Fast Guide to Density Functional Calculations

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Outline of this talk

I. From the many-particle problem to the Kohn-Sham functional

II. How to perform a total energy calculation
   → more in L3 – L7

III. From the total energy to materials science
   → more in L8 – L21

General 'condensed-matter' Hamiltonian

$$(\hat{T}^e + \hat{T}^{ion} + \hat{V}^{e-e} + \hat{V}^{e-ion} + \hat{V}^{ion-ion})\Psi = E\Psi$$

wavefunction $\Psi(\mathbf{r_1}, \cdots \mathbf{r_N}; \mathbf{R_I}, \cdots \mathbf{R_M})$

electronic coordinates $\mathbf{r_k}$, $k = 1, \cdots N$

ionic coordinates $\mathbf{R_I}$, $I = 1, \cdots M$

$$\hat{T}^e = \sum_{k=1}^{N} \frac{\mathbf{p}_k^2}{2m} \qquad\qquad \hat{T}^{ion} = \sum_{I=1}^{M} \frac{\mathbf{P}_I^2}{2M_I}$$

$$\hat{V}^{e-e} = \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{k \neq k'}^{N,N} \frac{e^2}{|\mathbf{r_k} - \mathbf{r_{k'}}|}$$

$$\hat{V}^{ion-ion} = \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{I \neq I'}^{M,M} \frac{Z_I Z_{I'}}{|\mathbf{R_I} - \mathbf{R_{I'}}|}$$

$$\hat{V}^{e-ion}(\mathbf{r_k}, \mathbf{R_I}) = \sum_{k=1}^{N} \sum_{I=1}^{M} \mathbf{v_I^{ion}}(|\mathbf{R_I} - \mathbf{r_k}|)$$

Born-Oppenheimer approximation

convenient, frequently made approximation (but not compulsary)

separation of variables $\rightarrow$ parametric dependence on set of coord. $\{\mathbf{R_I}\}$

$$\Psi(\mathbf{r_1}, \cdots \mathbf{r_N}; \mathbf{R_1}, \cdots \mathbf{R_M}) = \sum_\nu \Lambda_\nu(\{\mathbf{R_I}\}) \Phi_{\nu,\{\mathbf{R_I}\}}(\mathbf{r_k})$$

electronic Schrödinger equation

$$H^e_{\{\mathbf{R_I}\}} \Phi_{\nu,\{\mathbf{R_I}\}}(\mathbf{r_k}) = E^e_{\nu,\{\mathbf{R_I}\}} \Phi_{\nu,\{\mathbf{R_I}\}}(\mathbf{r_k})$$

$$H^e = T^e + V^{e-e} + V^{e-ion}$$

frequently made approximations:

- neglect of non-adiabatic couplings (terms of order m/M_I)
- only one $\Lambda_\nu \neq 0$ (in a solid, this means neglect of electron-phonon couplings)

$\rightarrow$ electronic and nuclear degrees of freedom decouple !

Limitations of Born-Oppenheimer

- doesn't account for correlated dynamics of ionic and electronic coordinates
  Example:
  suprafluid He3, polaron-induced superconductivity

- breakdown of the restriction to a single ground-state Born-Oppenheimer surface
  Example:
  chemoluminescence

- breakdown of the adiabatic approximation
  Example:
  excitation of surface plasmons during scattering of an ion from a metal surface → time-dependent density functional theory

electronic many-particle Hamiltonian

$$\left[\sum_{k=1}^{N} \frac{\nabla_k^2}{2m} + v^{(0)}(\mathbf{r_k}) + \sum_{k \neq k'}^{N,N} \frac{1}{2} W(\mathbf{r_k}, \mathbf{r'_k}) \right] \Phi(\mathbf{r_1}, \cdots \mathbf{r_N}) = E\Phi(\mathbf{r_1}, \cdots \mathbf{r_N})$$

$$W(\mathbf{r}, \mathbf{r'}) = \frac{e^2}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r'}|}$$

$$v^{(0)}(\mathbf{r}) = \sum_{I=1}^{M} v_I^{ion}(|\mathbf{R_I} - \mathbf{r}|)$$

still many (for a typical solid: 10^{23}) degrees of freedom

The many-particle problem can be solved only for small systems (atoms, molecules and clusters).

