Quantitative Low Energy Ion Scattering: achievements and challenges

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Layout

• Intro

• Low energy ion scattering
  → ESA : ions only

• Achievements:
  → surface composition analysis
    o Scattering potential
    o Charge exchange
    o information depth

• Challenges
  → subsurface information
    o stopping power ↔ reionization probability

→ TOF-LEIS
Low Energy Ion Scattering

projectiles: noble gas ions, large scattering angle (no grazing collisions)

\[ J_i^+ = I_0 \cdot P_i^+ \cdot c_i N_s \cdot \frac{d\sigma_i}{d\Omega} \cdot \Omega \cdot \eta_+ \]

Surface composition analysis

- \( J_i^+ \) ... detected ion current (ions/sec)
- \( I_0 \) ... primary ion current (ions/sec)
- \( c_i \) ... atomic surface concentration
- \( N_s \) ... atomic surface density (atoms/cm\(^2\))
- \( P_i^+ \) ... ion fraction of atom \( i \)
- \( d\sigma_i/d\Omega \) ... scattering cross section (atom \( i \))
- \( \Omega \) ... detector solid angle
- \( \eta_+ \) ... detector efficiency (incl. transmission)

\( E_0 = 0.5\text{-}10\text{keV} \)
Low Energy Ion Scattering

ESA: only ions detected ↔ surface sensitivity

\[ J_i^+ = I_0 \cdot P_i^+ \cdot c_i N_s \cdot \frac{d\sigma_i}{d\Omega} \cdot \Omega \cdot \eta_+ \]

3 keV He\(^+\) → Ta & O

Sensitivity factor \( S_i^+ \)

(B. Bruckner, 2015)

binary surface Ta & O: \( c_{Ta} + c_O = 1 \)
Low Energy Ion Scattering

ESA: only ions detected ↔ surface sensitivity

$3 \text{ keV He}^+ \rightarrow \text{Ta} & \text{O}$

Relative yield

$C_i = \frac{\frac{J_i^+}{I_0 \eta_i N_0} \sigma_i}{P_i^+} \equiv A_i^+$

$C \ldots \text{expt. constant}$

(B. Bruckner, 2015)

$\text{binary surface Ta} & \text{O: } c_{Ta} + c_O = 1 \leftrightarrow$

$\frac{A_{Ta}^+}{P_{Ta}^+} + \frac{A_O^+}{P_O^+} = \frac{1}{C}$
Scattering cross section

Screened Coulomb potential: \( V(r) = V_c(r) \cdot \Phi \left( \frac{r}{a} \right) \quad \Phi(r/a) \) ...screening function

\[ \frac{d\sigma}{d\Omega} \text{ depends on } \Phi(r/a) \text{ model} \]

\[ \Phi(r/a) = \sum_{i=1}^{3} b_i \cdot \exp(-c_i \cdot r/a) \]

\[ \frac{(d\sigma_{\text{scr}}/d\Omega)}{(d\sigma_{R}/d\Omega)} \]

Energy \( E \) [keV]  

\[ \frac{d\sigma_{\text{ZBL}}}{d\sigma_{\text{TFM}}} \]

He \( \rightarrow \) Au  \( \theta = 135^\circ \)
Surface composition analysis

ESA: only ions detected ↔ surface sensitivity

$3 \text{ keV He}^+ \rightarrow \text{Ta} & \text{O}$

$A^+ \text{Ta} \leftrightarrow A^+ \text{O}$

$A^+_\text{Ta} \leftrightarrow A^+ \text{O}$

$\text{ESA spectrum}$

$\text{secondary ions}$

$\equiv A_j^+$

$\frac{J_i^+}{I_0 N_0 \left( \frac{d\sigma}{d\Omega} \right)_i} \equiv \frac{p_j^+ \eta^+}{C A_i^+ p_i^+}$

constant?

→ charge exchange!

