Electronic Structure

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Summary

- Importance of Electronic Structure Theory
- What is Electronic Structure Theory
- Some personal examples

Impact of Electronic Structure Theory

Top 15 PR articles ranked by PR citations (June 2003)

Publication				Citations	Title	Authors	Type	Area
PR	140	A1133	1965	3227	Self-Consistent Equations...	W. Kohn and L. J. Sham	Theory	Cond. Mat.
PR	136	B864	1964	2460	Inhomogeneous Electron Gas	P. Hohenberg and W. Kohn	Theory	Cond. Mat.
PRB	23	5048	1981	2079	Self-Interaction Correction...	J. P. Perdew and A. Zunger	Theory	Cond. Mat.
PRL	45	566	1980	1781	Ground State of the Electron...	D. M. Ceperley and B. J. Alder	Theory	Cond. Mat.
PR	108	1175	1957	1364	Theory of Superconductivity	J. Bardeen, L. N. Cooper and J. R. Schrieffer	Theory	Cond. Mat.
PRL	19	1264	1967	1306	A Model of Leptons	S. Weinberg	Theory	Particle
PRB	12	3060	1975	1259	Linear Methods in Band Theory	O. K. Anderson	Theory	Cond. Mat.
PR	124	1866	1961	1178	Effects of Configuration...	U. Fano	Theory	Atomic
RMP	57	287	1985	1055	Disordered Electronic Systems	P. A. Lee and T. V. Ramakrishnan	Review	Cond. Mat.
RMP	54	437	1982	1045	Electronic Properties of 2D...	T. Ando, A. B. Fowler, and F. Stern	Review	Cond. Mat.
PRB	13	5188	1976	1023	Special Points for Brillouin-Zone...	H. J. Monkhorst and J. D. Pack	Theory	Cond. Mat.
PRL	42	673	1979	965	Scaling Theory of Localization...	E. Abrahams, P. W. Anderson, et al.	Theory	Cond. Mat.
RMP	49	435	1977	910	Theory of Dynamical Critical	P. C. Hohenberg and B. I. Halperin	Review	Cond. Mat.
RMP	66	1125	1994	899	Vortices in High-Temperature	G. Blatter et al.	Review	Cond. Mat.
PRB	43	1993	1991	892	Efficient Pseudopotentials...	N. Troullier and J. L. Martins	Theory	Cond. Mat.

- Citations of PR articles by PR articles. As an example of a closed directed graph.
- Shows journal bias. Theory or review and condensed matter.
- 7 out of 15 most cited papers are in electronic structure theory. 5 of those 7 (in yellow) are technical, 2 (in red) are seminal.

Electronic Structure

- Around 1930 it was clear that quantum mechanics described the properties of materials (atoms, molecules, solids).
- Heisenberg even said that what was left to be done was "*chemistry*"
  - Condensed matter systems are complex
    - Only trivial systems have exact solutions
    - Computers are needed for calculations
  - Understanding, not numbers
    - The electronic energy per atom of Al is of the order of 5000 eV. The difference in energy between superconductor and normal Al is 0.0001 eV.
  - Condensed matter physics is useful

Electronic Structure

Schrodinger equation

$$H\Phi(\mathbf{r}_1, \xi_1, \ldots, \mathbf{r}_m, \xi_m, \mathbf{R}_1, \Xi_1, \ldots, \mathbf{R}_n, \Xi_n) = E\Phi(\mathbf{r}_1, \xi_1, \ldots, \mathbf{r}_m, \xi_m, \mathbf{R}_1, \Xi_1, \ldots, \mathbf{R}_n, \Xi_n)$$

Hamiltonian

$$H = \sum_{i=1}^{n} -\frac{1}{2M_i}\nabla^2_{\mathbf{R}_i} + \sum_{j=1}^{m} -\frac{1}{2}\nabla^2_{\mathbf{r}_j} + \sum_{i<j} \frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|} + \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,j} \frac{Z_i}{|\mathbf{R}_i - \mathbf{r}_j|}$$

Symmetry constraints

$$\Phi(\ldots, \mathbf{r}_i, \xi_i, \ldots, \mathbf{r}_j, \xi_j, \ldots) = -\Phi(\ldots, \mathbf{r}_j, \xi_j, \ldots, \mathbf{r}_i, \xi_i, \ldots)$$

Atomic Units

Here we will be using the system of atomic units: $\hbar = m_e = e^2/4\pi\varepsilon_o = 1$, where m_e is the electron mass and e its charge. In this system, the unit of energy is the Hartree (≈ 27.212 eV), the unit of length is the Bohr (≈ 0.527 Å), the speed of light is $c \simeq 137$ (the inverse of the fine structure constant, $\alpha = e^2/4\pi\epsilon_0\hbar c$), and the unit of time is $\approx 2.4 \times 10^{-17}$ seconds.

What is the problem

- Function of 10^{23} variables in a solid
- Smallest orbital has a size 1/Z
- One needs 10 Z x 10 Z x 10 Z points per atom to describe space
- Antisymmetry is non-trivial to implement
- Electrons and ions have different energy and time-scales

What is the solution

- Separate the atoms from the nuclei
  - Born-Oppenheimer adiabatic approximation
- Electrons move in the mean field of other electrons
  - Density Functional Theory
  - Local density approximation (LDA)
  - Beyond LDA
- Treat core and valence electrons differently
  - Pseudopotential
  - Muffin-tin spheres: LAPW, LMTO,...

Born-Oppenheimer

- Electronic hamiltonian

$$H_e = \sum_{j=1}^{m} -\frac{1}{2}\nabla^2_{\mathbf{r}_j} + \sum_{i<j} \frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|} + \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,j} \frac{Z_i}{|\mathbf{R}_i - \mathbf{r}_j|}$$

$$H_e \Psi^{(k)}(\mathbf{r}_1, \ldots, \mathbf{r}_m; \mathbf{R}_1, \ldots, \mathbf{R}_n) = U^{(k)}(\mathbf{R}_1, \ldots, \mathbf{R}_n) \Psi^{(k)}(\mathbf{r}_1, \ldots, \mathbf{r}_m; \mathbf{R}_1, \ldots, \mathbf{R}_n)$$

- Wavefunction

$$\Phi(\mathbf{r}_1, \ldots, \mathbf{r}_m; \mathbf{R}_1, \ldots, \mathbf{R}_n) \simeq \Psi^{(k)}(\mathbf{r}_1, \ldots, \mathbf{r}_m; \mathbf{R}_1, \ldots, \mathbf{R}_n) \chi^{(k,q)}(\mathbf{R}_1, \ldots, \mathbf{R}_n)$$

- Nuclear motion

$$H_N^{(k)} = \sum_{i=1}^{n} -\frac{1}{2M_i}\nabla^2_{\mathbf{R}_i} + U^{(k)}(\mathbf{R}_1, \ldots, \mathbf{R}_n)$$

$$H_N^{(k)} \chi^{(k,q)}(\mathbf{R}_1, \ldots, \mathbf{R}_n) = E^{(k,q)} \chi^{(k,q)}(\mathbf{R}_1, \ldots, \mathbf{R}_n)$$

Variational Principle

- Redefining the hamiltonian

$$H = T + U + V$$

$$T = \sum_i -\frac{1}{2}\nabla^2_{\mathbf{r}_i}$$

$$U = \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$$V = \sum_i v(\mathbf{r}_i)$$

- Variational principle

$$E[v] = \min_{\Psi \in A} \langle \Psi \mid H \mid \Psi \rangle$$

$$A = \{\Psi \mid \Psi(\ldots, \mathbf{r}_i, \ldots, \mathbf{r}_j, \ldots) = -\Psi(\ldots, \mathbf{r}_j, \ldots, \mathbf{r}_i, \ldots) \quad \text{and} \quad \langle \Psi \mid \Psi \rangle = 1\}$$

Density Functional Theory

- The universal density functional

$$F[\rho] = \min_{\Psi \in A_\rho} \langle \Psi \mid T + U \mid \Psi \rangle$$

$$A_\rho = \{\Psi \mid \Psi \in A \quad \text{and} \quad m \int \mathrm{d}^3 r_2 \ldots \int \mathrm{d}^3 r_m |\Psi(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_m)|^2 = \rho(\mathbf{r})\}$$

- The energy functional

$$E_v[\rho] = \int \rho(\mathbf{r}) v(\mathbf{r}) \, \mathrm{d}^3 r + F[\rho]$$

Properties of the Energy Functional of Density

- The minimum of $E_v[\rho]$ is the ground state energy E_0
- For the ground state ρ_0 we have $E_v[\rho_0]=E_0$

Thomas-Fermi theory

- Oldest DFT

$$F[\rho] = \int t_s(\rho(\mathbf{r}))\rho(\mathbf{r})\,\mathrm{d}^3r + \frac{1}{2}\iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,\mathrm{d}^3r\,\mathrm{d}^3r'$$

$$t_s(\rho) = \frac{3}{10}(3\pi^2)^{2/3}\rho^{2/3}$$

  - The kinetic energy is from the uniform electron gas

Kohn-Sham DFT

- Kinetic energy functional

$$T_0[\rho] = \min_{(f_1,\ldots,f_k,\phi_1,\ldots,\phi_k)\in B_\rho} \sum_{i=1}^{k} f_i \langle \phi_i \mid -\frac{1}{2}\nabla^2 \mid \phi_i \rangle$$

$$B_\rho = \{(f_1,\ldots,f_k,\phi_1,\ldots,\phi_k) \mid \langle \phi_i \mid \phi_j \rangle = \delta_{ij}, \quad 0 \le f_i \le 1, \quad \sum_{i=1}^{k} f_i |\phi_i(\mathbf{r})|^2 = \rho(\mathbf{r})\}$$

- Exchange and correlation functional

$$E_{xc}[\rho] = F[\rho] - \frac{1}{2}\iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,\mathrm{d}^3r\,\mathrm{d}^3r' - T_0[\rho]$$

Kohn-Sham equations

- minimization

$$\min_{\rho} E_v[\rho] = \min_{\rho}\Big(T_0[\rho] + \int \rho(\mathbf{r}) v(\mathbf{r})\,\mathrm{d}^3r + \frac{1}{2}\iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,\mathrm{d}^3r\,\mathrm{d}^3r' + E_{xc}[\rho]\Big)$$

- Kohn-Sham equations

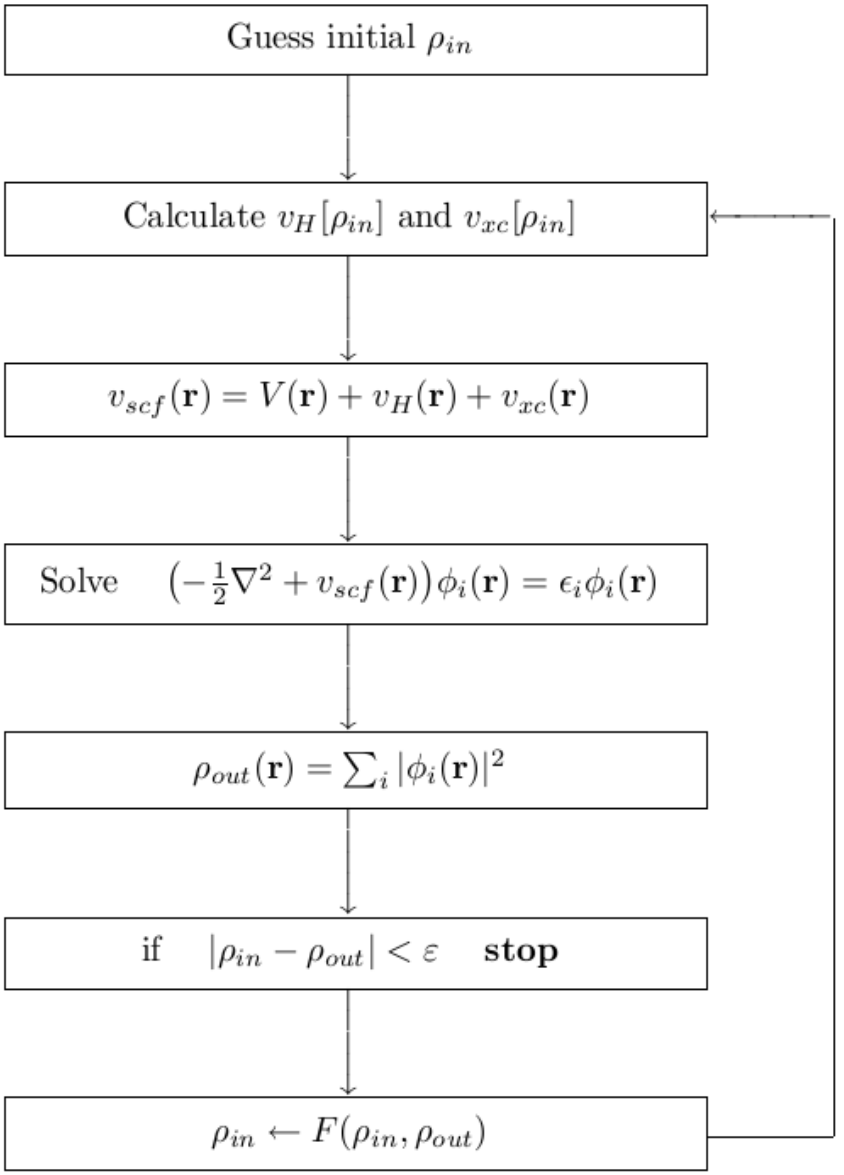
$$\{-\frac{1}{2}\nabla^2 + v(\mathbf{r}) + v_H(\mathbf{r};\rho] + v_{xc}(\mathbf{r};\rho]\}\phi_j(\mathbf{r}) = \epsilon_j\phi_j(\mathbf{r})$$

