Variational quantum Monte Carlo for solid surfaces

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motivation

- increasing resolution of experiments
- many-body effects in real materials
- indirect approach of other 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; Si, Ge, GaAs
- microscopical understanding of solid surfaces by comparison of theory and experiment

$\Longrightarrow$ application of QMC for solid surfaces

GaAs (110) as prototype for semiconductor surfaces

single particle formulations

- exact many-particle Schrödinger equation
  $H\Psi(1..N) = E\Psi(1..N)$ with Hamiltonian

$$H = -\frac{1}{2}\sum_{i=1}^{N}\Delta_i + V_{nn} + \sum_{i=1}^{N} V_{ne}(\vec{r}_i) + \frac{1}{2}\sum_{i\neq j=1}^{N} V_{ee}(\vec{r}_{ij})$$

  but: eigenvalue problem too difficult for $N > 1$

- approximations: LDA , GGA
  but: a posteriori justification

- Hartree-Fock (HF):
  H exact, $\Psi_S = \det(\phi_i(\vec{r}_j))$

- Configuration Interaction (CI):
  H exact, $\Psi = \sum_k \alpha_k \Psi_{S,k}$

- selfenergy-GW

QMC in general

$$\frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \int \frac{|\Psi|^2}{\int|\Psi|^2}\frac{H\Psi}{\Psi} \approx \frac{1}{M}\sum_{i=1}^{M}\frac{H(\vec{Y}_i)\Psi(\vec{Y}_i)}{\Psi(\vec{Y}_i)}$$

random walk

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

One electron coordinate is changed per step.

$$E = \frac{1}{M}\sum_{i=1}^{M}\frac{H(\vec{Y}_i)\Psi(\vec{Y}_i)}{\Psi(\vec{Y}_i)}, \qquad \sigma(E) = \frac{1}{\sqrt{M}}\sqrt{\mathrm{Var}\left(\frac{H\Psi}{\Psi}\right)}$$

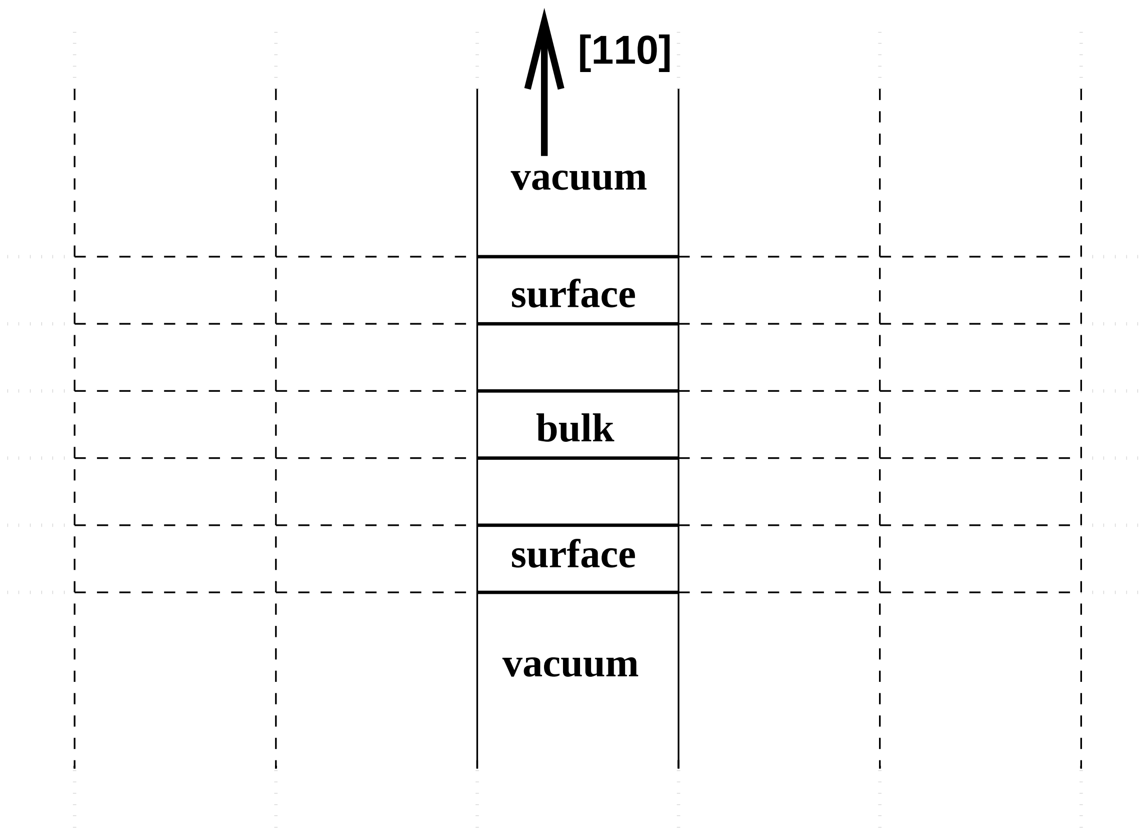
statistical mean and variance: purely statistical error

variational ansatz for Ψ $\quad\rightarrow\quad$ $\dfrac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \mathbf{min!}$ $\quad$ (Ritz)

