Forces and relaxation

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Slides: courtesy of Shobhana Narasimhan

Outline

- Forces and the Hellman-Feynman Theorem
- Stress (v. briefly)
- Techniques for minimizing a function
- Geometric optimization using forces

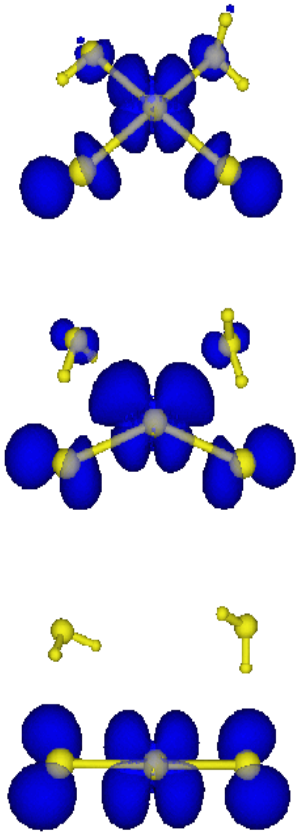
Calculation of forces from first principles

-) Model consists of atomic nuclei and electrons

-) Atomic nuclei follow classical mechanics

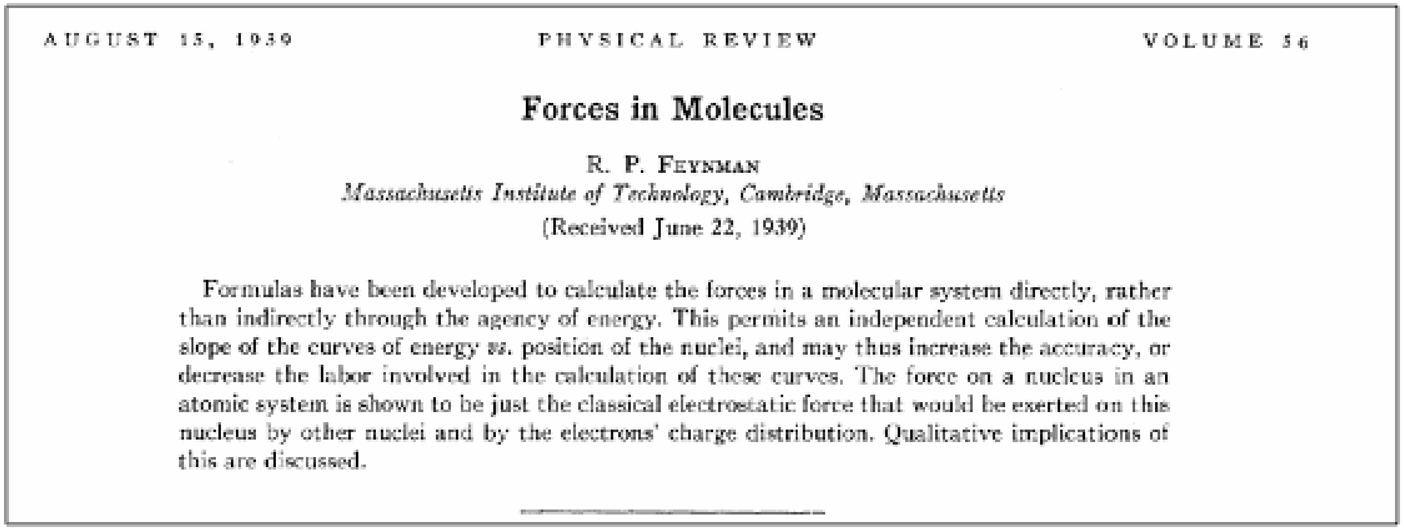
-) Electrons are quantum particles

-) Adiabatic approximation → during motion, electrons are always in the instantaneous ground state



Forces

- Need for geometry optimization and molecular dynamics.
- Can also use to get phonons.
- Could get as finite differences of total energy - too expensive!
- Use force (Hellmann-Feynman) theorem.
- Richard Feynman's Senior Thesis! (when he was 21…)



AUGUST 15, 1939 PHYSICAL REVIEW VOLUME 56

Forces in Molecules

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(Received June 22, 1939)

Formulas have been developed to calculate the forces in a molecular system directly, rather than indirectly through the agency of energy. This permits an independent calculation of the slope of the curves of energy *vs.* position of the nuclei, and may thus increase the accuracy, or decrease the labor involved in the calculation of these curves. The force on a nucleus in an atomic system is shown to be just the classical electrostatic force that would be exerted on this nucleus by other nuclei and by the electrons' charge distribution. Qualitative implications of this are discussed.

