EPFL

Electron-matter interactions: Elastic scattering (I)

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Contents

Introduction to e⁻ scattering

- Electron wave: wavelength and speed
- Plane wave for free electron: solving the Schrödinger eq.
- Plane wave in uniform potential
- Scattering by atomic potential
- Mott formula

Elastic scattering
Object: no change
of state

Fast e^-: - no change in
energy or λ

- change in
momentum

The electron wave

– wave / particle duality

- De Broglie relations: $\lambda = \dfrac{h}{p}$ $\qquad E_{\mathrm{el}} = \hbar\omega$ $\quad \left(\hbar = \frac{h}{2\pi}\right)$ $\quad (= h\nu)$ (1.1)

λ: wavelength
h: Planck's constant
p: momentum

Energy of e⁻ $\qquad \omega = 2\pi\nu$

- Momentum given by: $p = mv$ where $m = \dfrac{m_0}{\left(1 - v^2/c^2\right)^{1/2}} = \gamma m_0$ (1.2)

v: speed of e⁻
m: relativistic mass of e⁻
m_0: rest mass of e⁻

γ: Lorentz factor

- Relativistic total energy of electron: $W = mc^2 = E_{\mathrm{kin}} + m_0 c^2$ (1.3)

– Einstein eq.

E_{kin}: Kinetic energy of e⁻

The electron wave: λ

- Electron accelerated by potential difference (high tension) E_0:

$E_{kin} = eE_0$

E_0 in kV [EELS: E_0 in keV]

- Find relativistic wavelength:

$$W^2 = (eE_0 + m_0c^2)^2 = m^2c^4 \Rightarrow m^2c^2 = \left(m_0c + \frac{eE_0}{c}\right)^2$$

$$\text{Also: } m^2v^2 = m^2c^2 - m_0^2c^2 = \left(m_0c + \frac{eE_0}{c}\right)^2 - m_0^2c^2$$

$$\Rightarrow m^2v^2 = 2m_0eE_0 + \frac{e^2E_0^2}{c^2} = 2m_0eE_0\left[1 + \frac{eE_0}{2m_0c^2}\right]$$

$$\text{And: } m^2v^2 = p^2 = \left(\frac{h}{\lambda}\right)^2$$

Equate

$$\lambda = \frac{h}{\left[2m_0eE_0\underbrace{\left(1 + \frac{eE_0}{2m_0c^2}\right)}_{\text{Relativistic correction}}\right]^{1/2}} \qquad (1.4)$$

HT (kV)	λ (pm)
80	4.18
100	3.70
200	2.51
300	1.97

The free electron: v

- Find speed of electron:

From before: $eE_0 = mc^2 - m_0c^2$

and: $m = \gamma m_0 = \dfrac{m_0}{\left(1 - \frac{v^2}{c^2}\right)^{\frac{1}{2}}}$

Therefore: $\left(\dfrac{m}{m_0}\right)^2 = \left(\dfrac{eE_0}{m_0c^2} + 1\right)^2 = \dfrac{1}{\left(1 - \frac{v^2}{c^2}\right)}$

$\Rightarrow 1 - \dfrac{v^2}{c^2} = \dfrac{1}{\left(1 + \frac{eE_0}{m_0c^2}\right)^2}$

$$v = c\sqrt{1 - \frac{1}{\left(1 + \frac{eE_0}{m_0c^2}\right)^2}}$$

HT (kV)	v
80	$0.50c$
100	$0.55c$ (1.5)
200	$0.70c$
300	$0.78c$

Plane wave: wave function

Express e^- wave as a wave function

- Wave function of type: $$\psi(\vec{r},t) = \psi_0 \exp(2\pi i \vec{k}.\vec{r} - i\omega t) \qquad (1.6)$$

time

Normalizable pre-factor

position vector

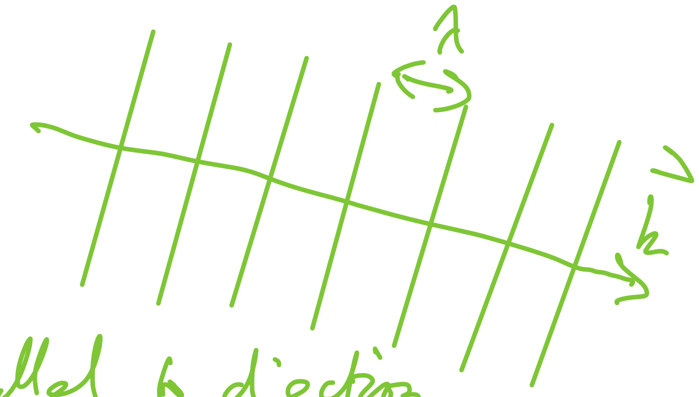
$|\psi|^2$: probability of finding e^- in a unit volume

where: $$|\vec{k}| = \frac{1}{\lambda} \qquad (1.7)$$

Greater energy $\Rightarrow \lambda \downarrow$

$\Rightarrow |\vec{k}| \uparrow$

$\vec{k}$: wave vector



$\vec{k}$ parallel to direction of propagation

Define $|\vec{k}|$ as for crystallography

$\cancel{|\vec{k}| = \frac{2\pi}{\lambda}}$

Plane wave: Schrödinger equation

Solve scattering problem by finding solutions to Schr. eq.

