

A fast guide to density functional calculations

P. Kratzer

*Fritz-Haber-Institut der MPG
D-14195 Berlin-Dahlem, Germany*

- I. From the many-particle problem to the Kohn-Sham functional
- II. How to perform a total energy calculation
- III. From the total energy to materials science

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 $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{R}_1, \dots, \mathbf{R}_M)$

electronic coordinates $\mathbf{r}_k, k = 1, \dots, N$

ionic coordinates $\mathbf{R}_I, I = 1, \dots, M$

$$\hat{T}^e = \sum_{k=1}^N \frac{\mathbf{p}_k^2}{2m}$$

$$\hat{T}^{ion} = \sum_{I=1}^M \frac{\mathbf{P}_I^2}{2M_I}$$

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

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

$$\hat{V}^{e-ion}(\mathbf{r}_k, \mathbf{R}_I) = \sum_{k=1}^N \sum_{I=1}^M v_I^{ion}(|\mathbf{R}_I - \mathbf{r}_k|)$$

Born-Oppenheimer approximation

separation of variables

parametric dependence on set of coord. $\{\mathbf{R}_I\}$

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{R}_1, \dots, \mathbf{R}_M) = \sum_{\nu} \Lambda_{\nu}(\{\mathbf{R}_I\}) \Phi_{\nu, \{\mathbf{R}_I\}}(\mathbf{r}_k)$$

electronic Schrödinger equation

$$H_{\{\mathbf{R}_I\}}^e \Phi_{\nu, \{\mathbf{R}_I\}}(\mathbf{r}_k) = E_{\nu, \{\mathbf{R}_I\}}^e \Phi_{\nu, \{\mathbf{R}_I\}}(\mathbf{r}_k)$$

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

is obtained if we neglect

- non-adiabatic couplings (usually terms of order m/M_I)
- electron-phonon couplings Λ_{ν} between different electronic states

Limitations of this approach

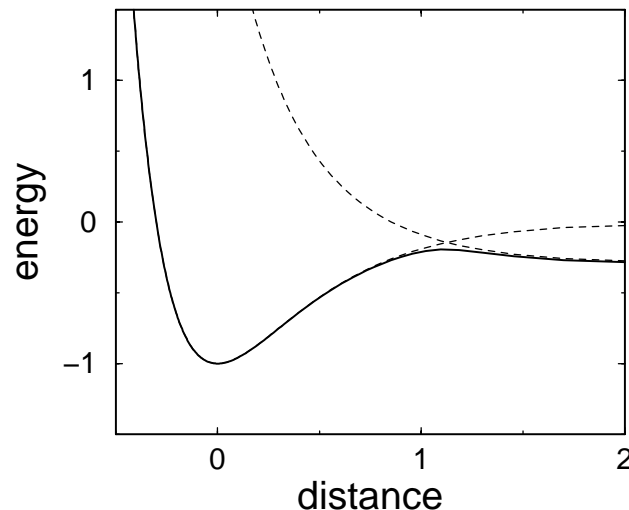
- doesn't account for correlated dynamics of ionic and electronic coordinates

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 theories (e.g. TD-DFT)

electronic many-particle Hamiltonian

$$\left[\sum_{k=1}^N \frac{\nabla_k^2}{2m} + v^{(0)}(\mathbf{r}_k) + \sum_{k \neq k'}^{N,N} \frac{1}{2} W(\mathbf{r}_k, \mathbf{r}'_k) \right] \Phi(\mathbf{r}_1, \dots, \mathbf{r}_N) = E \Phi(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

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

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

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

The many-particle problem can be solved only for rather small systems (atoms, molecules and clusters) using established methods of quantum chemistry (e.g. configuration interaction).

Density Functional Theory

Kohn-Hohenberg theorem:

For a 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. This allows for the definition of a **universal** functional \mathcal{F} with

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

Kohn-Sham theorem:

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

T_0 : kinetic energy of a system of non-interacting particles

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

Kohn-Sham (single particle) Hamiltonian

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

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

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

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

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

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

with the **effective potential**

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

The total energy (for static ions)

