Field emission from the first principles: Effect of point defects on the value of the workfunction

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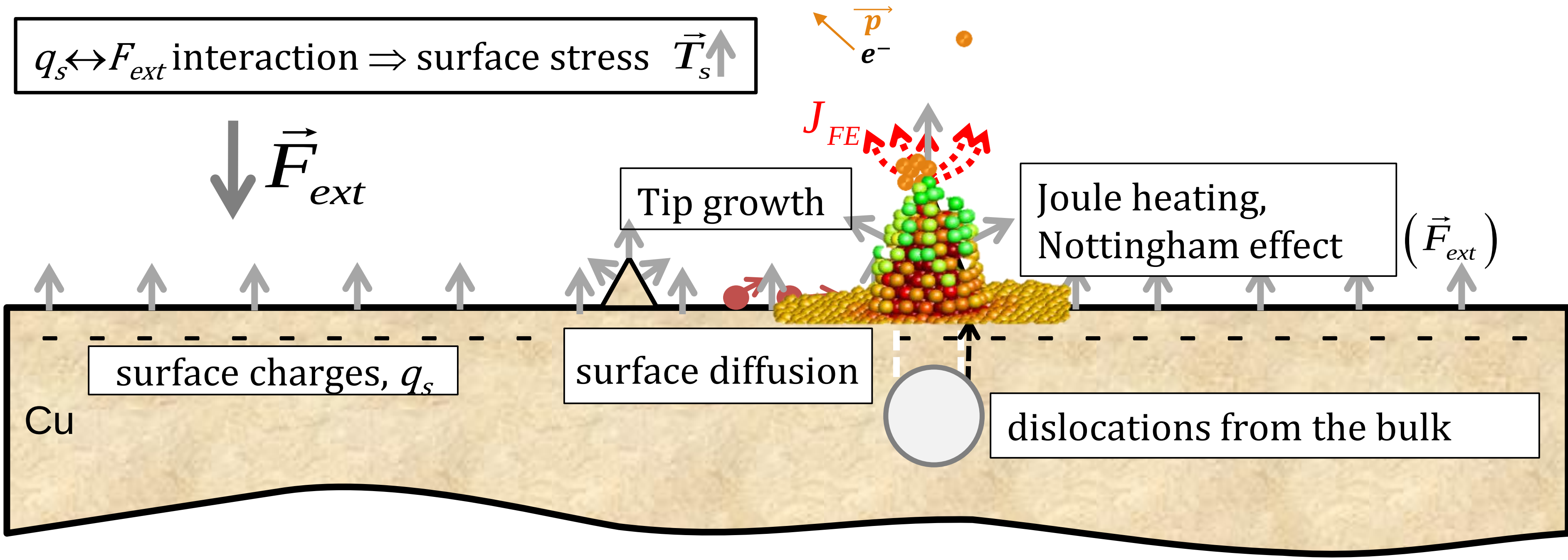
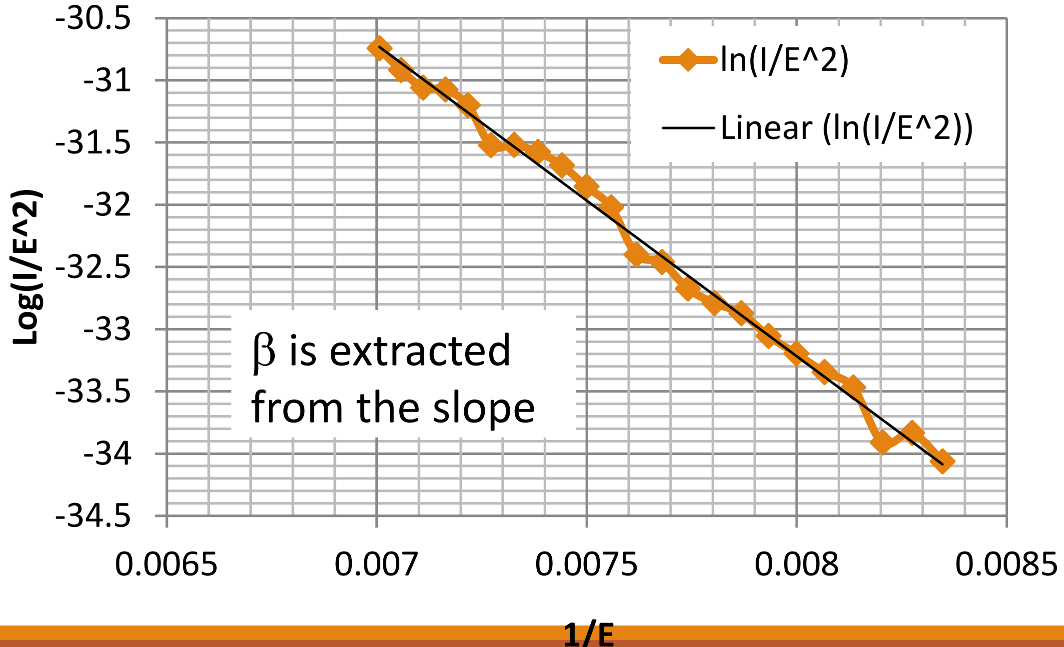
Mechanisms *on* and *under* the surface in the presence of electric fields

