SURFACE GREEN'S-FUNCTION METHOD
LCAO IMPLEMENTATION AND APPLICATIONS TO SURFACE CALCULATIONS

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Abstract: We present an efficient implementation of a surface Green's-function (SGF) method for atomistic modeling of surfaces using density functional theory in a pseudopotential localized basis set approach. Contrary to the traditional slab model for surface calculations, the SGF method couples the surface region to a bulk electron reservoir. The surface is thereby described as a truly semi-infinite system, where charge transfer between the reservoir and the surface region is naturally included. We demonstrate the versatility of the SGF method in several applications to surface physics and chemistry problems that are inherently difficult to properly address with the traditional slab method.

LCAO implementation in the Atomistix ToolKit package

$$\mathbf{H}^{KS} = \begin{pmatrix} \ddots & \vdots & \vdots & \vdots & \vdots \\ \cdots & \mathbf{V}_{BB}^\dagger & \mathbf{H}_B & \mathbf{V}_{BB} & 0 \\ \cdots & 0 & \mathbf{V}_{BB}^\dagger & \mathbf{H}_B & \mathbf{V}_{SB} \\ \cdots & 0 & 0 & \mathbf{V}_{SB}^\dagger & \mathbf{H}_S \end{pmatrix}$$

$$\mathbf{G}_S(\epsilon) = [(\epsilon + i\delta)\mathbf{S}_S - \mathbf{H}_S - \mathbf{\Sigma}(\epsilon)]^{-1}$$

○ The density matrix of the surface region is calculated from the finite Green's-function matrix for the surface region only, which couples the surface electronic structure to the bulk reservoir through the self-energy matrix.

○ Highly efficient implementation based on Green's function methods[1,2,3], similar to two-terminal device calculations with ATK[4]. Scaling with surface region thickness:
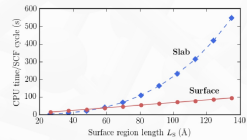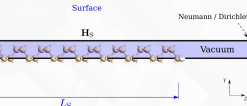- SGF: $O(M^\alpha N)$, $2 < \alpha \leq 3$
- Slab: $O(M^3 N^3)$

Work Functions

○ The work function is the energy required to remove an electron from the Fermi level of a cleaved crystal to the vacuum level.

○ Slab calculations: Slow and oscillatory convergence of predicted work functions with surface thickness.

○ SGF calculations: Fast and reliable work function predictions

Band Alignment in Semiconductor Heterostructures

Charge transfer and penetration of electronic states across the interface.

Figure 6| Valence and conduction band energies of a Ge(001) surface against surface thickness.
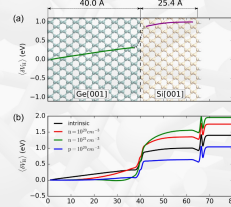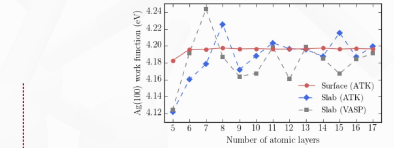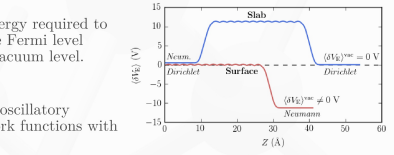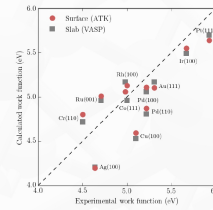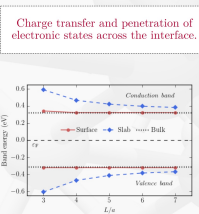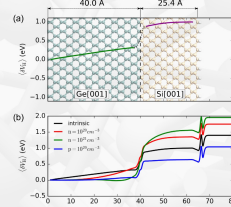
Figure 7| Silicon thin-film on a Ge(001) substrate. Doping the Ge substrate changes the electrostatic potential across the heterostructure.

