

Molecular and materials modelling

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About the course

327-5102-00L Molecular and Materials Modelling

Semester	Frühjahrssemester 2017
Dozierende	D. Passerone Carlo Pignedoli
Periodizität	jährlich wiederkehrende Veranstaltung
Lehrsprache	Englisch

Katalogdaten Leistungskontrolle Lernmaterialien Lehrveranstaltungen Einschränkungen Angeboten in Übersicht

Studiengang	Bereich	Typ
Materialwissenschaft Master	Wahlfächer	W ⓘ
Physik Master	Allgemeine Wahlfächer	W ⓘ
Rechnergestützte Wissenschaften Bachelor	Physik	W ⓘ
Rechnergestützte Wissenschaften Master	Physik	W ⓘ

The ability to select a suitable atomistic approach to model a **nanoscale system**, and to employ a simulation package to compute quantities providing a **theoretically sound explanation** of a given **experiment**.

This includes knowledge of empirical force fields and insight in **electronic structure theory**, in particular **density functional theory (DFT)**.

Understanding the advantages of **Monte Carlo** and **molecular dynamics (MD)**, and how these simulation methods can be used to compute various **static and dynamic material properties**.

Basic understanding on how to simulate different spectroscopies (IR, STM, X-ray, UV/VIS).

Performing a basic **computational experiment**: interpreting the experimental input, choosing theory level and model approximations, performing the calculations, collecting and representing the results, **discussing the comparison to the experiment**.

Course contents

1. **24.2** DP: Intro, potentials, NEB, clusters, force fields
2. **3.3** DP: Molecular dynamics: basics and quantities accessible to experiment
3. **10.3** CP: Monte Carlo methods and connections to experiment
4. **17.3** DP: Modeling surfaces: metals and semiconductors in classical MD
5. **24.3** DP: Free energy methods and connection to experiment
6. **31.3** DP: Quantum Chemistry and computing electronic properties
7. **7.4** DP: Density functional theory (1): basics and running a DFT simulation
8. **28.4** CP: Band structure in solids and connection with experiment (1)
9. **5.5** DP: Density functional theory (2): improving the agreement with experiment
10. **12.5** CP: Band structure in solids and connection with experiment (2)
11. **19.5** DP: Molecules on surfaces: connection to experiment
12. **26.5** CP: Scanning Tunnelling Microscopy and other microscopy techniques
13. **2.6** DP: Ultraviolet spectroscopy using DFT and beyond methods

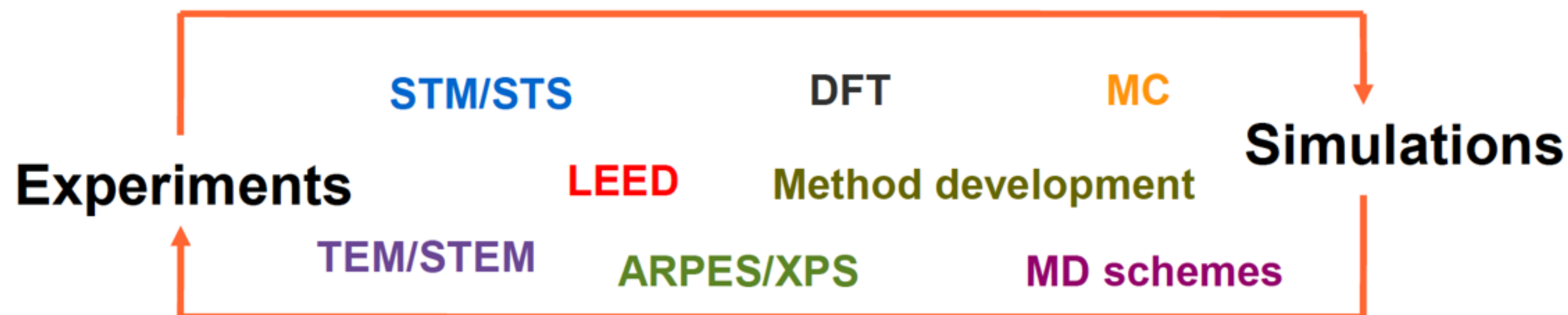
Timetable

- Spring semester 2017
- Friday 14-16 (Theory)
- Friday 16-18 (Exercises)
- 4 KP
- Oral exam

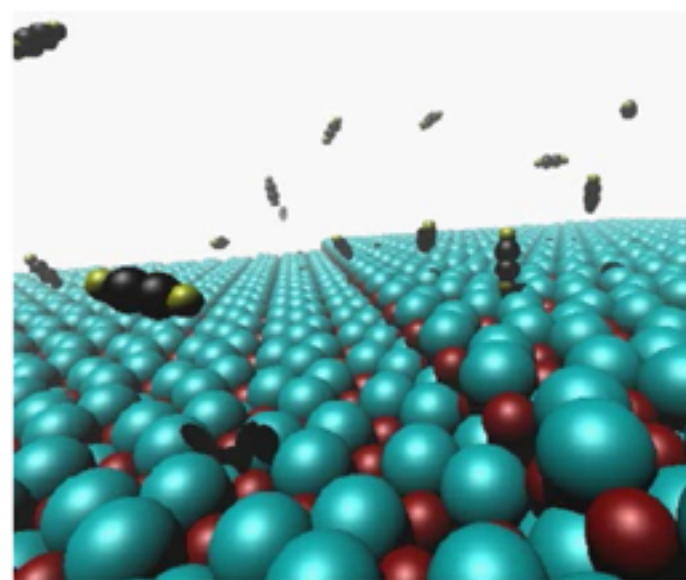
Motivation from all day's work

nanotech@surfaces

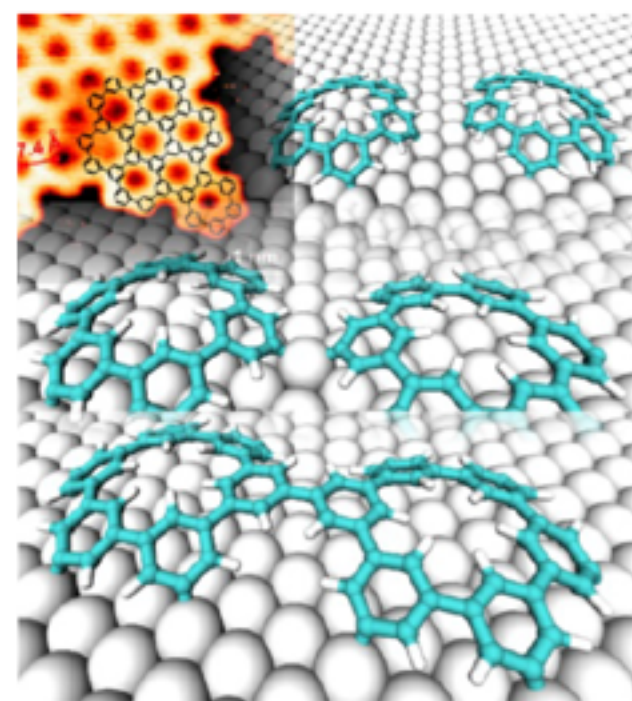
SUPPORT from simulations



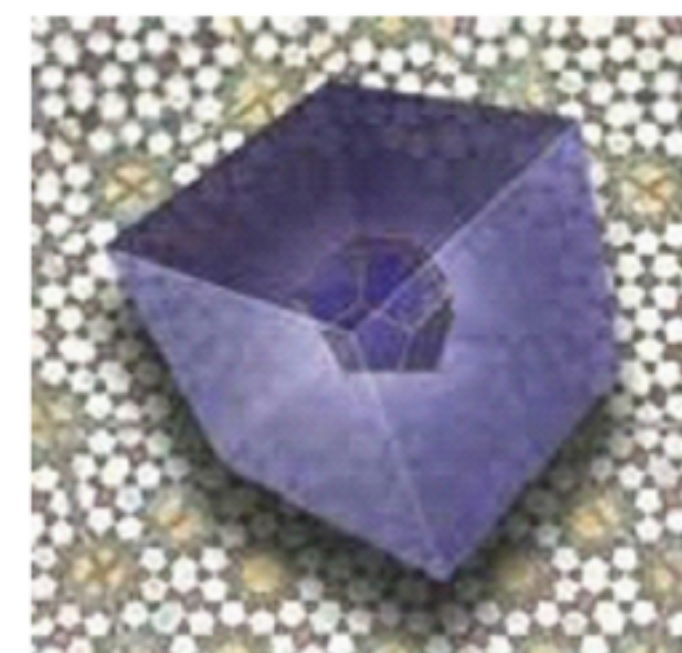
DESIGN and PREDICTION of experiments



Design of improved catalysts



Molecular engineering at surfaces

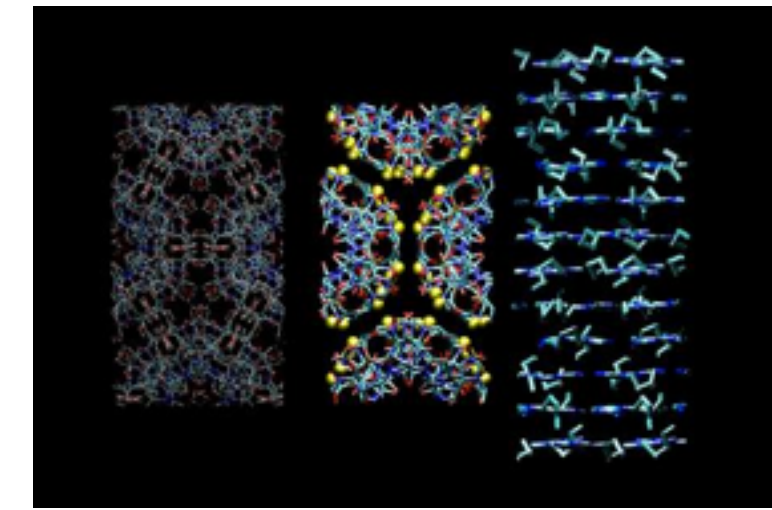


Complex metallic alloys with outstanding resistance to corrosion

Sampling conformational space

- Next lectures: how to explore the conformational space in an efficient way
- History dependent methods (local elevation, metadynamics)
- Accelerated dynamics methods
- Replica of several simulations at different temperatures (replica exchange)
- Monte Carlo simulation

Simulating nuclei+electrons



- Solving Schrödinger equation for several atoms (see next lectures for DFT)
- Dynamics: Discretizing the equation of motion with timesteps of the order of fractions of femtosecond; expensive wavefunction optimizations at each timestep
- Explicit solvent effects

More simply... classical approach

- Electrons are treated implicitly: only nuclei are considered
- Classical equations of motion govern the dynamics (e.g., Newton's equation)
- No solution of the quantum electronic problem at each dynamics step
- Electron effect is embedded in the interaction: example, a C-C bond
- This is valid only under some assumptions

Example: forces and pressures

- Distinguishing between forces and pressures...

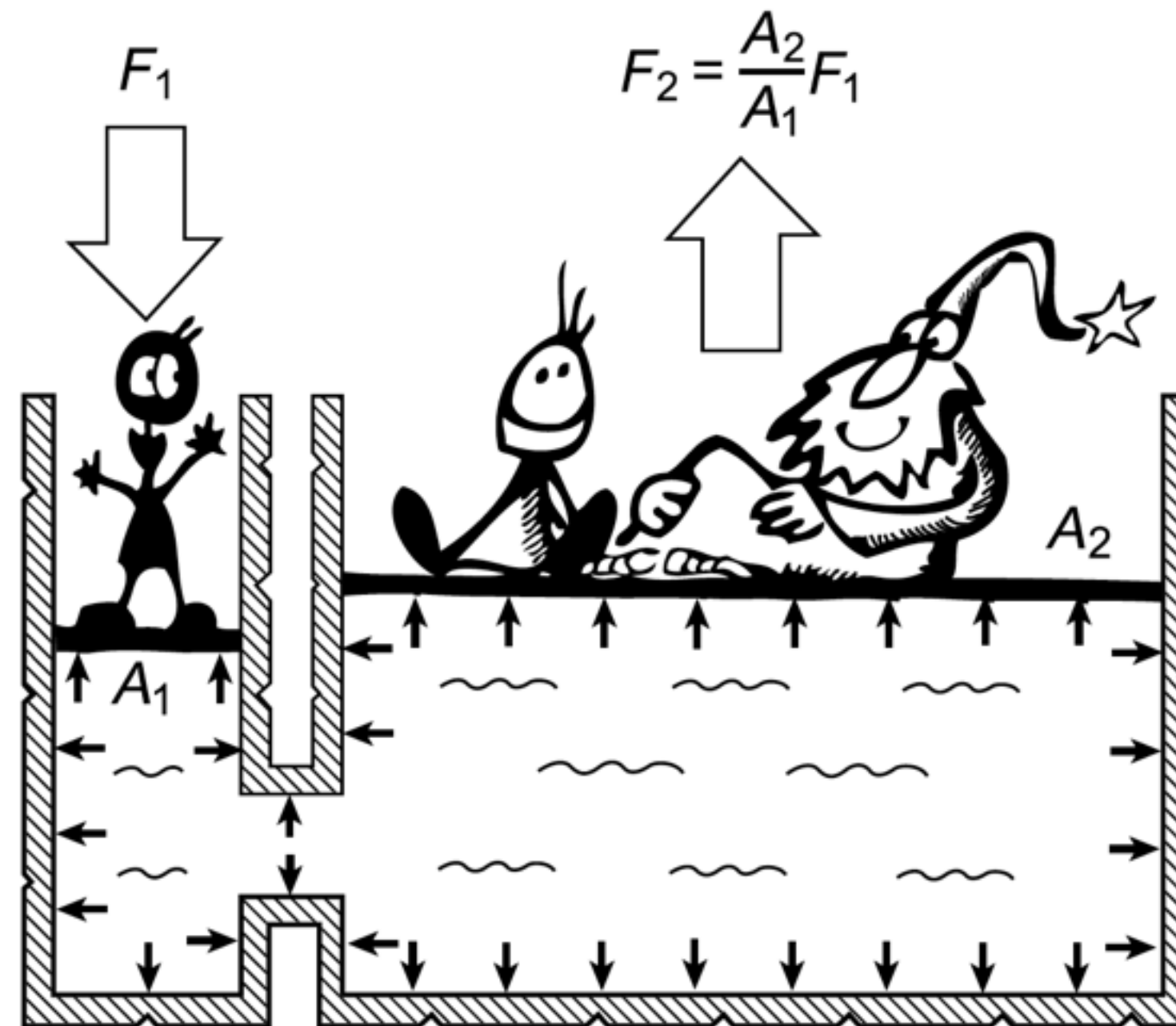
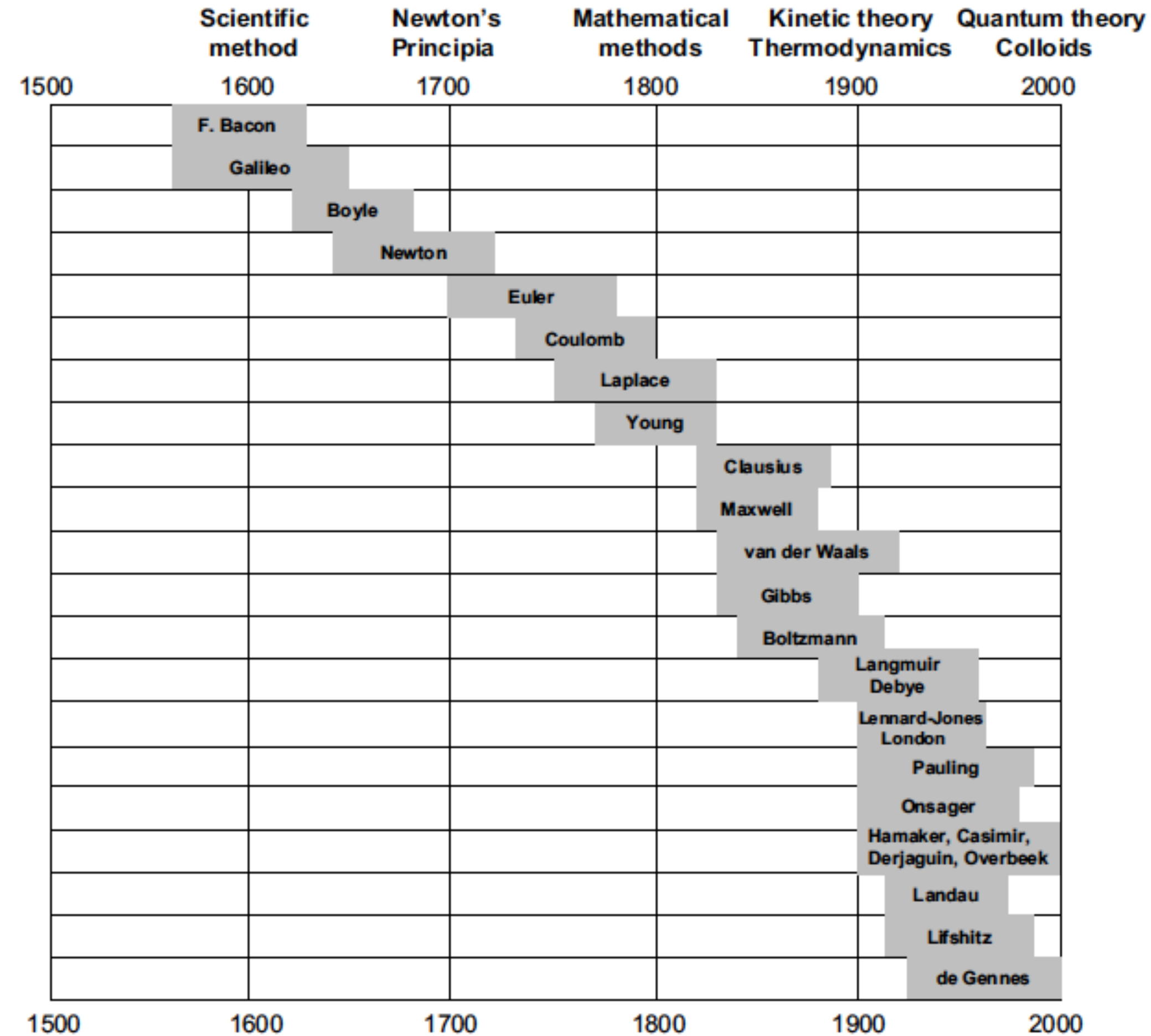


FIGURE 1.2 When discussing the “strength” of an interaction, it is important to clearly distinguish among the forces, energies, pressures, and so on. All of these have different units: force (N), energy (J), pressure (N m^{-2} or Pa), and so on. As will become apparent in future chapters, a bond may have a high bond *energy* but a low *force* needed to break it. Thus, simply talking about the “strength” of a bond may not mean anything. This figure illustrates the difference between *force* (F) and *pressure* ($\text{Force}/\text{Area} = F/A$), where a light load or force F_1 on the left lifts a heavier load F_2 on the right. At equilibrium, the *pressure* within a liquid at the same level must be the same everywhere (continuous), so motion occurs in the direction where the *pressure*, not the *force*, is lowest. In Chapter 9 we shall see how the difference between force and energy also requires consideration of the time (rate) and the temperature of an interaction. [Source: Figure reproduced from Watkins, 2000.]

A preliminary view of intermolecular forces

Table 1.1 Scientists Who Made Major Contributions to Our Understanding of Intermolecular Forces (including some whose contribution was indirect)



A preliminary view of intermolecular forces

- $w(r)$ is the pair potential
- The force is obtained by differentiating the energy with respect to distance

$$\mathbf{F}(\mathbf{r}) = F(r)\hat{\mathbf{r}} \quad F(r) = -\frac{dw(r)}{dr}$$

- The stabilising repulsive “Pauli exclusion” interactions (not shown) usually follow an exponential function

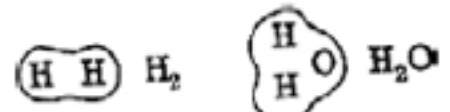

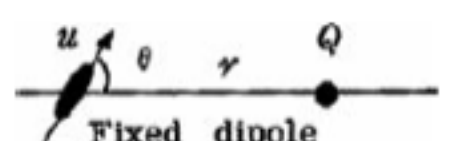
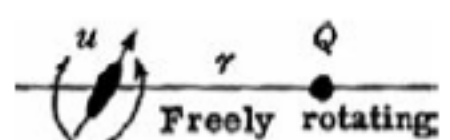
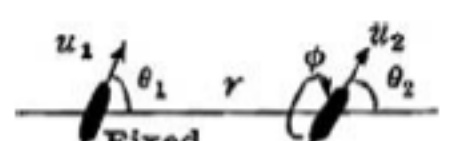
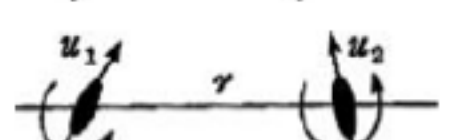
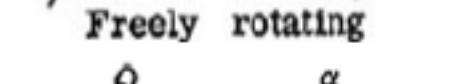
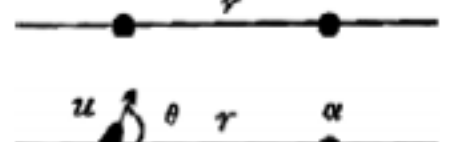
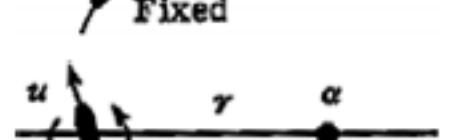

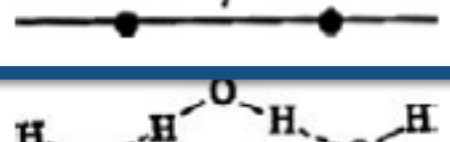
$$w_{\text{rep}}(r) \propto e^{-\frac{r}{r_0}}$$

- For simplicity and computational convenience Pauli exclusion interactions are modeled as power laws

$$w_{\text{rep}}(r) \propto +\frac{1}{r^n} \quad (n = 9 \dots 12)$$

Picture from: J. Israelachvili, Intermolecular and Surface Forces, Academic Press.

Table 2.2 Common Types of Interactions and their Pair-Potentials $w(r)$ between Two Atoms, Ions, or Small Molecules in a Vacuum ($\epsilon = 1$)^a

Type of interaction	Interaction energy $w(r)$
Covalent, metallic 	Complicated, short range
Charge-charge 	$+Q_1Q_2/4\pi\epsilon_0r$ (Coulomb energy)
Charge-dipole 	$-Qu \cos \theta/4\pi\epsilon_0r^2$
	$-Q^2u^2/6(4\pi\epsilon_0)^2kTr^4$
Dipole-dipole 	$-u_1u_2[2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi]/4\pi\epsilon_0r^3$
	$-u_1^2u_2^2/3(4\pi\epsilon_0)^2kTr^6$ (Keesom energy)
Charge-non-polar 	$-Q^2\alpha/2(4\pi\epsilon_0)^2r^4$
Dipole-non-polar 	$-u^2\alpha(1 + 3 \cos^2 \theta)/2(4\pi\epsilon_0)^2r^6$
	$-u^2\alpha/(4\pi\epsilon_0)^2r^6$ (Debye energy)
Two non-polar molecules 	$-\frac{3}{4} \frac{h\nu\alpha^2}{(4\pi\epsilon_0)^2r^6}$ (London dispersion energy)
Hydrogen bond 	Complicated, short range, energy roughly proportional to $-1/r^2$

^a $w(r)$ is the interaction free energy or pair-potential (in J); Q , electric charge (C); u , electric dipole moment (C m); α , electric polarizability ($\text{C}^2 \text{m}^2 \text{J}^{-1}$); r , distance between the centers of the interacting atoms or molecules (m); k , Boltzmann constant ($1.381 \times 10^{-23} \text{J K}^{-1}$); T , absolute temperature (K); h , Planck's constant ($6.626 \times 10^{-34} \text{J s}$); ν , electronic absorption (ionization) frequency (s^{-1}); ϵ_0 , dielectric permittivity of free space ($8.854 \times 10^{-12} \text{C}^2 \text{J}^{-1} \text{m}^{-1}$). The force $F(r)$ is obtained by differentiating the energy $w(r)$ with respect to distance r : $F = -dw/dr$. The stabilizing repulsive “Pauli Exclusion” interactions (not shown) usually follow an exponential function $w(r) \propto \exp(-r/r_0)$, but for simplicity they are usually modeled as power laws: $w(r) \propto +1/r^n$ (where $n = 9-12$).

Dispersion forces

1. They are long-range forces and, depending on the situation, can be effective from large distances (greater than 10 nm) down to interatomic spacings (about 0.2 nm).
2. These forces may be repulsive or attractive, and in general the dispersion force between two molecules or large particles does not follow a simple power law.
3. Dispersion forces not only bring molecules together but also tend to mutually align or orient them, though this orienting effect is usually weaker than with dipolar interactions.
4. Dispersion forces are not additive; that is the force between two bodies is affected by the presence of other bodies nearby. This is called the **nonadditivity of an interaction**.

“Classical” interpretation

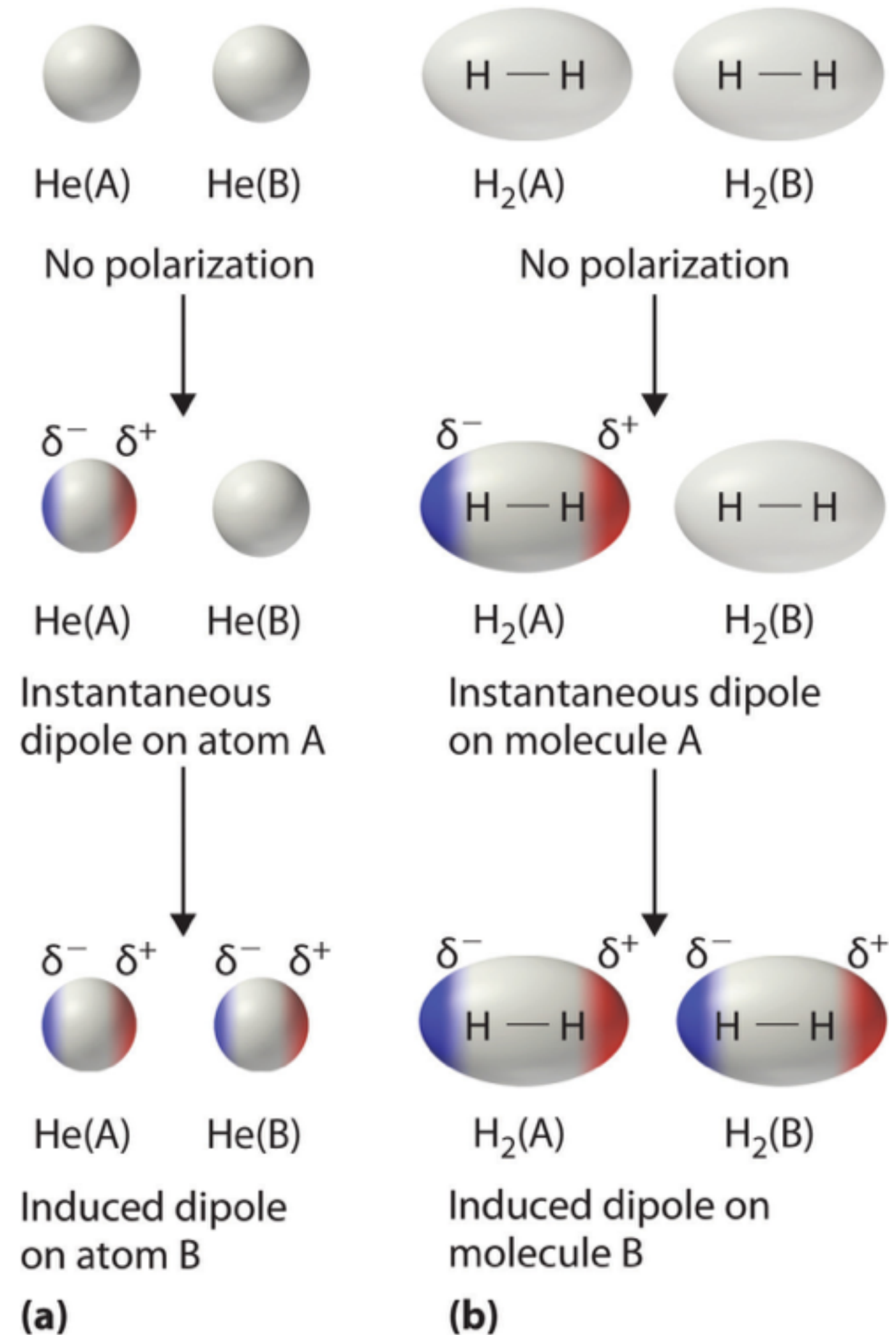
Intuitive origin of dispersion forces:

for a non-polar atom such as He, the time average of its dipole moment is zero.

At any instant, however, there exists a finite dipole moment (instantaneous position of electrons).

This generates an electric field. That polarises any neutral atom around, giving rise to a dipole moment.

The resulting interaction leads to an attractive force with finite time average.



Does it come close to the truth?

- Consider a Bohr model, namely one electron orbiting around the nucleus at the Bohr radius $a_0 = 0.52918 \text{ Angstrom}$ imposed by the De Broglie condition, namely that the orbit contains an integer number of wavelengths (quantum mechanics)
- Compute the instantaneous dipole and the corresponding interaction with the **induced dipole** of another atom, this gives (α is the polarizability of the second atom)

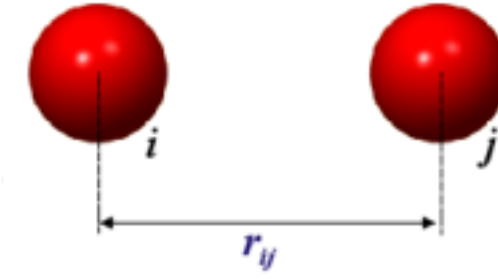
$$w(r) = -u^2 \alpha_0 / (4\pi\epsilon_0\epsilon)^2 r^6 = -(a_0 e)^2 \alpha_0 / (4\pi\epsilon_0)^2 r^6$$

- Using quantum mechanical perturbation theory, London found in 1937:

$$w(r) = \frac{-C_{\text{disp}}}{r^6} = -\frac{3}{4}\alpha_0^2 h\nu / (4\pi\epsilon_0)^2 r^6 = -\frac{3}{4}\alpha_0^2 I / (4\pi\epsilon_0)^2 r^6$$

- while dispersion forces are quantum mechanical (in determining the instantaneous, but fluctuating, dipole moments of neutral atoms), the ensuing interaction is still essentially electrostatic—a sort of quantum mechanical polarization force.
MORE DETAILS IN A FURTHER LECTURE

Lennard-Jones potential



- van der Waals interactions stem from induced dipole-induced dipole interaction, and, together with a repulsive part originating from Pauli repulsion, represent the nonelectrostatic part of the interaction between non-bonded atoms. The origin is purely quantum, and the modelization of this kind of interaction is a very active field also within the *ab initio* simulation community.

- Possible forms of the **Lennard-Jones** potential are:

$$E_{12-6}(\{r_{ij}\}; \sigma(i, j), \epsilon(i, j)) = \sum_i^{N_{\text{atoms}}} \sum_{j>i}^{N_{\text{atoms}}} 4\epsilon(i, j) \left[\left(\frac{r_{ij}}{\sigma(i, j)} \right)^{-12} - \left(\frac{r_{ij}}{\sigma(i, j)} \right)^{-6} \right]$$

$$E_{12-6}(\{r_{ij}\}; C_{12}(i, j), C_6(i, j)) = \sum_i^{N_{\text{atoms}}} \sum_{j>i}^{N_{\text{atoms}}} C_{12} r_{ij}^{-12} - C_6 r_{ij}^{-6}$$

- when we will face DFT and light absorption, we will discuss operative recipes to compute the coefficients

Combination rules for van der Waals

- When dealing with pairs of atoms of different kind, different combination rules can be used, for example (Lorentz and Berthelot, XIX century)

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad \epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}}$$

- One combination rule which is also used to connect to measurable properties is the Slater-Kirkwood expression, where $N(i)$ and $N(j)$ are the effective number of electrons in valence (outer) shells of the atom

$$C_6(i, j) = K \frac{\alpha(i)\alpha(j)}{(\alpha(i)/N(i))^{1/2} + (\alpha(j)/N(j))^{1/2}}$$

$$C_{12}(i, j) = \frac{1}{2}C_6(i, j) [R(i) + R(j)]^6$$

- Polarizabilities α can be measured experimentally, they measure the ability of forming instantaneous dipole upon application of an external electric field.

Lennard-Jones potential: a worked example (Israelachvili)

Worked Example 1.2

Question: The Lennard-Jones potential

$$w(r) = -A/r^6 + B/r^{12} \quad (1.7)$$

is a special case of the Mie potential, Eq. (1.6).¹³ In this potential the attractive (negative) contribution is the van der Waals interaction potential, which varies with the inverse-sixth power of the distance (Chapter 6). Make a sketch of how the energy $w(r)$ and force $F(r)$ vary with r . What does the Lennard-Jones potential predict for (i) the separation $r = r_e$ when the energy is at the minimum (equilibrium) value, w_{\min} ; (ii) the ratio of w_{\min} to the purely attractive van der Waals component of the interaction potential at r_e ; (iii) the ratio of r_e to r_0 defined by $w(r_0) = 0$; (iv) the ratio of r_s to r_0 , where r_s is the separation where the magnitude of the (attractive adhesion) force is maximum, F_{\max} ; and (v) the effective spring constant k of the bond for small displacements about the equilibrium position?

In the interaction between two atoms, the values of A and B are known to be $A = 10^{-77} \text{ J m}^6$ and $B = 10^{-134} \text{ J m}^{12}$. What is w_{\min} for this interaction in units of kT at 298 K, the spring constant in units of N m^{-1} , and the maximum adhesion force F_{\max} between the two atoms? Is this force measurable with a sensitive balance?