$\rightarrow$ wavefunction-based methods

- Configuration-interaction, Coupled Cluster method
- Quantum Monte Carlo method

Density Functional Theory

Hohenberg-Kohn theorem:

For any given external potential $v^{(0)}$, the wavefunctions can be considered as functionals in the space of ground state densities, n:

$$E_{v^{(0)}}[n] = \langle \Phi[n]| \hat{T}^e + \frac{1}{2}\hat{W} + \hat{v}^{(0)} |\Phi[n]\rangle$$

The energy functional is stationary at the ground state energy, and the true ground state density n_0 coincides with n at the stationary point. Therefore a universal functional $\mathcal{F}$ exists with the property

$$E_{v^{(0)}}[n] = \mathcal{F}[n] + \int d\mathbf{r}\ v^{(0)}(\mathbf{r})n(\mathbf{r})$$

Proof:

'$\Phi[n] \mapsto n$':   trivial

'$n \mapsto \Phi[n]$':   Note that $v_{ext} \to n \overset{\text{Raleigh-Ritz}}{\mapsto} \Phi[n]$

Also: $v_{ext} \mapsto \Phi[n]$. Thus, $E_{v^{(0)}}[n]$ is uniquely defined.

Kohn-Sham theorem

idea: decompose $\mathcal{F}[n]$ into its major contributions

$$\mathcal{F}[n] = T_0[n] + \frac{1}{2} \int \int d\mathbf{r}\, d\mathbf{r}'\, n(\mathbf{r}) W(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') + E_{XC}[n]$$

T_0:   kinetic energy of a system

                                    of non-interacting particles

$E_{XC}[n]$ exchange-correlation energy

                                    defined as 'the rest' $\rightarrow$ approximations

$V_{XC}[n](r) := \frac{\delta E_{XC}[n]}{\delta n(r)}$:   exchange-correlation potential

popular approximations for $E_{XC}[n]$:

- local-density approximation (LDA)
- generalized gradient approximations (GGAs)
- exact exchange formalism (EXX)

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Kohn-Sham Hamiltonian

To find the stationary point, we do variations at fixed $N = \int d\mathbf{r}\, n(\mathbf{r})$, which leads to

$$\frac{\delta E_{v^{(0)}}}{\delta n(\mathbf{r})} = \mu \qquad \text{(Lagrange parameter)}$$

If we write the density as a sum over single-particle functions,

$$n(\mathbf{r}) = \sum_{\mathbf{j=1}}^{\mathbf{N}} \sum_{\mathbf{k \in BZ}} |\varphi'_{\mathbf{j,k}}(\mathbf{r})|^{\mathbf{2}},$$

the variational principle $\delta E_{v^{(0)}}[\varphi^*]/\delta\varphi^*(\mathbf{r}) = \mathbf{0}$ leads to the Kohn-Sham equations

$$\left(-\frac{\nabla^2}{2m} + V_{\mathbf{eff}}[n](\mathbf{r}) \right) \varphi_{j,\mathbf{k}}(\mathbf{r}) = \epsilon_{j,\mathbf{k}}\, \varphi_{j,\mathbf{k}}(\mathbf{r})$$

with the effective potential

$$V_{\mathbf{eff}}[n](\mathbf{r}) = v_{R_I}^{(0)}(\mathbf{r}) + \int d\mathbf{r}' \frac{e^2 n(\mathbf{r}')}{4\pi\epsilon_0 |\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{XC}[n]}{\delta n}(\mathbf{r}).$$

How can we specify E_{XC} ?

At this point, we need to make approximations to get further.

