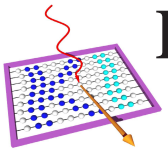

Layer resolved many-body calculations for surfaces of solids

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Introduction

Variational quantum Monte Carlo (VMC) directly includes many-body effects at solid surfaces

- total energy optimization and variational principle
- exact Hamiltonian with full Coulomb interactions
- ab initio nonlocal pseudopotential
- correlated many-particle trial wave function $\Psi=\Psi_S\,\Psi_J$ of *Slater-Jastrow* type for up to 400 electrons
- parameterized localized orbitals in Ψ_S
- confinement term v_{cf} in Ψ_J variationally rules localization to the surface system
- thin film geometry with 8 resp. 12 layers (2x2 supercell, 256 resp. 384 electrons)
- comparison of two surface models of GaAs(110): ideal vs. Duke
- stepwise optimization:
  confinement (V_{cf}, S_{cf})
  dangling bond s-p (ζ_s, ζ_p, γ_p)
  dangling bond angle (ϑ)
- surface ion displacement ("phonon")

Integration

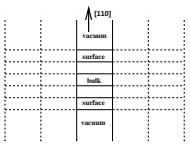
Total energy as expectation value of the Hamiltonian by highdimensional stochastic integration over electronic degrees of freedom $\vec{Y}$
(λ: set of variational parameters)

$$E_\lambda = \frac{\langle\Psi_\lambda|H|\Psi_\lambda\rangle}{\langle\Psi_\lambda|\Psi_\lambda\rangle} = \int \frac{|\Psi_\lambda(\vec{Y})|^2}{\int|\Psi_\lambda(\vec{Y})|^2\,d\vec{Y}}\,\frac{H(\vec{Y})\,\Psi_\lambda(\vec{Y})}{\Psi_\lambda(\vec{Y})}\,d\vec{Y}$$

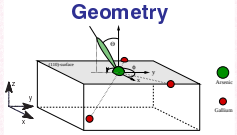
$$\approx \frac{1}{M}\sum_{i=1}^{M}\frac{H(\vec{Y}_i)\,\Psi_\lambda(\vec{Y}_i)}{\Psi_\lambda(\vec{Y}_i)}, \quad \sigma_\lambda(E_\lambda) = \frac{1}{\sqrt{M}}\sqrt{\mathrm{Var}\,\frac{H\Psi_\lambda}{\Psi_\lambda}}$$

Metropolis algorithm for importance sampling of integration points

Boundary conditions of integration: 2D-periodic in the surface plane:

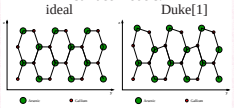


Geometry



surface models:

ideal Duke[1]



Hamiltonian

The Hamiltonian consists of:

+ kinetic energy,

+ nonlocal pseudopotential [2,3] (*Hamann-Schlüter*, d as local)

+ 2D-periodic Coulomb interactions like

$$\sum_{\mathbf{R}_\parallel}\frac{Z_a\,Z_b}{|\mathbf{r}_a-\mathbf{r}_b-\mathbf{R}_\parallel|}$$

evaluated with 2D-*Ewald* summation technique and used per interpolation.

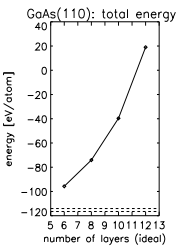
Jellium

Divergent 2D-lattice summations brought to convergence by introducing a neutralizing background charge in each interaction, the sum of which cancels out in the total energy.

Splitting into symmetric part v^s plus dipole part

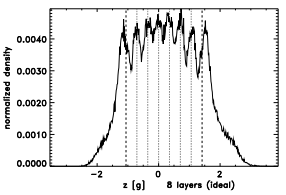
Delocalization & finite size

Pure bulk-derived VMC scheme shows bad finite size behaviour:

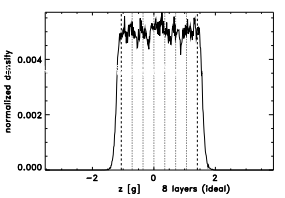


Explanation:

Electrons drift too far into vacuum regions due to repelling effect of the *Jastrow* factor, as shown by the z-resolved density:



Introduction of a confinement factor into the trial wave function leads to better, i.e. energetically more favourable, z-sampling:



Wave function

The many-particle trial wave function Ψ_λ with variational parameters λ consists of two parts:

× The ***Jastrow*** factor accounts for correlation (u, bulk parameter A) and confinement (v_{cf}, parameters V_{cf}, S_{cf}, L_{cf}):

$$\Psi_J(\{\vec{r}_{ij},\sigma_{ij}\},\{z_i\}) = \exp\Big(-\sum_{i<j}u(\vec{r}_{ij},\sigma_{ij})\Big)\times \exp\Big(-\sum_i v_{cf}(z_i)\Big)$$

$$u(\vec{r}_{ij},\sigma_{ij}) = A\Big(\frac{1}{r_{ij}}+v^s(\vec{r}_{ij})\Big)\Big(1-e^{-r_{ij}/F(\sigma_{ij})}\Big)$$

$$v_{cf}(z) = \frac{\epsilon V_c L}{2}\big(\tanh(S_{cf}(z-z^c-\epsilon L_{cf}))+\epsilon\big)$$

The two-particle term exp(-u) decreases when two particles come close to each other leading to a **smoothing** of the electronic density.

The confinement term exp(-v_{cf}) rules the **localization** to the whole surface system.

× The ***Slater*** determinant with parameterized localized orbitals $\phi_{\alpha\mu}$ (linear combination of 4s- and 4p-orbitals of Ga and As; α: As-ion index, μ: tetrahedral direction)

$$\Psi_\lambda(\vec{r}_1\sigma_1\ldots\vec{r}_N\sigma_N) = \Psi_S(\{\vec{r}_i\})\,\Psi_J(\{\vec{r}_{ij},\sigma_{ij}\},\{z_i\})$$

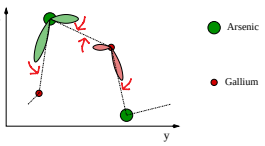
$$\Psi_S(\{\vec{r}_i\}) = \det(\phi_k(\vec{r}_i)) = D^\uparrow D^\downarrow$$

$$\phi_{\alpha\mu}(\vec{r}) = \phi^{\mathrm{As}}_{\alpha\mu}(\vec{r}) + \beta\,\phi^{\mathrm{Ga}}_{\alpha\mu}(\vec{r})$$

$$\phi^{\mathrm{DB}}_{\alpha\mu}(\vec{r}) = \phi^{\mathrm{As}}_s(|\vec{r}-\vec{R}^{\mathrm{As}}_\alpha|/\zeta_s) + \gamma_p\sum_{i=x,y,z}\tau^i_{\alpha\mu}(\vartheta,\phi)\,\phi^{\mathrm{As}}_{p_i}(|\vec{r}-\vec{R}^{\mathrm{As}}_\alpha|/\zeta_p)$$

Surface specific parameters are:
ζ_s, ζ_p (contraction), γ_p (s-p-weight), ϑ (polar angle) in the dangling bond orbital.

The other p-orbital coefficients $\tau_{\alpha\mu}$ are adjusted automatically to relaxation:

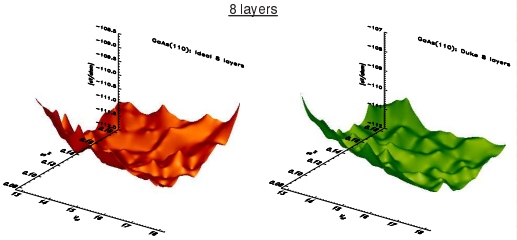


Confinement optimization

Total energy vs. confinement parameters V_{cf}, S_{cf} for GaAs (110)

ideal surface — Duke surface

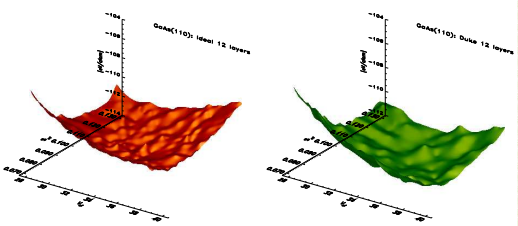
8 layers



$E_{8,i}$ = -111.46 eV/atom @ (V_{cf}|S_{cf})=(15.3|0.139)

