencies between ω and $\omega + d\omega$. When multiplied by $\bar{n}\hbar\omega$ this will give the energy inside the corresponding frequency interval.

Let's do the classical part. Imagine a cubic box $L \times L \times L$. A standing wave

$$L = m \frac{\lambda_m}{2} , \quad m = 1, 2, \dots$$

or

$$\left|\vec{k}\right| = m\frac{\pi}{L}$$

The above is valid for k_x , k_y and k_z . Thus, possible \vec{k} form a cubic lattice with lattice constant π/L . We need only the positive part, thus 1/8, but 2 polarizations. Now consider two spheres with radii k and k + dk. The number of states

$$\rho_k dk = \frac{1}{8} \times 2 \times 4\pi k^2 dk \left(\frac{\pi}{L}\right)^{-3} = \frac{V}{\pi^2} k^2 dk$$

We now go to the ω -space with $\omega = ck$:

$$\rho_{\omega}d\omega = \rho_k dk$$

thus

$$\frac{1}{V}\rho_{\omega} = \frac{1}{V}\rho_k \frac{dk}{d\omega} = \frac{\omega^2}{\pi^2 c^3}$$

Now multiply by quantum:

$$\frac{1}{V}d\omega\bar{n}\hbar\omega\rho_{\omega} = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{d\omega}{e^{\hbar\omega/k_B T} - 1}$$

This is the spectral density $W_T(\omega)d\omega$ - the Planck distribution. HW. Plot in good dimensionless variables.

One has max of W_T at

$$\hbar\omega_{\rm max} \approx 2.8 k_B T$$

- Wien's displacement law. HW. Show this

For the total spectral density

$$W_T(\omega)d\omega = \frac{k_B^4 T^4}{\pi^2 c^3 \hbar^3} \int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^2 k_B^4 T^4}{15c^3 \hbar^3}$$

HW. Check this and calculate the Stephen-Boltzmann constant.

A chart with electromagnetic spectrum will be given in class



FIG. 3: Motion of a charged particle in magnetic field, \vec{B} which points i the vertical, z-direction with or without electric field, \vec{E} (which points in the y-direction, behind the page, when non-zero). First picture (E = 0), the particle has no z-component of velocity and moves in a circle in the x,y plane. 2d picture (E = 0) - particle has a non-zero z-component of velocity and moves in a helix. 3d picture ($E \neq 0, v_z = 0$) - the particle drifts in the x-direction. [The latter is important in understanding the Hall effect].

III. MOTION OF CHARGED PARTICLES

$$\vec{F} = q\left(\vec{E} + \vec{v} \times \vec{B}\right)$$

Solution is hard, and can be obtained analytically only when both fields are uniform and perpendicular to each other - see Fig. 3.

1. Conventions for pictures and motion in magnetic field only

Problems with magnetism are always 3D. To simplify graphics, will use a 2D convention, as in Fig. 4.

| × | × | × | × | × | × | × | × | × | \odot |
|---|---|---|---|---|---|---|---|---|---------|---------|---------|---------|---------|---------|---------|---------|---------|
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FIG. 4: Convention for 2D pictures of magnetic field. Left - field goes into the page; right - field goes out of the page.

$$\vec{F} = q\vec{v} \times \vec{B} \tag{5}$$

See Fig. 5.

Example: separation of particles by charges and masses - see Fig. 6.

A. Circular motion of a particle

See Fig. 7.

$$m\frac{v^2}{r} = qvB$$

Thus,

$$r = \frac{mv}{qB}$$

This is the experimental way to find q/m for elementary particles, and eventually to find their masses (which otherwise are very small).

Period of revolution:

$$T = \frac{2\pi r}{v} = 2\pi \frac{m}{qB}$$

Doest not depend on the velocity (energy) of a particle (!)



FIG. 5: Magnetic force on a positive particle, $\vec{F} = q\vec{v} \times \vec{B}$. Note that \vec{F} (blue) is perpendicular to both \vec{v} (red) and \vec{B} (green), and reaches maximum when \vec{v} and \vec{B} are perpendicular to each other. For parallel (or antiparallel) \vec{v} and \vec{B} the force would be zero.

B. Relativistic particles

$$v \sim c$$

For cyclotron frequency - correct, but

$$m \to rac{m}{\sqrt{1 - v^2/c^2}}$$

Conservation of energy should include mc^2 :

$$E = \sqrt{c^2 p^2 + m^2 c^4}$$

Limits:

classical $v \ll c$, thus $p \ll mc$ and

$$E \approx mc^2 + \frac{p^2}{2m}$$



FIG. 6: Separation of particles of different signs in the magnetic field, as first observed in connection with radioactive decay. The positive (red) particles deviate to the right (they were called "alphaparticles" and later turned to be nuclei of Helium). The negative (blue) particles deviate left. (they were called "beta-particles" and turned out to be electrons). Neutral particles (green) do not deviate. (they were called "gamma-particles", and turned out to be quanta of electromagnetic radiation). Note that the path of negative particles is more curved, due to smaller mass.

ultrarelativistic, $v \approx c$

 $E \approx cp$

photon!

HW. use $p = mv/\sqrt{1 - v^2/c^2}$ and plot E(v)

Only voltage changes E (!)

Why relativistic important?

a) v/c - small, but accuracy very high. b) high accelerating voltage HW. express m_ec^2 in MeV.



FIG. 7: Circular motion of a positive particle in magnetic field. The velocity of a particle is shown in red, and the magnetic force (blue) provides a centripetal force for circular motion. The period of revolution is independent of the velocity (!) - a faster particle will make a larger circle, completing the revolution in the same time.

Dr. Vitaly A. Shneidman, Phys 719, 3d Lecture

IV. ELEMENTS OF QUANTUM MECHANICS (QM): DE BROGLIE WAVE

$$\lambda = \frac{h}{p}$$
 or $\vec{k} = \vec{p}/\hbar$

HW1: find λ for an (a) 1eV electron, (b) a 1eV neutron, (c) a 0.1 mg dust particle with a speed 100 m/s.