(B. Bruckner, 2015)
Charge exchange (He ions)

- **Auger neutralization (AN)**
  is possible at any ion energy $E$ & at any surface atom

- **Resonant charge exchange** (reionization, res. neutralization)
  (reionization & resonant neutralization)
  \[ E > \text{threshold energy } E_{th} \leftrightarrow R_{\min}(E_{th}, \vartheta) < R_{\text{crit}} \]

- **Quasi resonant neutralization** (qRN)
  resonant levels at atom and ion
  (→ quantum oscillations, difficult quantification)
Charge exchange (He ions)

- **Auger neutralization (AN)**
  is possible at any ion energy $E$ & at any surface atom

- **Resonant charge exchange** (reionization, res. neutralization)
  (reionization & resonant neutralization)
  $E >$ threshold energy $E_{th} \leftrightarrow R_{min}(E_{th}, \mathcal{J}) < R_{crit}$

- Quasi resonant neutralization (qRN)
  resonant levels at atom and ion
  ($\rightarrow$ quantum oscillations $\rightarrow$ difficult quantification)

**How to do quantitative composition analysis?**

**How to obtain surface sensitivity?**
Auger Neutralization (AN)

Auger transition rate $\Gamma_A$

$\Gamma_A$ depends on electron density parameter $r_s$

$\rightarrow \Gamma_A(r_s(x,y,z))$ in front of a surface

Typically, $\langle \Gamma_A \rangle \approx 1 \ldots 2 \cdot 10^{15}/s$
Auger Neutralization (AN)

Rate equation (1D) for survival probability $P^+$

$$dP^+ = -P^+ \cdot \Gamma_A(z)dt = -P^+ \frac{\Gamma dz}{v_\perp}$$

→ survival probability $P^+ = \exp\left(-\frac{v_c}{v_\perp}\right)$ with $v_c = \int_0^\infty \Gamma_A(z)dz$

(He$^+$ remains He$^+$)

$v_c$ ... characteristic velocity ↔ AN efficiency

$v_c \approx 1 \ldots 2 \cdot 10^5 \text{m/s} \approx 0.1 \text{ a.u.}$

Typically, $\langle z \rangle \approx 1\text{Å}$ ... information depth due to AN
Energy spectrum of scattered ions in AN regime

all detected ions are „survivals“ ↔ no charge exchange
$P^+(1/v_\perp)$ in the AN regime

He$^+ – Cu$: for $E < 2.1$ keV, only AN is possible

ion signal: 1$^{\text{st}}$ atomic layer dominates

$P^+ = \exp(-v_c/v_\perp)$

variation of geometry

variation of energy

$\nu_c = 1.92 \cdot 10^5 \text{ m/s}$

Summary AN regime

- **Information depth**
  high AN rate and long dwell time $\rightarrow$ information depth $\approx 1$ ML

- **Quantitative composition analysis**
  AN depends on DOS $\rightarrow$ matrix effects to be expected
  $\rightarrow$ not first choice for composition analysis
Resonant charge exchange in a close collision

\[ R_{\text{min}} < R_{\text{crit}} \rightarrow \text{overlap of orbitals} \]
\[ \rightarrow \text{electron promotion (atomic collision)} \]
\[ \rightarrow \text{is active for } E > E_{\text{th}} \]

Avoided crossings are typical of adiabatic surfaces and arise because the adiabatic electronic states corresponding to the surfaces are often mixtures of two simple molecular orbital (i.e., covalent) or valence bond (i.e., ionic) electronic structures (cf. the NaCl example used to explain the non-crossing rule), where the original energy functions do cross.

A surface where actual intersections are substituted for the avoided crossings is termed a diabatic surface.