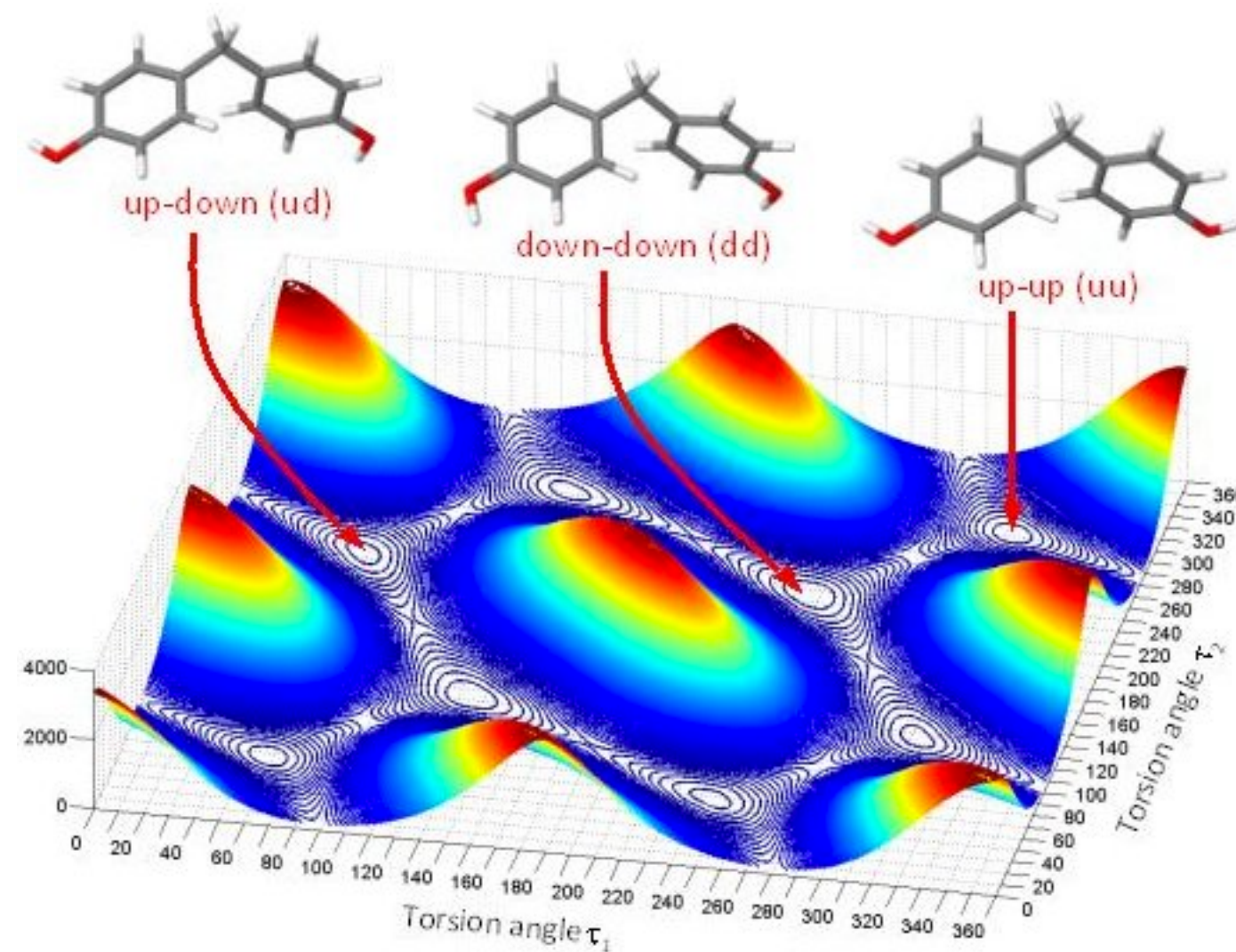
Answer:

- Figure 1.4 shows scaled plots of $w(r)$ and $F(r)$ for the given values of A and B , showing the various zero points, minima, points of inflexion, and asymptotic values of the energy and force functions, and the relationship between them.
- $w(r)$ is minimum when $dw/dr = 0$. This occurs at $r = r_e = (2B/A)^{1/6} = 0.355$ nm.
- Substituting r_e into Eq. (1.7) gives
$$w(r_e) = w_{\min} = -A^2/4B = -A/2r_e^6 = -2.5 \times 10^{-21} \text{ J} \rightarrow 2.5 \times 10^{-21} / 4.1 \times 10^{-21} = 0.61 \text{ kT}$$
at 298 K.
- $w_{\min}(r_e)/w_{\text{VDW}}(r_e) = (-A/2r_e^6)/(-A/r_e^6) = \frac{1}{2}$.
- Since $w(r) = 0$ at $r = r_0 = (B/A)^{1/6}$, we obtain $r_e/r_0 = 2^{1/6} = 1.12$. Thus, $r_0 = 0.316$ nm.
- The force is given by $F = -dw/dr$, and F_{\max} occurs at $d^2w/dr^2 = 0$ —that is, when $r = r_s = (26B/7A)^{1/6}$. Thus, $r_s/r_0 = (26/7)^{1/6} = 1.24$, and $r_s = (26B/7A)^{1/6} = 0.3935$ nm.
- $F_{\max} = -dw/dr = -6A/r^7 + 12B/r^{13}$ at $r = r_s = 0.3935$ nm.
Thus, $F_{\max} = -(126A^2/169B)/(26B/7A)^{1/6} = -1.89 \times 10^{-11} \text{ N} = -18.9 \text{ pN}$ (attractive).
- The effective spring constant or stiffness is defined by
$$k = |(dF/dr)_{r_e}| = d^2w/dr^2 = 42A/r^8 - 156B/r^{14}$$
at $r = r_e = (2B/A)^{1/6}$, giving
$$k = |42A(2B/A)^{-4/3} - 156B(2B/A)^{-7/3}| = 18(A^7B^{-4}/2)^{1/3} = 14.3 \text{ N m}^{-1}.$$
- The best conventional laboratory balance can measure down to $0.1 \mu\text{g}$ (about 10^{-9} N). To measure weaker forces, one needs specialized techniques. The *Atomic Force Microscope* (AFM) can measure forces down to 1 pN (see Section 12.8), while forces as small as 10^{-15} N (1 fN) can now be measured between molecules or small colloidal particles in solution using various optical techniques (see Chapter 12).

Potential energy surface

It is the graph of the potential... problem: usually the number of variables is of order $3N$... we draw cuts, projections, or we define global variables for the systems (gyration radius, other order parameters...)

$$V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$$



This is a simple case as a function of two torsional angles of this molecule (Müller group, Bochum). **All other coordinates are optimised to their equilibrium value.**

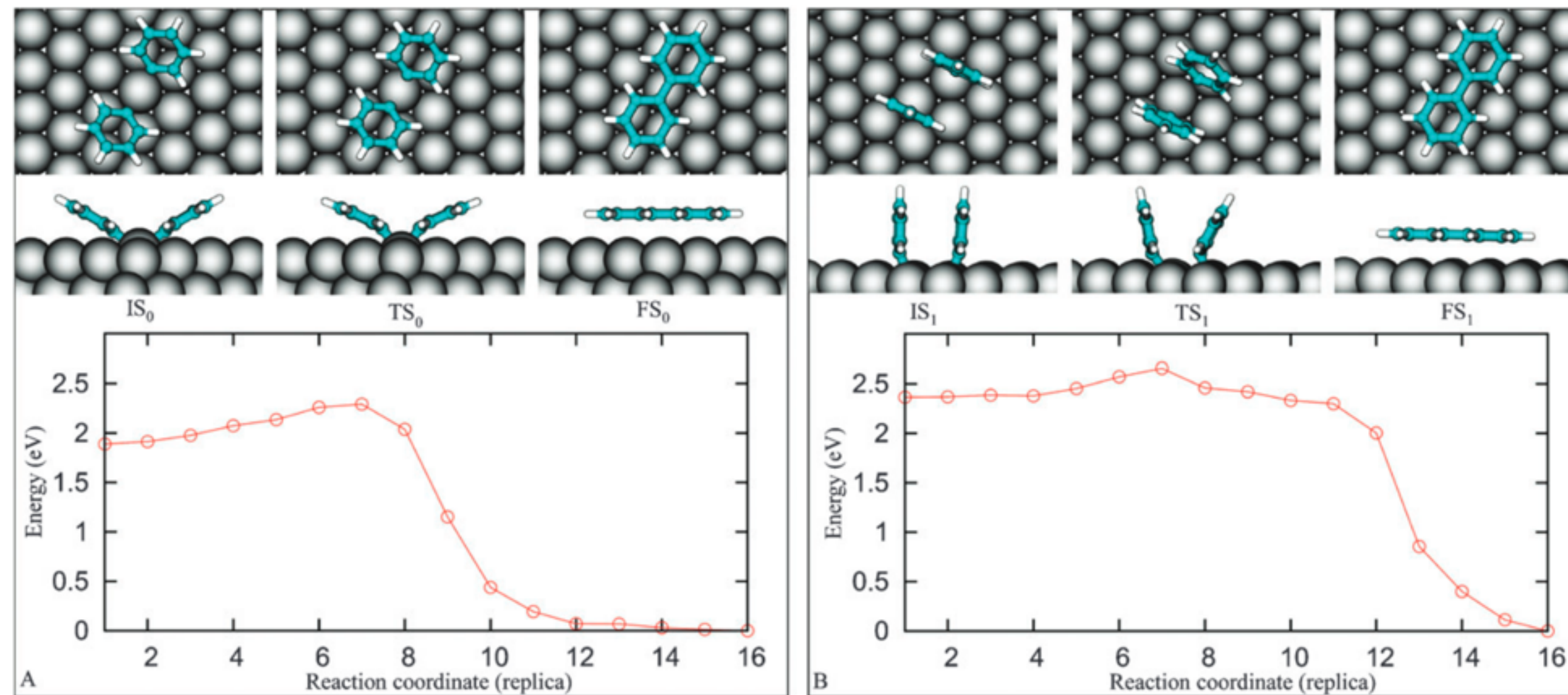
Locating stationary points

The potential energy of the system is a function of atomic coordinates:

$$V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$$

and the forces can be obtained by derivation; setting them to zero gives us maxima, minima and transition states.

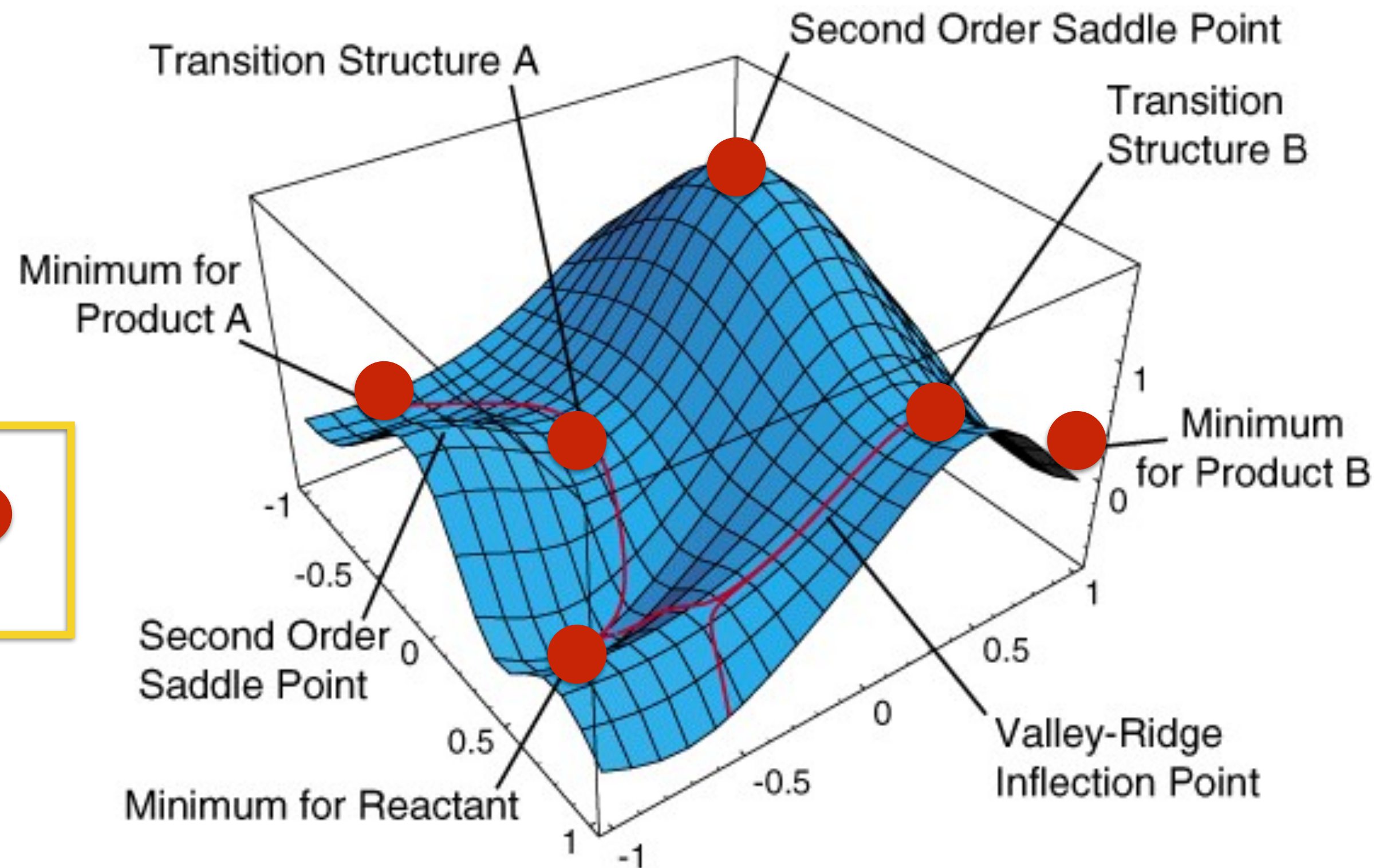
$$F_i = -\frac{\partial V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)}{\partial r_i} = 0 \quad \forall i$$



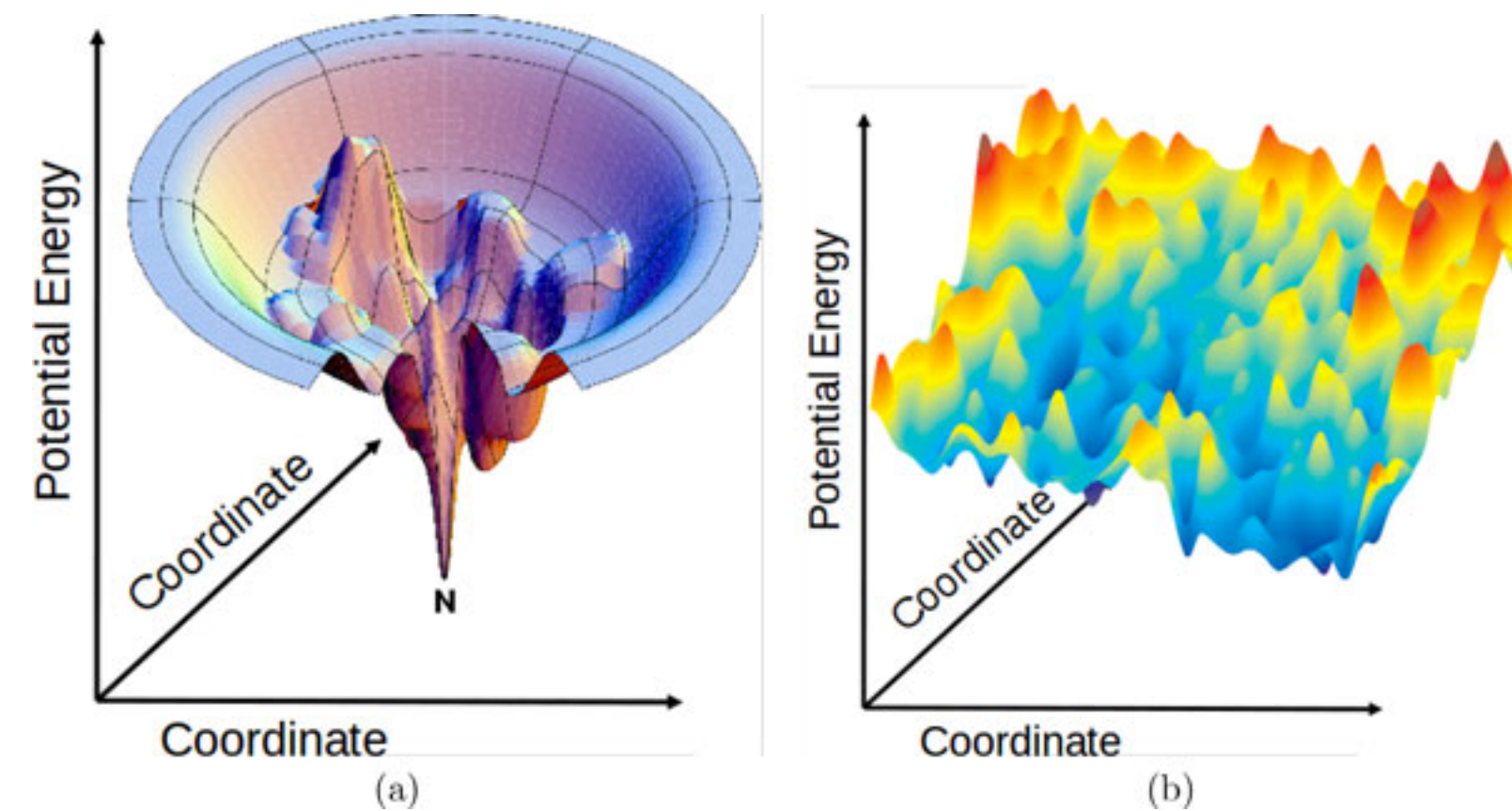
Potential Energy Surface: minima and transition states

Potential Energy Surface describes the energy of the system as a function of the coordinates. It is in principle known as soon as the **interaction** model is defined. Marked are the points of zero gradient of the potential

$$F_i = -\frac{\partial V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)}{\partial r_i} = 0 \quad \forall i$$



Methods to locate minima



- **WITHOUT** gradients: evaluate V on a grid of points, maybe in a clever way, and then locate the minimum value of V . Trivial but computationally intensive,
- **WITH** gradients:
 - Steepest descent
 - Non-linear conjugate gradient
 - Broyden-Fletcher-Goldfarb-Shanno (BFGS)
 - L-BFGS
- Such methods can be **INSUFFICIENT** to describe the thermodynamics of a system, for example if we are in a situation like (b), typical of molecules interacting with a solvent... next lectures: **FREE ENERGY METHODS**.

Non-linear conjugate gradients

1. Calculate the steepest direction: $\Delta x_n = -\nabla_x f(x_n)$,
2. Compute β_n according to one of the formulas below,
3. Update the conjugate direction: $s_n = \Delta x_n + \beta_n s_{n-1}$
4. Perform a line search: optimize $\alpha_n = \arg \min_{\alpha} f(x_n + \alpha s_n)$,
5. Update the position: $x_{n+1} = x_n + \alpha_n s_n$,

- Fletcher–Reeves

$$\beta_n^{FR} = \frac{\Delta x_n^T \Delta x_n}{\Delta x_{n-1}^T \Delta x_{n-1}}.$$

- Polak–Ribière:

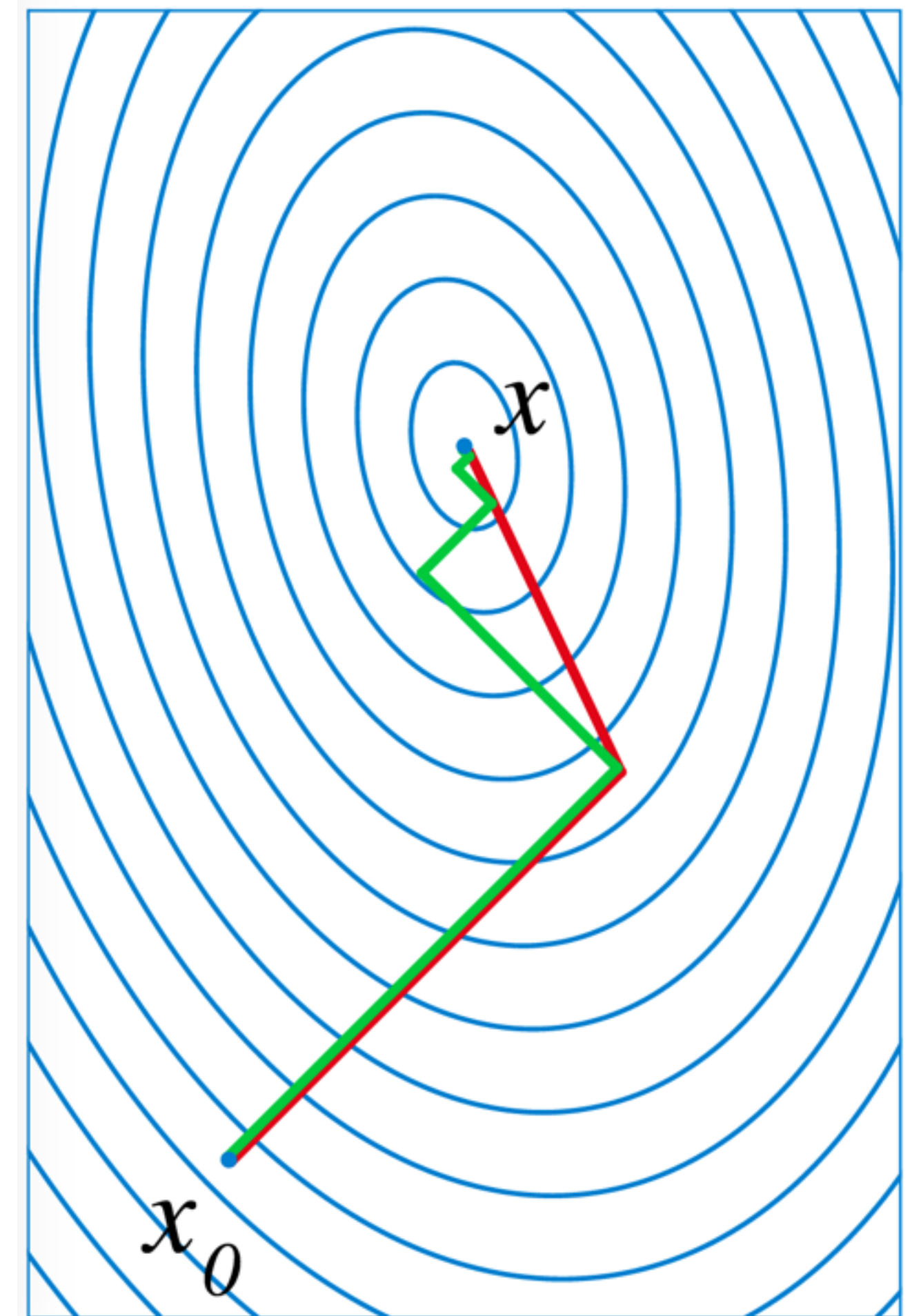
$$\beta_n^{PR} = \frac{\Delta x_n^T (\Delta x_n - \Delta x_{n-1})}{\Delta x_{n-1}^T \Delta x_{n-1}}.$$

- Hestenes–Stiefel:

$$\beta_n^{HS} = -\frac{\Delta x_n^T (\Delta x_n - \Delta x_{n-1})}{s_{n-1}^T (\Delta x_n - \Delta x_{n-1})}.$$

- Dai–Yuan:

$$\beta_n^{DY} = -\frac{\Delta x_n^T \Delta x_n}{s_{n-1}^T (\Delta x_n - \Delta x_{n-1})}.$$



BFGS

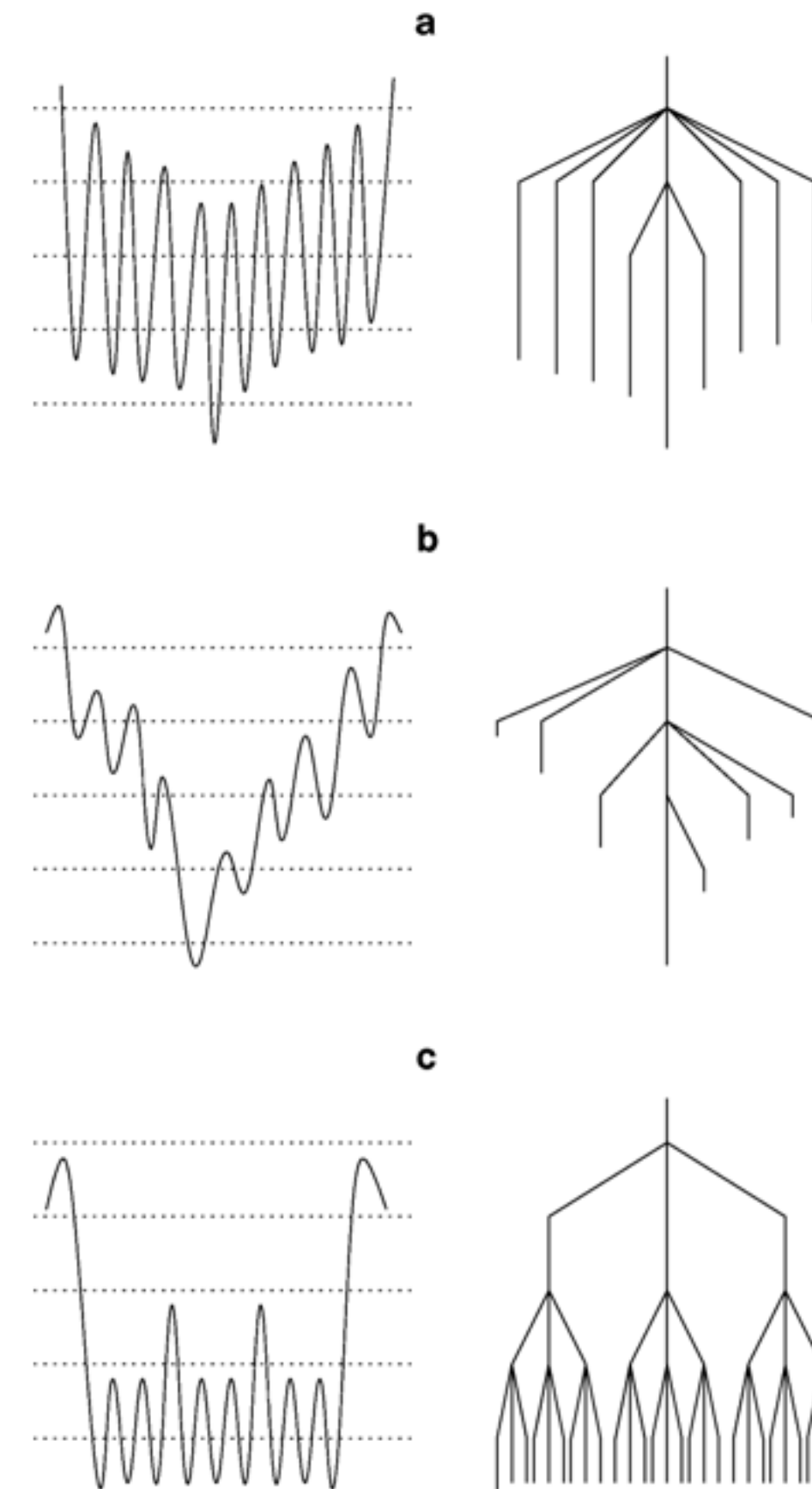
In quasi-Newton methods, the Hessian matrix of second derivatives doesn't need to be evaluated directly. Instead, the Hessian matrix is approximated using updates specified by gradient evaluations (or approximate gradient evaluations). Quasi-Newton methods are generalizations of the secant method to find the root of the first derivative for multidimensional problems.

From an initial guess \mathbf{x}_0 and an approximate Hessian matrix B_0 the following steps are repeated as \mathbf{x}_k converges to the solution:

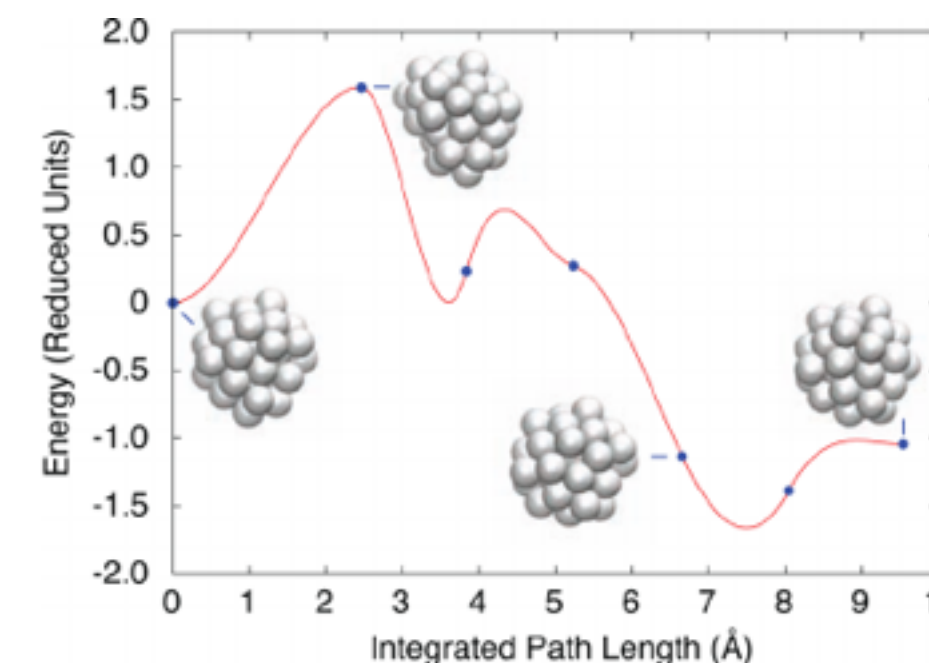
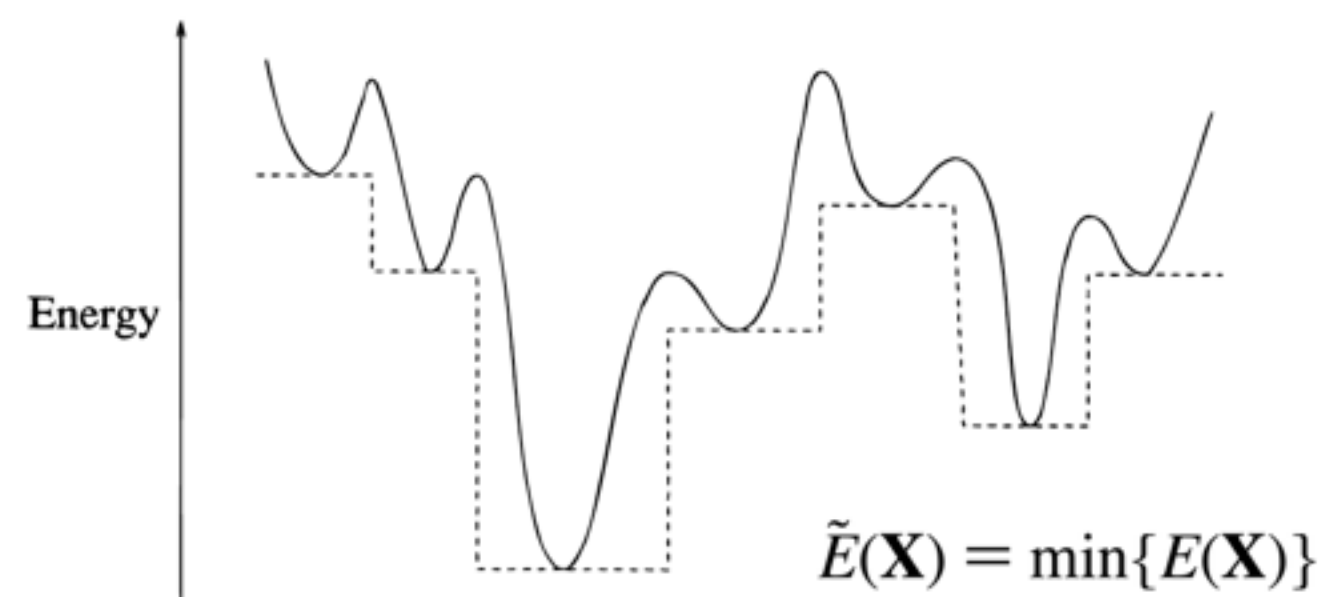
1. Obtain a direction \mathbf{p}_k by solving $B_k \mathbf{p}_k = -\nabla f(\mathbf{x}_k)$.
2. Perform a **line search** to find an acceptable stepsize α_k in the direction found in the first step, then update
$$\mathbf{x}_{k+1} = \mathbf{x}_k + \alpha_k \mathbf{p}_k.$$
3. Set $\mathbf{s}_k = \alpha_k \mathbf{p}_k$.
4. $\mathbf{y}_k = \nabla f(\mathbf{x}_{k+1}) - \nabla f(\mathbf{x}_k)$.
5.
$$B_{k+1} = B_k + \frac{\mathbf{y}_k \mathbf{y}_k^T}{\mathbf{y}_k^T \mathbf{s}_k} - \frac{B_k \mathbf{s}_k \mathbf{s}_k^T B_k}{\mathbf{s}_k^T B_k \mathbf{s}_k}.$$

Potential energy surfaces in a complex system

- As a function of the coordinates, the interaction potential can show several local minima
- Such local minima are connected by transition states at various energies. Classically such transition states can be overcome by the system only if the total energy allows that
- Thus it makes sense to draw “disconnectivity graphs” for energy landscapes
- **a**, The 'weeping willow' results from a gentle funnel with large barriers.
- **b**, The 'palm tree' results from a steeper funnel with lower barriers.
- **c**, The 'banyan tree' results from a rough landscape.
- Problem of how to reach the **global minimum** of the PES
- Example of strategy: **basin hopping method** (Wales and Doye): the exploration of the PES is done in a modified energy landscape, where each basin of attraction has the constant energy of the corresponding local minimum



