

Relaxation and Molecular Dynamics

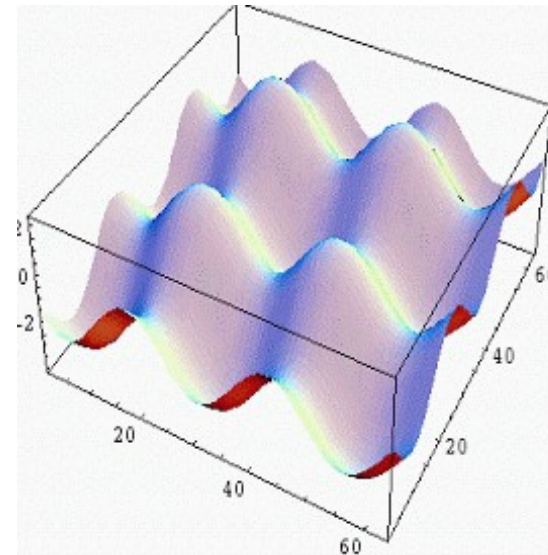
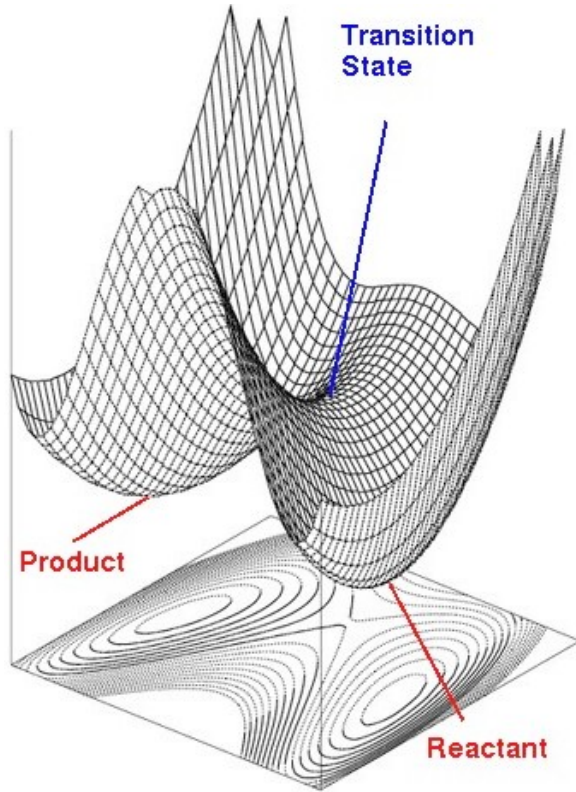


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Optimisation



- Local vs global minima
- PES is harmonic close to minima

Theory of Optimization

$$E(x + \delta x) = E(x) + G(x)\delta x + \frac{1}{2}H(x)\delta x^2 + \dots$$

Gradients

Hessian

$$\delta x = -\alpha H(x)^{-1} G(x)$$

$\alpha=1$ for quadratic region

Methods of Optimization

- Energy only:
 - simplex
- Energy and first derivatives (forces):
 - steepest descents (poor convergence)
 - conjugate gradients (retains information)
 - approximate Hessian update
- Energy, first and second derivatives:
 - Newton-Raphson
 - BFGS updating of Hessian (reduces inversions)
 - Rational Function Optimization (for transition states/ and soft modes)

SIESTA presently uses conjugate gradients

Optimization in SIESTA(1)

- ❑ Set runtime to conjugate gradients:
MD.TypeOfRun CG
- ❑ Set maximum number of iterative steps:
MD.NumCGsteps 100
- ❑ Optionally set force tolerance:
MD.MaxForceTol 0.04 eV/Ang
- ❑ Optionally set maximum displacement:
MD.MaxCGDispl 0.2 Bohr

Optimisation in SIESTA(2)

- ❑ By default optimizations are for a fixed cell
- ❑ To allow unit cell to vary:
MD.VariableCell true
- ❑ Optionally set stress tolerance:
MD.MaxStressTol 1.0 Gpa
- ❑ Optionally set cell preconditioning:
MD.PreconditionVariableCell 5.0 Ang
- ❑ Set an applied pressure:
MD.TargetPressure 5.0 GPa

Advice on Optimization in SIESTA

- Make sure that your MeshCutoff is high enough:
 - Mesh leads to space rippling
 - If oscillations are large convergence is slow
 - May get trapped in wrong local minimum

siesta: Atomic forces (eV/Ang):

1	-0.303027	-1.280971	0.567721
2	2.853904	0.005572	0.953702
3	-1.431055	2.487200	0.957536
4	-1.355350	-2.348017	0.895960

Tot	-0.235529	-1.136217	3.374919
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Max	2.853904	
Res	1.538755	$\text{sqrt}(\text{Sum } f_i^2 / 3N)$

Max	2.853904	constrained
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siesta: Atomic forces (eV/Ang):

1	0.006491	-0.000001	-0.695690
2	0.609572	0.000000	0.253077
3	-0.309017	0.538586	0.252556
4	-0.309017	-0.538586	0.252556

Tot	-0.001972	-0.000001	0.062500
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Max	0.695690	
Res	0.389268	$\text{sqrt}(\text{Sum } f_i^2 / 3N)$