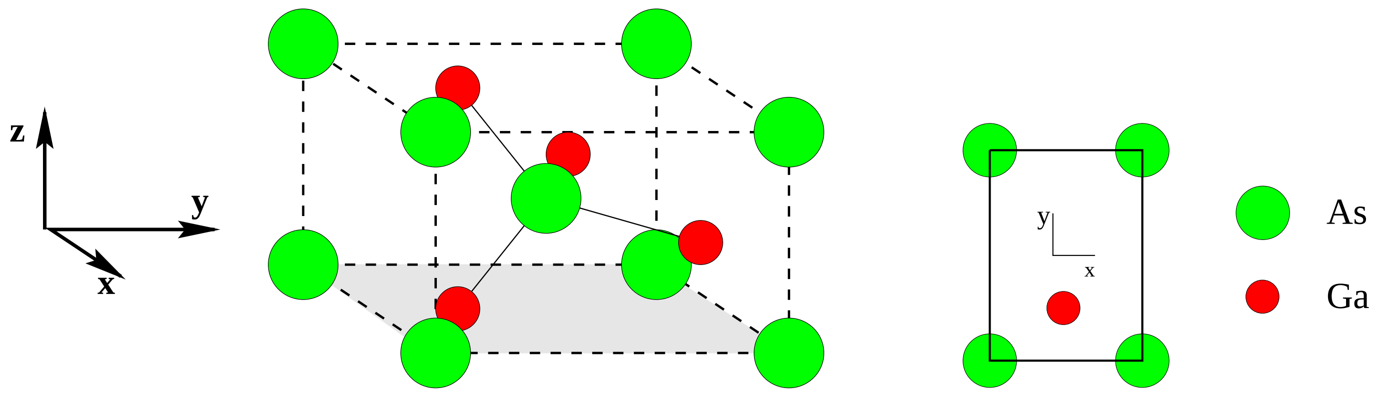
boundary conditions:

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

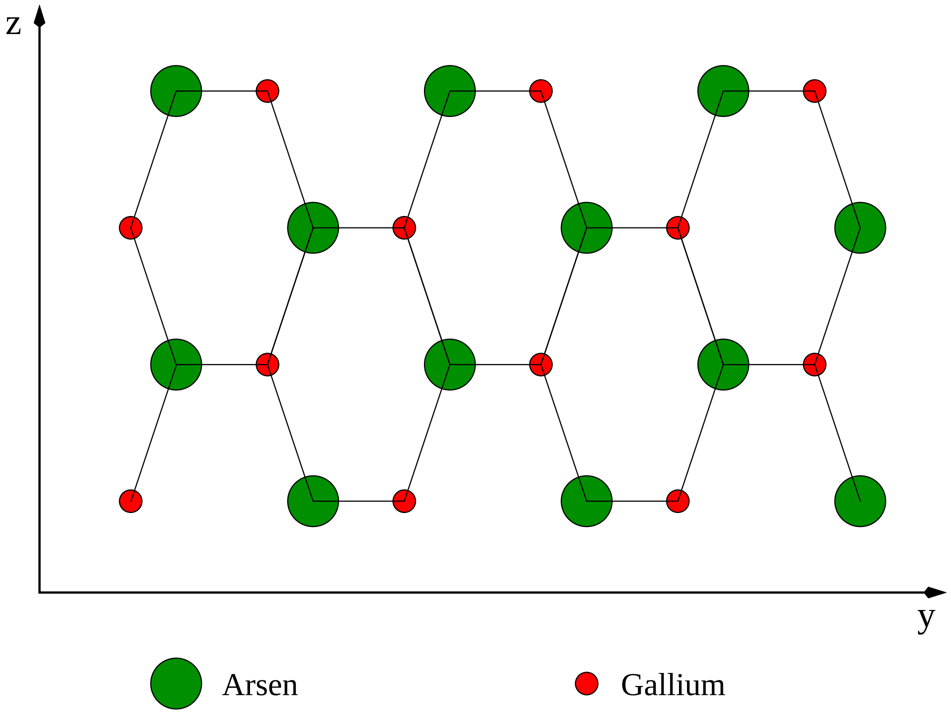
geometry

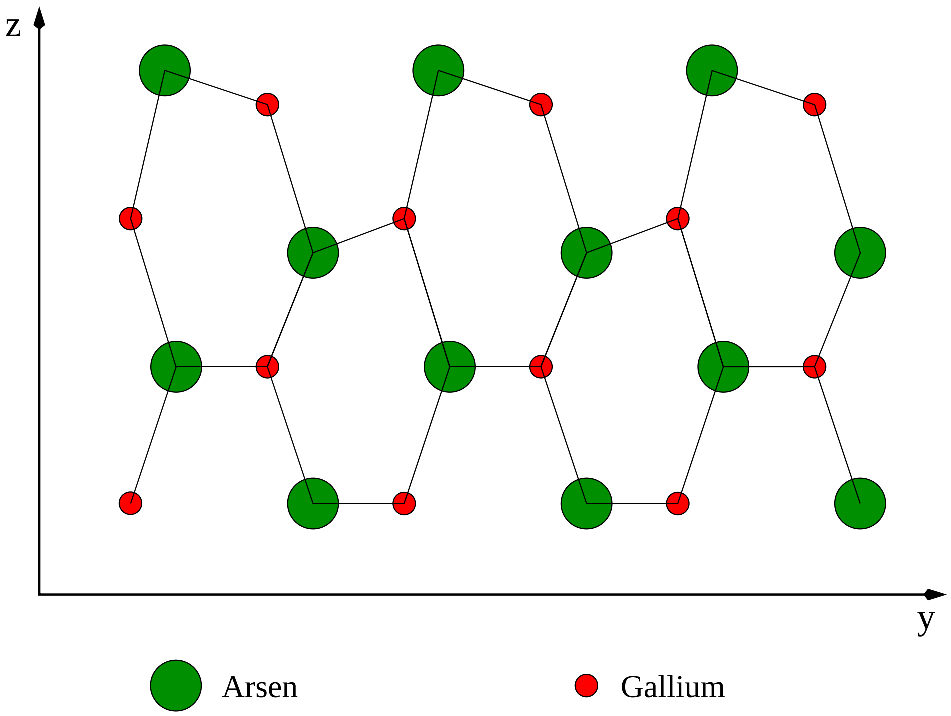


GaAs (110)



ideal (110) surface and Duke model





QMC for solid surfaces

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

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

- correlated many-particle trial wave function Ψ_N of Slater-Jastrow type with 7 variational surface parameters λ_i:

$$\Psi_N[\lambda] = \Psi_S[\lambda_1 \ldots \lambda_4] \times \Psi_J^{cf}[\lambda_5 \ldots \lambda_7]$$

