Variational quantum Monte Carlo (VMC) for real inhomogeneous systems

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outline
introduction to VMC

simulation of a solid surface:
random walk, Hamiltonian, wave function
results for Duke model of GaAs(110)

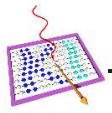
simulation of phonons (bulk/surface): first results

Electronic structure and dynamics

- quantum effects in experimental systems and devices
- increasing resolution of experiments
- indirect approach of other theoretical methods in a single particle picture (LDA,GGA,HF,CI,GW)
- Quantum Monte Carlo as reference method for:
  atoms
  homogeneous electron gas
  solids: H, Li, N; C, Si, Ge, GaAs
- microscopical understanding of electronic and dynamical properties in real inhomogeneous systems

$\Longrightarrow$ application of Variational quantum Monte Carlo to solid surfaces and phonons

GaAs(110) as prototype of a solid surface
optical phonons in long wavelength limit



VMC

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

λ: set of variational parameters in Ψ_λ

random walk: Importance sampling, Metropolis

$$\vec{Y}_i := (\vec{r}_1\sigma_1, \ldots, \vec{r}_N\sigma_N) \quad \vec{Y}_i{}' = \vec{Y}_i + \delta\vec{Y}_i \text{ (random)}$$

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

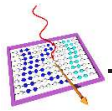
statistical mean and variance: purely statistical error

variational principle for ground states: $E_0 \leq \min(E_\lambda) =: E^*_\lambda$

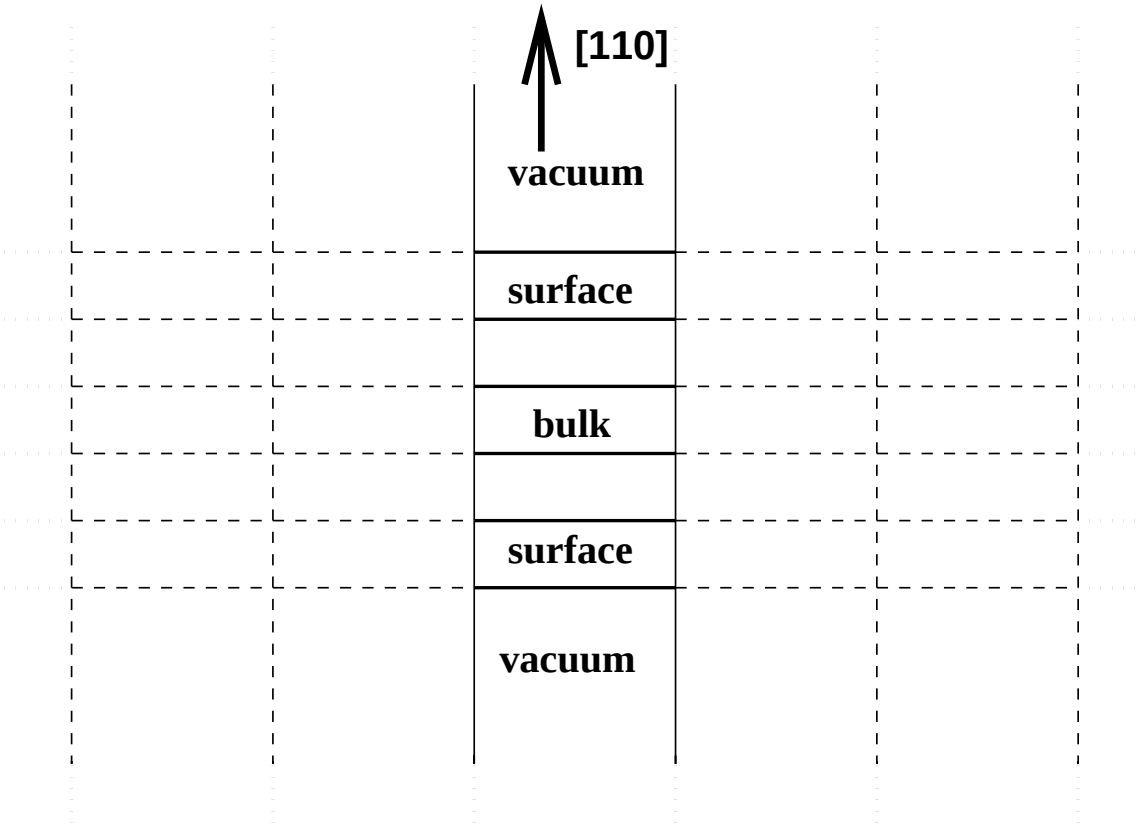
weighted least square fit of energy E as quadratic form in λ

boundary conditions:

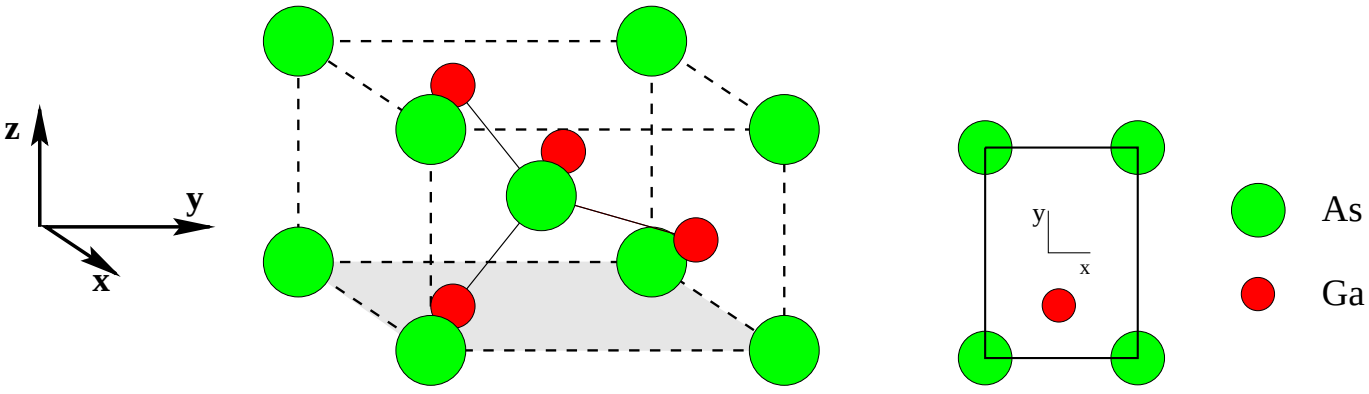
+ normalizibality for atomic systems: $\int_{-\infty}^{\infty} d^3r$
+ periodic boundary conditions for solids: $\int_\Omega d^3r$
+ finite layer geometry for solid surfaces: $\int_{-\infty}^{\infty} dz \int_{\Omega_s} d^2r_\parallel$

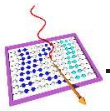


Geometry

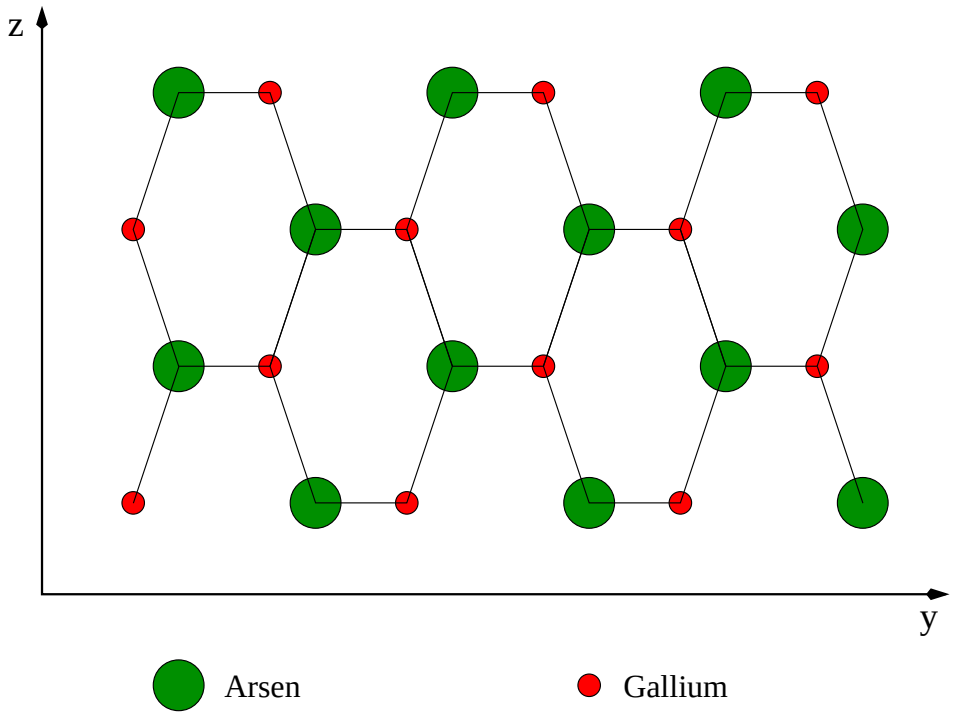


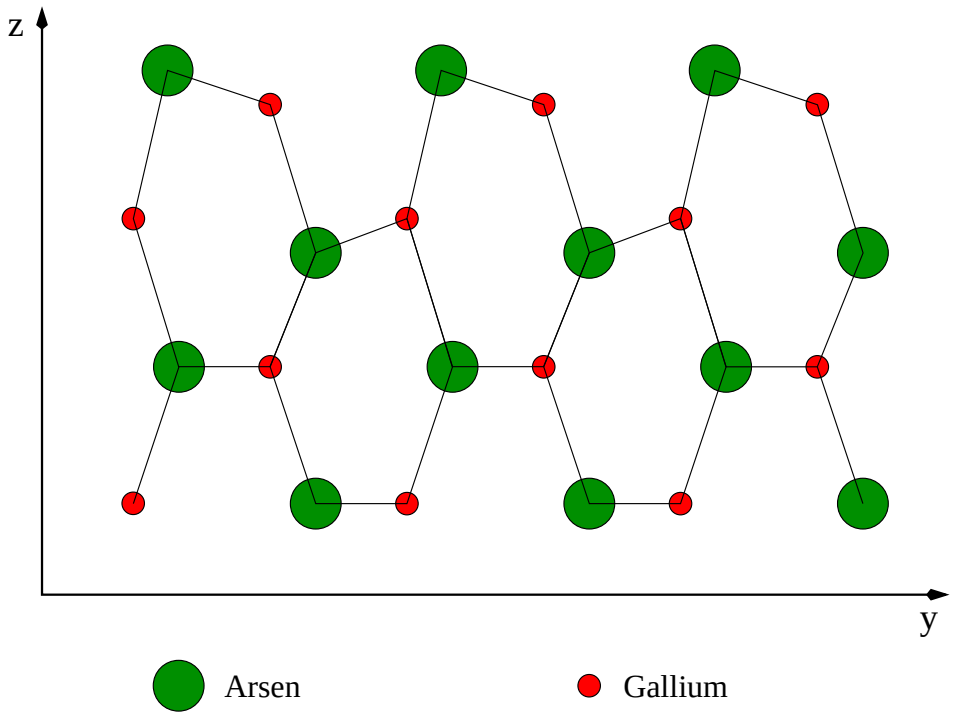
GaAs (110)