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

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

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

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

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

How can we specify E_{XC}

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

Example: local density approximation (LDA)

$$\begin{aligned} E_{XC}[n(\mathbf{r})] &= \int d\mathbf{r} e_{XC}[n(\mathbf{r})] n(\mathbf{r}) \\ &\approx \int d\mathbf{r} [e_X^{hom}(n(\mathbf{r})) + e_C^{hom}(n(\mathbf{r}))] n(\mathbf{r}) \end{aligned}$$

$$\begin{aligned} e_X^{hom}(n) &= -(81/64\pi)^{1/3} n^{1/3}(\mathbf{r}) \\ &\quad -0.1423(1 + 1.0529\sqrt{r_s} + 0.3334r_s)^{-1} && \text{if } r_s \geq 1, \\ e_C^{hom}(n) &= \begin{cases} -0.0480 + 0.0311 \ln r_s - 0.0116r_s + 0.002 r_s \ln r_s & \text{if } r_s \geq 1, \\ -0.0480 + 0.0311 \ln r_s - 0.0116r_s + 0.002 r_s \ln r_s & \text{if } r_s < 1. \end{cases} \end{aligned}$$

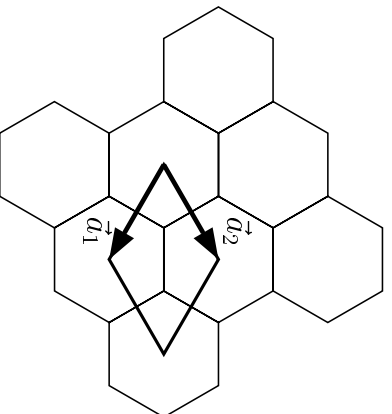
$r_s := (4\pi n(\mathbf{r})/3)^{-1/3}$ Wigner-Seitz radius

[see, e.g. Perdew & Zunger, PRB 23 5048 (1981)]

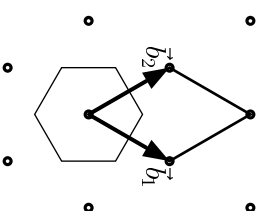
Periodic systems

crystal structure = Bravais lattice & translational symmetry group \mathcal{T} & symmetries of the basis compatible with the Bravais lattice point group \mathcal{P} basis

Example: two-dimensional 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 $\vec{b}_1, \vec{b}_2, \vec{b}_3$

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

($\{ijk\} = \{123\}$ & cyclic permutations of indices)

Bloch functions

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

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

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,

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

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.

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

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

Self-consistency cycle

Harris functional

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

update charge density

$$n^{(i)}(\mathbf{r}) = \sum_{\mathbf{k}}^{N_{\mathbf{k}}} \sum_j^{n_B} f_{j,\mathbf{k}} |\varphi_{j,\mathbf{k}}^{(i)}(\mathbf{r})|^2$$

with $f_{j,\mathbf{k}} = [\exp((\varepsilon_{j,\mathbf{k}} - \epsilon_F)/kT) - 1]^{-1}$. In principle, we are interested in $T \rightarrow 0$, but finite T helps to stabilize the SC loop.

$$\begin{aligned} \tilde{E}_{tot}[n^{(i+1)}] &= T_0[n^{(i)}] + \int d\mathbf{r} v_{\mathbf{R}_I}^{(0)}(\mathbf{r}) n^{(i)}(\mathbf{r}) \\ &+ E^{e-e}[n^{(i)}(\mathbf{r})] + E_{XC}[n^{(i)}] + V_{\mathbf{R}_I}^{ion-ion} \end{aligned}$$

Kohn-Sham functional: $\tilde{E}_{tot}[n_0] = E_{tot}[n_0]$ with self-consistent density n_0

Variational properties

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

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

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

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

This can be used to define the 'double' functional

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

with the variational properties

$$\begin{aligned} E_{\text{tot}}^D[n_0 + \delta n, V_{\text{eff}}[n_0]] - E_{\text{tot}}^D[n_0, V_{\text{eff}}[n_0]] &= c_1 (\delta n)^2 \\ E_{\text{tot}}^D[n_0, V_{\text{eff}}[n_0] + \delta v] - E_{\text{tot}}^D[n_0, V_{\text{eff}}[n_0]] &= c_2 (\delta v)^2. \end{aligned}$$

Normally, one has $c_1 > 0, c_2 < 0$. The Harris functional, in this notation, is $E_{\text{tot}}^D[n^{(i-1)}, V_{\text{eff}}[n^{(i-1)}]]$.