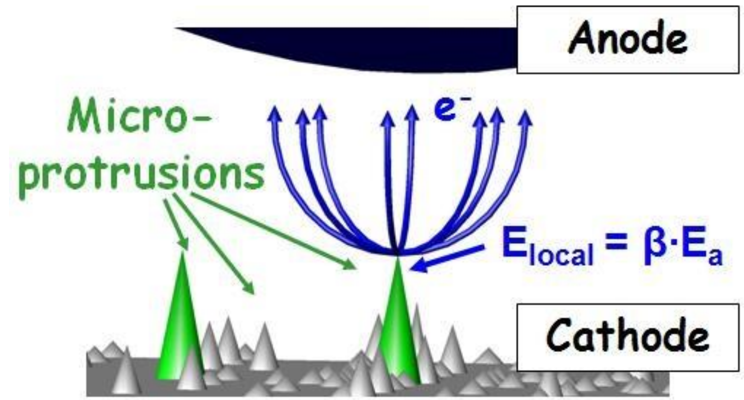


Field emission - β measurement

An I-V scan from a flat surface, performed at limited current, fits to the classical Fowler-Nordheim formula, where $[j_{FE}] = A/m^2$, [E] = MV/m and [ϕ] = eV (usually 4.5 eV).

$$j_{FE} = \frac{1.54 \cdot 10^6 (\beta \cdot E)^2}{\phi} \exp(10.41 \cdot \phi^{-1/2}) \exp\left(\frac{-6.53 \cdot 10^3 \phi^{3/2}}{\beta E} \right)$$



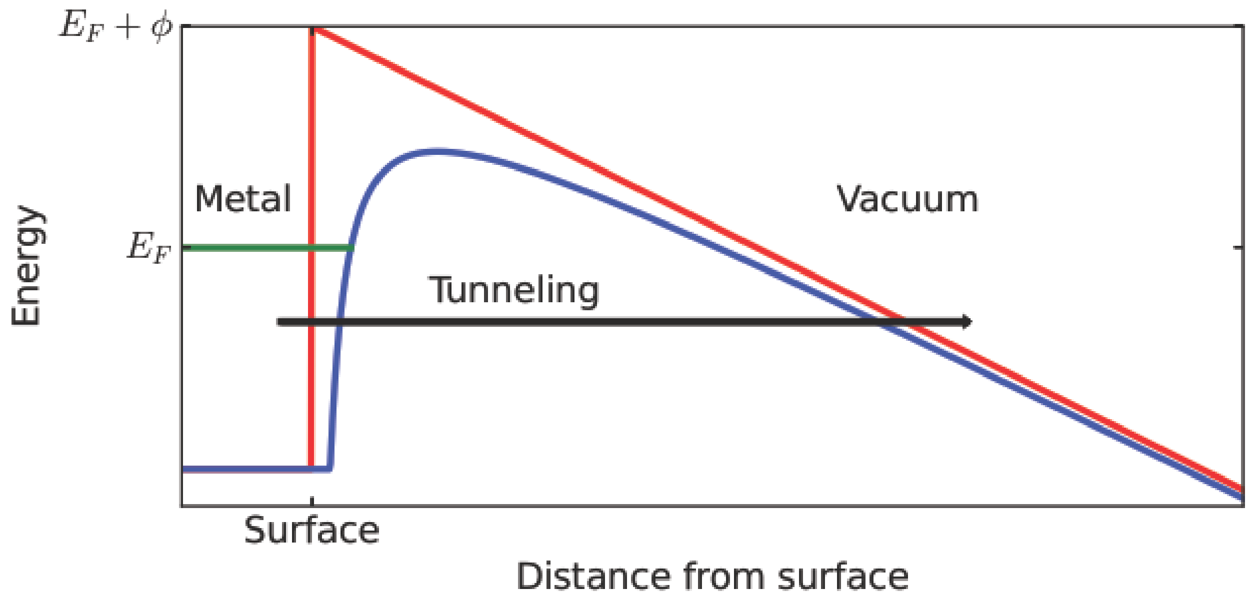


Field Emission

Emission of electrons by tunneling due to an electrostatic field

Dependent on field strength and material/surface

- Potential barrier from surface to vacuum
- The value of a local field determines the width of the barrier
- The value of workfunction, on the other hand, may affect the shape of the barrier to a significant extent



Purpose of the study

Defects present on the surface may alter the energetics in the vicinity of it and, thus, the value of the workfunction may also alter.

Since the phenomenon of the field emission is based on the transmission of electrons through the barriers, this probability must be calculated based on the quantum-mechanical considerations:

- Compute work functions
- Compute tunneling currents
- Compute field enhancement factors

Quantum-mechanical approach

VASP: DFT software

- Plane wave DFT software developed at the University of Vienna
- Relatively fast & accurate (DeltaCodesDFT)
- Interface slightly inconvenient

Kwant: Quantum transport software

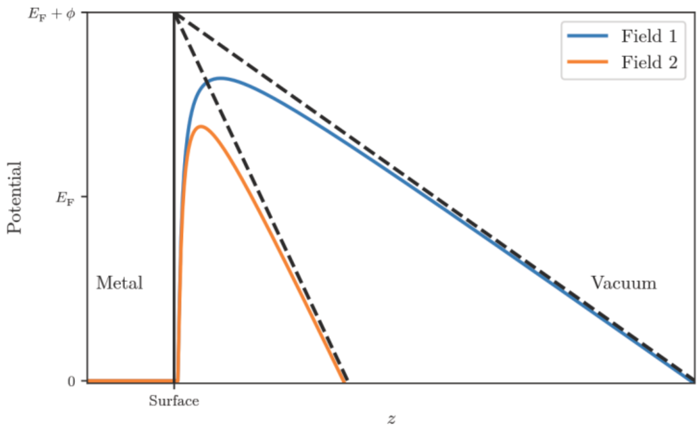
- Quantum transport with tight-binding Hamiltonians
- Faster than conventional solvers
- Convenient Python interface

Calculation of field emission currents

Field emission current is defined by the supply function $N(E,T)$ and the transmission probability:

$$J(F,T) = e\int_0^\infty \mathrm{d}E_z\, N(E_z,T)D(E_z,F)$$

These can be calculated if a jellium model for electrons in metals is assumed and the potential has a triangular shape.



