Basics III: Ionic Relaxation, Stress & Cell Shapes, Phonons and Molecular Dynamics

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Outline

1. Ionic Relaxation
   - Introduction
   - Algorithms used in VASP
   - INCAR parameters in VASP, Problem Handling
2. Lattice Relaxation
   - Cell Volume Optimization
   - INCAR parameters in VASP
3. Phonons
   - Introduction
   - INCAR Parameters, Problem Handling
4. Molecular Dynamics
   - Introduction
   - MD Algorithms implemented in VASP
   - Thermostats implemented in VASP

Introduction

Basic Considerations

- Hermiticity of $\hat{H} \longrightarrow$ forces on the atoms can be calculated via the Hellmann-Feynman theorem

$$\nabla_I \epsilon_0(\vec{R}) = \frac{\partial}{\partial \vec{R}_I} \langle \Psi_0 \mid H_e(\vec{R}) \mid \Psi_0 \rangle = \langle \Psi_0(\vec{R}) \mid \nabla_I H_e(\vec{R}) \mid \Psi_0(\vec{R}) \rangle$$

- Forces acting on the ions are given by the expectation value of the gradient of the electronic Hamiltonian in the ground-state
- atomic coordinates in a cell with fixed cell shape: Hellmann-Feynman forces
- geometry of the unit cell (volume, shape): Hellmann-Feynman stresses

Introduction

. . . Basic Considerations

- in equilibrium: $E(\vec{R}, V, \mathrm{cellshape}\ldots) = \min.$
- (1): find the atoms' positions $\vec{R}$ minimizing E
- $\Rightarrow$ search for the (local) minimum of $E(\vec{R}) = f(\vec{x})$ with, f expanded around equilibrium $\vec{x}^0$

$$\begin{aligned} f(\vec{x}) &\approx a + \vec{b}\vec{x} + \frac{1}{2}\vec{x}\mathbf{B}\vec{x} = \bar{a} + \frac{1}{2}(\vec{x} - \vec{x}^0)\mathbf{B}(\vec{x} - \vec{x}^0) \\ \mathbf{B} &= \mathbf{B}_{ij} = \frac{\partial^2 f}{\partial x_i \partial x_j} \quad \text{Hessian matrix} \end{aligned}$$

- at a stationary point the gradient of f $(\vec{g}_i(\vec{x}))$ vanishes: $\vec{g}_i(\vec{x}) = \frac{\partial f}{\partial x_i} = \sum_j \mathbf{B}_{ij}(\vec{x}_j - \vec{x}_j^0) = 0$
- at a minimum: $\mathbf{B}$: has to be positive definite

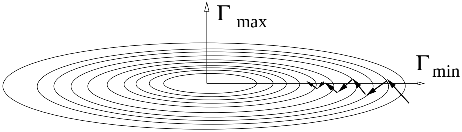
Introduction

... Basic Considerations: Newton Algorithm

1. start with an arbitrary point $\vec{x}^1$
2. calculate the gradient of f at $\vec{x}^1$:
   $g(\vec{x}^1) = \frac{\partial f}{\partial \vec{x}} = \mathbf{B}(\vec{x}^1 - \vec{x}^0)$
3. perform a step
   $\longrightarrow \vec{x}^2 = \vec{x}^1 - \mathbf{B}^{-1}\vec{g}(\vec{x}^1)$

- in practice: **B** is approximated by the largest eigenvalue of the Hessian matrix, $\Gamma_{\mathrm{max}}(\mathbf{B})$
- steepest descent algorithm

Introduction



Steepest Descent Algorithm

1. guess $\vec{x}^1$
2. calculate $\vec{g}(\vec{x}^1)$
3. step along the steepest descent direction $\vec{x}^2 = \vec{x}^1 - \frac{1}{\Gamma_{\max}} \vec{g}(\vec{x}^1)$
4. repeat 2+3 $\longrightarrow$ converged geometry

Introduction

Convergence of the Steepest Descent Algorithm

- minimize the number of steps requested to reach the afforded accuracy in the ion positions: step-widths along $\vec{g}(\vec{x}^1)$
- Eigenvalues of **B**: vibrational modes of the system
  - Γ_{max}: "hardest mode" maximum stable step width
  - Γ_{min}: "softest mode" slowest convergence
- to reduce the error in *all* components to a certain fraction, the number of steps can be estimated from $\frac{\Gamma_{\mathrm{max}}}{\Gamma_{\mathrm{min}}}$
- use preconditioning of **B** to speed up convergence

Algorithms used in VASP

Overview

- aims:
  1. reach asymptotic convergence rates
  2. maintain the relaxation history
- Quasi-Newton Schemes (DIIS): direct inversion in the iterative subspace
- Conjugate Gradient (GC): search directions are conjugated to the previous seach directions
- Damped Molecular Dynamics (MD): minimization problem is cast into a simulated annealing approach

Algorithms used in VASP

The Quasi-Newton Algorithm

- simple Quasi-Newton Scheme: for a set of points $\vec{x}^i$ and gradients $\vec{g}^i$ $(i = 1, \ldots, N)$
- find a linear combination of $\vec{x}^i$ which minimizes $\vec{g}^i$
- constraint: $\sum_i \alpha_i = 1$:

$$\begin{aligned}\vec{g}^i(\sum_i \alpha^i \vec{x}^i) &= \mathbf{B}(\sum_i \alpha^i \vec{x}^i - \vec{x}^0) \\ &= \mathbf{B}(\sum_i \alpha^i \vec{x}^i - \sum_i \alpha^i \vec{x}^0) \\ &= \sum_i \alpha^i \mathbf{B}(\vec{x}^i - \vec{x}^0) = \sum_i \alpha^i \vec{g}^i\end{aligned}$$