Total energy calculations and thermodynamics

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

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

Structural relaxation:

Minimize $F(T, V)$ (or E_{tot} , respectively)

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:

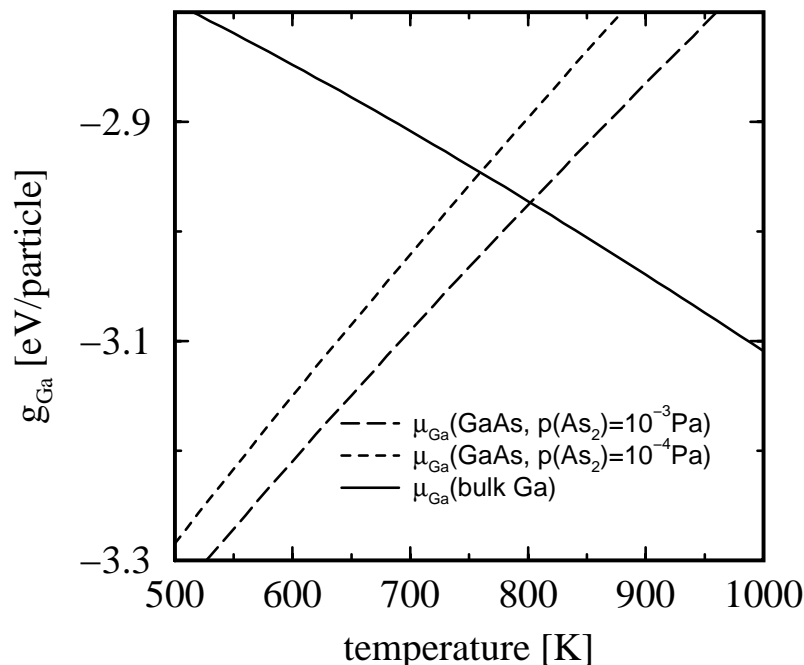
- equilibrium between two structural phases
- equilibrium between a solid and its vapor

Example: Thermal decay of GaAs



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

$G_{\text{As}}(p, T)$ from ideal two-atomic gas, $S_{\text{GaAs}}^{\text{ion}}$ and $S_{\text{Ga}}^{\text{ion}}$ 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. Kratzer *et al.*, Phys. Rev. B **59**, 15246 (1999)]

Finite electronic temperature

occupation numbers from Fermi distribution

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

→ The program actually computes the free energy F !

entropy of the electronic system

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

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 observable quantities

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 $T = 0$:

$$F(T = 0, V) = E_{tot}(V)$$

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

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

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

C) second derivatives

Examples:

1. force constant matrix

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

→ calculation of phonon spectrum, vibrational entropy, . . .

2. particle number fluctuations

→ chemical **softness** and **hardness**

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

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

Note: When calculating second derivatives, the response of the density must be taken into account.

→ 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: transport effective mass, magneto-resistance developing field
- optical/spectroscopic properties
Examples: photoemission spectra, cross sections for light absorption
topic beyond Kohn-Sham theory, encouraging progress recently
:
many other applications

Transport theory based on first-principles

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, there is no strict proof that the Fermi **surface** is represented correctly in DFT. Further, in a **Kohn-Sham theory**, $\epsilon_{j,\mathbf{k}}$ cannot be identified with the excitation energy of quasiparticles or quasiholes. One can only show

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

[supposing that E_{XC} is a continuously differentiable function of particle number]

Still one may use

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

as an approximation to the **effective mass tensor**.

The **transport cross section** for impurity scattering can be calculated from the 'golden rule' expression,

$$d\sigma(\hat{\mathbf{k}}, \hat{\mathbf{k}}') = 2\pi/\hbar (1 - \hat{\mathbf{k}}\hat{\mathbf{k}}') |V_{\mathbf{k},\mathbf{k}}|^2 \rho(\epsilon_{\mathbf{k}'}) d\hat{\mathbf{k}}',$$

using ρ , the density of states at the Fermi energy, from a DFT calculation as input.

Simulation techniques

In many materials science problems length scales much larger than the atomic scale are involved (e.g. in phase transitions, line defects, plastic deformation, etc.). Further, one is interested in dynamic (rather than static) properties, and evolution on time scales as long as seconds.

These problems require simulation techniques which build upon the reliability of the first-principles approach, but extend its range of applicability.

molecular dynamics

- to follow dynamical processes in time, e.g. chemical reactions
scale: several hundred atoms, pico-seconds
- for calculation of vibrational properties & phonons
(Fourier transform of time correlation functions)
- as a way to calculate the free energy at finite T
(performing a time average)

statistical physics

statistical treatment of a discrete Hamiltonian with parameters taken from DFT calculations

kinetics

description of 'rare' events using rate laws