Example: local density approximation (LDA)

$$E_{XC}[n(\mathbf{r})] = \int d\mathbf{r}\, e_{XC}[n(\mathbf{r})]\, n(\mathbf{r})$$

$$\approx \int d\mathbf{r}\, [e_X^{hom}(n(\mathbf{r})) + e_C^{hom}(n(\mathbf{r}))]\, n(\mathbf{r})$$

$$e_X^{hom}(n) = -(81/64\pi)^{1/3} n^{1/3}(\mathbf{r})$$

$$e_C^{hom}(n) = \begin{cases} -0.1423(1 + 1.0529\sqrt{r_s} + 0.3334 r_s)^{-1} & \text{if} \quad r_s \geq 1, \\ \\ -0.0480 + 0.0311\ln r_s - 0.0116 r_s + 0.002 \quad r_s \quad \ln r_s \\ & \text{if} \quad r_s < 1. \end{cases}$$

$r_s := (4\pi n(\mathbf{r})/3)^{-1/3}$ Wigner-Seitz radius

[see, e.g. J. Perdew & A. Zunger, Phys. Rev. B **23** 5048 (1981)]

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The total energy (for static ions)

two equivalent definitions:

$$
\begin{aligned}
E_{tot}[n] &= T_0[n] + \int d\mathbf{r}\, v_{\mathbf{R}_i}^{(0)}(\mathbf{r})n(\mathbf{r}) + \frac{1}{4\pi\epsilon_0}\int d\mathbf{r}\int d\mathbf{r}'\,\frac{e^2 n(\mathbf{r})n(\mathbf{r}')}{2|\mathbf{r}-\mathbf{r}'|} \\
&\quad + E_{XC}[n] + V_{\mathbf{R}_I}^{ion-ion}
\end{aligned}
$$

$$
E_{tot}[n] = \sum_{j=1}^{N}\sum_{\mathbf{k}\in BZ}\varepsilon_{j,\mathbf{k}} + \Delta E^{e-e}[n] + \Delta E_{XC}[n] + V_{\mathbf{R}_I}^{ion-ion}
$$

$$
\Delta E^{e-e}[n] = -\frac{1}{4\pi\epsilon_0}\int d\mathbf{r}\int d\mathbf{r}'\,\frac{e^2 n(\mathbf{r})n(\mathbf{r}')}{2|\mathbf{r}-\mathbf{r}'|} = -E^{e-e}[n]
$$

$$
\Delta E_{XC}[n] = E_{XC}[n] - \int d\mathbf{r}\, V_{XC}[n](\mathbf{r})\mathbf{n}(\mathbf{r})
$$

E_{tot} is stationary with resp. to variations of n around n_0, but the individual terms are not !

Periodic systems

crystal structure =

Bravais lattice   &   basis

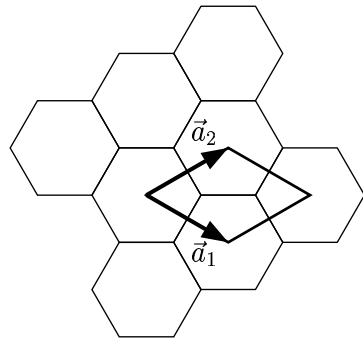translational symmetry   symmetries of the basis compatible
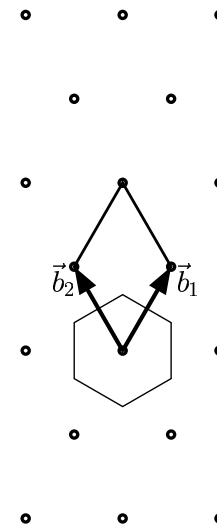
with the Bravais lattice

group $\mathcal{T}$ point group $\mathcal{P}$

Example: twodimensional honeycomb lattice

(Bravais lattice if a basis of two atoms is used)

lattice vectors $\vec{a}_1, \vec{a}_2, \vec{a}_3$

Brillouin zone (BZ)

reciprocal lattice vectors $\vec{b}_1, \vec{b}_2, \vec{b}_3$

$$\vec{b}_i = 2\pi/\Omega \, (\vec{a}_j \times \vec{a}_k)$$

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Bloch functions

Since H commutes with the elements of $\mathcal{T}$, the wave functions must be of the form

$$\varphi_{j,\mathbf{k}}(\mathbf{r} + \mathbf{R}) = \mathrm{e}^{i\mathbf{k}\mathbf{R}} \varphi_{j,\mathbf{k}}(\mathbf{r}), \quad \text{(Bloch's theorem)}$$

for any $\mathbf{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$.