- diamagnetic ground state, fixed spins
- T $= 0$
  minimum energy principle for the ground state

Wave function

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

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

α: As-ion index
μ: bond direction

dangling bond orbital

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

Jastrow factor

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

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

$\epsilon =$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

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

$$\sum_{\vec{R}^i_{\|}} \Big(\frac{1}{|\vec{r} - \vec{R}^i_{\|}|} - \frac{1}{z_0 \cdot \Omega^s_0} \int\limits_{-\frac{z_0}{2}}^{+\frac{z_0}{2}} \int\limits_{\Omega^s_0} \frac{-1}{|\vec{r} - \vec{R}^i_{\|} - \vec{R}|} \, d\vec{R}_{\|} dR_z \Big)$$

<u>aim:</u> 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

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

<u>result:</u> $v_{2D}(\vec{r}) =$

$$\boxed{\begin{aligned} &\sum_{\vec{R}^i_{\|}} \left(\frac{1}{|\vec{r} - \vec{R}^i_{\|}|} - \frac{1}{|\vec{r} + \alpha \operatorname{sign}(z)\, \vec{e}_z - \vec{R}^i_{\|}|} \right) + \\ &+ \frac{2\pi}{\Omega^s_0} \sum_{\vec{G}_{\|} \neq 0} \frac{\exp\left(i\, \vec{G}_{\|} \cdot \vec{r}_{\|} - |\vec{G}_{\|}|(|z| + \alpha) \right)}{|\vec{G}_{\|}|} + \\ &+ \frac{2\pi}{\Omega^s_0} \begin{cases} -\alpha & : \quad z \notin [-\frac{z_0}{2}, +\frac{z_0}{2}] \\ -\alpha - |z| + \frac{1}{z_0} \left(\left(\frac{z_0}{2}\right)^2 + z^2 \right) & : \quad z \in [-\frac{z_0}{2}, +\frac{z_0}{2}]. \end{cases} \end{aligned}}$$

Hamiltonian

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

$$\hat{T} = -\frac{1}{2}\sum_i \Delta_i$$

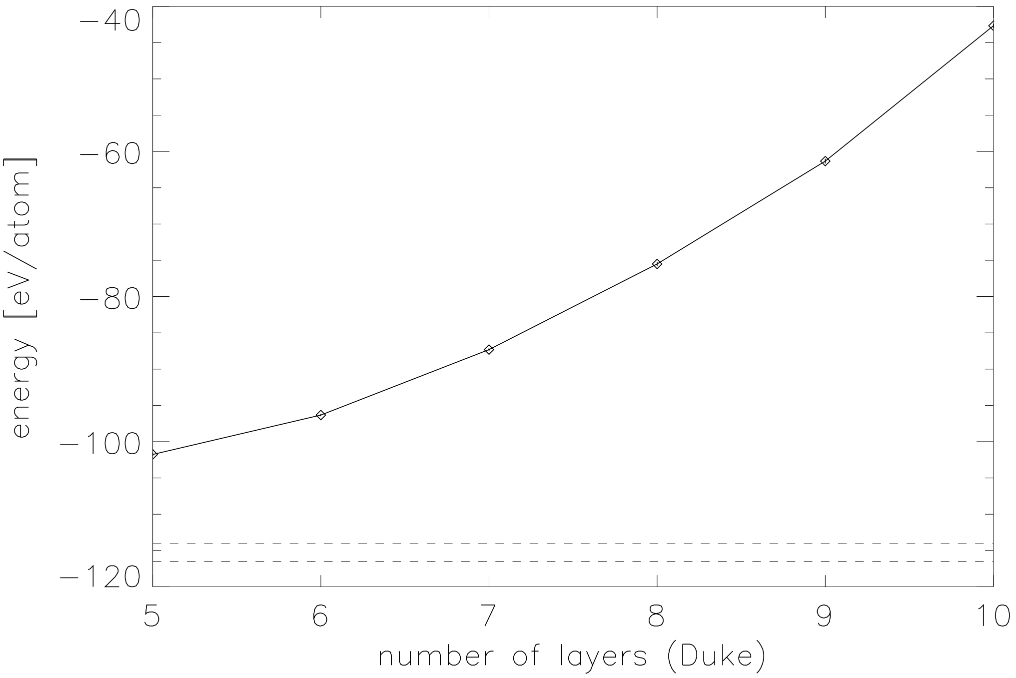
$$\hat{V} = \hat{V}^{\mathrm{l}}_{PP} + \hat{V}^{\mathrm{nl}}_{PP} + \hat{V}_c$$