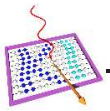




Ideal and Duke GaAs(110)







VMC for solid surfaces

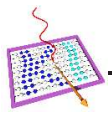
- simulation cell with finite number N of particles
- Born-Oppenheimer approximation
- inner shells replaced by nonlocal pseudopotential
  $\longrightarrow\ N = 200 - 1000$
- full interacting Hamiltonian for valence electrons

$$\hat{H} = \hat{T} + \hat{V}^{\mathrm{l}}_{PP} + \hat{V}^{\mathrm{nl}}_{PP} + \hat{V}_{ee} + \hat{V}_{ei} + E_{ii}$$

- 2D Ewald method for Coulomb interaction
- fixed Jellium leads to exact cancellation of Jellium contributions in total energy
- correlated many-particle trial wave function Ψ_N of Slater-Jastrow type with 7 variational surface parameters λ_i:

$$\Psi_N[\lambda] = \Psi_S[\lambda_1 \ldots \lambda_4] \times \Psi_J[\lambda_5 \ldots \lambda_7]$$

- stepwise optimization of energy
- diamagnetic ground state, fixed spins



Wave function

$$\Psi(\vec{r}_1\sigma_1 \ldots \vec{r}_{\rm N}\sigma_{\rm N}) = \Psi_S(\{\vec{r}_i\}) \times \Psi_J(\{\vec{r}_{ij}, \sigma_{ij}\}, \{z_i\})$$

Slater determinant

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

α: As-ion index

μ: bond direction

dangling bond orbital

$$\begin{aligned}\phi^{\rm DB}_{\alpha\mu}(\vec{r}) &= \gamma^{\rm As}\phi^{\rm As}_s([\vec{r} - \vec{R}^{\rm As}_\alpha]/\zeta_s) \\ &+ \gamma_{\rm p} \sum_{{\rm i}=x,y,z} \tau^{\rm i}_{\alpha\mu}(\theta)\ \phi^{\rm As}_{p_{\rm i}}([\vec{r} - \vec{R}^{\rm As}_\alpha]/\zeta_p)\end{aligned}$$

Jastrow factor

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

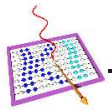
$$v_{cf}(z) = \frac{\epsilon V_{cf}}{2}\left[\tanh\left(S_{cf}(z - z^\epsilon - \epsilon L_{cf})\right) + \epsilon\right]$$

ϵ =sign(z)

z^ϵ: slab borders

$$u(\vec{r}, \sigma) = A\, v_{2D}(\vec{r})\ \left(1 - e^{-r/F(\sigma)}\right)$$

v_{2D}: 2D Ewald potential



Ewald's method in 2D

$$v_{2D}(\vec{r}) =$$

$$\sum_{\vec{R}_\parallel^i} \left(\frac{1}{|\vec{r} - \vec{R}_\parallel^i|} - \frac{1}{z_0 \cdot \Omega_0^s} \int_{-\frac{z_0}{2}}^{+\frac{z_0}{2}} \int_{\Omega_0^s} \frac{-1}{|\vec{r} - \vec{R}_\parallel^i - \vec{R}|} \, d\vec{R}_\parallel dR_z \right)$$

aim: evaluate $v_{2D}(\vec{r})$ fast and accurately

$\longrightarrow$ Ewald's method in 2D:

transform long ranged parts of $v_{2D}(\vec{r})$ into Fourier space

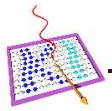
$$\sum_{\vec{R}_\parallel^i} f(\vec{R}_\parallel^i) \equiv \sum_{\vec{R}_\parallel^i} g(\vec{R}_\parallel^i, \alpha) + \sum_{\vec{G}_\parallel} h(\vec{G}_\parallel, \alpha) \quad \forall \alpha$$

result: $v_{2D}(\vec{r}) =$

$$\sum_{\vec{R}_\parallel^i} \left(\frac{1}{|\vec{r} - \vec{R}_\parallel^i|} - \frac{1}{|\vec{r} + \alpha \, \mathrm{sign}(z) \, \vec{e}_z - \vec{R}_\parallel^i|} \right) +$$

$$+ \frac{2\pi}{\Omega_0^s} \sum_{\vec{G}_\parallel \neq 0} \frac{\exp\left(i \, \vec{G}_\parallel \cdot \vec{r}_\parallel - |\vec{G}_\parallel| (|z| + \alpha) \right)}{|\vec{G}_\parallel|} +$$

$$+ \frac{2\pi}{\Omega_0^s} \begin{cases} -\alpha & : \quad z \notin [-\frac{z_0}{2}, +\frac{z_0}{2}] \\ -\alpha - |z| + \frac{1}{z_0} \left(\left(\frac{z_0}{2}\right)^2 + z^2 \right) & : \quad z \in [-\frac{z_0}{2}, +\frac{z_0}{2}]. \end{cases}$$