- Schrödinger equation: $$\underbrace{\hat{H}\psi(\vec{\mathbf{r}},t)}_{\text{Hamiltonian}} = \underbrace{i\hbar\frac{\partial\psi(\vec{\mathbf{r}},t)}{\partial t}}_{\text{Energy operator } \hat{E}} \quad (1.8)$$

- Energy of electron eigenstate E_{eig}:

$$\hat{E}\psi(\vec{r},t) = E_{eig}\psi(\vec{r},t)$$

$$\psi = \psi_0 \exp(2\pi i\,\vec{k}\cdot\vec{r} - i\omega t) \Rightarrow \hbar\omega\,\psi(\vec{r},t) = E_{eig}\,\psi(\vec{r},t)$$

$$\Rightarrow \boxed{E_{eig} = \hbar\omega}$$

de Broglie relation

Plane wave: Schrödinger eq. for free e⁻

- Hamiltonian: $$\hat{H} = \underbrace{\frac{\hat{p}^2}{2m}}_{\text{Kinetic energy}} + \underbrace{V(\vec{\boldsymbol{r}},t)}_{\text{Potential energy}} \quad (1.9)$$

- Momentum operator: $$\hat{p} = -i\hbar\nabla \quad (1.10)$$

∇: Laplacian

$\nabla = \frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z}$

Free e^- in vacuum

- Solve considering $V(\vec{\boldsymbol{r}},t) = 0$:

$\hat{H}\psi(\vec{r},t) = -\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r},t) = E_{eig}\psi(\vec{r},t)$

$\Rightarrow -\frac{\hbar^2}{2m} \cdot -4\pi^2 k^2 \psi(\vec{r},t) = E_{eig}\psi(\vec{r},t) \Rightarrow \boxed{E_{eig} = \frac{h^2 k^2}{2m}}$

$k^2 = \frac{2m_e E_0}{h^2}$

Plane wave: Schrödinger eq. for free e⁻

- Energy of electron: $E_{\text{eig}} = \hbar\omega$ $\qquad E_{\text{eig}} = \dfrac{h^2k^2}{2m}$ (1.11)

- From now on use a *time independent* wave function for the electron plane wave:

– time invariant system

$\Rightarrow \quad \psi = \psi_0 \exp(2\pi i \vec{k}.\vec{r})$

- Schrödinger equation simplifies to:

$$-\frac{\cancel{h^2}}{4\pi^2 . \cancel{2m}} \nabla^2 \psi(\vec{r}) = E_{\text{eig}}\, \psi(\vec{r}) = \frac{\cancel{h^2} k^2}{\cancel{2m}} \psi(\vec{r})$$

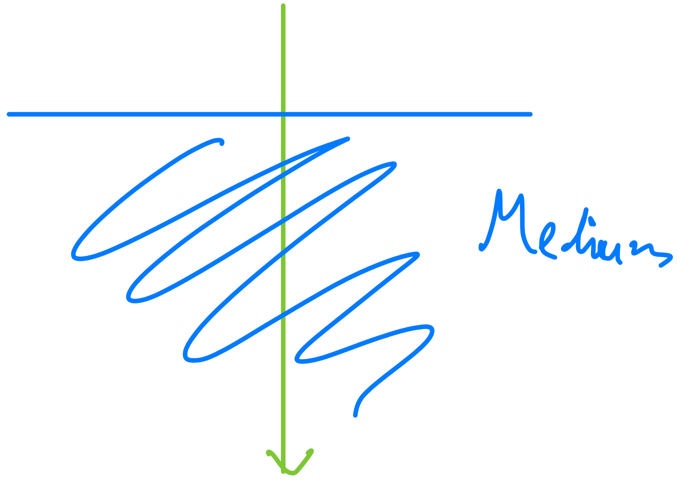
$$\nabla^2\psi(\vec{\mathbf{r}}) + 4\pi^2 k^2 \psi(\vec{\mathbf{r}}) = 0 \qquad (1.12)$$

Choose $\psi_0 = 1$

- Solutions: $\underbrace{\psi = \exp(2\pi i \vec{\mathbf{k}}.\vec{\mathbf{r}})}$ and $\psi = \exp(-2\pi i \vec{\mathbf{k}}.\vec{\mathbf{r}})$ (1.13)

Choose for e^- wave travelling in direction $\vec{k}$

e⁻ in uniform potential field



- Suppose electron travels in uniform potential field:

$V(\vec{r}) = V$ – potential energy

- Schrödinger equation becomes:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + V\psi(\vec{r}) = E_{ei}\psi(\vec{r})$$

$$\Rightarrow -\frac{h^2}{8\pi^2 m}\nabla^2\psi(\vec{r}) + V\psi(\vec{r}) = E_{ei}\psi(\vec{r})$$

Effect of uniform potential ?

e⁻ in uniform potential field

- Schrödinger eq.: $$-\frac{h^2}{8\pi^2 m}\nabla^2\psi(\vec{\mathbf{r}})+V\psi(\vec{\mathbf{r}})=E_{\text{eig}}\psi(\vec{\mathbf{r}}) \qquad (1.14)$$