The wavevector $\mathbf{k}$ is an index specified by a point in the first Brillouin zone (elementary cell of the reciprocal lattice), and the number of such points is equal to the number of lattice sites in the crystal.

Due to Bloch's theorem, it suffices to calculate φ in just one elementary cell,

$$\varphi_{j,\mathbf{k}}(\mathbf{r}) = \mathrm{e}^{i\mathbf{k}\mathbf{r}} u_{j,\mathbf{k}}(\mathbf{r})$$

where u is a lattice-periodic function.

In practice, sums over $\mathbf{k}$ are evaluated by summing over a discrete set of (special) $\mathbf{k}$-points.

Brillouin zone sampling

Problem: Calculate the BZ average of the Fourier transform $\tilde{u}$ of a lattice-periodic function u

$$\sum_{\mathbf{k} \in \text{BZ}} \tilde{u}(\mathbf{k}) \approx \sum_{\mathbf{k}_i}^{i_{max}} w_i \tilde{u}(\mathbf{k}_i) \tag{1}$$

accurately using a small set of sampling points and weights, $\mathbf{k}_i$ and w_i. $\{\mathbf{R}\}_s$ is a set of lattice vectors invariant under the n_P operations in $\mathcal{P}$. For this purpose, define symmetrized plane waves ('stars')

$$A_s(\mathbf{k}) = \frac{1}{n_P} \sum_{\{\mathbf{R}\}_s} e^{i\mathbf{k}\mathbf{R}} \qquad \text{as basis set expansion for } \tilde{u}(\mathbf{k}).$$

Idea: If the $\mathbf{k}_i$ and w_i are such that

$$\sum_{i=1}^{i_{max}} w_i A_s(\mathbf{k}_i) = 0 \quad \text{for all s=1,M}$$

then Eq. 1 holds except (small) contributions from 'stars' of order $> M$. **Caution:** statement only holds for continuously differentiable function $\tilde{u}(\mathbf{k})$.

Basic steps in an electronic structure calculation

1. guess a starting charge density
   (e.g. superposition of atomic densities)

2. set up the Hamiltonian for this charge density (usually done in a small, preliminary basis set)

3. diagonalize this approximative Hamiltonian

4. use the eigenvalues and wavefunctions to set up a new charge density

5. try to improve the wavefunctions using the variational principle for E_{tot}, thereby simultaneously approaching self-consistency

$$n^{(i-1)} \rightarrow V_{eff}^{(i-1)} \rightarrow \varepsilon_{j,\mathbf{k}}^{(i-1)}, \varphi_{j,\mathbf{k}}^{(i-1)} \rightarrow n^{(i)} \rightarrow V_{eff}^{(i)} \rightarrow \varepsilon_{j,\mathbf{k}}^{(i)}, \varphi_{j,\mathbf{k}}^{(i)} \cdots$$

Variational properties

At the stationary point, the Kohn-Sham equations lead us to

$$T_0[n] = \sum_{j=1}^{N} \sum_{\mathbf{k} \in BZ} \varepsilon_{j,\mathbf{k}} - \int d\mathbf{r} \, n(\mathbf{r}) V_{\text{eff}}[n](\mathbf{r})$$

For the non-consistent case, we may introduce the generalization

$$T_0[n, V_{\text{eff}}] = \sum_{j=1}^{N} \sum_{\mathbf{k} \in BZ} \varepsilon_{j,\mathbf{k}}[V_{\text{eff}}] - \int d\mathbf{r} \, n(\mathbf{r}) V_{\text{eff}}(\mathbf{r})$$