Hamiltonian

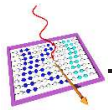
$i = 1 \ldots \mathrm{N}$: electrons
$\alpha = 1 \ldots \mathrm{NK}$: ions

$$\begin{aligned} \hat{T} &= -\frac{1}{2}\sum_i \Delta_i \\ \hat{V} &= \hat{V}^{\mathrm{l}}_{PP} + \hat{V}^{\mathrm{nl}}_{PP} + \hat{V}_c \end{aligned}$$

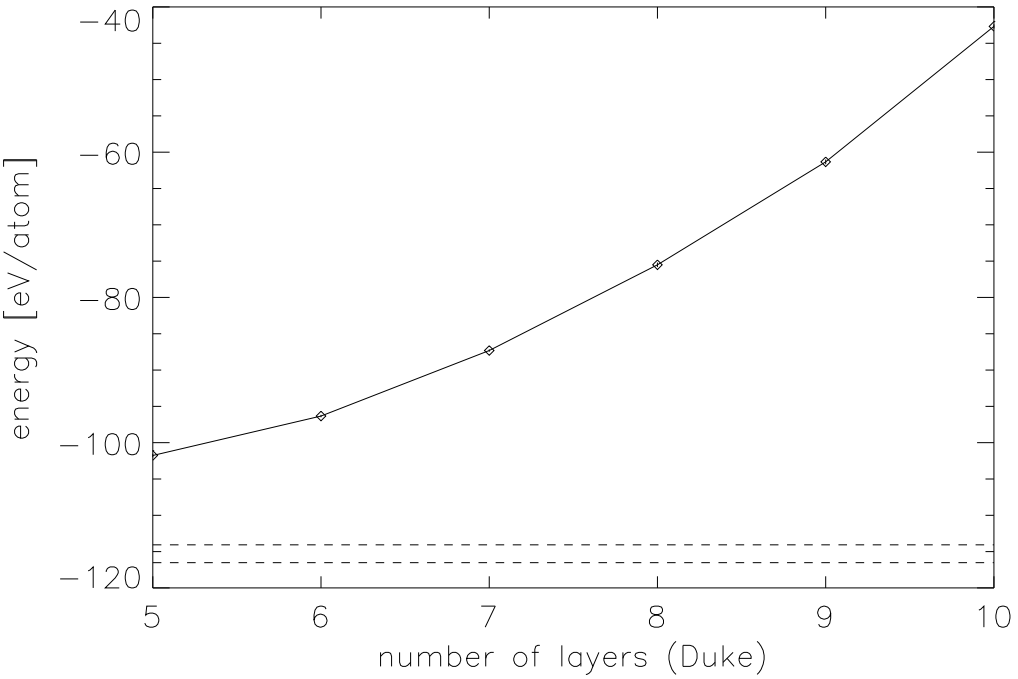
$$\hat{V}^{\mathrm{nl}}_{PP} = \sum_{\alpha,i}\sum_{l} V_{\alpha,l}(r_{\alpha i}) \frac{Y_{l0}(0,0)\int_{r'=r_{\alpha i}} Y^*_{l0}(\Omega_{r'})\,\psi(\ldots,\vec{r}_i=\vec{r}',\ldots)\,d\Omega_{r'}}{\psi(\ldots,\vec{r}_i,\ldots)}$$

$$\begin{aligned} \hat{V}_c &= \hat{V}_{ee} + \hat{V}_{ei} + E_{ii} \\ &= \frac{1}{2}\sum_{i\neq j} v_{2D}(\vec{r}_{ij}) - \sum_{i,\alpha} Z_\alpha\, v_{2D}(\vec{r}_{i\alpha}) + \\ &\quad + \frac{1}{2}\sum_{\alpha\neq\alpha'} Z_\alpha Z_{\alpha'}\, v_{2D}(\vec{r}_{\alpha\alpha'}) + \\ &\quad + V_{fJ}(\{z_.,z'_.\}) \end{aligned}$$

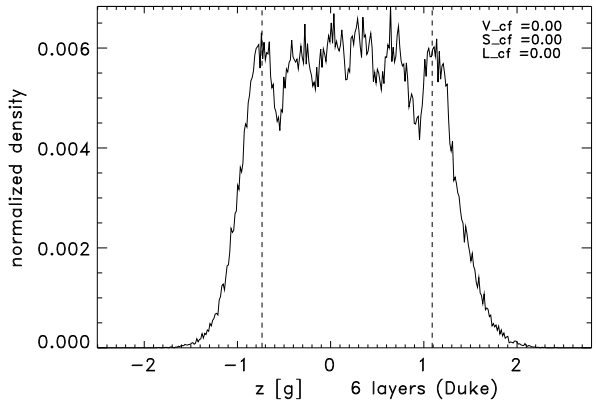
dipol-like contribution due to fixed Jellium