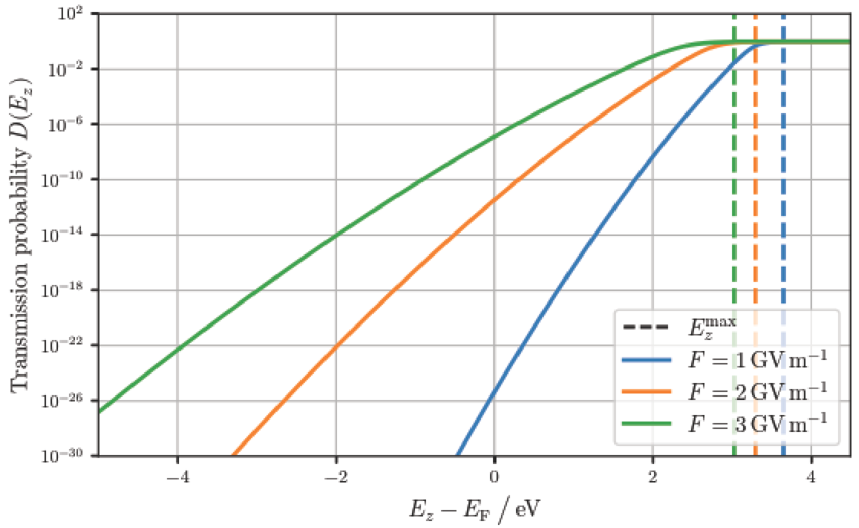
Calculating the transmission probability for the Schottky–Nordheim barrier in the Murphy and Good approximation for an electron with the normal energy E_z and assuming isotropic supply function, we obtain the formula, which allows to calculate the field emission currents:

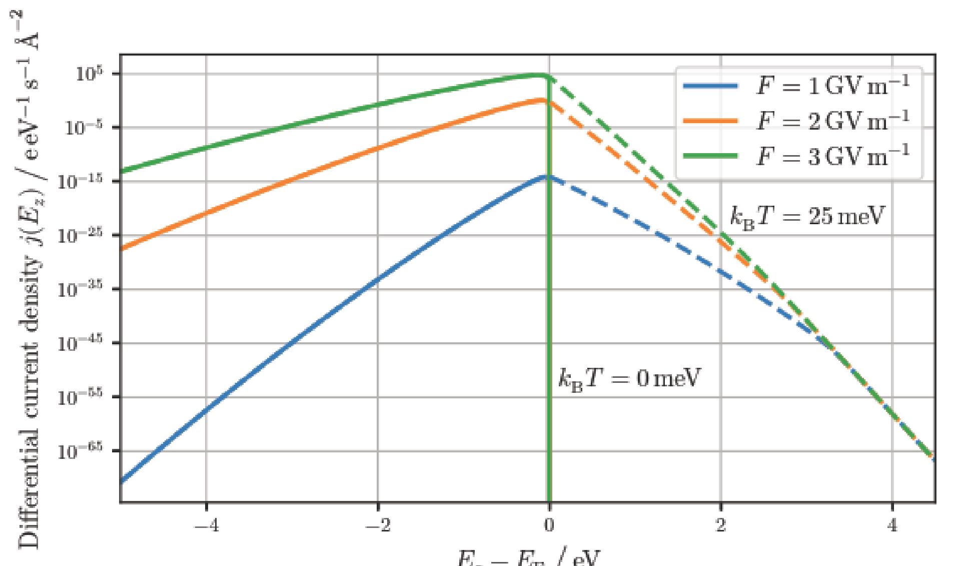
$$\boxed{N(E_z) = \int_{E_z}^\infty \mathrm{d}E\,\frac{f_{\mathrm{FD}}(E)\rho(E)}{\sqrt{8mE}}\,.}$$

$$J(F,T) = \frac{emk_\mathrm{B}T}{2\pi^2\hbar^3}\left\{\int_0^{E_z^{\max}}\mathrm{d}E_z\,\frac{\ln\left[1+\exp\left(\frac{E_\mathrm{F}-E_z}{k_\mathrm{B}T}\right)\right]}{1+\exp[Q(E_z,F)]} + \int_{E_z^{\max}}^\infty \mathrm{d}E_z\,\ln\left[1+\exp\left(\frac{E_\mathrm{F}-E_z}{k_\mathrm{B}T}\right)\right]\right\}$$

Calculation of current density at different electric fields

The transmission probability and differential current density for the Schottky–Nordheim barrier. The work function is ϕ = 4.76 eV, the value determined for the (111) copper surface in this work.