- For uniform potential ϕ_0: potential energy $V = -e\phi_0$

From before: $E_{eig} = eE_0$

Therefore $\nabla^2\psi(\vec{r}) + \frac{8\pi^2 me}{h^2}[E_0+\phi_0]\psi(\vec{r}) = 0$

For $\psi = \exp(2\pi i \vec{k}\cdot\vec{r})$: $-\cancel{4\pi^2}k^2 + \frac{\cancel{8\pi^2}^{\,2} me}{h^2}[E_0+\phi_0] = 0$

$\Rightarrow k^2 = \frac{2me}{h^2}[E_0+\phi_0]$

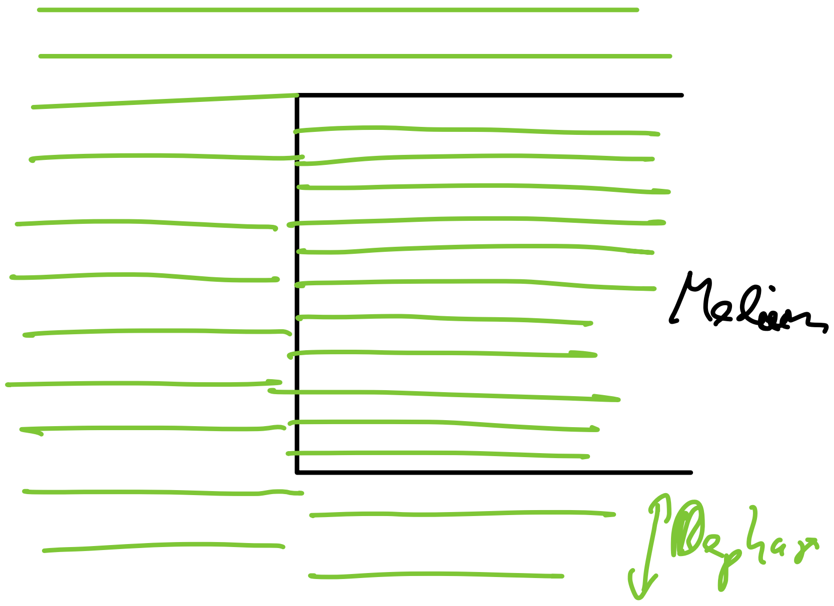
For free e⁻ in vacuum

Effect of potential ϕ_0:

$k\uparrow \Rightarrow \lambda\downarrow$

e⁻ wave travels faster

e⁻ in uniform potential field



- For uniform potential ϕ_0 derive refractive index n:

Say $n = \frac{v_\phi}{v_0}$

$p = mv = \frac{h}{\lambda} \Rightarrow v = \frac{h}{m\lambda} = \frac{hk}{m}$

$n \simeq \frac{k_\phi}{k_0} = \left(\frac{E_0+\phi_0}{E_0}\right)^{\frac{1}{2}}$

$$n = \sqrt{\left(1+\frac{\phi_0}{E_0}\right)} \qquad (1.15)$$

Phase difference between wave travelling in vacuum and passing through medium

$\Downarrow$

Holo with TL

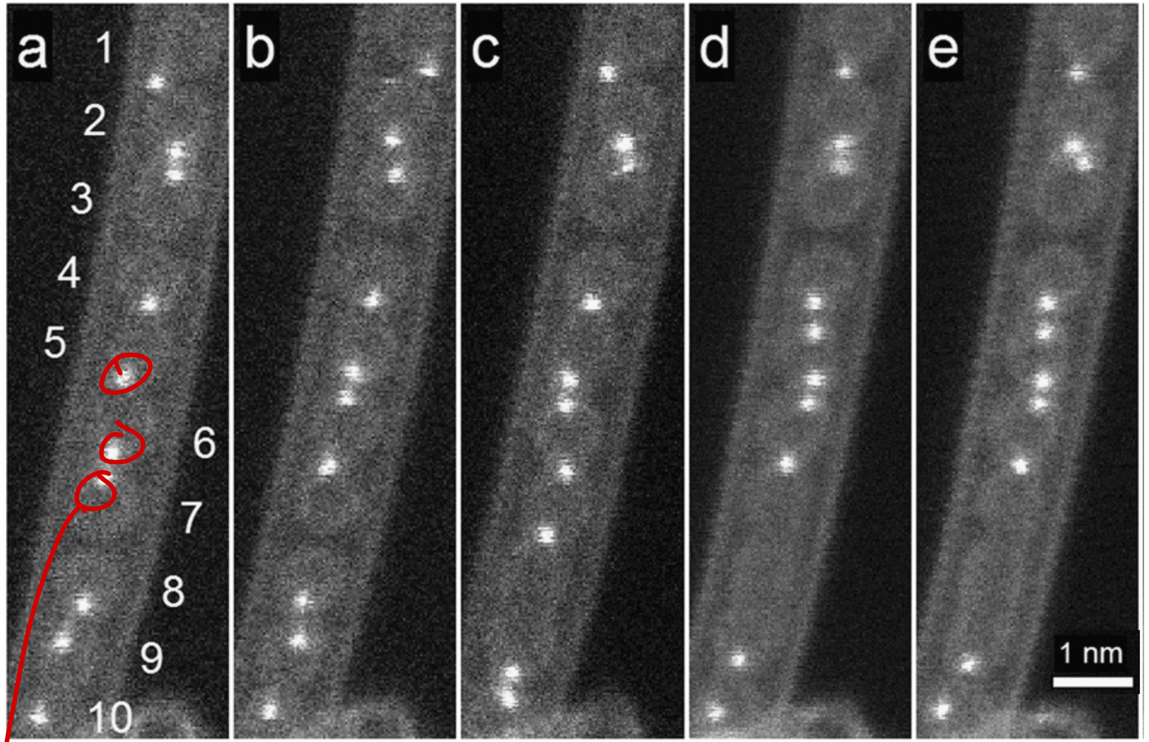
- Typical $\phi_0 \approx$ 10–20 V:

– Average charge of nuclei screened by atomic e^-

$\Rightarrow n \simeq 1 + 5 \times 10^{-5}$

TEM imaging of individual atoms

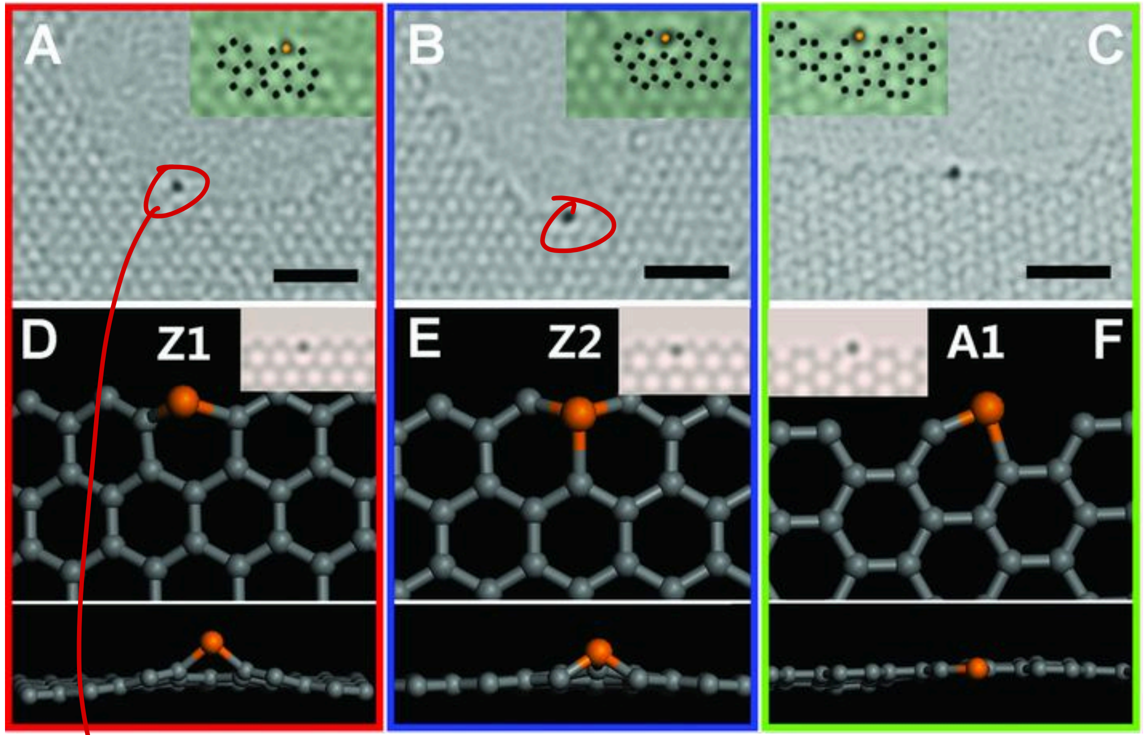
Measure scattering by a single atom



Cs-corrected canning TEM (STEM) time sequence of Er atoms in carbon nanotube “pea pods”

O.L. Krivanek et al. Ultramicroscopy **110** (2010) 935–945

Er atom



Cs-corrected high resolution TEM of single Fe atoms at edge of graphene monolayer

J. Zhao et al. Science **343** (2014) 1228–1232

Fe atom

Schrödinger eq. for atomic potential $\phi(\vec{\boldsymbol{r}})$

- Aim: study scattering of plane wave by single atomic potential described by function $\phi(\vec{\boldsymbol{r}})$:

- Rewrite equation 1.14: $-\dfrac{h^2}{8\pi^2 m}\nabla^2\psi(\vec{\boldsymbol{r}}) + V\psi(\vec{\boldsymbol{r}}) = E_{\text{eig}}\psi(\vec{\boldsymbol{r}})$

Now $V = -e\,\phi(\vec{r})$

$$\nabla^2\psi(\vec{\boldsymbol{r}}) + \frac{8\pi^2 me}{h^2}\left[E_0 + \phi(\vec{\boldsymbol{r}})\right]\psi(\vec{\boldsymbol{r}}) = 0 \qquad (1.16)$$

