Image potential

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If the charged particles such as cations and anions become close to the metal surface (electrode), electrons on the metal surface screen the electric field from the charged particles to prevent the penetration of the field inside the metal. This screening generate the charge at the surface and interacts the charge above the surface. The electrostatic interaction can be described by the screened charges are located the virtual charge shown in Fig. below.

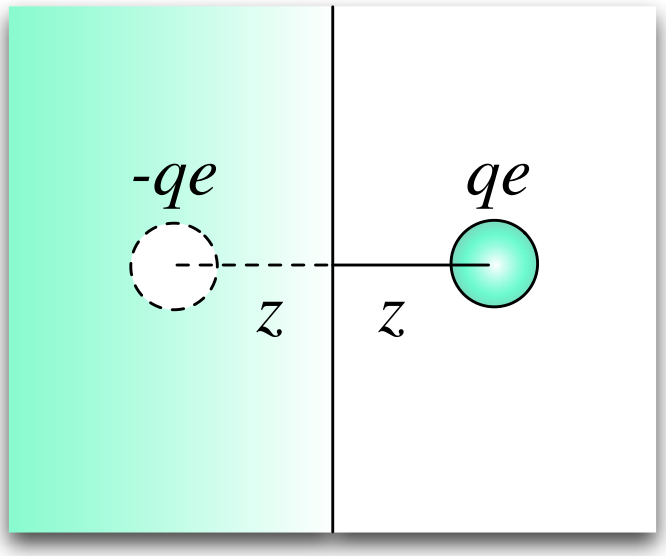

Figure 1: image potential of charged particle

The force on the charge above the surface becomes

$$\mathbf{F}_z = -\frac{1}{4\pi\epsilon_0}\frac{q^2e^2}{(2z)^2} = -\frac{q^2e^2}{16\pi\epsilon_0 z^2} \tag{1}$$

The electric field $\mathbf{E}$ and the potential ϕ are

$$\mathbf{F}_z = qe\mathbf{E}_z, \quad \mathbf{E}_z = -\frac{qe}{16\pi\epsilon_0 z^2}, \quad \mathbf{E}_z = -\mathrm{grad}\phi \tag{2}$$

$$\phi(z) = -\frac{1}{4\pi\epsilon_0}\frac{qe}{4z} \tag{3}$$

From the first-principles calculation based on the density functional theory, we can not get the image potential if we use some purtabation theory.

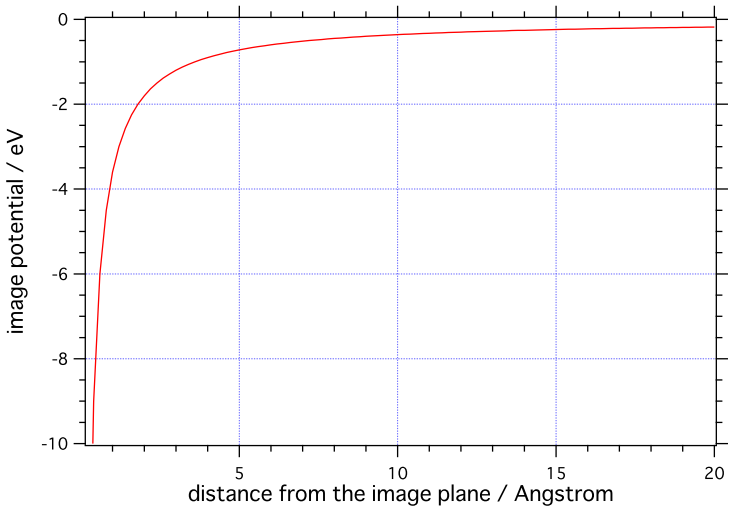

Figure 2: z dependence of the image potential of charged particle

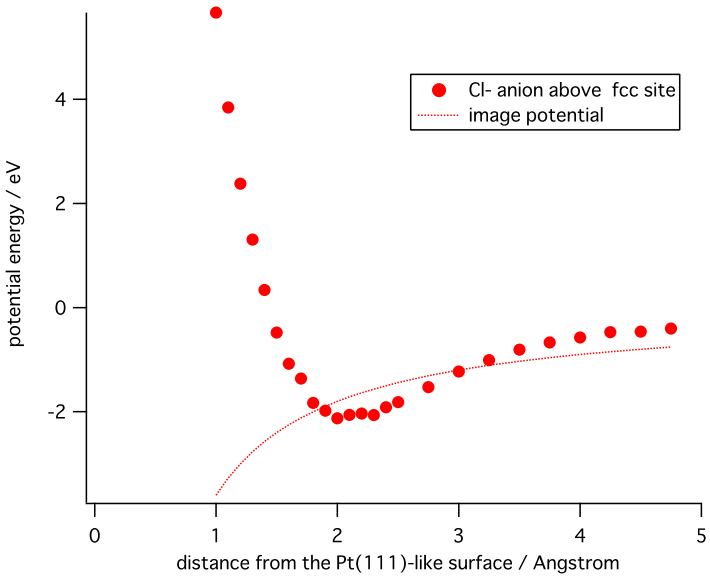

Figure 3: image potential and potential energy of Cl- anion on Pt(111) surface calculated by ab-initio method