If the nuclei are assumed to move slowly, then they are likely to follow a single, adiabatic energy surface, even in the region of an avoided crossing. If the nuclei have sufficient velocity, then the Born-Oppenheimer approximation breaks down and the nuclei may effectively “ignore” the gap in the avoided crossing and simply cross over to the other adiabatic surface, adopting that configuration. This is termed non-adiabatic behaviour can be modelled, to some extent, by a diabatic representation.

\[ \text{He}^+ \rightarrow \text{Al} \]

\[ R_{\text{crit}} \approx 0.1 \text{ Å} \leftrightarrow E_{\text{th}} \approx 2 \text{ keV} \rightarrow \text{AN dominant} \]

\[ \text{Ta: } R_{\text{crit}} \approx 0.5 \text{ Å} \leftrightarrow E_{\text{th}} \approx 0.4 \text{ keV} \rightarrow \text{RN, RI dominant} \]

\[ \text{Al: } R_{\text{crit}} \approx 0.5 \text{ Å} \leftrightarrow E_{\text{th}} \approx 0.2 \text{ keV} \]
Resonant charge exchange in a close collision

\[ P^+ = P^+_{in} \cdot (1 - P^+_{RN}) \cdot P^+_{out} + (1 - P^+_{in}) \cdot P^+_{RI} \cdot P^+_{out} \]

Survivals (no AN, no RN)  reionized projectiles (AN+RI)
Resonant charge exchange in a close collision

\[ P^+ = P_{in}^+ \cdot (1 - P_{RN}) \cdot P_{out}^+ + (1 - P_{in}^+) \cdot P_{RI} \cdot P_{out}^+ \]

Survivals (no AN, no RN)  reionized projectiles (AN+RI)

AN: \[ P^+ = \exp(-v_c/v_\perp) \] (survival probability)

RN: \[ P_{RN} = 1 - \exp(-v_{RN}/v) \] … neutralization probability due to rate \( \Gamma_{RN} \)

RI: \[ P_{RI} = \exp(-v_{RI}/v) \] … reionization probability due to rate \( \Gamma_{RI} \)

rates \( \Gamma_{RI}, \Gamma_{RN} \): ???

RN, RI scale with velocity \( v \)
**$P^+$: Variation of geometry**

$$E = E_{th}: P_{RI} = P_{RN} = 0$$

$$E > E_{th}: P_{RI} > 0, P_{RN} > 0$$

(D. Roth, 2016)
$P^+$: Variation of geometry

$He^+ \rightarrow Au$-poly, CuAu(100)

(D. Roth, 2016)
Reionization $\text{He}^+ - \text{Al}_{\text{poly}}$

- is active for $E > E_{th}$ (threshold energy)

**empirical fact:**

variation of $E \to P^+ = e^{-v_R/v_\perp}$

$P^+_{\text{expt}} \ll P^+_{\text{AN}} \leftrightarrow \text{RN dominant}$

$v_R \gg v_c$

Low ion signal

$\langle \text{charge state} \rangle \approx 0$

(S. Rund et al., 2011)
4 keV He\(^+\) → Ta: ion spectrum

4 keV → Ta

surface peak
(survivals and reionized proj.)

reionization background
(subsurface backscattering)

charge exchange
penetration to deeper layers & reionization @ surface: \( \Rightarrow \) information depth is due to \( P_{\text{out}}^+ \) (no AN on way out)

\[
J_{RI}^+(1) = \sigma(R_{\text{crit}}) \cdot P_{RI} \cdot P_{\text{out}}^+
\]
\[
J_{RI}^+(2) = \sigma(R_{\text{crit}}) \cdot P_{RI} \cdot (P_{\text{out}}^+)^3 = J_{RI}^+(1) \cdot P_{\text{out}}^{+2}
\]
\[
J_{RI}^+(3) = \sigma(R_{\text{crit}}) \cdot P_{RI} \cdot (P_{\text{out}}^+)^5 = J_{RI}^+(1) \cdot P_{\text{out}}^{+4}
\]
\[
\vdots
\]
\[
J_{RI}^+ = J_{RI}^+(1) \cdot (1 + (P_{\text{out}}^+)^2 + (P_{\text{out}}^+)^4 + \ldots)
\]

\[
J_{RI}^+ = \frac{J_{RI}^+(1) \text{[1st layer]}}{1 - (P_{\text{out}}^+)^2} \approx J_{RI}^+(1) \text{[1st layer]}
\]
MC-simulations and charge exchange

modeling the reionization background in TRIM
by introducing a minimum number of additional parameters

