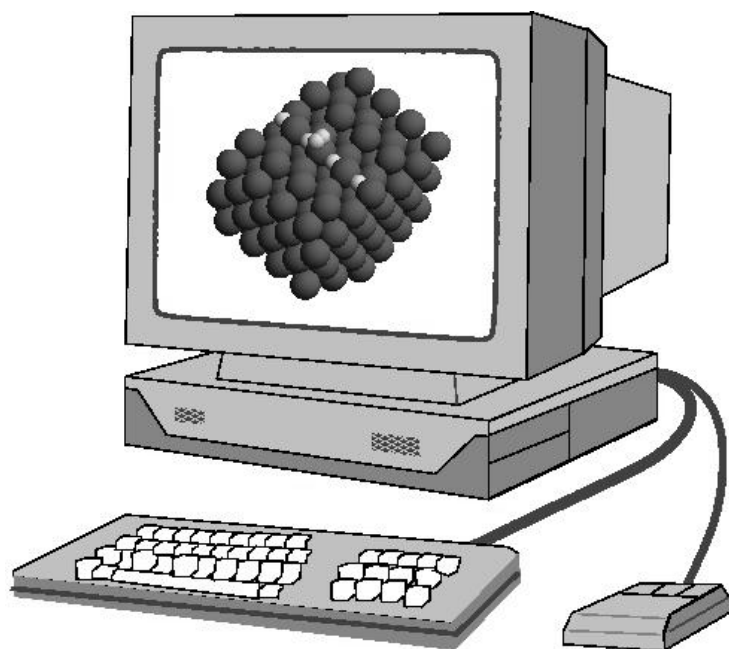


Theoretische Simulation und Modellierung

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<http://www.uni-ulm.de/theochem>



1. Einführung
2. Lehrplan
3. Vorlesung

Contents

1. Introduction
2. Molecular Modeling
3. Statistical Mechanics and Monte Carlo methods
4. Molecular dynamics
5. Quantum Mechanics
6. Multiscale Modeling

Computational Quantum chemistry

Virtual chemistry lab



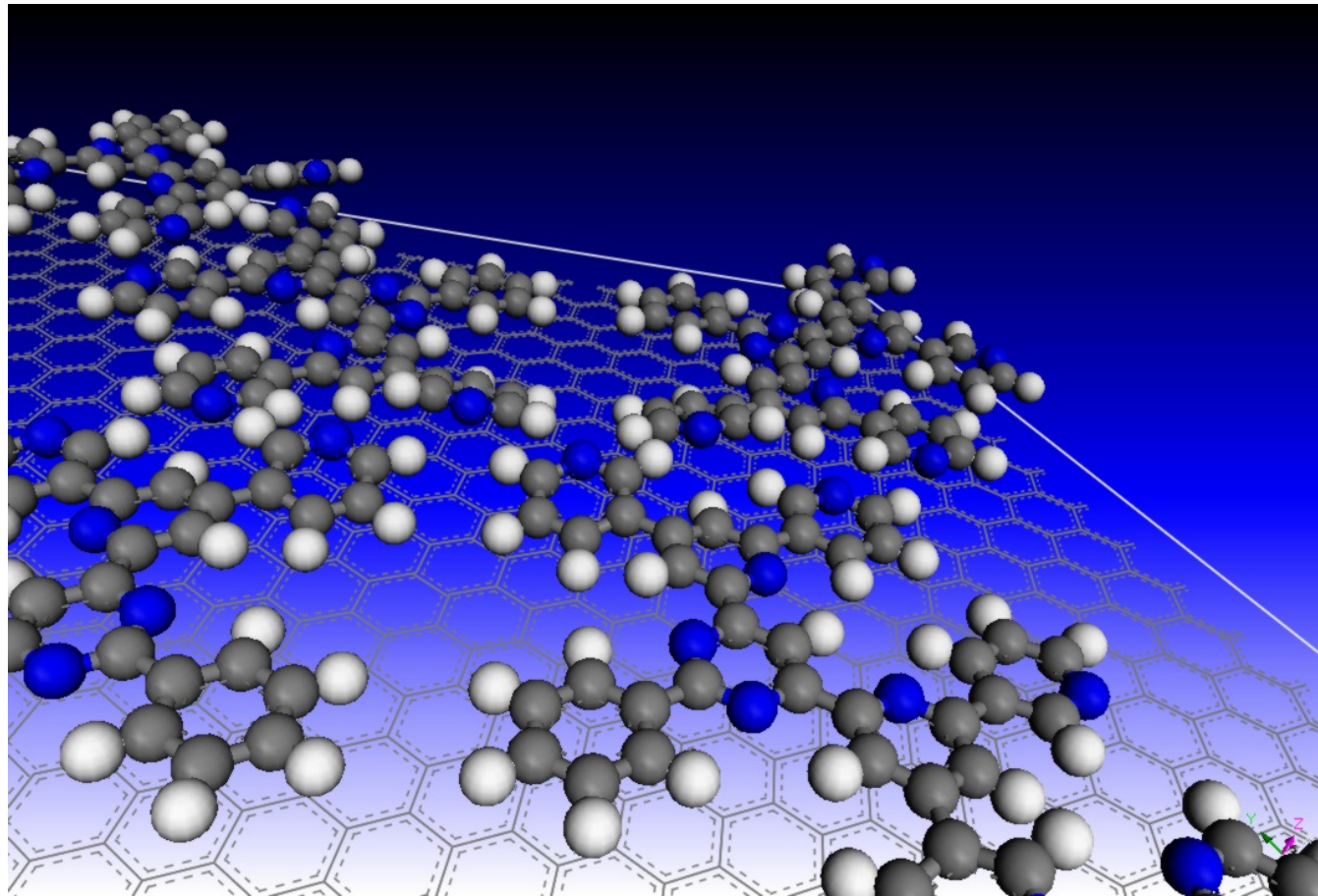
Inst. f. Theoretische Chemie, O25

Computational Chemistry

- Evaluation of the electronic, geometric and chemical properties of molecules, surfaces and solids with modern methods of electronic structure theory
- Quantum chemical program packages (Gaussian, NWChem, . . .) and Plane-Wave-Methods (VASP, Abinit, . . .)
- Empirical programs, e.g. force fields and code development
- **Analysis and visualisation of the results**

Adsorption of organic molecules

Study of the electronic, chemical, catalytic and optic properties of organic molecules on anorganic substrates