Note: ANY p, including relativistic (!). Relation to energy: from

$$E_{rel} = \sqrt{c^2 p^2 + m^2 c^4}$$

non-relativistic $p = \sqrt{2mE}$ where $E = E_{rel} - mc^2$, the kinetic energy, and

$$\lambda = \frac{h}{\sqrt{2mE}}$$

HW2. Express this as $const/\sqrt{E}$ with *E* energy of an electron expressed in eV. Relativistic: $m \to 0, p \to E/c$ and

$$\lambda = \frac{hc}{E}$$

This is exactly as for a photon: $E = h\nu$, and $\lambda = c/\nu$

Myth: for a good understanding of QM you always need the Shrödinger equation. No! In very many cases the de Broglie picture is sufficient, and allows for a deep analogy with optics (see below).

A. Experiments

Thompson (1927) analogy of X-ray diffraction and electron diffraction pictures of a thin foil.

Davisson-Germer (1927). Studies of single crystal. $\lambda = d \sin \theta$.

HW3: Consider the DG experiment for Ni with d = 0.215 nm, E = 54 eV, $\theta = 50^{\circ}$. Find λ and compare with theory.

B. Analogy with optics

- 1. Double slit diffraction
- 2. Barrier penetration (Tunneling).

$$\frac{p^2}{2m} + U(x) = E$$
$$p = \sqrt{2m \left(E - U\right)}$$



FIG. 8: Double slit diffraction of electrons for different energies. Intensity (arb. units) is plotted vs. distance on the screen in cm. Distance between slits is 2 nm and the distance to the screen is 1 cm. Note that for higher energies the oscillations become so fast that it is impossible to resolve them, and experimentally a bell-shaped curve will be observed.

classical: E < U - forbidden. QM:

$$\Psi \sim \exp\left(ikx\right)$$

with $k = p/\hbar$. If E > U - oscillates, if E < U exponential decay. For a rectangular barrier ("mirror" in optics).

$$\Psi \sim \exp\left\{-\frac{|p|}{\hbar}x\right\}$$

Transmission probability

$$D \sim |\Psi|^2 = \exp\left\{-2\frac{|p|d}{\hbar}\right\}$$

d-barrier thickness. More general (non-rectangular barrier)

$$D \sim \exp\left\{-2\int \sqrt{2m(U-E)}dx/\hbar\right\}$$

with integration over classically forbidden region E < U.

3. Reflection above the barrier

$$R = 1 - D$$

4. Uncertainty principle

$$\delta x \delta p \geq \hbar/2$$

or

$$\delta x \ge \pi \lambda$$

5. Standing waves

Major application - Atom:

- a) lowest energy state, thus STABILITY of matter
- b) discrete energy levels

Atom - separate topic.

Questions: meaning of Ψ the "wave equation"

V. INTERMISSION: NEUTRON SCATTERING

Neutrons provide an excellent illustration of a de Broglie wave. Detail and specific methods will be discussed in class.

Energies of neutrons vs. X-Rays (p about the same):

$$E_{ph} = cp$$
, $E_n = \frac{p^2}{2m} = \frac{1}{2}vp \ll E_{ph}$

Methods:

- ineleastic neutron scattering: mostly from hydrogen
- high-resolution neutron powder diffractometry
- small-angle neutron scattering
- residual stress measurement
- neutron reflectometry

VI. THE SHRÖDINGER EQUATION (SE)

- A. What is Ψ ?
- M. Born:

$$|\Psi|^2$$

proportional to probability density. Two situations:

• infinite motion. In classics - E > U(x) for all accessible x. Experimental - scattering problem.

$$\int \left|\Psi(x)\right|^2 dx = \infty$$

• finite motion. In classics - $E \ge U(x)$ only for a finite interval of x. Experimental - discrete energy levels.

$$\int |\Psi(x)|^2 \, dx = 1$$

B. How to construct a SE?

The Hamilton operator

$$H = \frac{p^2}{2m} + U(x) \rightarrow \hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x)$$

$$\hat{H}\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

Steady-state: fixed E

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar}$$

$$\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + \left[E - U(x)\right]\psi = 0$$

Free particle: U = 0.

$$\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + E\psi = 0$$
$$\psi(x) \propto e^{\pm ikx}$$

with $k = \sqrt{2mE}$. And

$$\Psi(x,t) \propto e^{\pm ikx - i\omega t}$$

with $\omega = E/\hbar$. Note: k, ω - very large(!)

More general, if $U = const \neq 0$ similar, but $k = p/\hbar = \sqrt{2m(E-U)}/\hbar$ and can be imaginary if E < U (classically forbidden region). Boundary conditions: ψ and ψ' continuous.

Example-HW-small project. Calculate the reflection coefficient from a potential wall: U(x) = 0 for x < 0 and $U(x) = U_0$ for x > 0. Hint:

$$\psi(x) = e^{ik_1x} + Be^{-ik_1x}, \ k_1 = \sqrt{2mE}/\hbar, \ x < 0$$

(incident + reflected wave) and

$$\psi(x) = e^{ik_2x}, \ k_2 = \sqrt{2m(E - U_0)}/\hbar, \ x > 0$$

and

 $R = |B|^2$

Example-HW. Discrete spectrum: U(x) = 0 for 0 < x < a and $U(x) = +\infty$ otherwise.

C. Harmonic oscillator

$$U(x) = \frac{1}{2}m\omega^2 x^2$$

SE:

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} \left(E - \frac{1}{2}m\omega^2 x^2 \right) \psi = 0$$

or with $\zeta = x \sqrt{m\omega/\hbar}$,

$$\psi'' + \left(\frac{2E}{\hbar\omega} - \zeta^2\right)\psi = 0$$

here E must be discrete to satisfy

$$\int_{-\infty}^{\infty} \psi^2(x) dx < \infty$$

. One has

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega\tag{6}$$

Wave functions:

$$\psi_n \propto e^{-\zeta^2/2} H_n(\zeta)$$

with

$$\psi_0 \propto e^{-\zeta^2/2}$$

corresponding to the lowest energy state. Otherwise,

$$H_n(\zeta) = (-1)^n e^{\zeta^2} \frac{d^n e^{-\zeta^2}}{d\zeta^n}$$

HW: plot several $\psi_n.$

VII. SHRÖDINGER EQUATION (CONT.)

so far mostly stationary SE; now more dynamic properties. To be specific, we consider discrete spectrum. Mathematically, this is the most demanding lecture of our course, but we will survive... A *Mathematica* file coherent.nb can be of extra help (and contains some graphics), although you will need further instructions if you never used *Mathematica* before. Much of the discussion, especially the part related to physics, will be added in class.