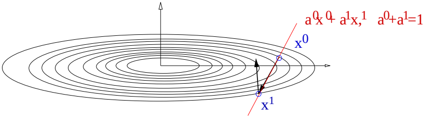
- gradient: *linear* in its arguments

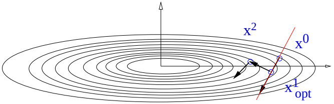
Algorithms used in VASP

The Full DIIS Algorithm

1. start with a single initial point $\vec{x}^i$
2. steepest descent step along gradient $\vec{g}(\vec{x}^1) : \vec{x}^2 = \vec{x}^1 - \lambda \vec{g}^1$
3. $\longrightarrow$ new gradient $\vec{g}^2 = \vec{g}(\vec{x}^2)$
4. search for the minimal gradient in the subspace spanned by $\vec{g}^i$:$\longrightarrow$ $\vec{g}_{\mathrm{opt}} = \sum_i \alpha^i \vec{g}^i$
5. calculate the corresponding position $\vec{x}_{\mathrm{opt}} = \sum_i \alpha^i \vec{x}^i$
6. $\longrightarrow \vec{x}^3 = \vec{x}_{\mathrm{opt}} - \lambda \vec{g}_{\mathrm{opt}}$

Algorithms used in VASP





full DIIS

- start with single initial point x^0
- steepest descent step (sds)
- opt. position $\vec{x}^1_{\text{opt}}$
- sds from $\vec{x}^1_{\text{opt}}$ along $\vec{g}_{\text{opt}} \longrightarrow \vec{x}^2$
- $\longrightarrow \vec{g}(\vec{x}^2)$
- linearity $\longrightarrow$ gradient is known in 2D
- minimize f exactly

Algorithms used in VASP

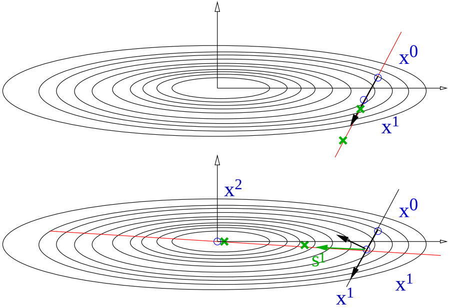
The Conjugate-Gradient Algorithm (CG)

- search directions: conjugated to the previous seach directions
- start with $\vec{x}^0$
  1. steepest descent step along gradient with line minimization
  2. gradient at the current position $\vec{g}(\vec{x}^N)$
  3. conjugate $\vec{g}(\vec{x}^N)$ to the previous search direction:

$$\vec{s}(\vec{x}^N) = \vec{g}(\vec{x}^N) + \gamma \vec{g}(\vec{x}^{N-1}), \quad \gamma = \frac{(\vec{g}(\vec{x}^N) - \vec{g}(\vec{x}^{N-1})) \cdot \vec{g}(\vec{x}^N)}{\vec{g}(\vec{x}^{N-1}) \cdot \vec{g}(\vec{x}^{N-1})}$$

  4. line minimization along $\vec{s}^N$
  5. if $\vec{g}$ is not sufficiently small: continue with 1
- search directions are orthogonal (step 3): $\vec{s}^N \mathbf{B} \vec{s}^M \quad \forall N, M$
- CG finds the min. of a quadratic function with k DOF in $k+1$ steps exactly

Algorithms used in VASP



The CG Algorithm

- sds from $\vec{x}^0$ along $\vec{g}^0$
- trial step(s) $\times$, $N_\times \geq 1$), $\longrightarrow \vec{x}^1$
- $\longrightarrow$ new $\vec{g}^1 = \vec{g}(\vec{x}^1)$
- conjugate $\vec{g}^1$: $\longrightarrow$, $\vec{s}^1$
- $\vec{s}^1$ points directly towards the minimum
- minimization along $\vec{s}^1$

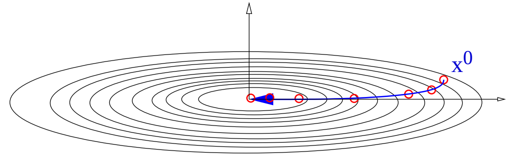
Algorithms used in VASP

Damped MD (MD)

- atoms' positions $\vec{x}$ are regarded as dynamic degrees of freedom
- forces (=gradients) accelerate the motion of the atoms
- equation of motions of the atoms: $\ddot{\vec{x}} = -2\alpha\vec{F} - \mu\dot{\vec{x}}$
- introduce an additional friction term μ
- integration of this eqation: simple velocity Verlet algorithm

$$\begin{aligned} \vec{v}_{N+1/2} &= \Big((1-\mu/2)\vec{v}_{N-1/2} - 2\alpha\vec{F}_N\Big)/(1+\mu/2) \\ \vec{x}_{N+1} &= \vec{x}_N + \vec{v}_{N+1/2} \end{aligned}$$

Algorithms used in VASP



Damped MD (MD)

- “rolling ball” with friction (μ)
- μ too small: minimum overshot, back-acceleration
- μ too large: relaxation slows down

INCAR Parameters in VASP

Overview

Algorithm	main flag	additional flags	termination
DIIS	`IBRION =1`	`POTIM, NFREE`	`EDIFFG`
CG	`IBRION =2`	`POTIM`	`EDIFFG`
damped MD	`IBRION =3`	`POTIM, SMASS`	`EDIFFG`