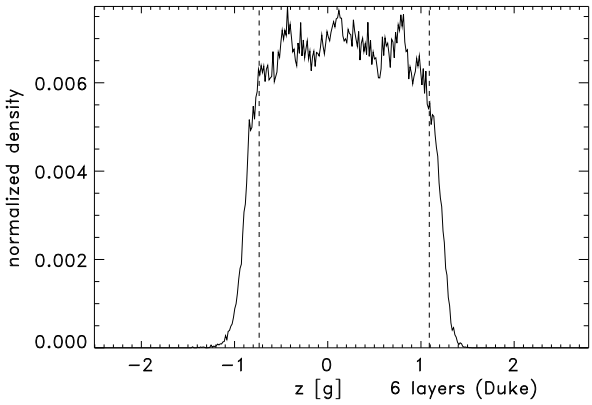


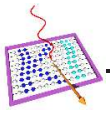
Finite size asymptotics of E



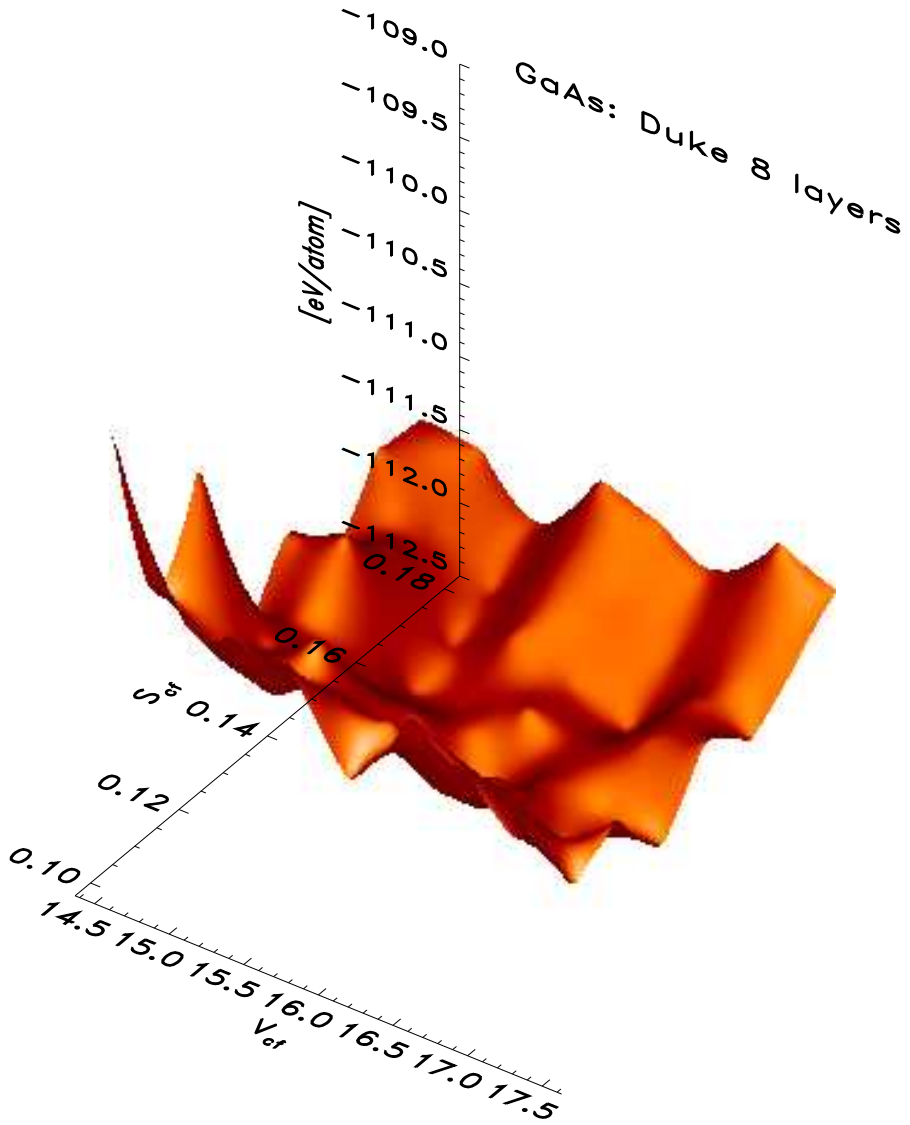
z-sampling





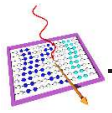


Confinement

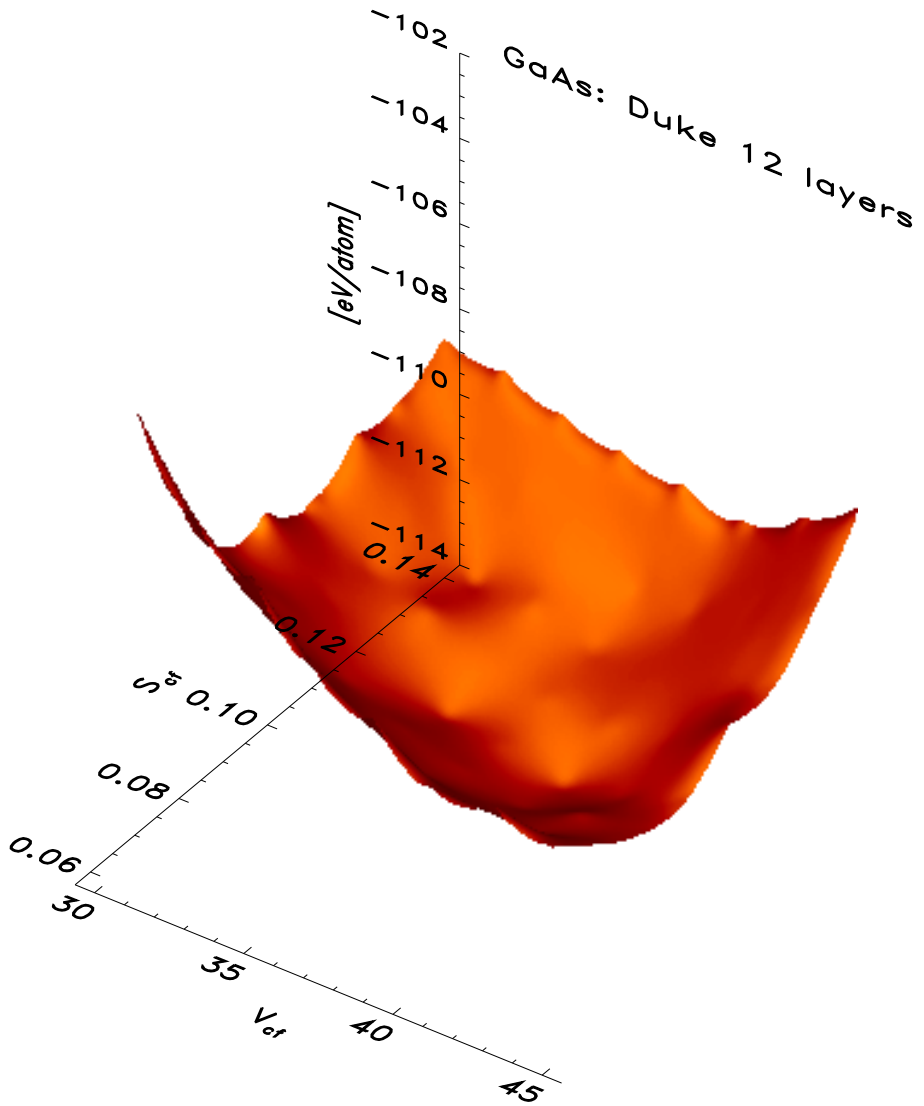