Hellmann-Feynman Theorem

- Want to calculate force on ion I:

$$\mathbf{F}_I = -\frac{d}{d\mathbf{R}_I}\langle\Psi|H|\Psi\rangle$$

- Get three terms:

$$\mathbf{F}_I = -\langle\Psi|\frac{\partial H}{\partial \mathbf{R}_I}|\Psi\rangle - \langle\frac{\partial\Psi}{\partial \mathbf{R}_I}|H|\Psi\rangle - \langle\Psi|H|\frac{\partial\Psi}{\partial \mathbf{R}_I}\rangle$$

- When $|\Psi\rangle$ is an eigenstate,

$$H|\Psi\rangle = E|\Psi\rangle$$

-Substitute this…

Hellmann-Feynman Theorem (contd.)

- The force is now given by

$$\begin{aligned}\mathbf{F}_I &= -\langle\Psi|\frac{\partial H}{\partial \mathbf{R}_I}|\Psi\rangle - E\langle\frac{\partial\Psi}{\partial \mathbf{R}_I}|\Psi\rangle - E\langle\Psi|\frac{\partial\Psi}{\partial \mathbf{R}_I}\rangle \\ &= -\langle\Psi|\frac{\partial H}{\partial \mathbf{R}_I}|\Psi\rangle - \xcancel{E\frac{\partial}{\partial \mathbf{R}_I}\langle\Psi|\Psi\rangle}\end{aligned}$$

- Note that we can now calculate the force from a calculation at ONE configuration alone – huge savings in time.
- If the basis depends on ionic positions (not true for plane waves), would have extra terms = Pulay forces.
- If $|\Psi\rangle$ is not an exact eigenstate (electronic calculation not well converged), may get big errors in forces calculated using this prescription!

Using H-F Theorem in a (plane-wave) DFT calculation

- Force on ion I given by:

$$\mathbf{F}_I = -\frac{\partial E(\mathbf{R})}{\partial \mathbf{R}_I} = -\left\langle \Psi(\mathbf{R}) \left| \frac{\partial H_{BO}(\mathbf{R})}{\partial \mathbf{R}_I} \right| \Psi(\mathbf{R}) \right\rangle$$

$$\mathbf{F}_I = -\int n_{\mathbf{R}}(\mathbf{r}) \frac{\partial V_{\mathbf{R}}(\mathbf{r})}{\partial \mathbf{R}_I} d\mathbf{r} - \frac{\partial E_N(\mathbf{R})}{\partial \mathbf{R}_I}$$

where

$V_{\mathbf{R}}(\mathbf{r})$ =(pseudo)potential due to ion cores

and $E_N(\mathbf{R})$ = interaction of ions with each other.

Hellmann-Feynman forces

In the Born-Oppenheimer approximation the total energy $E[R_I^{3N},\rho(R_I^{3N})]$ is a function of ionic coordinates R_I^{3N} and defines a 3N-dimensional hyper-surface, called Potential Energy Surface (PES).

The forces acting on the ions are given by (minus) the gradient of the total energy. Using Hellmann-Feynman theorem:

$$\mathbf{F}_I = -\frac{\partial E(\mathbf{R})}{\partial \mathbf{R}_I} = -\left\langle \Psi(\mathbf{R}) \left| \frac{\partial H_{BO}(\mathbf{R})}{\partial \mathbf{R}_I} \right| \Psi(\mathbf{R}) \right\rangle$$

$$\mathbf{F}_I = -\int n_{\mathbf{R}}(\mathbf{r}) \frac{\partial V_{\mathbf{R}}(\mathbf{r})}{\partial \mathbf{R}_I} d\mathbf{r} - \frac{\partial E_N(\mathbf{R})}{\partial \mathbf{R}_I}$$