A. The superposition principle

$$\Psi(x,t) = \sum_{k} a_k \Psi_k(x,t) = \sum_{k} a_k \psi_k(x) e^{-iE_k t/\hbar}$$
(7)

Here $|a_k|^2$ give the probability to be in the k-th state; in particular

$$\sum_{k} |a_k|^2 = 1$$

There exists an orthogonality condition

$$\int_{-\infty}^{\infty} dx \psi_k(x) \psi_m(x) = 0 , \quad m \neq k$$

(for a discrete spectrum all ψ_k can be real-valued in 1D). Thus,

$$a_k = \int_{-\infty}^{\infty} dx \psi_k(x) \Psi(x,t) e^{+iE_k t/\hbar}$$

HW verify the orthogonality condition for the WF (a) of the rectangular box and (b) of the harmonic oscillator

Example - might skip it in class. The coherent states of an oscillator (Shrödinger).

$$\Psi(x,t) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \exp\left\{\frac{i\beta(t)x}{\hbar} - \frac{m\omega(x-\alpha(t))^2}{2\hbar} - \frac{i\omega t}{2} - i\frac{\alpha(t)\beta(t)}{2\hbar}\right\}$$

 α and β can be selected arbitrary, but satisfying the classical equations of motion for the same harmonic oscillator; α has a meaning of $\bar{x}(t)$ (*HW-optional-show this*) and β is the average momentum $\bar{p}(t)$. Now one can expand

$$\Psi = \sum_{n=0}^{\infty} a_n \Psi_n$$

with

$$\Psi_n(x,t) = \psi_n(x) \exp\left\{-i\left(n+\frac{1}{2}\right)\omega\right\}$$

and with $\psi(x)$ (now with the coefficient) given by

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} \exp\left(-\frac{m\omega}{2\hbar}x^2\right) H_n\left(x\sqrt{\frac{m\omega}{\hbar}}\right) \tag{8}$$

HW (optional) Show that

$$w_n = |a_n|^2 = e^{-\bar{n}} \frac{\bar{n}^n}{n!}$$

(Poisson distribution)

with

$$\bar{n} = \frac{1}{\hbar\omega} \left(\frac{\beta^2}{2m} + \frac{m\omega^2 \alpha^2}{2} \right)$$

B. Periodic perturbations

we consider the SE

$$i\hbar\frac{\partial\Psi}{\partial t} = \left(\hat{H}_0 + \hat{V}\right)\Psi$$

and at any time look for a solution

$$\Psi = \sum_{k} a_k(t) \Psi_k^{(0)} \tag{9}$$

where $\Psi_k^{(0)}$ are eigenfunctions of a non-perturbed Hamiltonian

$$i\hbar\frac{\partial\Psi_k^{(0)}}{\partial t} = \hat{H}_0\Psi_k^{(0)}$$

From the orthogonality condition one has

$$i\hbar \frac{da_m}{dt} = \sum_k V_{mk}(t)a_k$$

with

$$V_{mk} = \int dx \Psi_m^{(0)*} \hat{V} \Psi_k^{(0)} \equiv V_{mk} e^{i\omega_{mk}t} , \quad \omega_{mk} = \frac{E_m^{(0)} - E_k^{(0)}}{\hbar}$$

We now solve the above equations using iterations. let us start from the *n*-th state: $a_n^{(0)} = 1$ and $a_k^{(0)} = 0$ for $n \neq k$. We will use the 2d index to emphasize the *n*-th level. From the 1st iteration:

$$i\hbar \frac{a_{kn}^{(1)}}{dt} = V_{kn}(t)$$

or

$$a_{kn}^{(1)} = -\frac{i}{\hbar} \int V_{kn}(t) dt = -\frac{i}{\hbar} \int V_{kn} e^{i\omega_{kn}t} dt$$

Consider now a periodic perturbation

$$\hat{V} = 2\hat{F}(x)\cos(\omega t) = \hat{F}\left(e^{i\omega t} + e^{-i\omega t}\right)$$

Thus,

$$V_{kn}(t) = V_{kn}e^{i\omega_{kn}t} = F_{kn}\left\{\exp\left[i\left(\omega_{kn}-\omega\right)t\right] + \exp\left[i\left(\omega_{kn}+\omega\right)t\right]\right\}$$

After integration,

$$a_{kn}^{(1)} = -\frac{F_{kn}e^{i\omega_{kn}t}}{\hbar} \left(\frac{e^{i\omega t}}{\omega_{kn}+\omega} + \frac{e^{-i\omega t}}{\omega_{kn}-\omega}\right)$$

VIII. SHRÖDINGER EQUATION IN 3D; THE HYDROGEN ATOM

Main differences from 1D:

- discrete spectrum can be degenerate
- a shallow well can have no discrete level
- angular momentum becomes crucial (there is no such in 1D)

A. Elementary theory of hydrogen levels

$$P_{ang} = pr$$

Quantization:

$$2\pi r = n\lambda_{dB} = n\frac{h}{p} = n\frac{2\pi\hbar}{p}$$

$$P_{ang} = n\hbar$$

(Bohr). The rest is classical (CGS):

$$\frac{mv^2}{r} = \frac{e^2}{r^2}$$
$$r = \frac{P_{ang}^2}{me^2}$$
$$U = -\frac{e^2}{r} = -2K , \quad K = \frac{mv^2}{2}$$

Thus,

$$E = -\frac{mv^2}{2} = -\frac{e^2}{2r} = -\frac{me^4}{2n^2\hbar^2}$$

In SI units and with Z > 1:

$$U = -\frac{Ze^2}{4\pi\epsilon_0 r}$$

$$E = -\frac{Z^2 m e^4}{2n^2 \left(4\pi\epsilon_0\hbar\right)^2}$$

HW: Calculate for n = 1

IX. SCHRÖDINGER EQUATION IN 3D: THE HYDROGEN ATOM

The Hamilton operator

$$H = \frac{p^2}{2m} + U(\vec{r}) \rightarrow \hat{H} = -\frac{\hbar^2}{2m}\hat{\Delta} + U(\vec{r})$$
$$\hat{\Delta} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}, \quad \text{i.e.} \quad \hat{\Delta}\psi = \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}$$

Look for a steady-state solution:

$$\hat{H}\psi\left(\vec{r}\right) = E\psi\left(\vec{r}\right) \tag{10}$$

In spherical coordinates one has

$$\hat{\Delta} = \hat{\Delta}_r - \frac{1}{r^2}\hat{l}^2 \tag{11}$$

with \hat{l}^2 given by

$$\hat{l}^2 = -\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) - \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2}$$
(12)

$$\hat{\Delta}_r = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r}$$
(13)

(although specific form of these operators mostly will not be required...)