- 4 keV He → Cu:
  
  Good agreement for $\Gamma_A = 1.635 \cdot 10^{15}$/s
Surface composition analysis

$P^+ (\text{He} - \text{Si})$ – influence of oxygen exposure

\[ \text{He}^+ \rightarrow \text{Si} \]
\[ \text{He}^+ \rightarrow \text{SiO}_2 \]

\[ \frac{S}{\sigma(E)} \] (a.u.)

\[ \frac{\text{Relat. ion yield } J^+}{(d\sigma/d\Omega)/E} \]

\[ \frac{1}{v^+} + \frac{1}{v^-} \] (s/m)

\( E^{-4} \)

(Hidde Brongersma, 1992 (?)

\[ \frac{A_{\text{Si}}^+}{P_{\text{Si}}^+} + \frac{A_{\text{O}}^+}{P_{\text{O}}^+} = \frac{1}{C} \]

(T. Jansens et al., 2003)
charge exchange

\[ P^+ (\text{He} - \text{Al}) - \text{influence of oxygen} \]

He\(^+ \) → Al\textsubscript{metal}:

\[ v_R = 2.2 \times 10^5 \text{ m/s} \]

He\(^+ \) → Al\textsubscript{2O}\(_3\):

\[ v_R = 2.4 \times 10^5 \text{ m/s} \]

1/\(v_\perp\) → 0: \(P^+ \rightarrow 0.45\)

(Barbara Bruckner, 2014)
Surface composition analysis

\[ P^+ (\text{He} - \text{Ta}) - P^+ (\text{He} - \text{Ta}_2\text{O}_5) \]

Linear dependence signal - concentration!

Reionization regime is best suited for composition analysis

But: physics of reionization is not yet understood!

(Barbara Bruckner, 2014)
Summary reionization regime

Information depth

polycrystals: surface peak $\rightarrow$ information depth $\approx 1$ ML

quantitative surface composition analysis

probabilities $P_{RN}$, $P_{RI}$: depend only weakly on band structure

$\rightarrow$ „absence of matrix effects“!
Characterization of graphene

Achievements

3 keV He\(^+\) → CH\(_x\) / graphene / metals? /Si

(Stan Prusa et al, Langmuir, 2015)
Characterization of graphene layers

3 keV He$^+$ $\rightarrow$ CH$_x$ / graphene / metals? / Si

(Stan Prusa et al, Langmuir, 2015)
Achievements

Characterization of graphene layers

$3 \text{ keV He}^+ \rightarrow \text{CH}_x / \text{graphene} / \text{metals?} / \text{Si}$

(Stan Prusa et al, Langmuir, 2015)
Challenges: subsurface information

\[ \text{He}^+ \rightarrow \text{subsurface Hf}: \]

- Required input: \( dE/dx \) in Al\(_2\)O\(_3\)
- Multiple scattering
- Reionization at surface

(Philipp Brüner, 2014)
Reionization → subsurface information

Final energy ↔ penetration depth?

Reionization background
(subsurface backscattering)

Surface peak
(survivals)

4 keV → Ta

Final energy ↔ penetration depth?
TRBS + charge exchange ↔ experiment

TRBS ↔ experiment:

\[ N_{\text{expt}}(E) = N_{\text{TRBS}}(E) \cdot p_{RI,\text{eff}} \]

\[ p_{RI,\text{eff}} = P_{RI} \cdot P_{\text{out}}^{+} \]

\( p_{RI,\text{eff}} \) is a surface property

Electronic stopping
Multiple scattering
Path length increase
**Summary quantification**

**Reionization**: best suited for composition analysis 😊
- no matrix effects!
- charge exchange still lacks basic understanding 😞

**Auger regime**: not recommended for composition analysis 😞
- band structure (matrix effects) effects to be expected

**quasi resonant neutralization**: not recommended for composition analysis 😞
- $P^+$ oscillation amplitudes of a factor ~ 3,
- $P^+$ depends on band structure
Summary information depth