- Substitute in: $k^2 = \dfrac{1}{\lambda^2} = \dfrac{2meE_0}{h^2}$ $\qquad U(\vec{\boldsymbol{r}}) = \dfrac{2me}{h^2}\phi(\vec{\boldsymbol{r}})$ $\qquad (1.17)$

Effective potential

$\Rightarrow \nabla^2\psi(\vec{r}) + 4\pi^2\left[k^2 + U(\vec{r})\right]\psi(\vec{r}) = 0$

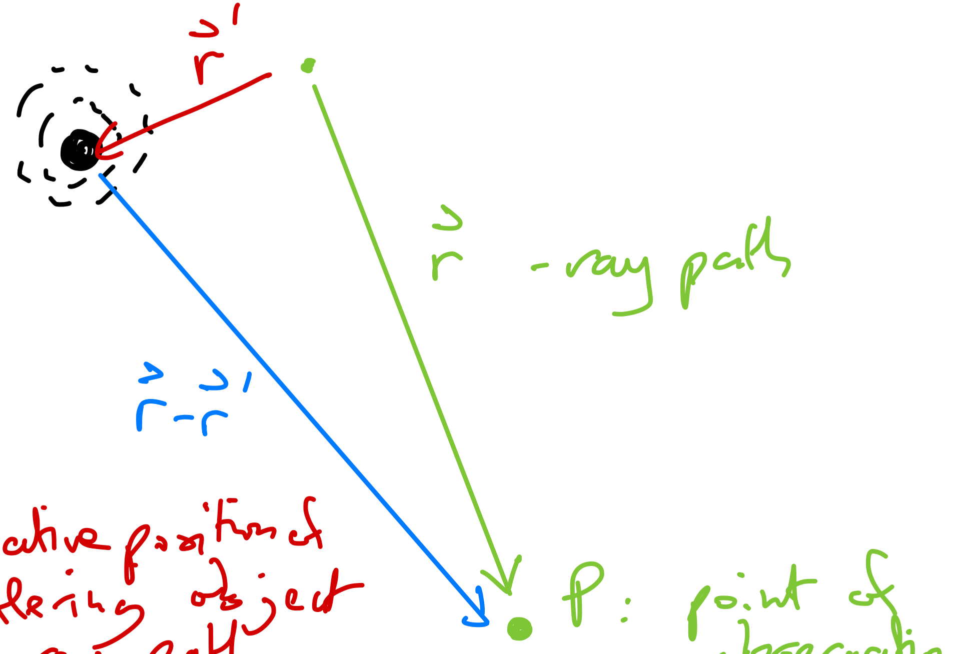
Schrödinger eq. for atomic potential $\phi(\vec{r})$

- Equation: $$\nabla^2\psi(\vec{\boldsymbol{r}})+4\pi^2\left[k^2+U(\vec{\boldsymbol{r}})\right]\psi(\vec{\boldsymbol{r}})=0 \qquad (1.18)$$

  has integral form (see Mott and Massey): $$\psi(\vec{\boldsymbol{r}})=\psi_0(\vec{\boldsymbol{r}})+\pi\int\frac{\exp\{2\pi ik|\vec{\boldsymbol{r}}-\vec{\boldsymbol{r}}'|\}}{|\vec{\boldsymbol{r}}-\vec{\boldsymbol{r}}'|}U(\vec{\boldsymbol{r}}')\psi(\vec{\boldsymbol{r}}')\mathrm{d}\vec{\boldsymbol{r}}' \qquad (1.19)$$

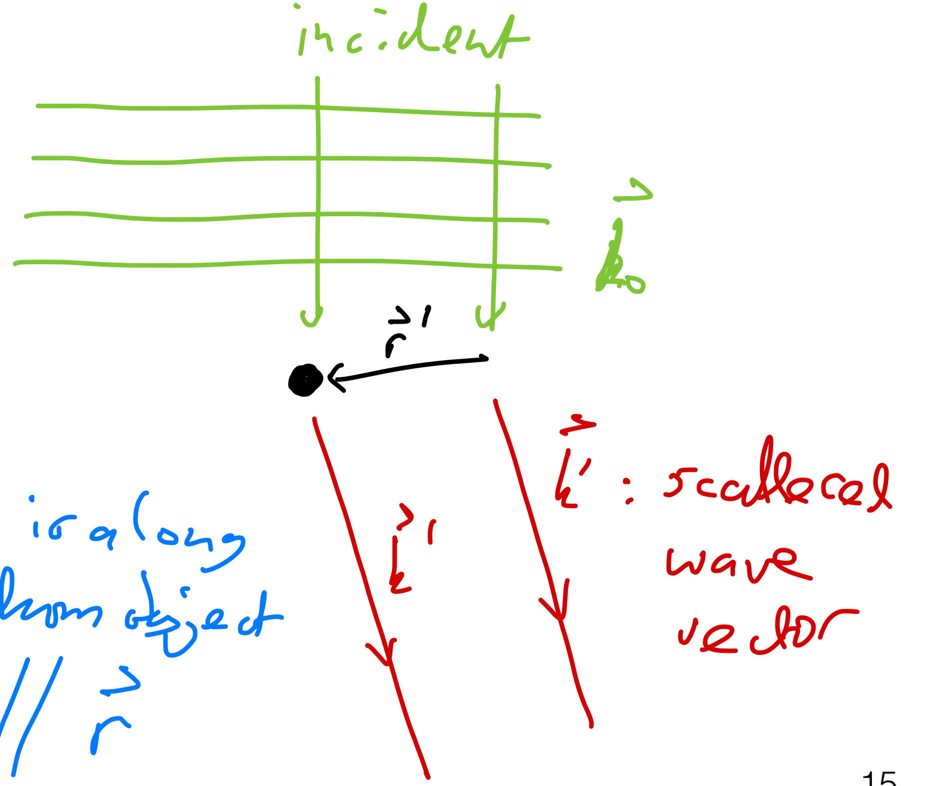
$\psi_0(\vec{r})$: incident wave function