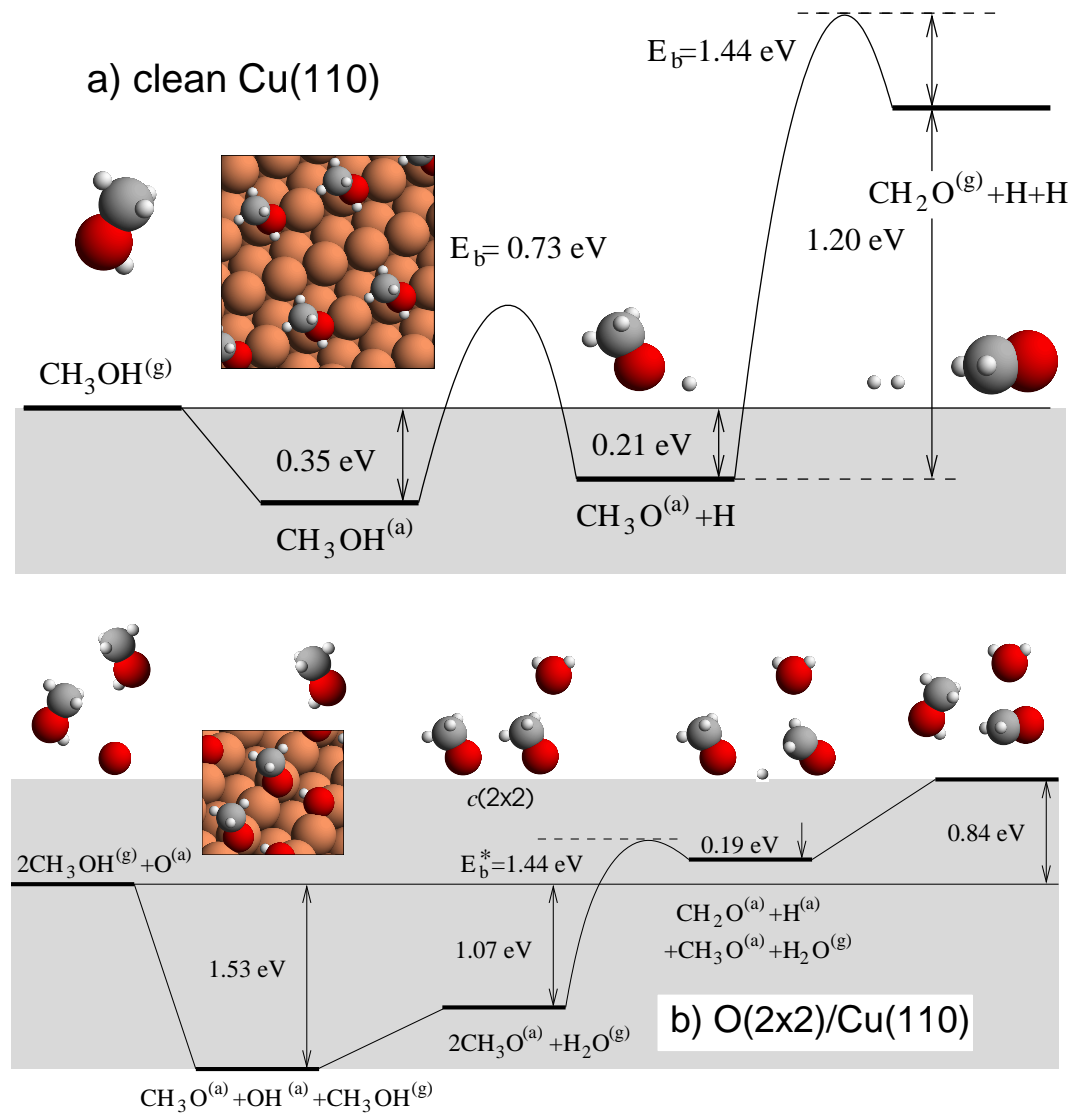


Structure of oligopyridine on graphite

Close collaboration with experimental groups

Surface reactions: Methanol oxidation on $O(2 \times 2)/Cu(110)$

S.Sakong and A. Groß, J. Catal. **231**, 420 (2005).



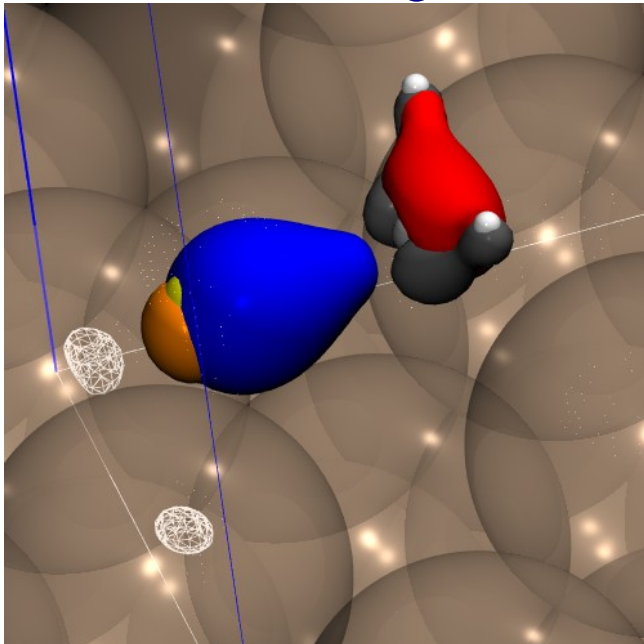
Energy scheme of the partial oxidation of CH_3OH on clean and (2×2) oxygen-precovered Cu(110)

Methanol oxidation on Cu: Analysis of the electronic structure

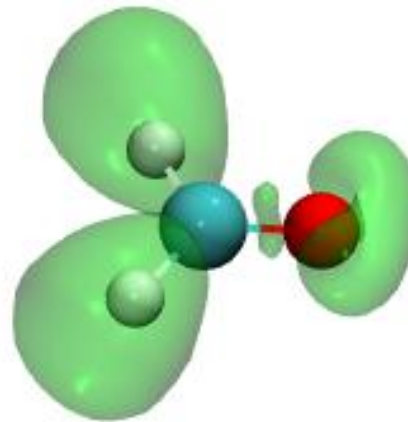
S.Sakong and A. Groß, J. Catal. **231**, 420 (2005).

CH₂O/Cu(110): Chemical interaction analyzed using electronic orbitals and charge densities