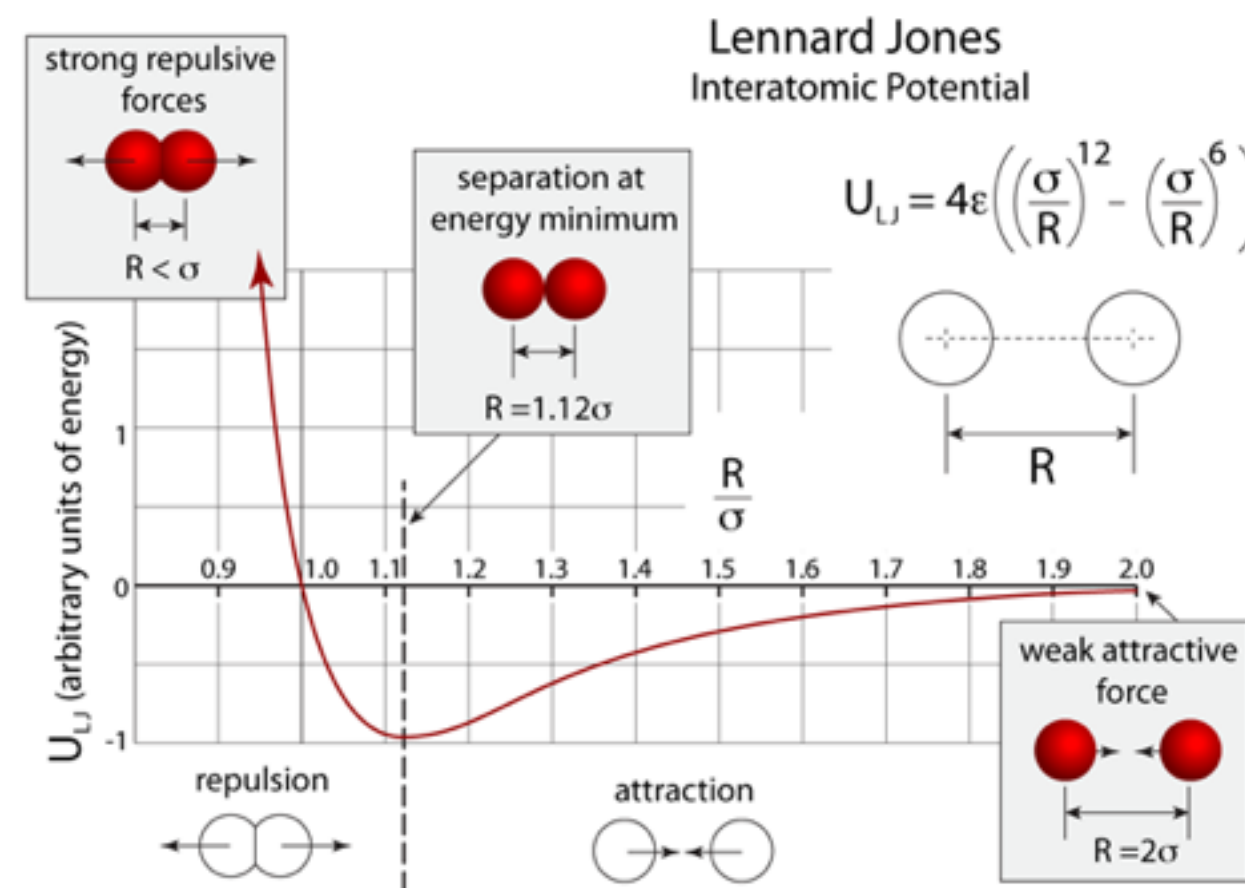
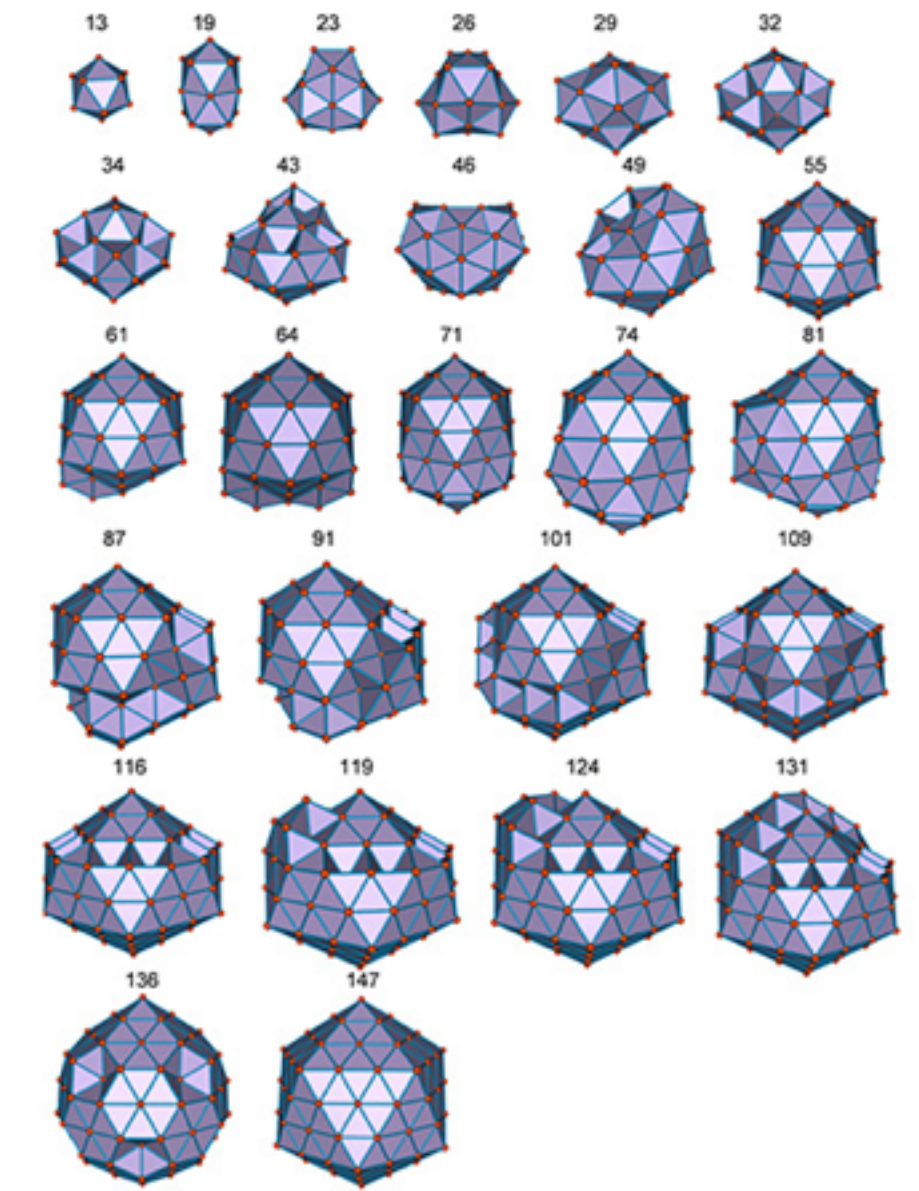
From the following article:
Archetypal energy landscapes
 David J. Wales, Mark A. Miller and Tiffany R. Walsh
Nature **394**, 758-760(20 August 1998)
 doi:10.1038/29487



Local minima are connected by transition states

Lennard-Jones clusters (see <http://doye.chem.ox.ac.uk/research/clusters.html>)

- Clusters are finite aggregates of atoms or molecules, which can contain from a few to tens of thousands of atoms or molecules, and so they provide a bridge between isolated atoms and molecules and bulk matter.
- In this intermediate size regime it is particularly interesting to observe the emergence of properties that involve the collective behaviour of the atoms and molecules and to see how these properties evolve to the familiar bulk-like behaviour.
- LJ clusters are clusters of atoms interacting only via dispersion forces: typically, noble gas atoms (He) Ar, Ne, Kr, Xe, Rn

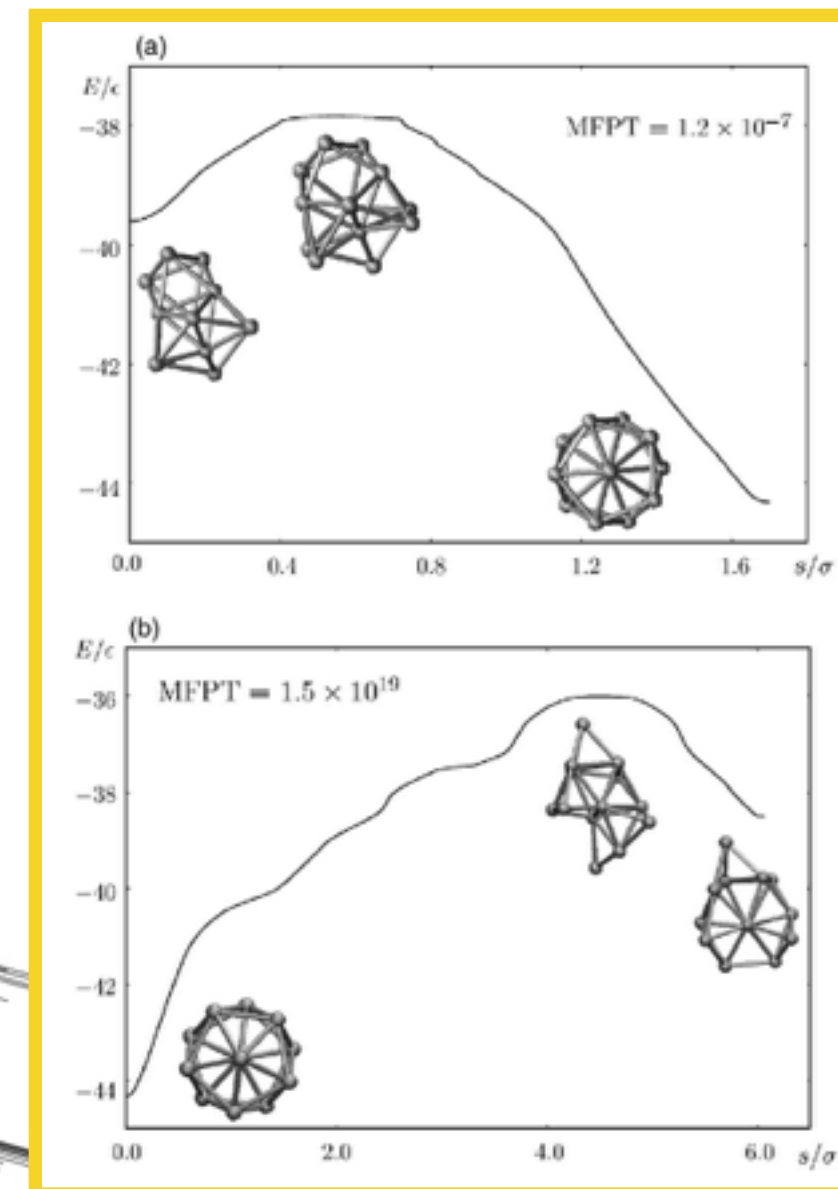
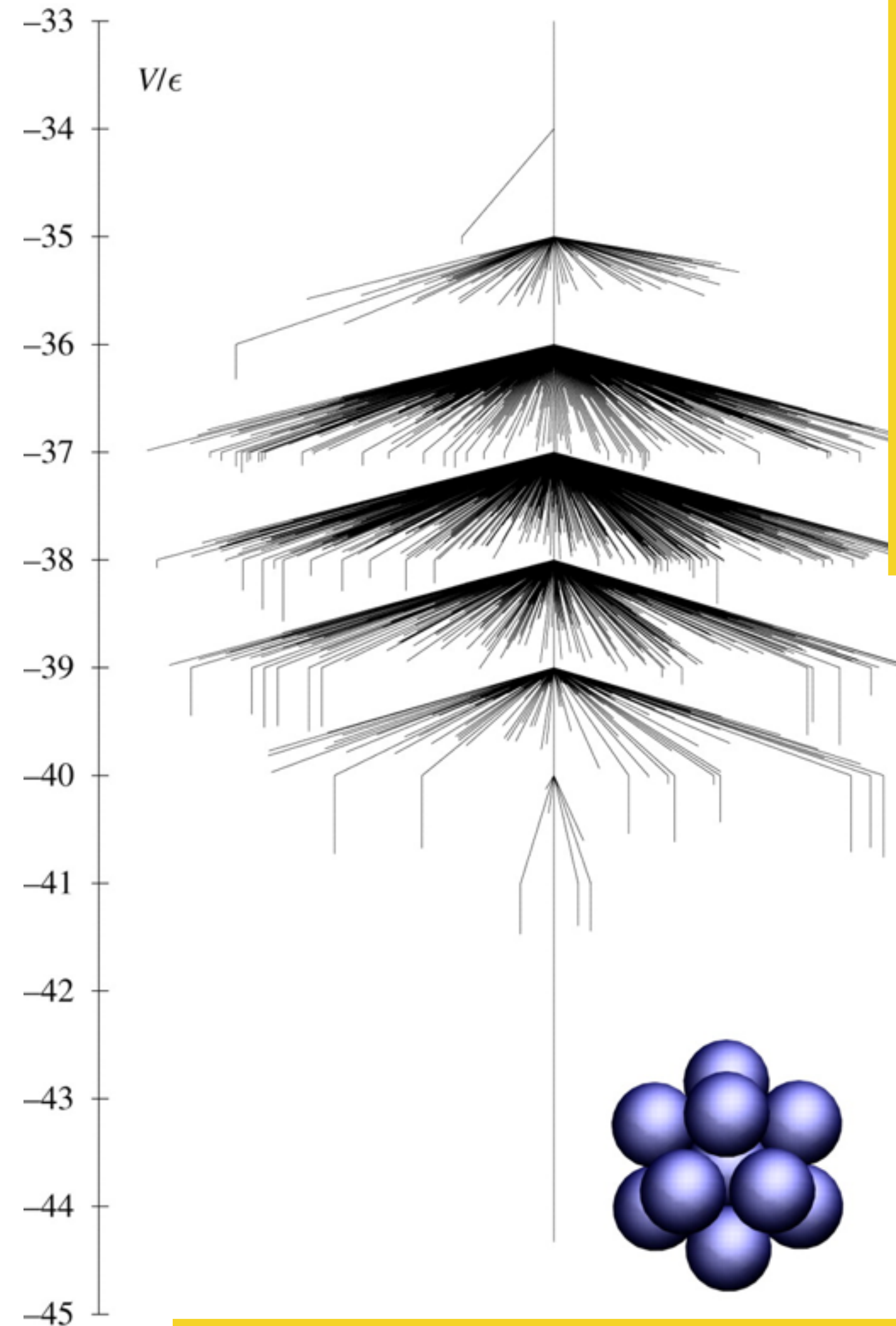


<http://atomsinmotion.com/>

- They can be observed experimentally, and they are IDEAL for testing algorithms for exploring energy surfaces: only pairwise interaction, growing complexity of the PES, rich thermodynamics....
- Given the kind interaction, all properties of (say) Ar clusters are basically the same for Ne, Kr, Xe... upon rescaling of lengths and energies. **THIS IS AN APPROXIMATION** (rather valid in this case).
- For this reason, a cluster of N argon atoms is called in the computational community: LJ- N cluster.

Disconnectivity graphs

- To construct a potential energy disconnectivity graph from a connected set of local minima, we first choose an energy spacing, ΔV , and then determine how the minima are partitioned into subsets (superbasins) at threshold energies $V_0, V_0 + \Delta V, V_0 + 2\Delta V, \dots$
- The subsets are groups of minima, which can interconvert via transition states that lie below the potential energy threshold. At sufficiently high energy, all the minima can interconvert without exceeding the threshold (unless there are infinite barriers) and there is a single superbasin.
- As we lower the threshold energy, the superbasins progressively split apart, and the disconnectivity graph follows this splitting by connecting subgroups to the parent superbasin at the threshold energy above.
- Eventually, the superbasins split into individual local minima, which are represented by points at the corresponding potential energy on a vertical scale, connected to the parent superbasin at the closest superbasin energy above.
- Disconnectivity graph for the LJ13 cluster including 1467 local minima identified for this system.
- **Inset:** examples of transition paths connecting adjacent minima. The height of the barrier can be connected to the transition rate that determines the **kinetics** of phase transformation: here MFPT = Mean first passage time

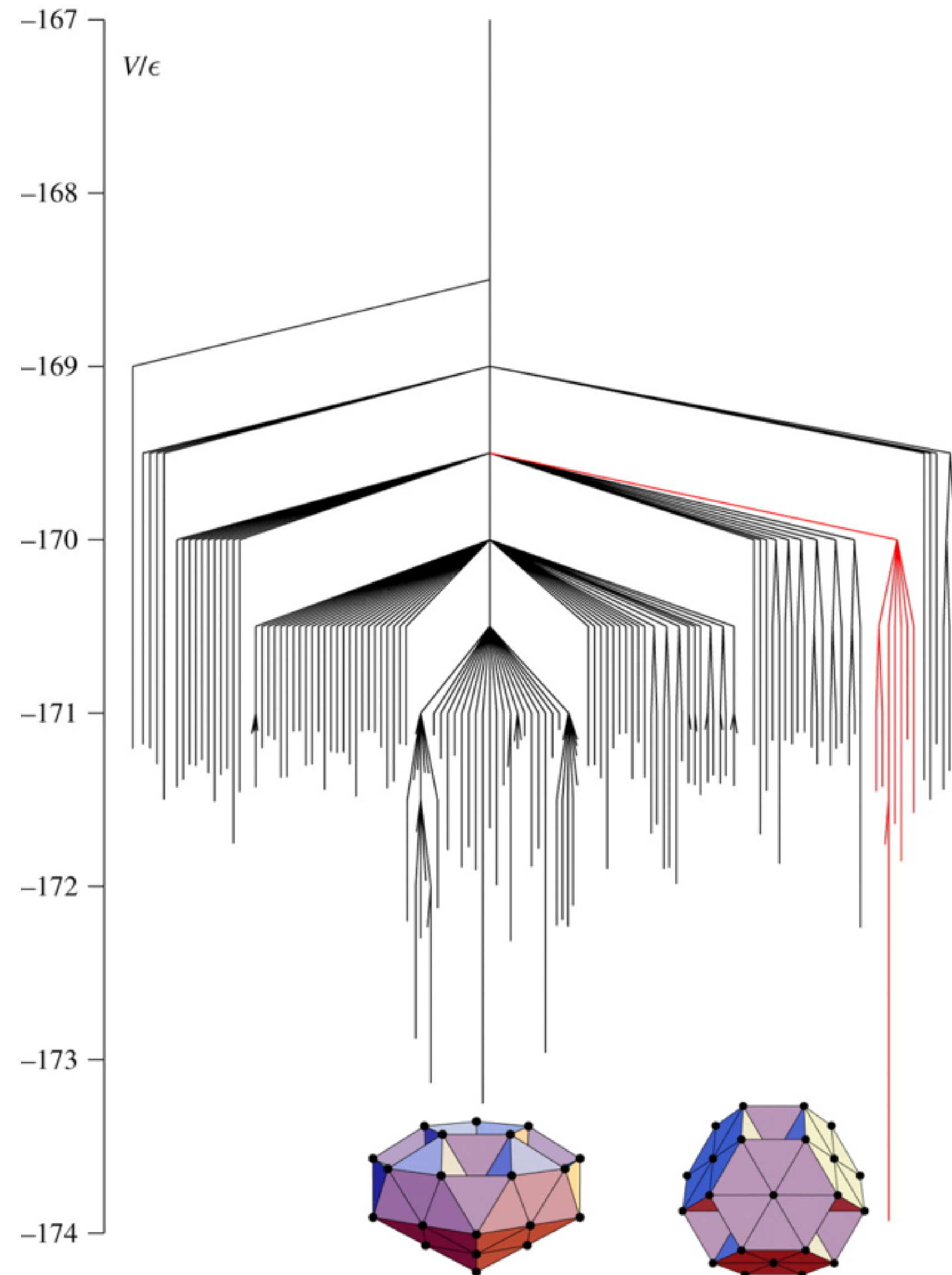


D. J. Wales, Comparison of double-ended transition state search methods. The Journal of Chemical Physics 127, 134102 (2007).

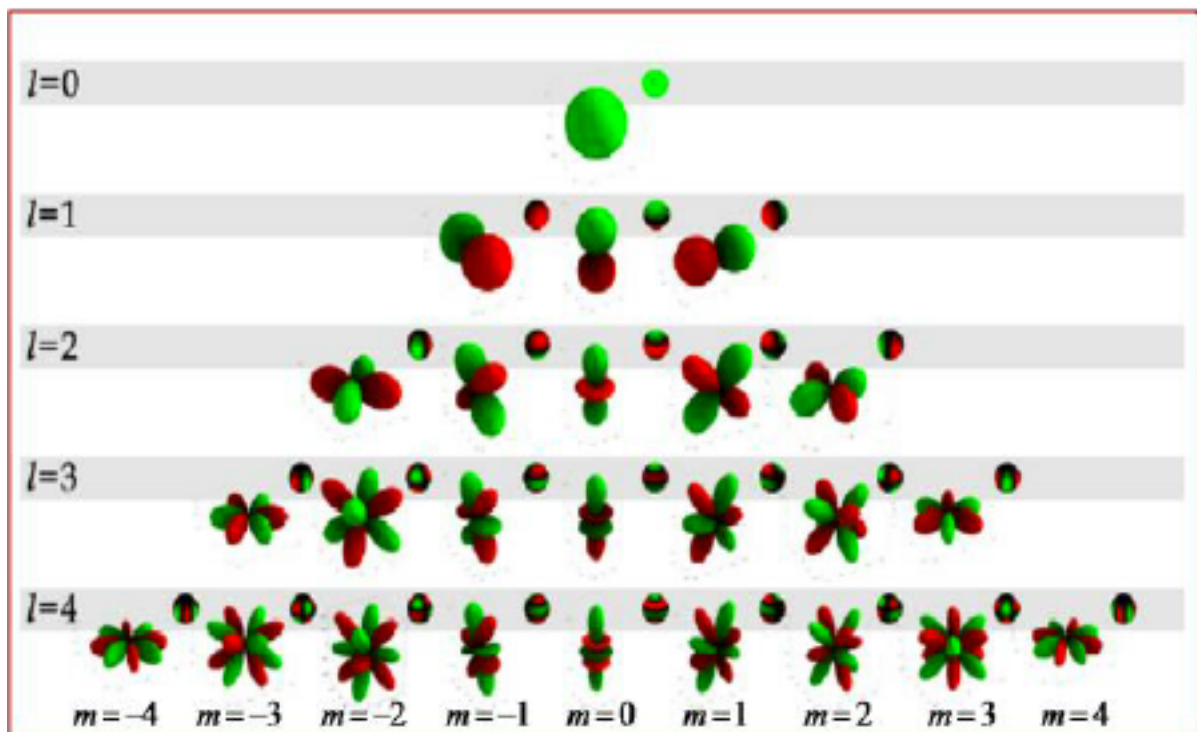
Disconnectivity graph for LJ38

- In this case, there are two competing morphologies separated by a high barrier, corresponding to an incomplete Mackay icosahedron and a truncated octahedron (fcc).
- Branches of the graph associated with minima based on the octahedron are coloured red.

Wales, D. J. Decoding the energy landscape: extracting structure, dynamics and thermodynamics. *Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences* 370, 2877–2899 (2012).

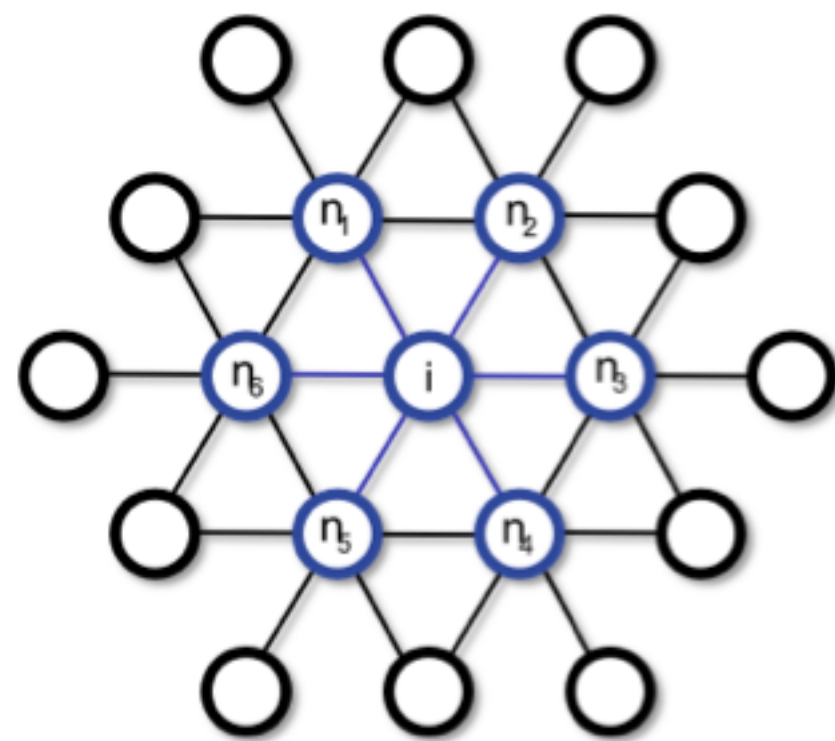


How to identify classes of structures: Steinhardt order parameters



(Robin Green, Spherical Harmonic Lighting: The Gritty Details)

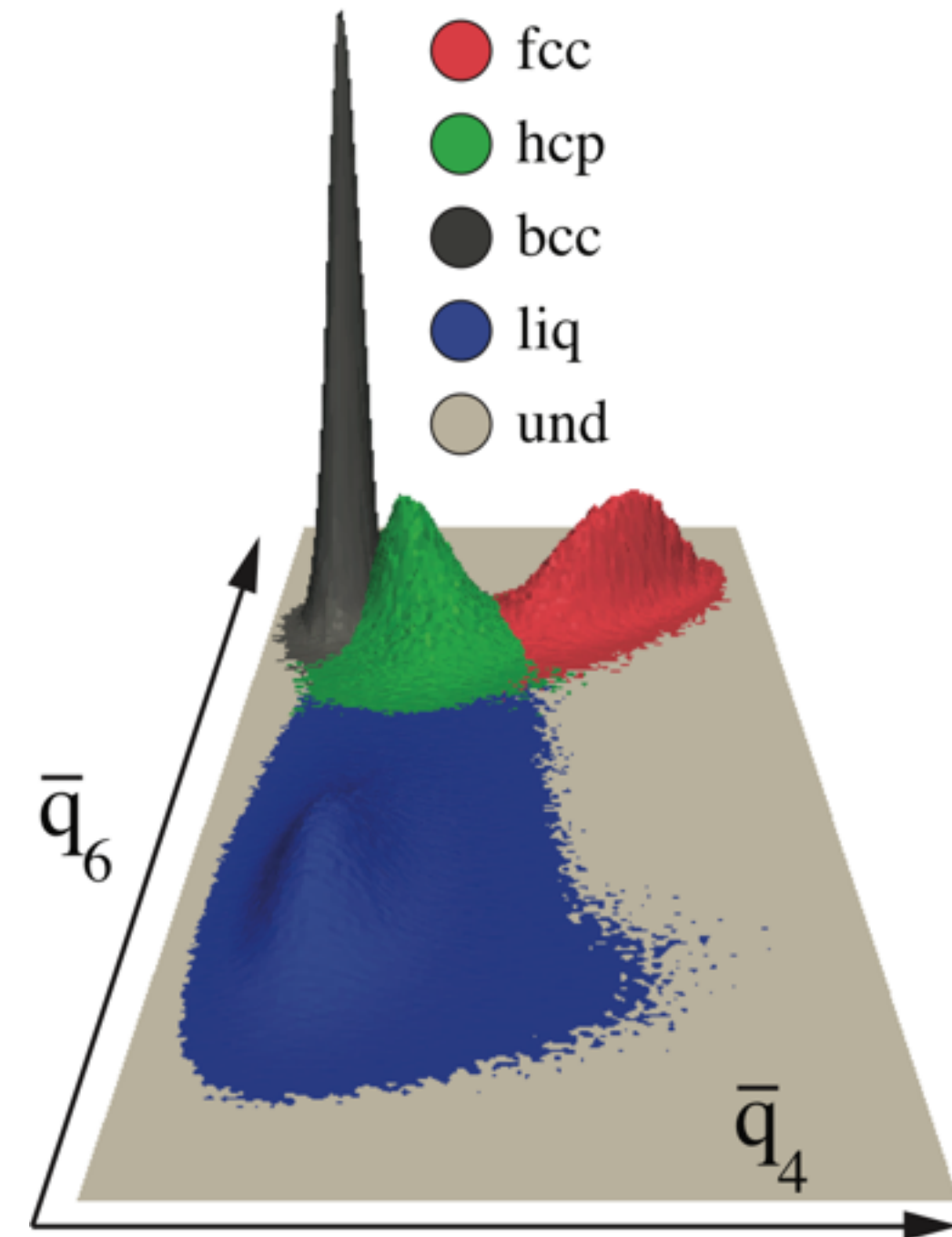
- Steinhardt parameters measure the local order in the neighbourhood of an atom and are able to distinguish between solid and liquid structures as well as between different symmetries in ordered structures.
- They are a function of the vectors joining neighbouring atoms (bonds).
- They use **spherical harmonics**, that have maxima in particular directions on a sphere upon varying the index l
- q_4 and q_6 are useful for liquid-solid transitions



$$q_{lm}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{lm}(r_{ij})$$

$$\bar{q}_{lm}(i) = \frac{q_{lm}(i) + \sum_{k=0}^{N_b} q_{lm}(k)}{N_b + 1}$$

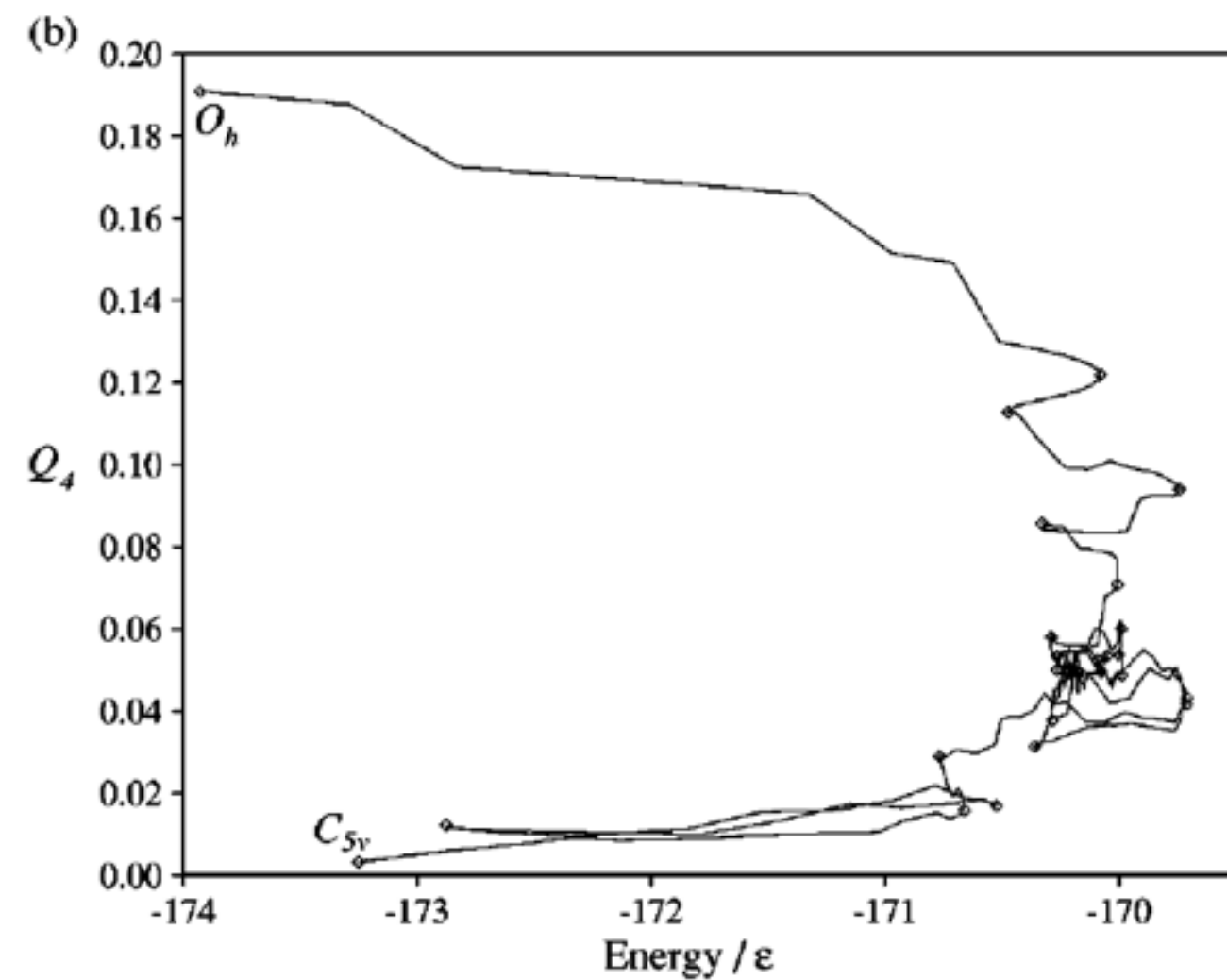
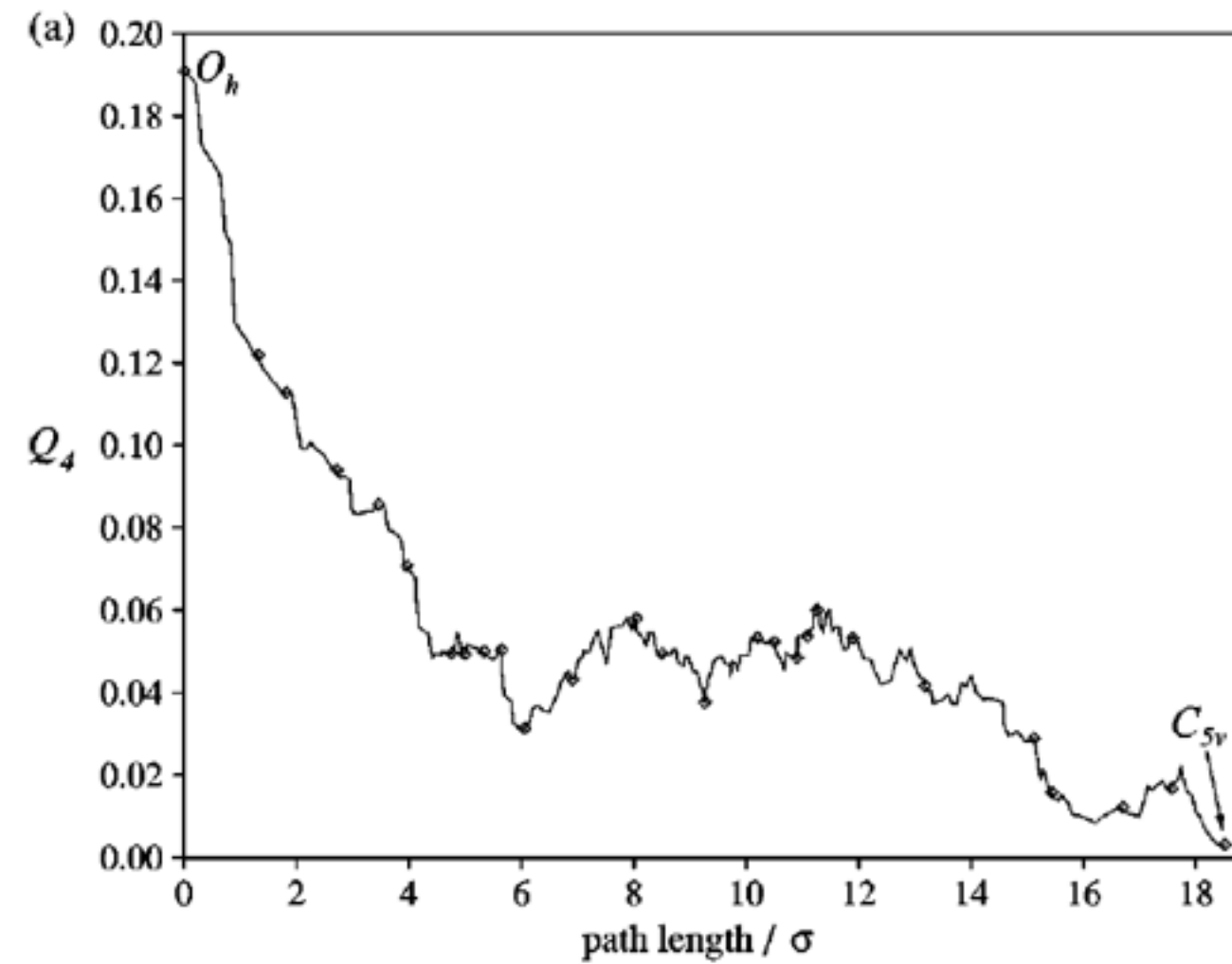
$$\bar{q}_l(i) = \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^l |\bar{q}_{lm}(i)|^2}$$