where the electron-nucleus interaction and the electrostatic ion-ion interaction,

$$V_{\mathbf{R}}(\mathbf{r}) = -\sum_I \frac{Z_I e^2}{|\mathbf{r} - \mathbf{R}_I|} \qquad E_N(\mathbf{R}) = \frac{e^2}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$

depend only on the ionic positions

Hellmann-Feynman forces

$$\mathbf{F}_I = -\int n_{\mathbf{R}}(\mathbf{r}) \frac{\partial V_{\mathbf{R}}(\mathbf{r})}{\partial \mathbf{R}_I} d\mathbf{r} - \frac{\partial E_N(\mathbf{R})}{\partial \mathbf{R}_I}$$

The evaluation of forces is then a cheap byproduct of the electronic structure calculation.

The quality of forces depends on the quality of the electronic structure calculation!

From the forces:

- **structural optimization. Equilibrium condition given by**

$$\mathbf{F}_I \equiv -\frac{\partial E(\mathbf{R})}{\partial \mathbf{R}_I} = 0$$

- **molecular dynamics**
- **higher-order derivatives (phonons, ...)**

Stress

- Strain: $\mathbf{r}_\alpha \rightarrow (\delta_{\alpha\beta} + \epsilon_{\alpha\beta})\mathbf{r}_\beta$
- Stress: $\sigma_{\alpha\beta} = -\frac{1}{\Omega}\frac{\partial E}{\partial\epsilon_{\alpha\beta}}$
- Stress Theorem (Nielsen & Martin, 1985) → as for forces, can calculate at a single configuration.
- What if the primitive lattice vectors (specifying unit cell) are not optimal?
  - Forces on atoms may = 0
  (e.g., an FCC crystal with wrong lattice constant)
  - Stress will not be zero, however.
    < 0 → cell would like to expand.
    > 0 → cell would like to contract.

Use of forces (and stresses)

Forces can be used for 2 main applications

1) To study the dynamics of the system (molecular dynamics, phonons)

2) To identify the energy minima in the space of possible atomic configurations and geometries (relaxation)

Geometric Optimization

- Want to move the atomic positions around until the lowest-energy equilibrium configuration is obtained.

- At equilibrium,

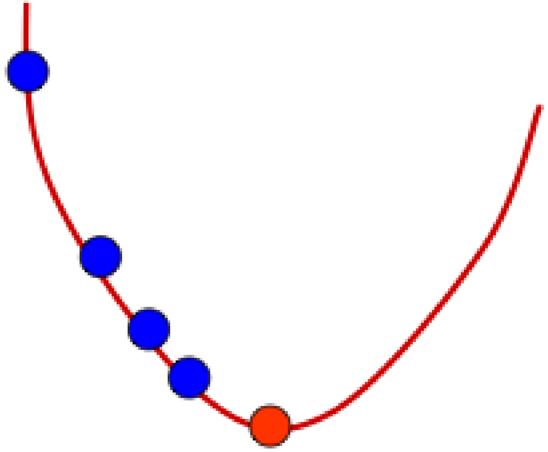
$$\boxed{\mathbf{F}_I \equiv -\frac{\partial E(\mathbf{R})}{\partial \mathbf{R}_I} = 0} \quad \text{for all } I.$$

- We are searching for a minimum in a $3N_I$-dim space.

Minimization in 1-D using gradients

- Consider a function $f(x)$; we want to find x_0, the value of x where the function has its minimum value.
- Iterative methods: successive approximations $x^1, x^2, x^3, \ldots x^n \ldots x_0$
- Can take several small downhill steps, in the direction opposite the gradient $f'(x^n)$.