$$E = -111.7 \text{ eV/atom} \ @ \ (16.4|0.139|3.0)$$

8 layers

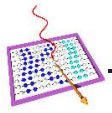


Confinement

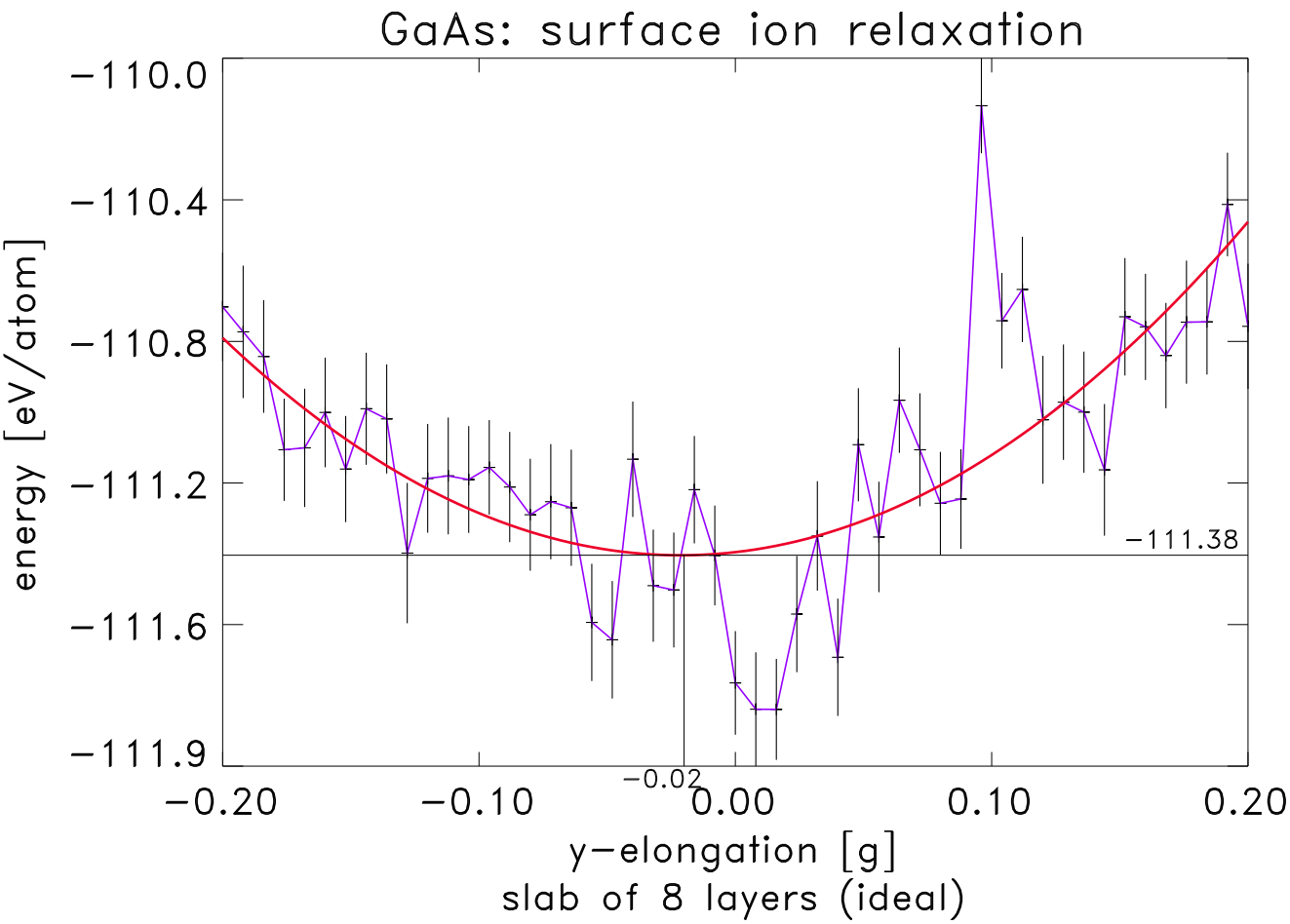


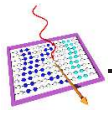
$$E = -111.8 \text{ eV/atom} \ @ \ (39.9|0.099|4.3)$$