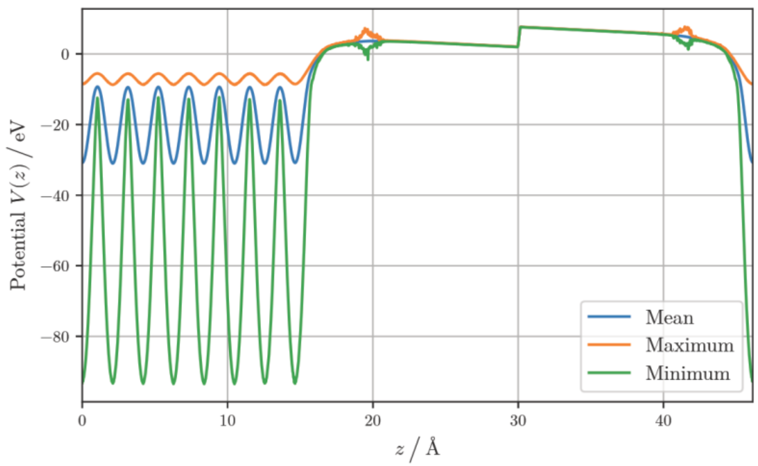


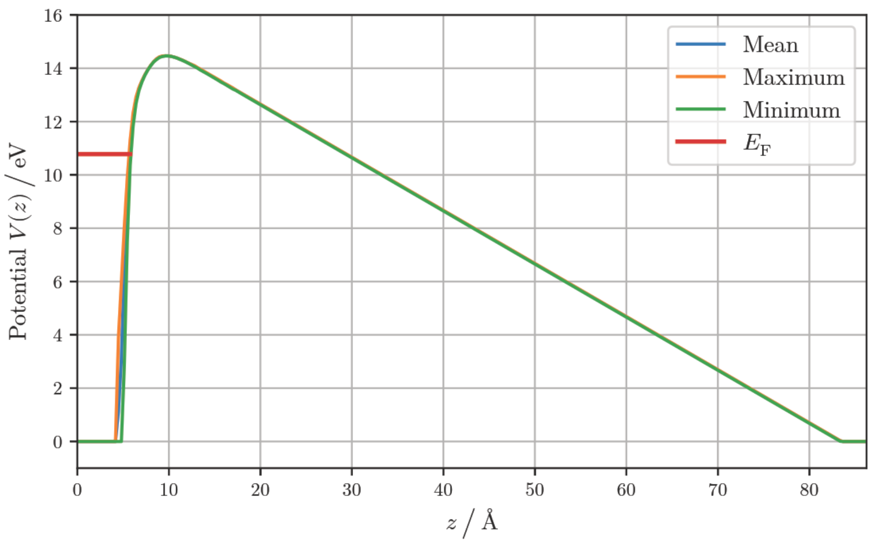


Potential near the flat surface in VASP

Electrostatic potential as it is obtained from VASP calculations cannot be used directly for transmission probability calculations.

Special processing is needed to smoothen the fluctuations and increase the vacuum gap that the potential can naturally drop below 0 eV (Fermi level)





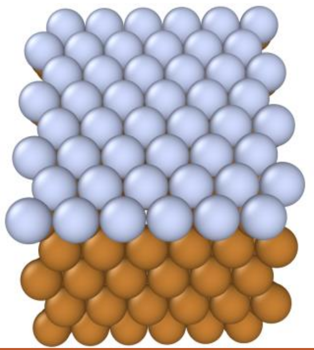
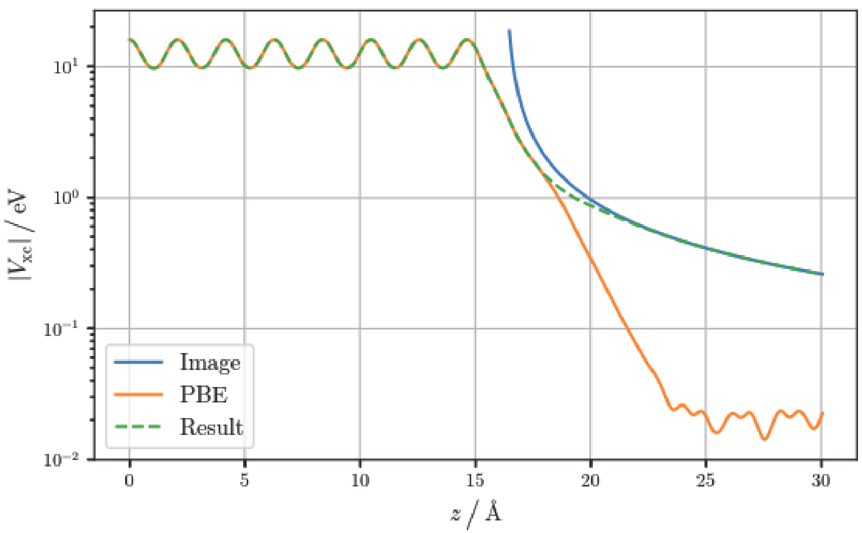


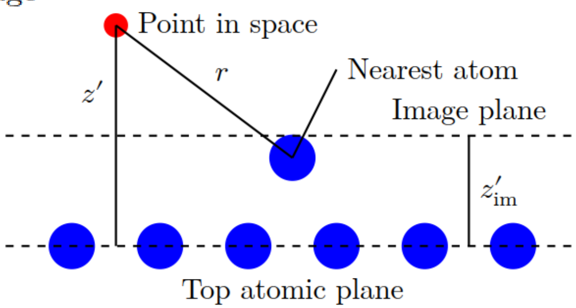
Image potential further away from surface

Both LDA and GGA functionals do not give correct asymptotic form of the potential in the vacuum above a metal surface, vanishing exponentially into the vacuum, since they cannot describe long-range correlation due to their local or semilocal nature.