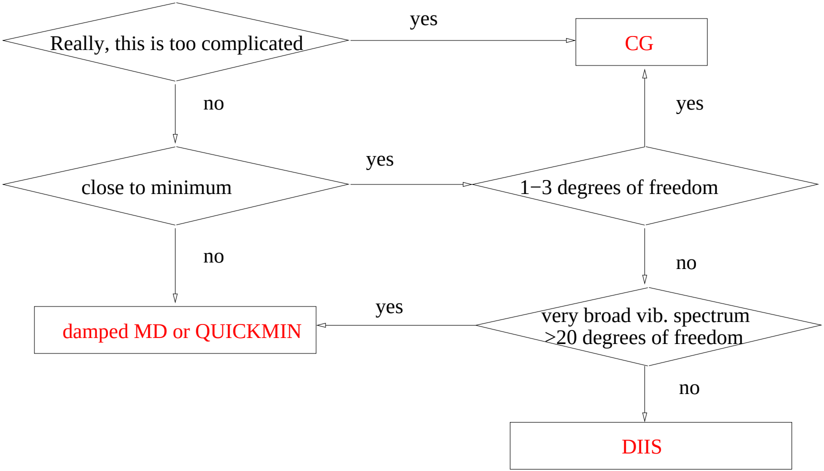
- `EDIFFG` “convergence criterium”:
  - $\texttt{EDIFFG} > 0: \quad |(E^N - E^{N-1})| < \texttt{EDIFFG}$
  - $\texttt{EDIFFG} < 0: \quad |\vec{F}_i^N| < |\ \texttt{EDIFFG}\ | \quad \forall i = 1, N_{\mathrm{ions}}$

INCAR Parameters in VASP

Parameter Usage by the Algorithms of VASP

- DIIS
  - `POTIM (=0.5)` generally determines the step size (no line minimizations)
  - `NFREE` # of ionic steps stored in the iteration history: for the set of points $\vec{x}^i$ and gradients $\vec{g}^i$ $(i = 1, \ldots, N)$
    `NFREE (=5)` $= \max(N)$
- CG
  - `POTIM (=0.5)` : size of the *first trial step*, the subsequent line minimization is performed using Brent's algorithm
- damped MD: in $\vec{v}_{N+1/2} = \Big((1-\mu/2)\vec{v}_{N-1/2} - 2\alpha\vec{F}_N\Big)/(1+\mu/2)$
  - `POTIM` $\approx \alpha$, good choices: $0.15 <$ `POTIM` <0.4
  - `SMASS (=0.4)` $\approx \mu$, which should be $\approx 2\sqrt{\Gamma_{\mathrm{min}}/\Gamma_{\mathrm{max}}}$

Choice of the most Appropriate Algorithm



Really, this is too complicated

yes

CG

no

close to minimum

yes

1−3 degrees of freedom

yes

no

no

damped MD or QUICKMIN

yes

very broad vib. spectrum
>20 degrees of freedom

no

DIIS

Problem Handling

(Some Other) Reasons for Bad Convergence

- unreasonable starting geometry (POSCAR)
  - lattice parameters, atomic positions
  - check OUTCAR for interatomic distances, forces of the input geometry, external pressure, (if `ISIF` > 0)
- sub-optimal settings of (some) INCAR parameters
  - bad electronic convergence of (one of) the ionic steps $\longrightarrow$ wrong forces
  - check OSZICAR for the convergence of each ionic step: dE, charge density convergence
  - increase `NELM`, decrease the (spin density) mixing parameters
  - choose a different BZ-integration method `ISMEAR, SIGMA`
  - choose a different electronic relaxation algorithm `ALGO`
  - basis sets too small ($\longrightarrow$ aliasing errors)
- is the $\vec{k}$-mesh appropriate? (modify KPOINTS)

Problem Handling

Aliasing Errors

- related to errors caused by the truncated FFT grid
- folding theorem: $\rho = \int \psi_n^* \psi_n$ (V_G^H) contain components up to $2n = 2G_{\mathrm{cutoff}}$ after back-transformation from ρ_r to ρ_G (V)
- residual Vector $(V\psi)$: components up to $3G_{\mathrm{cutoff}}$
- Fourier grid has to include all wave-vectors up to $2G_{\mathrm{cutoff}}$.
- if this is not the case: $\longrightarrow$ aliasing ("wrap around") errors: components of ρ are wrapped around from the other side of the box due to the periodicity
- high frequency components are aliased to low-frequency components

Problem Handling

Drifts in the Forces

- impact of aliasing errors on the results::
- in a lattice with perfect translation symmetry: if all atoms of the cell are shifted by the same translation vector,
    - E has to remain exactly the same
    - forces sum up to 0: $\sum_{i=1}^{N_{\mathrm{at}}} \vec{F}_i = 0$
- aliasing errors destroy the translational invariance:
- $\Rightarrow$ atoms equivalent by symmetry are equivalent no longer
- $\Rightarrow$ drifts
- BUT VASP symmetrizes ρ and $\vec{F}$ explicitely unless `ISYM=0`

Problem Handling

Drifts in the Forces

- to reduce drifts in the forces (written in OUTCAR)
- bulk & surfaces: increase the precision `ENCUT, PREC`
- surfaces: in 3D periodic cell, the origin of the cell is arbitrary, i.e. the slab may start drifting through the vacuum
  - keep (at least) one layer fixed (`Selective Dynamics` option in POSCAR)
  - polar surfaces: include dipole corrections (`IDIPOL, LDIPOL`) to avoid artificial electrostatic forces across the vacuum layer

Outline

Cell Volume Optimization

Introduction

- the equilibrium volume V_{eq} and shape of a crystal calculated from *ab initio* depend on the XC-type used:
  - LDA: overbinding $\longrightarrow$ a_0 too small
  - PBE, PW91: underbinding $\longrightarrow$ a_0 too large
  - results are improved using specially designed functionals (PBEsol, HSE),...
- $\Rightarrow$ accurate calculations should always be performed for the cell at equilibrium for the respective XC-type to avoid artifacts (unless there is good reason not to do so)