$$\hat{V}^{\mathrm{nl}}_{PP} = \sum_{\alpha,i}\sum_l$$

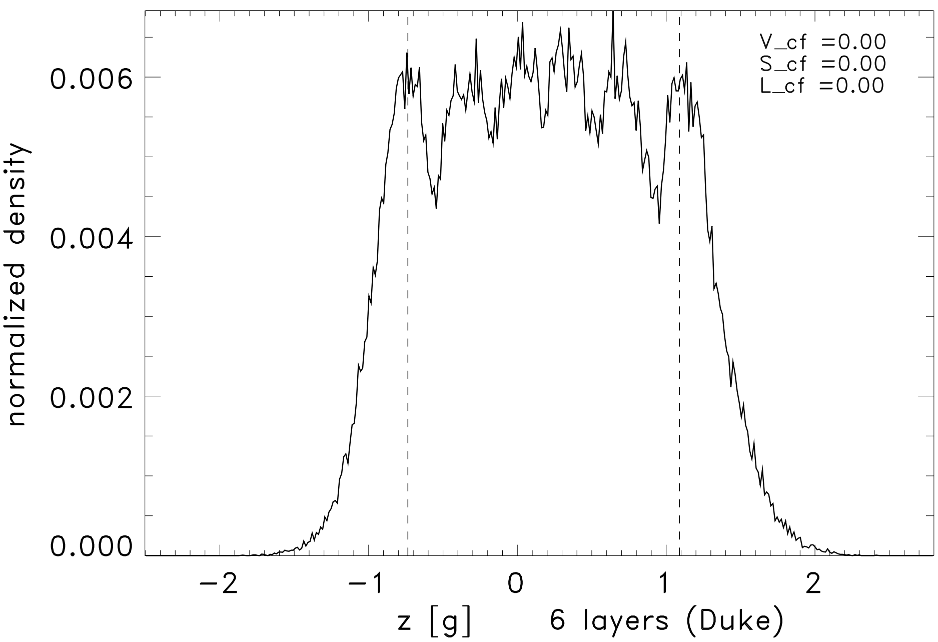
$$V_{\alpha,l}(r_{\alpha i})\frac{Y_{l0}(0,0)\int_{r'=r_{\alpha i}} Y^*_{l0}(\Omega_{r'})\,\psi(\ldots,\vec{r}_i=\vec{r}\,',\ldots)\,d\Omega_{r'}}{\psi(\ldots,\vec{r}_i,\ldots)}$$