$$\boxed{x^{n+1} = x^n - \beta^{(n)} f'(x^n)}$$

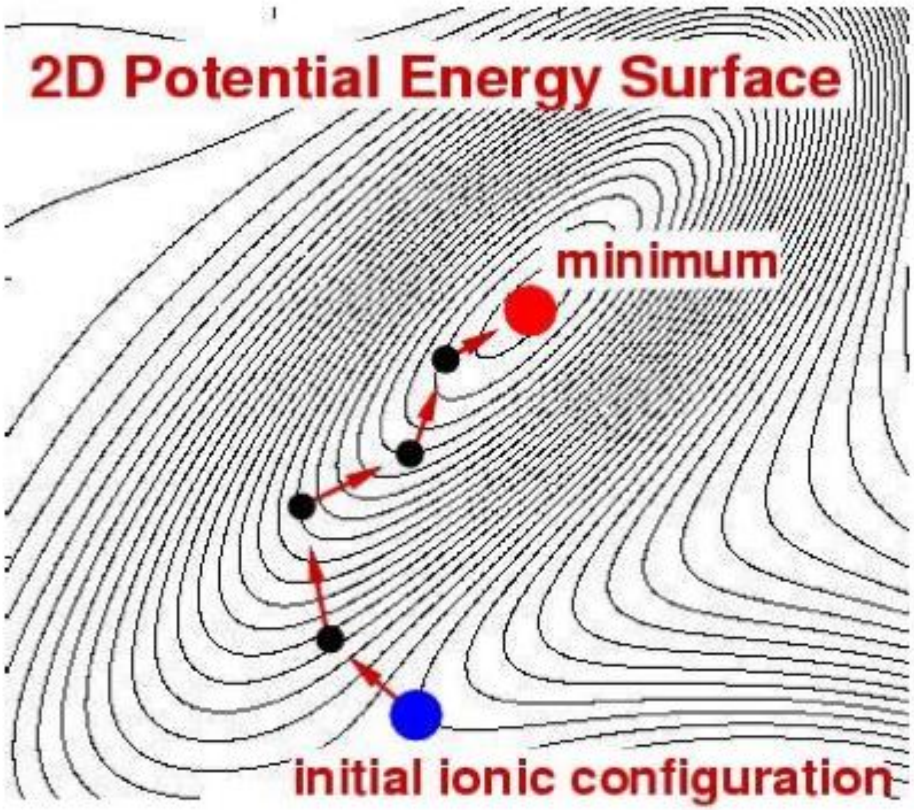


- Might take a long time to converge.

Note: need first derivatives

Structural optimizations

Several algorithms for searching an equilibrium configuration, close to the initial ionic configuration (a local minimum of the PES). For example:



Steepest Descent optimisation

$$\dot{X}_I^{3N} = F(X_I^{3N})$$

discretisation

$$X_{k+1} = X_k - \lambda \frac{g_k}{|g_k|}$$

gradient unitary vector

Quasi-Newton ionic relaxation

the Broyden Fletcher Goldfarb Shanno algorithm

Taylor expansion of the energy around a stationary point (X_{k+1}):

$$s_k = X_{k+1} - X_k$$

Hessian matrix

$$E(X_{k+1}) - E(X_k) = g(X_k) \cdot s_k + \frac{1}{2} s_k^T H_k s_k$$

gradient vector

Quasi-Newton ionic relaxation

the Broyden Fletcher Goldfarb Shanno algorithm

Equivalently, for the gradient vector we have:

$$g(X_{k+1}) - g(X_k) = H_k s_k$$

Stationary condition:

Newton-Raphson step:

$$\|g(X_{k+1})\|_\infty = 0 \quad \Longrightarrow \quad s_k^{NR} = -H_k^{-1} g_k$$

Quasi-Newton ionic relaxation

the Broyden Fletcher Goldfarb Shanno algorithm

trust radius

$$s_k^{NR} = -H_k^{-1} g_k$$

$$X_{k+1} = X_k + T_k^L \frac{s_k^{NR}}{|s_k^{NR}|}$$

The inverse Hessian matrix is updated using the BFGS scheme:

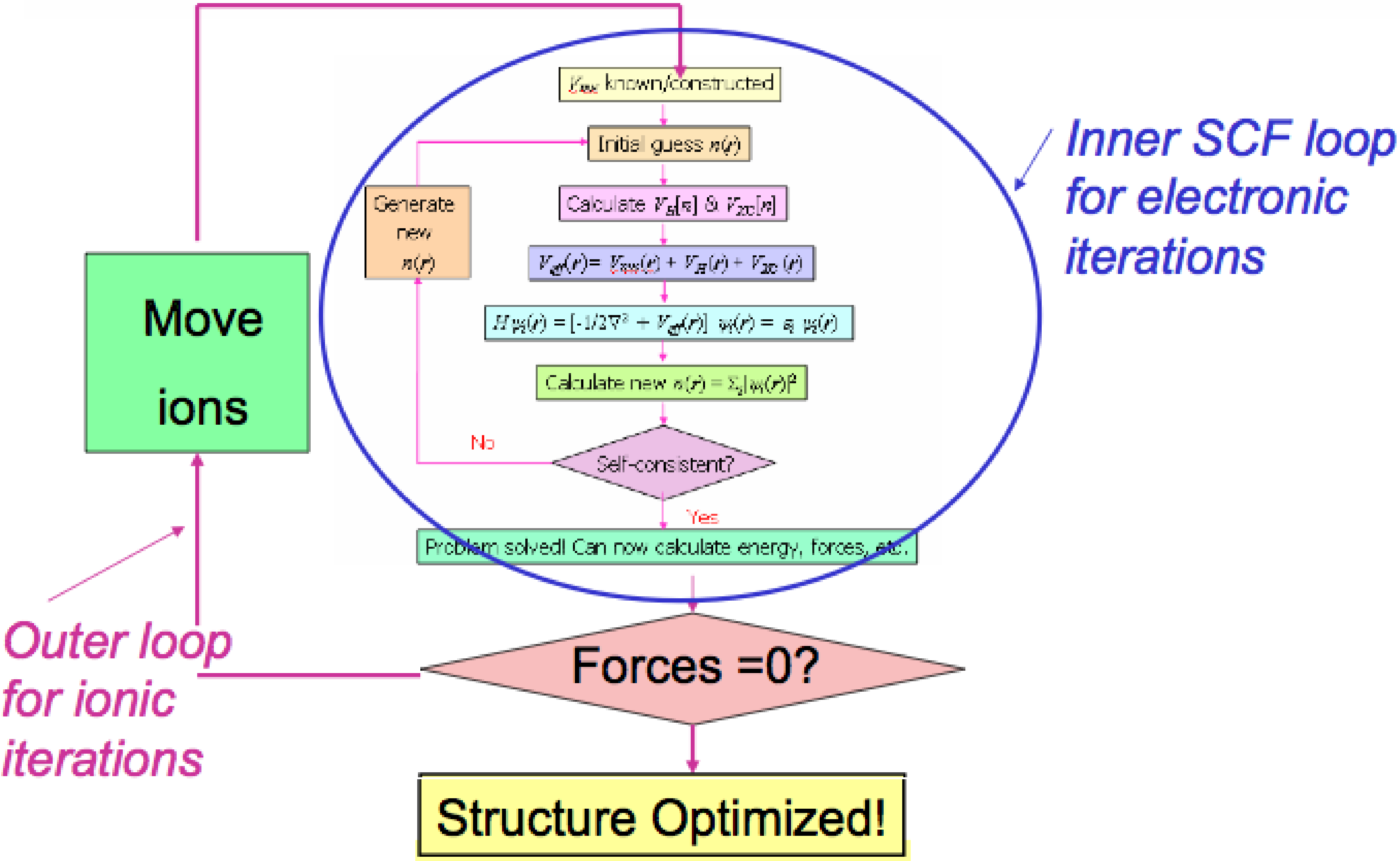
$$H_{k+1}^{-1} = H_k^{-1} + \left(1 + \frac{\gamma_k^T H_k^{-1} \gamma_k}{s_k^T \gamma_k}\right) \frac{s_k s_k^T}{s_k^T \gamma_k} - \left(\frac{s_k \gamma_k^T H_k^{-1} + H_k^{-1} \gamma_k s_k^T}{s_k^T \gamma_k}\right)$$