Wolfgang Lechner, University of Vienna
<https://homepage.univie.ac.at/wolfgang.lechner/nucleation.html>

P. Steinhardt, D. Nelson, and M. Ronchetti, Phys. Rev. B 28, 784 (1983).

q4 in the LJ38 cluster



Along a transition pathway from the global minimum to an icosahedral one, the q_4 parameter signals the change of symmetry

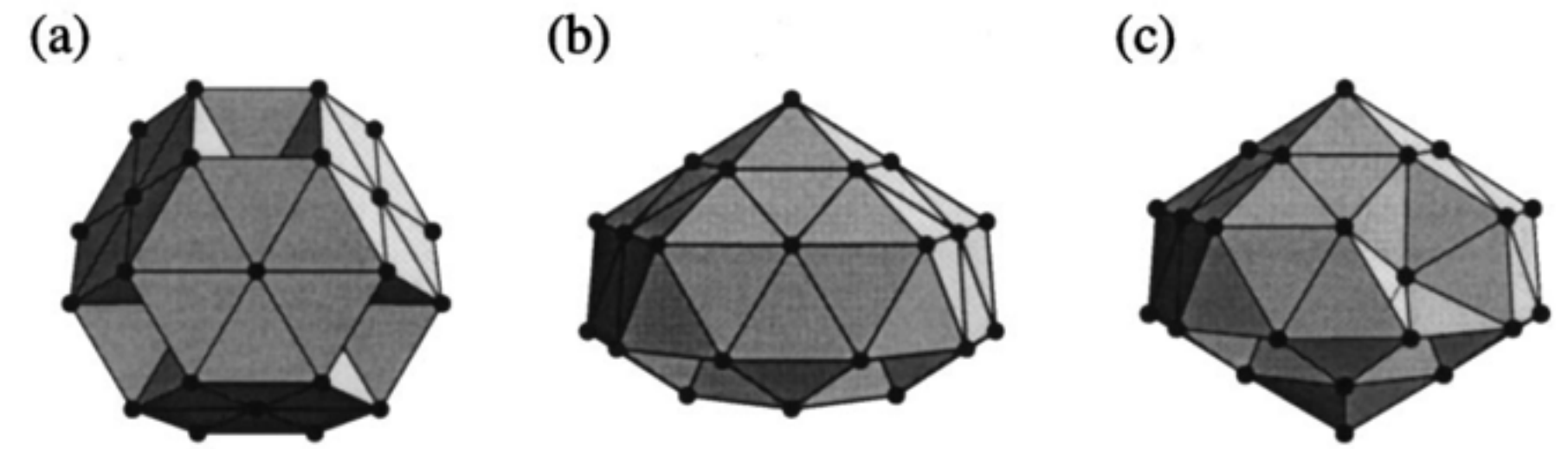
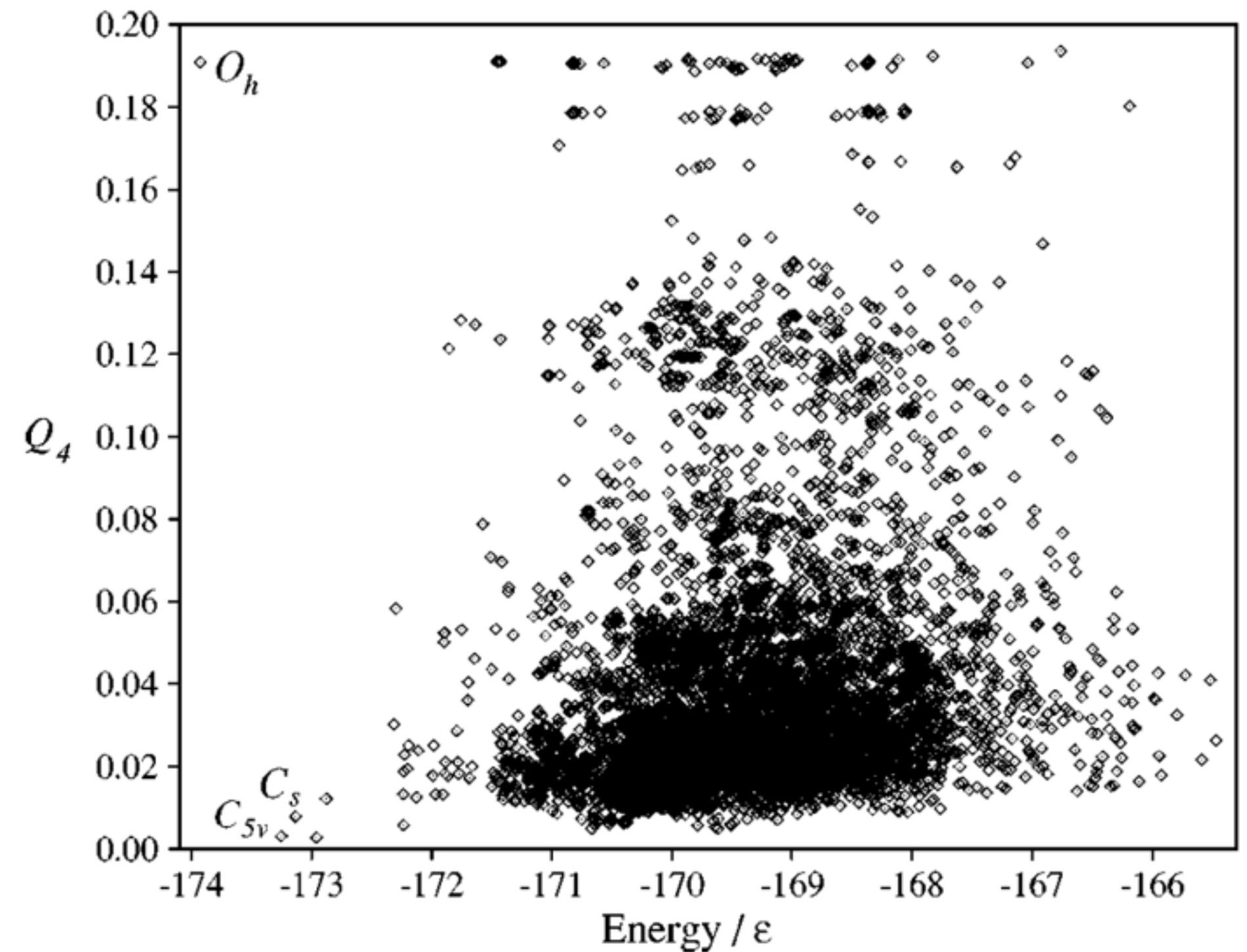
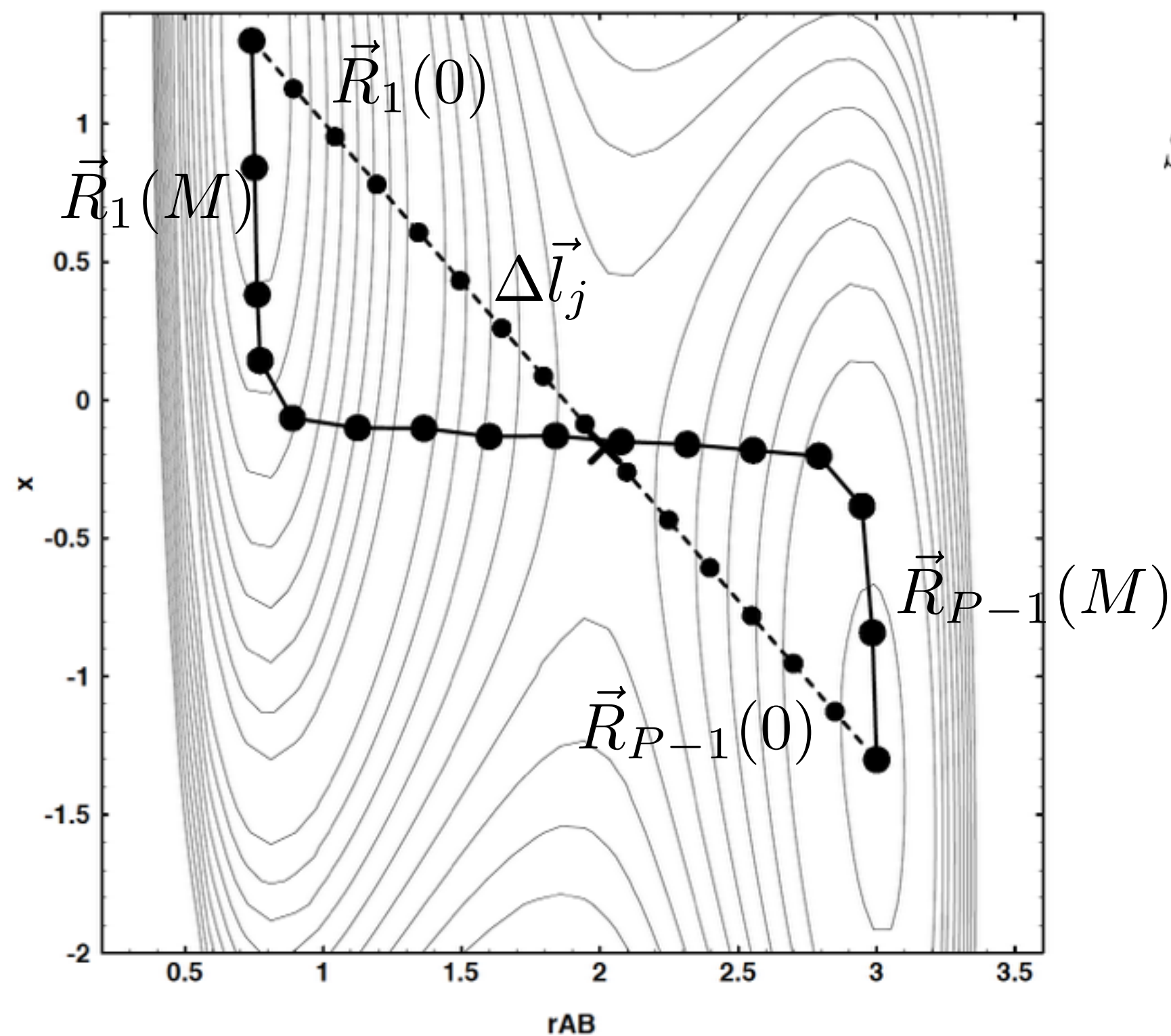


FIG. 1. (a) The LJ_{38} global minimum, an fcc truncated octahedron ($E = -173.928\,427\epsilon$; point group O_h). (b) Second lowest energy minimum of LJ_{38} ($E = -173.252\,378\epsilon$; point group C_{5v}). (c) Third lowest energy minimum ($E = -173.134\,317\epsilon$; point group C_s). The structures in (b) and (c) are both incomplete Mackay icosahedra.



Locating transition states: for today, only band method...

In chain-of-states methods, several images (or 'states') of the system are connected together by a spring of a certain spring constant to trace out a path. If the images are connected with springs of zero natural length and the object function is defined as (Elber and Karplus). Such function is minimized iteratively, until at convergence (step M), should pass through the transition state. Not only, but the path will be called “**Minimum energy path**” (MEP) being the the lowest-energy path connecting two minima on a potential energy surface.



$$S^{EK}(\vec{R}_1, \dots, \vec{R}_{P-1}) = \frac{1}{\sqrt{\sum_j |\Delta \vec{l}_j|^2}} \sum_{j=1}^{P-1} V(\vec{R}_j) |\Delta \vec{l}_j| + \sum_{j=1}^P \lambda \left(|\Delta \vec{l}_j| - \sqrt{\frac{\sum_j |\Delta \vec{l}_j|^2}{P}} \right)^2$$

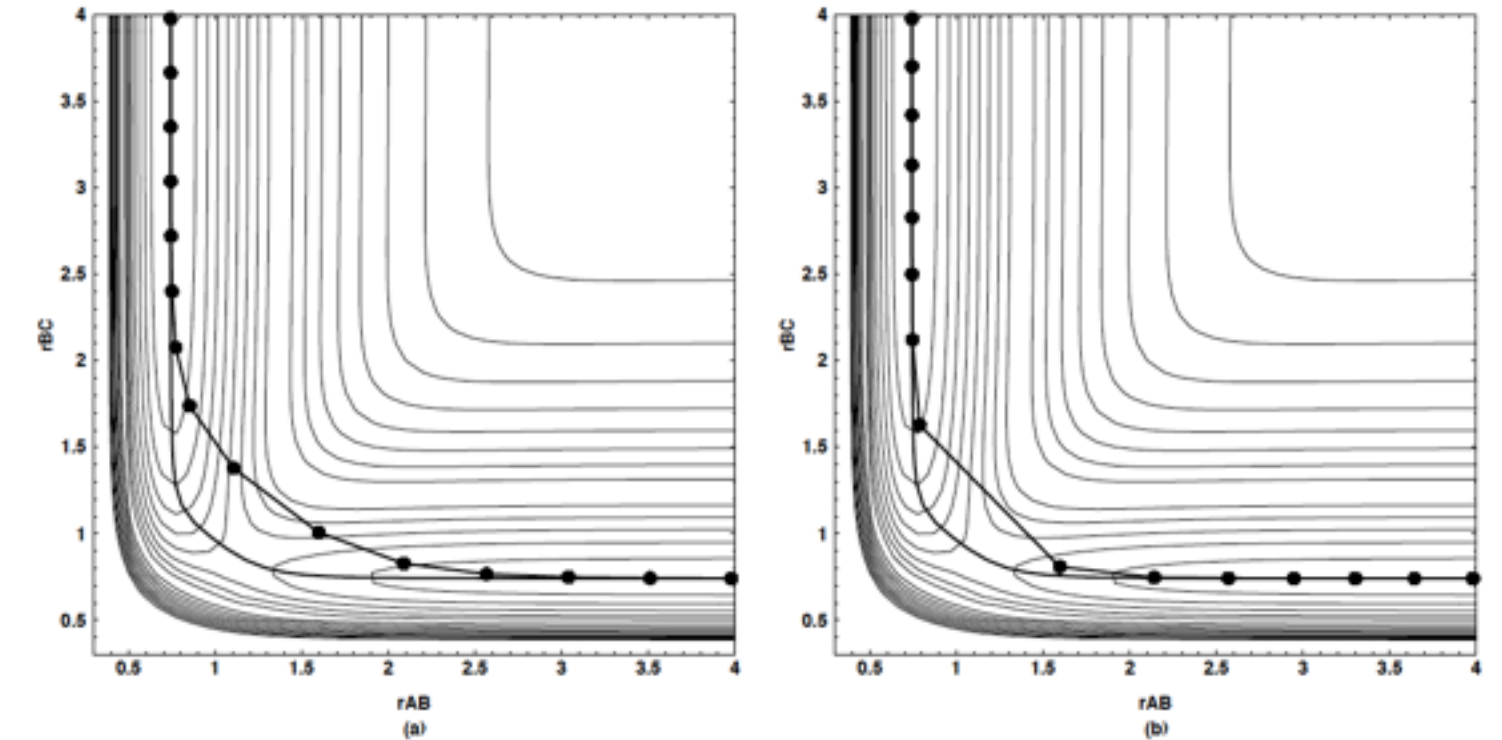
Nudged elastic band (Jonsson)

Band methods can show corner cutting and other problems.

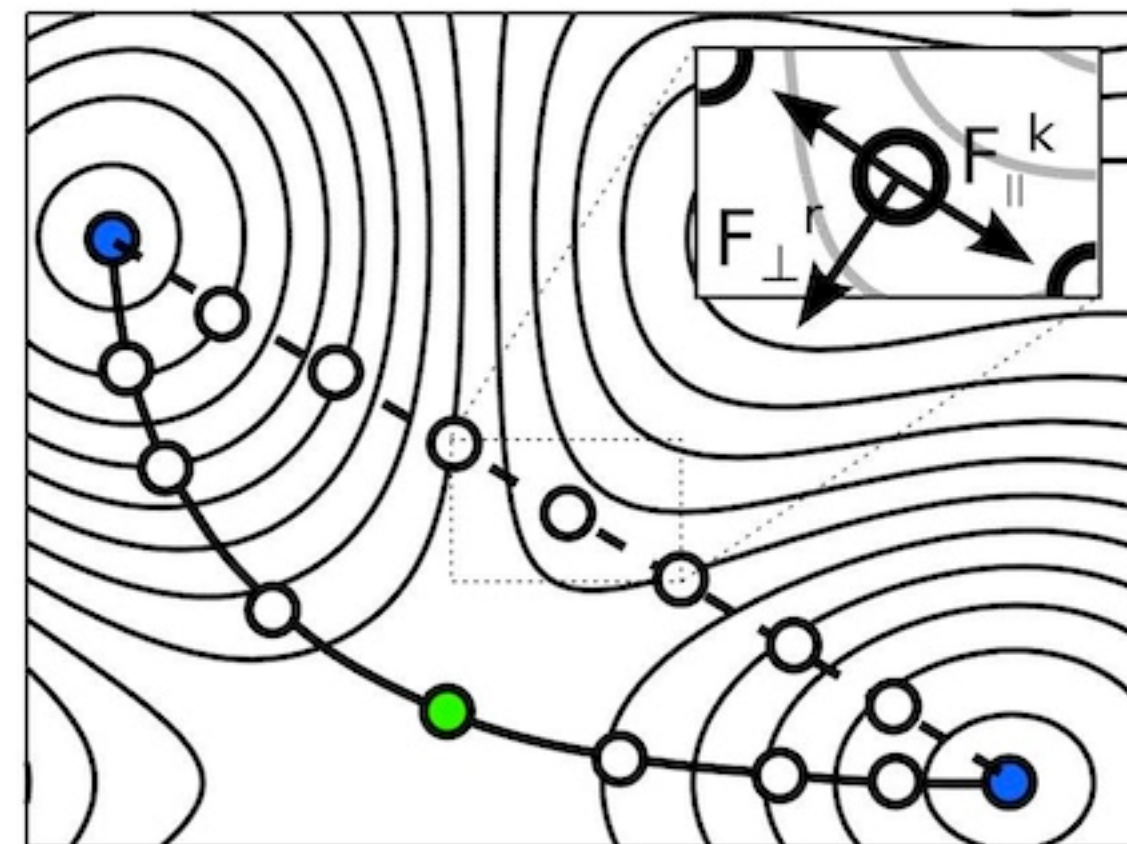
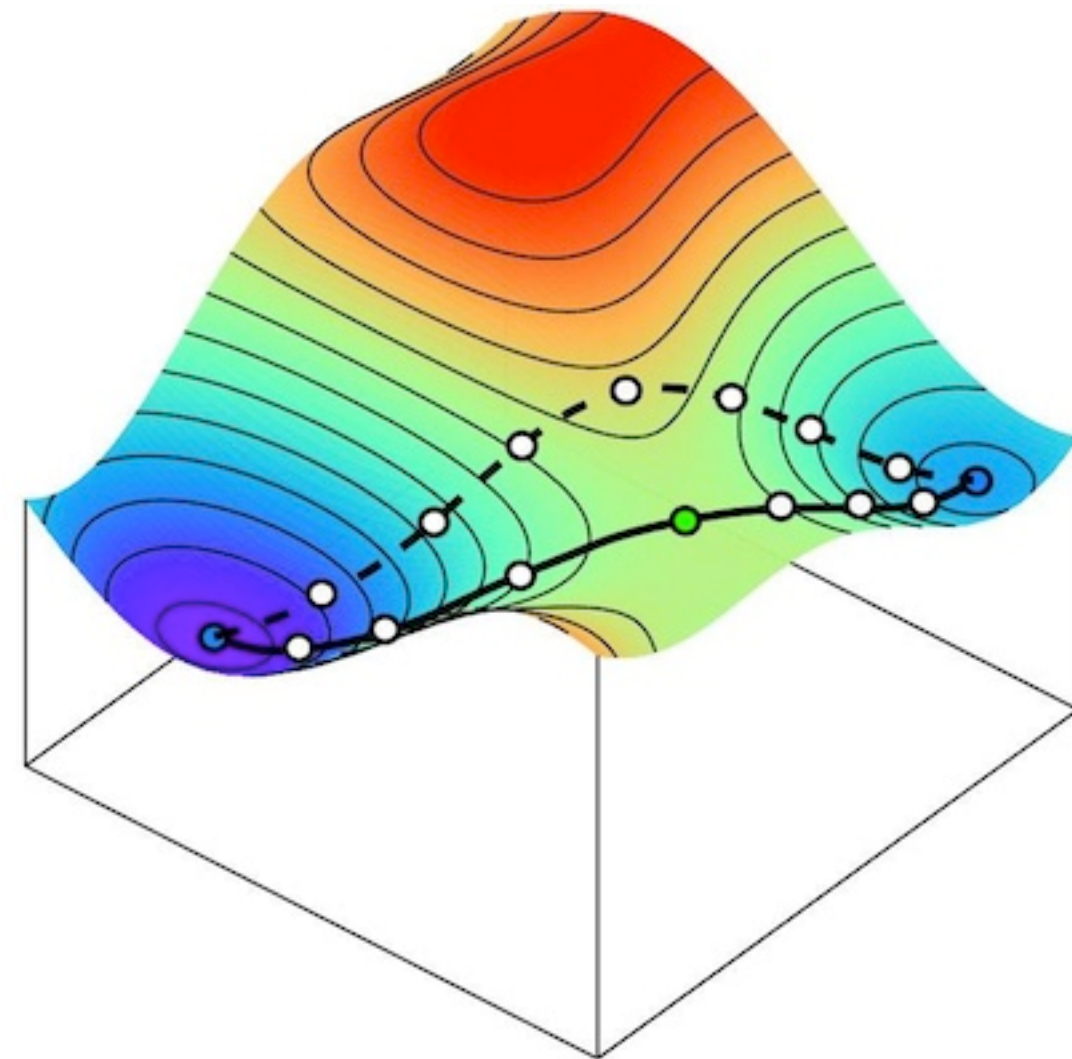
The problem with corner cutting results from the component of the spring force which is perpendicular to the path and tends to pull images off the Minimum Energy Path.

In the NEB method, a minimization of an elastic band is carried out where the perpendicular component of the spring force and the parallel component of the true force are projected out.

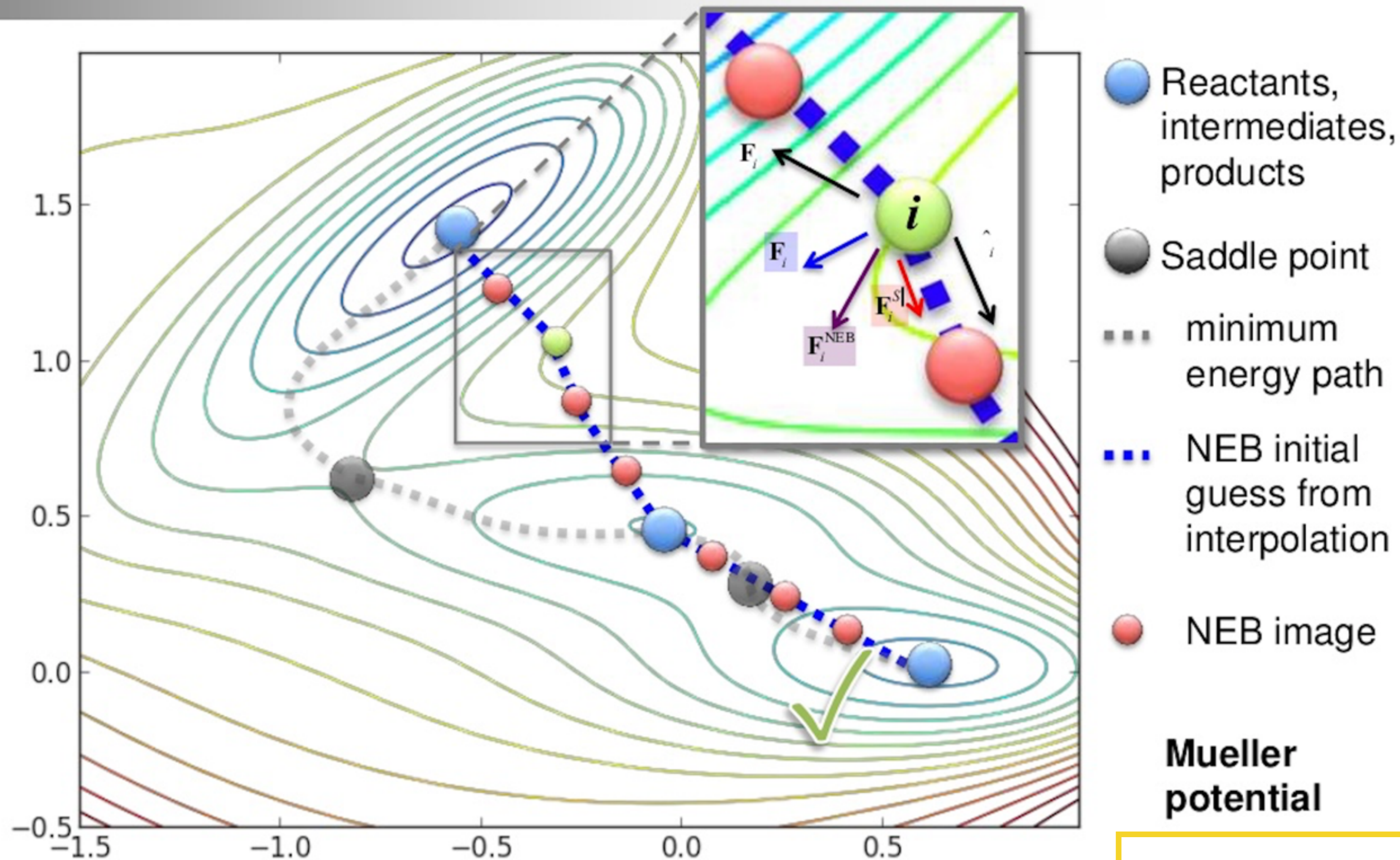
$$V^{LEPS}(r_{AB}, r_{BC}) = \frac{Q_{AB}}{1+a} + \frac{Q_{BC}}{1+b} + \frac{Q_{AC}}{1+c} - \left[\frac{J_{AB}^2}{(1+a)^2} + \frac{J_{BC}^2}{(1+b)^2} + \frac{J_{AC}^2}{(1+c)^2} - \frac{J_{AB}J_{BC}}{(1+a)(1+b)} - \frac{J_{BC}J_{AC}}{(1+b)(1+c)} - \frac{J_{AB}J_{AC}}{(1+a)(1+c)} \right]^{\frac{1}{2}} \quad (17)$$



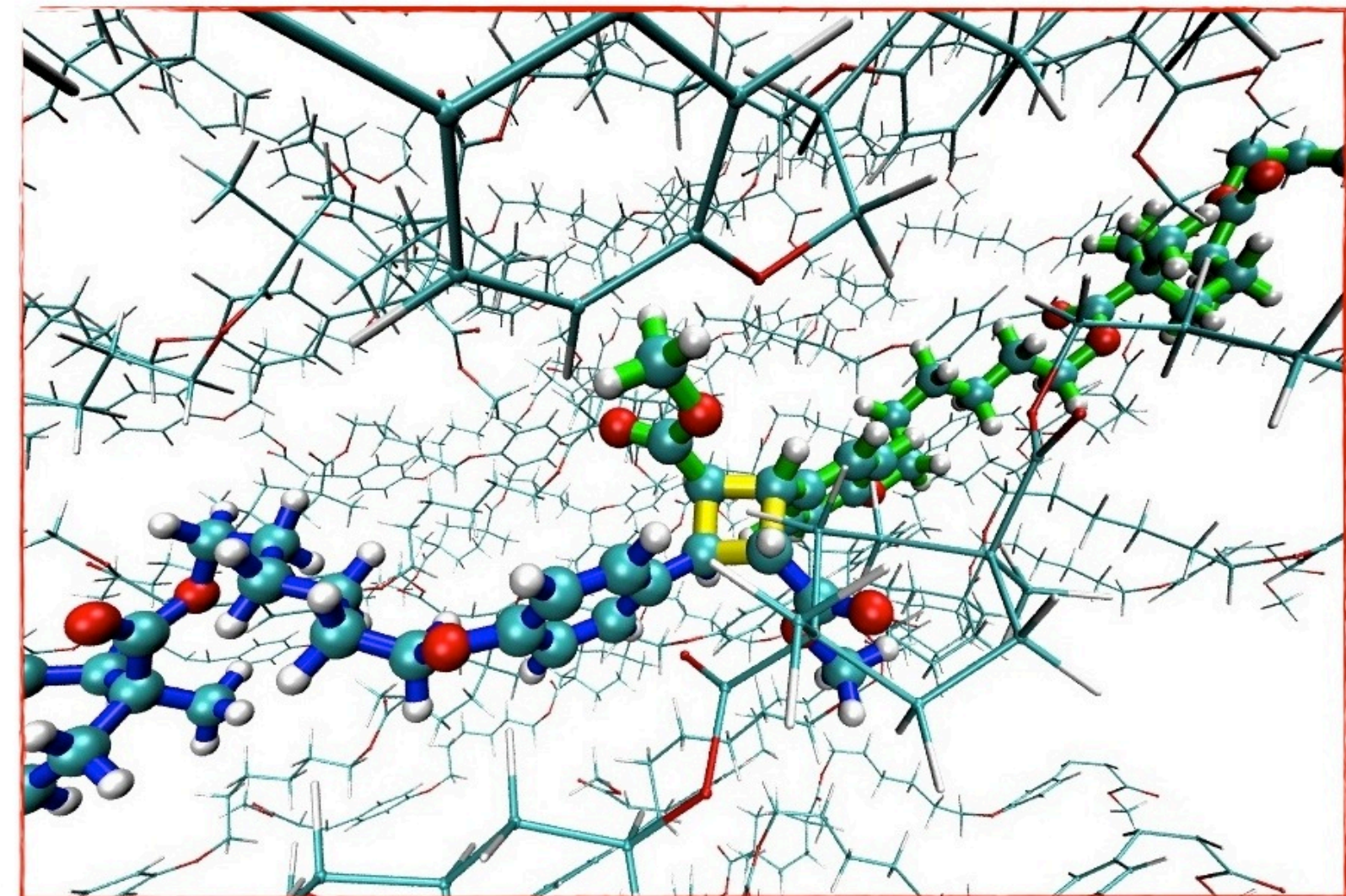
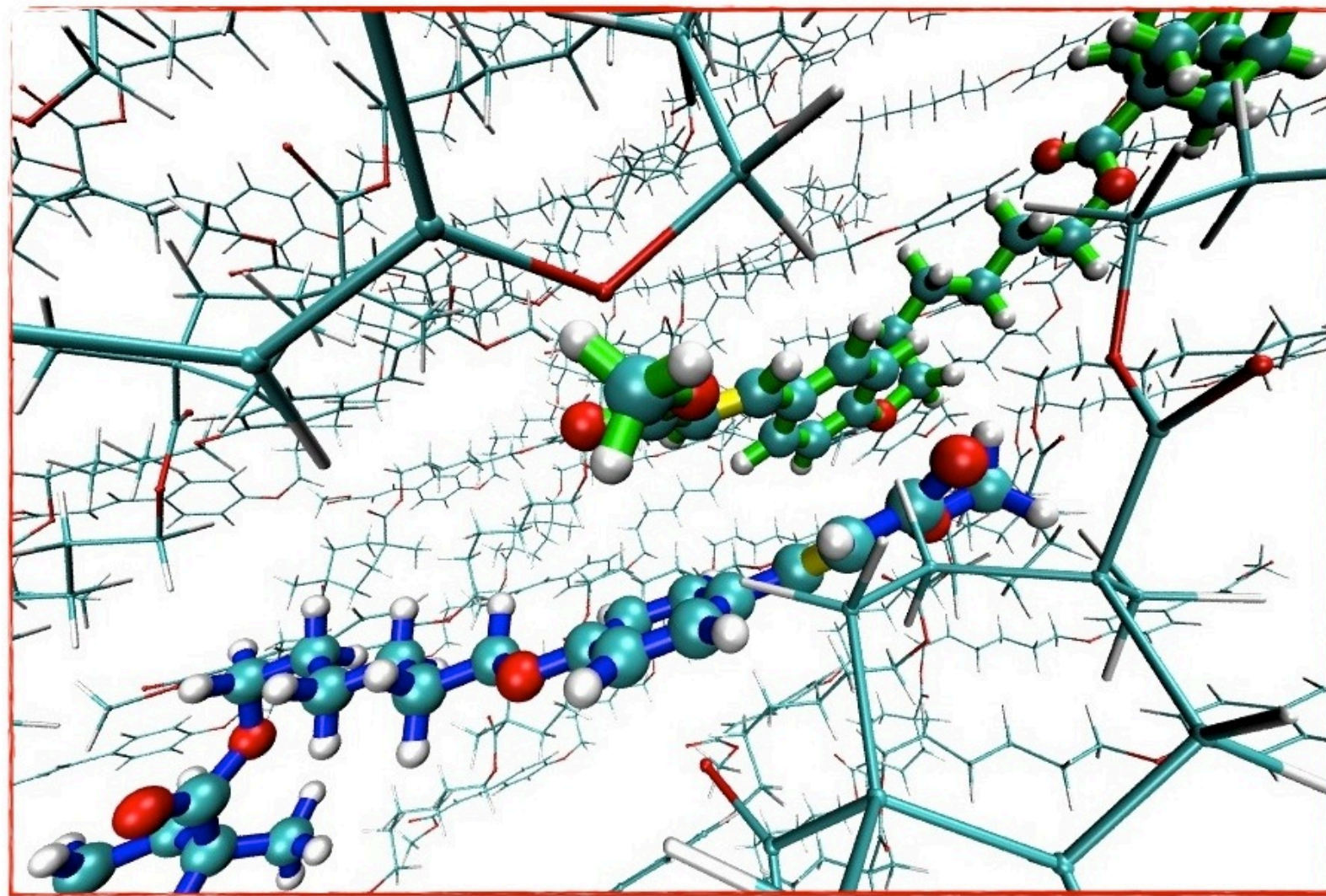
$$\vec{F}_i^0 = -\vec{\nabla}V(\vec{R}_i)|_{\perp} + \vec{F}_i^s \cdot \hat{\tau}_{\parallel} \hat{\tau}_{\parallel}$$



Another toy model to test the NEB (Jonsson et al.)