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

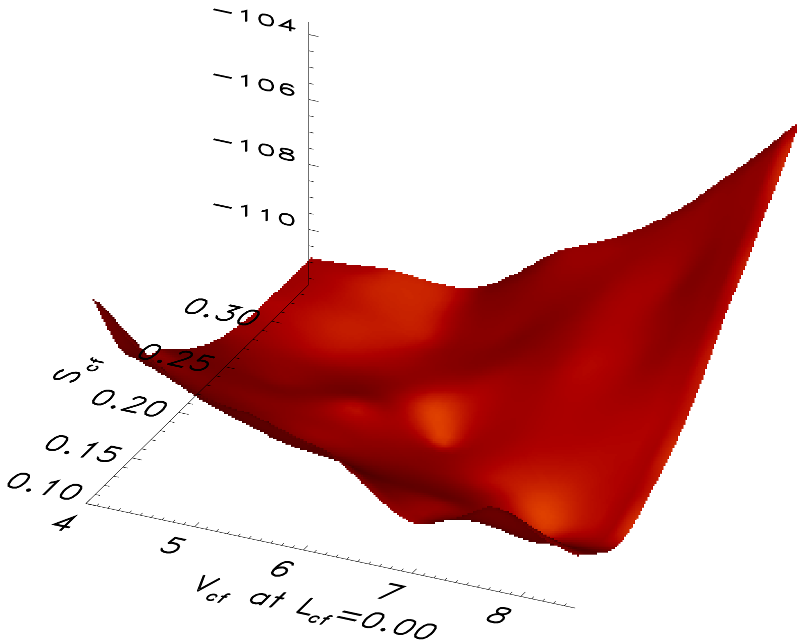
no confinement

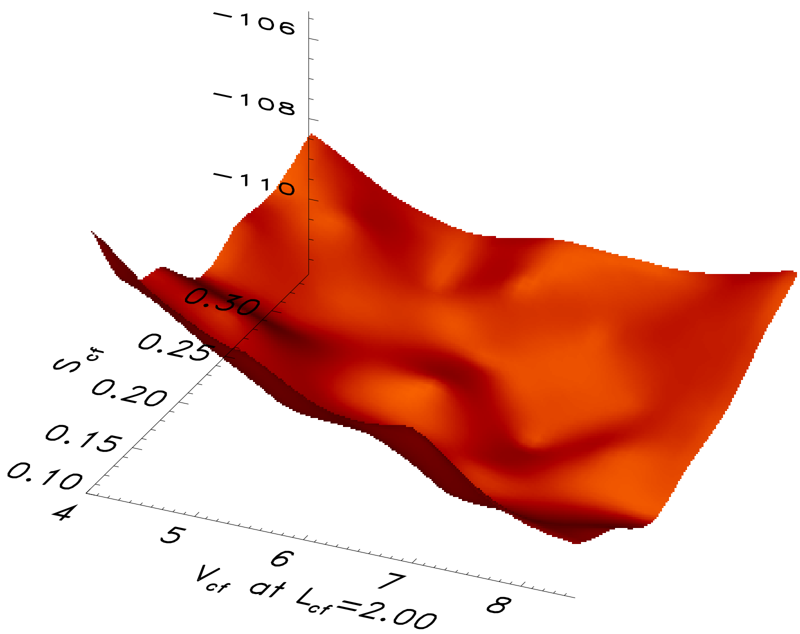


z-sampling

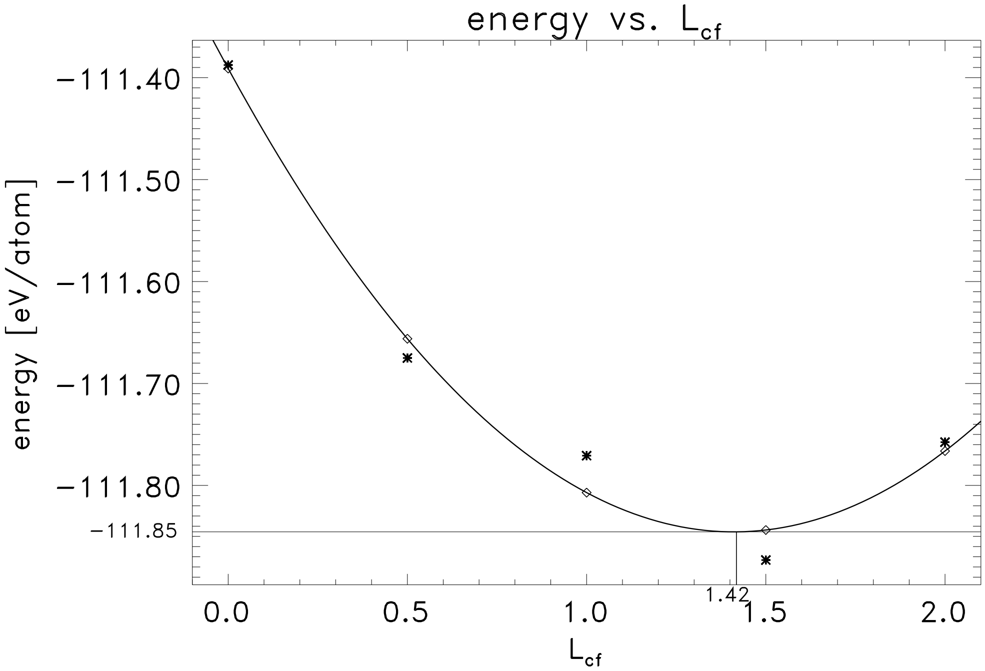


confinement optimization



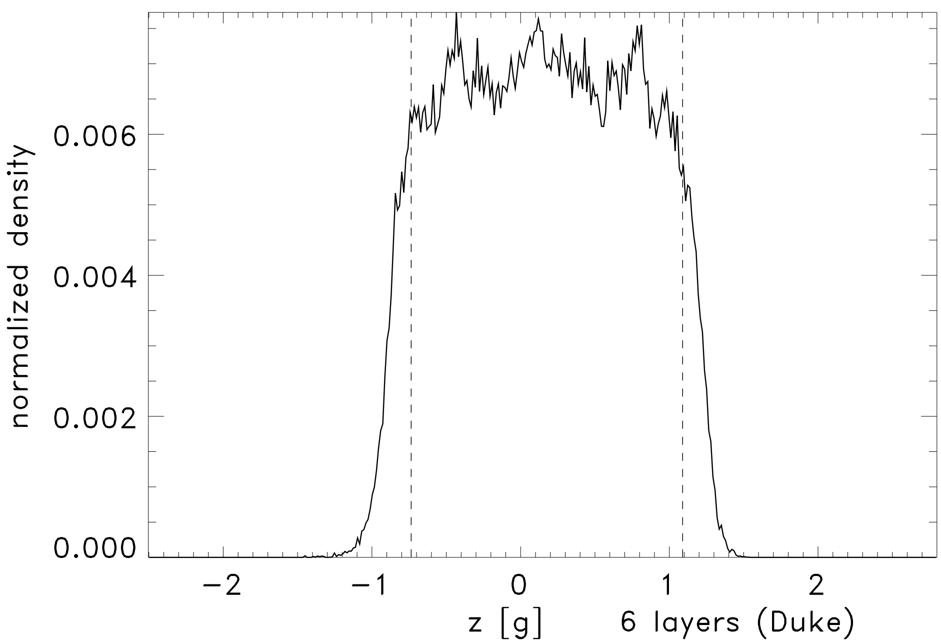


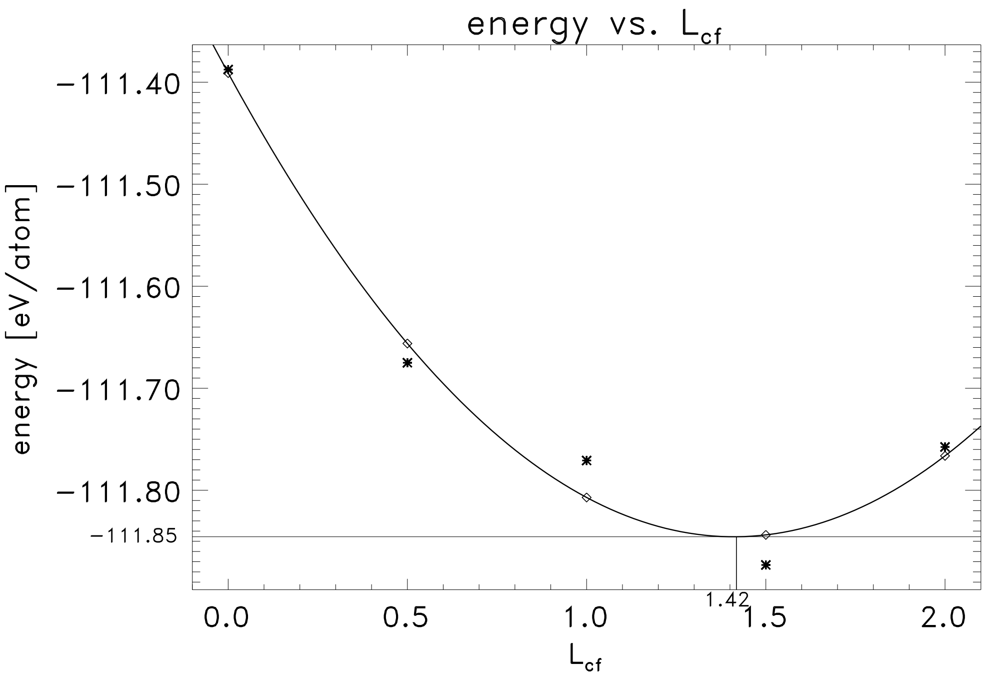
slab of 6 layers (Duke)