We merge the existing exchange-correlation functional with the image potential

$$V_{\mathrm{XC}} = f(x)V_{\mathrm{XC}}^{\mathrm{PBE}} + (1 - f(x))V_{\mathrm{XC}}^{\mathrm{Image}}$$

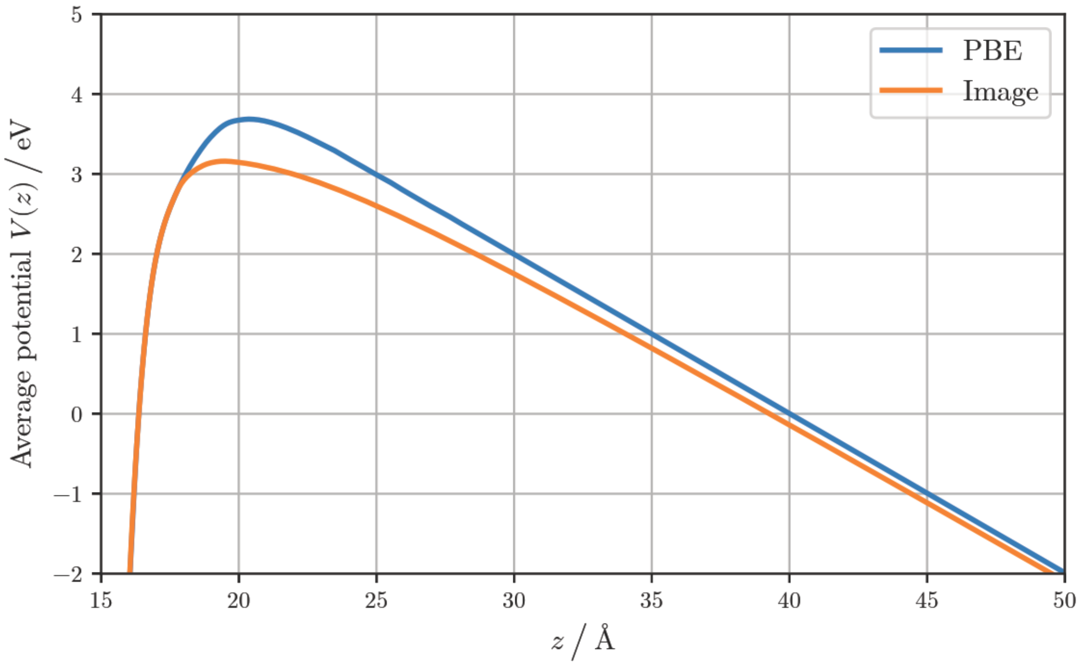




$$f(x) = \begin{cases} 1.0 & x \leq 0 \\ \exp(-x/\lambda_x) + [1 - \exp(-x/\lambda_x)]\exp(-x) & x > 0 \end{cases}$$

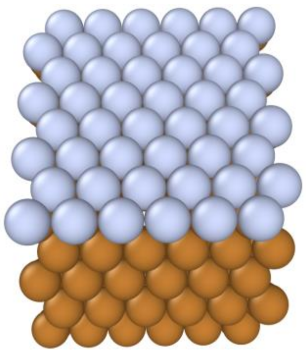
Image potential further away from surface

Final shape of the corrected potential for a system with a clean surface and an applied electric field of 2 GV m−1. The image potential decreases the barrier height by approximately 0.5 eV and makes the barrier slightly thinner. This has the effect of increasing the emitted current by approximately one order of magnitude.



Workfunction at the surface defects in VASP

Clean



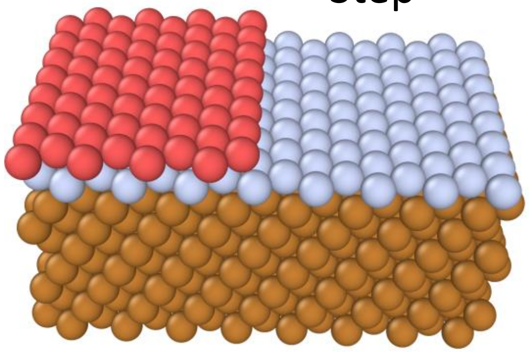
Clean: 4.76 eV (lit. 4.85 eV exp. / 4.78 eV DFT)

Step: 4.66 eV (−0.10 eV)

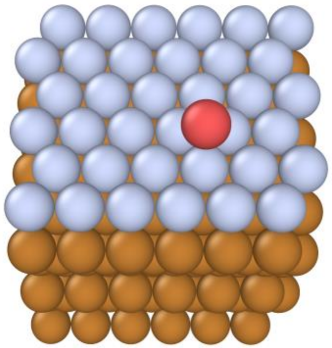
Adatom: 4.44 eV (−0.32 eV)

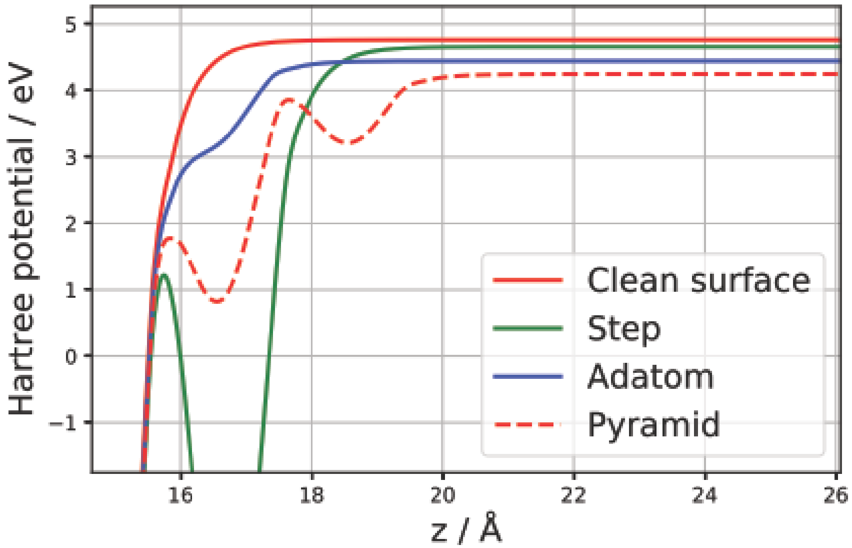
Pyramid: 4.25 eV (−0.51 eV)