$$v_H(\mathbf{r};\rho] = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,\mathrm{d}^3r'$$

$$v_{xc}(\mathbf{r};\rho] = \frac{\delta E_{xc}[\rho]}{\delta\rho(\mathbf{r})}$$

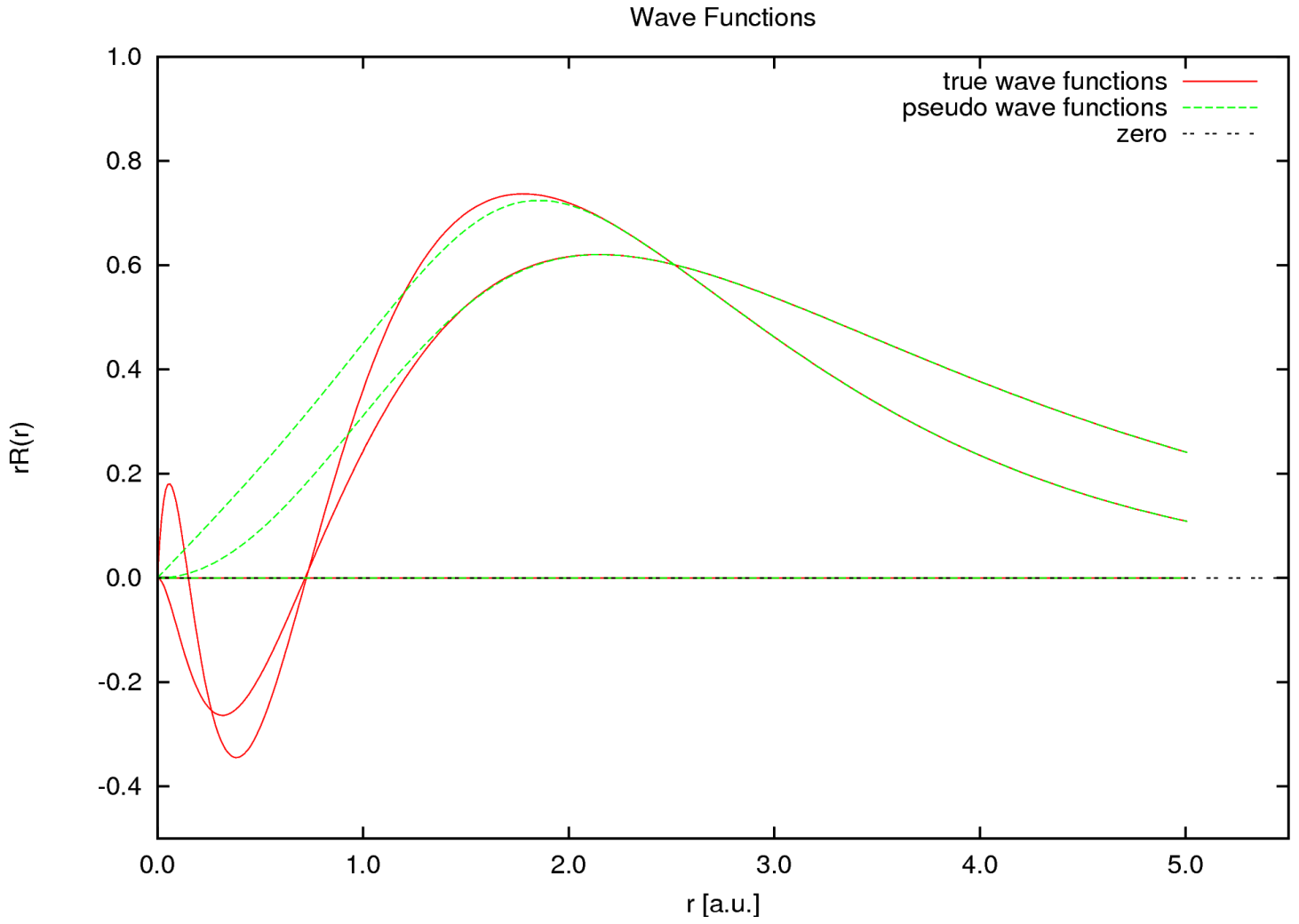
$$\rho(\mathbf{r}) = \sum_{i=1}^{k} f_i|\phi_i(\mathbf{r})|^2$$

Self Consistent Cycle



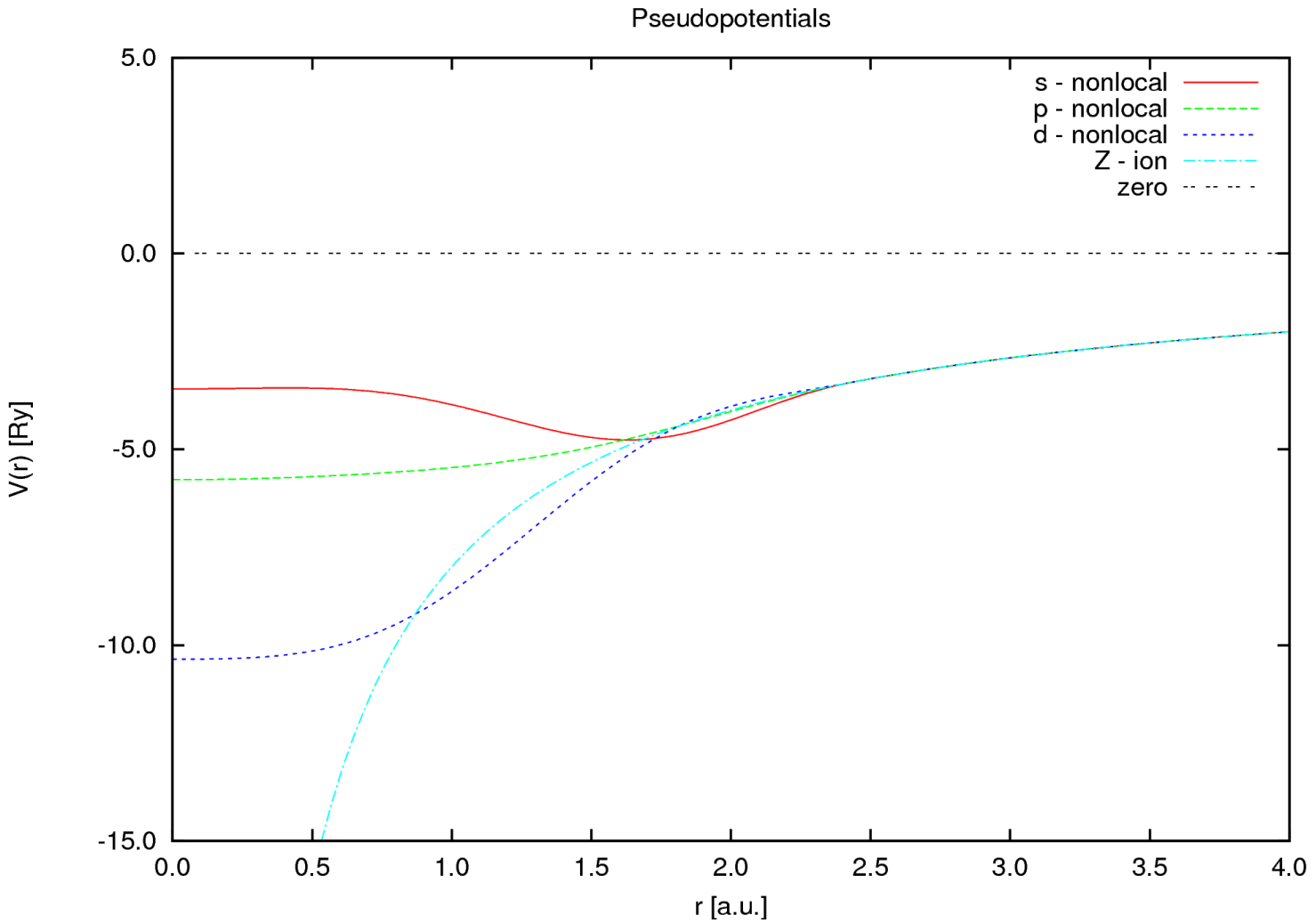
Pseudowavefunctions

True and pseudo-wavefunctions of Si



Pseudopotential

Pseudopotential for Si



Basis Sets

- Plane waves
  - $e^{i\vec{k}\cdot\vec{r}}$
- Gaussians
  - $e^{-\alpha r^2}$
- Numeric, augmented plane waves, muffin-tin orbitals,...

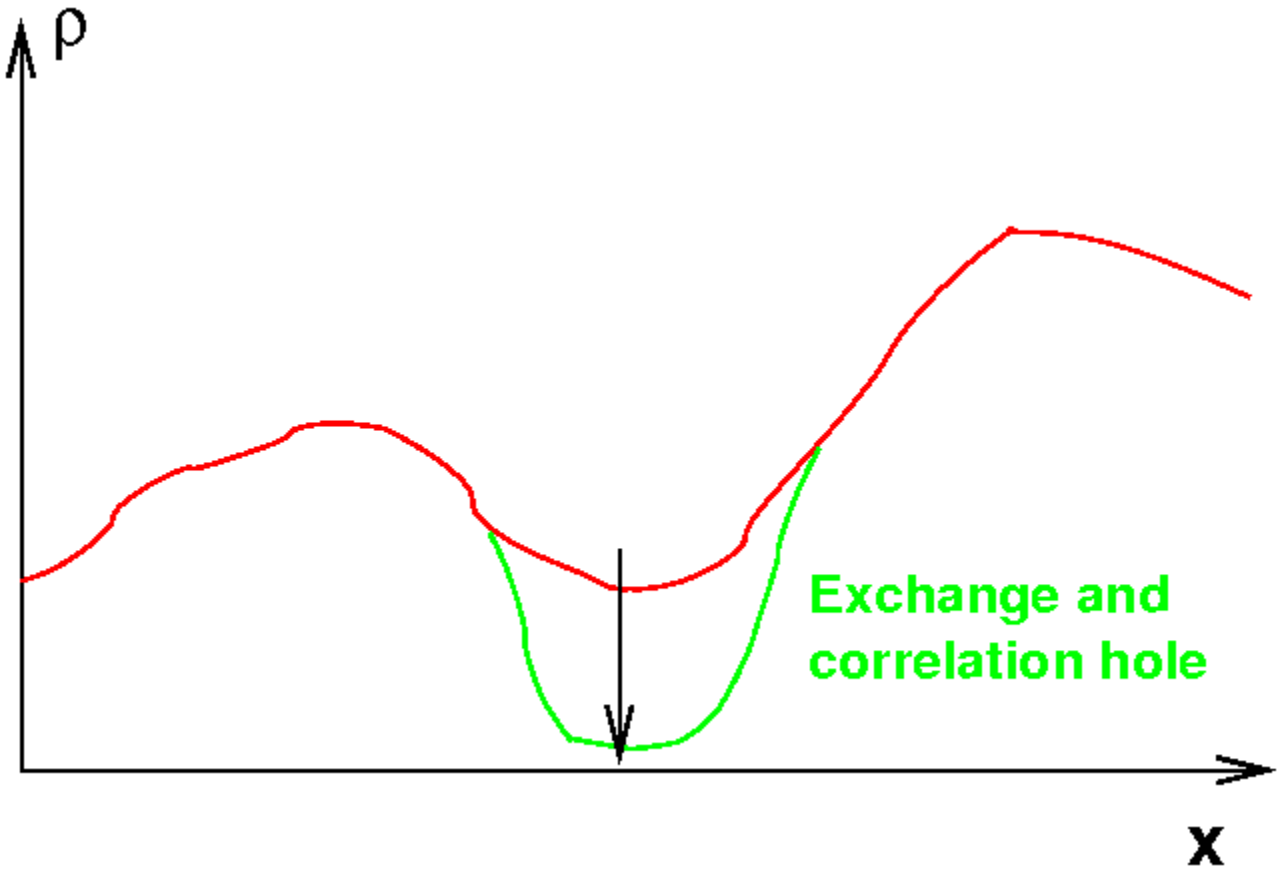
Local Density Approximation (LDA)

- All the many-body complexity is hidden in the exchange and correlation functional.
- The LDA approximation is

$$E_{\mathrm{xc}}[\rho] = \int \rho(\vec{r})\epsilon_{\mathrm{xc}}(\rho(\vec{r}))\,\mathrm{d}^3r$$

Why LDA works

- The xc corresponds to the interaction with one hole.
- The depth and width of the hole are determined by the local electron density.