Classical MD: Force fields



Molecular dynamics and its evolution

P.H. Hünenberger and W.F. van Gunsteren

Empirical classical interaction functions for molecular simulation

In: "Computer Simulation of Biomolecular Systems, Theoretical and Experimental Applications", Vol. 3, W.F. van Gunsteren, P.K. Weiner, A.J. Wilkinson eds., Kluwer Academic Publishers, Dordrecht, The Netherlands, (1997), pp. 3-82

http://link.springer.com/chapter/10.1007%2F978-94-017-1120-3_1#

Empirical classical interaction functions for molecular simulation

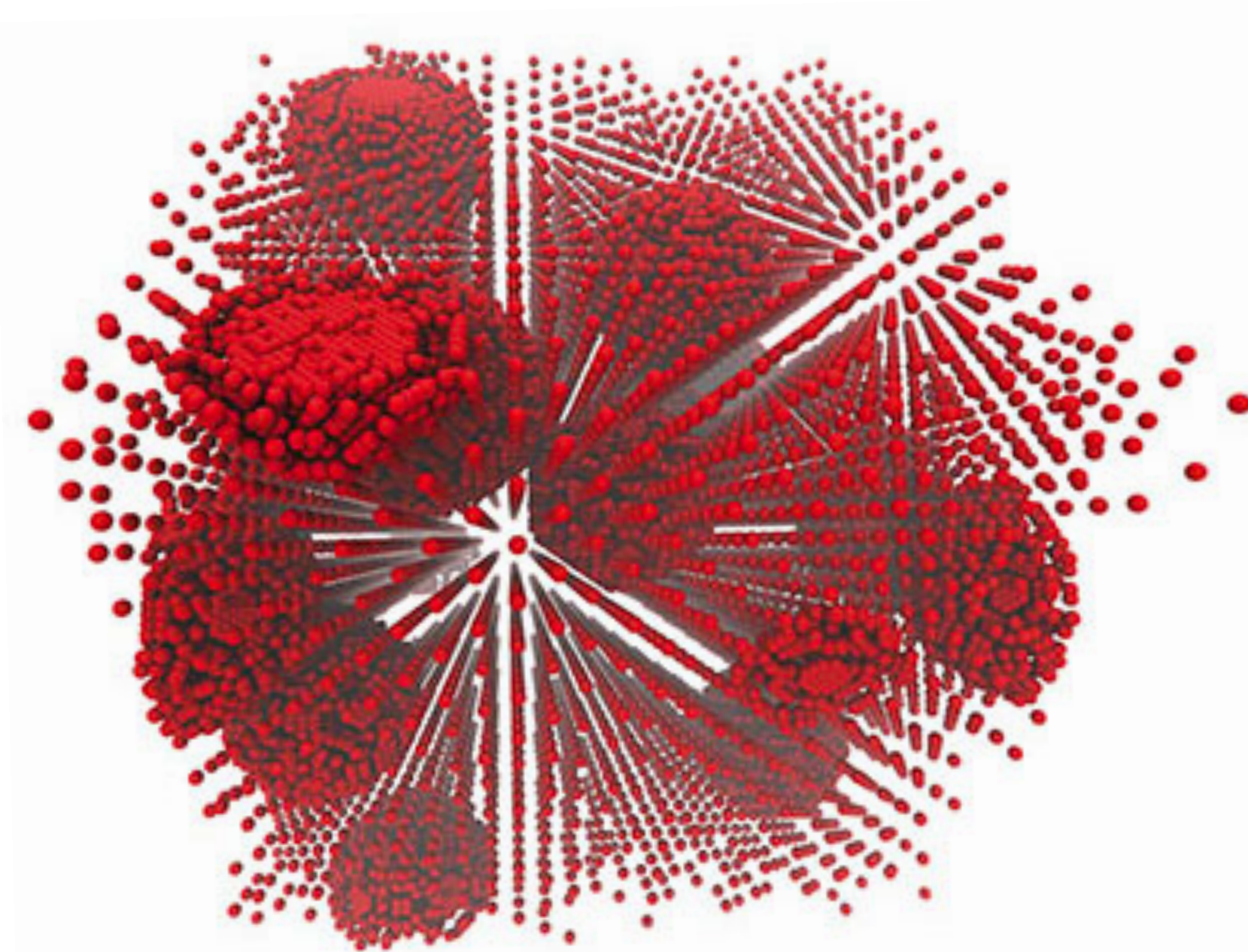
P.H. Hünenberger and W.F. van Gunsteren

Laboratory of Physical Chemistry, ETH-Zentrum, CH-8092 Zürich, Switzerland

1. Introduction

With the continuing increase of the power of computers, the past decades have seen a rapid increase in the number, performance and accuracy of theoretical computational methods in chemistry [1,2]. One can distinguish three major classes of methods for the theoretical study of molecular properties, listed in order of decreasing computational expenses: (i) *ab initio* molecular orbital methods [3]; (ii) semiempirical molecular orbital methods [4,5]; and (iii) empirical classical force-field methods. The computational expenses of *ab initio* methods are of order $O(N_f^4)$ (Hartree–Fock level) or higher (configuration interaction, many-body perturbation theory), N_f being the number of basis functions used. Density functional approaches and semiempirical methods scale as $O(N_f^3)$ or lower. The costs of empirical methods scale as $O(N_a^2)$ down to nearly $O(N_a)$, where N_a stands for the number of elementary particles (atoms or groups of atoms). Independently of the scaling with the system size, the evaluation of an empirical interaction function remains usually much cheaper than any other method (size of the prefactor to the scaling) and currently allows for the simulation of systems typically up to 10^5 – 10^6 atoms

1997: 10^5 – 10^6 atoms



Germany 2013: $(4.125 \cdot 10^{12})$ particles on Garching's SuperMUC, 146,016 cores used to reach an actual processing power of 591.2 teraFLOPS!!!!

In liquid form, 4.125 trillion molecules of the noble gas krypton would occupy the volume of a cube whose edges are 6.3 micrometers long. Thus the simulation computation pushes forward into a domain in which it should soon be possible to directly compare the results of simulations with the results of measurements – an important advance on the way to reliable insights into properties of matter.

Why simulation? Which choices?

- Hühnenberger + van Gunsteren 1997: HvG97

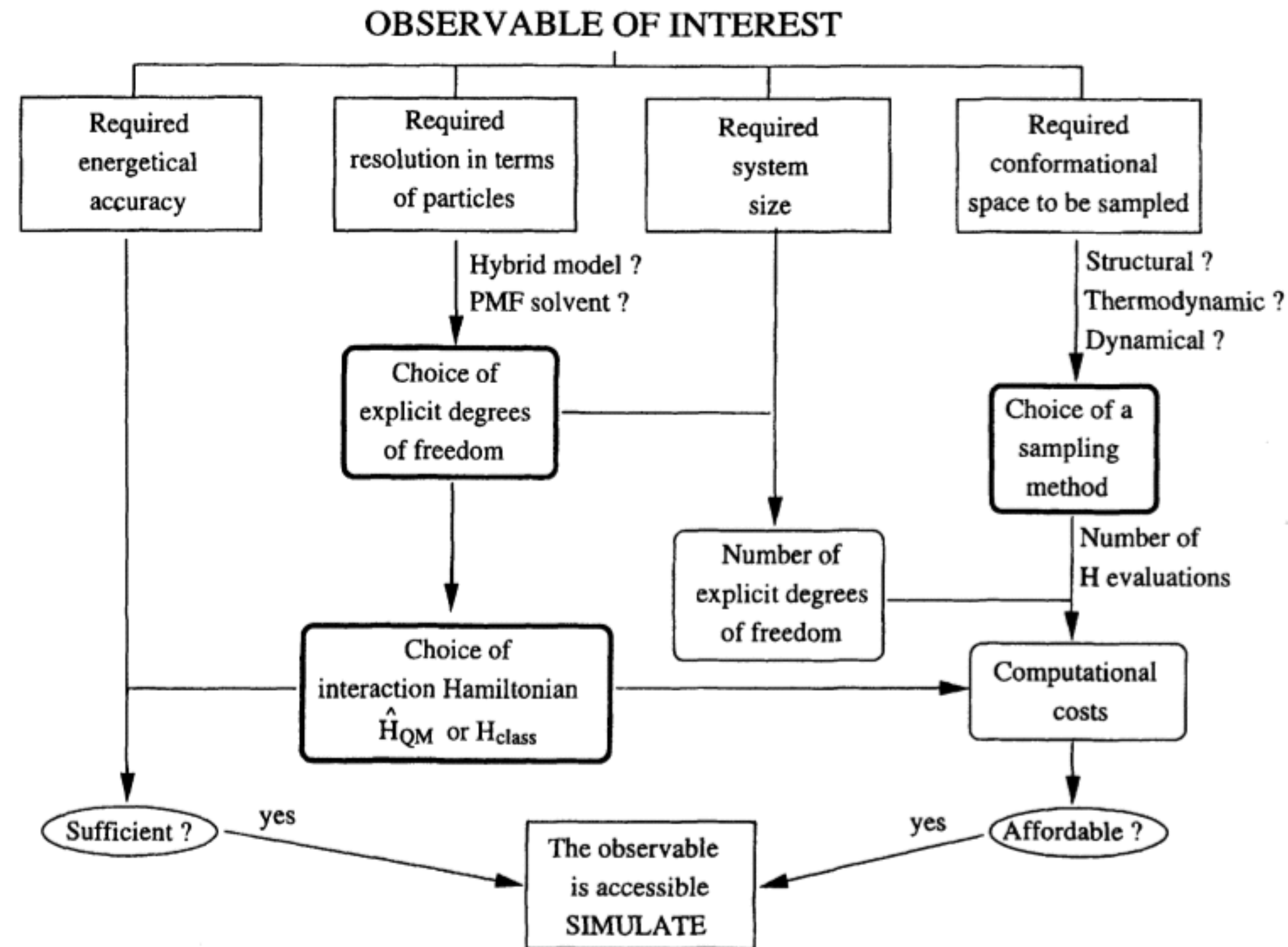


Fig. 1. Schematic representation of the basic choices made while building a model of the molecular system in order to simulate an observable of interest. The thick-line boxes represent the three essential choices and the global scheme of the present text.

Choice of the explicit degrees of freedom of the model

The choice of the elementary unit is the first step in the design of an empirical force field. This choice affects:

- the computational effort
- the extent of conformational space that can be searched (timescale)
- maximum resolution in terms of particles and processes
- the energetical accuracy in the interactions
- the type of observables that can be accessible

Hierarchy of explicit degrees of freedom

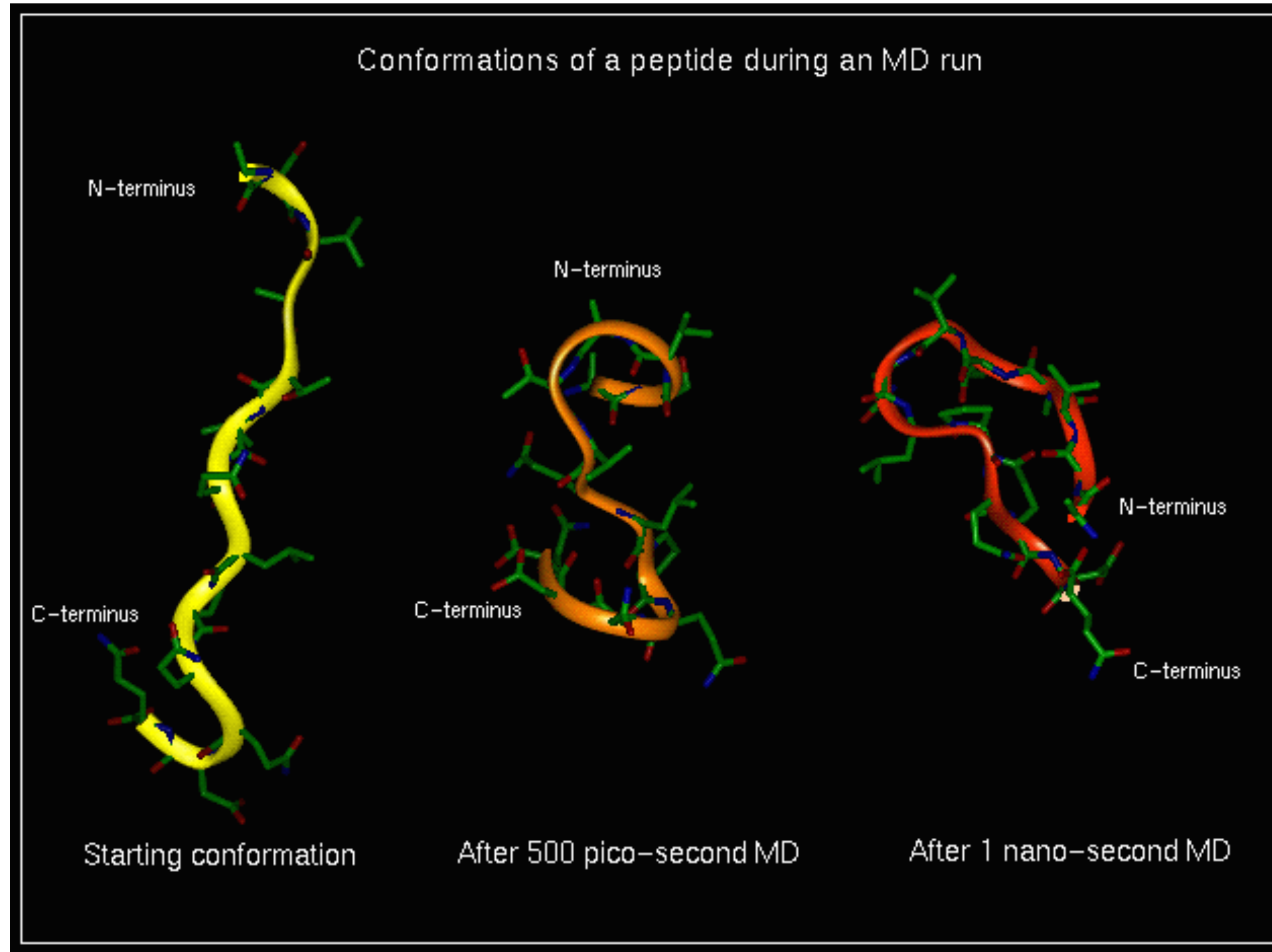
Table 1 *Hierarchy of explicit degrees of freedom included in the model*

Elementary unit	Phase	Type of interaction (operator/function)	Degrees of freedom averaged out	Reference
Electrons and nuclei	Gas phase	<i>Ab initio</i> , density functional: First-principles quantum mechanical Hamiltonian, Born–Oppenheimer surface	None	[3]
		Semiempirical: Approximated Hamiltonian	None	[4,5]
	Explicit solvent	<i>Idem</i> , supermolecule methods	None	[14]
	Implicit solvent	<i>Idem</i> , additional reaction field contribution	Solvent	[15–19]
United atoms	Gas phase			
All atoms		Classical empirical interaction function	Electronic	[64, 77]
United atom (aliphatic groups only)		<i>Idem</i>	Aliphatic H	[64, 77]
United atom (all CH _n groups)		<i>Idem</i>	All H bound to C	[64, 77]
United atoms (all)		<i>Idem</i>	All H	[64, 77]
<i>Idem</i>	Explicit solvent	<i>Idem</i> , including explicit solvent terms	<i>Idem</i>	[12]
<i>Idem</i>	Implicit solvent	<i>Idem</i> , possible corrections in the functional form, parameters, by additional terms or in the equations of motion	Solvent	[12]
Atom groups as ‘bead(s)’ E.g. amino acids in proteins represented by one or a few beads	Implicit solvent (or crystal)	Statistics-based interaction function	Side chain	[25]
Molecules Represented by a sphere, a rod or a disk	Liquid phase (or crystal)	Average intermolecular interaction function	Intramolecular	[257]

Kind of force fields

- **Gas-phase force fields**
- **Condensed-phase force fields:**
 - A. Molecules**
 - B. Polymers
 - C. Solids**
- Mean-solvent force fields
- Low-resolution force fields
- Hybrid force fields

Need of a classical approximation

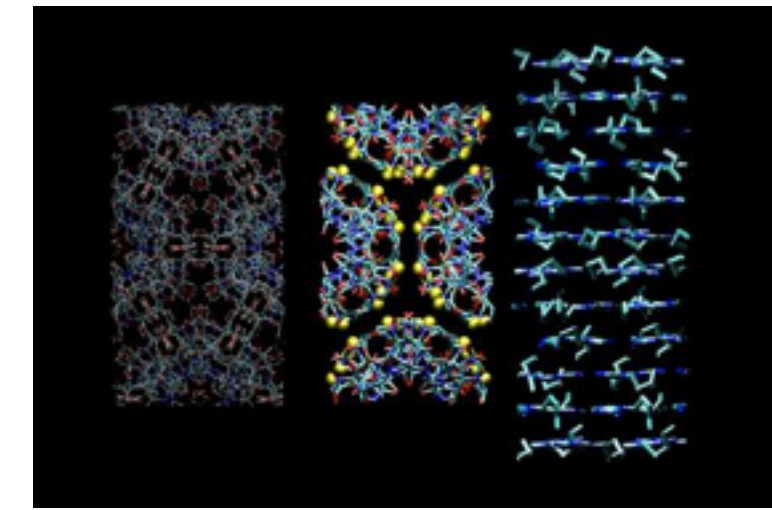


Length and time scale problems

Sampling conformational space

- Next lectures: how to explore the conformational space in an efficient way
- History dependent methods (local elevation, metadynamics)
- Accelerated dynamics methods
- Replica of several simulations at different temperatures (replica exchange)
- Monte Carlo simulation

Simulating nuclei+electrons



- Solving Schrödinger equation for several atoms (see next lectures for DFT)
- Dynamics: Discretizing the equation of motion with timesteps of the order of fractions of femtosecond; expensive wavefunction optimizations at each timestep
- Explicit solvent effects

More simply... classical approach

- Electrons are treated implicitly: only nuclei are considered
- Classical equations of motion govern the dynamics (e.g., Newton's equation)
- No solution of the quantum electronic problem at each dynamics step
- Electron effect is embedded in the interaction: example, a C-C bond
- This is valid only under some assumptions

Possible interaction terms (from HvG97, p. 37)

Table 2 *n*-Body interaction terms found in common force fields

(n)	Subset	Type	Term
1	All atoms	P	Kinetic energy
	Charged atoms	P	Interaction with an external electric field
	Surface atoms	P	Stochastic/frictional force on a macromolecule
	Listed or all atoms	U	Atomic positional restraining
2	All-atom pairs	P	Pairwise nonbonded interaction (point charges, point charge/point dipole etc., van der Waals, solvent accessible surface area interaction)
	Bonded atoms	P	Covalent bond
	H-bonded atoms	P	H-bonding interaction (acceptor–donor)
	Listed atom pairs	U	Distance restraining
3	All-atom triples	P	Triple nonbonded interactions (expensive, seldom used)
	Atoms in bond angle	P	Covalent bond-angle bending
	Pairs of bond	P	Bond–bond cross-term
	Bond in angle	P	Bond–angle cross-term
4	Atoms in dihedrals	P	Torsional interaction, improper dihedral interaction
	H-bonded atoms	P	H-bonding (acceptor-antecedent, acceptor, hydrogen, donor)
	Pairs of angle	P	Angle–angle cross-term (around one centre)
	Atoms in dihedral	P	Bond–dihedral cross-term (central bond), angle–angle–torsion cross-term
	Atoms in dihedral	U	J-value restraining, local elevation
≥ 5	Covalent neighbours	P	Other cross-terms among bonds, angles and dihedrals
N	All atoms	P	Point polarizability
	All atoms	U	Radius of gyration unfolding force

(n): order of the term, i.e. the number of particles involved in the interaction term, N indicates all atoms; Subset: subset of atoms for which the term is calculated, either from a list or all atoms (pairs, triples, respectively); Type: physical (P) or ‘unphysical’ (U) term.

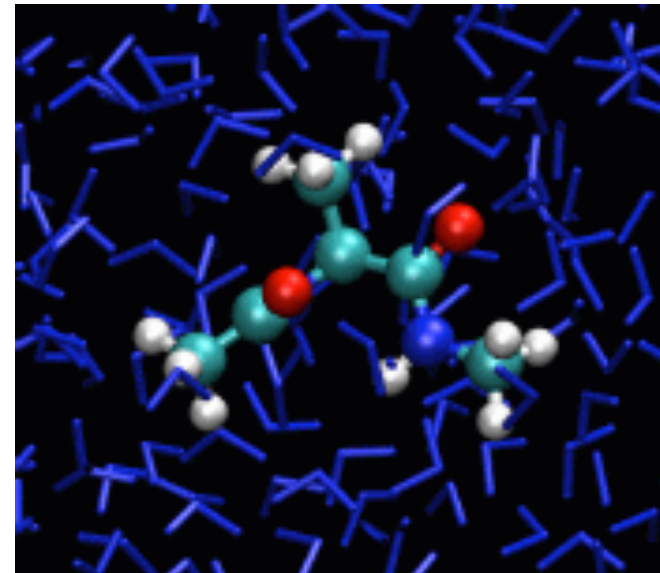
Assumptions underlying empirical interaction functions (p. 25)

“The only justification of empirical force fields resides in their ability to reproduce and predict a vast amount of experimental results... It is useful to try to understand the reason of the agreement (or the cause of discrepancies) by considering the relationship between the energy terms of the force field and the underlying QM reality” Important assumptions are:

- Implicit degrees of freedom and the assumption of weak correlation
example: fluctuations of implicit electronic degrees of freedom can be neglected at fixed nuclei
- Energy terms and the assumption of transferability
Functionally simple energy terms valid in several “physical situations” and not around a given stable configuration of a molecule
- Coordinate redundancy and the assumption of transferability
There are more than $3N-6$ energy terms...
- Choices made in the averaging process
A certain energy term is resulting on averaging different molecular situation (all, for example, with a C-C single bond)

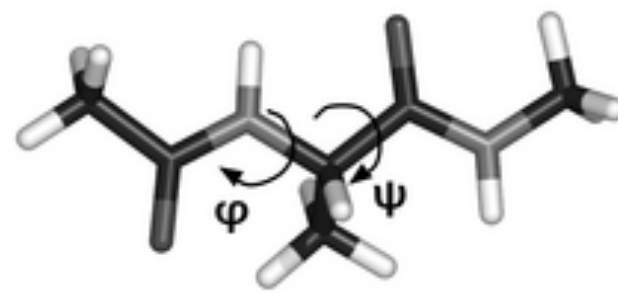
Preparing the model for a molecule

1. Getting the coordinates from some database (e.g., pdb file)



ATOM	ID	Element	x	y	z	x2	y2	z2	Element
ATOM	1	HC1	6.274	2.310	-2.248	0.00	0.00	0.00	H
ATOM	2	CT1	5.273	1.875	-2.280	0.00	0.00	0.00	C
ATOM	3	HC1	5.330	0.863	-1.872	0.00	0.00	0.00	H
ATOM	4	HC1	4.958	1.814	-3.324	0.00	0.00	0.00	H
ATOM	5	C	4.257	2.702	-1.481	0.00	0.00	0.00	C
ATOM	6	O	3.131	2.238	-1.290	0.00	0.00	0.00	O
ATOM	7	N	4.520	2.085	-1.035	0.00	0.00	0.00	N

2. Defining the topology



```

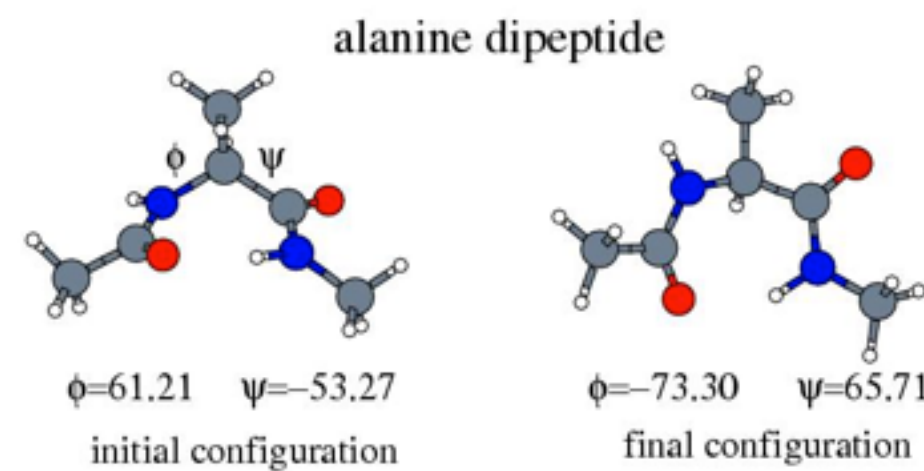
21 !NBOND
  2      3      2      4      1      2      11      12
11      13      11      14      9      10      7      8
19      20      19      21      19      22      17      18
  5      6      5      7      2      5      15      16
15      17      9      11      9      15      7      9
17      19

36 !NTHETA
  5      7      8      4      2      5      3      2      4
  3      2      5      1      2      3      1      2      4
  1      2      5      15      17      18      13      11      14
12      11      13      12      11      14      10      9      11
10      9      15      9      11      12      9      11      13
  9      11      14      8      7      9      7      9      10
21      19      22      20      19      21      20      19      22
18      17      19      17      19      20      17      19      21
17      19      22      6      5      7      5      7      9
  2      5      6      2      5      7      16      15      17
15      17      19      11      9      15      9      15      16
  9      15      17      7      9      11      7      9      15

45 !NPHI
  6      5      7      8      5      7      9      10
  4      2      5      6      4      2      5      7
  3      2      5      6      3      2      5      7
  2      5      7      8      1      2      5      6
  1      2      5      7      16      15      17      18
15      17      19      20      15      17      19      21
15      17      19      22      14      11      9      15
13      11      9      15      12      11      9      15
10      9      11      12      10      9      11      13
10      9      11      14      10      9      15      16
10      9      15      17      9      15      17      18
  8      7      9      10      8      7      9      11
  8      7      9      15      7      9      11      12
  7      9      11      13      7      9      11      14
18      17      19      20      18      17      19      21
18      17      19      22      5      9      7      8
15      19      17      18      6      5      7      9
  5      7      9      11      5      7      9      15
  2      5      7      9      16      15      17      19
11      9      15      16      11      9      15      17
  9      15      17      19      7      9      15      16
  7      9      15      17      2      7      5      6
  9      17      15      16
    
```

```

BONDS
!
!V(bond) = Kb(b - b0)**2
!
!Kb: kcal/mole/A**2
!b0: A
!
!atom type Kb      b0
!
CT1  HC1  340.00000000  1.090000000
CT3  HC2  340.00000000  1.090000000
CT2  H11  340.00000000  1.090000000
N    H    434.00000000  1.010000000
CT4  H12  340.00000000  1.090000000
C    O    570.00000000  1.229000000
C    N    490.00000000  1.335000000
CT1  C    317.00000000  1.522000000
CT2  CT3  310.00000000  1.526000000
CT2  C    317.00000000  1.522000000
N    CT2  337.00000000  1.449000000
N    CT4  337.00000000  1.449000000
    
```

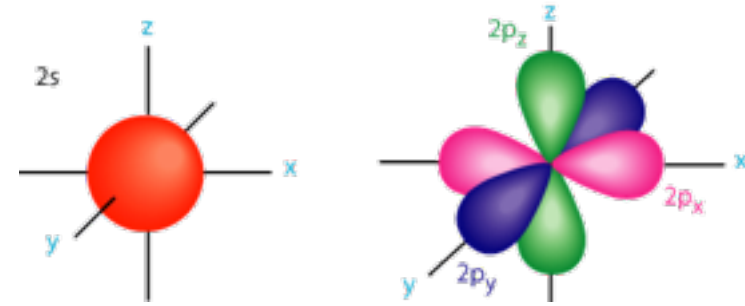


3. Defining the interaction parameters

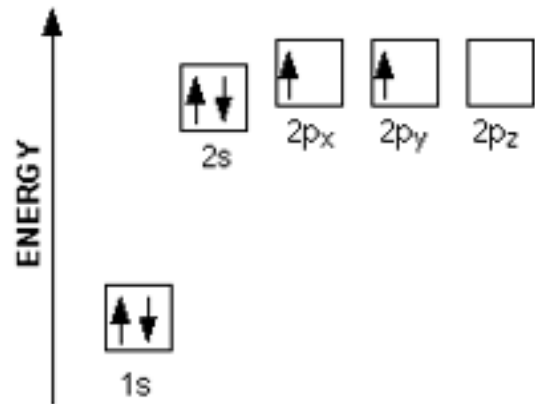
The first step is always the atom type definition

No.	Atom type	Description	No.	Atom type	Description
1	c	sp ² carbon in C=O, C=S	2	c1	sp ¹ carbon
3	c2	sp ² carbon, aliphatic	4	c3	sp ³ carbon
5	ca	sp ² carbon, aromatic	6	n	sp ² nitrogen in amides
7	n1	sp ¹ nitrogen	8	n2	sp ² nitrogen with 2 subst., real double bonds
9	n3	sp ³ nitrogen with 3 subst.	10	n4	sp ³ nitrogen with 4 subst.
11	na	sp ² nitrogen with 3 subst.	12	nh	amine nitrogen connected to aromatic rings
13	no	Nitrogen in nitro groups	14	o	sp ² oxygen in C=O, COO ⁻
15	oh	sp ³ oxygen in hydroxyl groups	16	os	sp ³ oxygen in ethers and esters
17	s2	sp ² sulfur (p=S, C=S, etc.)	18	sh	sp ³ sulfur in thiol groups
19	ss	sp ³ sulfur in —SR and S—S	20	s4	hypervalent sulfur, 3 subst.
21	s6	hypervalent sulfur, 4 subst.	22	p2	sp ² phosphorus (C=P, etc.)
23	p3	sp ³ phosphorus, 3 subst.	24	p4	hypervalent phosphorus, 3 subst.
25	p5	hypervalent phosphorus, 4 subst.	26	hc	hydrogen on aliphatic carbon
27	ha	hydrogen on aromatic carbon	28	hn	hydrogen on nitrogen
29	ho	hydrogen on oxygen	30	hs	hydrogen on sulfur
31	hp	hydrogen on phosphorus	32	f	any fluorine
33	cl	any chlorine	34	br	any bromine
35	i	any iodine			
36	cc(cd)	inner sp ² carbon in conjugated ring systems	37	ce(cf)	inner sp ² carbon in conjugated chain systems
38	cp(cq)	bridge aromatic carbon in biphenyl systems	39	cu	sp ² carbon in three-membered rings
40	cv	sp ² carbon in four-membered rings	41	cx	sp ³ carbon in three-membered rings
42	cy	sp ³ carbon in four-membered rings	43	nb	aromatic nitrogen
44	nc(nd)	inner sp ² nitrogen in conjugated ring systems, 2 subst.	45	ne(nf)	inner sp ² nitrogen in conjugated chain systems, 2 subst.
46	pb	aromatic phosphorus	47	pc(pd)	inner sp ² phosphorus in conjugated ring systems, 2 subst.
48	pe(pf)	inner sp ² phosphorus in conjugated chain systems, 2 subst.	49	px	conjugated phosphorus, 3 subst.
50	py	conjugated phosphorus, 4 subst.	51	sx	conjugated sulfur, 3 subst.
52	sy	conjugated sulfur, 4 subst.	53	h1	hydrogen on aliphatic carbon with 1 electron-withdrawal group
54	h2	hydrogen on aliphatic carbon with 2 electron-withdrawal groups	55	h3	hydrogen on aliphatic carbon with 3 electron-withdrawal groups
56	h4	hydrogen on aromatic carbon with 1 electron-withdrawal group	57	h5	hydrogen on aromatic carbon with 2 electron-withdrawal groups

