

Exploring Potential Energy Surface

Introduction to Molecular Modeling



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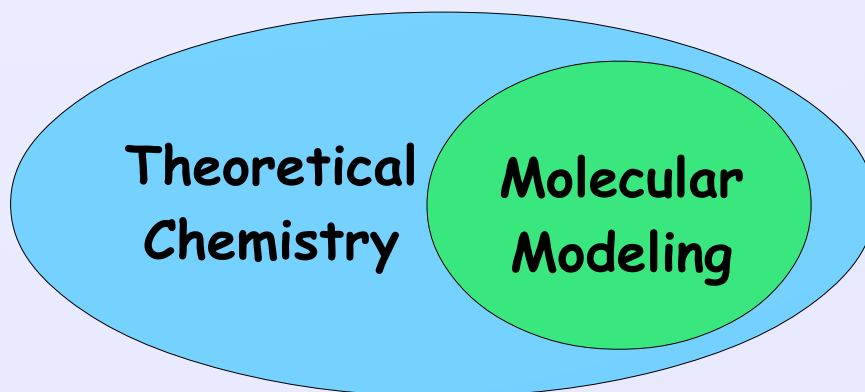
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Some Definitions

- ❑ **Theory** is a group of ideas meant to explain a certain topic of science, such as a single or collection of fact(s), event(s), or phenomenon(a).
<http://en.wikipedia.org/wiki/Theory>
- ❑ **Theoretical physics chemistry** is a branch of physics chemistry which employs mathematical models and abstractions of physical (chemical) objects and systems to rationalize, explain and predict natural phenomena. http://en.wikipedia.org/wiki/Theoretical_physics
- ❑ **Molecular Modeling \approx Computational Chemistry** means implementation & application computer codes for studying properties of (hopefully reasonable models of real) molecules & solids ('*experiments in silico*').



Selected Literature

- ❑ C. J. Cramer "Essentials of Computational Chemistry" Wiley 2004.
- ❑ F. Jensen "Introduction to Computational Chemistry" Wiley 2006.
- ❑ L. Piela "Ideas of Quantum Chemistry" Elsevier, 2013.
- ❑ E. G. Lewars "Computational Chemistry" Springer 2011.
- ❑ J. Leszczyński (ed.) "Handbook of Computational Chemistry Vol. 1", Springer 2012.
- ❑ & many others...

Non-relativistic Quantum Mechanics

Erwin with his psi can do

Calculations quite a few.

But one thing has not been seen:

Just what does psi really mean?

//Gar Manches rechnet Erwin schon

//Mit seiner Wellenfunktion.

//Nur wissen m'ocht man gerne wohl,

//Was man sich dabei vorstell'n soll.

Ernest Hückel (Felix Bloch's transl. from German)

- ❑ N-particle Ψ is a function of $4N+1$ variables $\{N^*(3 \text{ spatial}+1 \text{ spin})+ \text{time}\}$ without any physical meaning.
- ❑ $|\Psi|^2$ is probability density. $\hat{O}\Psi = \lambda\Psi \Rightarrow$ eigenvalues are observables.
- ❑ Ψ obeys time dependent (TD) Schrödinger equation (SE):

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}(\mathbf{x}^N, t) \Psi(\mathbf{x}^N, t) \quad , \quad \mathbf{x}^i = (x_1^i, x_2^i, x_3^i, \sigma^i)$$

- ❑ Stationary cases: $\Psi(\mathbf{x}^N, t) = \Phi(\mathbf{x}^N) \exp(-iE/\hbar t)$ then $|\Psi|^2$ not TD and Ψ is solution to time-independent SE

$$\hat{H}(\mathbf{x}^N) \Psi = E \Psi(\mathbf{x}^N) \quad .$$

Non-relativistic QM for Molecules & Solids

- ▣ Exact non-relativistic (Coulomb) Hamiltonian (a. u.: $e, m_e, \hbar = 1$).

$$\hat{H} = \hat{T}_{nuc} + \hat{V}_{nuc-nuc} + \hat{T}_e + \hat{V}_{nuc-e} + \hat{V}_{ee} = \sum_I \left(-\frac{1}{2M_I} \nabla_I^2 \right) + \sum_{I>J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} + \\ + \sum_i \left(-\frac{1}{2} \nabla_i^2 \right) + \sum_{I,i} \left(-\frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} \right) + \sum_{i>j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

i. e. c infinite, no magnetic interactions.

- ▣ Relativistic effects become important for core electrons in heavy atoms ($Z > 40$) and can be:

- included in effective core potentials, one solves SE only for valence electrons - works for structures, energetics, IR, UV-Vis.
- added a posteriori as perturbation to Coulomb \hat{H} .

Dealing with Nuclei

- Translation of center of mass is separable from other motions.
- Because $m \ll M$, we assume that e follows immediately movements of nuclei, thus

$$\hat{H} = \hat{T}_{nuc}(\mathbf{R}^N) + \hat{H}_e(\mathbf{r}^n, \mathbf{R}^N)$$

$$\text{has eigenfunction } \Psi(\mathbf{R}^N, \mathbf{r}^n) \approx \Psi_{nuc}(\mathbf{R}^N) \Psi_e(\mathbf{r}^n; \mathbf{R}^N)$$

$$\text{each obeying } \hat{T}_{nuc} \Psi_{nuc} = T_{nuc} \Psi_{nuc} \quad \wedge \quad \hat{H}_e \Psi_e = E_e(\mathbf{R}^N) \Psi_e$$

$\Psi_e(\mathbf{r}^n; \mathbf{R}^N)$ denotes Ψ_e for given \mathbf{R}^N ; $V_{nn}(\mathbf{R}^N)$ included in \hat{H}_e .