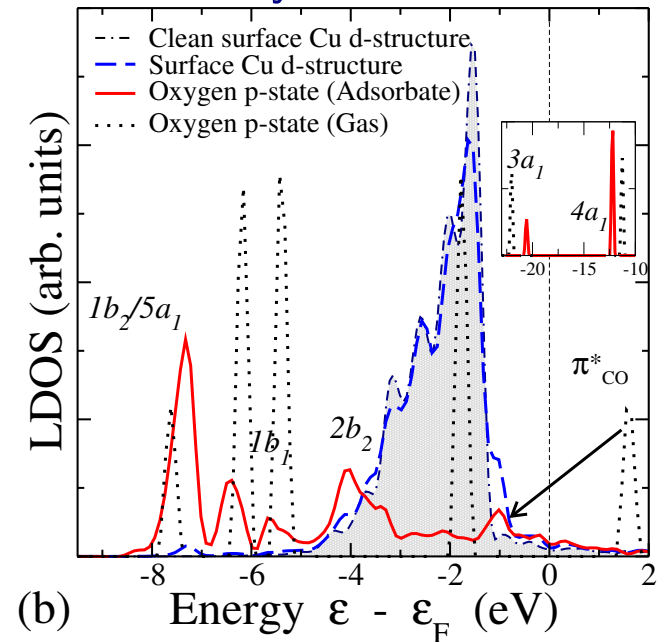
Partial charges



Electron
localisation



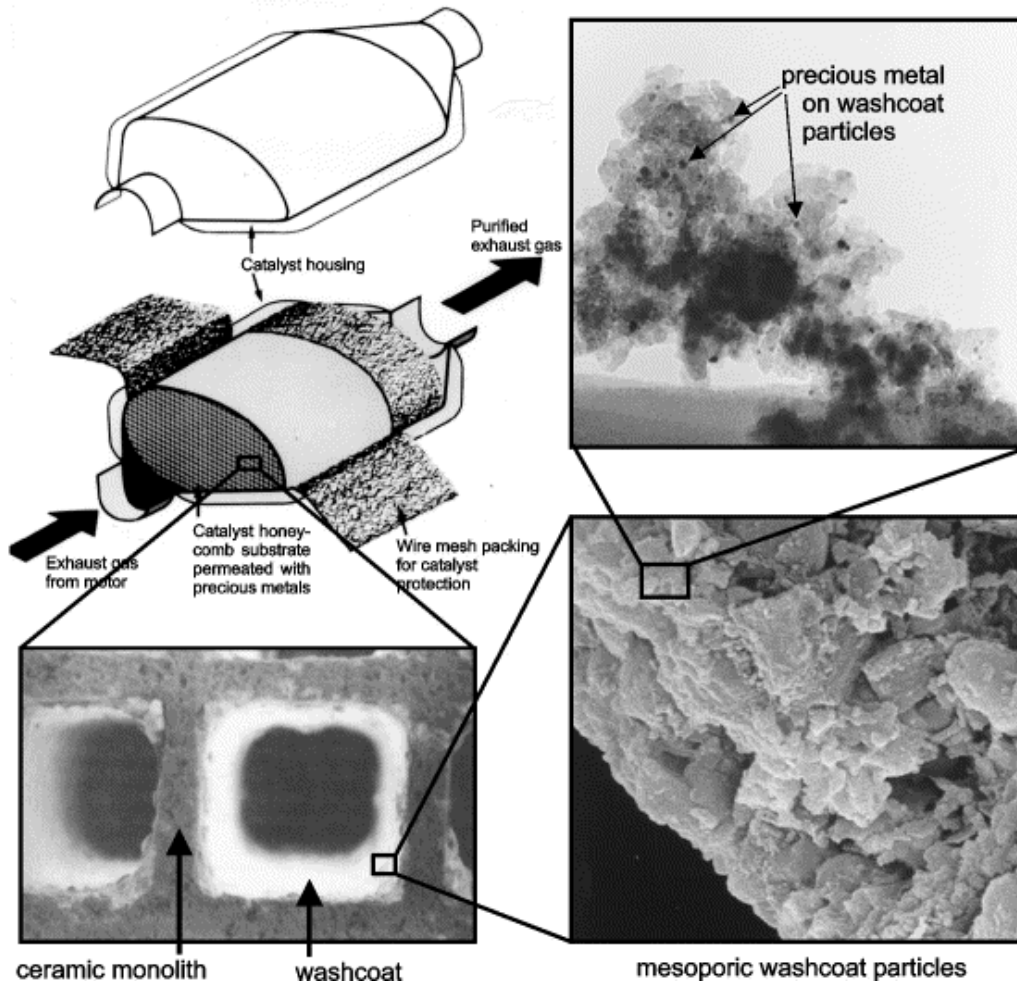
Density of states



Detection of the electronic factors that determine the reactivity

Exhaust catalyst

Structure of the exhaust catalyst



H.-J. Freund, Surf. Sci. **500**, 271 (2002)

Elementary steps in the CO oxidation

Without movies

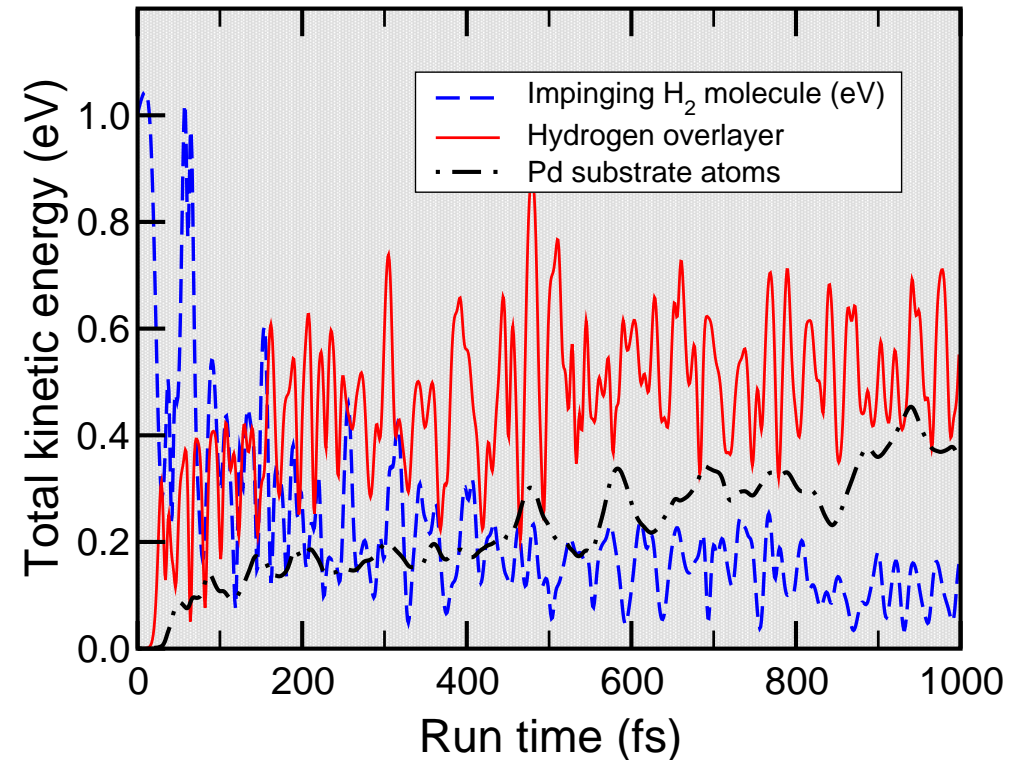
Schematic animation of the CO oxidation
(C.Stampfl, FHI Berlin)