First we use just spherical symmetry (but not specific U(r)). Look for

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

From

$$\hat{\Delta}\psi + \frac{2m}{\hbar^2} \left[E - U(r)\right]\psi = 0$$
$$Y\hat{\Delta}_r R - \frac{R}{r^2}\hat{l}^2Y + (E - U)RY\frac{2m}{\hbar^2} = 0$$

Now divide both sides by RY and multiply by r^2 :

$$\frac{r^2}{R}\hat{\Delta}_r R + \frac{2m(E-U)r^2}{\hbar^2} = \frac{1}{Y}\hat{l}^2 Y$$
(14)

Note that the l.h.s depends only on r while the r.h.s only on θ , ϕ . Thus, both sides should be a *const* $\equiv \lambda$. We thus achieved separation of variables using physical understanding of symmetry. The rest is math. First consider

 $\hat{l}^2 = \lambda Y$

now look for

$$Y(\theta, \phi) = \Phi(\phi) \times \Theta(\theta)$$

and repeat separation of variables. (HW -optional - do that). Recall that key to discrete eigenvalues - BC. Periodicity in ϕ leads to

$$Y(\theta,\phi) = e^{im\phi} \times \Theta(\theta) , \quad m = 0, \pm 1, \pm 2, \dots$$

(HW -optional - show that). For θ dependence harder (polynomials in $\cos \theta$, but pure math: Y_{lm} - spherical harmonics.

$$\hat{l}^2 Y_{lm} = l(l+1)Y_{lm} \tag{15}$$

Note no m - degeneracy of levels(!). (m - "magnetic quantum number", l - "orbital quantum number").

Now go back to radial

$$\hat{\Delta}_r R + \left\{ \frac{2m}{\hbar^2} \left[E - U(r) \right] - \frac{l(l+1)}{r^2} \right\} R = 0$$

r is the only variable, but l enters as a parameter. Solve (also pure math) - Bohrs formula for $E_n \propto -1/n^2$. Radial WF: R_{nl} will not need explicitly; (optional HW, nevertheless find it in a textbook, and plot).

Summary:

$$\Psi_{nlm}\left(r,\theta,\phi\right) = e^{-iE_{n}t/\hbar}R_{nl}(r)Y_{lm}\left(\theta,\phi\right)$$

with

$$n = 1, 2, 3, \dots, l \le n - 1, m = 0, \pm 1, \pm 2, \dots, \pm (l - 1)$$

n - principal quantum number. Levels - VERY degenerate. Why? System very symmetric. Field - less symmetry; Stark effect (\vec{E}) and Zeeman effect \vec{B}), splitting of levels.

(for more on plotting electronic density in hydrogen - see P. Tam, *Mathematica for Physicists*).



FIG. 9: Electronic densities in the excited hydrogen atom

A. Transitions between levels

Emission - hard; absorption - can be calculated.

If V is a weak perturbation potential, transition rate is proportional to

$$\int \Psi_{n_1 l_1 m_1} V \Psi_{n_2 l_2 m_2}$$

Now can treat almost classically: $\vec{E}(t) \simeq \vec{E}_0 \cos(\omega t)$ (Why no kx? - recall that $\lambda = 2\pi/k \gg a$, the size of the atom). Now $\vec{D} = e\vec{r}$ - the dipole moment and

$$V = \vec{D} \cdot \vec{E}_0 \cos(\omega t)$$

- transitions only for $E_1 E_2 = \hbar \omega$
- very many $\int \Psi_{n_1 l_1 m_1} V \Psi_{n_2 l_2 m_2} = 0$ from symmetry
- alowed:

$$\Delta l = \pm 1 , \ \Delta m = 0, \pm 1$$

X. QUANTUM ASPECTS OF EMISSION AND ABSORPTION; LASER

So far quantum mechanics was used to explain the discrete energy levels. After that ligh emission and absorption almost classical. In particular, in AES intensity is proportional to the Boltzmann population of the excited level. There are, however, limitations to this description.

A. Einstein's coefficients

Consider a 2-level system with $E_j > E_i$. let

 B_{ij} - probability of absorption

 A_{ji} probability of spontaneous emission.

Supposedly, if $\rho(\nu)$ is the density of photons with $h\nu = E_j - E_i$, and n_i , n_j are populations of the levels (i.e., numbers of atoms in each state), the rate of absorption is

$$B_{ij}n_i\rho(\nu) - A_{ji}n_j$$
, WRONG!

Why?

Consider equilibrium

$$n_j^{eq}/n_i^{eq} = \exp\left\{-\frac{E_j - E_i}{k_B T}\right\}$$

(the Boltzmann distribution), then

$$\rho^{eq}(\nu) = (A_{ji}/B_{ij}) \exp\left\{-\frac{E_j - E_i}{k_B T}\right\} , \text{ WRONG!!!}$$

must be Planck distribution. Thus, need induced transitions $B_{ji}\rho(\nu)$ ("stimulated"). Then, rate of absorption is

$$B_{ij}n_i\rho(\nu) - B_{ji}n_j\rho(\nu) - A_{ji}n_j$$

Now with $h\nu = E_j - E_i$

$$\rho^{eq}(\nu) = \frac{A_{ji}}{B_{ij}e^{h\nu/k_BT} - B_{ji}}$$

compare this with Planck

$$\rho(\nu)^{eq} = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{h\nu/k_B T} - 1}$$

0

Thus:

$$B_{ij} = B_{ji}$$

(to ensure symmetry for very strong fields) and

$$B_{ij} = A_{ij} \left(\frac{c^3}{8\pi h\nu^3} \right)$$

Idea of a laser: let $n_j > n_i \ll n_j^{eq}$, inverse population. An incident photon with $h\nu = E_j - E_i$ will cause Bn_i up transitions and Bn_j down transitions. The number of photoons will increase, leading to amplification of light.