- Born-Oppenheimer approximation

taking $\langle \Psi_e(\mathbf{r}^n; \mathbf{R}^N) | \hat{T}_{nuc} | (\mathbf{R}^N) \Psi_e(\mathbf{r}^n; \mathbf{R}^N) \rangle \approx 0$ one gets:

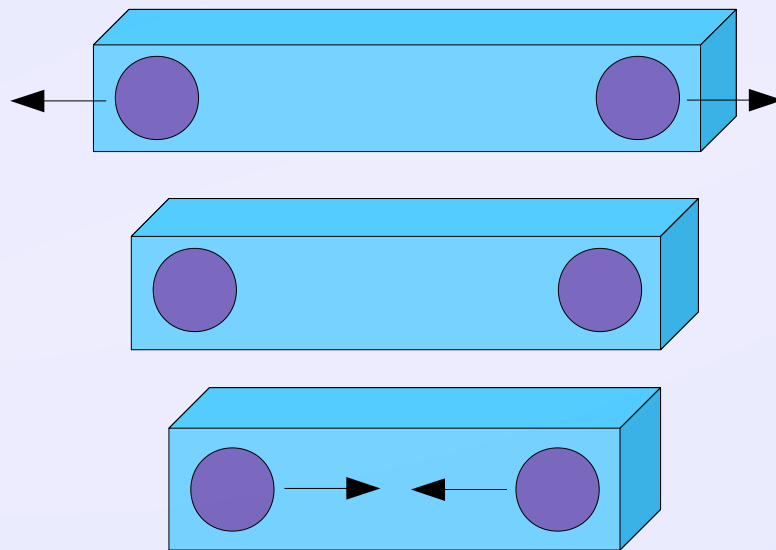
$$(\hat{T}_{nuc} + \hat{H}_e) \Psi_{nuc} \Psi_e = (T_{nuc} + E_e(\mathbf{R}^N)) \Psi_{nuc} \Psi_e \quad / : \Psi_e$$

$$\hat{T}_{nuc} \Psi_{nuc} + \frac{1}{\Psi_e} (\hat{H}_e \Psi_e) \Psi_{nuc} = (T_{nuc} + E_e(\mathbf{R}^N)) \Psi_{nuc} \quad / \leftarrow \hat{H}_e \Psi_e = E_e \Psi_e$$

$$(\hat{T}_{nuc} + E_e(\mathbf{R}^N)) \Psi_{nuc} = (T_{nuc} + E_e(\mathbf{R}^N)) \Psi_{nuc}$$

Born-Oppenheimer approx. in practice

- ❑ Electron E forms potential for movements of nuclei.
- ❑ Imagine metal balls embedded in rubber - the oscillation of balls (nuclei) depends on elastic constant of rubber (electron energy); if system rotates then centrifugal force will additionally affects oscillation.

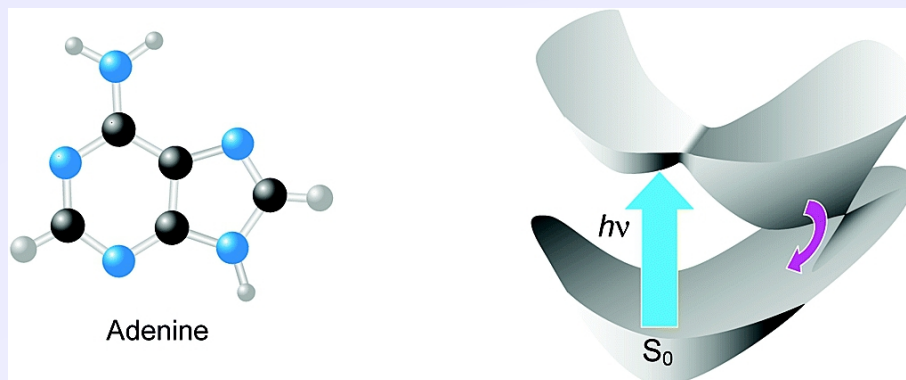


(after L. Piela 'Idee Chemii Kwantowej' PWN, 2005).

Does BO Approx. Work?

- Well, usually; BO approx. relies on assumption that gap between electronic states \gg gap between vibrational states.
- If both gaps are comparable, then vibrational (de)excitation can change electronic states.

- Non-BO effects:

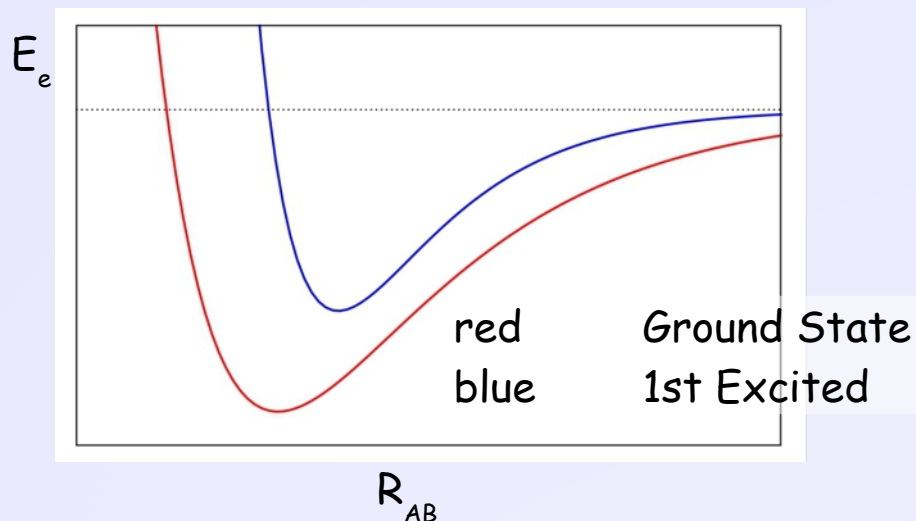


Kang & co. JACS, 2002, 124, 129

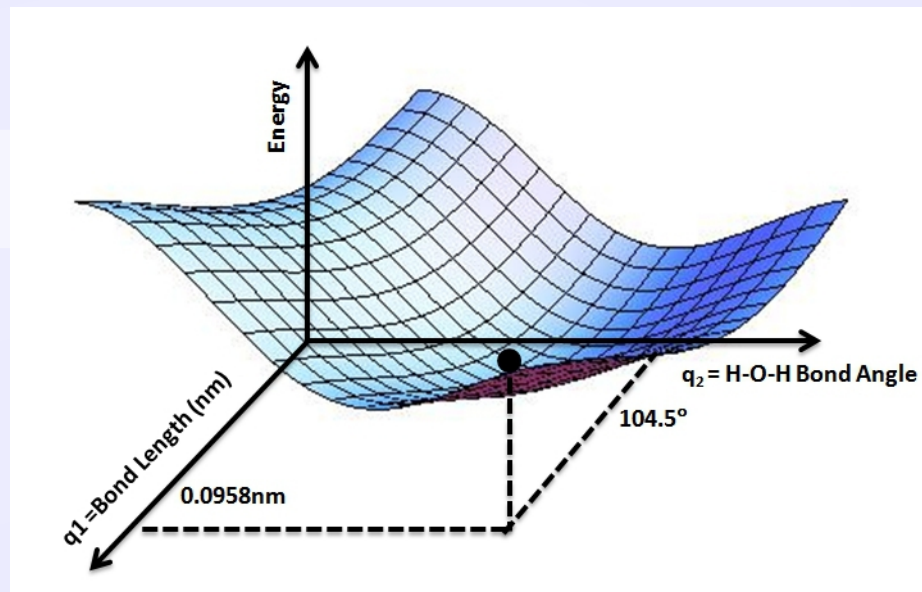
- photochemical reactions
 - dissociation of molecules
 - Jahn-Teller effect/Peierls distortion
 - electric resistivity, superconductivity.
- Treatment of non-BO effects - coupling between different Ψ_e :
$$\left\langle \Psi_e^i(\mathbf{r}^n; \mathbf{R}^N) \left| \hat{T}_{nuc}(\mathbf{R}^N) \right| \Psi_e^j(\mathbf{r}^n; \mathbf{R}^N) \right\rangle \neq 0$$

Potential Energy (Hyper)Surface (PES)

- ▣ E_e can be plotted as a function of $3N$ cartesian nuclear coord. or $3N-6$ ($3N-5$ for linear molecule) internal coord. (translations & rotations separated).