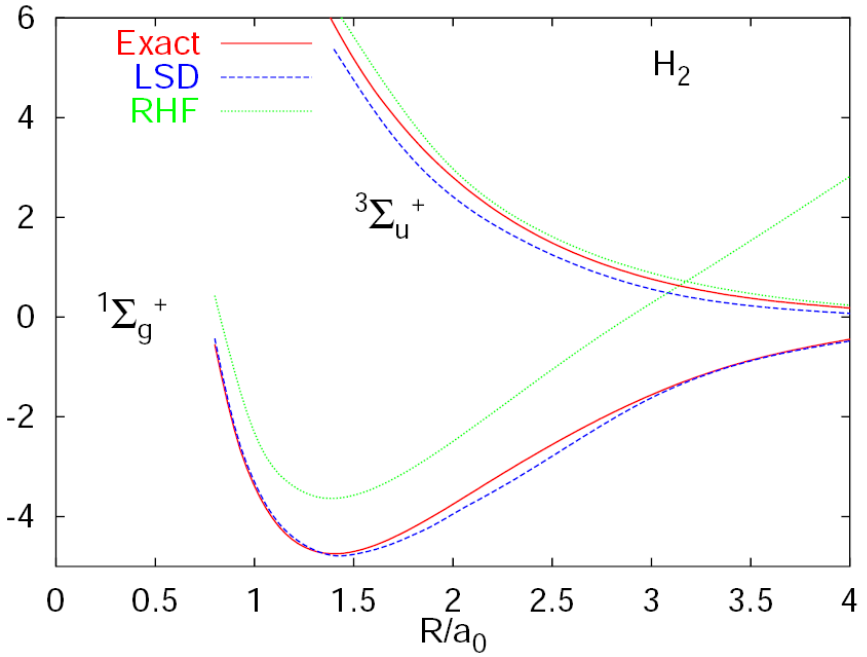
How good is it

- The basic approximation: local density approximation works within 5%. Fails for optical properties
- Beyond LDA is more precise. Works for local properties.

Outline of 2nd part of talk

- Examples of structural optimization
- The problem of finding a global minimum
- Possible Strategies
- Tests
- Conclusions

The total energy surface



- With modern electronic structure theory (in particular density functional theory) we can calculate the total energy of a system as a function of the position of the nuclei (Born-Oppenheimer adiabatic approximation)

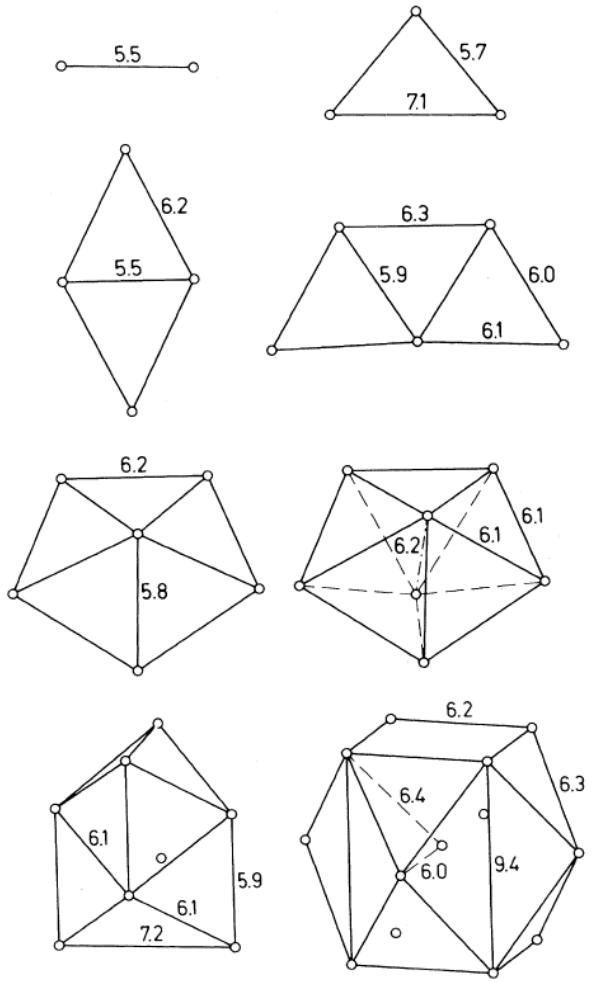
$$E(\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_n)$$

Finding the equilibrium geometry

- The equilibrium geometry / crystal structure is given by the minimum of $E(\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_n)$
- Finding a local minimum is “easy”, just go downhill following the forces

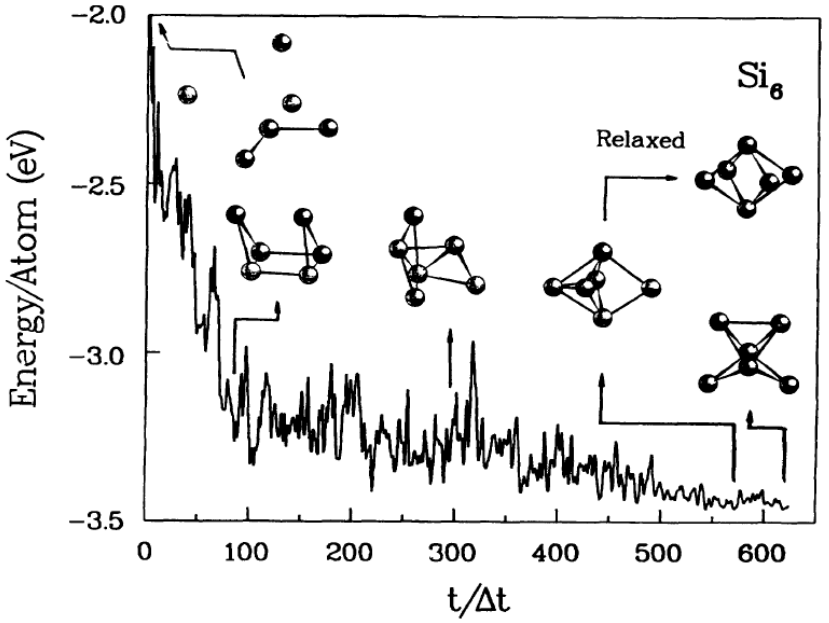
$$\vec{F}_j(\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_n) = -\vec{\nabla}_j E(\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_n)$$

Simple metal clusters



- Na clusters, 0.14 Mflop/s
  PRL 53, 655 (1984)
- $\vec{R}^{(n+1)} \Leftarrow \vec{R}^{(n)} + a\vec{F}^{(n)}$
- Recognition of symmetry (by inspection)
- Start points at random

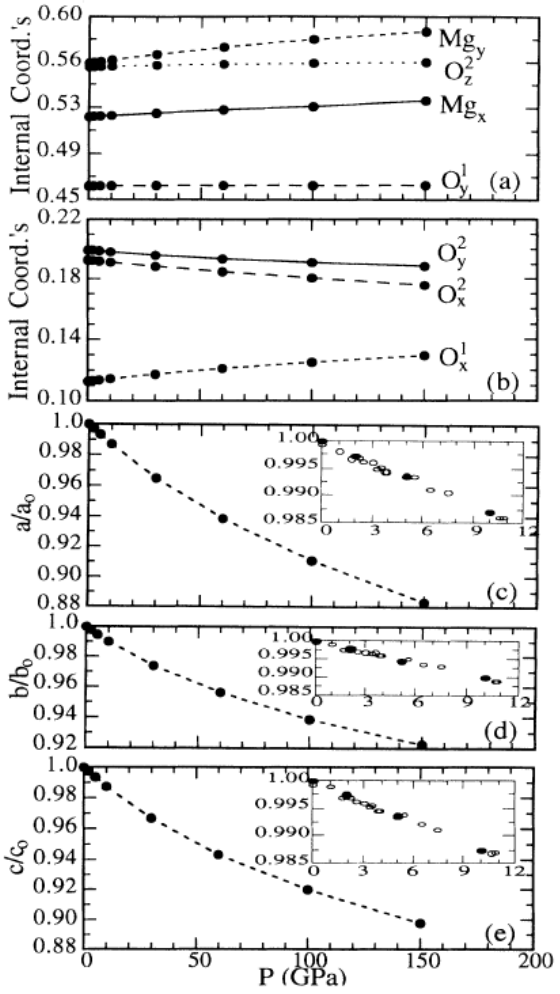
Semiconductor clusters



- Si clusters, 200 Mflop/s, PRL 68, 2956 (1992)
- Langevin molecular dynamics at a decreasing T temperature

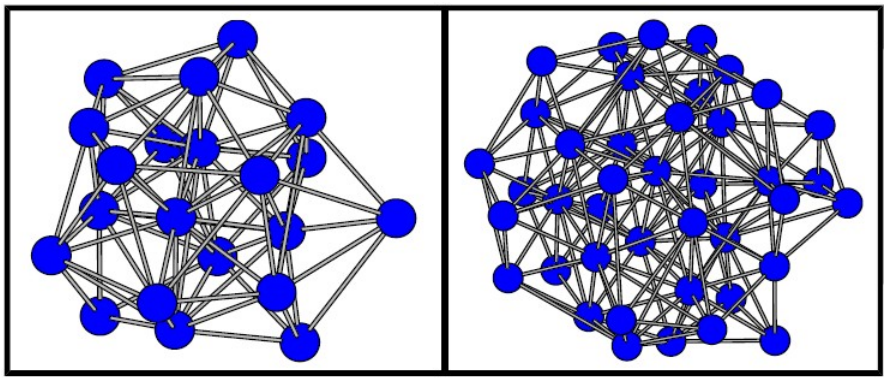
$$m\vec{a}_j = \vec{F}_j - g\vec{v}_j + \vec{F}_{random}(T)$$