Cell Volume Optimization

Strategies to obtain V_{eq}

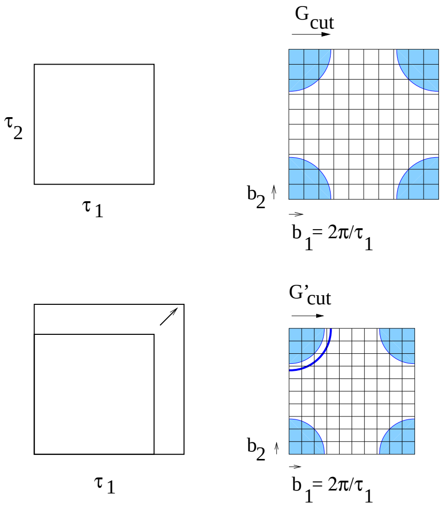
- "by hand": series of calculations at different cell volumes, $\longrightarrow$ $V_{eq} = V(\min(E(V))$:
  very old-fashioned, almost impracticable for non-cubic cells
- "by hand": fitting to thermodynamic equations:
  eg. Birch-Murnaghan fit
- VASP: automatic optimization, based on the calculated Hellmann-Feynman stresses
- the automatic geometry optimization sensitively depends on the quality of the used basis sets:
  - E-cutoffs (completeness of the basis set), FFT-grids
  - $\vec{k}$-meshes

Cell Volume Optimization

Energy Cutoff: Basis Sets

- at each $\vec{k}$, the plane waves that are included in the basis have to fulfill the criterium $\frac{\hbar^2}{2m_e}|\vec{G}+\vec{k}|^2 < E_{\mathrm{cutoff}}$
- E_{cutoff} defined by `ENCUT`: default: max(`ENMAX`), given in `POTCAR` for each element
- $E_{\mathrm{cutoff}} \approx \vec{G}^2 \Rightarrow \approx$ changes of cell volume and -shape
- $\Rightarrow$ the default cutoff should only be used for calculations with fixed cell-shape and -volume, eg.
    - frozen phonons
    - surface and adsorption calculations
    - MD (NVT ensemble)

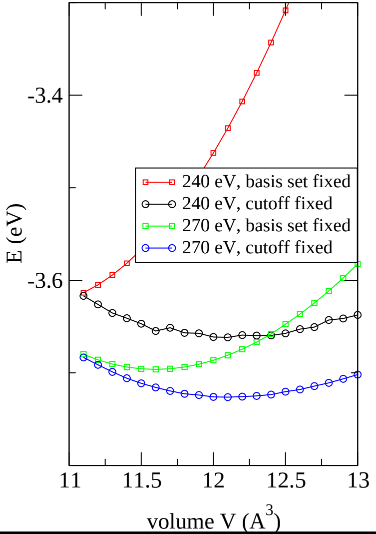
Cell Volume Optimization



explanation:

- lattice expanded $\tau_1 \longrightarrow \tau_1'$
- cutoff decreases by a a factor $\frac{\tau_1}{\tau_1'}$
- effective cutoff G_{cut}' is lower
- E is overestimated for larger Vs
- the apparent V_{eq} is too small

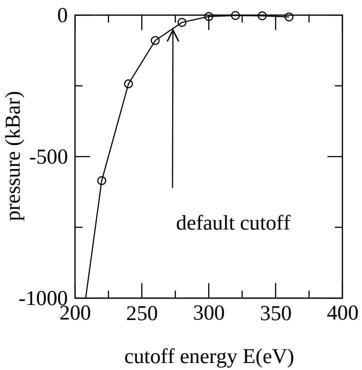
Cell Volume Optimization



Improvement using fixed basis sets?

- start from WAVECAR with `ISTART` =2
- NO!!, because
- $E^{\text{effective}}_{\text{cutoff}}$ decreases with increasing V
- $\Rightarrow$ quality of the basis set becomes worse with increasing V
- $\Rightarrow$ $\min(E(V))$ is shifted
- dense $\vec{k}$ meshes necessary to obtain smooth curves $(|\vec{k} + \vec{G}|^2)$!

Cell Shape relaxations



Stress Tensor

- VASP does not adopt the basis set in a run
- stress tensor σ_{ij}: implicitely calculated with a fixed-basis-set setup
- for Cu (270eV): contraction predicted by error (p=-50 kB)
- increase `ENCUT` (by 30%) to
  - perform lattice relaxations
  - calculate stress tensors and pressure ($P = \frac{1}{3}\mathrm{Tr}\sigma_{ij}$)

Cell Shape relaxations

"recipe" for Determining Cell Shapes

- always use an increased cutoff: `ENCUT` = 1.3*max(`ENMAX`)
- do it step-wise:
  1. start with 1-2 steps (`NSW`) from your guessed input geometry (coarse pre-relaxation)
  2. delete `WAVECAR`
  3. continue from `CONTCAR` with slightly more steps
  4. repeat 1-3 until the remaining pressure (and stress tensor components) are in accordance with the afforded accuracy
- if the space-group of the system is known, use `ISYM = 2` to avoid symmetry violations due to numerical errors

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Introduction

Basics

- vibrations of the crystal lattice influence
  - elastic
  - thermodynamic
  - optical
  - electronic transport properties
  - “soft modes” indicate
    phase transitions (bulk) or
    dissociation (dissociative adsorbtion processes)

Introduction

Basics

- if atom m in cell l of a crystal $\vec{R}_0(lm)$ is displaced by $\vec{u}$ $\longrightarrow \vec{R}(lm) = \vec{R}_0(lm) + \vec{u}(lm)$
- kinetic energy: $T = \frac{1}{2}\sum_{lm\alpha} M_m \dot{u}_\alpha^2(lm)$, potential energy: expanded

$$V(\vec{R}(lm)) = \underbrace{V_0(\vec{R}_0(lm))}_{=V_0=0} + \underbrace{\sum_{lm\alpha} \frac{\partial V(\vec{R}(lm))}{\partial R_\alpha(lm)} u_\alpha(lm)}_{=0 \text{ in equilibrium}}$$

$$+ \frac{1}{2} \sum_{lm\alpha, l'm'\beta} \underbrace{\frac{\partial^2 V(\vec{R}(lm))}{\partial R_\alpha(lm)\partial R_\beta(l'm')}}_{\Phi_{\alpha\beta}(ll'mm') \text{ force constant}} u_\alpha(lm) u_\beta(l'm')$$