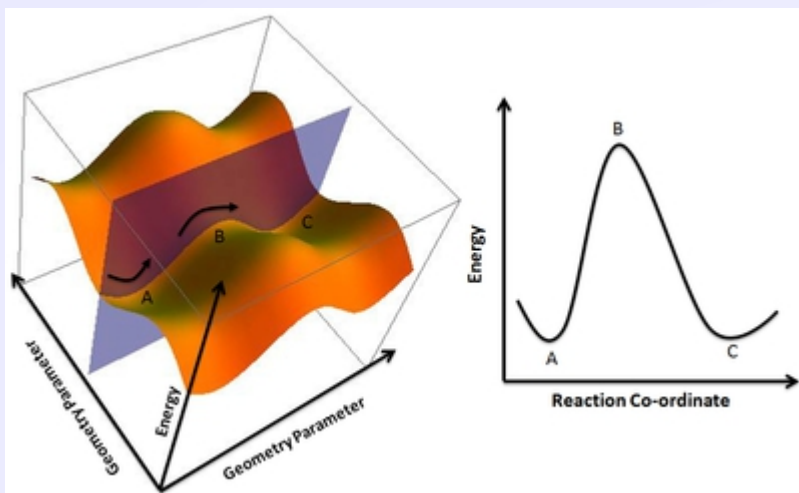
Ground state PES for H_2O molecule, assuming equal H-O bonds.



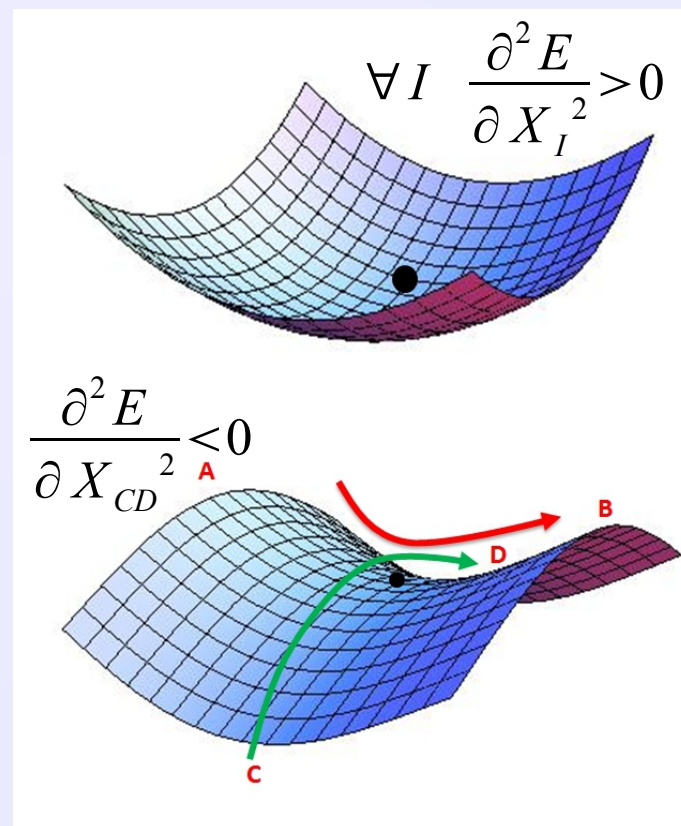
- ▣ In BO approx. for a given electronic state we have uniquely define electron E for given set of (mean) positions of nuclei.
- ▣ If masses of el. & nuc. were similar, we could only talk about total E for a given set of mean values of position operators of el. & nuc.

Places Worth Visiting on PES

- Stationary points: $\text{grad}_{\mathbf{R}} E_e = \mathbf{0}$.
- Typically the objects of interests are (local) minima, which corresponds to (meta)stable conformations & 1st order saddle points, which are transition states in chemical reactions.



*Reaction coordinate - geometric parameter changing during reaction; can be bond, angle or more complex function of \mathbf{R}^N .



Geometry Optimization

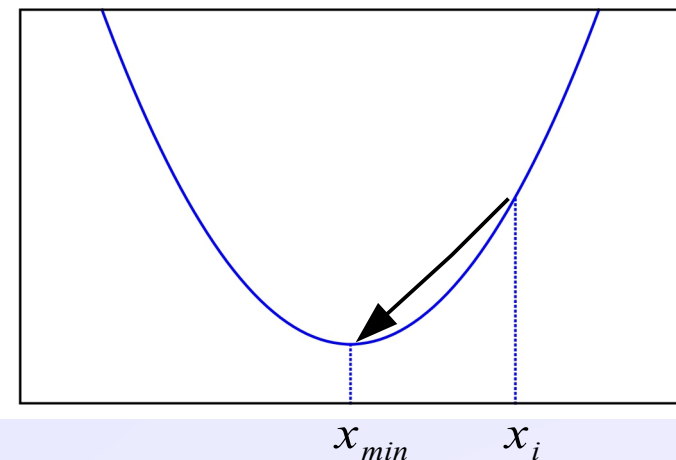
- ❑ Main techniques of looking for E minima
 - (i) without gradients,
 - (ii) with numerical gradients & 2nd derivatives,
 - (iii) with analytical gradients & numerical 2nd derivatives,**
 - (iv) with analytical gradients & 2nd derivatives.

- ❑ Typically (iii) is chosen, as the compromise between efficiency & time of calculation, the most time consuming part is the calculation of 2nd derivative matrix (Hessian).

- ❑ Among (iii) one of the most popular ones are (quasi) Newton-Raphson methods.