optimum confinement in 3 parameter space

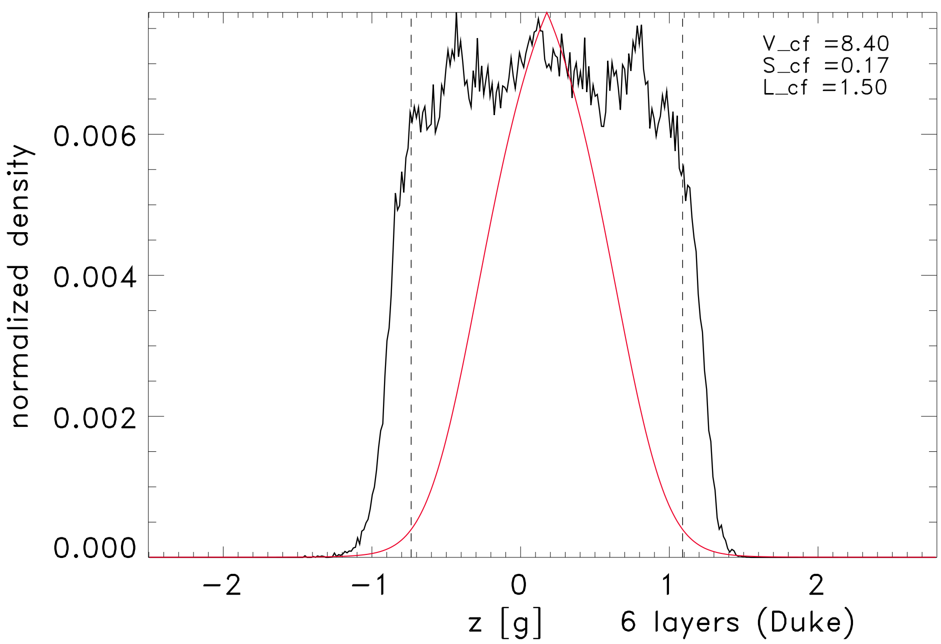
z-sampling



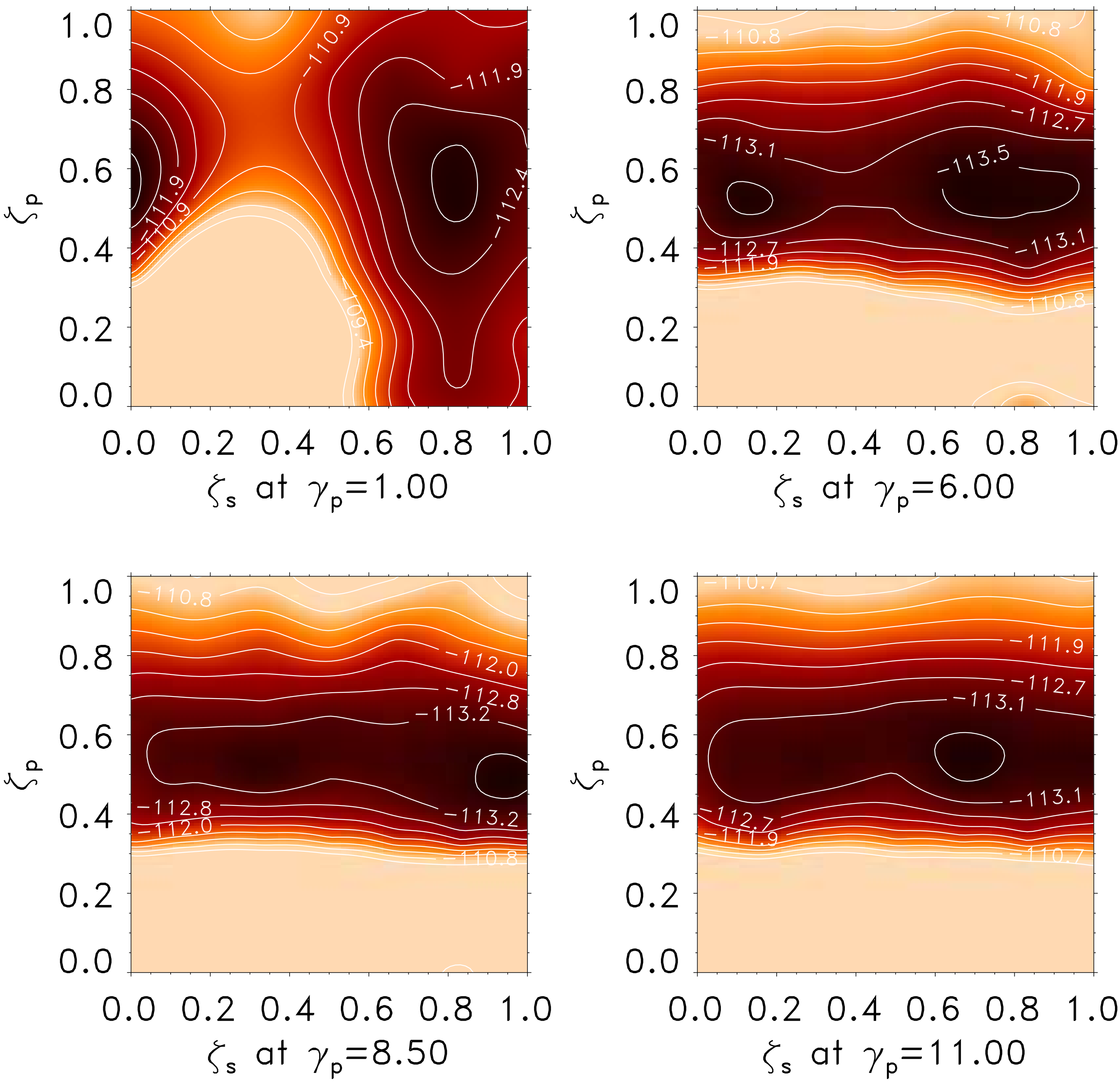


optimum confinement in 3 parameter space

z-sampling & confinement factor



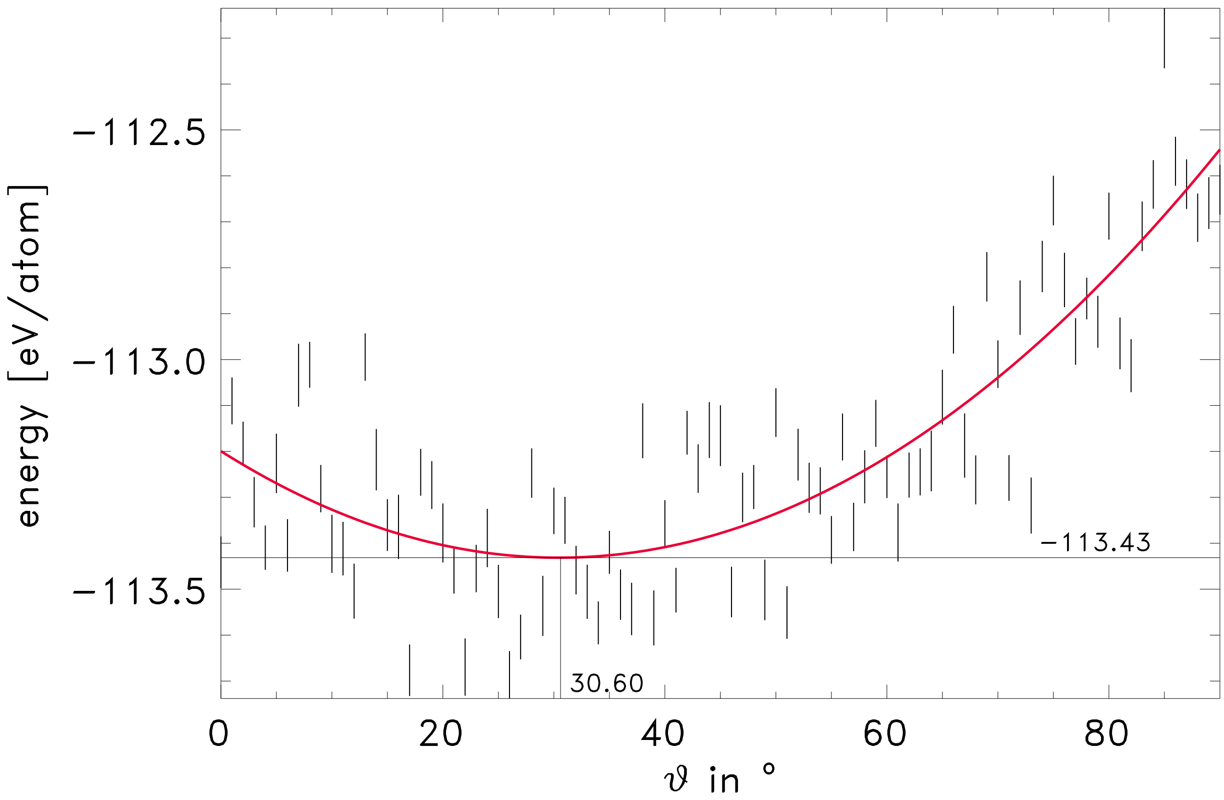
dangling bond parameters



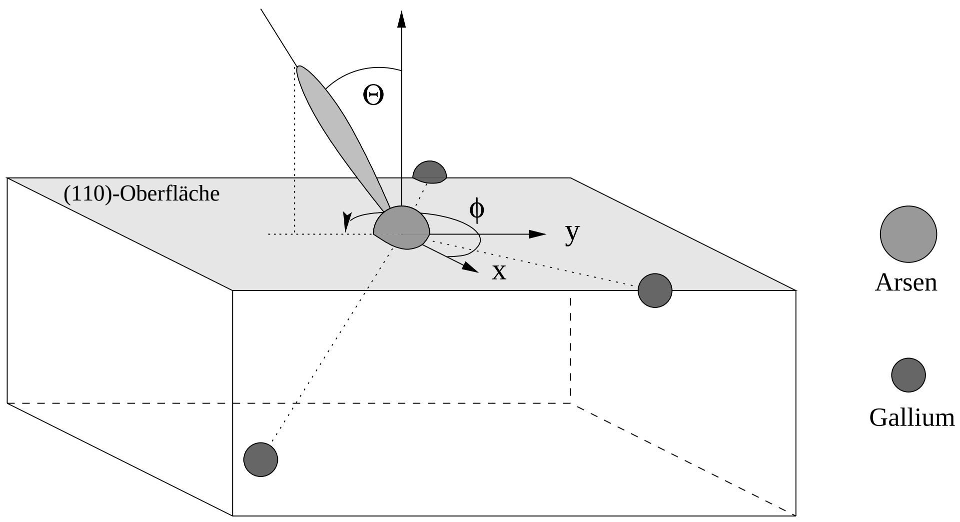
orbital contraction parameters ζ_s, ζ_p

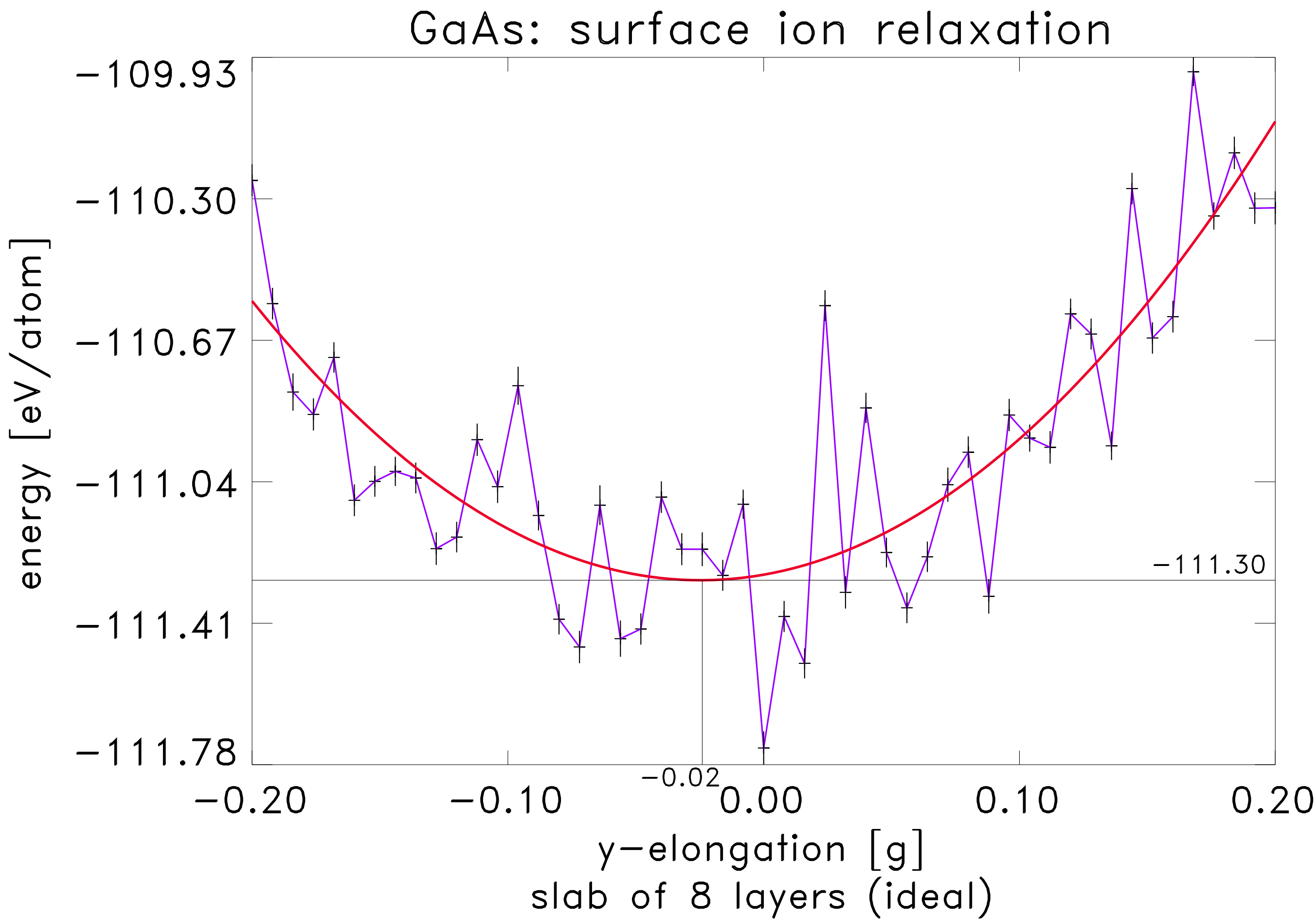