Step

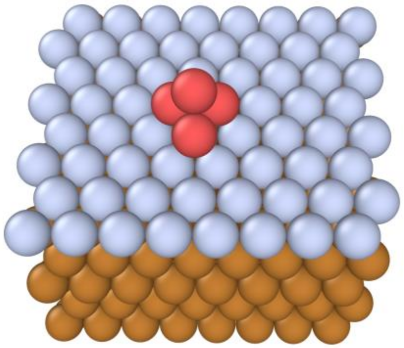


Adatom



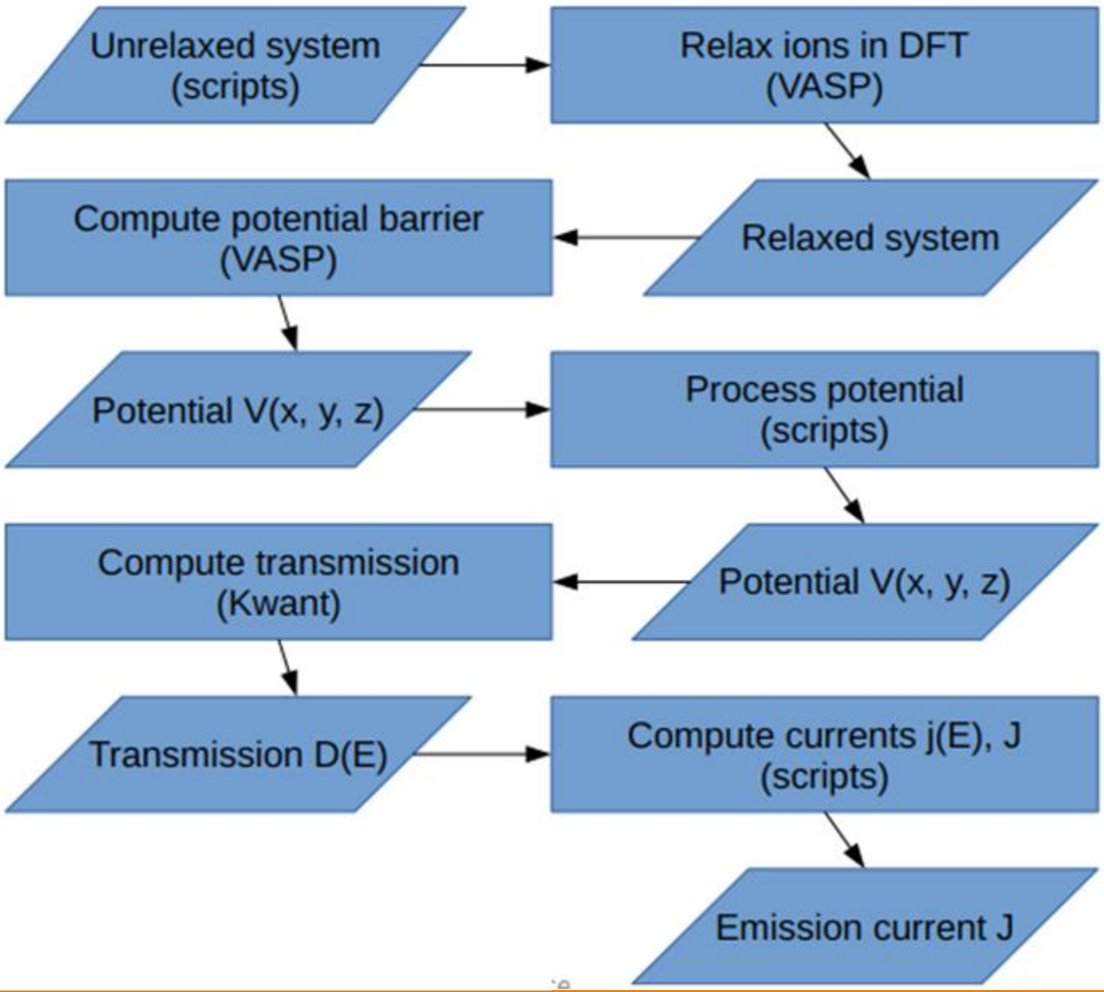


Pyramid



How to compute the emission current

Workflow



Main approximations

Slab model for the DFT calculations

Ad-hoc addition of image potential

- Failure of common PBE exchange-correlation functional
- SA-TPSS with correct behavior not usable