- $\Phi_{\alpha\beta}(ll'mm')$: derivative taken at $\vec{R}(lm) = \vec{R}_0(lm)$

Introduction

Basics

- $\Phi_{\alpha\beta}(ll'mm')$: component α of the force acting on atom (lm), caused by the displacement of atom $(l'm')$ in direction β
- equations of motion

$$M_m \ddot{u}_\alpha(lm) = -\frac{\partial V}{\partial u_\alpha(lm)} = -\sum_{l'm'\beta} \Phi_{\alpha\beta}(ll'mm') u_\beta(l'm')$$

- use symmetry
- harmonic ansatz: $u_\alpha(lm,t) = \sqrt{M_m} e_\alpha(m) e^{i\vec{q}\vec{R}_l} e^{i\omega t}$

$$\omega^2 e_\alpha(m) = \sum_{\beta,m'} e_\beta(m') \underbrace{\left(\sum_{l'} (M_m M_{m'})^{-\frac{1}{2}} \Phi_{\alpha\beta}(ll'mm') e^{i\vec{q}(\vec{R}_{l'}-\vec{R}_l)}\right)}_{D_{\alpha\beta}(mm',\vec{q}) \quad \text{dynamical} \quad \text{matrix}}$$

Phonons

Bulk

- VASP calculates phonons at the zone-center
  $\Rightarrow$ supercell approach
- the elements of the Hessian Matrix are calculated either by
  - finite displacement of the ions:
    `IBRION = 5,6; NFREE, POTIM`
    assume: displacements are within the harmonic limit
  - using density functional perturbation theory `IBRION = 7,8`
- the tags making use of the symmetry (`IBRION = 6,8`) can be used in vasp.5.2 only

Phonons

Vibrational Modes of Molecules

- select vibrational modes of interest using `Selective Dynamics` in POSCAR (eg. change of the modes of a molecules upon adsorption on a surface)
- vibrational frequencies of adsorbates: usually calculated accurately if
  - only the adsorbate itself and the NN substrate atoms are not kept fixed
  - in any case: test how many “shells” have to be included to converge the frequencies
  - saves computing time

Problem Handling

possible sources of errors

- negative frequencies (imaginary modes):
  - *may* indicate structural instabilities (mode softening),
  - or: calculation not properly converged ⟶ increase `EDIFF` from the default value
- VASP.4.6 only: `POTIM` has to be set explicitely: recommended `POTIM = 0.015` or smaller, the default value (0.5) certainly is *not* within the harmonic limit. ⟶ unreasonable frequencies
- VASP can *not* continue from an unfinished run. ⟶ for the calculation of eg vibration frequencies of adsorbates (large number of atoms in the unit cell): reduce the calculated vibration modes to a reasonable number

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Introduction

General Remarks

- classical equations of motion (EOM) for atoms in a microcanocical NVE ensemble (p: momenta , q: positions)

$$H(p,q) = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{m_i} + V(q_1, ...q_n)$$

$$\frac{dp}{dt} = -\frac{\partial H(p,q)}{\partial q} \quad , \quad \frac{dq}{dt} = \frac{\partial H(p,q)}{\partial p}$$

- ergodic hypothesis: ensembe and time averages are related:

$$\langle A \rangle_H = \frac{\int dpdqA(q)e^{-\frac{H}{k_B T}}}{\int dpdqe^{-\frac{H}{k_B T}}} = \frac{1}{\tau}\int_0^{\tau} dtA(t)$$

- $\Rightarrow$ MD can be used to compute observables A.

MD Algorithms implemented in VASP

Standard Version

- standard MD: on the Born-Oppenheimer surface, Hellmann-Feynman forces, Thermostat: Nosé
- Newtonian EOM for the set of atoms i, $M_i\ddot{\vec{R}}_i(t) = -\frac{\partial E}{\partial \vec{R}_i(t)}$
- $\longrightarrow$ coupled set of equations, wavefunctions kept are orthonormal via a Lagrangian multiplier λ_{ij}

$$\mu\ddot{\psi}_i(\vec{r},t) = -\frac{\delta E}{\delta\psi_i^*(\vec{r},t)} + \sum_j \lambda_{ij}\psi_j(\vec{r},t)$$

- Verlet algorithm with damping factor (friction term) μ

$$\begin{aligned}\vec{v}_{N+1/2} &= ((1-\mu/2)\vec{v}_{N-1/2} - 2\alpha\vec{F}_N)/(1+\mu/2)\\ \vec{x}_{N+1} &= \vec{x}_N + \vec{v}_{N+1/2}\end{aligned}$$

MD Algorithms implemented in VASP

Introduction: (Chemical) Reactions

- for any reaction, according to Arrhenius' law:

$$\frac{dc_0(i)}{dt} = -k c_0(i) \quad k = Ae^{-\frac{\Delta E^{\ddagger}}{k_B T}}, \quad A: \text{Arrhenius prefactor}$$

- Eyring-Polanyi theory: $k = \frac{k_B T}{h} e^{-\frac{\Delta A^{\ddagger}}{k_B T}}$
$\Delta A^{\ddagger}$... free energy difference between the transition state (‡) and the initial state (0).
- the free energy A can be evaluated via statistical thermodynamics:

$$A_i = -k_B T \log Q_i \Rightarrow k = -\frac{k_B T}{h} \cdot \frac{Q^{\ddagger}}{Q^0} \quad Q: \text{ partition function}$$