A protoppelaser is just 2 mirrors with reflectivity $R_1 \approx 1$ and $R_2 < 1$. The distance is $L = m\lambda/2$. Let β be gain per ion (related to Einstein coefficients) and $N = n_j - n_i$. Round trip 2L, thus gain intensity

$$e^{2N\beta L}$$

. Losses are

 $R_1 R_2 e^{-2\alpha l}$

(α - attenuation coefficient). For stable operation:

$$R_1 R_2 e^{2L(N\beta - \alpha)}$$

How to create inverse population?

3 level: $E_1 < E_3 < E_2$ and $A_{23} \gg A_{31}$. Strong (and long) pumping leads to $n_2 \approx n_1$ and lasing between 3 and 1.

4-level: $E_1 < E_4 < E_3 < E_2$ with $A_{23} \gg A_{34}$. Lasing between 3 and 4. Advantage: don't have to exceed n_1 .

XI. VIBRATIONAL AND ROTATIONAL SPECTRA OF MOLECULES. RAMAN SPECTROSCOPY

A. Estimations

Why so well separated?

$$\omega_{el} \gg \omega_{vib} \gg \omega_{rot}$$

Large parameter $\sqrt{m_e/M}$ - will explain in class.



FIG. 10: Relative intensities of spectral lines of hypothetical molecule shaped as a spherical top with rotational inertia $I = 3 \cdot 10^{-47} kg \cdot m^2$. On the *x*-axes is the number *J*.

- vibrations almost classical. Natural frequencies ω_{vib} give discrete levels $\hbar \omega_{vib}(n+1/2)$, but only one line per frequency, $\lambda = 2\pi c/\omega_{vib}$ (anharmonicity - more lines, but also near-classical)
- rotational more quantum. Discrete spectrum from periodicity of the WF in angle. Also, classical part is much harder.

$$E(J,\nu) = hcw_e\left(\nu + \frac{1}{2}\right) - hcw_{exe}\left(\nu + \frac{1}{2}\right)^2 + hcB_\nu J(J+1)$$
(16)

with

$$B_{\nu} = B_e - \alpha_e \left(\nu + \frac{1}{2}\right) , \quad B_e = 10.593 cm^{-1} , \quad \alpha_e = 0.3072 cm^{-1}$$
$$w_e = 2990.9 cm^{-1} , \quad w_{exe} = 52.82 cm^{-1}$$

(see *Physical Chemistry with Mathematica*, although an old version of *Mathematica* is used there)



FIG. 11: Rotational-vibrational spectrum of a diatomic molecule HCl from eq. (11).



FIG. 12: Rotational spectrum of NH_3 with $I_A = I_B = 2.816 \cdot 10^{-47} kg \cdot m^2$ and $I_C = 4.437 \cdot 10^{-47} kg \cdot m^2$ (oblate top).

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FIG. 13: Molecular (red) and virtual (blue) energy levels and types of spectroscopy.

XII. APPLICATIONS: INFRARED AND RAMAN SPECTROSCOPIES

A. Quantum

see Fig. 13 Note: Intensity of anti Stokes grows with T.

B. Classical

Why classical? - Intensities! Dipole moment

 $d = E\alpha$

 α - polarizability

 $E = E_0 \cos\left(\omega t\right)$

If Ω - natural frequency of the molecule

$$\alpha = \alpha_0 + \alpha' \delta r \cos((\Omega t))$$

Thus,

$$d(t) = \alpha_0 E_0 \cos(\omega t) + \frac{1}{2} \alpha' \delta r E_0 \left\{ \cos\left[(\omega - \Omega) t \right] + \cos\left[(\omega + \Omega) t \right] \right\}$$

the 1st trem is Rayleigh, the 2d is Raman Stokes, the 3d - Anti Stokes

Difference: let Q be generalized coordinates associated with vibrations. The

 $I\propto \alpha_0^2$, Rayleigh

$$I \propto \left(\frac{\partial \alpha}{\partial Q}\right)^2 \bar{Q}^2$$
, Raman

XIII. PHONONS

A. Linear monoatomic chain

Let g -spring constant; \boldsymbol{u}_l - displacement from equilibrium. Force

$$F_{l} = g(u_{l+1} - u_{l}) - g(u_{l} - u_{l-1})$$

or

$$m\ddot{u}_{l} = g\left(u_{l+1} + u_{l-1} - 2u_{l}\right)$$

Acoustic wave:

$$a \cdot l \to x , \ (\dots) \to a^2 \frac{\partial^2 u}{\partial x^2}$$

with $m/a = \rho$, linear density, and ag = G

$$\rho \frac{\partial^2 u}{\partial t^2} = G \frac{\partial^2 u}{\partial x^2}$$

or

$$\frac{\partial^2 u}{\partial t^2} = v^2 \frac{\partial^2 u}{\partial x^2}$$

with the "speed of sound"

$$v^2 = G/\rho = a^2g/m$$

Any u(x - vt) - solution. E.g., $\exp\{i(\omega t - kx)\}\$ with any ω , k with $\omega = kv$.

Return to discreet:

look for

$$u_l \propto \exp\left\{i\left(\omega t - kx\right)\right\}, \ x = la$$

Then,

$$-m\omega^{2} = g\left[e^{ika} + e^{-ika} - 2\right] = g\left[e^{ika/2} - e^{-ika/2} - \right]^{2}$$

Or,

$$\omega(k) = \sqrt{\frac{4g}{m}} \left| \sin\left(\frac{ka}{2}\right) \right|$$

For $k \to 0, \, \omega \approx kv$.

$$-\frac{\pi}{a} < k < \frac{\pi}{a}$$

Brillouin zone. See figure (and file phonons.m with m = M).

Debye frequency:

$$\omega_{\rm max} \sim \frac{v}{a} \sim 10^{13} - 10^{14} Hz$$

(infrared)

B. 3D - monoatomic

Three accoustic branches - 1 longitudinal and 2 transverse.