Hybridization

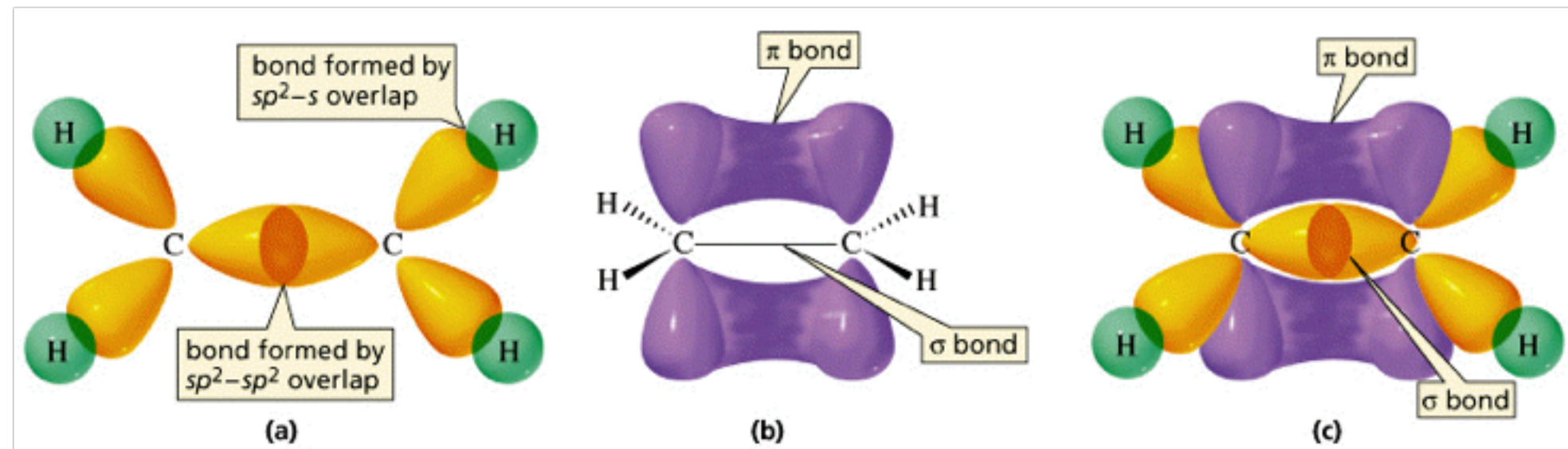


	Linear	Trigonal planar	Tetrahedral	Trigonal bipyramidal	Octahedral
Atomic orbitals mixed	one s one p	one s two p	one s three p	one s three p one d	one s three p two d
Hybrid orbitals formed	two sp	three sp ²	four sp ³	five sp ³ d	six sp ³ d ²
Unhybridized orbitals remaining	two p	one p	none	four d	three d
Orientation					

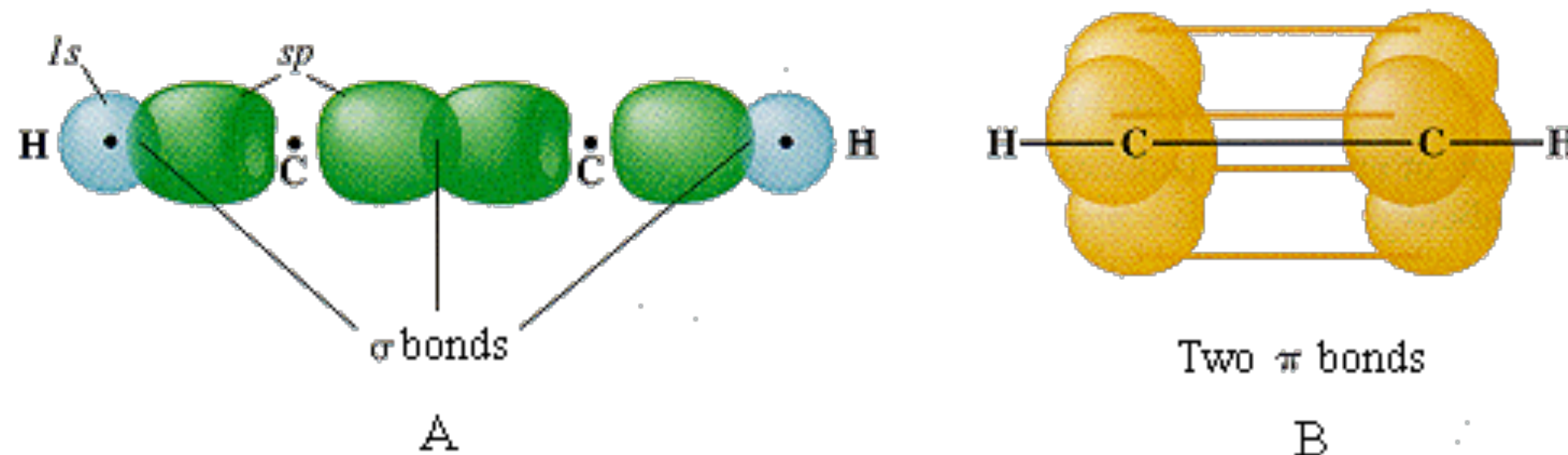


<http://www.education.com/study-help/article/valence-bond-theory/>

Example: carbon: $1s^2 2s^2 2p^2$



four valence electrons per atom
ethylene: double bond



acetylene: triple bond


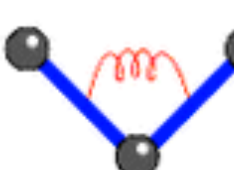

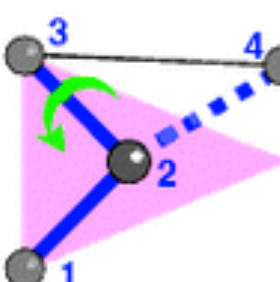
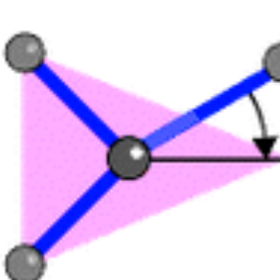
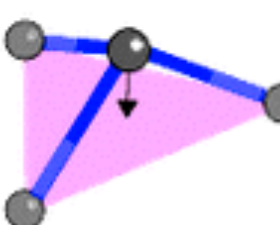
<http://chemwiki.ucdavis.edu/>

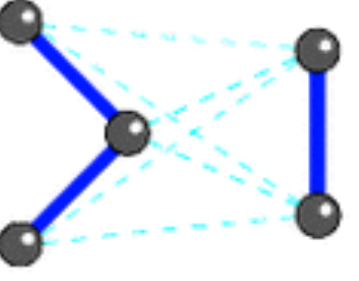
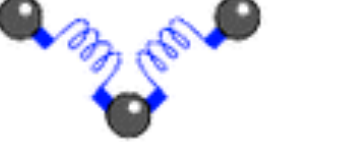
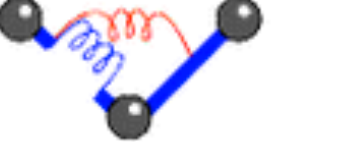

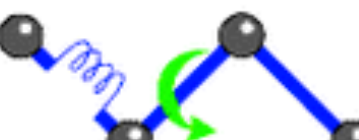
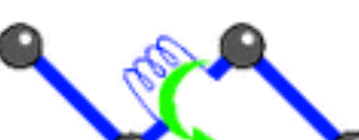
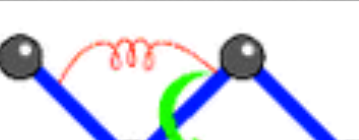
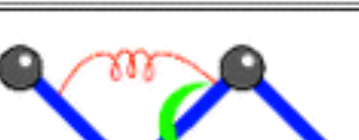

The classical Hamiltonian: AMBER force field

$$\begin{aligned} V(\mathbf{r}) &= E_{\text{bonded}} + E_{\text{nonbonded}} \\ &= \sum_{\text{bonds}} K_b (b - b_0)^2 + \sum_{\text{angles}} K_\theta (\theta - \theta_0)^2 \\ &+ \sum_{\text{dihedrals}} (V_n/2)(1 + \cos[n\phi - \delta]) \\ &+ \sum_{\text{nonbij}} (A_{ij}/r_{ij}^{12}) - (B_{ij}/r_{ij}^6) + (q_i q_j / r_{ij}) \end{aligned}$$

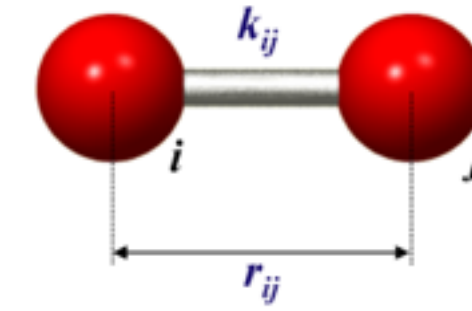
A visual summary from a commercial software (from Accelrys)

Table 24. Common potential terms in major forcefields supported by Accelrys

name	illustrated	form of the term	forcefield ¹
quadratic bond-stretching		$k(r - r_0)^2$	AMBER, CHARMM, UFF
quartic bond-stretching		$k_2(r - r_0)^2 + k_3(r - r_0)^3 + k_4(r - r_0)^4$	CFF
Morse bond-stretching		$k \left[1 - e^{-\alpha(r - r_0)} \right]^2$	CVFF, ESFF
quadratic angle-bending		$k(\theta - \theta_0)^2$	AMBER, CHARMM, CVFF
quartic angle-bending		$k_2(\theta - \theta_0)^2 + k_3(\theta - \theta_0)^3 + k_4(\theta - \theta_0)^4$	CFF
cosine angle-bending		various	ESFF, UFF
single-cosine torsion		$k(1 + \cos(n\phi - \phi_0))$ or similar	AMBER, CHARMM, CVFF
three-term cosine torsion		$k_1[1 - \cos(\phi - \phi_{01})] + k_2[1 - \cos(2\phi - \phi_{02})] + k_3[1 - \cos(3\phi - \phi_{03})]$	CFF
cosine-Fourier torsion		$k(1 \pm \cos n\phi)$	UFF
sin-cos torsion		$k_\phi \left(\frac{\sin^2 \theta_1 \sin^2 \theta_2}{\sin^2 \theta_1^0 \sin^2 \theta_2^0} + \text{sign} \frac{\sin^n \theta_1 \sin^2 \theta_2}{\sin^n \theta_1^0 \sin^2 \theta_2^0} \cos[n\phi] \right)$	ESFF
improper cosine out-of-plane		$k[1 + \cos(n\chi - \chi_0)]$ or similar	AMBER, CVFF, UFF
improper quadratic out-of-plane		$k(\chi - \chi_0)^2$	CHARMM
improper square out-of-plane, improp		$k\chi^2$	CVFF
Wilson (or umbrella) out-of-plane		$k\chi^2$	CFF, ESFF, UFF
		$k(\cos \chi - \cos \chi_0)^2$	UFF
pyrimid-height out-of-plane		not used	none

6-9 van der Waals		$\left[\frac{r_{ij}^{*9}}{r_{ij}^9} - \frac{r_{ij}^{*12}}{r_{ij}^{12}} \right]$ or $\epsilon [2(r^*/r)^9 - 3(r^*/r)^6]$	CFF, ESFF, UFF
6-12 van der Waals		$\left[\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^6} \right]$ or $\epsilon [(r^*/r)^{12} - 2(r^*/r)^6]$	AMBER, CHARMM, CVFF
electrostatic		$\frac{q_i q_j}{\epsilon r_{ij}}$ or similar	AMBER, CFF, CHARMM, CVFF, ESFF, UFF
quadratic bond-bond		$k(r - r_0)(r' - r'_0)$	CFF, CVFF ²
quadratic bond-angle		$k(r - r_0)(\theta - \theta_0)$	CFF, CVFF
angle-angle		$k(\theta - \theta_0)(\theta' - \theta'_0)$	CFF, CVFF
end bond-torsion		$(b - b_0)[k_1 \cos \phi + k_2 \cos 2\phi + k_3 \cos 3\phi]$	CFF
center bond-torsion		$(b' - b'_0)[k_1 \cos \phi + k_2 \cos 2\phi + k_3 \cos 3\phi]$	CFF
angle-torsion		$(\theta - \theta_0)[k_1 \cos \phi + k_2 \cos 2\phi + k_3 \cos 3\phi]$	CFF
angle-angle-torsion		$k \cos \phi (\theta - \theta_0)(\theta' - \theta'_0)$	CFF, CVFF
improper out-of-plane--out-of-plane, improper		$k[1 - \cos 2\chi]^{1/2}[1 - \cos 2\chi']^{1/2}$	CVFF

Bond energy terms

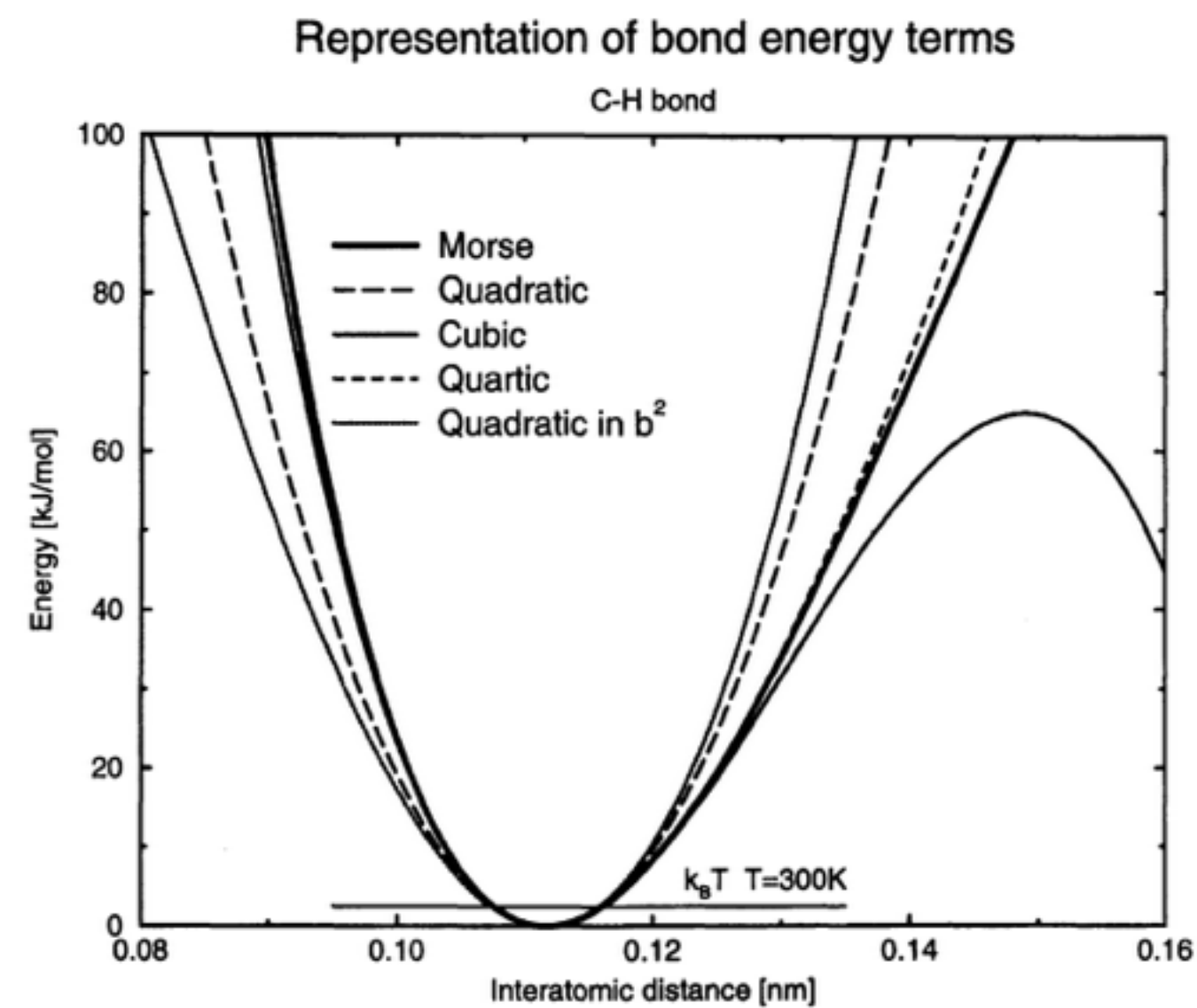


- Assuming that the system will not deviate “too much” from equilibrium, a quadratic expansion is valid

$$U_b(r) = K (r - r_{eq})^2$$

- although a Morse expansion would be more faithful to the exact result.

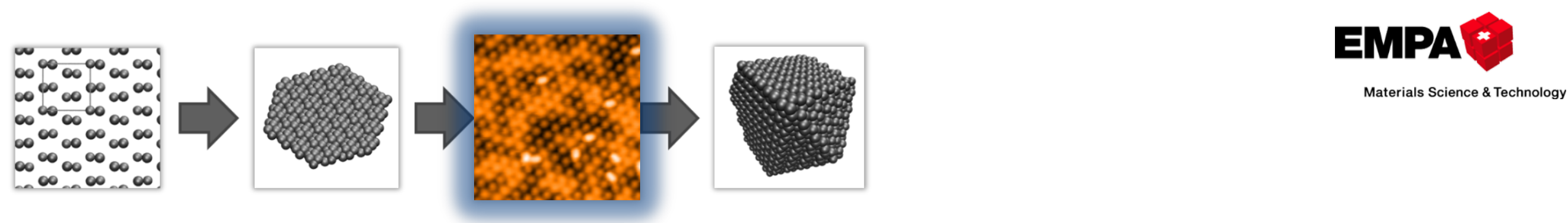
$$U(d) = D_e \left[1 - e^{-a(d-d_0)} \right]^2$$



Typical bond parameter values

Atom pair	r_{eq} in Å	K_r in kcal/ (molÅ ²)
C = O	1.229	570
C - C2	1.522	317
C - N	1.335	490
C2 - N	1.449	337
N - H	1.01	434

An example from real experiments (Jan Prinz, Empa)

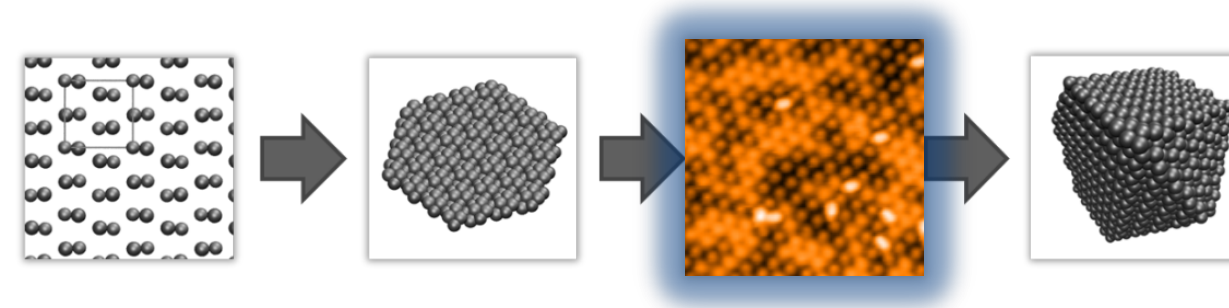


Probing molecule-surface interactions
using CO as a test molecule

Adsorption of a small molecule on the surface
of an intermetallic PdGa compound

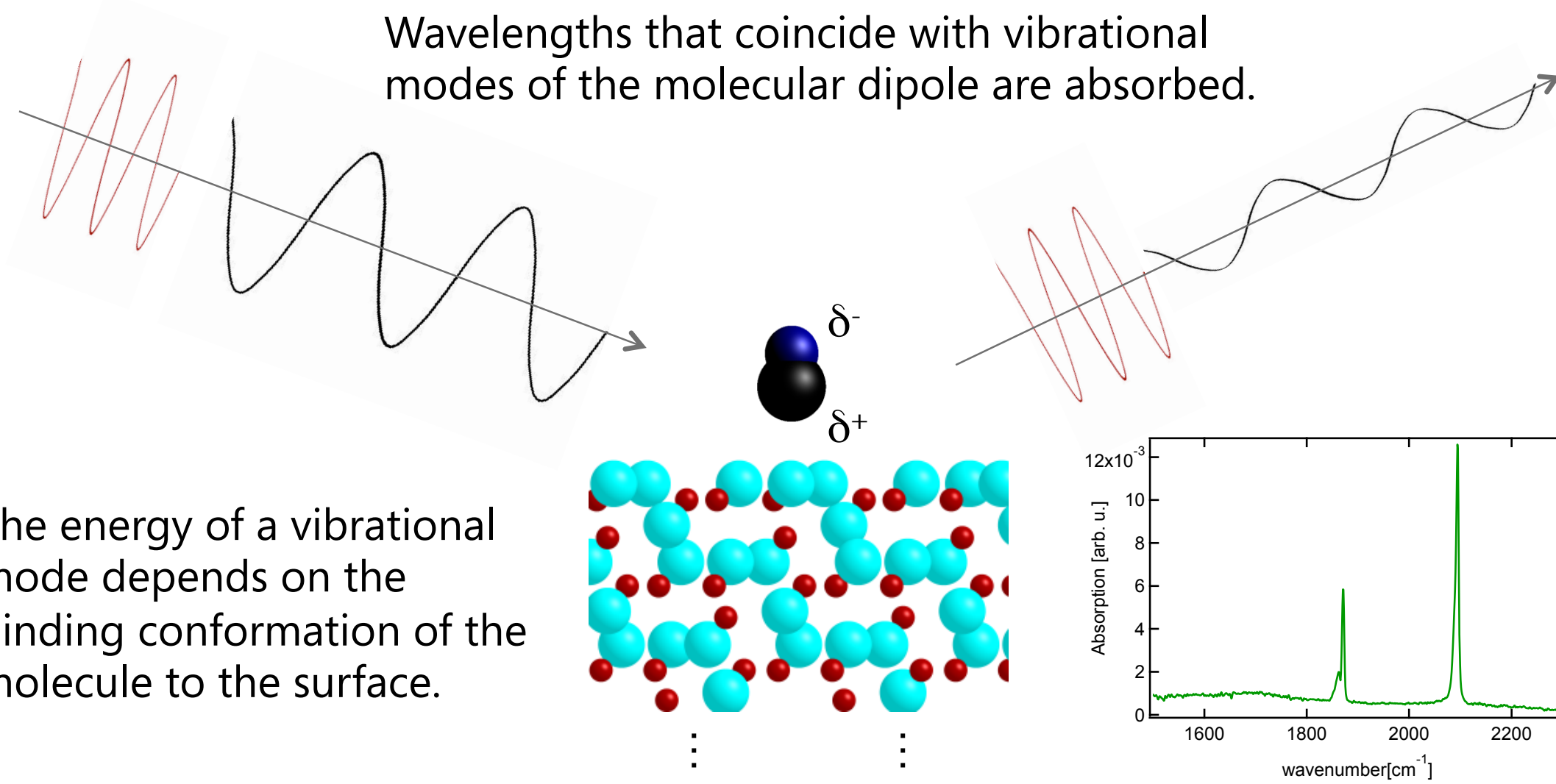
Pd/Ga site?

Hollow/bridge/top site?



FTIR (Fourier Transform Infrared Spectroscopy)
RAIRS (Reflection Absorption Infrared Spectroscopy)

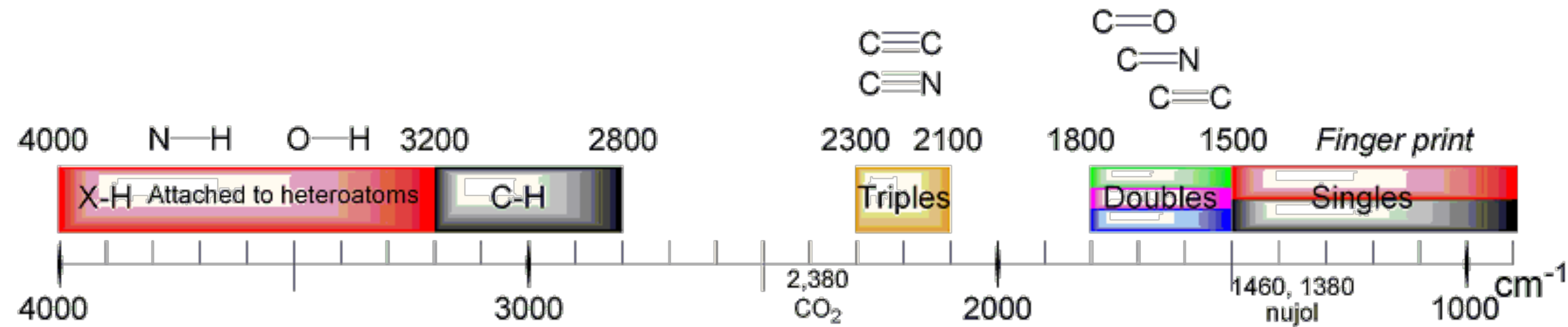
Wavelengths that coincide with vibrational modes of the molecular dipole are absorbed.



The energy of a vibrational mode depends on the binding conformation of the molecule to the surface.

Wavenumber [cm ⁻¹]	Absorption [arb. u.]
1850	~5.5
2100	~11.5

Extracting bond strength: infrared spectroscopy



The absorption wavenumber for a stretching vibration is related to both the force constant k between the two atoms and the mass of the two atoms (m_1 and m_2) by Hooke's law:

$$\bar{\nu} = \frac{1}{2\pi c} \left[k \left(\frac{m_1 + m_2}{m_1 \cdot m_2} \right) \right]^{1/2}$$

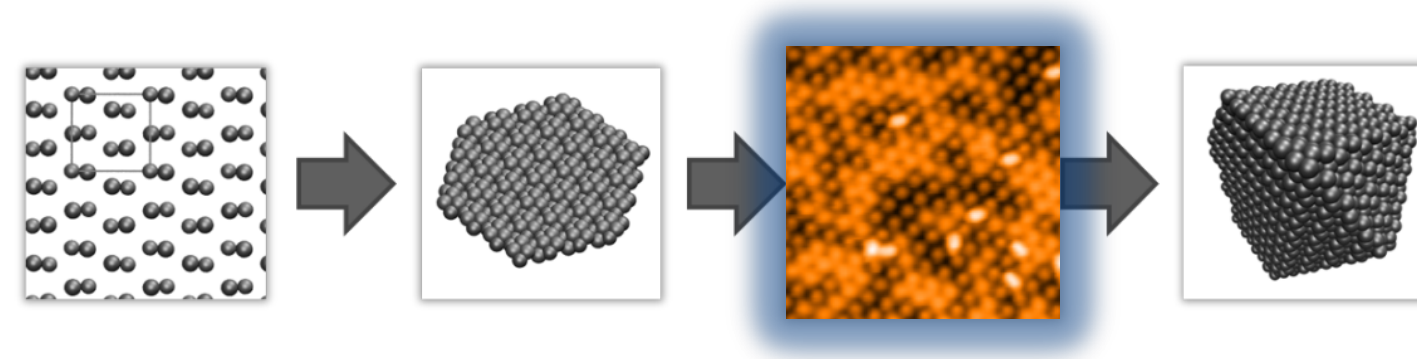
From this relationship, two important trends in the wavenumber for stretching vibrations can be deduced.

1. As the bond strength increases, the wavenumber increases. For example:

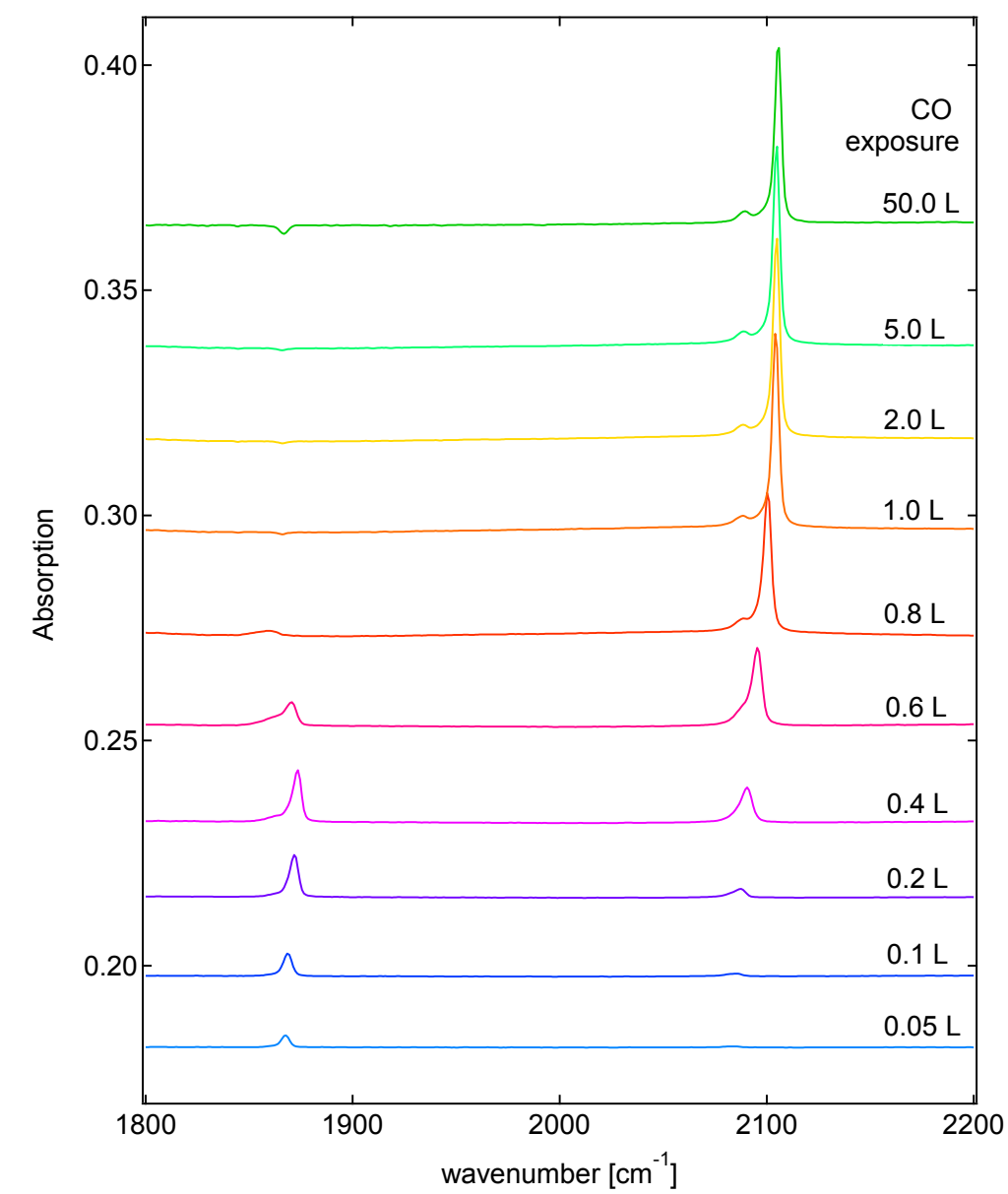
Bond stretch	C-C	C=C	C≡C	C-H	=C-H	≡C-H
Wavenumber of Absorption (cm ⁻¹)	1200	1650	2150	2900	3100	3300

2. As the mass of one of the two atoms in the bond increases, the wavenumber decreases (assuming the change in bond strength is relatively small). For example,

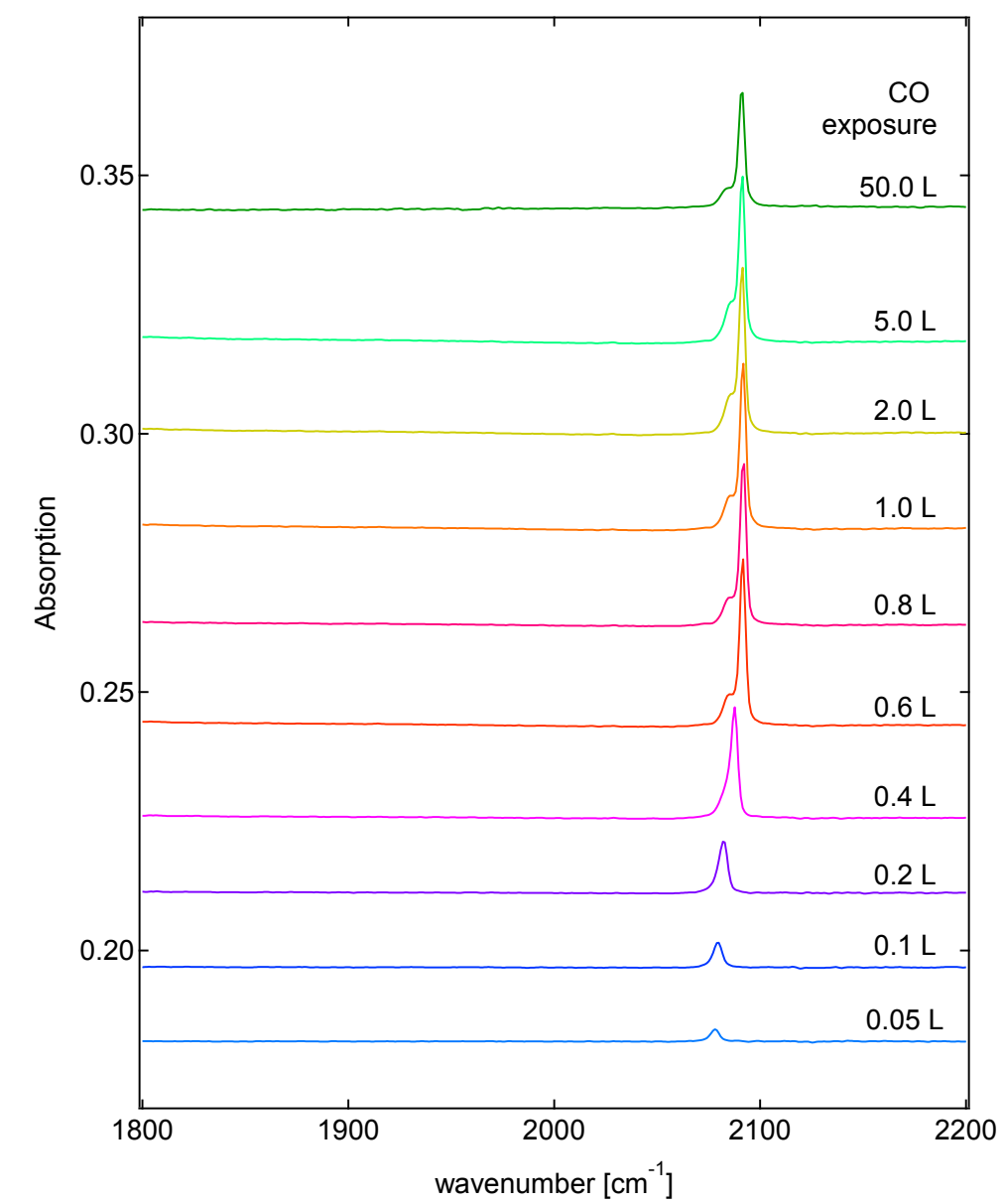
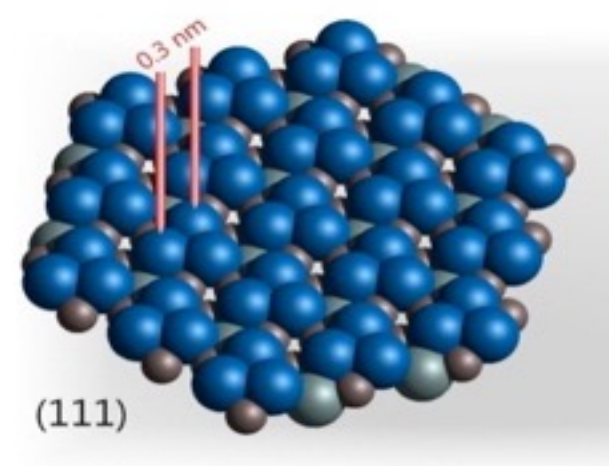
Bond stretch	C-H	C-D	C-C	C-O	C-Cl	C-Br	C-I
Wavenumber of Absorption (cm ⁻¹)	3000	2100	1200	1100	800	550	500