Introduction

Some Statistics' Basics

- Q^{tot} for species i $Q_i^{\mathrm{tot}} = Q_i^{\mathrm{trans}} Q_i^{\mathrm{rot}} Q_i^{\mathrm{vib}} Q_i^{\mathrm{elecronic}}$
  in extended systems with translational symmetry:
  Q_i^{trans} and Q_i^{rot} are constant and cancel out
- Q_i^{vib}: $Q_i^{\mathrm{vib}} = \prod_{i=1}^{M} \frac{e^{-\frac{h\nu_i}{2k_B T}}}{1-e^{-\frac{h\nu_i}{k_B T}}}$ (harmonic approx.)
- $Q_i^{\mathrm{electronic}}$: $Q_i^{\mathrm{el}} = e^{-\frac{E_i}{k_B T}} \Rightarrow \frac{Q_i^{\mathrm{el},\ddagger}}{Q_i^{\mathrm{el},0}} = e^{-\frac{\Delta E_i^{\ddagger}}{k_B T}}$
- the reaction constant k is given as

$$k = -\frac{k_B T}{h} \cdot \frac{Q^{\mathrm{vib},\ddagger}}{Q^{\mathrm{vib},0}} \cdot e^{-\frac{\Delta E_i^{\ddagger}}{k_B T}}$$

MD Algorithms implemented in VASP

Advanced MD Techniques

- standard version of MD:
  - uses Carthesian coordinates
  - transition states: obtained using the Nudged Elastic Band (NEB) method
  - $\longrightarrow$ inefficient, slow for chemical reactions
- improvement: Advanced MD Techniques
  - instead of cartesian coordinates: use a more clever choice of delocalized, internal coordinates ξ (bond lenghts, -angles,. . .)
  - ergodic hypothesis used to calculate $\langle A \rangle$ via its time average
- implemented in VASP.5 by Tomas Bucko
- compile VASP with `-Dtbdyn` to replace standard MD by advanced MD techniques

MD Algorithms implemented in VASP

Advanced MD Techniques

- in systems with richly structured Potential Energy Hypersurfaces (PES): forces on the atoms might not drag the system over an energy barrier of the PES
- ⇒ the system gets stuck in a basin of the PES
- methods to avoid this behavior:
    - add a bias potential $\tilde{V}(\xi)$ to enhance the sampling in regions of the PES with low probability $P(\xi_i)$ (eg transition state regions):
      "umbrella sampling"
    - constrain the MD by adding geometrical constraints via additional terms in the Lagrangian, enforcing the constraint
      "blue moon sampling"

MD Algorithms implemented in VASP

Advanced MD Techniques: Biased MD

- a bias potential $\tilde{V}(\xi)$ is used to enhance sampling of the internal coordinate $\xi(q)$

$$\begin{aligned} \tilde{H}(p,q) &= H(p,q) + \tilde{V}(\xi), \quad \xi = \xi(q) \\ \tilde{P}(\xi_i) &= \langle \delta(\xi(q) - \xi_i) \rangle_{\tilde{H}} = \frac{\int \delta(\xi(q) - \xi_i) e^{-\frac{\tilde{H}}{k_B T}} dpdq}{\int e^{-\frac{\tilde{H}}{k_B T}} dpdq} \end{aligned}$$

- 2. recover the correct distribution of A at the end by using

$$\langle A \rangle_H = \frac{\left\langle A(q) e^{\frac{\tilde{V}}{k_B T}} \right\rangle_{\tilde{H}}}{\left\langle e^{\frac{\tilde{V}}{k_B T}} \right\rangle_{\tilde{H}}}$$

MD Algorithms implemented in VASP

Advanced MD Techniques: Metadynamics

- additional DOFs (α) driving the reaction: ξ_α, $\dot{\xi}_\alpha$ (velocity) and mass μ_α, are coupled to the relevant geometrical parameters (collective variables $\Xi_\alpha(\mathbf{x})$) via harmonic springs with force constants k_α:

$$\mathcal{L} = \mathcal{L}_0 + \sum_{alpha} \frac{1}{2}\mu_\alpha \dot{\xi}_\alpha^{\,2} - \sum_{alpha} \frac{1}{2} k_\alpha (\Xi_\alpha(\mathbf{x}) - \xi_\alpha)^2 - \tilde{V}(t,\xi)$$

- $\tilde{V}(t,\xi) = h \sum_{i=1}^{t/t_G} e^{-\frac{|\xi(t)-\xi(it_G)|^2}{2w^2}}$
  sum of Gaussian hills (h_i, w_i) updated at every time-step t_G during the calculation
- t_G: 1-2 orders of magnitude $>$ than Δt of the MD
- $A(\xi)_{t=\infty} = -\lim_{t\to\infty} \tilde{V}(t,\xi) + \text{const}$

MD Algorithms implemented in VASP

Advanced MD Techniques: Constrained MD

- modify the Lagrange multiplier $\mathcal{L}$ by adding a term including all geometric constraints r :

$$\mathcal{L}(q,\dot{q})^* = \mathcal{L}(q,\dot{q}) + \sum_{i=1}^{r} \lambda_i \sigma_i$$

with $\sigma_i = \xi_i(q) - \xi_i$, ξ_i …fixed variable

1. standard leap-frog MD to obtain $\longrightarrow q_i(t+\delta t)$
2. use new positions to compute $\lambda_i \forall$ constraints
3. update $\vec{v}$ and q by adding a contribution due to the restoring force $(\approx \lambda) \longrightarrow q_i(t+\delta t)$
4. repeat 1-3 until $|\sigma(q)|$ matches the convergence criterium (SHAKE algorithm)