$$\gamma_k = g_{k+1} - g_k$$

Back to the Problem of Ionic Relaxation

- Function f to be minimized is total energy E_{tot} .
- Points $\mathbf{x}$ in $3N_I$-d space correspond to set of ionic coordinates $(x_1, y_1, z_1, x_2, y_2, z_2, \ldots x_{NI}, y_{NI}, z_{NI})$.
- Gradients $\nabla f(\mathbf{x})$ correspond to set of 3 components of forces on the N_I ions.
- Forces can be computed using Hellmann-Feynman theorem.
- Now use a minimization scheme to find the ionic positons that give the lowest value of E_{tot}, which is also when the forces on all ions are (close to) zero.

An Outer Loop: Ionic Relaxation



V_{ext} known/constructed

Initial guess $n(r)$

Calculate $V_H[n]$ & $V_{XC}[n]$

$V_{eff}(r) = V_{ext}(r) + V_H(r) + V_{XC}(r)$

$H\psi_i(r) = [-1/2\nabla^2 + V_{eff}(r)]\ \psi_i(r) = \varepsilon_i\ \psi_i(r)$

Calculate new $n(r) = \Sigma_i|\psi_i(r)|^2$

Self-consistent?

No

Generate new $n(r)$

Yes

Problem solved! Can now calculate energy, forces, etc.

Inner SCF loop for electronic iterations

Forces =0?

Move ions

Outer loop for ionic iterations

Structure Optimized!

Ionic Relaxation in PWscf

- Tell the program to carry out ionic relaxation, and say which method to use to find minimum

```
&control
calculation = ‘relax’
.
.
.
ion_dynamics = ‘bfgs’
               ‘damp’
```

Ionic Relaxation in PWscf (contd.)

- Say which atoms are to be moved & in which directions.

- e.g., for a four-layer Al(001) slab:

```
ATOMIC_POSITIONS
Al   0.000 0.000 2.828 0 0 1
Al   0.500 0.500 2.121 0 0 1
Al   0.000 0.000 1.414 0 0 0
Al   0.500 0.500 0.707 0 0 0
```

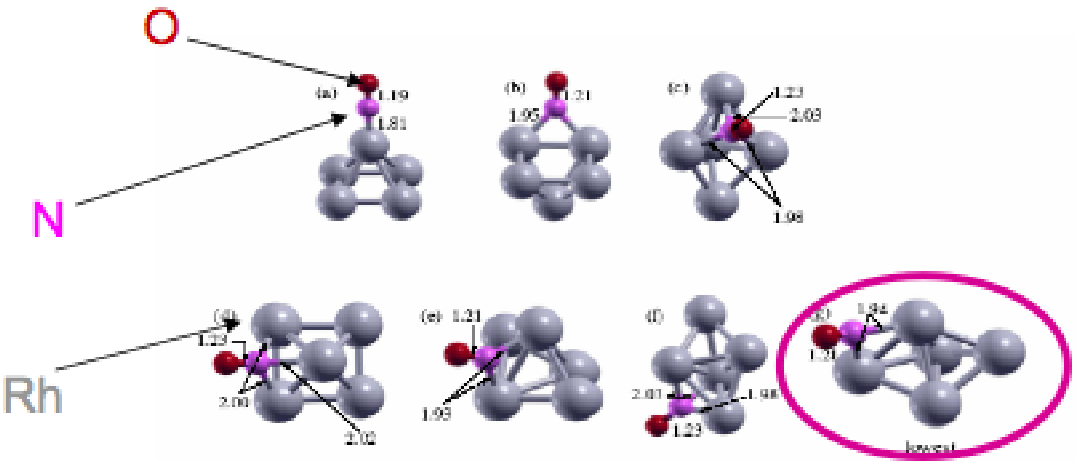
Allow these atoms to move only along z

Fix these atoms

Equilibrium Geometries

- In some cases, there are lots of equilibrium geometries (corresponding to local minima in the energy landscape).
- Finding the global minimum can be challenging!

e.g., NO adsorbed on a 5-atom Rh cluster:



Ghosh, Pushpa, de Gironcoli & Narasimhan

Calculation of forces from first principles

THE END