Doping level cm^{-3}	$Q_{Si} - Q_{p\text{-}Si}$ e/cm^2	Φ_b eV	ΔE_v eV	ΔE_c eV
$p = 10^{20}$	0	0.08	−0.41	−0.63
intrinsic	-0.63×10^{12}	0.34	−0.06	−0.30
$n = 10^{20}$	-2.44×10^{12}	0.39	0.28	0.27
$n = 10^{21}$	-6.70×10^{12}	0.15	0.50	0.27

Table | Band alignment parameters of the Ge(001)|Si interface for the four different doping levels of the Ge(001) sub-strate. $Q_{Si}(Q_{p\text{-}Si})$ is is the induced charge in the (p-doped)Si film, where $Q_{p\text{-}Si}=0.49\times10^{12}$ e/cm^2. Φ_b is the Schottky barrier at the Ge(001)|Si interface. ΔE_v (ΔE_c) is the offset between the Si film and bulk Ge valence (conduction) band minima. Note that the Q_{Si} charge is calculated by integrating the electron difference density over the Si film.
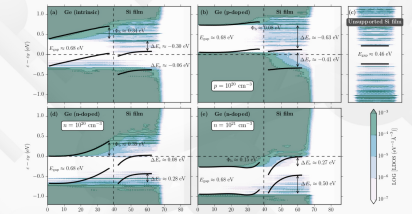

Figure 8| Band diagrams showing the local DOS across the Ge(001)|Si(001) heterostructure for different levels of Ge doping. Black lines indicate the band edges.

Surface States

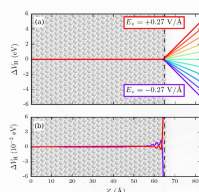### Field-induced Stark shift of the Ag(111) Shockley surface state

Bi2Se3(111) topologically protected surface state

Figure 9| Field-induced pertubations of the Ag(111) surface electronic structure may penetrate down several monolayers.
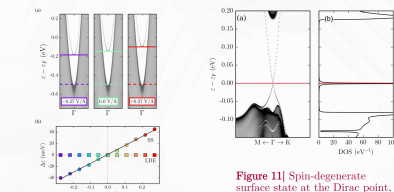
Figure 10| The lowest energy of the surface state (SS) depends linearly on the applied electric field, while the bulk lower band edge (LBE) stays constant.
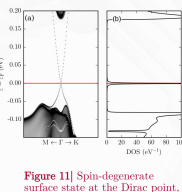
Figure 11| Spin-degenerate surface state at the Dirac point, 170 meV below the surface conduction band minimum.
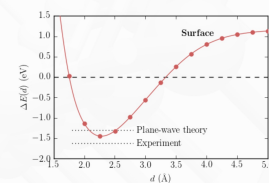
Surface Chemistry in External Electrostatic Fields

Figure 12| Zero-field potential-energy curve for atomic iodine adsorbed on Pt(111), calculated using the SGF method.
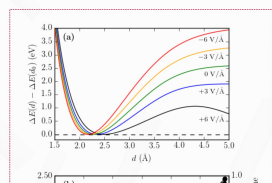
Figure 13| (a) Finite-field PECs given relative to the equilibrium-position energies. (b) Equilibrium I-Pt(111) separation distance (solid line, left y-axis) and Mulliken charge on the iodine atom (dashed line, right axis), both as a function of the applied field. Positive Mulliken charge means accumulation of electrons on the iodine atom.

Summary

○ We have developed a state-of-the-art implementation of the Green's-function formalism for accurate first-principles simulations of surfaces within the framework of density functional theory.

○ This SGF method allows us to model a surface as a truly semi-infinite system by coupling it to an electron reservoir.

○ We have presented several applications of the SGF method to surface science problems that are inherently difficult to properly address with the traditional slab method.

○ The computational cost of the Green's-function based surface calculations scales linearly with the thickness of the surface, and therefore outperforms cubic-scaling slab calculations for large systems.

Given the demonstrated advantages of the SGF method as implemented in Atomistix ToolKit, we expect it will contribute to extending the applicability of first-principles, atomistic modeling towards challenging problems in surface science.

References

[1] M. Brandbyge, J.-L. Mozos, P. Ordejon, J. Taylor, and K. Stokbro, Phys. Rev. B 65, 165401 (2002).
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[3] Daniele Stradi, Umberto Martinez, Anders Blom, Mads Brandbyge, and Kurt Stokbro, Phys. Rev. B 93, 155302 (2016).
[4] Atomistix ToolKit version 2017, QuantumWise A/S (www.quantumwise.com)

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