Free electron like density of states

- Isotropic in $\boldsymbol{k}$-space
- Free electron dispersion relation

Approximate wave functions as plane waves for computing transmission probability

Transmission probability only depends on normal energy

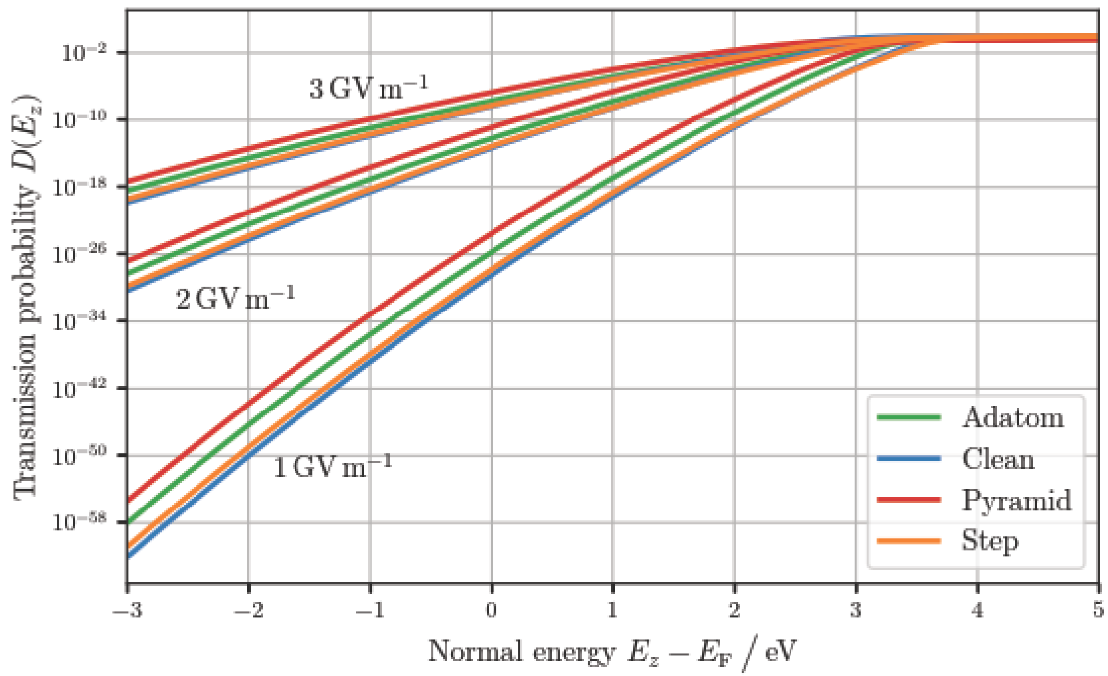
Transmission probability with surface defects

All curves are qualitatively similar

Note that all curves are almost parallel near the Fermi level

Slopes change only of at high energies near the top of the barrier which are irrelevant for field emission (according to the Fermi–Dirac statistics supply function vanishes).

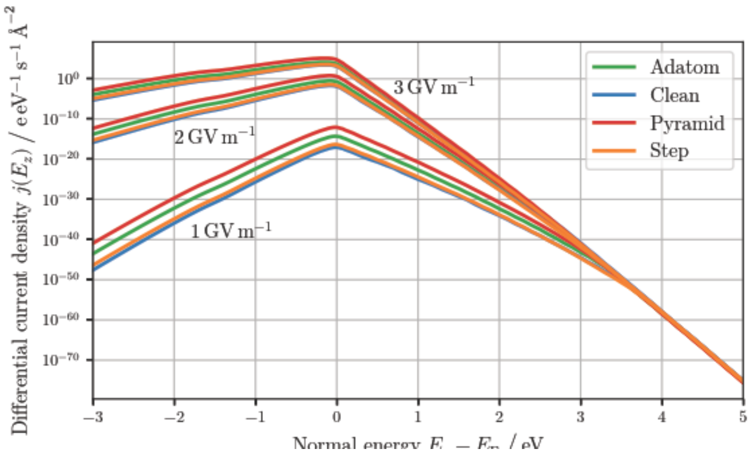
Stronger fields -> flatter curves -> the transmission probability is capped at unity and thus become equally large everywhere



Field emission currents

The total emitted current densities can be computed by integrating the differential current density in the whole energy range.

Field emission electron currents for the different systems and electric fields at zero temperature in e s^{-1} $Å^{-2}$. The results for the Schottky–Nordheim barrier are shown for comparison.



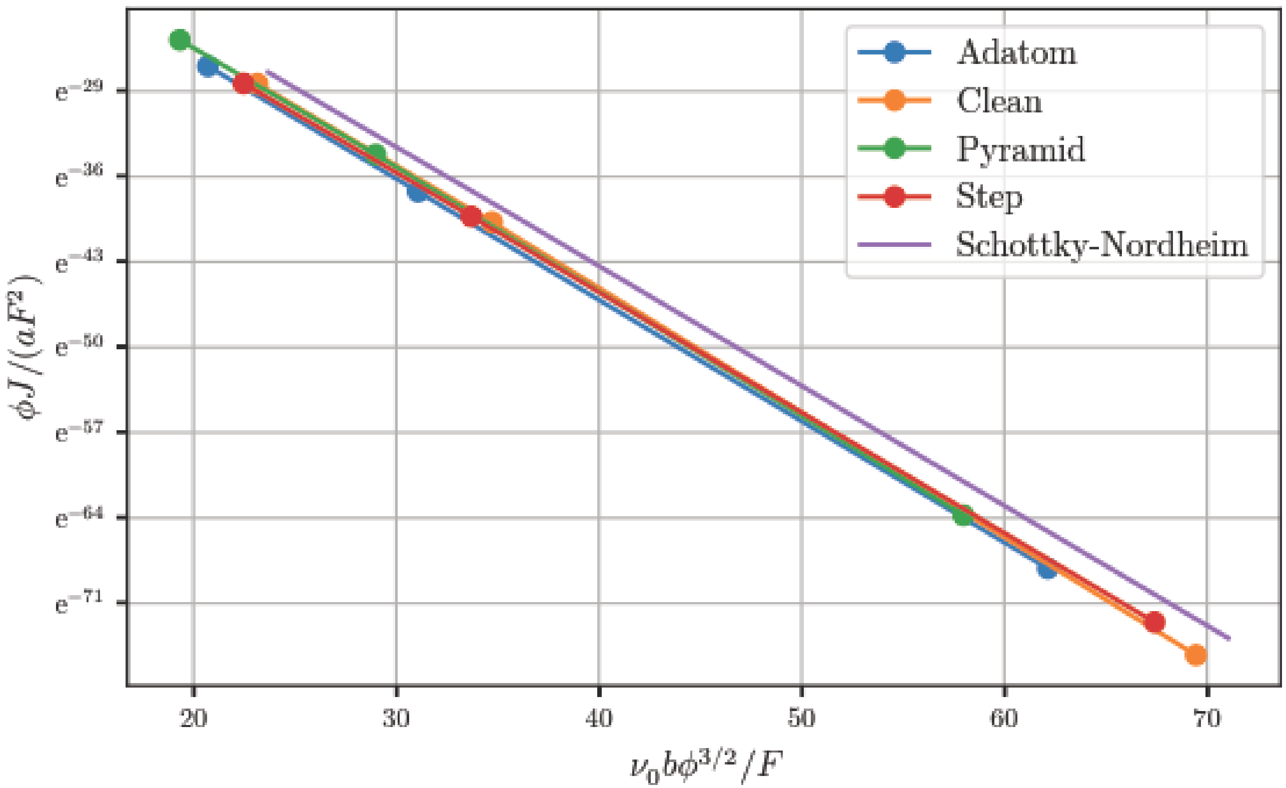
System \ Field	1 GV m^{-1}	2 GV m^{-1}	3 GV m^{-1}
S.–N. barrier	$2.47 \cdot 10^{-18}$	$1.37 \cdot 10^{-2}$	$2.93 \cdot 10^{3}$
Clean surface	$5.46 \cdot 10^{-19}$	$5.76 \cdot 10^{-3}$	$1.10 \cdot 10^{3}$
Step defect	$8.33 \cdot 10^{-18}$	$9.50 \cdot 10^{-3}$	$1.15 \cdot 10^{3}$
Adatom defect	$7.20 \cdot 10^{-16}$	$7.54 \cdot 10^{-2}$	$4.98 \cdot 10^{3}$
Pyramid defect	$5.95 \cdot 10^{-13}$	1.66	$4.45 \cdot 10^{4}$