- Scattering geometry:



$\vec{r}'$: relative position of scattering object (to ray path)

If P is along ray from object
$\vec{k}' \,//\, \vec{r}$



Schrödinger eq. for atomic potential $\phi(\vec{r})$

- For: $$\psi(\vec{r}) = \psi_0(\vec{r}) + \pi \int \frac{\exp\{2\pi i k |\vec{r} - \vec{r}'|\}}{|\vec{r} - \vec{r}'|} U(\vec{r}')\psi(\vec{r}')\mathrm{d}\vec{r}'$$
- Solution given by **Born series**: $\psi(\vec{r}) = \sum_{n=0}^{\infty} \psi_n(\vec{r})$
- First Born approximation: assume that $\psi(\vec{r})$ in integral can be replaced by $\psi_0(\vec{r})$

i.e. single scattering – "kinematical"

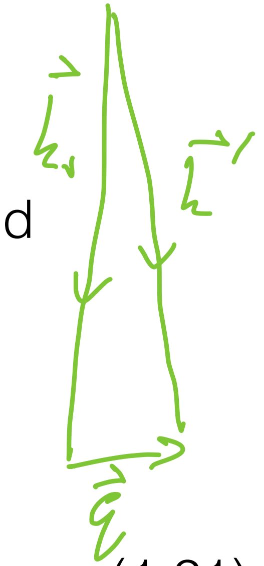
⇒ assuming scattering is very weak

- For plane incident wave $\psi_0(\vec{r}) = \exp\{2\pi i \vec{k}_0 \cdot \vec{r}\}$ this gives:

$$\psi(\vec{r}) = \psi_0(\vec{r}) + \underbrace{\psi_1(\vec{r})}_{\text{scattered wave}} = \exp\{2\pi i \vec{k}_0 \cdot \vec{r}\} + \pi \int \frac{\exp\{2\pi i k |\vec{r} - \vec{r}'|\}}{|\vec{r} - \vec{r}'|} U(\vec{r}') \exp\{2\pi i \vec{k}_0 \cdot \vec{r}'\} \mathrm{d}\vec{r}' \quad (1.20)$$

Scattering from atomic potential $\phi(\vec{r})$

Need to treat: $$\int \frac{\exp\{2\pi i k|\vec{r}-\vec{r}'|\}}{|\vec{r}-\vec{r}'|} U(\vec{r}')\exp\{2\pi i \vec{k}_0\cdot\vec{r}'\}d\vec{r}'$$



- Assume point of observation for $\vec{r}$ which is very large compared to scattering field

$$|\vec{r}-\vec{r}'| \simeq r$$

$$k|\vec{r}-\vec{r}'| = k(r^2 - 2\vec{r}\cdot\vec{r}' + r'^2)^{\frac{1}{2}} \simeq kr\left(1 - \frac{2\vec{r}\cdot\vec{r}'}{r^2}\right)^{\frac{1}{2}}$$

$r'^2 \sim 0$

$$\simeq kr - \left(k\frac{\vec{r}}{r}\right)\cdot\vec{r}' = kr - \vec{k}'\cdot\vec{r}'$$

- Scattering vector: $\vec{q} = \vec{k}' - \vec{k}_0$ (1.21)

$$\rightarrow \frac{\exp(2\pi i kr)}{r}\int U(\vec{r}')\exp\left[-2\pi i \underbrace{(\vec{k}' - \vec{k}_0)}_{\vec{q}}\cdot\vec{r}'\right]d\vec{r}'$$

- Then:

$$\psi(\vec{r}) = \psi_0(\vec{r}) + \psi_1(\vec{r}) = \exp\{2\pi i \vec{k}_0\cdot\vec{r}\} + \pi\frac{\exp\{2\pi i k r\}}{r}\int U(\vec{r}')\exp\{-2\pi i \vec{q}\cdot\vec{r}'\}d\vec{r}' \quad (1.22)$$

Scattering from atomic potential $\phi(\vec{\boldsymbol{r}})$

- Scattered wave: $$\psi_1(\vec{\boldsymbol{r}}) = \frac{2\pi me}{h^2}\frac{\exp\{2\pi ikr\}}{r}\int\phi(\vec{\boldsymbol{r}}')\exp\{-2\pi \mathrm{i}\vec{\boldsymbol{q}}\cdot\vec{\boldsymbol{r}}'\}\mathrm{d}\vec{\boldsymbol{r}}' \quad (1.23)$$