Newton-Raphson Method

E



$$E - E_{min} = k(x - x_{min})^2$$

$$\left(\frac{\partial E}{\partial x}\right)_i = 2k(x_i - x_{min}) \quad \wedge \quad \left(\frac{\partial^2 E}{\partial x^2}\right)_i = 2k$$

$$x_{min} = x_i - \left(\frac{\partial E}{\partial x}\right)_i \cdot \left(\frac{\partial^2 E}{\partial x^2}\right)_i^{-1}$$

For non-quadratic function iterative procedure must be applied

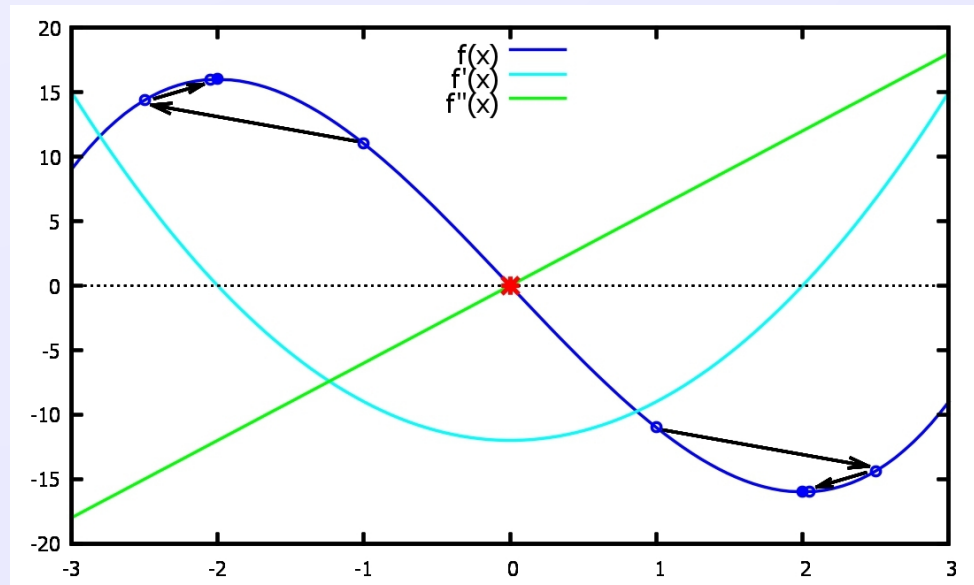
$$x_{i+1} = x_i - \left(\frac{\partial E}{\partial x}\right)_i \cdot \left(\frac{\partial^2 E}{\partial x^2}\right)_i^{-1} \quad \text{until} \quad |x_{i+1} - x_i| \approx 0 < \epsilon \quad \vee \quad |(\partial E / \partial X)_i| \approx 0 < \epsilon \quad \text{etc.}$$

E. g. $y = x^3 - 2x$

$$x_1 = 1.0, x_2 = 2.5, x_3 = 2.1, x_4 = 2.0$$

$$x_1 = -1.0, x_2 = -2.5, x_3 = -2.1, x_4 = -2.0$$

$$x_1 = 0.0 \text{ procedure fails } f''(0) = 0.$$



Quasi Newton-Raphson Method

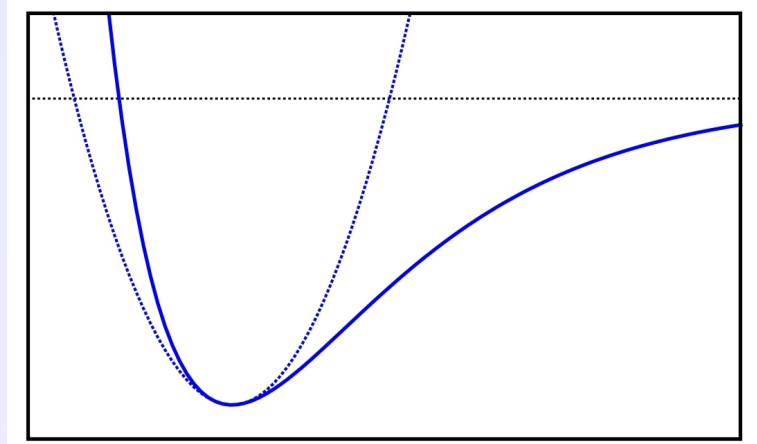
➤ PES around minimum is only approx. quadratic, iterative solution.

$$\begin{aligned} \text{➤ } E(X_i) - E_{min} &\approx \Delta X^T H \Delta X \rightarrow E \\ &\rightarrow g(X_i) = -H(X_i) \Delta X, \quad \Delta X = X_i - X_e \\ X_{i+1} &= X_i - g(X_i) \cdot H^{-1}(X_i) \end{aligned}$$

➤ H usually approximated:

$$H_{i+1}^{appr.} = f[H_i^{appr.}, g(X_{i+1}), g(X_i), X_{i+1}, X_i]$$

H_0 can be taken as unitary matrix.



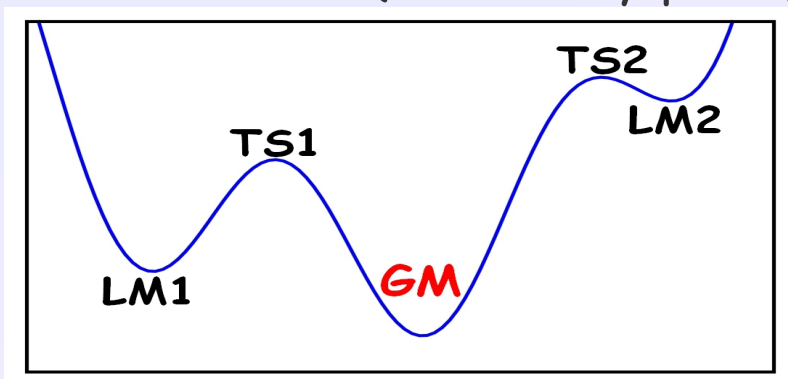
R_{AB}

➤ Iteration proceeds until gradients and/or change in X_i , E_i between consecutive sufficiently small.

$$X_k = \begin{pmatrix} X_k^1 \\ X_k^2 \\ \vdots \\ X_k^{3N} \end{pmatrix}, \quad g(X_k) = \begin{pmatrix} \frac{\partial E}{\partial X_k^1} \\ \frac{\partial E}{\partial X_k^2} \\ \vdots \\ \frac{\partial E}{\partial X_k^{3N}} \end{pmatrix}, \quad H(X_k) = \begin{pmatrix} \frac{\partial E}{\partial X_k^1 \partial X_k^1} & \frac{\partial E}{\partial X_k^1 \partial X_k^2} & \cdots & \frac{\partial E}{\partial X_k^1 \partial X_k^{3N}} \\ \frac{\partial E}{\partial X_k^2 \partial X_k^1} & \frac{\partial E}{\partial X_k^2 \partial X_k^2} & \cdots & \frac{\partial E}{\partial X_k^2 \partial X_k^{3N}} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial E}{\partial X_k^{3N} \partial X_k^1} & \frac{\partial E}{\partial X_k^{3N} \partial X_k^2} & \cdots & \frac{\partial E}{\partial X_k^{3N} \partial X_k^{3N}} \end{pmatrix}$$

(Dis)Advantages of Quasi-Newton method (& related ones)

- ❑ We are looking for **local** minima, usually there is no guarantee that the structure is of the lowest E .
- ❑ Results strongly depend on the **initial** guess, optimization procedures converge to the **nearest** minimum (stationary point).



