Primary electron can interact by different mechanisms with a surface:

1) **Coulomb or dipolar interaction**
   - excites whatever has a dynamical dipole moment:
     - electronic excitation (electron hole pairs, plasmons, dipole active vibrations of the substrate or of adsorbates

2) **Impact scattering**
   - excites losses with whatever momentum transfer but is usually weaker than dipole scattering

3) **Exchange interaction**
   - Generates magnetic excitations (Stoner pairs and magnons).

The energy loss probability is generally small (order of 10^{-2}) so that multiple losses are generally (but not always) negligible
Coulomb or dipole interaction

Usually for HREELS studies primary electron beams are employed with impact energies between 1 e 20 eV striking the surface at grazing incidence. EELS takes place however also for swift electrons and is used in TEM studies.

The energy loss is generated by the variable electric field generated by the moving electron. Such field induces screening charges. On metals the screening is perfect and the electric field lines are therefore normal to the surface. On semiconductors the screening is partial and the lines have a component parallel to the surface.

The Fourier transform of the time dependence of the electric field generates the frequency spectrum which extends over all frequencies up to a cut off given by the electron energy. The filed is just equivalent to while light. At the resonance frequencies of the substrate absorption takes place as for infrared spectroscopy.

Such energy is lost by the electron. The electron may be reflected by the surface before or after its energy loss and the two processes may interfere.

The cross section is given by the square of the matrix element and contains therefore the square of the dynamical dipole moment, $\mu$, of the relevant transition. It follows:

$$\frac{I}{I_0} = A \mu^2$$

with $I_0$ intensity of the elastically reflected beam
Volume:
high energy electron energy loss spectroscopy

Ex: Plasmon Losses vs film thickness
The Coulomb interaction goes like $r^{-2}$, and is thus long ranged. At large distances (10 nm) from the surface the latter is illuminated uniformly by the electric field, i.e. the dephasing is small over atomic distances. Dipolar excitations correspond therefore to small transferred momenta $q_\parallel$ or large wavelengths of the excitations. (dipole cone). The dipole cone is empty at the center since excitations with $q_\parallel \to 0$ imply very large distances of the electron to the sample and the fields are correspondingly weaker.

The loss probability is maximized when the phase velocity of the wave coincides with teh velocity of the electron parallel to the surface because the excitation takes place always in phase (surfing condition)

$$\frac{d^2 S}{d\omega d\Omega} = \frac{m^2 e^2 v^2_\perp}{2\pi^2 \hbar^5 \cos \theta_i} \frac{k_s P(q_\parallel, \omega)}{k_i q^2_\parallel}$$

$$\times \left| v_\perp q_\parallel (R_s + R_i) + i (R_i - R_s) (\omega - v_\parallel \cdot q_\parallel) \right|^2 \frac{1}{\left[ v^2_\perp q^2_\parallel + (\omega - v_\parallel \cdot q_\parallel)^2 \right]^2},$$
Three layer model

The dielectric function acquires a $q_\parallel$ dependence because of the finite width $W$ of the surface layer (e.g. the layer of adsorbates)

Loss function

$$P(q_\parallel, \omega) = \frac{2\hbar q_\parallel}{\pi} \left[ 1 + n(\omega) \right] \text{Im} \left[ \frac{-1}{\varepsilon(q_\parallel, \omega) + 1} \right]$$

Effective dielectric function

$$\varepsilon(q_\parallel, \omega) = \varepsilon_s(\omega) \left[ \frac{1 + \Delta(\omega) e^{-2q_\parallel W}}{1 - \Delta(\omega) e^{-2q_\parallel W}} \right]$$

$$\Delta = \frac{\varepsilon_b(\omega) - \varepsilon_s(\omega)}{\varepsilon_b(\omega) + \varepsilon_s(\omega)}.$$
Example: dependence of the energy loss induced by a Cs layer deposited on Si(111) 7x7 (electron beam impinges nearly normally to the crystal). At 1 monolayer (PL) the loss is due to the excitation of the surface plasmon. Notice the vanishing cross section at small momentum transfer. Beyond the monolayer thickness the loss spectrum is dominated by the multipole mode (max at $q_\parallel = 0$).

\[ \hbar \omega \ll E_i \quad \text{and} \quad \theta \ll 1 \]

\[ v^2 q^2 + (\omega - v_\parallel \cdot q_\parallel)^2 = 4E_i^2(\theta^2 + \theta_E^2) \cos^2 \theta_i \]

\[ \theta_E = \frac{\hbar \omega}{2E_i} \]

$E_i$ energy of the incident electrons

Ag surface
Plasmon
excited by HREELS at grazing incidence
Dependence on impact energy $E$

Adsorbate losses

$$\sum \propto \frac{1}{E}$$

Surface losses which are not confined to the surface but rather penetrate for a depth proportional to $q_{\parallel}$

$$\sum \propto \frac{1}{\sqrt{E}}$$

The most favorable angle is grazing since the electron maximises the time close to the surface. Grazing incidence and low impact energies are thus to be preferred. The most favourable condition is when the whole dipole cone is contained in the angular acceptance of the HREEL spectrometer.
Interference phenomena (LEED fine structures) and reflectivity structures

The loss process may take place either on the way to or on the way off the surface and the two processes may interfere. Such features may give rise to sharp structures close to resonance conditions associated to LEED fine structures since the scattering phase can then change over few hundred meV. In the experiment reported on the right the losses take place principally before reflection and the uniform loss intensity is modulated by the energy dependent reflectivity.
Selection Rules:
Coulomb scattering can only excite modes whose dynamical dipole moment is in the vertical direction (strictly for flat metal surfaces, relaxed for stepped surface and for semiconductors).

Symmetry tells whether a mode is observable, tells nothing about the intensity of the loss which depends on the dynamical dipole moment.
Example of chemical analysis

Ethylene on Pt(111) dissociates forming ethylydene and H. Ethylydene adsorbs with the CC axis vertical with respect to the surface giving rise to a strong dipole intensity for the vibration of that bond.
Impact scattering

\[
\frac{dS}{d\Omega} = \frac{m}{2\pi^2 \hbar^2} A \frac{\cos^2 \theta_s E_i}{\cos \theta_i} \left| \langle \{n_{q\|t}\}_s | f(k_s, k_i; \{R\}) | \{n_{q\|t}\}_i \rangle \right|^2
\]

The loss probability depends on the involved energy and grows thus with \(E\).

The collision takes place at small distances ... all possible momneta can be exchanged. The electron energy loss intensity is subject to interference like LEED vs \(E_i\) and angle \(\theta\)

E.g.: phonons on Ni(100)

The \(S_6\),mode, polarized parallel to the surface can be observed only in a narrow energy range
Measurements vs $q_{||}$ allow to measure the phonon dispersion curve and possible phonon anomalies (Kohn anomaly for W(110) H)
Magnetic excitations (exchange mechanism): surface magnons

Surface magnons are spin waves in ferromagnets. They have been observed very recently with SPEELS and the excitation corresponds to the inversion of the spin of the scattered electron. This process can only take place if the incident electron corresponds to the minority species on the magnetized surface. Notice that loss 3 is indeed present in the spectra only for one given polarization (either red or blue spectra) and that the latter is opposite for gain and loss processes. Surface Magnons exhibit a quadratic dispersion with $q_{||}$. 

![Graphs showing SPEELS spectra and dispersion relation.](image-url)