⇒ Atomic potential scatters a spherical wave

- Define scattering amplitude $f(\vec{\boldsymbol{q}})$ such that: $$\psi_1(\vec{\boldsymbol{r}}) = \frac{\exp\{2\pi ikr\}}{r}f(\vec{\boldsymbol{q}}) \quad (1.24)$$

- Therefore: $$f(\vec{\boldsymbol{q}}) = \frac{2\pi me}{h^2}\underbrace{\int_{-\infty}^{\infty}\phi(\vec{\boldsymbol{r}})\exp\{-2\pi \mathrm{i}\vec{\boldsymbol{q}}\cdot\vec{\boldsymbol{r}}\}\mathrm{d}\vec{\boldsymbol{r}}}_{\text{FT of } \phi(\vec{r})} \quad (1.25)$$

- sometimes referred to as "atomic scattering factor"

Mott formula derivation

Charge density of atomic e^-

- Introduce Poisson's equation: $$\nabla^2\phi(\vec{\boldsymbol{r}}) = -4\pi e\left[\underbrace{\rho_{\text{n}}(\vec{\boldsymbol{r}})}_{\text{Charge density of nucleus}} - \rho_{\text{e}}(\vec{\boldsymbol{r}})\right] \tag{1.26}$$

- First rewrite $f(\vec{\boldsymbol{q}})$:

Use : $\nabla^2 \exp[-2\pi i\vec{q}\cdot\vec{r}] = -4\pi^2 q^2 \exp[-2\pi i\vec{q}\cdot\vec{r}]$

Subst. in eq. 1.26

$$f(\vec{\boldsymbol{q}}) = -\frac{me}{2\pi h^2 q^2}\int_{-\infty}^{\infty}\phi(\vec{\boldsymbol{r}})\nabla^2\exp\{-2\pi \mathrm{i}\vec{\boldsymbol{q}}\cdot\vec{\boldsymbol{r}}\}\mathrm{d}\vec{\boldsymbol{r}} \tag{1.27}$$

- Integrating by parts gives: $$f(\vec{\boldsymbol{q}}) = -\frac{me}{2\pi h^2 q^2}\int_{-\infty}^{\infty}\nabla^2\phi(\vec{\boldsymbol{r}})\exp\{-2\pi \mathrm{i}\vec{\boldsymbol{q}}\cdot\vec{\boldsymbol{r}}\}\mathrm{d}\vec{\boldsymbol{r}} \tag{1.28}$$

- Substitute in $\nabla^2\phi(\vec{\boldsymbol{r}})$: $$f(\vec{q}) = \frac{2me^2}{h^2q^2}\int_{-\infty}^{\infty}[\rho_n(\vec{r}) - \rho_e(\vec{r})]\exp(-2\pi i\vec{q}\cdot\vec{r})\,d\vec{r}$$

Mott formula

- Scattering amplitude: $$f(\vec{\boldsymbol{q}}) = \frac{2me^2}{h^2q^2}\int_{-\infty}^{\infty}\left[\rho_n(\vec{\boldsymbol{r}}) - \rho_e(\vec{\boldsymbol{r}})\right]\exp\{-2\pi i\vec{\boldsymbol{q}}\cdot\vec{\boldsymbol{r}}\}d\vec{\boldsymbol{r}} \qquad (1.29)$$

- Charge density of nucleus: $$\rho_n(\vec{\boldsymbol{r}}) = Z\delta(\vec{\boldsymbol{r}}) \qquad (1.30)$$

  $\delta(\vec{r})$: delta function
  Z: atomic number

- Find: $$f(\vec{\boldsymbol{q}}) = \frac{2me^2}{h^2q^2}\left[Z - f_x(\vec{\boldsymbol{q}})\right] \qquad (1.31)$$

  ← Gaussian units

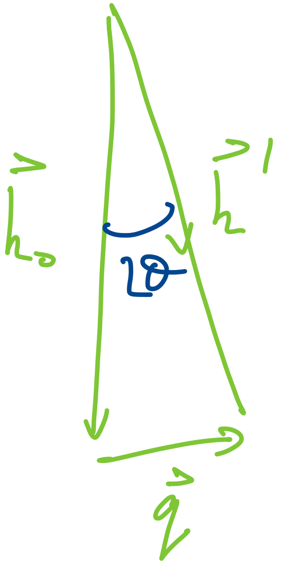
  $f_x(\vec{q})$: FT (atomic e^- density)
  – i.e. X-ray scattering factor – scattering by Coulomb field of atomic e^-

- In SI units: $$f(\vec{q}) = \frac{me^2}{2h^2q^2\pi\varepsilon_0}\left[Z - f_x(\vec{q})\right]$$

- Or for Bohr radius a_0: $$f(\vec{\boldsymbol{q}}) = \frac{1}{2\pi^2a_0q^2}\left[Z - f_x(\vec{\boldsymbol{q}})\right] \qquad (1.32)$$