$E_{8,d}$ = -111.59 eV/atom @ (V_{cf}|S_{cf})=(16.6|0.138)

12 layers



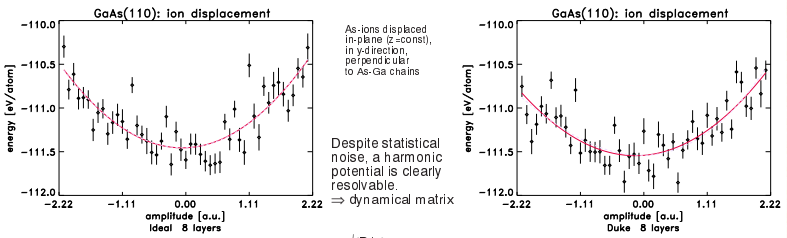
$E_{12,i}$ = -111.82 eV/atom @ (V_{cf}|S_{cf})=(32.7|0.103)

$E_{12,d}$ = -111.80 eV/atom @ (V_{cf}|S_{cf})=(34.5|0.103)

"Phonons"

Test case: sensitivity to relaxation of surface ions?

ideal, 8 layers — Duke, 8 layers



As-ions displaced in-plane (z=const), in y-direction, perpendicular to As-Ga chains

Despite statistical noise, a harmonic potential is clearly resolvable.
⇒ dynamical matrix

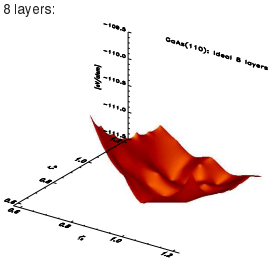
D = 6.64 eV/(a_0)^2 → ω = 37.0 meV ∗(1±0.09)

ω = √(D/μ)
μ = √(m_{As}·m_{Ga})

D = 5.80 eV/(a_0)^2 → ω = 34.6 meV ∗(1±0.09)

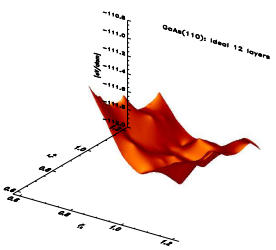
Dangling bond: contraction

8 layers:



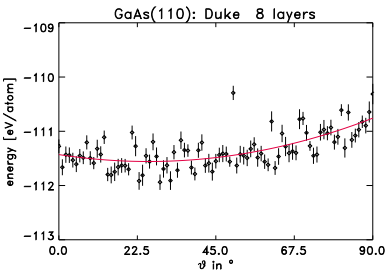
$E_{8,i}$ = -111.51 eV/atom @ (ζ_s|ζ_p)=(0.99|1.04)

12 layers:



$E_{12,i}$ = -111.81 eV/atom @ (ζ_s|ζ_p)=(0.97|1.15)

Dangling bond: angle



$E_{8,d}$ = -111.55 eV/atom @ ϑ=26°

Summary

! Bulk-derived VMC scheme shows poor finite size behaviour

! New confinement term gives much deeper total energy and better finite size behaviour

! Dangling bond properties resolvable

! Significant differences between Duke surface and ideal surface

! Surface ion relaxation shows harmonic dependence

Outlook

! Full optimization and finite size analysis

! Determination of pair correlation function

! New information about exchange-correlation functional

References

[1] C.B. Duke, S.L. Richardson, A. Paton, A. Kahn: *Surf. Sci.* **127**, L135 (1983).

[2] S. Fahy, X.W. Wang, S.G. Louie: *Phys. Rev. B* **42**, 3503 (1990).

[3] H. Eckstein, W. Schattke, M. Reigrotzki, R. Redmer: *Phys. Rev. B* **54**, 5512 (1996).

[4] R. Bahnsen, H. Eckstein, W. Schattke, N. Fitzer, R. Redmer: *Phys. Rev. B (2001) in press, scheduled for 15. Mai 2001.*

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