C. Applications of neutron scattering

Note that k0 and $k + 2\pi/a$ - same. in 3D: \vec{b} - vector of reciprocal lattice, analog of $2\pi/a$ (will study more in connection with crystallography). Let \vec{k} be the momentum of an emitted phonon, and \vec{K} the momentum of the neutron. Then,

$$\vec{K} = \vec{K}' + \vec{k} + n\vec{b}$$
, $n = 0, 1, 2, \dots$

• $\vec{k} = 0$ (no energy loss to phonon) and

$$\left|\vec{K}\right| = \left|\vec{K}'\right|$$

Bragg scattering

• n = 0 no diffraction. Spectroscopy.

$$\vec{K} = \vec{K}' + \vec{k}$$

Energy: $p^2/2m$ for a neutron, $\hbar\omega$ for a photon

$$\frac{\hbar^2 K^2}{2m} = \frac{\hbar^2 \left(K'\right)^2}{2m} + \hbar\omega \left(\vec{k}\right)$$

(see slides with experimental data)

D. Polyatomic lattice: Optical branches

will be discussed in class (also, see file phonons.m).

XIV. FREE ELECTRONS IN METALS: FERMI ENERGY

$$\Delta p_x \cdot L_x = 2\pi\hbar , \dots$$
$$\Delta k_x \cdot L_x = 2\pi , \dots$$
$$N = 2 \cdot \frac{4}{3}\pi K_F^3 \frac{1}{\Delta k_x \cdot \Delta k_y \cdot \Delta k_z} = V \frac{K_F^3}{\pi^2}$$
$$n = \frac{K_F^3}{3\pi^2}$$

(density of electrons)

Estimations:

$$n \sim 1/\mathring{A}^3$$
, $K_F \sim 1\mathring{A}^{-1}$

$$v_F \sim \frac{p_F}{m} = \frac{\hbar K_F}{m} \sim 10^6 \ m/s$$

$$E_F = \frac{\hbar^2 K_F^2}{2m} \sim 1.5 - 15 \ eV$$

HW: Find E_F *for* Ag with (cgs)

$$a_0 = \hbar^2 / me^2 = 0.529 \cdot 10^{-8} \ cm$$

and

$$r_s = \left(\frac{3}{4\pi n}\right)^{1/3}$$
$$K_F = 3.63 \left(\frac{a_0}{r_s}\right) \mathring{A}^{-1}$$
$$E_F = 50.1 \left(\frac{a_0}{r_s}\right)^2 eV$$
$$v_F = 4.20 \cdot 10^8 \left(\frac{a_0}{r_s}\right) cm/s$$

HW - show that

$$\rho(E) = \frac{1}{\exp\left\{\frac{E - E_F}{k_B T}\right\} + 1}$$

XV. ELECTRONS IN PERIODIC POTENTIAL: BANDS

$$\psi(\vec{r}) = e^{i\vec{q}\vec{r}}u_{\vec{q}}(\vec{r}) , \ u_{\vec{q}}(\vec{r}+\vec{a}) = u_{\vec{q}}(\vec{r})$$

(Bloch, 1929).

A. Dirac comb

$$U(x) = \frac{\hbar^2}{m} \Omega \sum_{n=-\infty}^{\infty} \delta(x - na)$$

see Fig. 14.



FIG. 14: Energy bands for the "Dirac comb" (Kronig-Penney model) for different values of the interaction potential.

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XVI. RUTHERFORD BACKSCATTERING SPECTROSCOPY (RBS)

A. Introduction

see Fig. 15 Estimation: energy to hit a nucleus

$$E[eV] = k_e e/r \sim 9 \cdot 10^9 1.6 \cdot 10^{-19}/10^{-14} \sim \dots$$

B. Differential and total cross-sections

$$d\sigma = \frac{dN}{n}$$
$$dN = 2\pi\rho d\rho \cdot n$$



FIG. 15: Scattering of positive particles by a heavy nucleus (upper figure). For small values of the impact parameter (distance from axes) particles are backscattered. For the same impact parameter the scattering angle is smaller for larger energies. Note that incoming particles never approach the nucleus ($\sim 10^{-14} m$) but are repelled by Coulomb forces. The lower figure shows negative particles with similar parameters. Note the symmetry - negative particles are scattered by the same angle, only deviate in an opposite direction. In principle, negative particles can hit the nucleus, although such events are extremely rare.

 $\rho \; [cm] \;$ - impact parameter

$$d\sigma = 2\pi\rho d\rho = 2\pi\rho \left(\theta\right) \left|\frac{d\rho}{d\theta}\right| d\theta$$

$$d\Omega = 2\pi\sin\theta d\theta$$

spherical angle

$$d\sigma = \frac{\rho\left(\theta\right)}{\sin\theta} \left| \frac{d\rho}{d\theta} \right| d\Omega \tag{17}$$

Total:

$$\sigma = \int_0^{4\pi} \frac{d\sigma}{d\Omega} d\Omega$$

Example: hard sphere (in class)

C. Rutherford formula

Motion in central field

$$U(r) = \frac{\alpha}{r}$$

can be described analytically (in class). Then, eq. (17) gives

$$d\sigma = \left(\frac{\alpha}{2mv_{\infty}^2}\right)^2 \frac{d\Omega}{\sin^4\left(\theta/2\right)} \tag{18}$$

Note: α^2 - sign does not matter. Thus, $d\sigma \propto Z^2$, the charge of the nucleus. Also, $d\sigma \propto E^{-2}$. Remarkable: quantum -same formula! (Mott & Gordon, 1928).

D. Energy exchange

Consider here head-on collisons only (in class).

$$E = E_0 \left(\frac{M-m}{M+m}\right)^2$$

Or with $K \equiv E_0/E$

$$\frac{M}{m} = \frac{\sqrt{K}+1}{\sqrt{K}-1}$$

XVII. MID-TERM EXAM



FIG. 16:

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XVIII. ELEMENTS OF CRYSTALLOGRAPHY

A. Bravais lattice

$$\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$
, $n_{1,2,3} = 0, \pm 1, \pm 2, \dots$

 $a_{1,2,3}$ - primitive vectors (non-unique -see fig. 17).

Not all lattices are Bravais, e.g honeycomb.