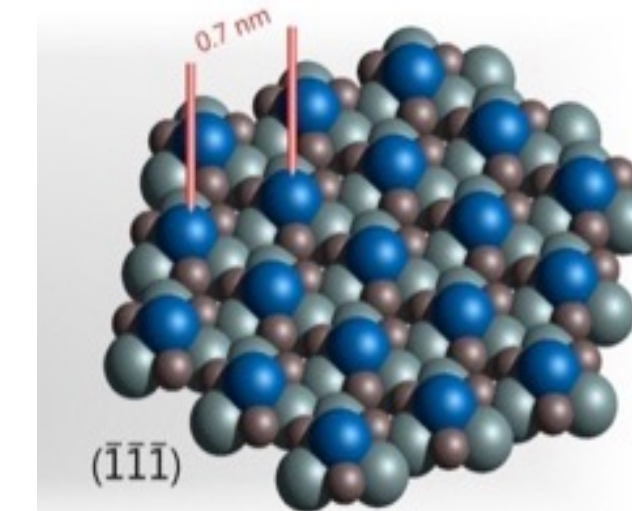
IR absorption as a function of CO exposure at liquid nitrogen temperatures

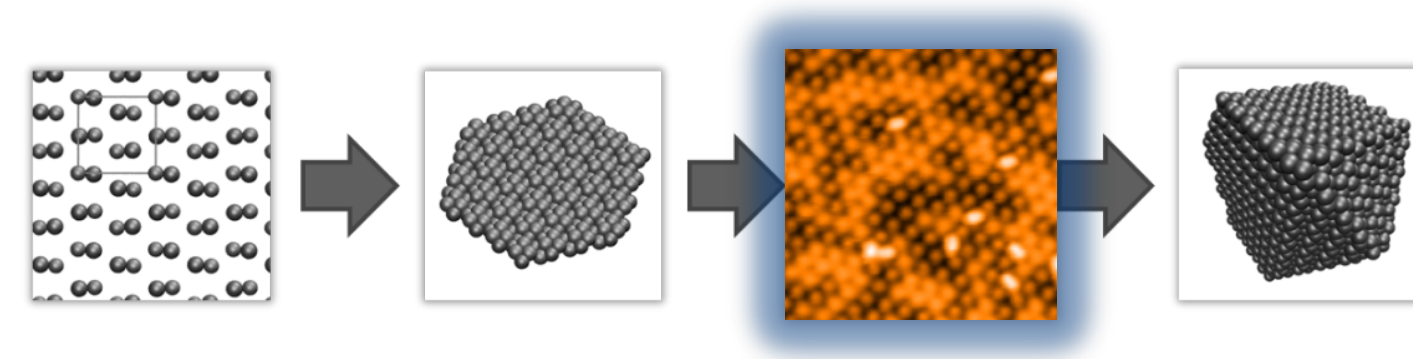


Molecule adsorbed on “Pd3”

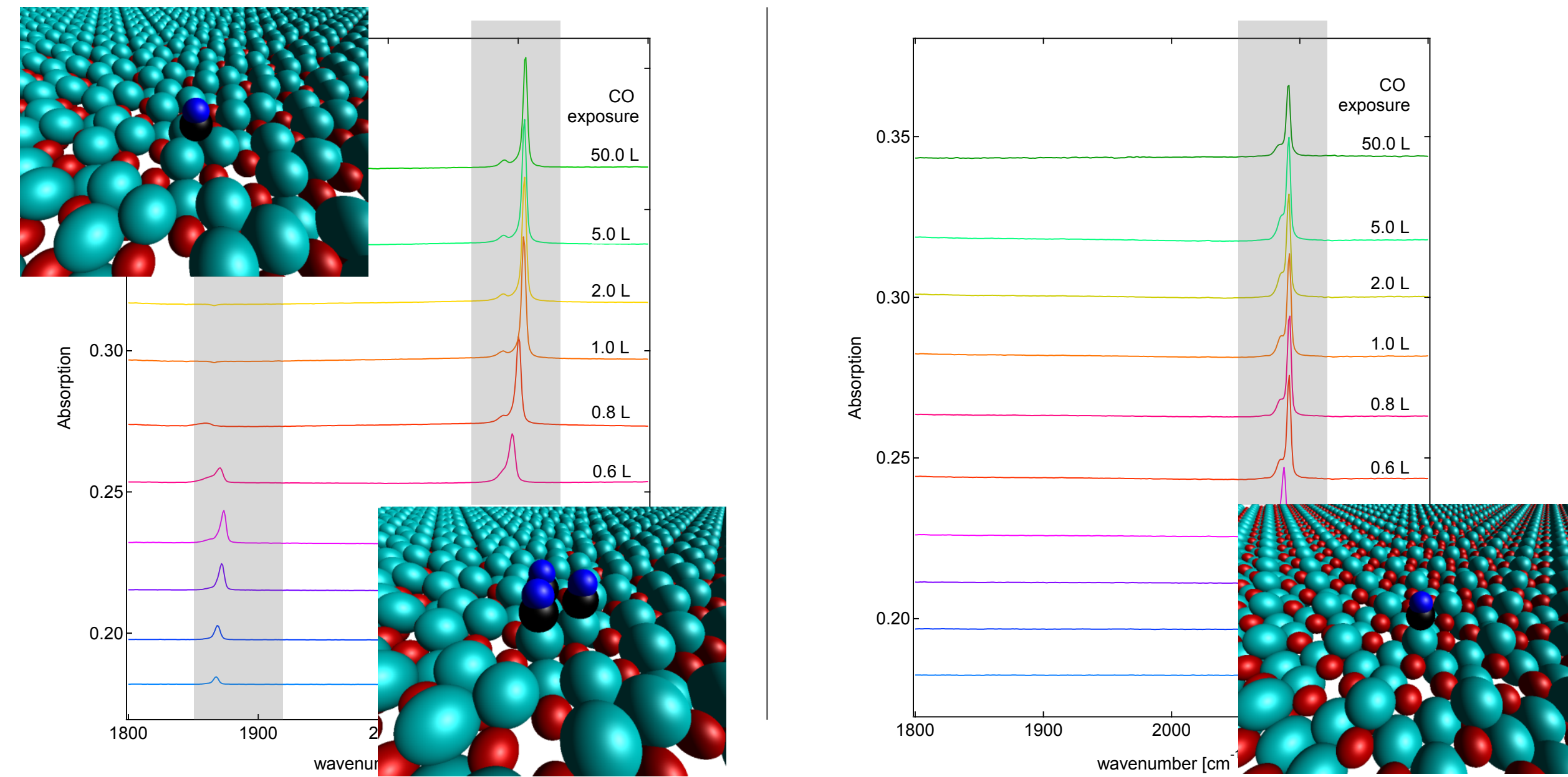


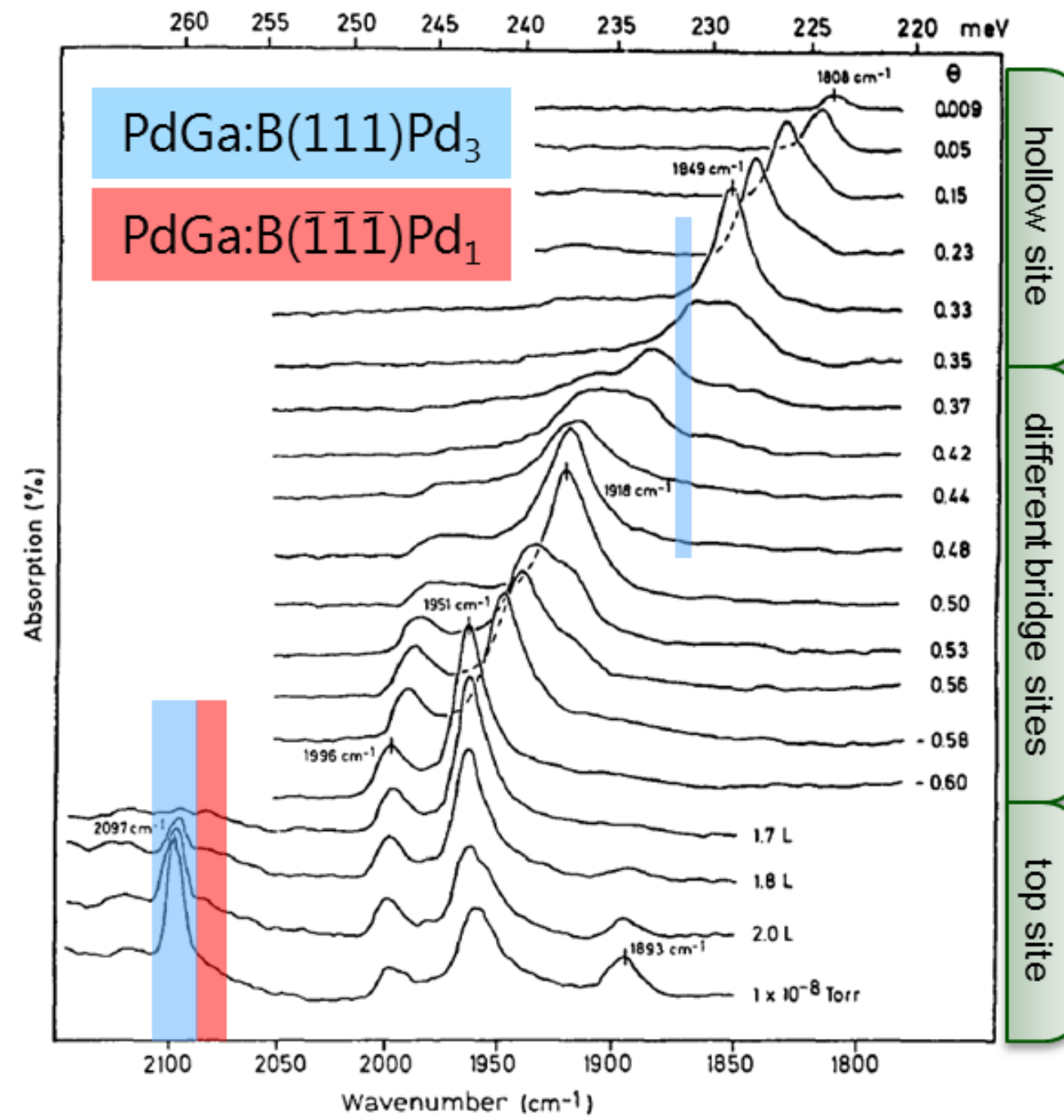
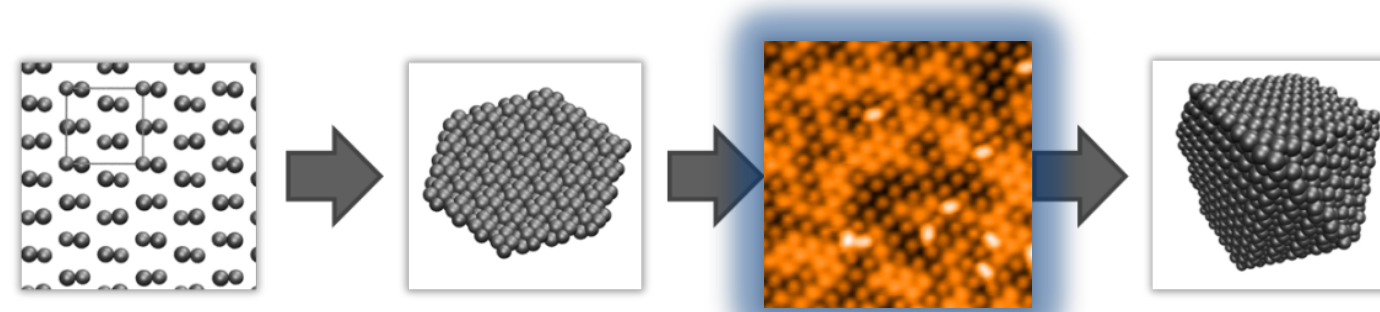
Molecule adsorbed on “Pd1”





IR absorption as a function of CO exposure at liquid nitrogen temperatures





Comparison to CO/Pd(111)
literature data

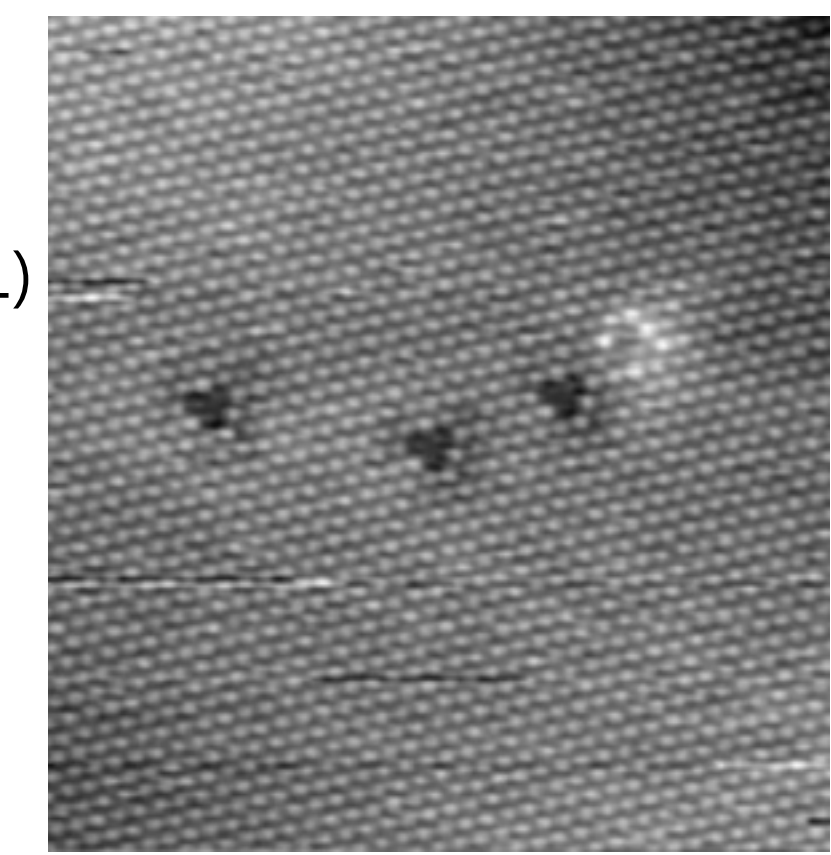


Fig. 20. IR absorption in the C–O stretch region as a function of increasing coverage for CO/Pd(111) at 90 K. After Ortega [53].

Surface Science Reports 3 (1983) 107–192
North-Holland Publishing Company

INFRARED REFLECTION-ABSORPTION SPECTROSCOPY OF ADSORBED MOLECULES

Friedrich M. HOFFMANN
Exxon Research and Engineering Company, Clinton Township, Annandale, New Jersey 08801, USA

Simulation with CP2K

High-performance computing Cluster *HYPATIA*

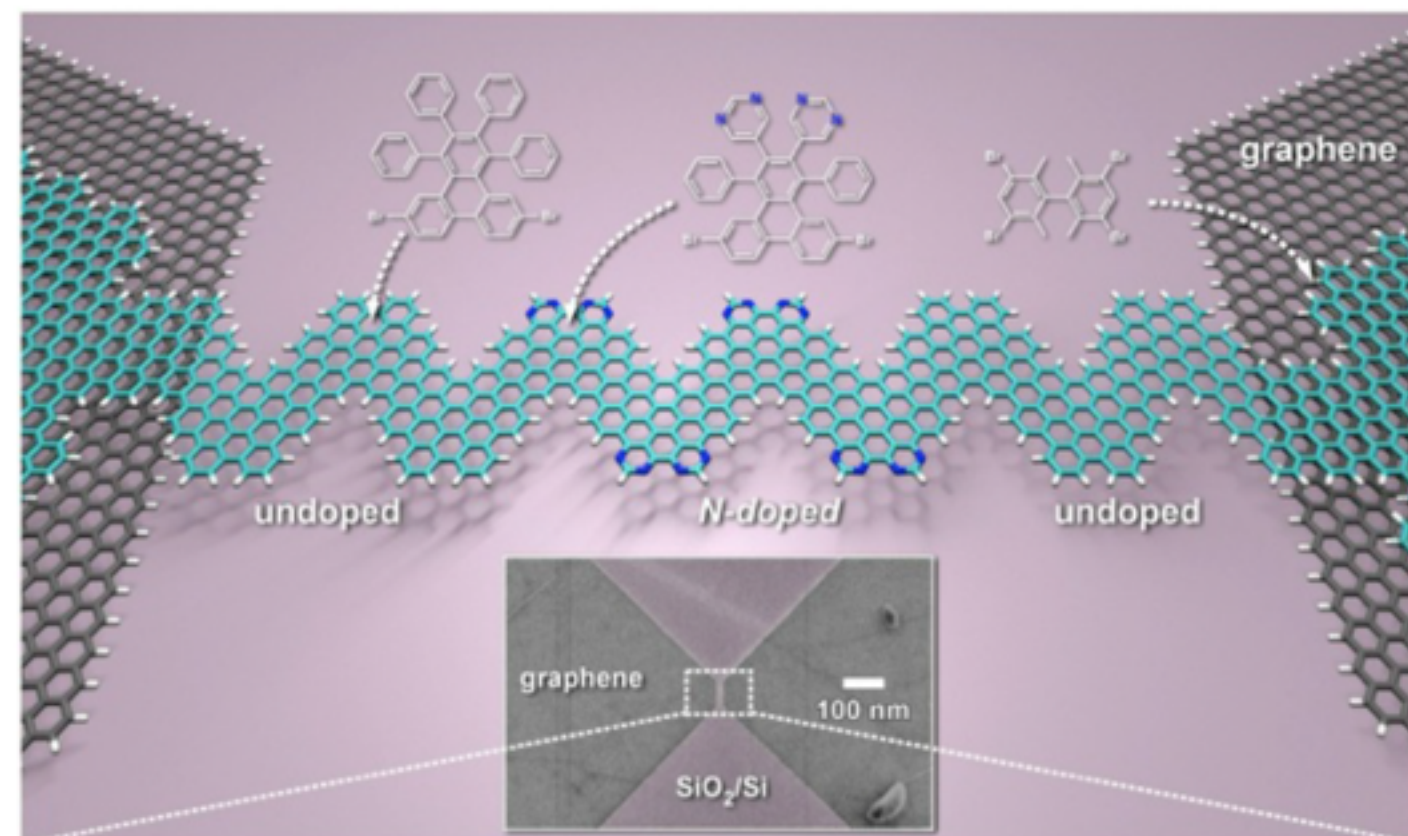
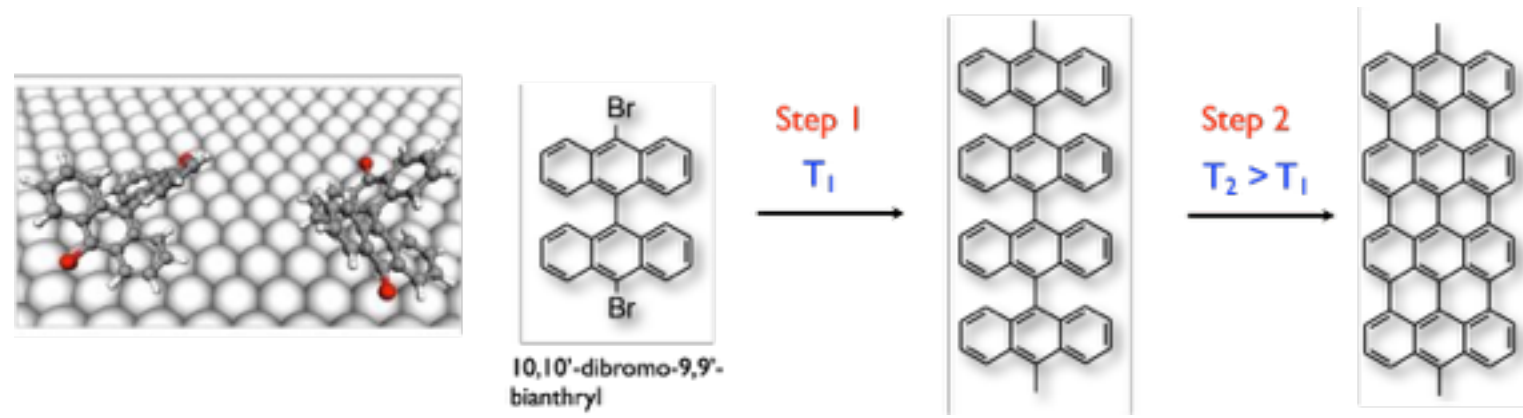
- Established 2007
- 6 Terabyte RAM
- 90 TB storage
- 13 Teraflops
- 1500 CORES



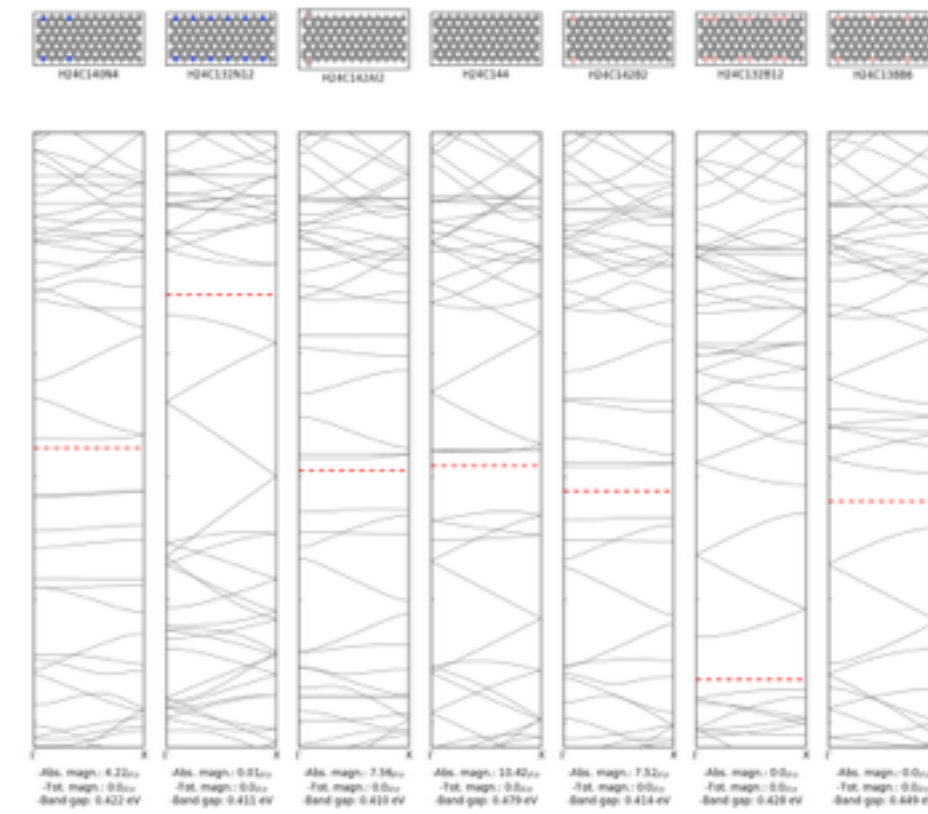
- 80% occupation 24h/7d by 15 Empa laboratories and 3 Eawag groups.
INDUSTRIAL NODES
- **Simulations at all scales from atomistic through meso/continuum (multiscale, engineering) to worldwide (climate, agriculture, flight noise)**
- **Our lab: classical and ab initio MD, advanced methods for electronic properties, exploration of free energy landscapes: all atomistic**

High-throughput screening of nanomaterials

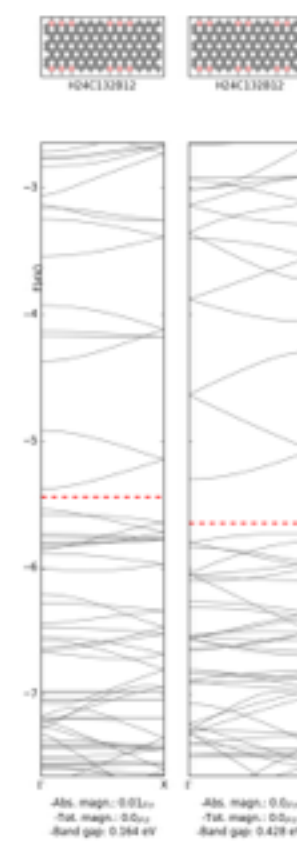
- Interplay with experiment/industry to define the problem
- Implement computer science-based workflows and data mining tools to automate calculations and inquiries
- Extract novel candidates for experiments and novel devices



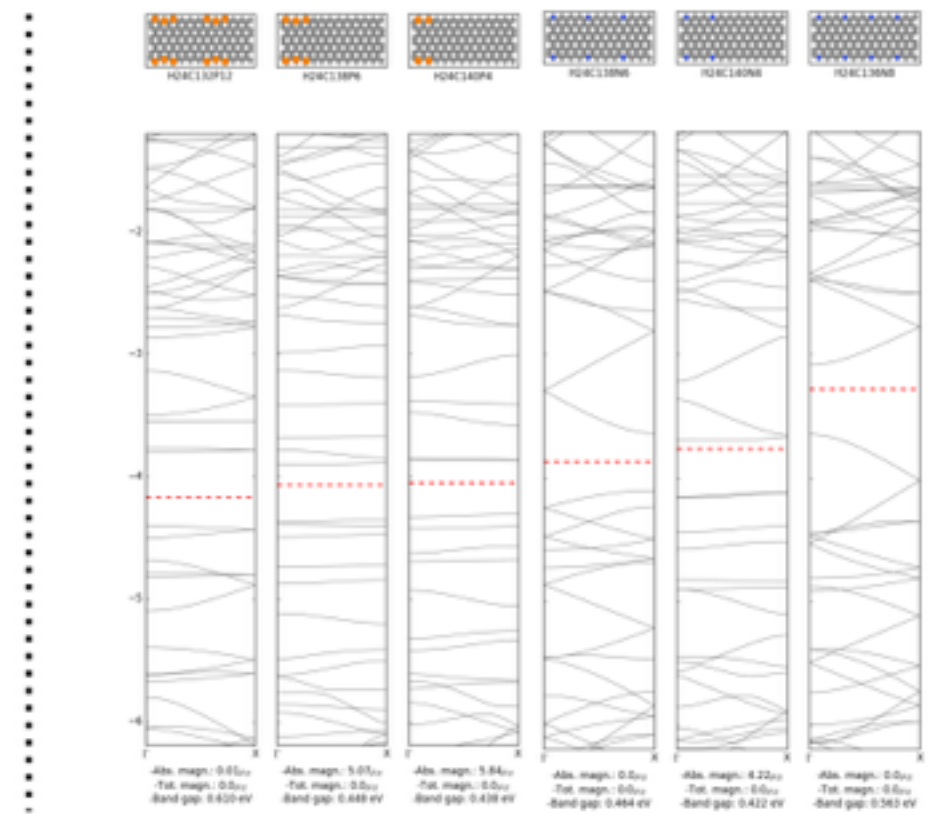
> verdi run select_bands.py --gap 0.4 0.5



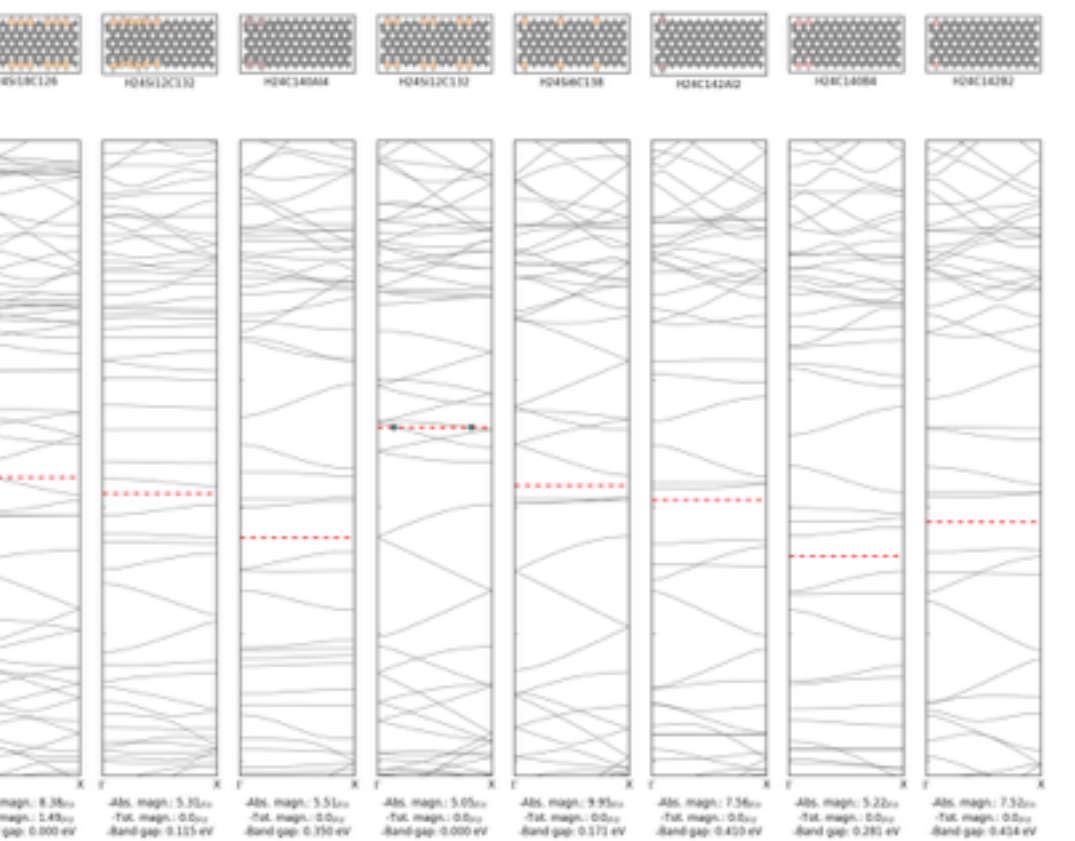
> verdi run select_bands.py --formula H24C132B12