This can be used to define the 'double' functional

$$E_{tot}^{D}[n, V_{\text{eff}}] = T_0[n, V_{\text{eff}}] + E^{e-e}[n] + E_{XC}[n] + V_{\mathbf{R}_I}^{ion-ion}$$

with the variational properties

$$E_{tot}^{D}[n_0 + \delta n, V_{\text{eff}}[n_0]] - E_{tot}^{D}[n_0, V_{\text{eff}}[n_0]] = c_1 (\delta n)^2$$

$$E_{tot}^{D}[n_0, V_{\text{eff}}[n_0] + \delta v] - E_{tot}^{D}[n_0, V_{\text{eff}}[n_0]] = c_2 (\delta v)^2.$$

Normally, one has $c_1 > 0, c_2 < 0$. Then, $E_{tot}^{D}[n^{(i-1)}, V_{\text{eff}}[n^{(i-1)}]]$ is a lower bound for the (coverged) total energy.

Total-energy and thermodynamics

The thermodynamic ground state is determined by the global minimum of
— the free energy of the system (for fixed volume)

$$F(T,V) \quad = \quad E_{tot}(T,V) - TS^e(T,V)$$
$$+E_{kin}^{ion}(T) - TS^{ion}(T,V)$$

Structural relaxation:

Minimize $F(T,V)$ (in practice: E_{tot})

Caution: ionic contribution to the free energy important if,

e.g.,anharmonic effects come into play

—or by the Gibbs free energy (for fixed pressure)

$$G(T,p) = F(T,V) + pV$$

Examples:

– equilibrium between two structurally different crystalline phases
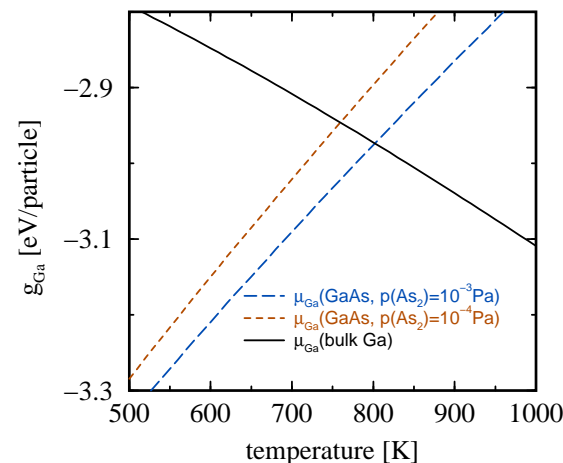– equilibrium between a solid and its vapor

Thermal decay of GaAs

$$GaAs \leftrightarrow Ga_{metal} + \frac{1}{2} As_2$$

$$G_{Ga}^{GaAs\ bulk}(p, T) = G_{GaAs}(T) - G_{As}(p, T).$$

$G_{As}(p, T)$ from ideal two-atomic gas, S_{GaAs}^{ion} and S_{Ga}^{ion} from Debye model of the solid.

Free enthalpy per Ga atom in bulk GaAs in thermodynamic equilibrium with As$_2$ vapor at two pressures, compared to the free enthalpy per Ga atom in elemental Ga.

[P. K., C.G. Morgan and M. Scheffler, Phys. Rev. B **59**, 15246 (1999)]

Finite electronic temperature

occupation numbers from Fermi distribution

$$f_{j,\mathbf{k}} = [\exp((\varepsilon_{j,\mathbf{k}} - \epsilon_F)/kT) - 1]^{-1}$$

$\rightarrow$ Computer codes actually calculate the free energy F !

entropy of the electronic system

$$S^e = 2k_B \sum_{j=1}^{n_B} \sum_{\mathbf{k} \in \mathrm{BZ}} [f_{j,\mathbf{k}} \ln f_{j,\mathbf{k}} + (1 - f_{j,\mathbf{k}}) \ln(1 - f_{j,\mathbf{k}})]$$