12 layers



Surface "phonons"

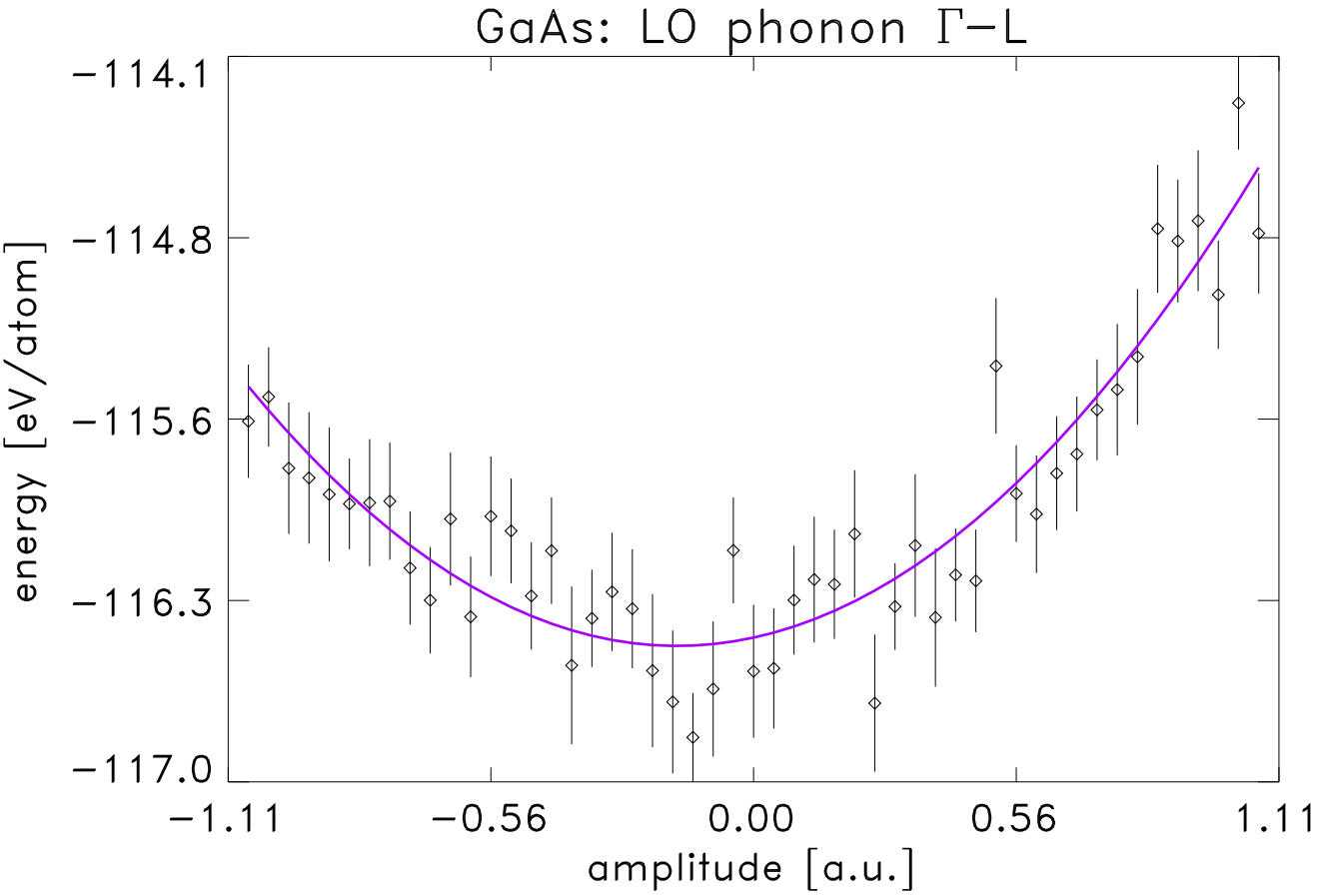




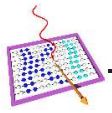
Bulk LO phonons

curvature $\rightarrow$ dynamical matrix $\rightarrow$ phonon frequencies $\omega_\lambda(\vec{q})$