$MgSiO_3$ Perovskite



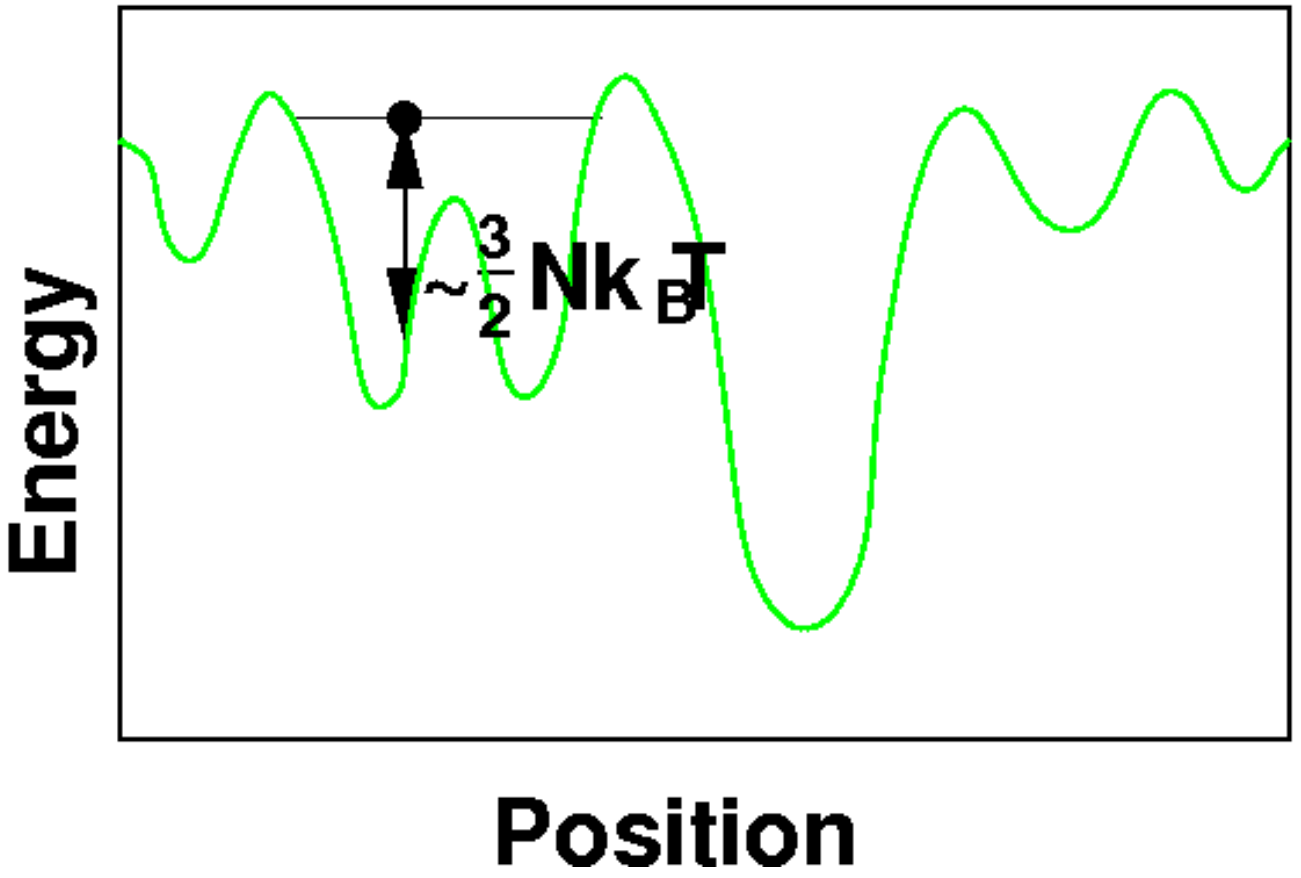
- Mineral that dominates Earth's mantle PRL 70, 3947 (1993)
- Variational cell shape molecular dynamics (cell parameters are fictitious dynamic variables), strongly damped

Large Na clusters



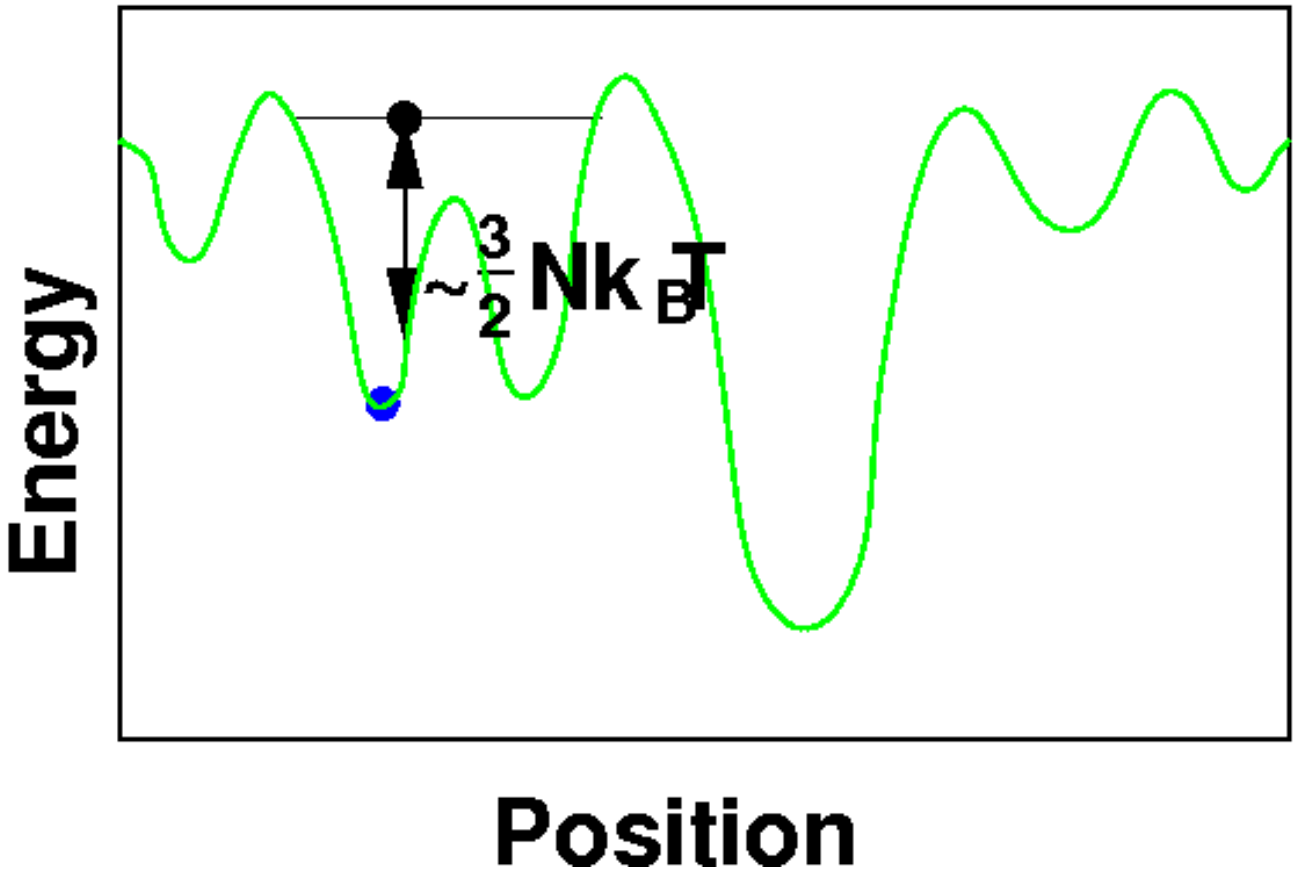
- J-walk Monte Carlo
  Lecture Notes 2001, Springer
- Monte-Carlo at two temperatures in simultaneous. Besides normal accept/reject of moves, once in a while the low and high temperature molecules are swapped.

What is the problem?



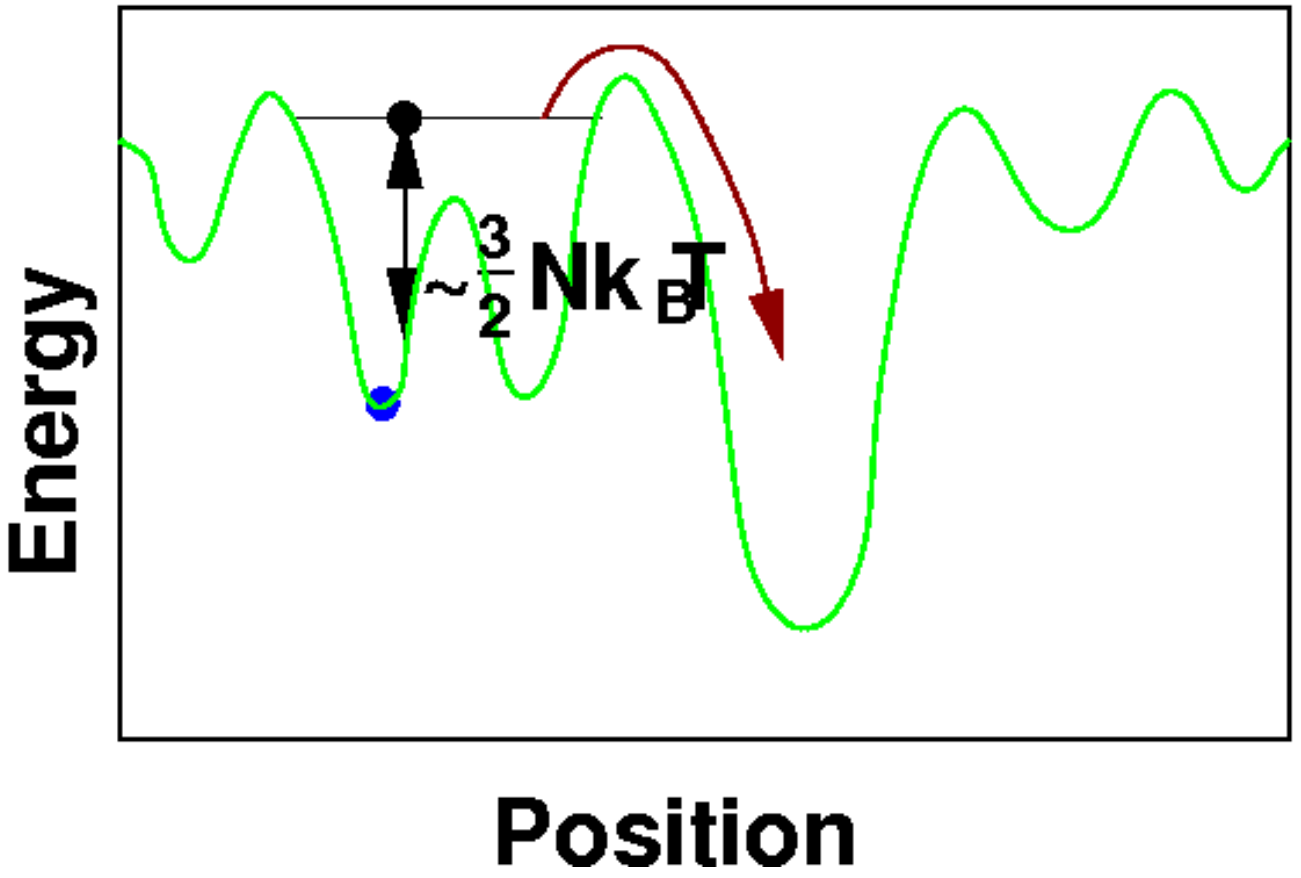
- Go fast to a minimum, but sample enough of the configuration sample to find a low minimum (hopefully the global minimum)

What is the problem?