For a (free-electron-like) metal, we have

$$F(T) = E(T=0) - \frac{\gamma}{2} T^2 + O(T^3)$$

$$E(T) = E(T=0) + \frac{\gamma}{2} T^2 + O(T^3)$$

extrapolation to zero electronic temperature

$$E(T=0) \approx [F(T) + E(T)]/2 = E(T) - S^e T/2$$

[see M. J. Gillan, J. Phys. Cond. Mat. **1**, 689 (1989)]

How to compute observables

A) energy differences

between different structures, formation energy of defects, heat of adsorption, ...

B) derivatives of the thermodynamic potentials E_{tot}, F or G

For simplicity's sake, we consider a system with constant volume at $T = 0$: $\qquad F(T = 0, V) = E_{tot}(V)$

- pressure $p = -\dfrac{\partial E_{tot}(V)}{\partial V}$

- bulk modulus $B = V\dfrac{\partial^2 E_{tot}(V)}{\partial V^2}$

- forces $\vec{F}_I$ on atom I (in electronic ground state)

$$\vec{F}_I = -\frac{\partial E_{tot}}{\partial \vec{R}_I} = -\sum_j^N \langle\, \varphi_{j,\mathbf{k}} | \partial H / \partial \vec{R}_I | \varphi_{j,\mathbf{k}} \,\rangle$$

due to the Hellmann-Feynman theorem

How to compute observables

C) second derivatives

Examples:

1. force constant matrix

$$\frac{\partial E_{tot}}{\partial \vec{R}_i \partial \vec{R}_j}$$

$\rightarrow$ calculation of phonon spectrum, vibrational entropy, ...

2. particle number fluctuations

$\rightarrow$ chemical **softness** and **hardness**

$$s(\mathbf{r}) = \left.\left(\frac{\partial n(\mathbf{r})}{\partial \mu}\right)\right|_{v,T} = \int \left(\frac{\delta^2 E_{tot}}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\right)^{-1} d\mathbf{r}'$$

$$h(\mathbf{r}) = \left.\frac{1}{2}\left(\frac{\partial \mu}{\partial n(\mathbf{r})}\right)\right|_{v,T} = \int \frac{\delta^2 E_{tot}}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\frac{n(\mathbf{r}')}{2N} d\mathbf{r}'$$

Note: When calculating second derivatives, the response of the density to the perturbation must be taken into account.
$\rightarrow$ Density Functional Perturbation Theory

What materials properties are accessible to calculation?

- **structural properties**
  Examples: structural phase transitions, surface reconstructions   yes

- **elastic properties**
  Examples: bulk modulus, C_{11}, C_{12}, C_{44}, …   yes

- **chemical properties**
  Examples: thermochemical stability of compounds, reactivity of surfaces   yes

- **transport properties**
  Examples: conductance of nanowires, magneto-resistence

    developing field

- **optical/spectroscopic properties**
  Examples: photoemission spectra, cross sections for light absorption
  topic beyond Kohn-Sham theory $\rightarrow$ time-dependent DFT

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many other applications

Electronic properties of materials

From the Kohn-Sham variational principle, we have

$$\frac{\delta E_{tot}}{\delta n(\mathbf{r})} = \mu = \epsilon_F \quad \text{in a metal}$$

However, one cannot proof that the Fermi surface is represented correctly in DFT. Further, in a Kohn-Sham theory, there is no straightforward relationship between $\epsilon_{j,\mathbf{k}}$ and the excitation energy of quasiparticles and quasiholes. One can only show Janak's theorem

$$\frac{\partial E_{tot}}{\partial f_{j,\mathbf{k}}} = \epsilon_{j,\mathbf{k}}.$$

[supposing that E_{XC} is a continuously differentiable function of particle number, which is not true in a finite system]

As a first approximation to the effective mass tensor, one may use

$$\left. \left(\frac{\partial \epsilon_{j,\mathbf{k}}}{\partial k_n \partial k_m} \right) \right|_{\epsilon=\epsilon_F} = (\mathbf{M}^{-1})_{nm}$$

For a better treatment, use time-dependent DFT !