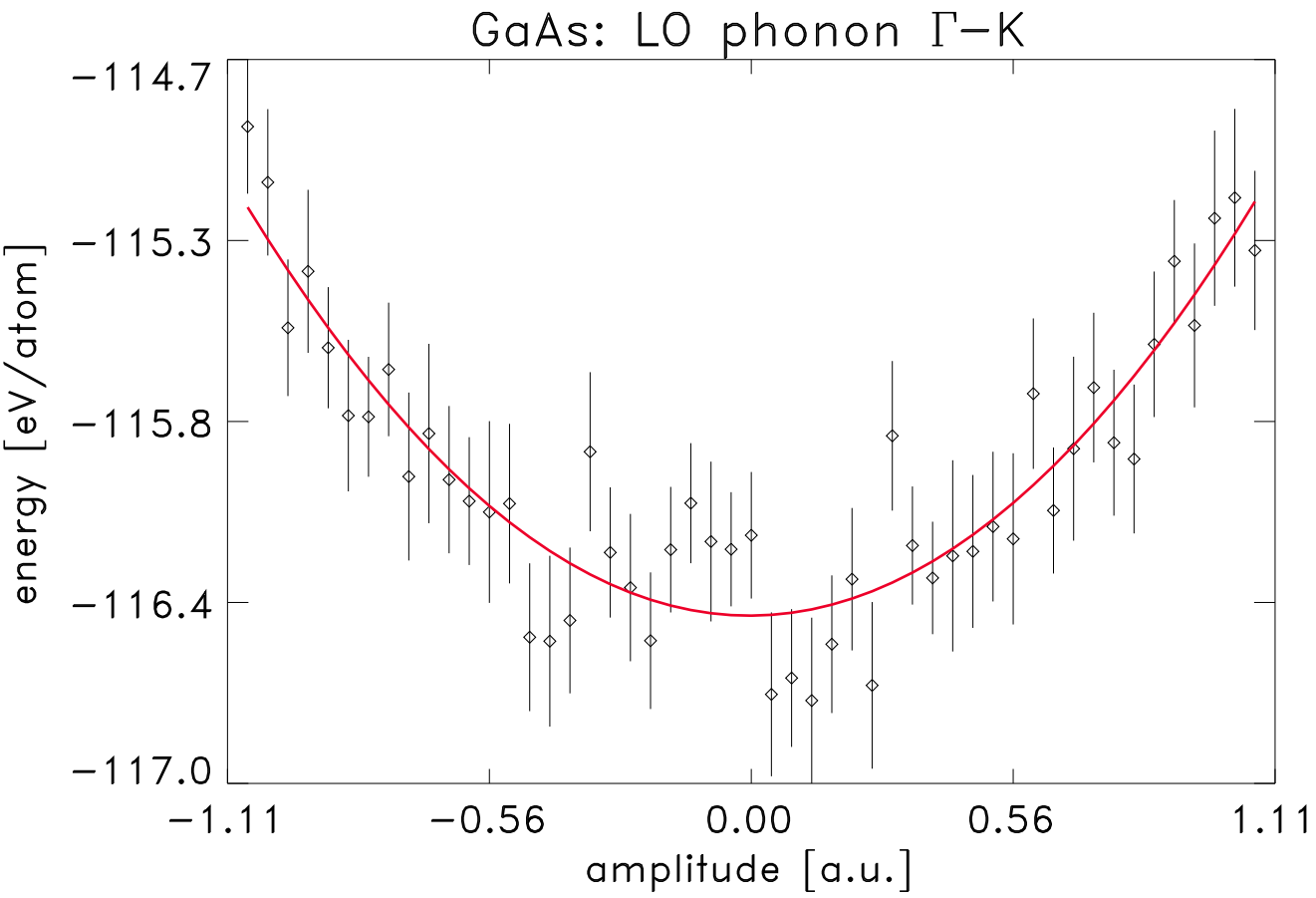
supercell approach, long wavelength limit $q \rightarrow 0$



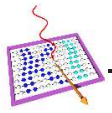
$$\omega_{LO} = 45.53 * (1 \pm 0.07)\text{meV}$$



Bulk LO phonons

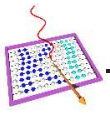


$$\omega_{LO} = 43.44 * (1 \pm 0.07)\text{meV}$$



Summary

- stochastic integration of many-body Hamiltonian
- boundary conditions and Ewald's method in 2D
- compensation of "Jastrow pressure" by confinement term
- determine elements of dynamical matrix within 5 meV

outlook

- surface wave function $\Psi_N = \ldots$
- pair correlation function $\rightarrow$ $E_{xc}[n]$
- excited states
- electron phonon coupling