1. BCC

$$\vec{a}_1 = a\hat{x} , \ \vec{a}_2 = a\hat{y} , \ \vec{a}_3 = \frac{a}{2} \left(\hat{x} + \hat{y} + \hat{z} \right)$$

or more symmetric

$$\frac{a}{2} \left(- \hat{x} + \hat{y} + \hat{z} \right) \;, \;\; \frac{a}{2} \left(\hat{x} - \hat{y} + \hat{z} \right) \;, \;\; \frac{a}{2} \left(\hat{x} + \hat{y} - \hat{z} \right)$$



FIG. 17:

2. FCC

$$\vec{a}_1 = \frac{a}{2} \left(\hat{y} + \hat{z} \right) , \ \vec{a}_2 = \frac{a}{2} \left(\hat{x} + \hat{z} \right) , \ \vec{a}_2 = \frac{a}{2} \left(\hat{x} + \hat{y} \right)$$

- 3. Coordination number
- 4. Primitive and Elementary cells
- 5. Wigner-Seitz cell

HW: try to sketch for triangular lattice

B. Bravais lattice with a basis

BCC: SC with

$$\vec{0}$$
, $\frac{a}{2}(\hat{x}+\hat{y}+\hat{z})$



FIG. 18:

FCC: SC with

$$\vec{0}$$
, $\frac{a}{2}(\hat{y} + \hat{z})$, $\frac{a}{2}(\hat{x} + \hat{z})$, $\frac{a}{2}(\hat{y} + \hat{x})$

Diamond: 2 FCC displaced by 1/4 of big diagonal Hexagonal CP: triangular + c-along z- axes

C. Reciprocal lattice

Define volume

$$v = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$$

$$\vec{b}_1 = \frac{2\pi}{v} \vec{a}_2 \times \vec{a}_3$$
$$\vec{b}_2 = \frac{2\pi}{v} \vec{a}_3 \times \vec{a}_1$$
$$\vec{b}_3 = \frac{2\pi}{v} \vec{a}_1 \times \vec{a}_2$$

Check:

reciprocal to SC - SC

reciprocal to BCC - FCC reciprocal to FCC - BCC

1. Brillouin zone

D. Atomic planes

1. Miller indices

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XIX. XRD

A. Theory (some)

Can use Maxwell equations as in optics, but

- $\lambda \sim a$ (not a continum) harder
- $\omega \gg \omega_{el}$ easier. Why?

 $\omega_{el} \sim v/a$

and

$$\omega \sim c/\lambda \sim c/a$$

Thus,

$$m\dot{\vec{v}} = e\vec{E}$$

Next, everything $\propto e^{-i\omega t}$;

 $\vec{v} = i e \vec{E} / m \omega$

Let $n(\vec{r})$ be the density of electrons.

$$\vec{j} = en\vec{v} = \frac{ie^2n}{m\omega}\vec{E}$$

(Note; \vec{j} along \vec{E}). Also note: $n(\vec{r})$, not $n(\vec{r}, t)$, i.e. only coherent scattering is considered. Now \vec{j} into the ME

$$\nabla \times \vec{H} = \frac{1}{c} \frac{\partial \vec{E}}{\partial t} + \frac{4\pi}{c} \vec{j} = -\frac{i\omega}{c} \left(1 - \frac{4\pi e^2 n}{m\omega^2} \right) \vec{E}$$

This is similar to optics, but n, not \bar{n} . Also note that

$$(\ldots) = \left(1 - \omega_p^2 / \omega^2\right)$$

Now the 2d standard ME can be invoked -see Landau-Lifshitz, vol.III for detail. Scattering cross-section: similar to particles. Intensity in angle $d\Omega$ to energy density in insident wave. Θ - deviation from original direction

$$\vec{q} = \vec{k}' - \vec{k}$$
, $q = k \sin \Theta$

In CGS:

$$d\sigma = \frac{1}{2} \left(\frac{e^2}{mc^2}\right)^2 \left(1 + \cos^2\Theta\right) \left|\int n\left(\vec{r}\right) e^{-i\vec{q}\cdot\vec{r}} dV\right|^2 d\Omega$$

HW: re-write this in SI units

Note the Fourier component of density. Optics limit:

$$\vec{q} \to 0 \;, \; |\ldots| \to \int n dV = \bar{n} V$$

(no difference between glass and crystal. Think where the anisotropy was lost).

Crystal:

$$n\left(\vec{r}\right) = \sum_{\vec{K}} n_{\vec{K}} e^{i\vec{K}\cdot\vec{r}}$$

 \vec{K} from reciprocal lattice. Now consider

$$\int dV \exp\left\{-i\left(\vec{q}-\vec{K}\right)\cdot\vec{r}\right\}$$

For $\vec{q} \neq \vec{K}$ rapid oscillations, $\int \rightarrow 0$. Thus,

 $\vec{q} = \vec{K}$

(Laue)

Theorem: Laue equivalent to Bragg.

Proof: consider a family of planes separated by d. Then,

$$\vec{K} = n\vec{K}_0 , \quad K_0 = \frac{2\pi}{d}$$

From Laue (K = q) and geometry

 $K=2k\sin\theta$

Thus,

$$\frac{2}{\lambda}\sin\theta = \frac{n}{d}$$

or

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

(Bragg)

B. Experimental

- 1. Ewald construction
- 2. Laue method

(non-monochromatic)

- 3. Rotating crystal (Bragg) method
- 4. Powder diffraction method

Particles large on atomic scale. Rings:

$$K = 2k\sin\left(\phi/2\right)$$

BCC (rec.):

$$K_1: K_2: K_3: K_4: \ldots = \frac{\sqrt{3}}{2}: 1: \sqrt{2}: \frac{\sqrt{11}}{2}: \ldots$$

(see xrdBCCr.nb)

FCC (rec.)

$$K_1: K_2: K_3: K_4: \ldots = \frac{\sqrt{2}}{2}: 1: \sqrt{3/2}: \sqrt{2}: \ldots$$

HW: rings were observed at the following angles (in deg.)

and

in each case identify the lattice type. Also, find the lattice constant a if $\lambda = 1.5 \text{\AA}$.