- ❑ But this is often exactly what we are looking for! Many existing substances are thermodynamically unstable/only kinetic stable with respect to **global** E minima. (e. g. diamond & graphite, wurtzite & zinc blende, *n*-butane & isobutane etc.).
- ❑ All discussion above refers to finding (local) minimum of E_e @ OK!
Real systems corresponds to (local) minima of **total** (e+nuc) **free energy/enthalpy** at given T, p !

Some Comments on Hessian & Frequencies

- ❑ What we got from optimization is 'static' structure. In reality atoms always moves, even in OK (zero point vibrations).
- ❑ Having exact H we can calculate ($\sqrt{\text{of eigenvalues}}$) vibrational frequencies in **harmonic approximation**.
- ❑ After optimization is completed, it is good custom to calc. freqs., to check if it true minimum/transition state was found.
- ❑ Having harmonic freqs. one can evaluate zero point E & estimate vibrational contributions to free energy @ given T .
- ❑ Searching for transition states usually more tricky than looking for minima, usually one needs really good guess structure & exact initial H .
- ❑ Anharmonicity becomes important when PES strongly deviates from quadratic form (e. g. weak hydrogen bonds) or @ high T (thermal expansion of solids).

Back to Energy

➤ But how to get electron E ?

- **Wavefunction based methods** ('*ab initio*' in chemists' jargon)

Hartree-Fock method (mean field method) - min. $E[\Psi]$ with Ψ being single determinant made of N 1-electron functions (spinorbitals).

Correlated methods - approx. to full **Configuration Interaction** expansion, Ψ_{CI} being a linear combination of determinants.

- **Density Functional Theory** $E[\Psi]$ replaced by $E[\rho]$
- **Semiempirical/Tight Binding methods** 'simplified HF', some integrals not calc., but fitted to exp. (spectroscopic) data.
- **Molecular Mechanics** 'balls & springs' molecules, classical treatment of atoms.

Molecular Mechanics

- **Molecular Mechanics (MM)** - parametrization of E_{el} as a function of atomic coordinates only.
- In general, not to be confused with **Molecular Dynamics (MD)** - solving (classical) equation of motion for atoms (nuclei); but yes, MD usually relies on MM type parametrization of PES.

$$E_{MM} = \underbrace{E_{stretching}(R_{ij}) + E_{bending}(\Theta_{ijk}) + E_{torsional}(\Phi_{ijkl})}_{E_{bond}} + \underbrace{E_{Coulomb}(R_{ij}) + E_{dispersion}(R_{ij})}_{E_{nonbond}}$$

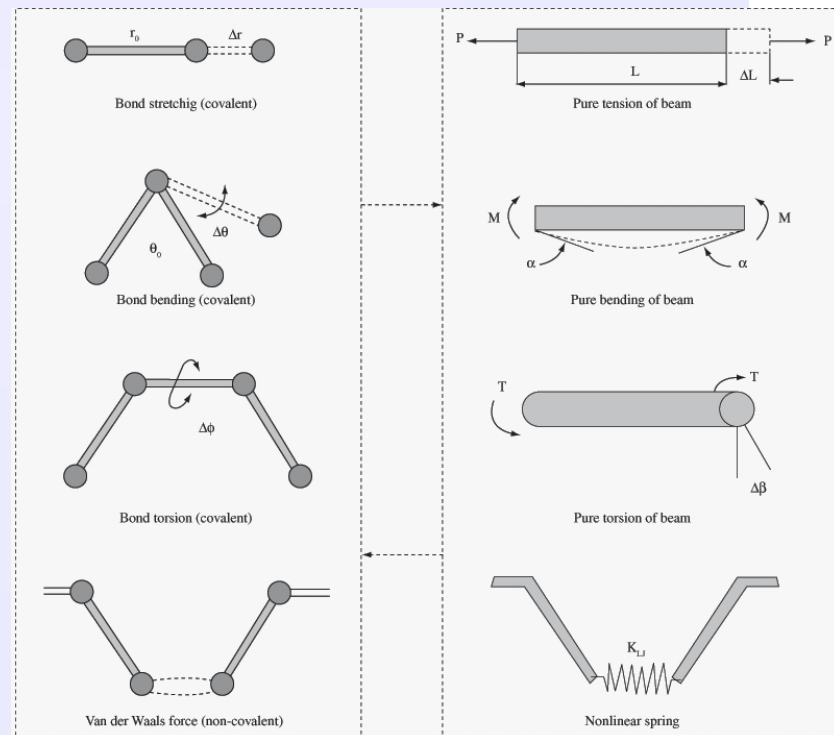


Fig. from Ferreira-Avila & Lacerda Mater. Res. 2008, 11, 325.

Force Fields

➤ **Force Fields (FF)/Interatomic Potentials Functions** - form (& set of parameters) used for description of interatomic interactions.

➤ 2-body interactions

Parameters

$$E_{\text{harmonic}} = k_R (R_{12} - R_0)^2$$

$$k_R, R_0$$

$$E_{\text{Morse}} = D_{eq} \left\{ \left[1 - \exp(-a(R_{12} - R_0)) \right]^2 - 1 \right\}$$

$$D_{eq}, a, R_0$$

➤ 3-body interactions

$$E_{\text{harmonic}} = k_{\Theta} (\Theta_{123} - \Theta_0)^2$$

$$k_{\Theta}, \Theta_0$$

$$E_{\text{Urey-Bradley}} = k_{UB} (R_{13} - R_0)^2$$

$$k_{UB}, R_0$$

➤ 4-body interactions

$$E_{\text{torsion}} = k_{\phi} (1 \pm \cos(\phi_{1234} - \phi_0))$$

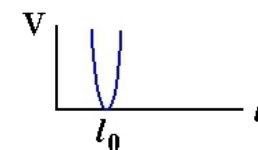
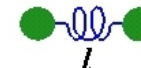
$$k_{\phi}, \phi_0$$

$$E_{\text{harmonic}}^{\text{improper torsion}} = k_{\omega} (\omega_{1234} - \omega_0)^2$$