Subsurface penetration for $\text{H}_2/(3 \times 3)7\text{H}/\text{Pd}(100)$

Dissociation

Energy redistribution

Without movies

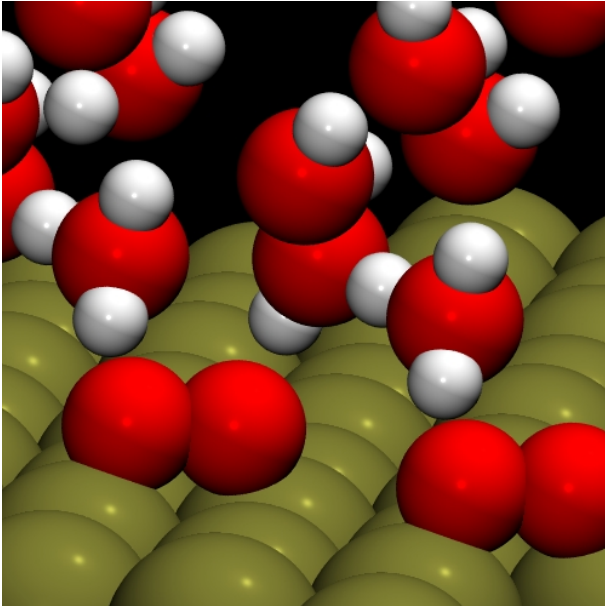


Concertive motion of two hydrogen atoms during subsurface penetration

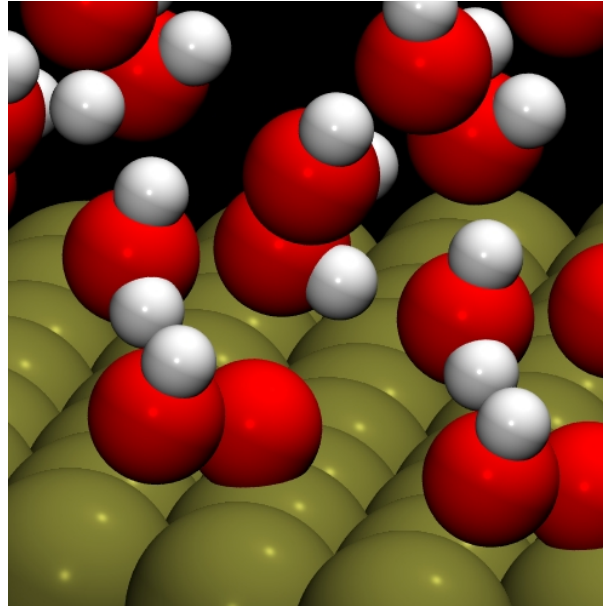
Elektrochemie und elektrochemische Katalyse

Interaktion O_2 mit einem Zundelion auf Pt(111) in einer wässrigen Umgebung

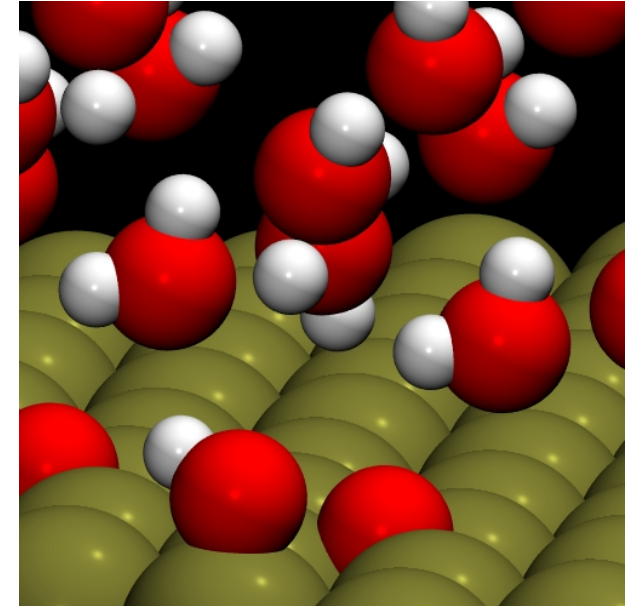
Initial configuration



Adsorbed OOH



Adsorbed O + OH



Presence of water leads to activation barriers for the oxygen reduction on Pt(111)

Study of systems that are relevant for the electrochemical energy conversion and storage

Ab initio molecular dynamics simulations of H₂ dissociation on water-covered Pt(111)

Trajectory

Discussion

Without movies

H₂ dissociation through thermalized disordered water layer

After dissociation, H atoms can move almost freely beneath the water layer

H atoms end up at top sites

Disordered water layer rearranges upon H adsorption

Quantum Mechanics: Hamiltonian

Chemistry:

Only electrostatic interaction taken into account \Rightarrow Hamiltonian:

$$H = T_{\text{nucl}} + T_{\text{el}} + V_{\text{nucl-nucl}} + V_{\text{nucl-el}} + V_{\text{el-el}} \quad (1)$$

Quantum Mechanics: Hamiltonian

Chemistry:

Only electrostatic interaction taken into account \Rightarrow Hamiltonian:

$$H = T_{\text{nucl}} + T_{\text{el}} + V_{\text{nucl-nucl}} + V_{\text{nucl-el}} + V_{\text{el-el}} \quad (1)$$

$$T_{\text{nucl}} = \sum_{I=1}^L \frac{\vec{P}_I^2}{2M_I} = \sum_{I=1}^L \frac{-\hbar^2}{2M_I} \vec{\nabla}_I^2, \quad (2)$$

$$T_{\text{el}} = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} = \sum_{i=1}^N \frac{-\hbar^2}{2m_i} \vec{\nabla}_i^2, \quad (3)$$

$$V_{\text{nucl-nucl}} = \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\vec{R}_I - \vec{R}_J|}, \quad (4)$$

$$V_{\text{nucl-el}} = -\frac{1}{4\pi\epsilon_0} \sum_{i,I} \frac{Z_I e^2}{|\vec{r}_i - \vec{R}_I|}, \quad (5)$$

$$V_{\text{el-el}} = \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}. \quad (6)$$

Schrödinger Equation

Nonrelativistic Schrödinger Equations:

$$H \Psi(\vec{R}, \vec{r}) = E \Psi(\vec{R}, \vec{r}). \quad (7)$$

$$i\hbar \frac{\partial \Psi(\vec{R}, \vec{r}, t)}{\partial t} = H \Psi(\vec{R}, \vec{r}). \quad (8)$$

Solution: Eigen and initial value problem, respectively, of a high-dimensional partial differential equation taking into account the appropriate quantum statistics (\rightarrow Pauli principle)

In principle we are ready here, however

Schrödinger Equation

Nonrelativistic Schrödinger Equations:

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In principle we are ready here, however

Solution of Schrödinger equation in closed form not possible

\Rightarrow Hierarchy of approximate and numerical methods

Theoretical Chemistry

P.A.M Dirac (1930):

“The underlying physical laws necessary for the mathematical theory of a large part of physics *and the whole of chemistry* are thus completely know, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.”

Born-Oppenheimer approximation

Atoms 10^4 to 10^5 heavier than electrons
(except for hydrogen and helium)

⇒ electrons are 10^2 to 10^3 times faster than the nuclei

Born-Oppenheimer of adiabatic approximation:
electrons follow motion of the nuclei instantaneously

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electrons follow motion of the nuclei instantaneously

Practical implementation:

Define electronic Hamiltonian H_{el} for fixed nuclear coordinates $\{\vec{R}\}$

$$H_{\text{el}}(\{\vec{R}\}) = T_{\text{el}} + V_{\text{nucl-nucl}} + V_{\text{nucl-el}} + V_{\text{el-el}}. \quad (9)$$

Nuclear coordinates $\{\vec{R}\}$ do not act as variables but as parameters

The Schrödinger equation for the electrons

$$H_{\text{el}}(\{\vec{R}\}) \Psi(\vec{r}, \{\vec{R}\}) = E_{\text{el}}(\{\vec{R}\}) \Psi(\vec{r}, \{\vec{R}\}). \quad (10)$$

Born-Oppenheimer approximation II

Schrödinger equation for the electrons

$$H_{\text{el}}(\{\vec{R}\}) \Psi(\vec{r}, \{\vec{R}\}) = E_{\text{el}}(\{\vec{R}\}) \Psi(\vec{r}, \{\vec{R}\}). \quad (11)$$