Simulation techniques

Challenges:

- length scales much larger than the atomic scale (e.g. in phase transitions, line defects, plastic deformation, …).
- dynamic properties, evolution on time scales as long as seconds (e.g. melting, crystal growth)

$\rightarrow$ combine the reliability of the first-principles approach with

molecular dynamics

- to follow dynamical processes in time, e.g. chemical reactions
  scale: several hundred atoms, pico-seconds
- for calculation of time correlation functions and phonons (using Fourier transformations)
- as a way to calculate the free energy (as a time average)

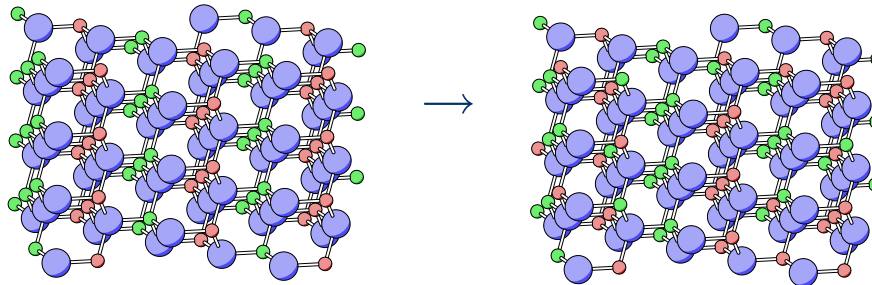statistical physics

kinetic modelling

Equilibrium statistical physics

To treat phenomena on large scales, map your problem to a model 'spin'
Hamiltonian, with parameters determined from DFT calculations.

Examples:

    order-disorder transition in alloys

    ordered ad-layers on surfaces

1. Calculate $\Delta E_{\text{DFT}}(\sigma, V)$ at $T = 0$ for many structures

2. Construct $\Delta E_{\text{CE}}(\sigma, V) = \sum_{k,m} d_{k,m} \Pi_{k,m}(\sigma) J_{k,m}(V)$
   $\Pi_{k,m}(\sigma)$ lattice-averaged spin product in k-atom-motif of type m
   $J_{k,m}(V)$ interaction parameters, fitted to DFT energies

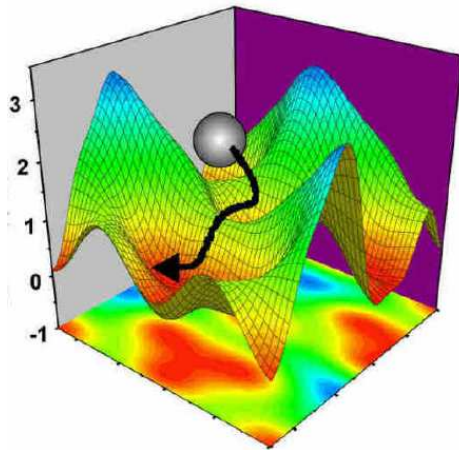3. Calculate partition function $Z = \langle \exp(-\Delta E_{CE}(\sigma, V)/k_B T) \rangle$

Kinetic Modeling of 'rare' events

Typical time interval τ between activated processes is too long to be covered by a Molecular Dynamics simulation.

Transition State Theory:

$$\tau^{-1} = \Gamma = \Gamma_0 \exp(-\Delta E / k_B T) \qquad \Gamma_0 = \frac{\prod^N \nu_k^{(i)}}{\prod^{N-1} \nu_k^{(TS)}}$$

Calculate these quantities using input from DFT calculations !

$\nu_k^{(i)}$: normal mode frequencies at energy minimum

$\nu_k^{(TS)}$: normal mode frequencies at transition state

ΔE: energy barrier

THE END

Enjoy the workshop !