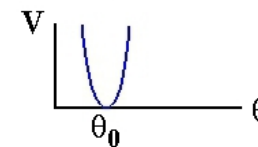
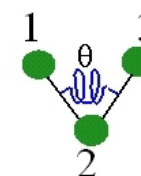
$$k_{\omega}, \omega_0$$

➤ **Cross terms, e. g.** $E_{\text{cross}} = k_{\text{cross}} (R_{12} - R_0)(\theta_{123} - \theta_0)$

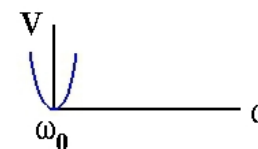
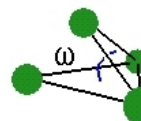
Bonds



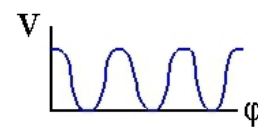
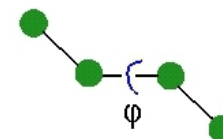
Angles



Improper
Dihedrals



Torsions



* Harmonic terms are the 1st non-0 terms in the Taylor expansion of E. ** Fig from:
employees.csbsju.edu/hjakubowski/classes/ch331/protstructure/mechdynam2.html

Force Fields – Nonbonded Terms

❑ Coulomb interactions

$$E_{Coulomb} = \frac{q_1 q_2}{R_{12}}$$

Parameters

$$q_1, q_2$$

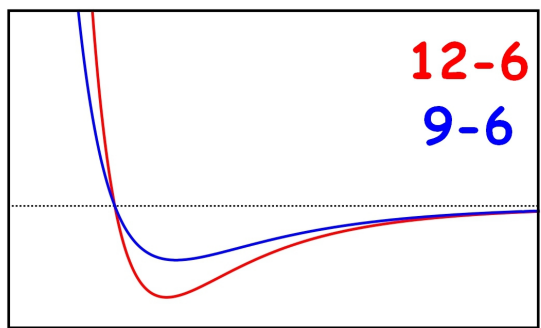
Atomic charge in MM is just an adjustable parameter!

Atomic charge is not an observable!

❑ Short range interactions = vdW attractions+Pauli repulsion.

$$E_{Lennard-Jones} = \frac{A}{R_{12}^m} - \frac{B}{R_{12}^n} = \epsilon \left[\left(\frac{n}{m-n} \right) \left(\frac{\sigma}{R_{12}} \right)^m - \left(\frac{m}{m-n} \right) \left(\frac{\sigma}{R_{12}} \right)^n \right]$$

$A, B \quad \vee \quad \epsilon, \sigma$



In L-J potential usually $m = 12$ or 9 , $n = 6$.

$$E_{Buckingham} = A \exp(-R_{12}/\rho) - \frac{B}{R_{12}^6} \quad A, \rho, B$$

$$E_{Axilrod-Teller} = k_{AT} \frac{1 + 3\cos(\theta_{123})\cos(\theta_{231})\cos(\theta_{312})}{(R_{12}R_{23}R_{13})^3} \quad k_{AT}$$

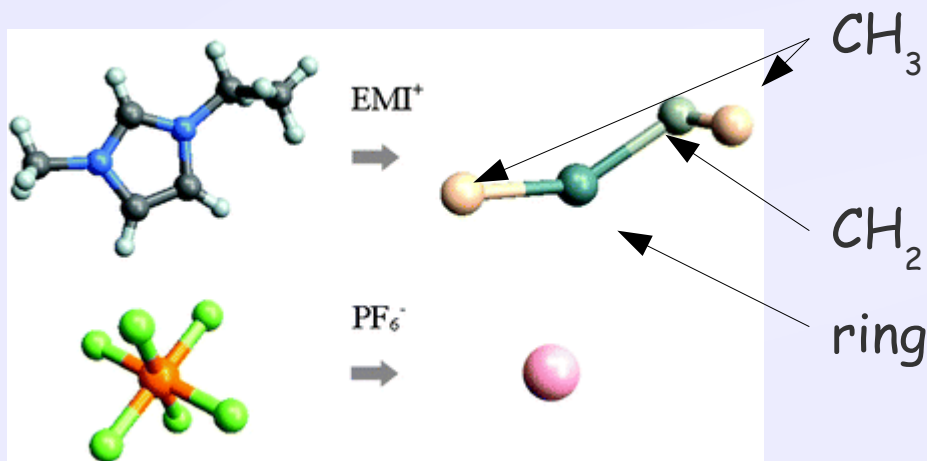
How to Get Proper Parameters?

$$\{C_i^{opt}\} \rightarrow \min \left\{ F(C_i) = \sum_i w_i [f_i^{obs} - f_i^{calc}(C_i)]^2 \right\}$$

- ❑ w_i - statistical weights; f_i - observables (structures, thermodynamical props., vibrational freqs., elastic constants etc.).
- ❑ f_i can be exp. values or calculated by higher level theor. methods.
- ❑ Fitting C_i is not unique (e. g. depends on the choice of w_i).
- ❑ The performance of a given FF depends on the type of observables it was fitted to - e. g. FF fitted to structural data may describe very poorly cohesion energy.
- ❑ There is always limited transferability of FF - e. g. parameters fitted for C-O bonds in alcohols don't work well for carbonates.

How Many Atoms Can You See?

- Generally, FFs need 'more elements' than in periodic table, e. g. for good description of hydrocarbons one needs different set of parameters for $C\ sp^3$, aliphatic sp^2 , aromatic sp^2 & sp .



Jeong & co. *PCCP*, 2010, 12, 2001.

- United Atom/Coarse Grained Approach:** 'atoms' in MM not necessarily are true atoms - to save time one can treat group of atoms as one 'superatom'.

More Tricky Issues

❑ Polarisability:

(1) Representing atoms as dipole moments with polarisability α_i :

$$\mu_i^{ind} = \alpha_i E(q_j, \mu_j^{ind}) \rightarrow E_{ind} = -\frac{1}{2} \sum_i \mu_i^{ind} E(q_j, \mu_j^{ind})$$

(2) Dividing atoms into 2 point charges: heavy core & massless shell interacting via harmonic potential & via Coulomb with other cores-shells; the positions of both core & shells are optimized.