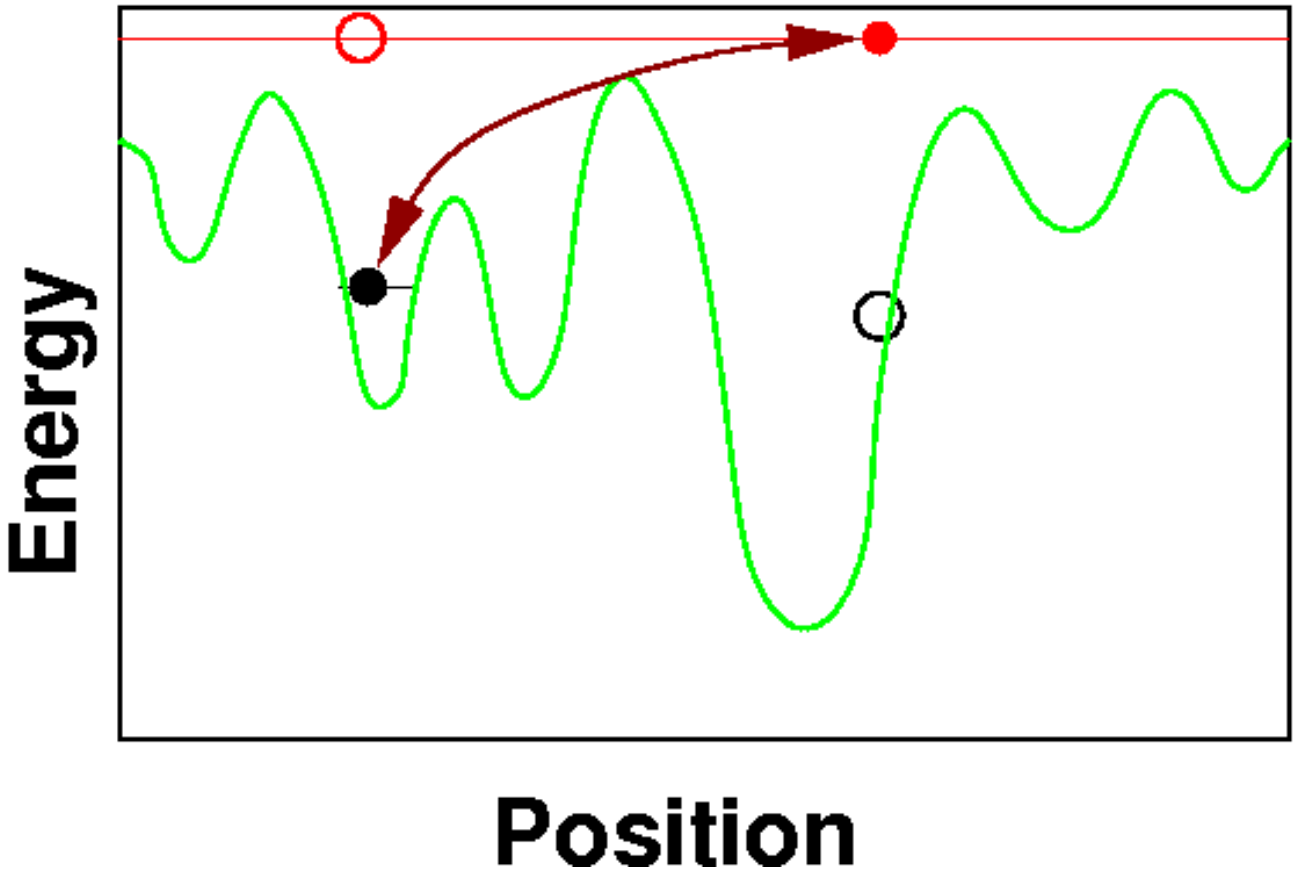
- Going downhill fast gets the configuration trapped in a local minimum

What is the problem?



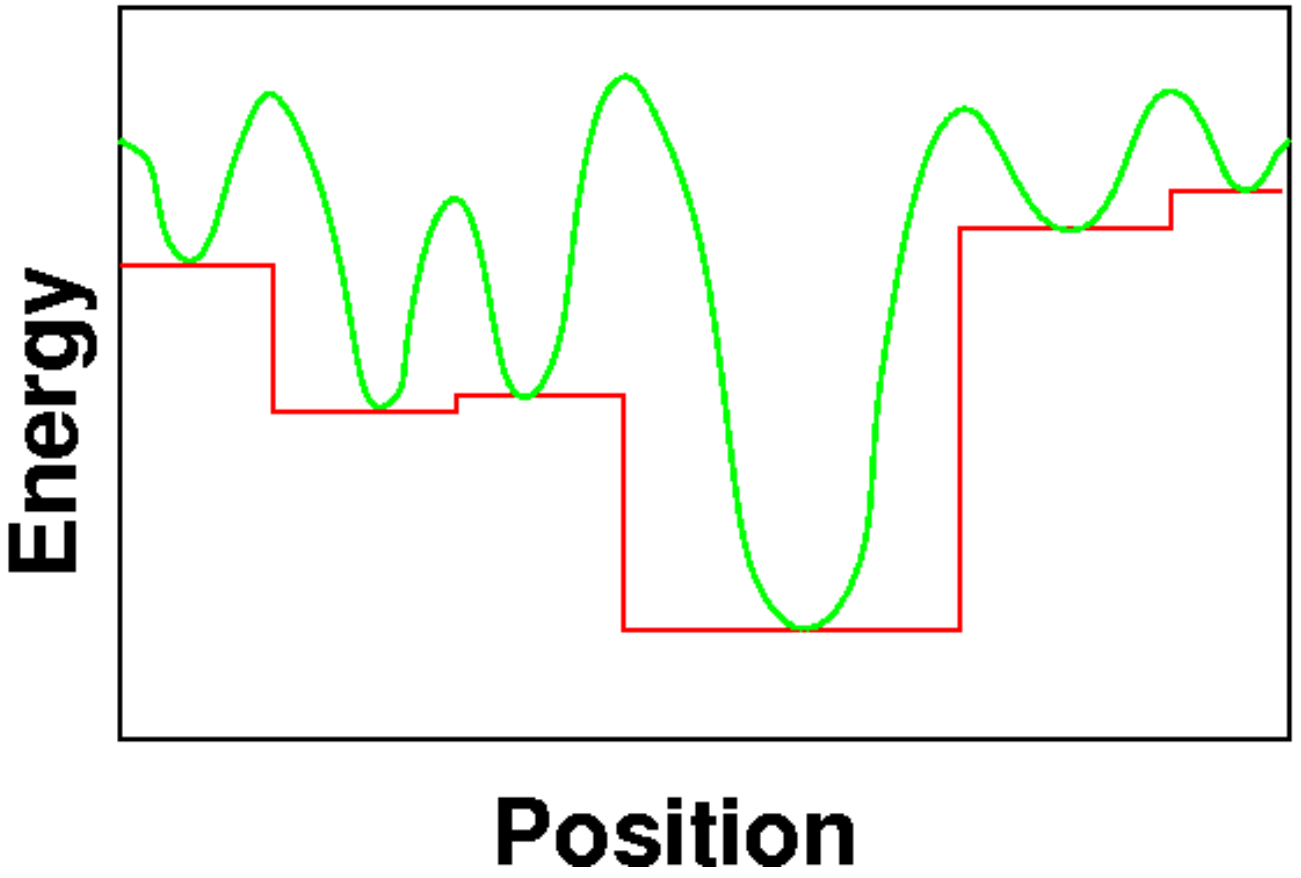
- With temperature fluctuations in molecular dynamics or Monte Carlo there is some chance of jumping over barriers

One solution



- With two temperatures in the J-Walk algorithm we can minimize fast and sample the configuration space at the same time.

Another Solution



- In the basin hopping method the original potential is replaced by the energy of the nearest minimum.

Modern strategies

- Change of the potential energy surface to eliminate barriers.
- Allow smart “global” moves instead of visiting neighboring configurations.

Genetic Algorithms

The idea behind genetic algorithms

- Nature is very efficient in the optimization of complex structures (living creatures)
  - Survival of the fittest
  - Evolution
    - Mutation (slow)
    - Sexual reproduction
- Artificial selection is even faster!!!!
- The process occurs at the molecular level in the genetic code **TCGAATTCG.....**

A thousand generations of artificial selection

A thousand generations of artificial selection

Problem we want to solve

- **We want to optimize geometries**
  - Clusters and molecules
  - Crystals
- In principle we just have to minimize the total energy (or enthalpy or free energy)
  - Phase space is too big => Monte Carlo, molecular dynamics simulated annealing, genetic algorithms

Genetic Algorithms

- J. Holland, *Adaptations in Natural and Artificial Systems,* 1975.
  - Represent the possible solutions in a “genetic” code
  - Start with some population {100101,010001,...}
  - Evolve the population with
    - Mutation: 100101 => 101101
    - Mating: 100101 + 010001 => 100001 + 010101
  - Selection of the fittest for the next generation (needs an objective function)

Key factors in genetic algorithms

- “Basically, if you get
  - The objective function right
  - The representation right
  - The operators right

  then variations on genetic algorithms and its parameters will result in only minor improvements”

Objective Function

- For geometrical optimization the total energy *E* is a good objective function. We want to minimize *E*
- From the objective function we have to derive a fitness function *F(E).* Lower energies must be attributed an higher fitness. There is a lot of freedom in choosing the fitness function. Linear, Boltzmann, step,...

Mutation

- We need mutation to be able to explore all phase space:
  - If we have {001001, 000110, 001010, 001101} mating will always result in a 00**** offspring.
- For a string of *N* bits the mutation probability of a bit is a fraction of 1/*N.* For example 0.05/*N*.
- Mutations occur in Nature.

Crossover

- 1 point:

  101001010101100 X 011011000101001 =>
  101001000101001

  Initial and final bits are always separated.

- 2 point:

  101001010101100 X 011011000101001 =>
  101011000101000

- Uniform:

  101001010101100 X 011011000101001 =>
  101001010101001

  Bits are crossed individually with a given probability (0.5).

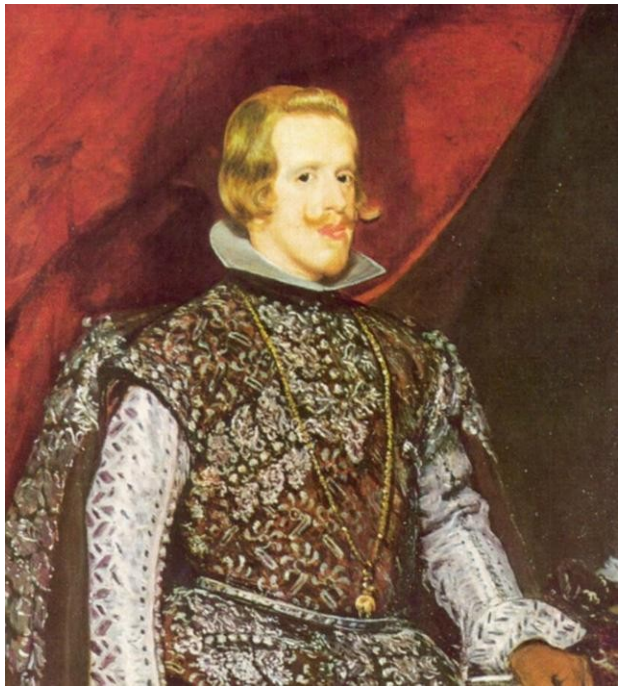
- Crossover occurs in nature before the formation of zigotic cells.

Survival of the fittest

- We have to apply a reasonable evolutionary pressure.
  - With low evolutionary pressure we converge slowly to the most fit genomes.
  - With high evolutionary pressure we may converge fast to a local minimum for all genomes, and without ecological diversity, the crossover mechanism does not explore efficiently the phase space.
- Both for the selection of parents to be crossed and for the survival into the next generation we use probabilities proportional to the fitness function *f(E)*.

The consequences of inbreeding

The consequences of inbreeding



Filipe III

João VI

Problem with clusters and crystals

Representing the (floating point) atomic coordinates by its bit representation is not efficient.