Max	0.695690	constrained
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Optimization

- ❑ Optimize internal degrees of freedom first
- ❑ Optimize unit cell after internals
- ❑ Exception is simple materials (e.g. MgO)
- ❑ Large initial pressure can cause slow convergence
- ❑ Small amounts of symmetry breaking can occur
- ❑ Check that geometry is sufficiently converged (as opposed to force - differs according to Hessian)
- ❑ SCF must be more converged than optimisation
- ❑ Molecular systems are hardest to optimise

At the end of the optimization:

outcoor: Relaxed atomic coordinates (fractional):

0.35283880	0.35283832	0.35283911	1	Al	1
0.14716104	0.14716153	0.14716182	1	Al	2
0.64716098	0.64716140	0.64716141	1	Al	3
0.85283870	0.85283826	0.85283867	1	Al	4
0.55515471	0.94484219	0.25000112	2	O	5
0.25000041	0.55515618	0.94484478	2	O	6
0.94484499	0.24999874	0.55515695	2	O	7
0.44484487	0.05515776	0.74999926	2	O	8
0.74999875	0.44484374	0.05515659	2	O	9
0.05515481	0.75000093	0.44484422	2	O	10

Using Constraints

- The following can currently be constrained:
 - atom positions
 - cell strains
- User can create their own subroutine (constr)
- To fix atoms:

```
%block GeometryConstraints  
position from -1 to -10 0.0 0.0 1.0  
%endblock GeometryConstraints
```

- To fix stresses:

```
%block GeometryConstraints  
stress 4 5 6  
%endblock GeometryConstraints
```

Stress notation: 1=xx, 2=yy, 3=zz, 4=yz, 5=xz, 6=xy

Molecular Dynamics 1

- Follows the time evolution of a system
- Solve Newton's equations of motion:
- Treats electrons Quantum mechanically
- Treats nuclei *classically* $F = \frac{\partial E}{\partial x} = m a = m \frac{d^2 x}{dt^2}$
- Hydrogen may raise issues: - tunnelling
- Allows study of dynamic processes
- Annealing of complex materials
- Examines the influence of temperature

Molecular Dynamics 2

- Divide time into a series of timesteps, δt
- Expand position, velocity and acceleration as a Taylor series in δt
- Based on an initial set of positions, velocities and accelerations extrapolate to the next timestep e.g.

$$v(t + \delta) \approx v(t) + a \cdot \delta \quad (\text{true for constant acceleration})$$

- Correct values for errors based on actual values
- Different algorithms depending on:
 - order of Taylor expansion
 - which expansions (x,v,a) are combined
 - timesteps at which values are extrapolated

Molecular Dynamics 3

- ❑ Timestep must be small enough to accurately sample highest frequency motion
- ❑ Typical timestep is 1 fs (1×10^{-15} s)
- ❑ Typical simulation length = 1 - 10 ps
- ❑ *Is this timescale relevant to your process?*
- ❑ Simulation has two parts:
 - equilibration (redistribute energy)
 - production (record data)
- ❑ Results:
 - diffusion coefficients
 - free energies / phase transformations (very hard!)
- ❑ *Is your result statistically significant?*

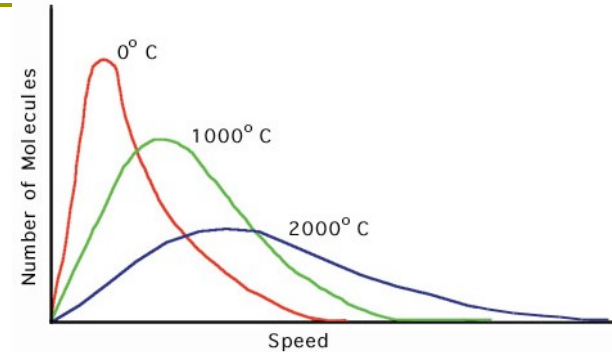
Molecular Dynamics in SIESTA(1)

- MD.TypeOfRun Verlet
NVE ensemble dynamics
- MD.TypeOfRun Nose
NVT dynamics with Nose thermostat
- MD.TypeOfRun ParrinelloRahman
NVE dynamics with P-R barostat
- MD.TypeOfRun NoseParrinelloRahman
NVT dynamics with thermostat/barostat
- MD.TypeOfRun Anneal
Anneals to specified p and T

Variable
Cell

Molecular Dynamics in SIESTA(2)

- Setting the length of the run:
MD.InitialTimeStep 1
MD.FinalTimeStep 2000
- Setting the timestep:
MD.LengthTimeStep 1.0 fs
- Setting the temperature:
MD.InitialTemperature 298 K
MD.TargetTemperature 298 K
- Setting the pressure:
MD.TargetPressure 3.0 Gpa
- Thermostat / barostat parameters:
MD.NoseMass /
MD.ParrinelloRahmanMass



Maxwell-Boltzmann

Annealing in SIESTA

- ❑ MD can be used to optimize structures:
MD.Quench true
- zeros velocity when opposite to force
- ❑ MD annealing:
MD.AnnealOption Pressure
MD.AnnealOption Temperature
MD.AnnealOption TemperatureAndPressure
- ❑ Timescale for achieving target
MD.TauRelax 100.0 fs