Dick & Overhauser *PR* **1958**, 112, 90.

$$\alpha_i = \frac{q_{shell}^2}{k_{core-shell}}$$

(3) Variable charges - Fluctuating Charge (FQ), Electronegativity Equalization (EE) - E minimized with constraints on electronegativity χ :

$$\chi_i = -\frac{\partial E}{\partial q_i}, \quad \sum_i q_i = const., \quad \chi_i^{min} = 0$$

Review: Cieplak & co. *J. Phys. Condens. Matt.* **2009**, 21, 333102.

& More More Tricky Issues

- MM for Metals: E expressed as a functional of electron density

Embedded Atom Method $E_{tot} = \sum_{i>j} E_{ij}^{repulsive} - \sum_i f(\rho_i), \quad \rho_i = \sum_{j \neq i} \rho_j(R_{ij})$

e. g. Finnis-Sinclair potential

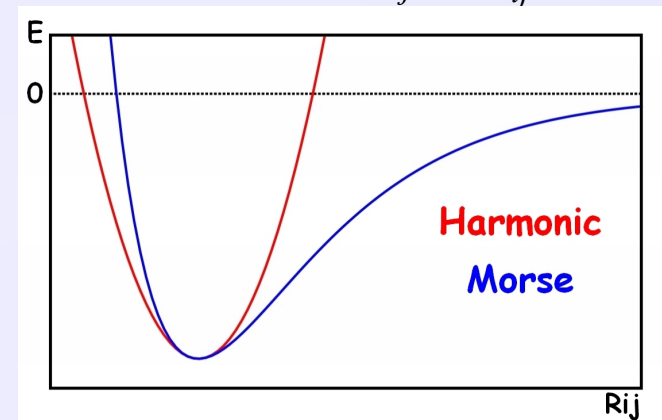
Finnis & Sinclair *Phil. Mag. A* **1984**, 50, 45. $f(\rho_i) = \sqrt{\rho_i} = \text{const} \cdot \sqrt{\left(\sum_{j \neq i} \frac{1}{R_{ij}}\right)}$

- Bond Breaking/Formation

Harmonic pot. cannot describe dissociation,

Morse pot. (roughly) correct.

Bond Order Potentials



$$E_{BO}(R_{ij}) = \sum_{i>j} E^{repuls}(R_{ij}) - b_{ij} E^{attract}(R_{ij}), \quad b_{ij} = b_{ij} \left(\sum_{k \neq i, j} f(R_{ij}, R_{ik}, \theta_{ijk}) \right)$$

Abell *PR-B* **1958**, 31, 6184; Tersoff *PR-B* **1988**, 37, 6991; Brenner & co. *JPCM* **2002**, 14, 783.

ReaxFF - more complicated dependence of atom electronic state vs interatomic distance. van Duin & co. *JPC-A* **2001**, 105, 9396.

Force Fields Market

❏ **Class I:** harmonic + 2-body nonb. terms, aim to reproduce structure.

(1) AMBER (Cornell & co. *JACS*, **1995**, 117, 5179; ambermd.org)

(2) CHARMM (Brooks & co. *J. Comp. Chem.* **1983**, 4, 187; charmm.org)

*Martin Karplus - Nobel Prize in chemistry 2014

(3) GROMOS (Scott & co. *JPC-A*, **1999**, 103, 3596) (4) & many others...

(1)-(3) both names of FF & program packages

(4) UFF - all atom FF, covering all periodic table, but moderately accurate (Rappe & co. *JACS* **1992**, 114, 10024).

❏ **Class II:** cross terms + anharmonic ones, should reproduce vibrations.

(1) COMPASS (Sun *JPC-B* **1998**, 102, 7338), (2) MMFF (Halgren *J. Comp. Chem.* **1998**, 17, 490), (3) new versions of AMBER, CHARMM, GROMOS, (4) etc.

❏ **Class III:** included polarisability, electronegativity etc.

e. g. AMOEBA (Ponder & co. *JPC-A* **2010**, 114, 2549)

➤ http://en.wikipedia.org/wiki/List_of_software_for_molecular_mechanics_modeling

➤ Free goodies

(1) LAMMPS <http://lammps.sandia.gov/>

(2) Tinker <http://dasher.wustl.edu/tinker/>

(3) GULP <https://projects.ivec.org/gulp/>

Quite universal softwares, Linux & Windows portable, variety of FF implemented, MM & MD, handle periodic boundary conditions.

(1), (2) more oriented toward soft matter & (bio)organic systems,

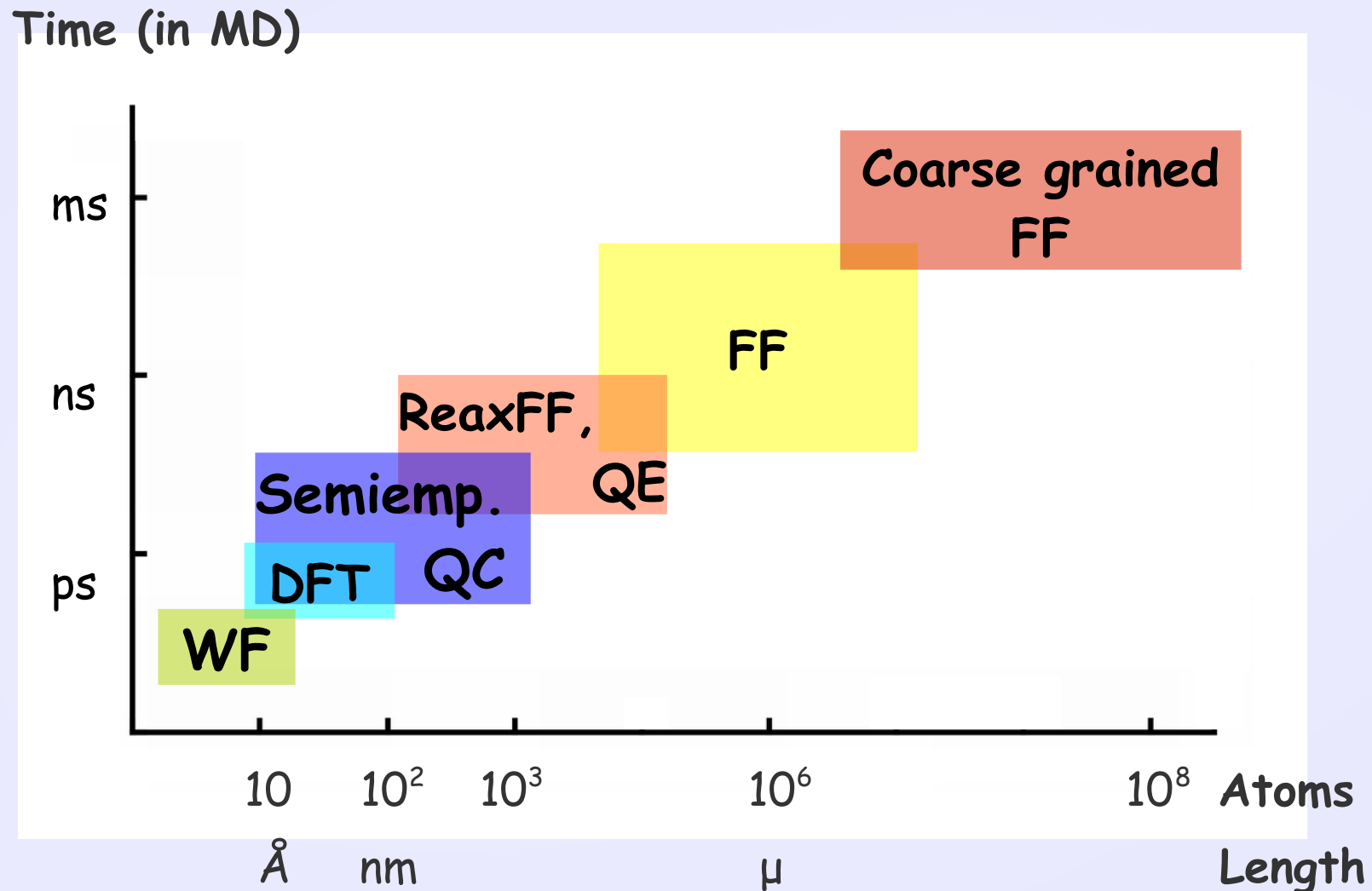
(3) more oriented toward solids.