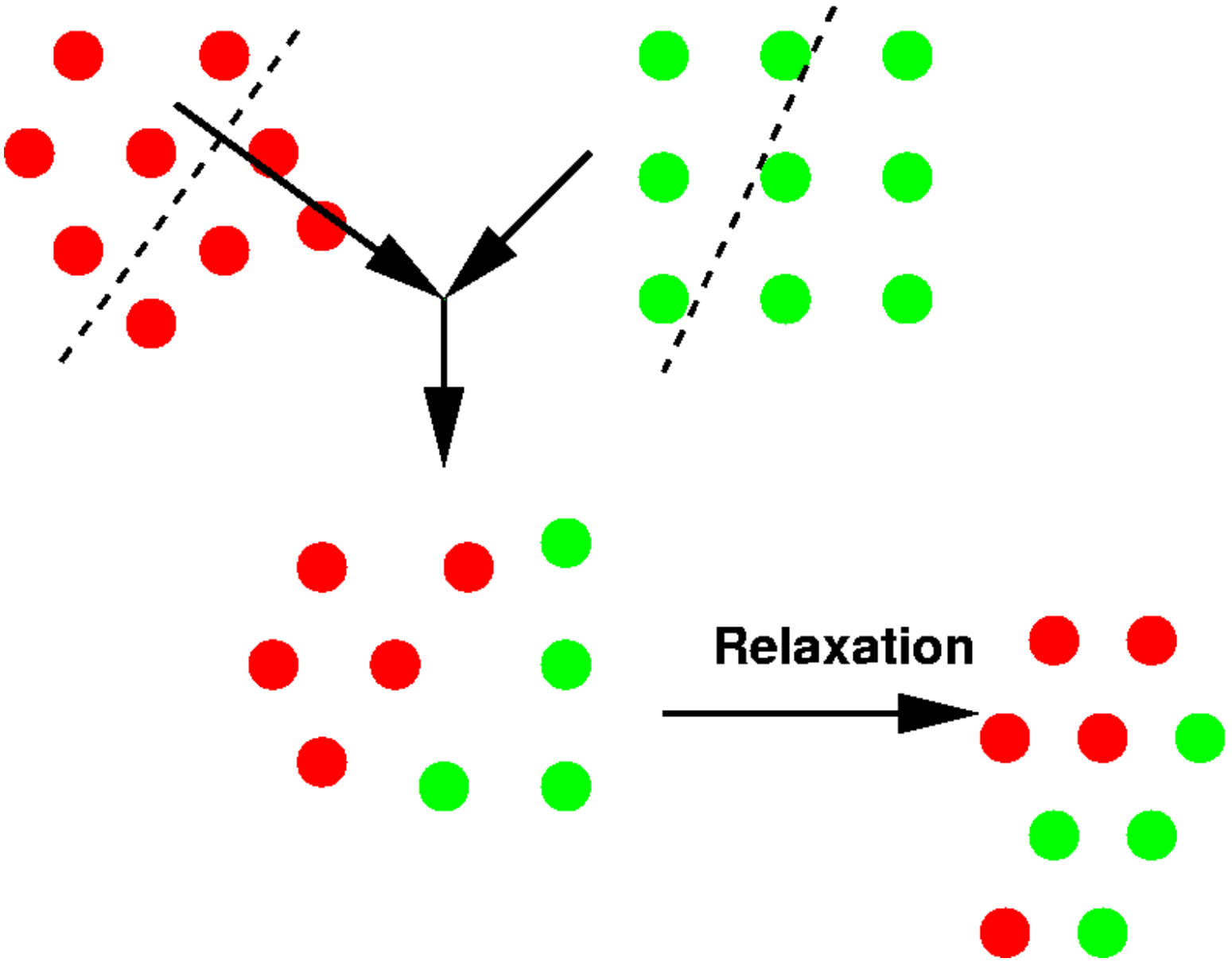
Molecular Geometry Optimization with a Genetic Algorithm

D. M. Deaven and K. M. Ho

PRL 75, 288 (1995)

- The structures are represented by the respective atomic coordinates. (Phenotype versus genome?)
- For crossover the parents are split in half and the offspring is constructed by gluing two halves from different parents.
- The offspring is relaxed to the nearest local minimum: Lamarckian evolution!!!

Crossover in Deaven and Ho



Application to crystals

- A genetic algorithm has been applied with success by A. Oganov to crystals. It is based on Deaven and Ho, and the secret is in the crossover operator, that is how to cut the crystals. The details have not been published.
- N. L. Abraham and M. I. J. Probert, PRB 73, 224104 (2006) say the trick is to do a periodic slice of the crystal.

Slicing the crystal

- The cut must have the periodicity of the crystal and should not depend on the choice of origin of the unit cell.
- Lattice vectors may be averaged.
- Structures are relaxed

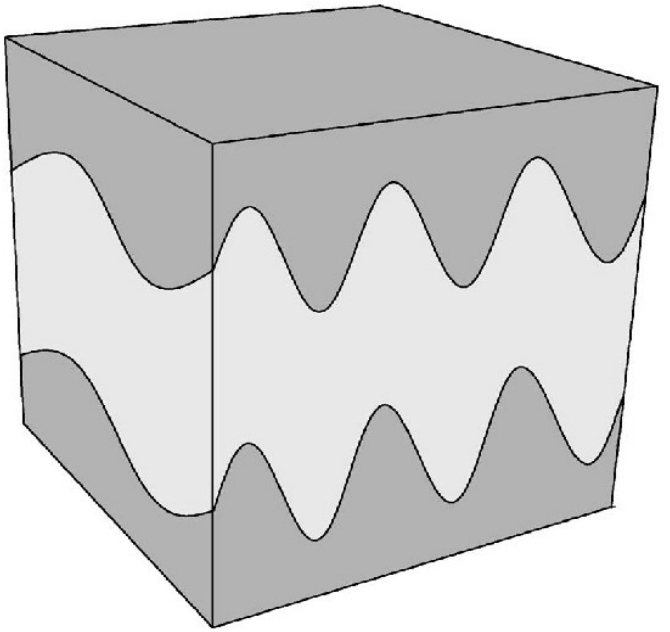


FIG. 2. Real-space representation of the periodic cuts in the crossover operation. Different wavelengths and amplitudes can be used for the cuts along the different cell directions. The cuts are calculated in fractional coordinates which allows crossover between parents with different cells. The dark gray sections represent one part of the cell, the light gray the other, and it is these parts that are swapped in crossover.

What we have done

- Implemented several optimization methods
  - Simple Monte Carlo and Descent from random configuration
  - Adaptative Monte-Carlo with basin hopping
  - Genetic algorithm
- Tested variants of the codes
  - Lennard-Jones clusters (empirical potential)
  - Carbon clusters (first principles – siesta)

Monte Carlo Basin Hopping

- To each configuration we associate the energy of the nearest minimum.
- Monte-Carlo move is made from the minimized configuration displacing all atoms.
- Temperature and size of displacement are adapted so that we visit different configurations.

Our genetic algorithm

- Slicing method
  - simple for clusters
  - elaborated for crystals
- Recognition of similar and identical structures to avoid inbreeding (in progress)
  - Search over all transformations to recognize identical structures
  - recognize structures of same type (tetrahedral coordination, closed packed,...)

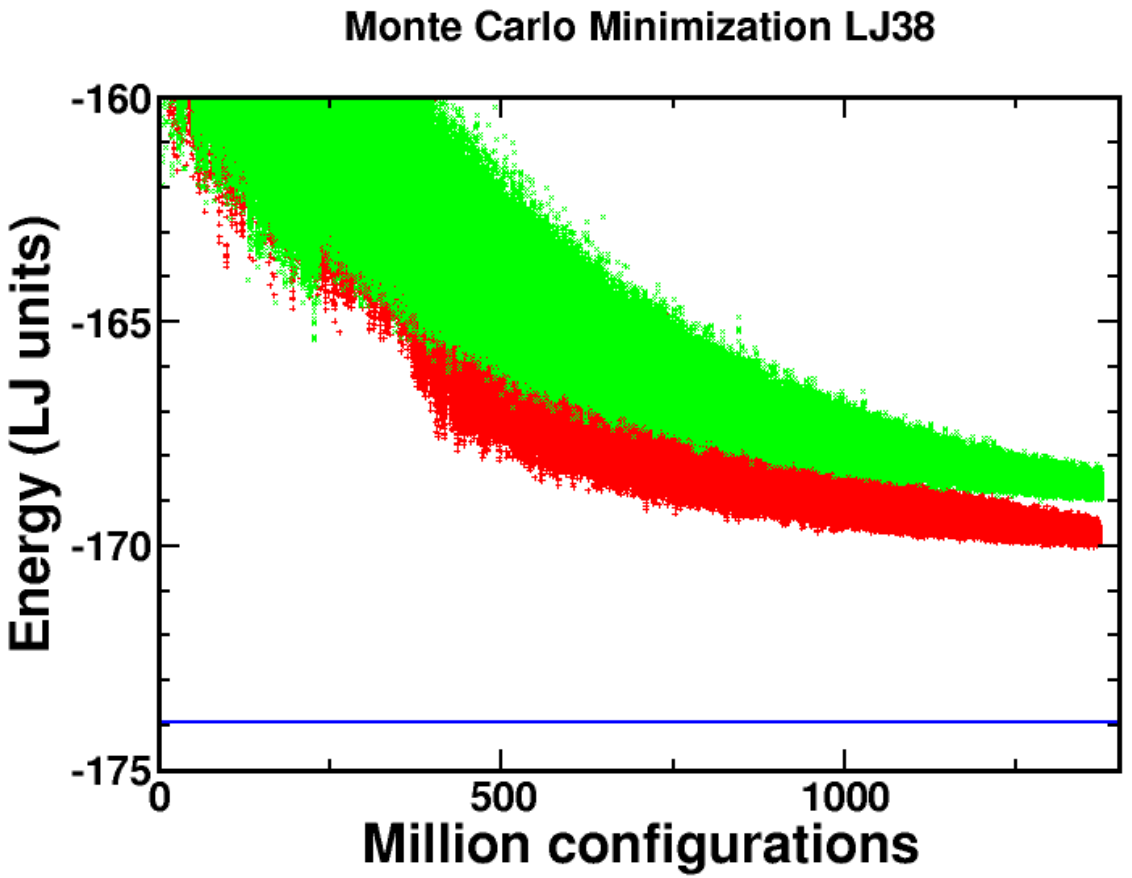
Slicing the crystal

- Define a periodic function $g(\vec{r}) = \sum a_j \exp(i\vec{G}_j \cdot \vec{r})$
- Each atomic position is associated with the value of the function at that point. The offspring crystal is built from the atoms with the larger positive and negative values of each parent crystal
- The coefficients a_j are obtained from a Monte-Carlo search that optimizes several criteria
  - The scar is simple
  - The stoichiometry is correct

Test case: Lennard Jones

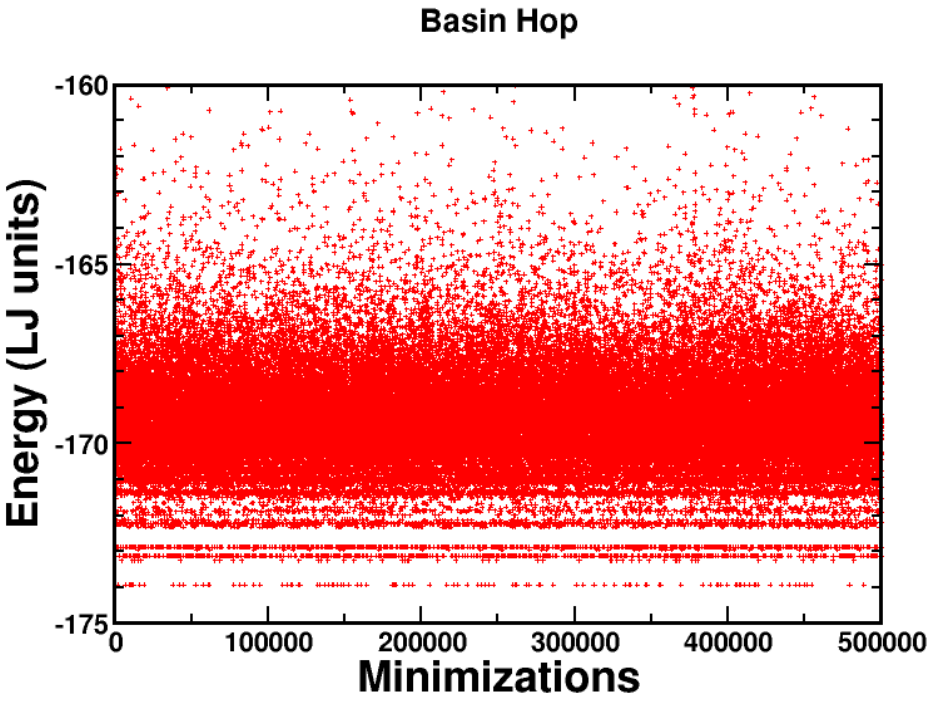
- Cluster with 38 atoms is an interesting test case
  - Ground state has an fcc structure
  - Most low energy structures have an icosahedral pattern
  - Empirical potential allows many calculations needed for statistics

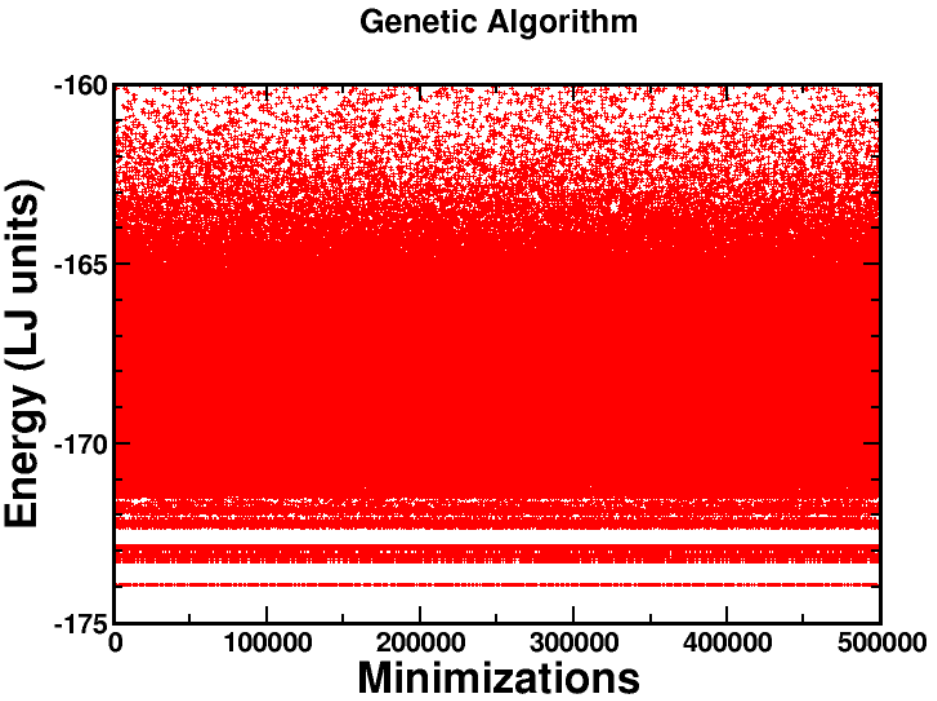
Old Monte Carlo



- After 1300 million moves an adaptative step Monte Carlo minimization fails to settle to the global minimum of LJ-38.