$E_{\text{el}}(\{\vec{R}\})$ Born-Oppenheimer energy surface: potential for the nuclear motion:

$$\{T_{\text{nucl}} + E_{\text{el}}(\vec{R})\} \chi(\vec{R}) = E_{\text{nucl}} \chi(\vec{R}). \quad (12)$$

Born-Oppenheimer approximation II

Schrödinger equation for the electrons

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If quantum effects negligible: classical equation of motion

$$M_I \frac{\partial^2 \vec{R}_I}{\partial t^2} = -\frac{\partial}{\partial \vec{R}_I} E_{\text{el}}(\{\vec{R}\}) \quad . \quad (13)$$

Born-Oppenheimer approximation (BOA) III

In the BOA electronic transitions neglected

Exact derivation: Expansion of Schrödinger equation in the small parameter m/M

BOA very successful, but still its validity hardly directly obvious

Born-Oppenheimer approximation (BOA) III

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Physical arguments

Systems with a band gap: electronic transitions improbable

Metals: electronic system strongly coupled
⇒ short lifetimes and fast quenching of electronic excitations

Interaction between molecules

Consider ions A and B with charge Q_A and Q_B , respectively

$$\vec{R}_{AB} = \vec{R}_B - \vec{R}_A, R_{AB} = |\vec{R}_{AB}|$$

Force of Q_A acting on Q_B

$$\vec{F}_{AB} = \frac{1}{4\pi\epsilon_0} \frac{Q_A Q_B}{R_{AB}^3} \vec{R}_{AB} \quad (14)$$

Force of Q_B acting on Q_A

$$\vec{F}_{BA} = \frac{1}{4\pi\epsilon_0} \frac{Q_A Q_B}{R_{AB}^3} \vec{R}_{BA} \quad (15)$$

$$F_{BA} = \frac{1}{4\pi\epsilon_0} \frac{Q_A Q_B}{R_{AB}^2} \quad (16)$$

Pairwise additive forces

Force of Q_A and Q_C acting on Q_B

$$\vec{F}_B = \frac{Q_B}{4\pi\epsilon_0} \left(Q_A \frac{\vec{R}_{AB}}{R_{AB}^3} + Q_C \frac{\vec{R}_{CB}}{R_{CB}^3} \right) \quad (17)$$

Charge distribution

$$Q_A = \int \rho(\vec{r}) d^3r \quad (18)$$

Force of Q_A acting on Q_B

$$\vec{F}_{AB} = \frac{Q_B}{4\pi\epsilon_0} \int \rho(\vec{r}) \frac{(\vec{R}_B - \vec{r})}{|\vec{R}_B - \vec{r}|^3} d^3r \quad (19)$$

Potential energy

$$U_{AB} = \frac{1}{4\pi\epsilon_0} \frac{Q_A Q_B}{R_{AB}} \quad (20)$$

Corresponds to the energy it costs to bring the two charges from infinity to the distance R_{AB}

Relation between force and potential energy; Energy in one dimension:

$$E = \frac{m}{2}v^2 + U(x) \quad (21)$$

Energy conservation, i.e. $dE/dt = 0$:

$$F = -\frac{dU}{dx}, \text{ in three dimensions : } \vec{F} = -\nabla U = -\left(\frac{\partial U}{\partial x}, \frac{\partial U}{\partial y}, \frac{\partial U}{\partial z}\right) \quad (22)$$

Force is directed along the steepest decent of U

Many-body interaction

Consider system of N atoms; If forces are additive

$$U_{\text{tot}} = \sum_{i=1}^{n-1} \sum_{j=i+1}^n U_{ij} = \frac{1}{2} \sum_{i \neq j}^{n,n} U_{ij} \quad (23)$$

General case

$$U_{\text{tot}} = U(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_n) \quad (24)$$

Formal expansion

$$U_{\text{tot}} = \sum_{\text{pairs}} U^{(2)}(\vec{R}_i, \vec{R}_j) + \sum_{\text{triples}} U^{(3)}(\vec{R}_i, \vec{R}_j, \vec{R}_k) + \dots + U^{(n)}(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_n) \quad (25)$$

Nature of the interaction

$$U = U_{\text{es}} + U_{\text{disp}} + U_{\text{rep}} \quad (26)$$

Electrostatic plus dispersive interaction plus Pauli repulsion

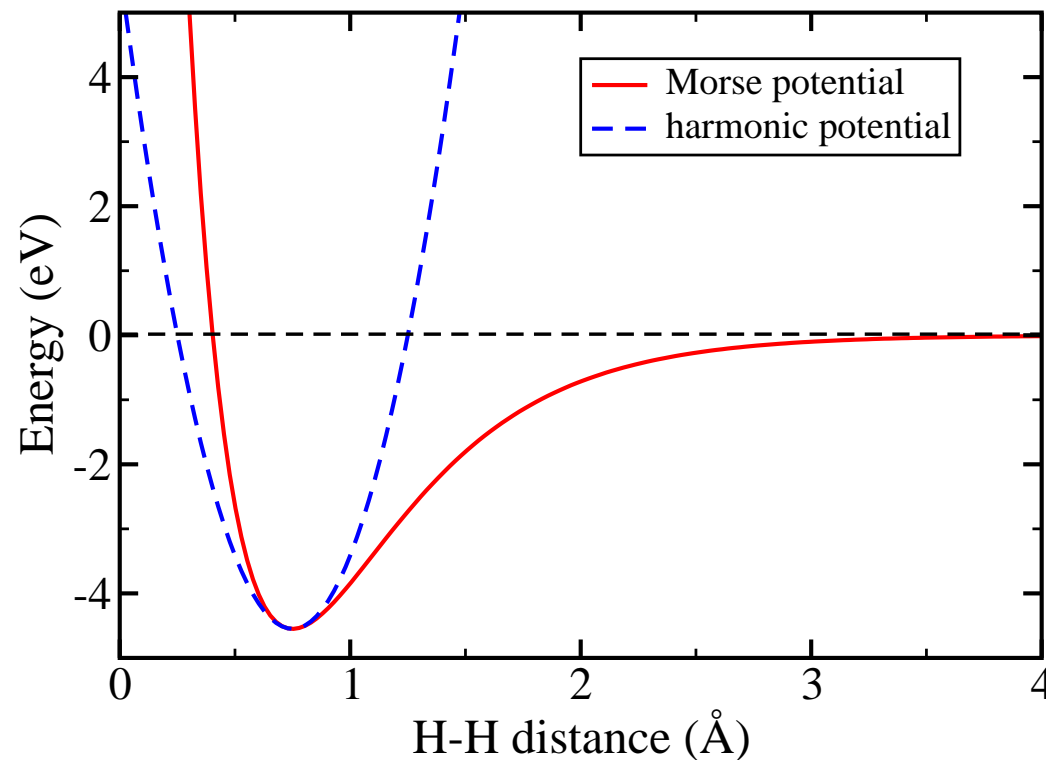
Vibrational potentials

Harmonic potential

$$U_{\text{vib}} = \frac{1}{2}k(R - R_e)^2, E_{\text{vib}} = \hbar\omega\left(v + \frac{1}{2}\right) \quad (27)$$