MD Algorithms implemented in VASP

Advanced MD Techniques: TD integration of A-gradients

- T. Bucko, J.Phys.Cond.Matt. **20**, 064211 (2008)
- the #DOF dynamical variables of $\hat{H}$ are split into
    - the active reaction variable $\xi^*(p_\xi, q_\xi)$, defining the reaction path $1 \longrightarrow 2$, (slow modes)
    - inactive set $\mathbf{q} = \{q_1, \ldots, q_{M-1}\}, p_\mathbf{q}$ (fast modes; not frozen, but do not contribute to the minimum A-path as their thermal motions are nearly harmonic)

$$\Delta A_{1 \longrightarrow 2} = \int_{\xi(1)}^{\xi(2)} d\xi \left(\frac{\partial A}{\partial \xi} \right)_{\xi^*}$$

- ξ is constrained to remain constant to $\xi^* \Rightarrow \dot{\xi} = 0$,
- also, $\Rightarrow p_\xi$ is not sampled in the MD

MD Algorithms implemented in VASP

Advanced MD Techniques: TD integration of *A*-gradients

the Hamiltonians of the constrained ($H^c_{\xi^*}$) and unconstrained (H) ensembles are:

$$\begin{aligned} H^c_{\xi^*} &= \frac{1}{2}\mathbf{p}^{\mathbf{t}}\mathbf{X}\mathbf{p} + V(\mathbf{q},\xi) \\ H &= H^c_{\xi^*} + p^t_\xi(\mathbf{Y}\cdot\mathbf{p}_q) + \frac{1}{2}(p^t_\xi Z p_\xi) \end{aligned}$$

with

$$X_{\alpha,\beta} = \sum_{i=1}^{M}\frac{1}{m_i}\frac{\partial q_\alpha}{\partial x_i}\frac{\partial q_\beta}{\partial x_i}, Y_\alpha = \sum_{i=1}^{M}\frac{1}{m_i}\frac{\partial \xi}{\partial x_i}\frac{\partial q_\beta}{\partial x_i}, Z = \sum_{i=1}^{M}\frac{1}{m_i}\left(\frac{\partial \xi}{\partial x_i}\right)^2$$

$(\alpha,\beta = 1,\dots M-1)$

MD Algorithms implemented in VASP

Advanced MD Techniques: TD integration of *A*-gradients

- constrained and unconstrained ensemble averages of a quantity $\mathcal{O}$ are related via a "blue moon" correction
  E.A.Carter *et.al.*, Chem.Phys.Lett **156**, 472 (1989)

$$\langle \mathcal{O} \rangle = \frac{\left\langle \mathcal{O} Z^{-\frac{1}{2}} \right\rangle_{\xi^*}}{\left\langle Z^{-\frac{1}{2}} \right\rangle_{\xi^*}}$$

- the constraints on the system to remain on the reaction path are included via the Lagrangian multiplier λ (accounting for the reaction coordinate, calculated using the SHAKE algorithm) in the modified Lagragian

$$\mathcal{L}^*(\mathbf{x}, \xi, \dot{\mathbf{x}}) = \mathcal{L}(\mathbf{x}, \dot{\mathbf{x}}) + \lambda(\xi\mathbf{x} - \xi)$$

MD Algorithms implemented in VASP

Advanced MD Techniques: TD integration of *A*-gradients

- the free energy gradients can then be calculated:

$$\left(\frac{\partial A}{\partial \xi}\right)_{\xi^*} = \frac{1}{< Z^{-\frac{1}{2}} >_{\xi^*}} \left\langle Z^{-\frac{1}{2}} \left[-\lambda_\xi + k_B T Z^{-1} \sum_{i=1}^{M} \frac{1}{m_i} \frac{\partial \xi}{\partial x_i} \frac{\partial Z}{\partial x_i} \right] \right\rangle_{\xi^*}$$

- crucial for blue moon ensemble techniques: appropriate choice of the parameter ξ

MD Algorithms implemented in VASP

Advanced MD Techniques: Slow Growth Approach

- linear change of the free-energy profile along a geometric parameter ξ from $\xi_{\text{initial state}} \longrightarrow \xi_{\text{final state}}$ with velocity $\dot{\xi}$
- irreversible work w^{irrev} to perform this transformation:

$$w_{1\to2}^{\text{irrev}} = \int_{\xi_{\text{i.s.}}}^{\xi_{\text{f.s.}}} \frac{\partial V(q)}{\partial \xi} \cdot \frac{\partial \xi}{\partial t} dt$$

- $w_{1\to2}^{\text{irrev}}$ is related to the free energy:

$$e^{-\frac{A_{1\to2}}{k_B T}} = \left\langle e^{-\frac{w_{1\to2}^{\text{irrev}}}{k_B T}} \right\rangle$$

- for infinitesimally small $\dot{\xi}$ (adiabatic transformation): $w_{1\to2}^{\text{irrev}} = \Delta A$ (free energy difference)

MD Algorithms implemented in VASP

Parinello-Rahman dynamics

- NpT ensembles with the enthalpy $H = E + pV$
- EOM of the atoms' and the lattice DOFs:

$$\mathcal{L}(s, \mathbf{h}, \dot{s}, \dot{\mathbf{h}}) = \frac{1}{2}\sum_{i=1}^{N} m_i \dot{s}_i^t \mathbf{h}^t \mathbf{h} \dot{s}_i - V(s, \mathbf{h}) + \frac{1}{2} W \mathrm{Tr}(\dot{\mathbf{h}}^t \dot{\mathbf{h}}) - p_{\mathrm{ext}} \Omega$$

  s_i: atomic positions, $\mathbf{h}$: matrix formed by the lattice vectors, $\Omega = \det h$: cell volume, $W[m]$: constant, mass of the lattice DOFs