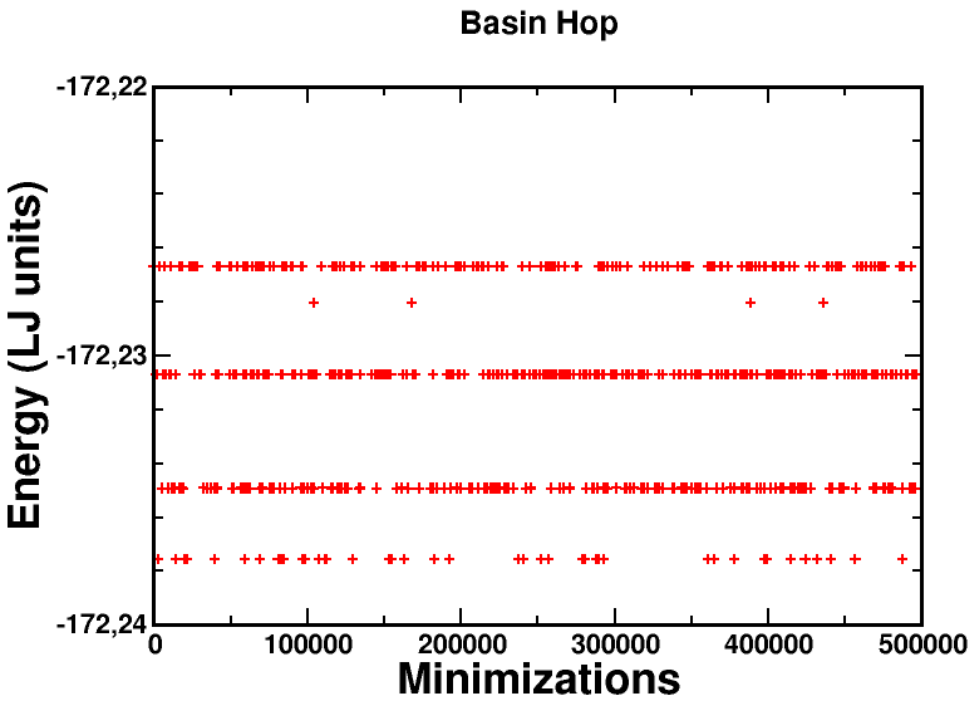
Basin hop and genetic on same scale

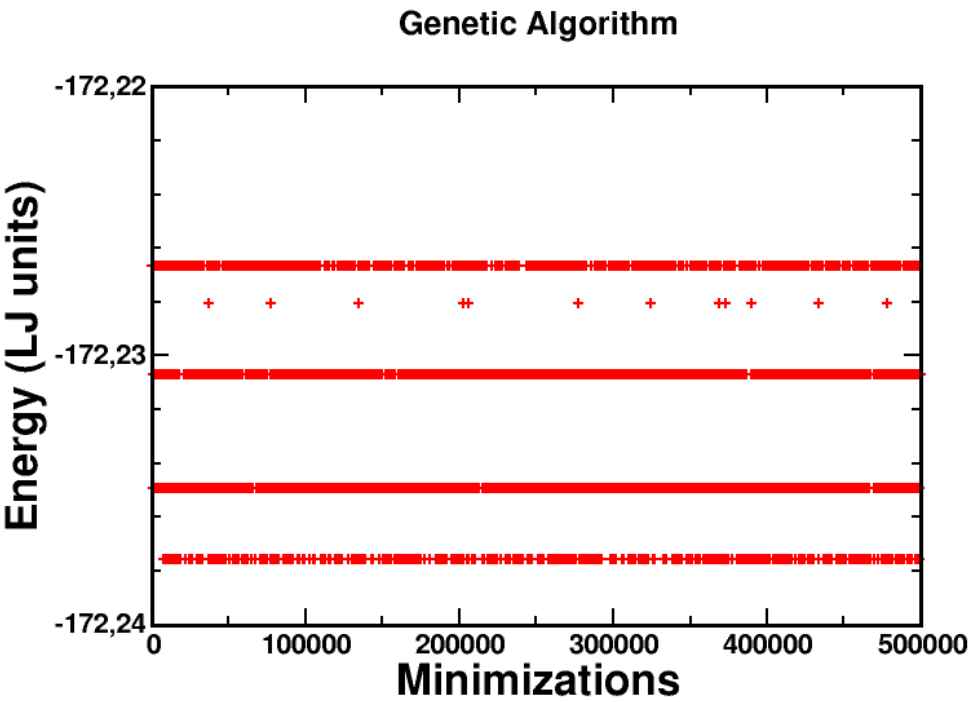




- Both basin hop and genetic algorithms find rapidly the ground state
- circa 20 times less configurations calculated
- genetic seems better

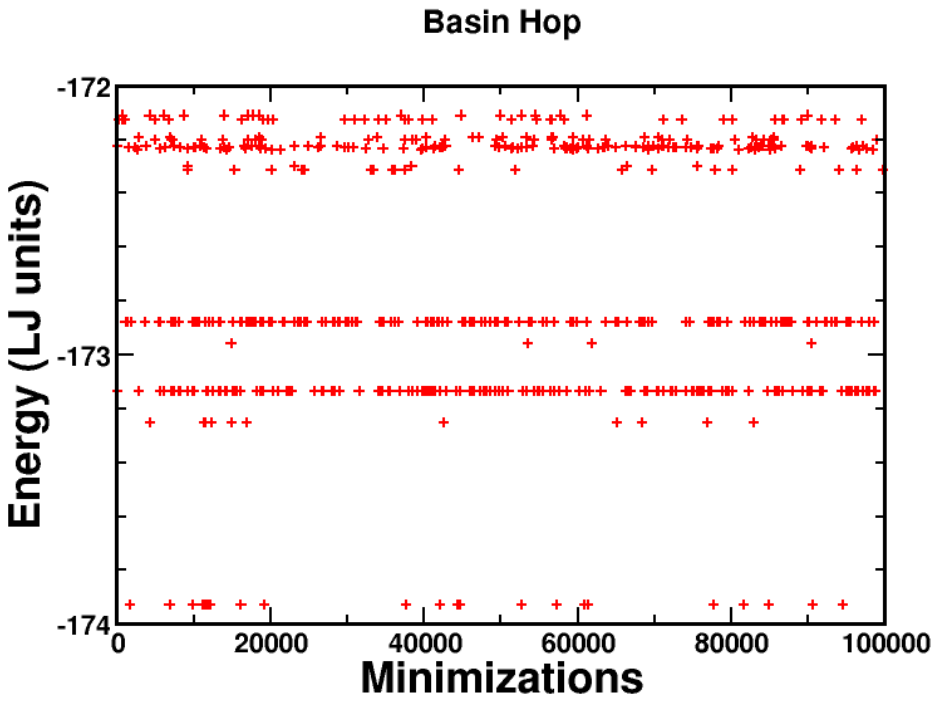
Rare configuration

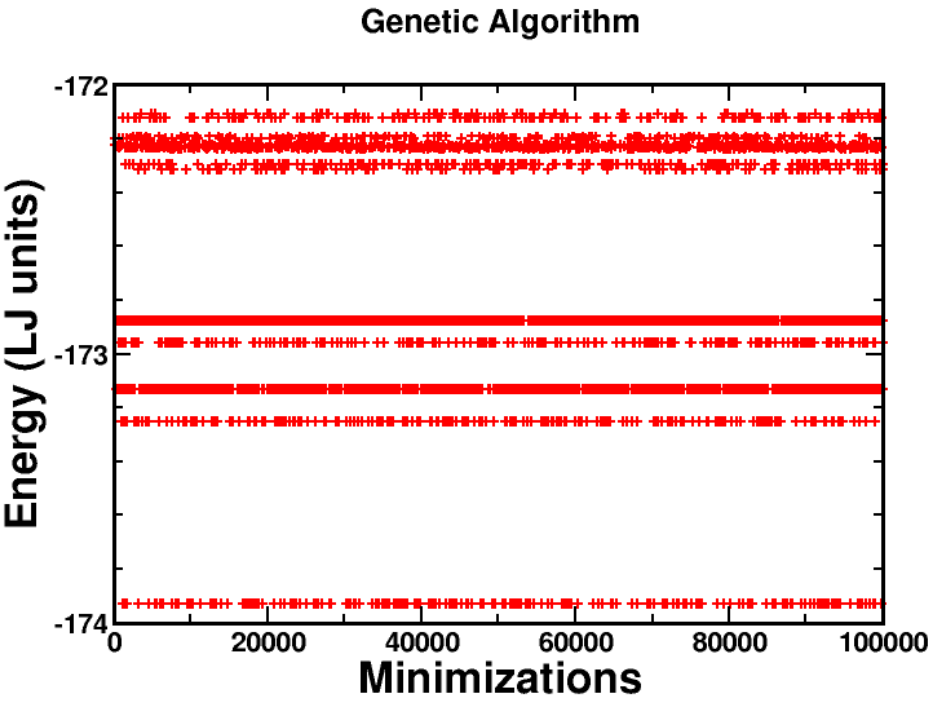




- There is a configuration that has a very small basin!!!
- Global optimization is an hard problem