> verdi run select_bands.py --gap 0.4 1.0 --cband -5.5 5.0

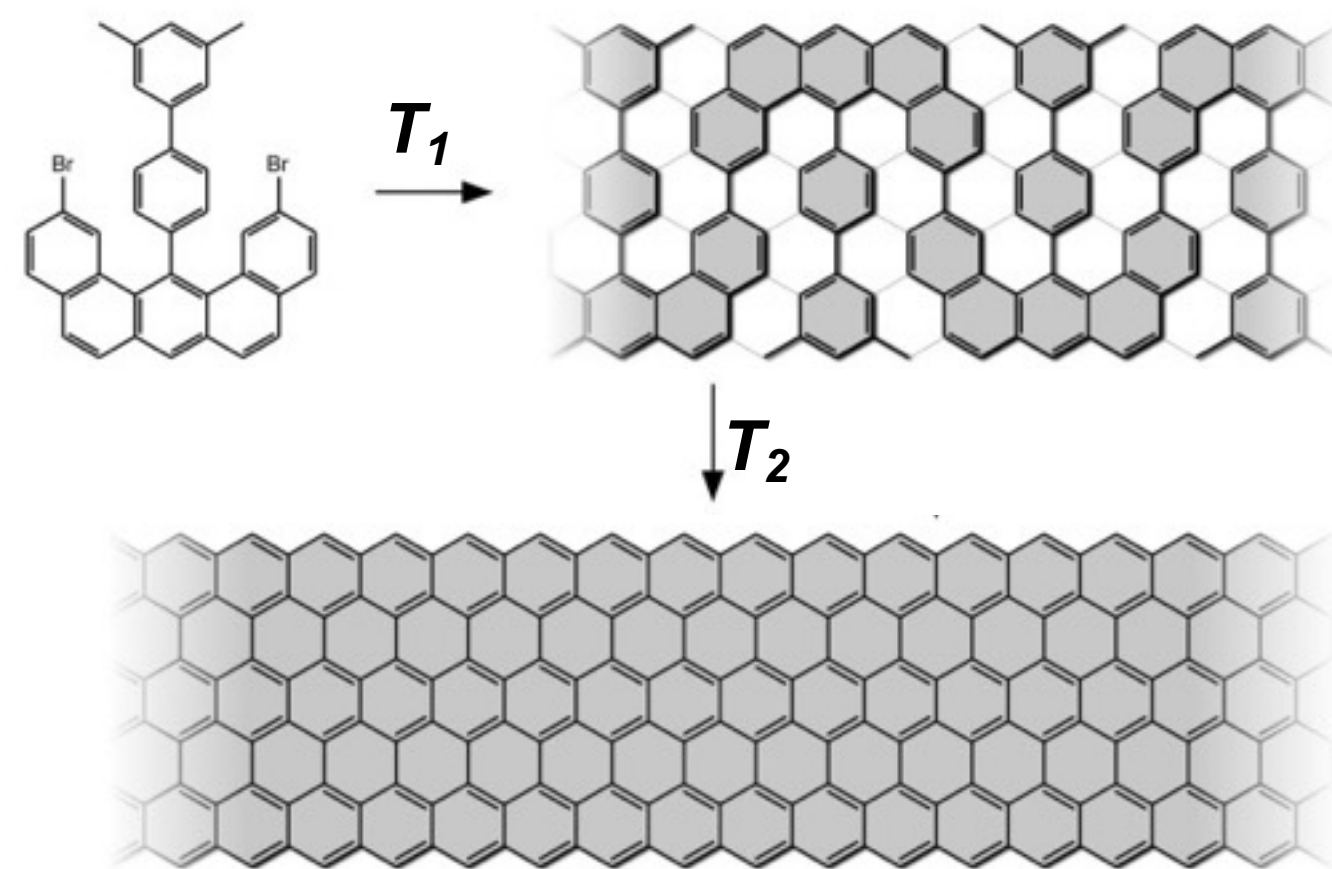


> verdi run select_bands.py --gap 0.4 1.0 --cband -5.5 5.0

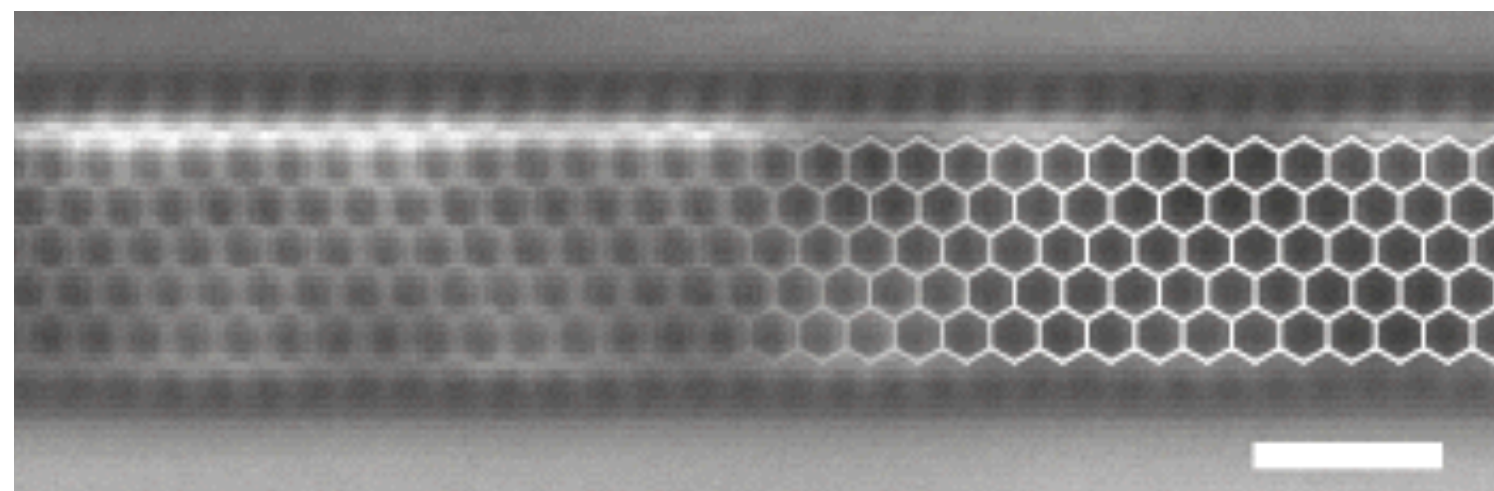


Synthesis

on Au(111)



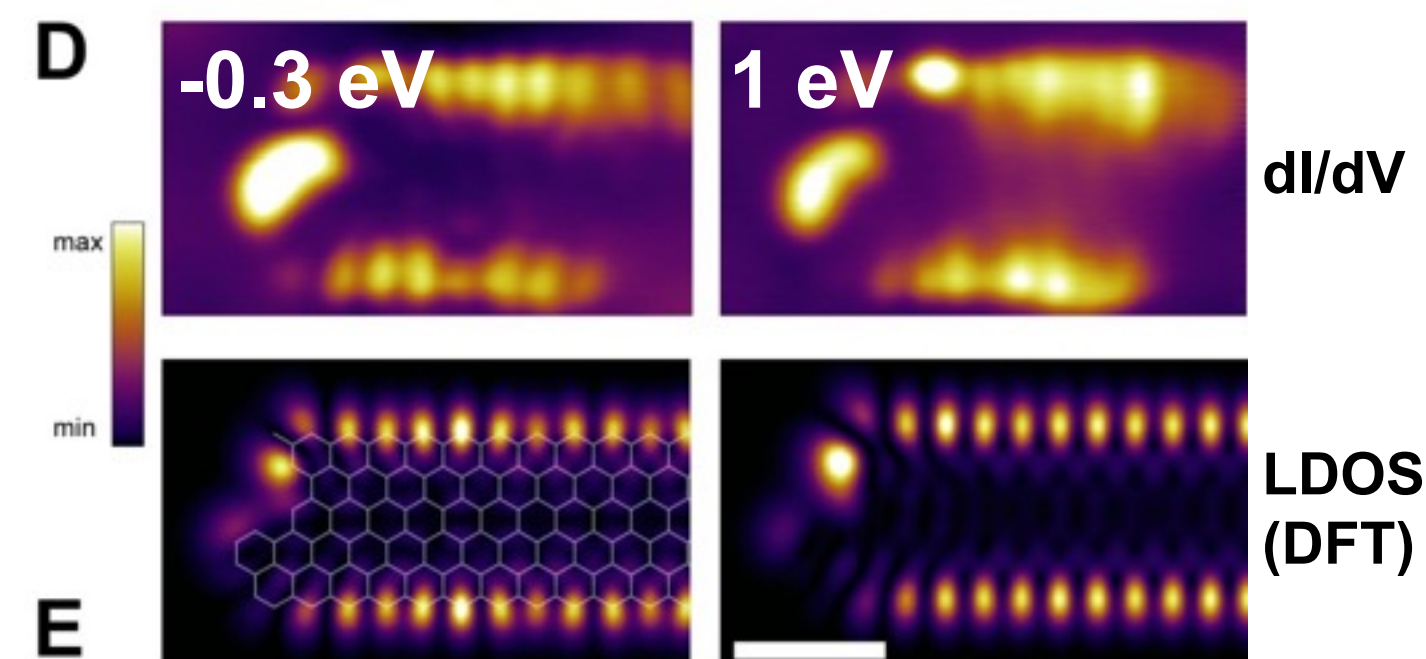
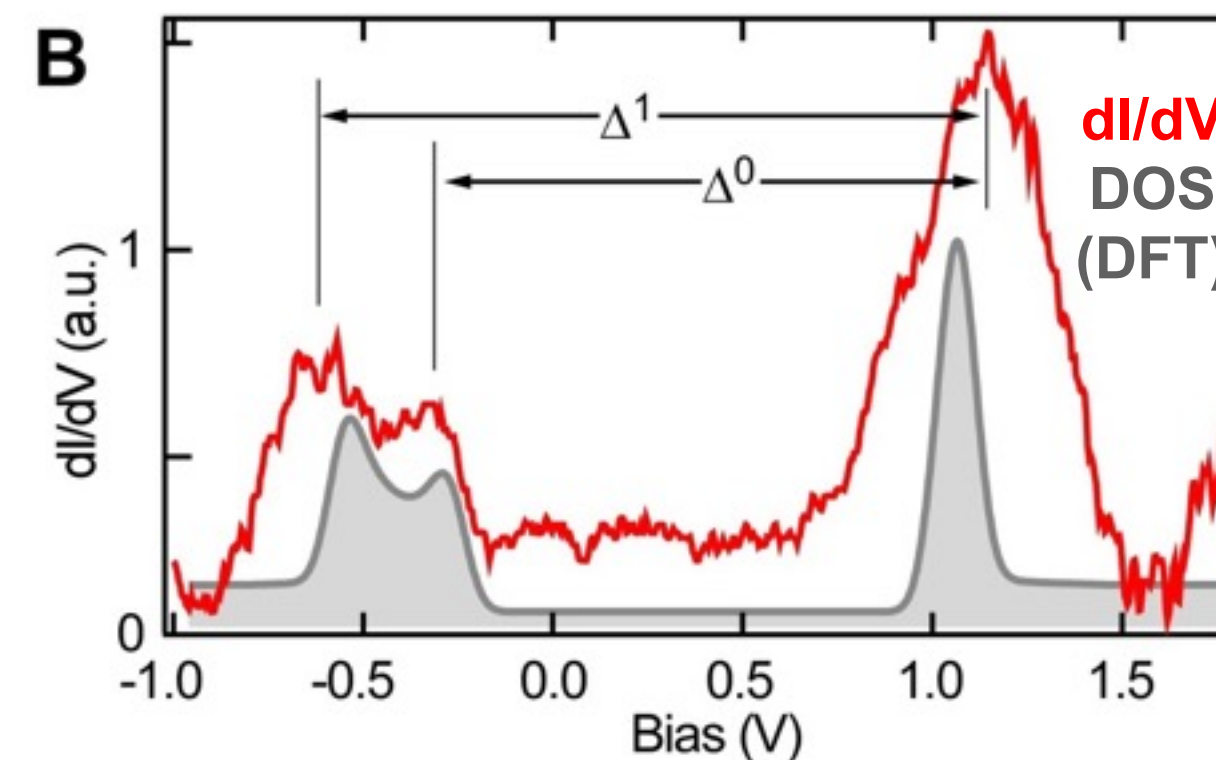
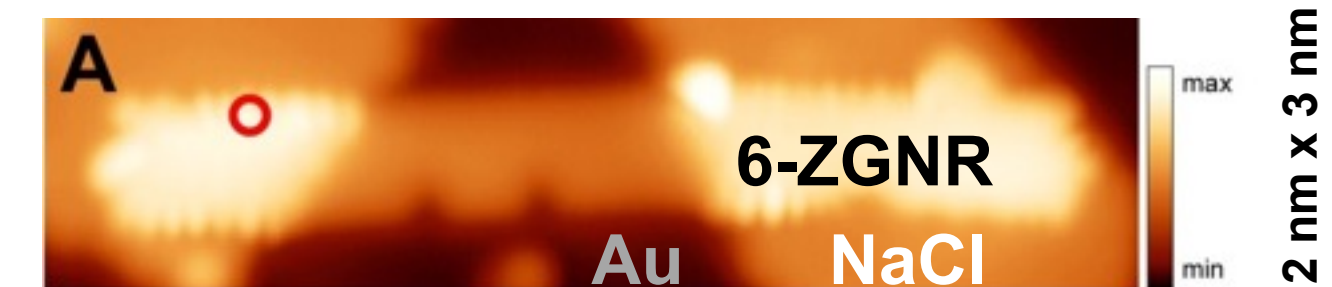
nc-AFM



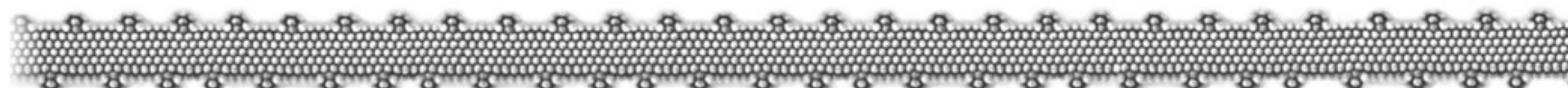
Edge state characterization: experiment and theory

STM-based manipulation onto NaCl

STM



P. Ruffieux, S. Wang, B. Yang, C. Sánchez-Sánchez, J. Liu, T. Dienel, L. Talirz, P. Shinde, C. A. Pignedoli, D. Passerone, T. Dumslaff, X. Feng, K. Müllen, R. Fasel
Nature **531**, 489 (2016)



What is CP2K?

CP2K is a freely available (GPL) program, written in Fortran 2003, to perform atomistic and molecular simulations of solid state, liquid, molecular and biological systems. It provides a general framework for different methods: density functional theory (DFT) using a mixed Gaussian and plane waves approach (GPW) using LDA, GGA, MP2, or RPA level of theory, classical pair and many-body potentials, semi-empirical (AM1, PM3, MNDO, MNDOd, PM6) Hamiltonians, Quantum Mechanics/Molecular Mechanics (QM/MM) hybrid schemes relying on the Gaussian Expansion of the Electrostatic Potential (GEEP).

Science with CP2K

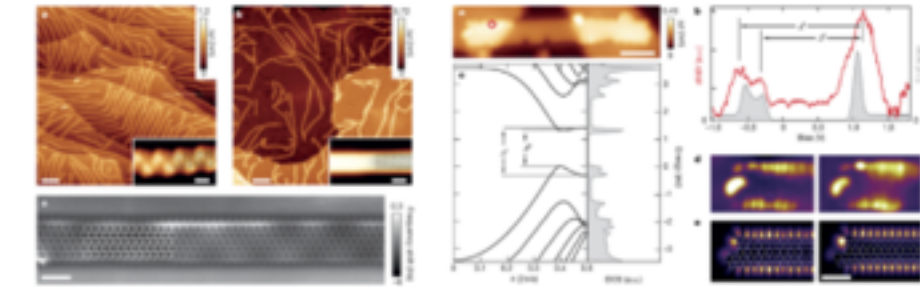
Surface-assisted synthesis of zigzag-edge graphene nanoribbons

LETTER

doi:10.1038/nature17151

On-surface synthesis of graphene nanoribbons with zigzag edge topology

Pascal Ruffieux^{1*}, Shiyong Wang^{2*}, Bo Yang^{2*}, Carlos Sánchez-Sánchez^{2*}, Jia Liu^{2*}, Thomas Dienel¹, Leopold Talirz¹, Prashant Shinde¹, Carlo A. Pignedoli^{1,3}, Daniele Passerone¹, Tim Dumslaff¹, Xinliang Feng², Klaus Müllen¹ & Roman Fasel^{1,3}



Pascal Ruffieux, Shiyong Wang, Bo Yang, Carlos Sánchez-Sánchez, Jia Liu, Thomas Dienel, Leopold Talirz, Prashant Shinde, Carlo A. Pignedoli, Daniele Passerone, Tim Dumslaff, Xinliang Feng, Klaus Müllen & Roman Fasel; 2016; On-surface synthesis of graphene nanoribbons with zigzag edge topology • *NATURE* 531: 489-492

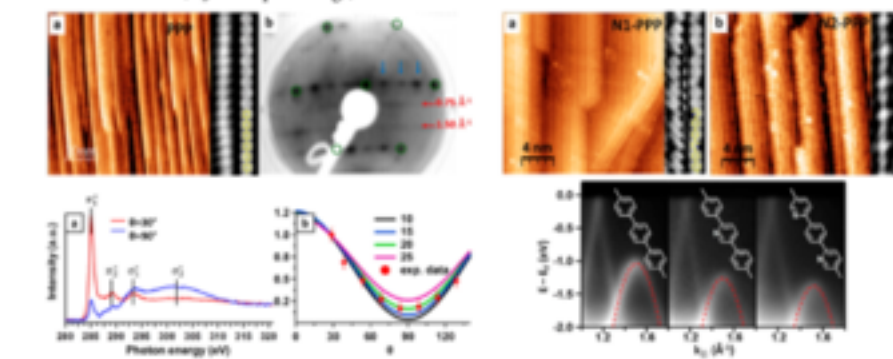
Simulating STM images of molecular wires

ACS NANO

ARTICLE

Tunable Band Alignment with Unperturbed Carrier Mobility of On-Surface Synthesized Organic Semiconducting Wires

Andrea Basagni¹, Guillaume Vasseur^{1,2}, Carlo A. Pignedoli¹, Manuel Vilas-Varela¹, Diego Peña¹, Louis Nicolas^{1,2}, Lucia Vitali^{1,3}, Jorge Lobo-Checa^{1,3}, Dimas G. de Oteyza^{1,2,3}, Francesco Sedona^{1,3}, Maurizio Casarin¹, J. Enrique Ortega^{1,2} and Mauro Sambi¹



Andrea Basagni, Guillaume Vasseur, Carlo A. Pignedoli, Manuel Vilas-Varela, Diego Peña, Louis Nicolas, Lucia Vitali, Jorge Lobo-Checa, Dimas G. de Oteyza, Francesco Sedona, Maurizio Casarin, J. Enrique Ortega & Mauro Sambi; 2016; Tunable Band Alignment with Unperturbed Carrier Mobility of On-Surface Synthesized Organic Semiconducting Wires • *ACS Nano* 10(2): 2644-2651

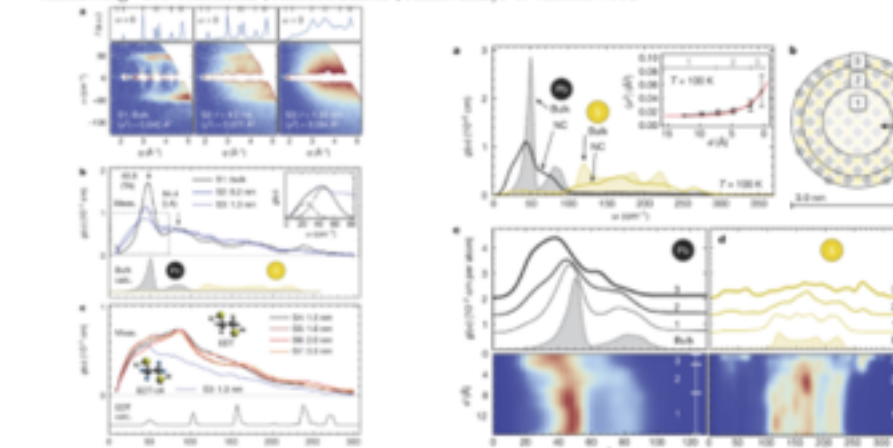
Strong electron-phonon coupling and fast multi-phonon transition rates

LETTER

doi:10.1038/nature16977

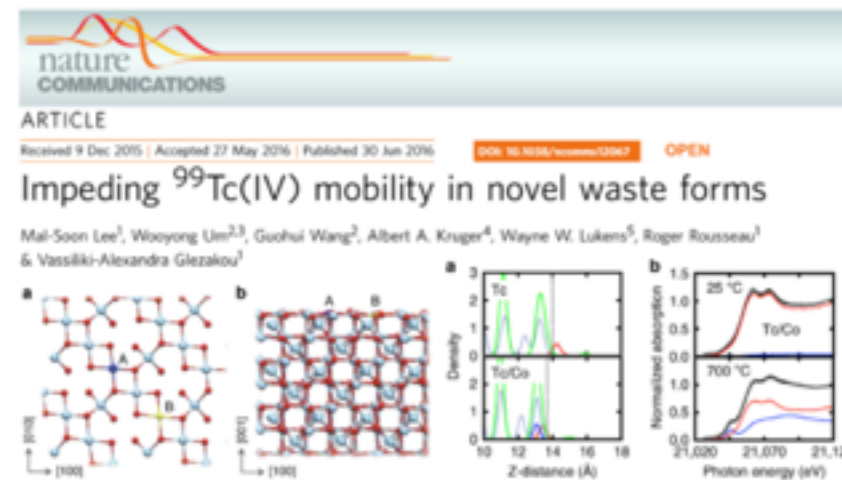
Soft surfaces of nanomaterials enable strong phonon interactions

Deniz Bozyigit¹, Nuri Yazdani¹, Maksym Yarema¹, Olesya Yarema¹, Weyde Matteo Mario Lin¹, Sebastian Volk¹, Kantawong Vuttivorakulchai¹, Mathieu Luisier¹, Fanni Juranyi¹ & Vanessa Wood¹



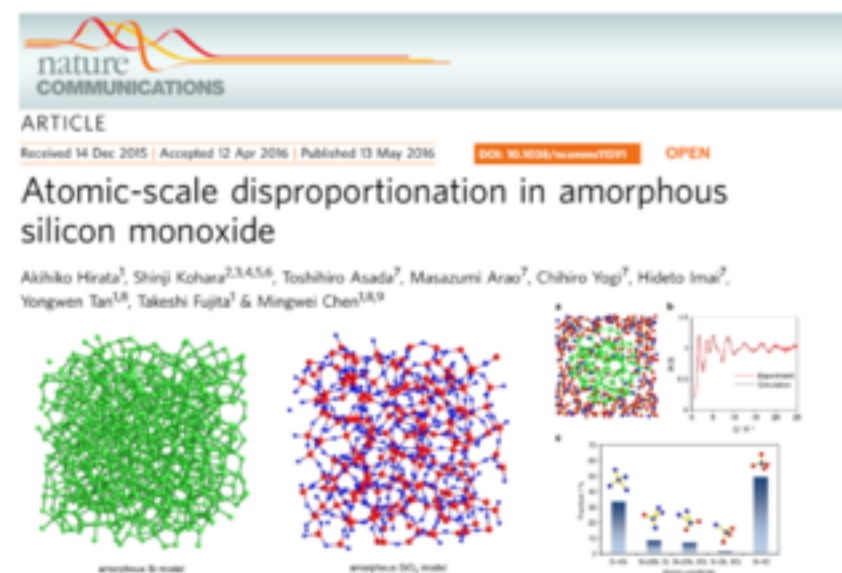
Deniz Bozyigit, Nuri Yazdani, Maksym Yarema, Olesya Yarema, Weyde Matteo Mario Lin, Sebastian Volk, Kantawong Vuttivorakulchai, Mathieu Luisier, Fanni Juranyi & Vanessa Wood; 2016; Soft surfaces of nanomaterials enable strong phonon interactions • *Nature* (2016), doi:10.1038/nature16977

AIMD on radioactive Technetium in glass waste form



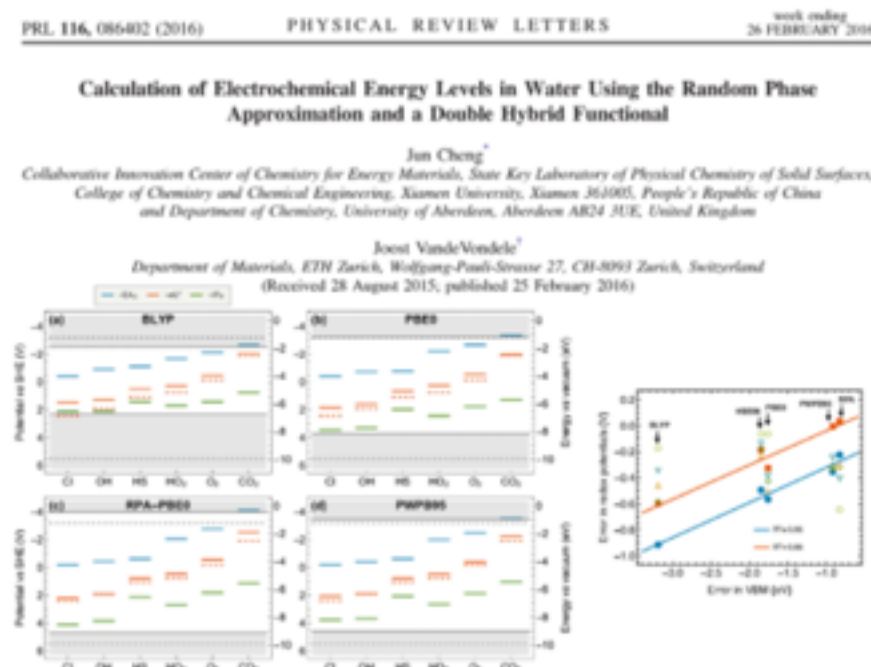
Mal-Soon Lee¹, Wooyong Um^{2,3}, Guohui Wang², Albert A. Kruger⁴, Wayne W. Lukens⁵, Roger Rousseau¹ & Vassiliki-Alexandra Glezakov²; 2016; Impeding ⁹⁹Tc(IV) mobility in novel waste forms • *Nat. Commun.* 7: 12067, 1-6

Structure of amorphous silicon monoxide



Akihiko Hirata¹, Shinji Kohara^{2,3,4,5,6}, Toshihiro Asada², Masazumi Arai⁷, Chihiro Yogi⁷, Hideto Imai⁷, Yongwen Tan^{1,8}, Takeshi Fujita¹ & Mingwei Chen^{1,9}; 2016; Atomic-scale disproportionation in amorphous silicon monoxide • *Nat. Commun.* 7: 11591, 1-7

Calculated water band positions and redox potentials using RPA and MD



Jun Cheng & Joost VandeVondele; 2016; Calculation of Electrochemical Energy Levels in Water Using the Random Phase Approximation and a Double Hybrid Functional [Phys. Rev. Lett. 116, 086402](https://doi.org/10.1103/PhysRevLett.116.086402)

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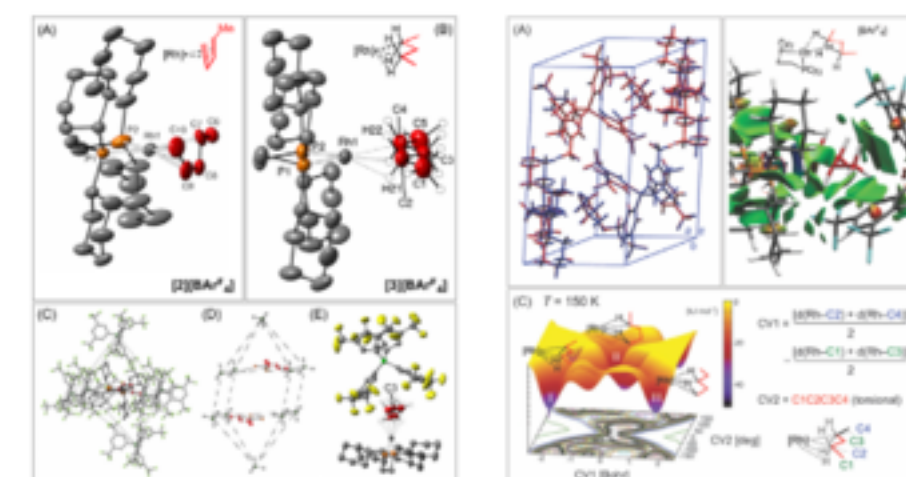
Rhodium-pentane σ -alkane complex

Alkane Complexes

International Edition: DOI: 10.1002/anie.201511269
German Edition: DOI: 10.1002/ange.201511269

A Rhodium-Pentane Sigma-Alkane Complex: Characterization in the Solid State by Experimental and Computational Techniques

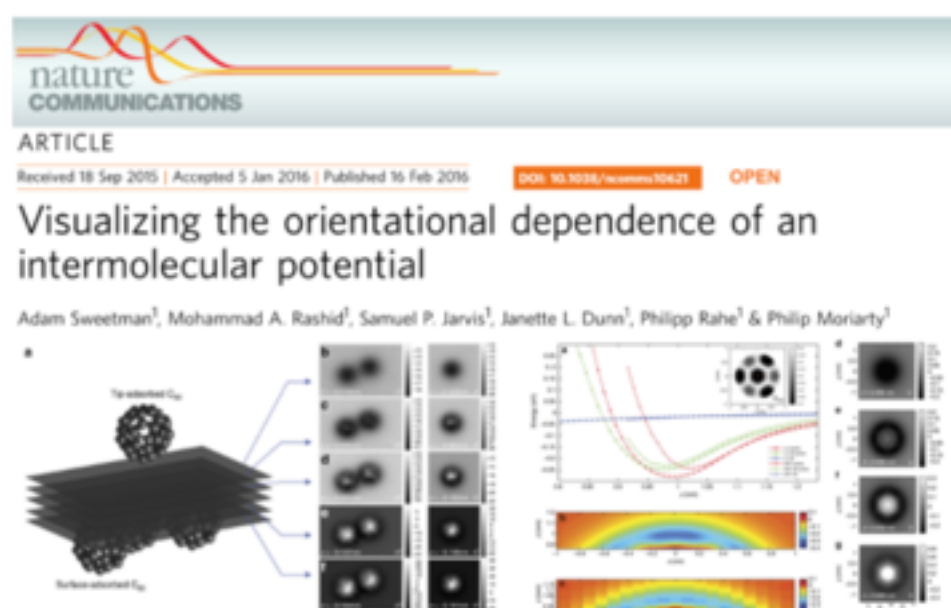
F. Mark Chadwick*, Nicholas H. Rees, Andrew S. Weller,* Tobias Krämer*, Marcella Iannuzzi, and Stuart A. Macgregor*



F. Mark Chadwick, Nicholas H. Rees, Andrew S. Weller, Tobias Krämer, Marcella Iannuzzi & Stuart A. Macgregor; 2016; A Rhodium-Pentane Sigma-Alkane Complex: Characterization in the Solid State by Experimental and Computational Techniques [Angew. Chem. Int. Ed. 2016, 55, 3677-3681](https://doi.org/10.1002/anie.201511269)
DOI: 10.1002/anie.201511269

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Modeling the interaction between fullerene molecules



Adam Sweetman, Mohammad A. Rashid, Samuel P. Jarvis, Janette L. Dunn, Philipp Rahe & Philip Moriarty; 2016; Visualizing the orientational dependence of an intermolecular potential [Nat. Commun. 7:10621, 1-7](https://doi.org/10.1038/ncom10621)

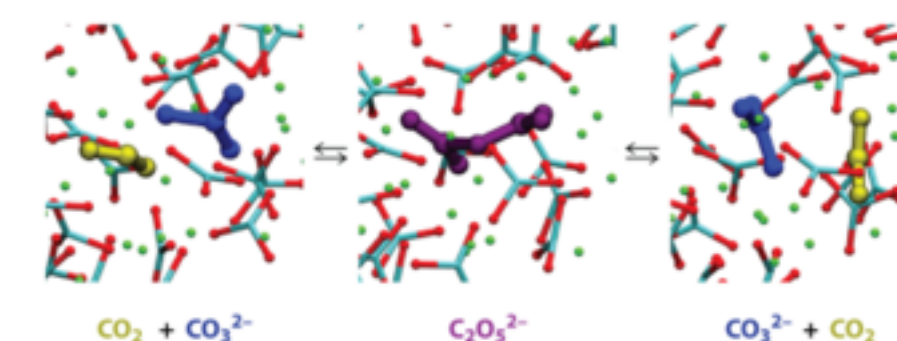
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Carbon dioxide solvation in molten carbonates

nature chemistry ARTICLES
PUBLISHED ONLINE: 29 FEBRUARY 2016 | DOI: 10.1038/nchem.2450

Carbon dioxide transport in molten calcium carbonate occurs through an oxo-Grothuss mechanism via a pyrocarbonate anion

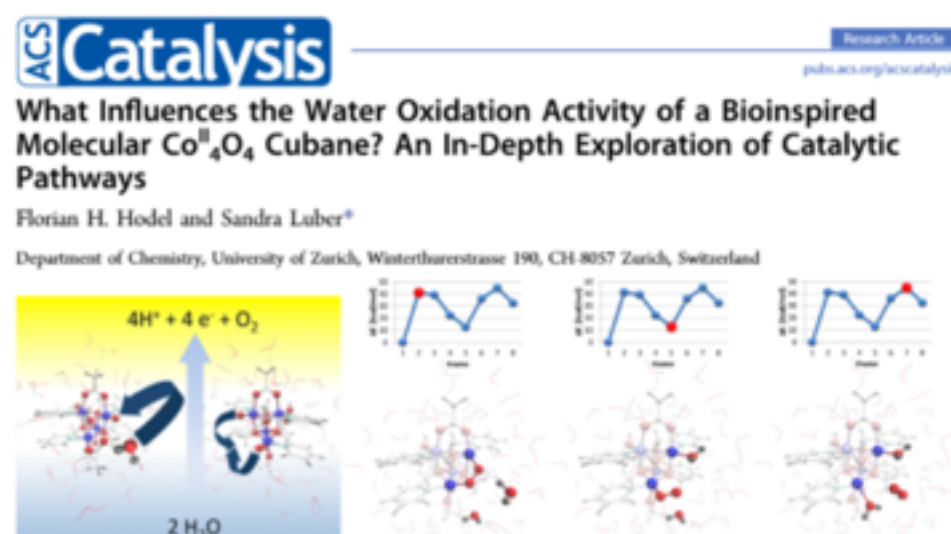
Dario Corradini^{1,2,3}, François-Xavier Coudert^{1*} and Rodolphe Vuilleumier^{1,2,4*}



Dario Corradini, François-Xavier Coudert & Rodolphe Vuilleumier; 2016; Carbon dioxide transport in molten calcium carbonate occurs through an oxo-Grothuss mechanism via a pyrocarbonate anion [Nature Chem. 2016, DOI: 10.1038/nchem.2450](https://doi.org/10.1038/nchem.2450)

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Investigation and design of a novel biomimetic water oxidation catalyst



Florian H. Hodel & Sandra Luber; 2016; What Influences the Water Oxidation Activity of a Bioinspired Molecular $\text{Co}^{\text{II}}_4\text{O}_4$ Cubane? An In-Depth Exploration of Catalytic Pathways [ACS Catal. 6\(3\): 1505-1517](https://doi.org/10.1021/acs.catal.5b02157)

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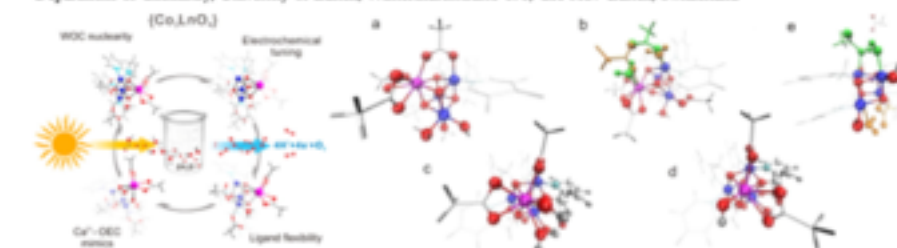
AIMD structure elucidation of novel nature-inspired water oxidation catalysts

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3d-4f $(\text{Co}^{\text{II}}_3\text{Ln}(\text{OR})_4)$ Cubanes as Bio-Inspired Water Oxidation Catalysts

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Fabio Evangelisti, René Moré, Florian Hodel, Sandra Luber & Greta Ricarda Patzke; 2015; 3d-4f $(\text{Co}^{\text{II}}_3\text{Ln}(\text{OR})_4)$ Cubanes as Bio-Inspired Water Oxidation Catalysts [J. Am. Chem. Soc. 137 \(34\): 11076-11084](https://doi.org/10.1021/ja511076a001)

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