Reionization regime: \( \approx 1 \) ML for polycrystals (depending on \( E \))
may be larger for single crystals (focusing collisions)

Auger regime: \( \approx 1 \) ML

quasi resonant neutralization: neutralizes much more effective than AN
information depth = 1 ML

😊
TOF-LEIS application: Cu/PET

3keV He
θ=129°

~3nm
TOF-LEIS application: Ag clusters/PET

Small clusters: buried in PET

Larger clusters: on PET, covered

(J M Flores-Camacho, 2011)
TOF-LEIS: growth Au on B

D. Primetzhofer et al., APL (2008)
Growth of Au on B

TOF-LEIS: 1 - 10 keV $\text{He}^+$ $\rightarrow$ Au nanostructures on B

Information on coverage and height?

D. Primetzhofer et al., APL (2008)
TRBS-Simulations: 1 Å

1.2 keV He$^+$ → Au (d = 1 Å)

\[ \langle h \rangle \quad f < 1 \]

D. Primetzhofer et al., APL (2008)
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charge exchange

(c) Quasiresonant neutralization

- **d-electrons (e.g., of Ge)** are quasi resonant with He 1s level
  $\rightarrow$ quantum oscillations!

Quantum oscillations

- d-electrons (e.g., of Ge) are quasi resonant with He 1s level
  → quantum oscillations!

(Erickson et al. (1975))
charge exchange

Quantum oscillations

Way in: at mixing distance $R_M$ the projectile „forgets“ its charge state

Collision: phase difference $\Delta \phi$ evolves between the two paths ($V_1$, $V_2$)
until projectile passes $R_M$ again

$qRN \equiv$ atomic collision: No dependence on $\alpha$, $\beta$,
no $1/v_\perp$ scaling!

$$\Delta \phi = \frac{1}{\hbar} \int \Delta V(t) dt = \frac{1}{\hbar} \int_{k_i}^{k_f} \frac{\Delta V(R)}{\bar{V}(R)} dR$$
$\rightarrow \Delta \phi$ from known $V_1(R)$, $V_2(R)$

$$I_+ = a_+ + b \cdot \cos^2(\Delta \phi/2) \ , \ I_0 = a_0 + b \cdot \sin^2(\Delta \phi/2)$$

$\rightarrow I_+$ oscillations are equidistant as $f(1/v)$
charge exchange

Interplay AN ↔ qRN ↔ RI

• **Threshold energy for reionization:** $E_f \approx 1200$ eV
  → for $E_f < 1200$ eV only Auger neutralization ↔ quasi-resonant neutral.

charge exchange

Quantum oscillations

- **d-electrons** are quasi resonant with He 1s level
  → quantum oscillations!

(Erickson et al., 1975)

(Smith et al., 1974)

(Zartner et al., 1978)
Quantitative $P^+$ for $\text{He}^+ \rightarrow \text{Ge}$

$P^+ \ll 1$: qRN is very effective

qRN works “one-way”: $\text{He}^+ \rightarrow \text{He}^0$

($\text{He}^0 \rightarrow \text{He}^+$ is not possible!)

No reionization up to 1.3 keV

$\rightarrow P^+ = \text{qRN-surviving probability}$

\[
P^+ = e^{-P_{\text{qRN}}} = e^{-v_{\text{qRN}}/v}
\]

$P^+ \approx 10^{-2}$ @ 1 keV ($v = 0.1 \text{ a.u.}$)

$\rightarrow v_{\text{qRN}} \approx 10^6 \text{ m/s} \approx 5 \cdot v_c$

$\rightarrow$ qRN dominates over AN

Information depth = 1 ML! (without reionization)

Oscillation amplitude $\approx$ factor 2: quantification
Quantitative $P^+$ for $\text{He}^+ \rightarrow \text{Ge}$

Information depth = 1 ML! (without reionization) 😊
Oscillation amplitude $\approx$ factor 2: quantification 😎

(Goebl et al., 2013)
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Peru
TOF-LEIS Experiment: ACOLISSA

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