1

1

FIG. 19: HCP with "small" and "large" atoms

C. Geometric structure factor

$$S_{\vec{K}} = \sum_{j} e^{i\vec{K}\cdot\vec{d}_{j}}$$
$$I_{\max} \propto |S_{\vec{K}}|^{2}$$

can go to zero - see xrd.nb

D. Different ions - atomic form-factor

$$S_{\vec{K}} = \sum_{j} f_j\left(\vec{K}\right) e^{i\vec{K}\cdot\vec{d}_j}$$

see xrd.nb and figures below. Also, you will have a Mathematica printout on form factor of a uniformly charged sherical ion. If a is the radius of ion,

$$f(K) \propto 2\pi \int_0^a dr r^2 \frac{\sin(kr)}{Kr}$$

The rest will be discussed in class.



FIG. 20: SC lattice with a basis with (a) different atoms, (b) identical finite size atoms, (c) identical point atoms

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XX. SELECTED APPLICATIONS

A. XPS

Analysis of electrons emitted from the surface (2-5nm) due to X-rays (the most common surface analysis). Sampling area - about 1 cm^2 , and small areas ~ 0. × 0.2 mm^2 can be achieved.

Detection limit: 1% of a monolayer for light elements - 0.1% for heavy. Only $\geq Li$ can be studied (Why?)

Basic relation:

$$E = h\nu - E_b$$

(More delicate recoil + interactions with electrons of other atoms - $\sim 1\%$ effect.

In solids - "chemical shift". Tabulations: Muilenburg, G. Handbook of X-ray ... (1979). Hard to find absolute energies, but comparison with tabulated - insight into chemical binding. Metals: E_b from Fermi level.

1. Instrumentation

X-ray source: often 2 anodes (Why? -later, to distinguish from Auger), e.g. Al, 1486.6 eV and Mg, 1253.6 eV + vacuum.

Energy analyzer: hemispherical (higher resolution) or cylindrical (higher efficiency): SLIDE/HANDOUT

2. Examples

SLIDE

B. Auger

Similar to XPS - analysis of electron enrgies (often, same instrumentation).

Incident radiation: X-rays or electrons. Electrons are easier to focus, thus can be used for scanning, $\sim 50 \ nm$ resolution.

Used to determine elements in the surface layer, 0.3 - 3nm and get info on the chemical state. Detection limit 0.01 - 0.001 at $\%, \gg XPS$.

Also, $\geq Li$

History: Auger, 1923 - discovered the process. Lander, 1952 - idea to use for surface analysis. Harris, 1967 - differentiation to enhance the Auger signal.

1. Fundamentas

in CLASS + SLIDE/HANDOUT

SLIDE/HANDOUT

C. SEM

1. General

A focussed electron beam is swept over a surface, and any of the reslting emissions are detected.

Image is formed on a cathode ray screen.

Large depth of focus (compared to optics). Resoluton as good as $\sim 3nm$.

Elemental analysis is possible through X-rays.

2. Specifics

Energies:

From surface:

incident beam - $30 \ KeV$ (SEM) - $100 \ KeV$ (TEM)

BS electrons - about the same (as in RBS, only very light)

secondary - < 50 eV

Auger - > 50 eV

+X-rays

Transmitted (for a thin film)

elestically scattered

inelestically scattered

DETECTORS:

BSE: concentric ring (direct line of sight)SE: see DIAGRAMSLIDE "figure 2"

D. TEM

SLIDE "figure 1a". Similar to optics, but "lenses" - magnetic field. Fixed lenses with variable f (current). Books - see syllabus.

Strong: resolution better than 0.2nm + both image and diffraction info. Individual dislocations can be imaged. But: slow and careful specimen preparation.

Crystal planes - similar to Bragg diffraction of X-rays, but λ - smaller, thus angles smaller. Interesting: relativistic corrections.

$$\sqrt{m^2c^4 + p^2c^2} = eV + mc^2$$

First approximation $p \ll mc$:

 $p\approx \sqrt{2meV}$

(HW -derive this, will be counted for the Exam) Second approximation (iteration)

$$p\simeq \sqrt{2meV}\left(1+\frac{eV}{2mc^2}\right)^{1/2}$$

(HW -derive this) with

$$2mc^2 \approx 1Mev$$

(HW - check this) and

 $\lambda = h/p$

one obtains

$$\lambda \ [nm] \simeq \frac{1.23 \ nm}{\sqrt{V \left(1 + 10^{-6}V\right)}}$$

(HW -derive this)

Example: V = 100kV, $\lambda = 0.0037nm$ (near-classical!) From

$$\lambda = 2d\sin(\theta)$$

and d = 0.15nm, one has $\theta \simeq 0.7^{\circ}$. Thus, Ewald spher - VERY LARGE:

$$k = 2\pi/\lambda \approx 1700 nm^{-1}$$

Compare this to reciprocal lattice with

$$K \sim 0.1 - 05 nm^{-1}$$

Thin films

$\Delta K \sim 2\pi/t$

(t-thickness). Kikuchi lines.

E. STM

Tunneling:

$$\psi_{out} \sim \exp\left(-\int_{x_1}^{x_2} |p| \, dx/\hbar\right)$$

For a rectangular barrier W = const this is

$$\exp\left(-d\sqrt{2mW}/\hbar\right)$$

Current:

$$I \sim \left|\psi_{out}^2\right| = \exp\left(-d_{[nm]} \cdot 1.62 \cdot \sqrt{W_{[eV]}}\right)$$

(HW - derive this)

HW (optional) generalize for
$$W = W_0 - Ex$$

Two modes : $I \approx const$, d - changes. Atomic scale profie, about 10Hz.

Or, $d \approx const$, record current, abot 1kHz.

Competition: thermal

$$I_{th} \sim \exp\left(-\frac{W}{kT}\right) \approx \exp\left(-40W_{[eV]}\frac{T_r}{T}\right)$$

Thus, for "clean" tunneling

$$T/T_r \ll \frac{20\sqrt{W_{[eV]}}}{1.62d_{[nm]}}$$

(HW - drive this)

Actual microscope: Bining and Roeher (1982). Key - atomically sharp tip. Resolution: $2\mathring{A}$ horisontal (parallel to surface) $0.02\mathring{A}$ vertical. (Why?)

Can operate in vacuum, air, liquid nitrogen. Best for metals and semiconductors with good conductivity (alternative - AFM).

Experimental: key precise mechanics, shielding from vibrations \rightarrow small size (then, $f_{res} \sim 5kHz$, compare to 20Hz in buildings)

XXI. AFM

Similar. New feature -soft cantilever spring to measure deflection.