- thermostat to be used: Langevin Thermostat

MD Algorithms implemented in VASP

MD-related files in VASP

- standard MD: `PCDAT` (OUT): pair correlation function
- advanced MD (-Dtbdyn)
  - `ICONST` (IN): constraints to geometry parameters (bond lengths, - angles, direct coordinates of $\vec{a}, \vec{b}, \vec{c}$, constraint status,. . .)
  - `PENALTYPOT` (IN): bias potentials (position in the space of active coordinates, height and width of the Gaussian hills)
  - `REPORT` (OUT): MD-related output
  - `HILLSPOT` (IN/OUT): Gaussian hills generated on the fly

Thermostats implemented in VASP

The Nosé Thermostat

- system is coupled to 1 additional DOF (=heat bath s)
- non-Hamiltonian EOM of the extended system:

$$\begin{aligned} M_I \ddot{\vec{R}}_I(t) &= -\frac{\partial E}{\partial \vec{R}_I(t)} - M_I \dot{\vec{R}}_I(t) \frac{\dot{s}(t)}{s(t)} \\ Q \frac{d(\dot{s}(t)/s(t))}{dt} &= -\sum_I M_I |\dot{\vec{R}}_I(t)|^2 - \underbrace{(3N-1)}_{\#DOF} k_B T \end{aligned}$$

- Q Nosé mass: response of s to the fluctuations of the ionic system
- characteristic frequency of the thermostat at T: $\omega_T^2 = \frac{2gk_BT}{Q}$
- equilibration ions – heat bath: coupling of the system to the Thermostat is most effective if ω_T is of the same order of magnitude of the characteristic frequency of the system to which it is coupled.

Thermostats implemented in VASP

The Nosé Thermostat

- coupling of the system to the thermostat via $\omega_T (\sim Q^-1)$ corresponds to a canonical ensemble at fixed temperature T:
- using the Nosé thermostat: conservation of the expectation value of the energy for the *combined* system (cell + thermostat)

$$\Omega = \Omega_{mc} + \frac{1}{2}(\frac{\dot{s}}{s})^2 + 3(N-1)k_B T \ln s$$

- micro-canonical ensemble: conservation of the energy Ω_{mc}:

$$\Omega_{mc} = \underbrace{T_{\rm ions}}_{E_{kin}} + \underbrace{E[\vec{R}_I, \psi_i, f_i]}_{\rm internal \quad E} + \underbrace{TS_{e^i}[f_i]}_{\rm electr. \quad entropy}$$

Thermostats implemented in VASP

Main Input Parameters for standard MDs (Nosé Thermostat)

- in `INCAR`
    - `IBRION = 0`: switches ionic relaxation algorithm to MD
    - `NSW`: number of MD steps (has to be given)
    - `SMASS`: choice of the ensemble
    - `POTIM`: time step in fs
    - `TEBEG, TEEND`: starting and final T (eg for simulated annealing)
    - `PREC = Normal`: recommended, (`Low` may lead to drifts)
- in `POSCAR` (optional): appended to the block of ionic positions, initial velocities $\vec{v}_{in}$ of the ions can be given (in Å/fs)

Thermostats implemented in VASP

INCAR: Choice of the Nosé mass: `SMASS`

- `SMASS = -3`: microcanonical ensemble: conservation of the total free energy ($\longrightarrow$ no thermostat), ions are accelerated by Hellmann-Feynman forces calculated from *ab initio*
- `SMASS = -2`: the initial velocities ($\vec{v}_{in}$) (read from `POSCAR`) are kept constant. actual step size: $\vec{v}_{in}$*`POTIM`
- `SMASS = -1`: rescaling of T after each `NBLOCK` step:
  - $T =$ `TEBEG` $+$ (`TEEND` - `TEBEG`) * NSTEP / `NSW`
  - between the T-jumps: microcanonical ensemble conditions
  - simulated annealing
- `SMASS = 0`: canonical ensemble; the Nosé mass Q is determined by VASP, averaging over 40 time-steps
- `SMASS` $>$ 0: Q set explicitely: it controls the frequency of T-oscillations

Thermostats implemented in VASP

The Andersen Thermostat

- coupling to the heat bath via random collisions of randomly chosen atoms with the heat bath $\longrightarrow$ stochastic impulsive forces on the atoms
- average number of collisions per atom and time-step: `ANDERSEN_PROB`
- `ANDERSEN_PROB` $= 0$ corresponds to a microcanonical NVE ensemble.
- VASP allows for up to 3 different sub-systems, coupled to 3 different Andersen thermostats

Thermostats implemented in VASP

The Langevin Thermostat

- T is maintained via modified EOMs:

$$M_I \ddot{\vec{R}}_I(t) = -\vec{F}_i + \vec{f}_i - \gamma_i \vec{p}_i$$

$\vec{f}_i$... random force with dispersion $\sigma_i = \frac{2 m_i \gamma_i k_B T}{\Delta t}$

  - NVT MD: `IBRION=0, ISIF=2, MDALGO=3`
  - NpT MD: `IBRION=0, ISIF=3, MDALGO=3`
    `LANGEVIN_GAMMA_L`: ...friction coefficient for the lattice DOF
    `PMASS`: mass for the lattice DOF
    (`PSTRESS`): forces acting on the lattice DOF:
    components of the stress tensor σ_{ij} are used to calculate the changes of the lattice constants and angles
    ⇒ increased `ENCUT` to avoid Pulay stress

Thermostats implemented in VASP

Choice of the Thermostat: `MDALGO`

- 0: standard MD as in VASP compiled without `-Dtbdyn`
- 1: Andersen
- 11: Metadynamics with Andersen
- 13: Andersen, up to 3 subsystems coupled to up to 3 independent Thermostats
- 2: Nosé Hoover
- 21: Metadynamics with Nosé Hoover
- 3: Langevin thermostat