Morse potential, $\beta = \frac{\omega}{2}\sqrt{2\mu/D_e}$

$$U_{\text{vib}} = D_e [1 - \exp(-\beta(R - R_e))]^2, E_{\text{vib}} = \hbar\omega\left(v + \frac{1}{2}\right) - \chi_e \hbar\omega\left(v + \frac{1}{2}\right)^2 \quad (28)$$



Molecular mechanics and force fields

Molecular Mechanics:

Application of classical mechanics to determinations of molecular equilibrium properties

Force field: Parametrized interaction potential

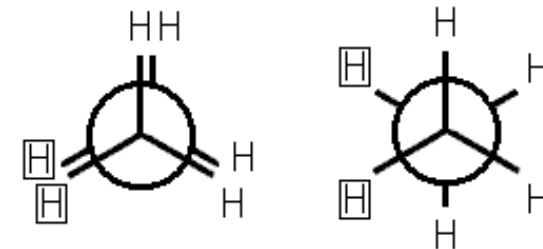
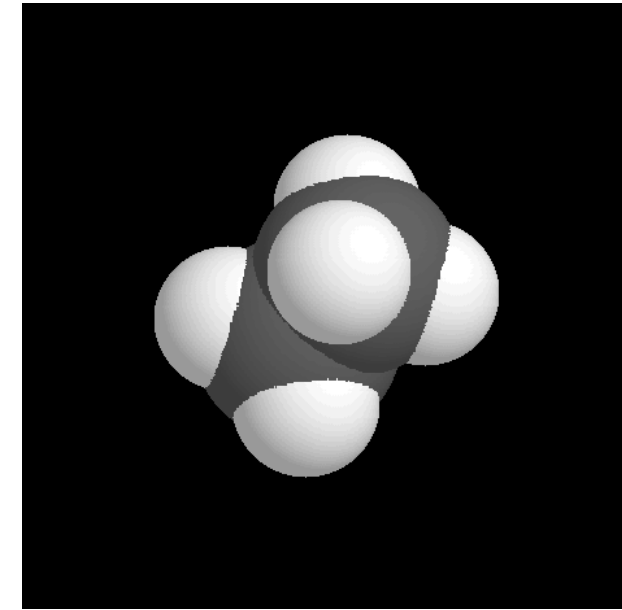
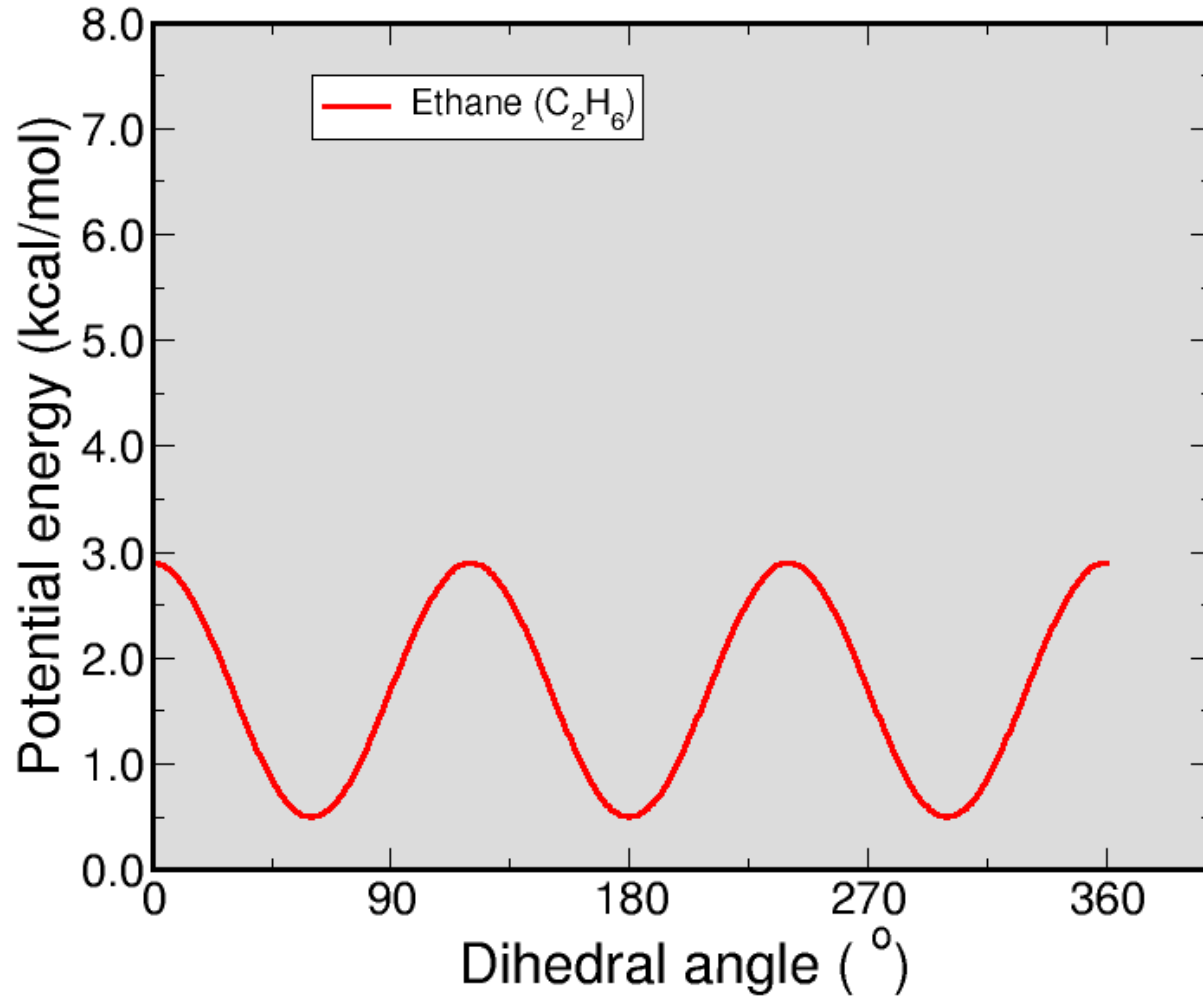
$$U = \sum_{\text{stretch}} U_{AB} + \sum_{\text{bend}} U_{ABC} + \sum_{\text{dihedral}} U_{ABCD} + \sum_{\text{inversion}} U_{ABCD} + \sum_{\text{nonbonded}} U_{AB} + \sum_{\text{Coulomb}} U_{AB} + \quad (29)$$

$$= \sum_{\text{bonds}} \frac{1}{2} k_{AB} (R_{AB} - R_{e,AB})^2 + \sum_{\text{bends}} \frac{1}{2} k_{ABC} (\Theta_{ABC} - \Theta_{e,ABC})^2 + \sum_{\text{dihedrals}} \frac{U_0}{2} (1 - \cos(n(\chi - \chi_0))) + \sum_{\text{inversions}} \frac{k}{2 \sin^2 \psi_e} (\cos \psi - \cos \psi_e)^2 + \sum_{\text{nonbonded}} \left(\frac{C_{AB}^{12}}{R_{AB}^{12}} - \frac{C_{AB}^6}{R_{AB}^6} \right) + \sum_{\text{charges}} \frac{1}{4\pi\epsilon_0} \frac{Q_A Q_B}{R_{AB}} \quad (30)$$