orbital weight parameter γ_p

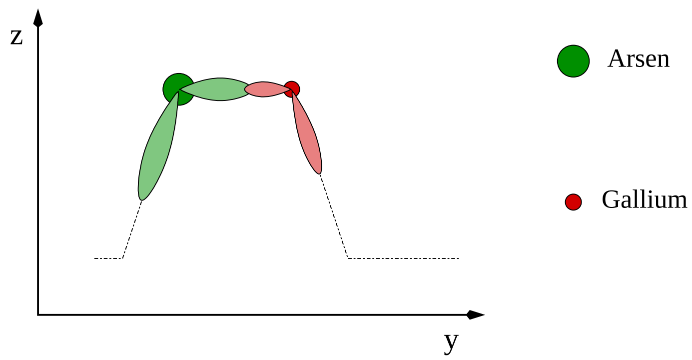
dangling bond angle

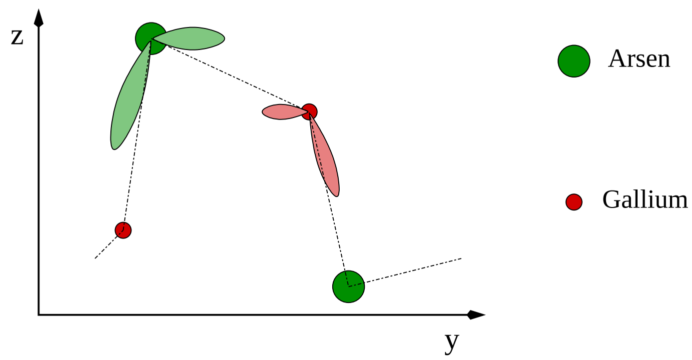


$\vartheta = \Theta$









adaptation of p-orbitals' coefficients $\vec{\tau}$

“At present QMC is 1000 times slower than DFT-LDA, every year a factor of 2 is pulled up. So in 10 years everything presented on this conference will be done by QMC.”

Volker Heine, Cambridge; cited from final talk of PSIK-Network - Conference 1996 in Schwäbisch Gmünd

summary

- stochastic integration of many-body Hamiltonian
- boundary conditions and Ewald's method in 2D
- Ψ? DB-orbital and confinement term
- compensation of "Jastrow pressure"
- dangling bond properties resolved
- towards dynamical matrix and molecular dynamics

outlook

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