Fowler-Nordheim plot

Linearized plot of Fowler-Nordheim equation

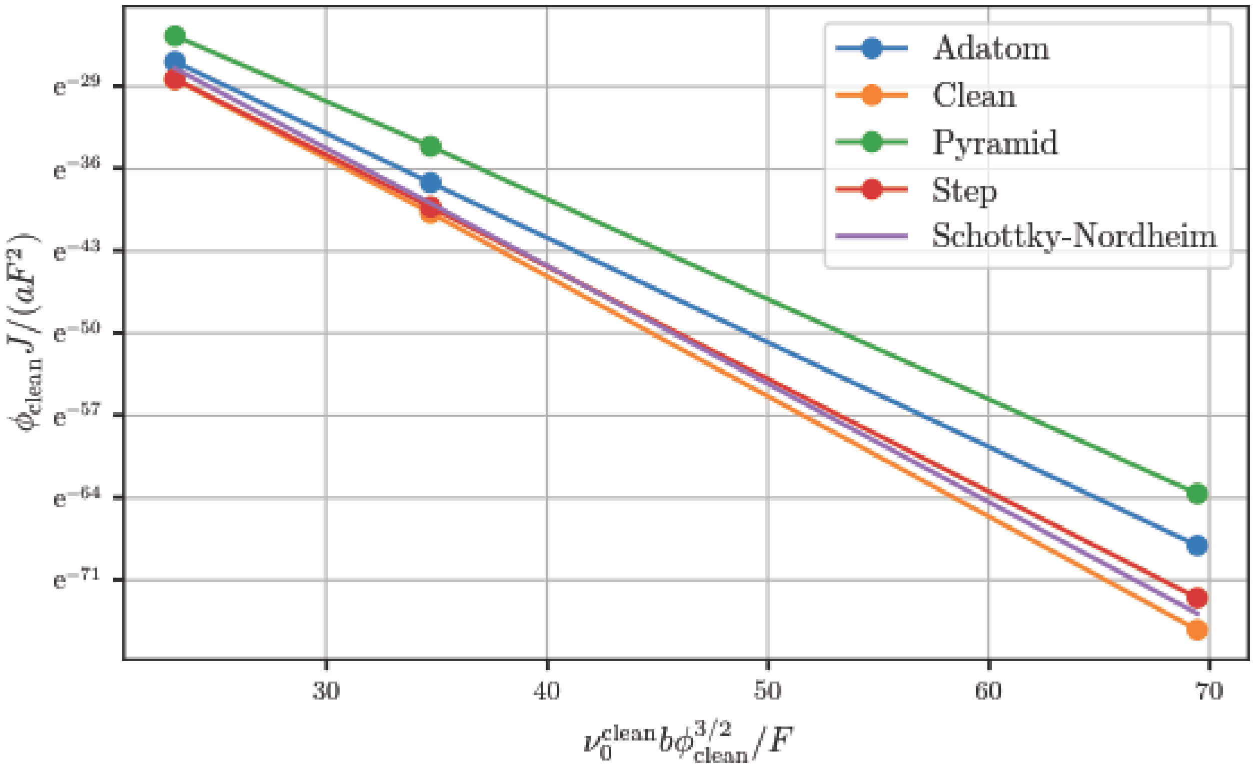
Approximately linear for metal emitters

Parallel lines ⇒ no field enhancement



Apparent geometric field enhancement

The apparent field enhancement factor of the adatom and pyramid defects are now approximately 1.14 and 1.24 respectively.



Summary

Now we have the method to compute:

- Work functions
- Emission currents
- Field enhancement factors

So far we showed:

- Rather moderate work function decrease with defects
- Increased current is due to decreased work function, not field enhancement

Thank you for your attention!