Potential curves

Torsional potential

Ethane

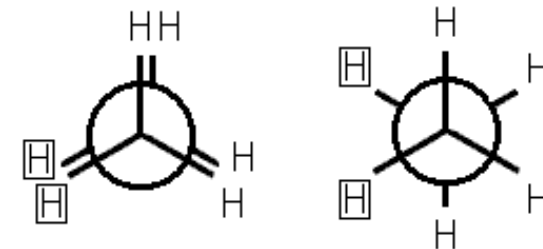
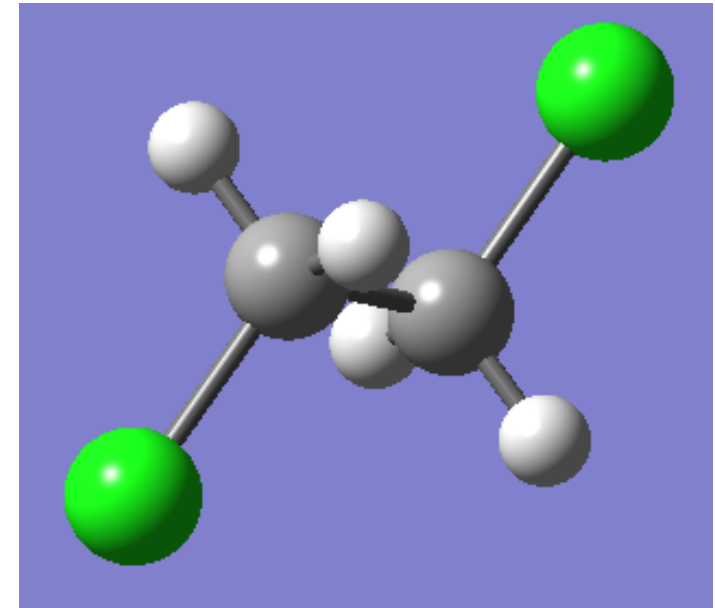
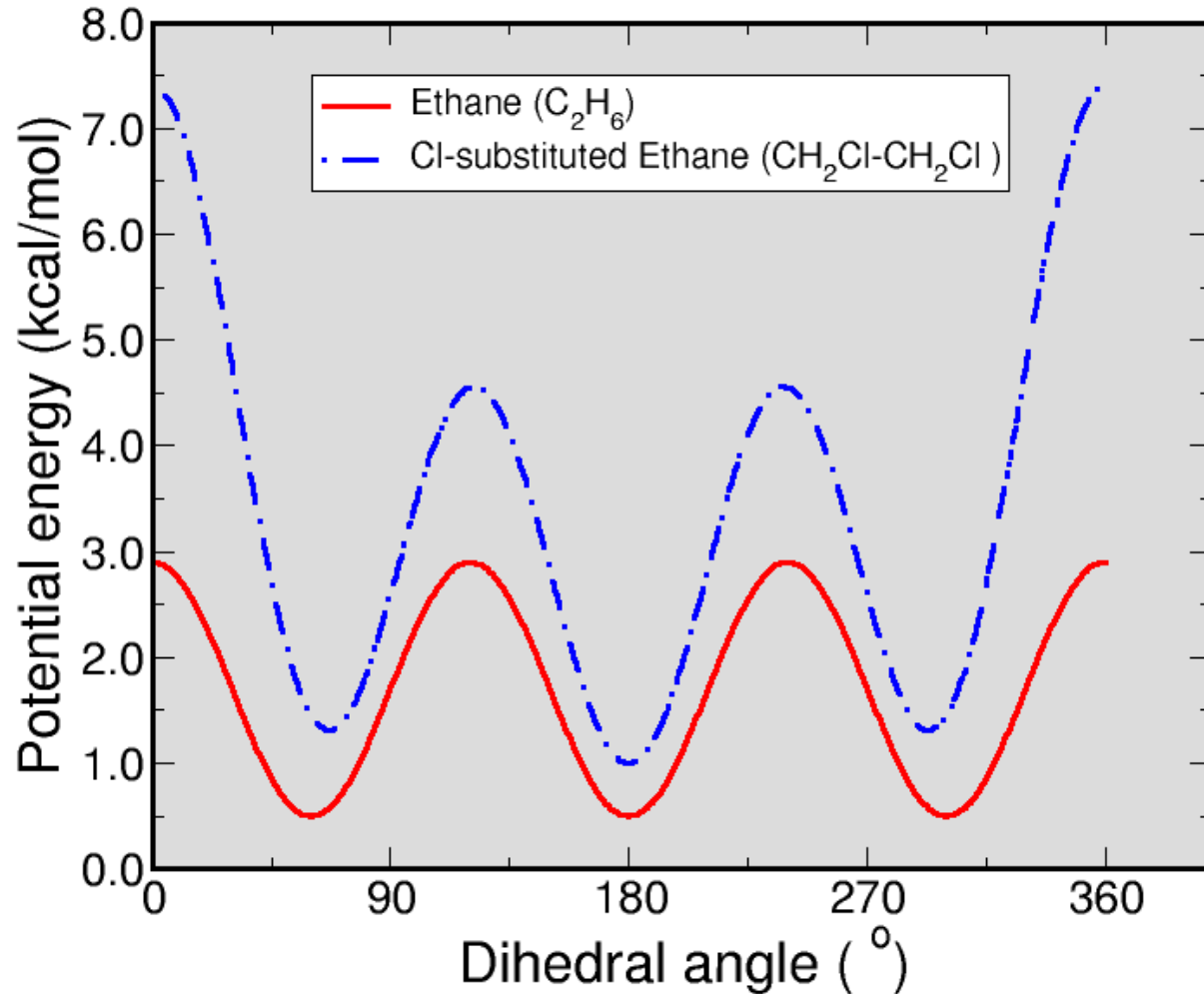