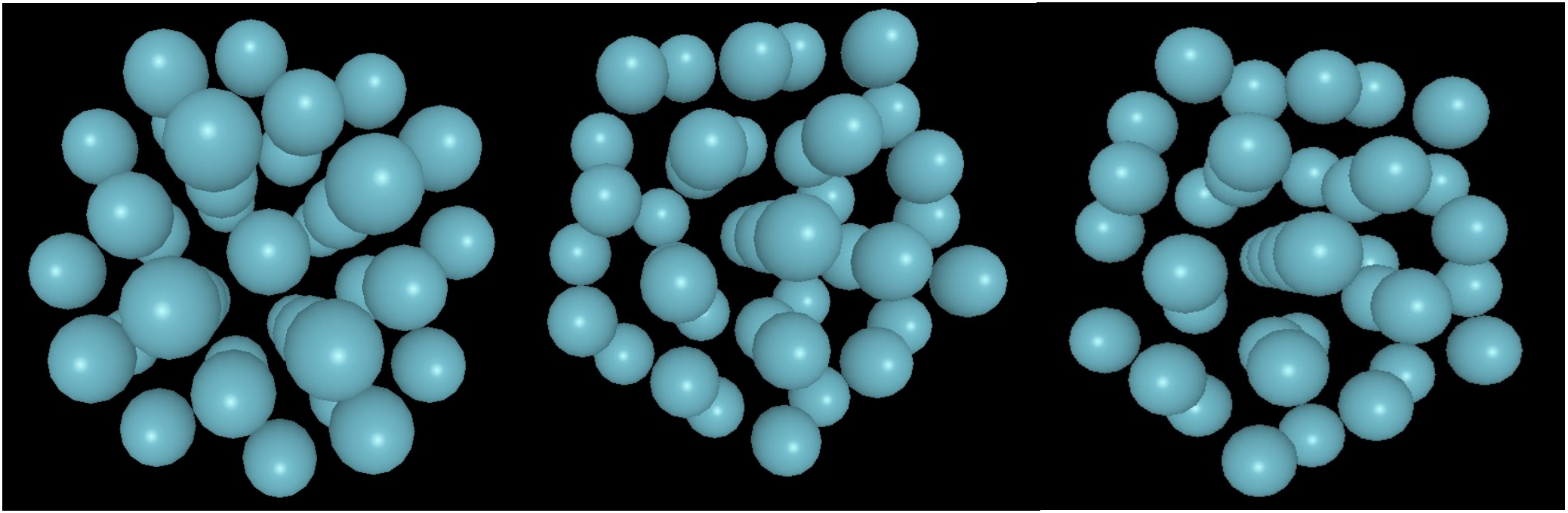
Zoomed picture





- Zooming in energy and number of minimizations we find the genetic algorithm more efficient

The LJ38



Equilibrium isomer

FCC Icosahedral

1st isomer

Icosahedral

Rare

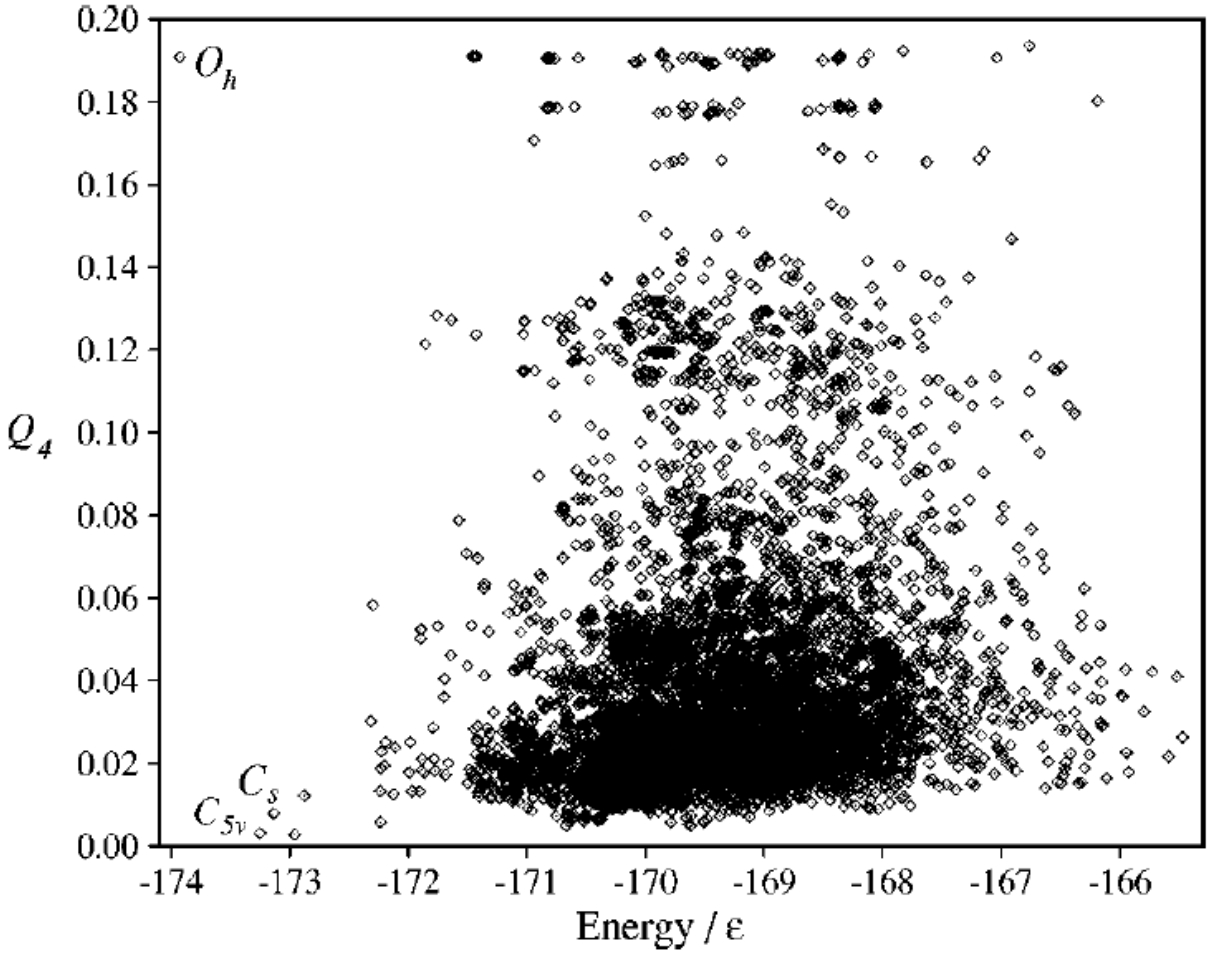
Pattern recognition

- Radial distribution function
- Angular distribution functions
- Nearest neighbor pattern
  - To each pair of atoms is associated a value based on a “soft Voronoi polyhedra” construction
    - Nearest neighbors get a value of 1
    - Distant neighbors get a value of 0
    - Values change continuously

Local coordination

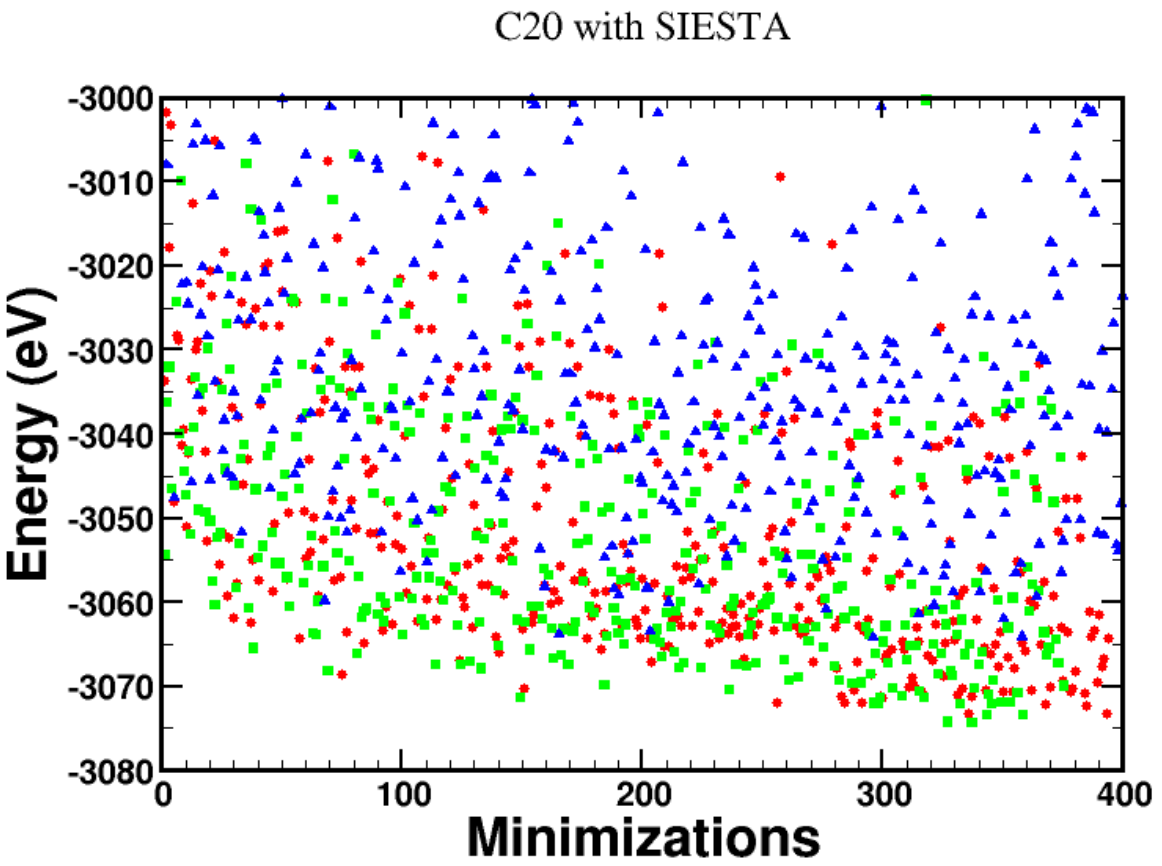
- For the nearest neighbors we make a sum of spherical harmonics $Q_{lm} = \sum c_{ij} Y_{lm}(\vec{R}_{ij})$
- We then aggregate them by angular momentum $Q_l = \sum_m Q_{lm}$
- Different types of structures have different patterns

Energy versus Q4 for LJ38



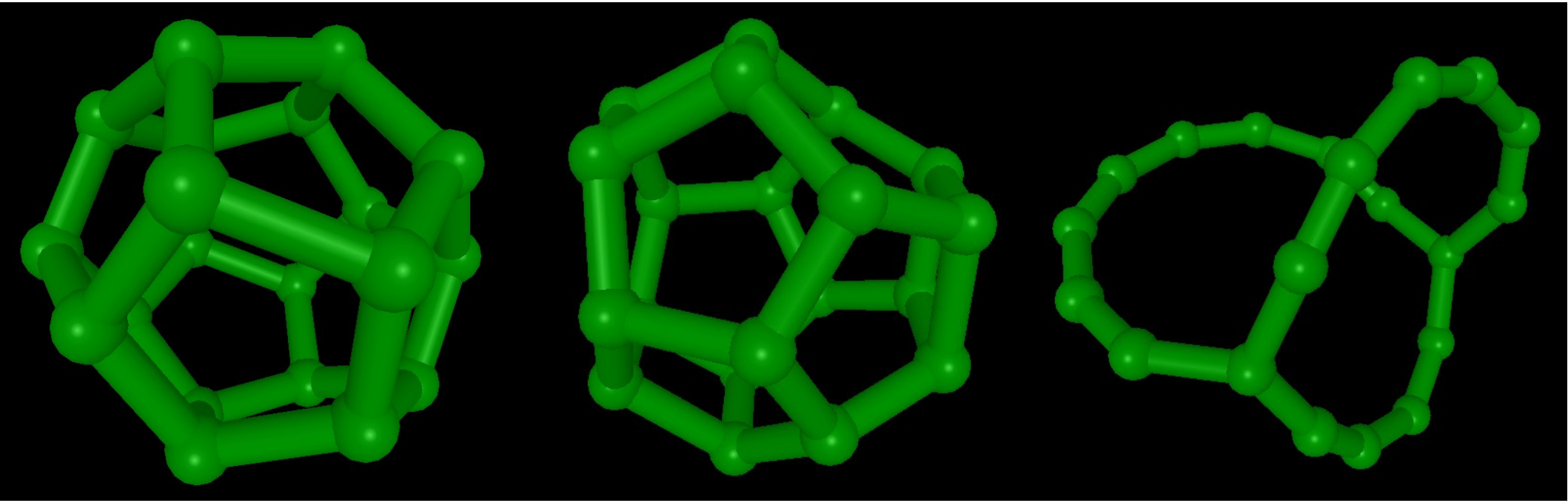
- There are thousands of minima.
- Most minima are amorphous.
- Very few minima have a fcc structure

Genetic algorithm test with SIESTA



- 3 short runs
  - green: lowest energy (dodecahedron)
  - red: lowest energy+defects (cage pentagons squares hexagons
  - blue: ring structure

C20 isomers from 3 runs with SIESTA



Icosahedron Cage 4-5-6 Ring

- one run got a ring ecosystem
- two runs got the cage structures

We want both in a single run: avoid inbreeding

Current work

- Clean-up for final implementation in plane-wave and siesta first principles codes.
- Optimize strategy for crystals.
- Reduce inbreeding

Conclusions

Electronic Structure Theory Works!!!!!