Scattering geometry

- Assume scattering by an angle 2θ



$$\frac{q}{2k} = \sin\theta = \frac{q\lambda}{2}$$

$$\Rightarrow q = \frac{2\sin\theta}{\lambda}$$

- Therefore atomic scattering amplitude:

$$f(\theta) = \frac{2me^2}{h^2} \cdot \frac{\lambda^2}{4\sin^2\theta}\left[Z - f_x(\theta)\right]$$

$$f(\theta) = \frac{me^2}{2h^2}\left(\frac{\lambda}{\sin\theta}\right)^2\left[Z - f_x(\theta)\right] \tag{1.33}$$

Amplitude of scattered wave @ unit distance

Scattered intensity

- Scattered intensity at unit distance: $I(\theta) = |f(\theta)|^2$ ← Measure intensity (1.34)

[$I(\theta) = \frac{d\sigma}{d\Omega}$ σ: scattering cross-section]

- For large scattering angles: $f_x(\vec{\boldsymbol{q}}) \to 0$ hence $I(\theta)_{\theta\to\pi/2} = |f(\theta)|^2_{\theta\to\pi/2} = \underbrace{\frac{4m^2e^4}{h^4q^4}Z^2}_{\text{Rutherford-like scattering}}$ (1.35)

General scattering is Mott scattering

Relative scattering strength

- Applying “bandwidth” nature of Fourier transform:

$$\Delta q \Delta r \simeq 1$$

Scattering distribution is mainly forward scattered

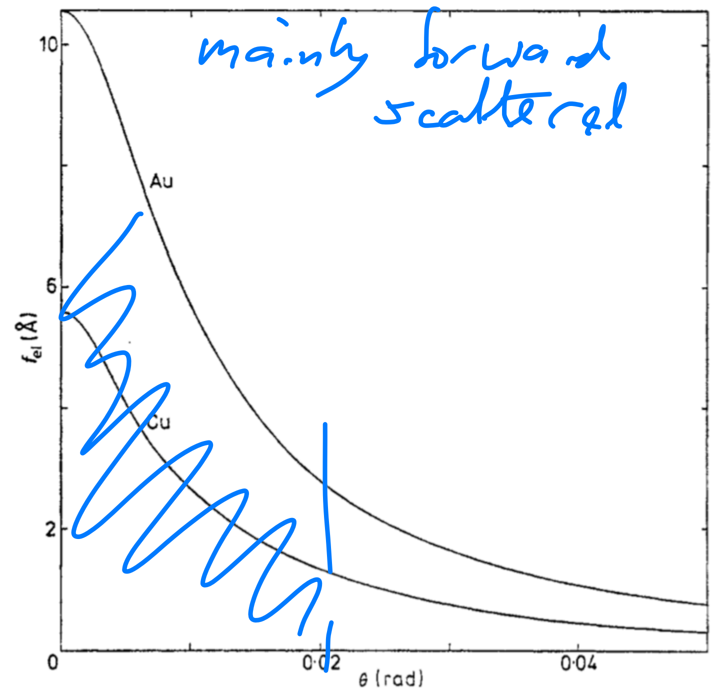


Figure 4. The first Born approximation scattering amplitude, $f^B(K')$, as a function of θ for 100 keV electrons incident upon single atoms of gold and copper. The plots have been made using the relativistic Hartree–Fock scattering amplitudes of Doyle and Turner (1968).

Δq: range of sca. angles over which $f(\vec{q})$ is large

Δr: range of values over which $\rho(\vec{r})$ is large

Atomic radius ~ 1 Å

$\Rightarrow \Delta q \sim 1\ \text{Å}^{-1} \simeq \frac{2\Delta\theta}{\lambda}$

$\lambda: 0.037$ Å $\Rightarrow \Delta\theta \simeq 20$ mrad (!)

Summary

Introduction to e⁻ scattering

- Free e⁻

$$\nabla^2\psi(\vec{\boldsymbol{r}})+4\pi^2k^2\psi(\vec{\boldsymbol{r}})=0$$

$$\psi=\exp(2\pi i\vec{\boldsymbol{k}}.\vec{\boldsymbol{r}})$$

$$|\vec{\boldsymbol{k}}|=\frac{1}{\lambda}$$

- Uniform potential

$$n=\sqrt{\left(1+\frac{\phi_0}{E_0}\right)}$$

$$k^2=\frac{2me}{h^2}[E_0+\phi_0]$$

- Scattering by atomic potential

$$f(\vec{\boldsymbol{q}})=\frac{2me^2}{h^2q^2}[Z-f_x(\vec{\boldsymbol{q}})]$$

Mott formula

Bibliography

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- Elastic and Inelastic Scattering in Electron Diffraction and Imaging, by Z.L. Wang, Plenum Press, New York 1995: Chapters 1 and 2
- Peter Rez: “Scattering Cross Sections in Electron Microscopy and Analysis” Microsc. Microanal. **7** (2001) 356–362. Note: $\vec{\boldsymbol{q}}_{\mathrm{Rez}=} 2\pi\vec{\boldsymbol{q}}$
- The Theory of Atomic Collisions Vol. 1, Third Edition, by N.F. Mott and H.S.W. Massey, Oxford Science Publications 4965