Cons of FF methods

- (-) Results strongly depends on (somewhat arbitrary) choice of FF (potential functions form & parametrization).
- (-) Limited transferability of FF from one system to the other.*
- (-) Problematic description of chemical reactivity.
- (-) Lack of direct insight into electronic structure & related spectroscopic quantities.

*Also principally it is never fully legal to combine parameters from different FF!

What Are Pros of FF?



One can do calc. for large models & long time scale MD!

Simple Example

🔖 GULP input - calculations for forsterite Mg_2SiO_4 .

[illegible]

Simple Example

```
#Initial geom. - exp. from Hazen Am. Mineral. 1976, 61, 1280.
cell
4.746000 10.180000 5.976000 90.000000 90.000000 90.000000
fractional
Si    core    0.426100    0.093900    0.250000
Mg1   core    0.000000    0.000000    0.000000
Mg2   core    0.991400    0.277200    0.250000
O1    core    0.766100    0.091900    0.250000
O2    core    0.220200    0.446900    0.250000
O3    core    0.277700    0.162800    0.033300
O1    shel    0.766100    0.091900    0.250000  #Initially shells
O2    shel    0.220200    0.446900    0.250000  #on cores
O3    shel    0.277700    0.162800    0.033300

space
P b n m
```

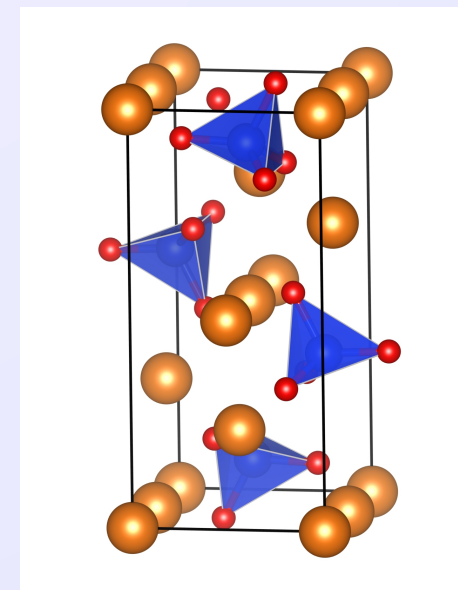
Simple Example

```
#Some more detailed options
maxcyc 1000           #no. of optimization cycles
output xtl            #output options, here: final geometry in .xtl format
dump every 1 gulp.res #dump restart file every iteration
switch rfo gnorm 0.001 #options for Rational Function Optimizer
accuracy 12           #accuracy for electrostatic summation
```

❏ Running calculations: `/(path)/gulp < GULP_input > GULP_output`

❏ & after 0.67 s on my old laptop...

	a	b	c(Å)	V(Å ³)
Exp.	4.746	10.180	5.976	288.73
Calc.	4.777	10.248	5.987	293.09
	K(GPa)	G(GPa)	v	
Exp.*	128	81	0.24	
Calc.**	152	75	0.29	



*Suzuki & co. *Phys. Chem. Mineral.* **1983**, 10, 38. **Hill definition.

Summary

- Most of chemistry can be explained in terms of **nonrelativistic QM**, relativistic correction can be introduced as a perturbations.
- The motions of "quantum electrons" & "semiclassical nuclei" can be separated within **Born-Oppenheimer approx.**
- Within **BO approx.** electron creates potential energy for (oscillatory) movements of nuclei. **Potential Energy Surface** is E_{el} plotted as the function of nuclei coordinates.
- Local minima of E_{el} corresponds to (meta)stable conformation of molecules/solids @ 0 K. For strongly bound systems & moderate T they should not differ much from exp. local minima of free energy @ finite T.

Summary

- Usually optimization techniques finds stationary points nearest to the guess structure - yes, it means that simulations must be done in **conscious** way.
- **Molecular Mechanics** is the parametrization of E_{el} as the function of interatomic distances, angles & torsions.
- **Force Field** is the functional form of this parametrization + set of parameters. Parametrization (always arbitrary) is performed for the set of exp. data &/or 'higher level' theoretical methods.
- **Molecular Dynamics** solves eqs. of motions for atoms - usually classical ones with use of FF.
- MM can be used in combination with quantum mechanics methods to study extended systems - small part of the system is treated at more accurate & computationally expensive methods, while the environment at cheaper & less accurate MM level. For example such **QM/MM** approach is popular in biochemistry - QM level for small active site & MM for the rest of enzyme.

- ❑ Accuracy of computational methods is accompanied by the growth of their computational demands. We can either perform accurate calculation for (often unrealistically:] small models or approximated calculations for large models.

The End (For A While)

Further Reading:

- GULP manual - really nice intro to MM, lot of refs.
<https://projects.ivec.org/gulp/help/manuals.html>
or Gale & Rohl *Mol. Simul.* **2003**, 29, 291.
- Good intro to MD by Furio Ercolessi
<http://www.fisica.uniud.it/~ercolessi/md/>

THANK YOU FOR YOUR ATTENTION!
(TO BE CONTINUED...)

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