Multiple minima

Potential curves

Torsional potential

Ethane and chlorine-substituted ethane



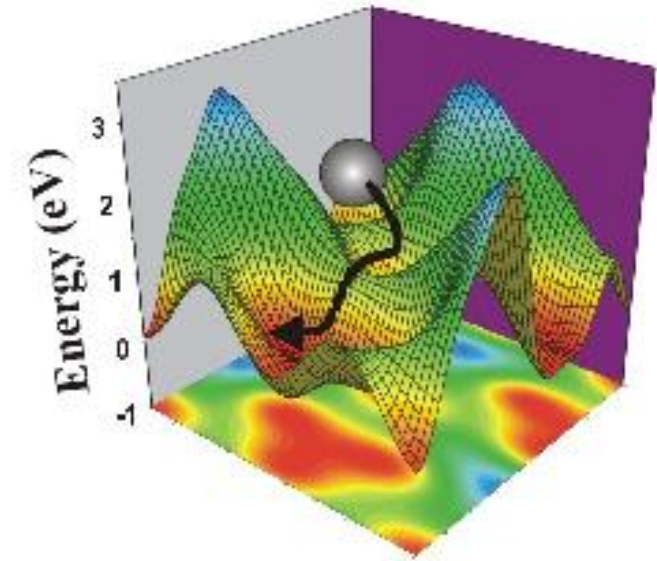
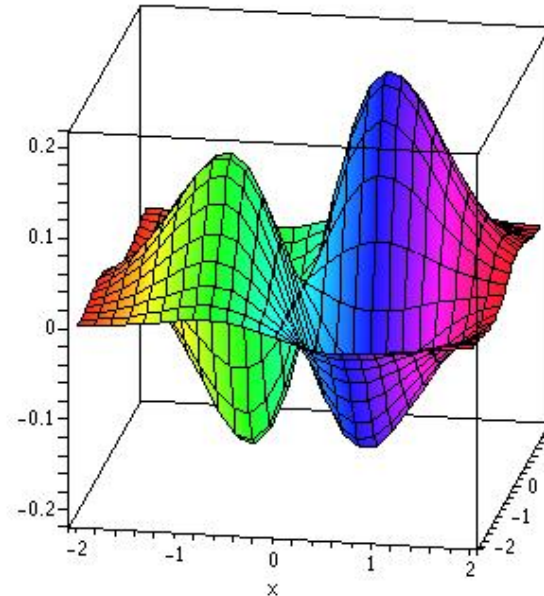
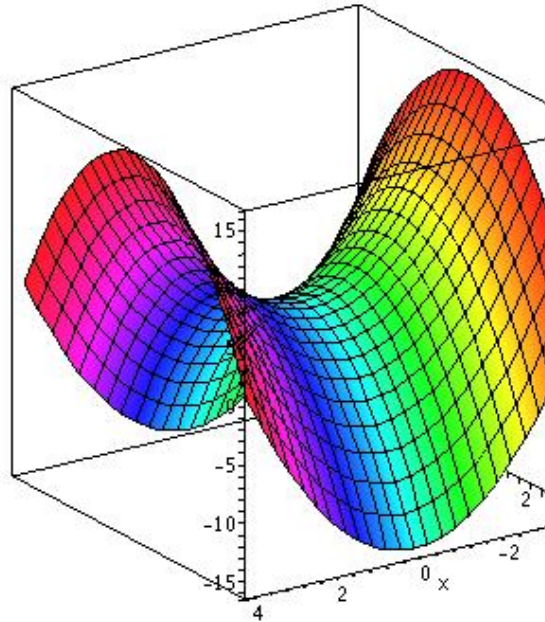
Multiple minima

Potential energy surfaces (PES)

Saddle point

Two minima

Multiple minima



FHI Berlin

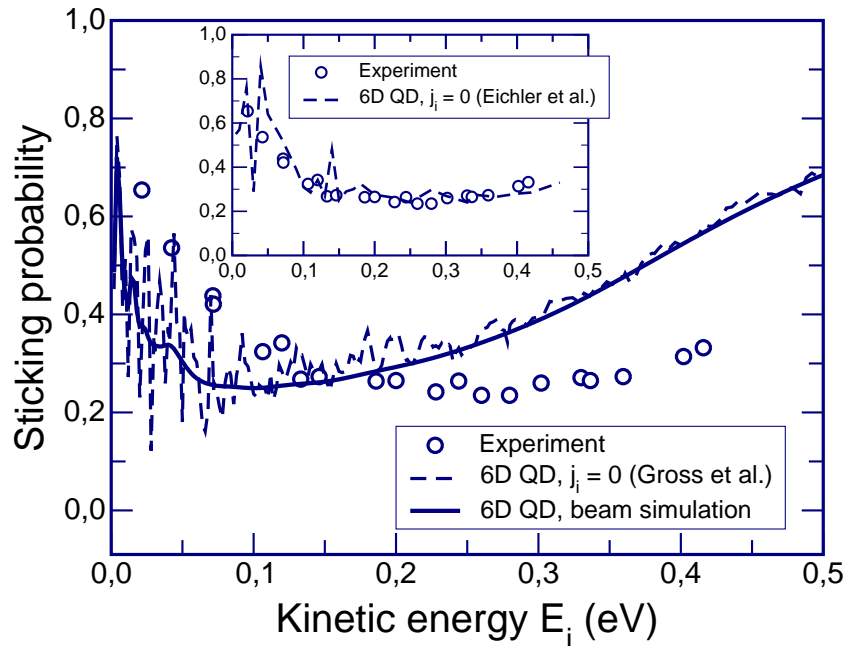
Saddle points correspond to transition states in chemical reaction,
minima to (meta)-stable intermediates

Reaction barriers are calculated as the difference between the the lowest saddle point
towards the product state and the energy minimum corresponding to the reactant state

$$E_{\text{barr}} = E_{\text{TS}} - E_{\text{ini}} \quad (31)$$

Sticking probability of H₂ on Pd(100)

Comparison theory-experiment



Exp.: K.D. Rendulic *et al.*, Surf. Sci. **208**, 404 (1989),

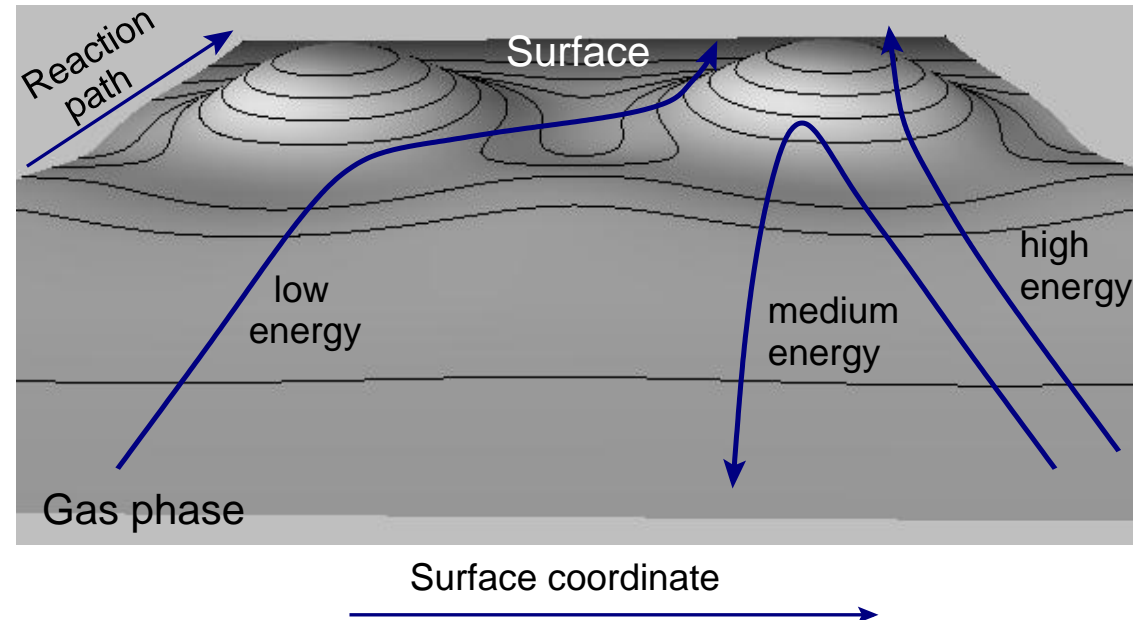
Theory: A. Groß *et al.*, PRL **75**, 2718 (1995).

All *six* hydrogen degrees of freedom treated quantum dynamically

Initial decrease in $S(E_i)$ caused by the suppression of the steering effect

Oscillations quantum effect: opening of new scattering channels with increasing energy

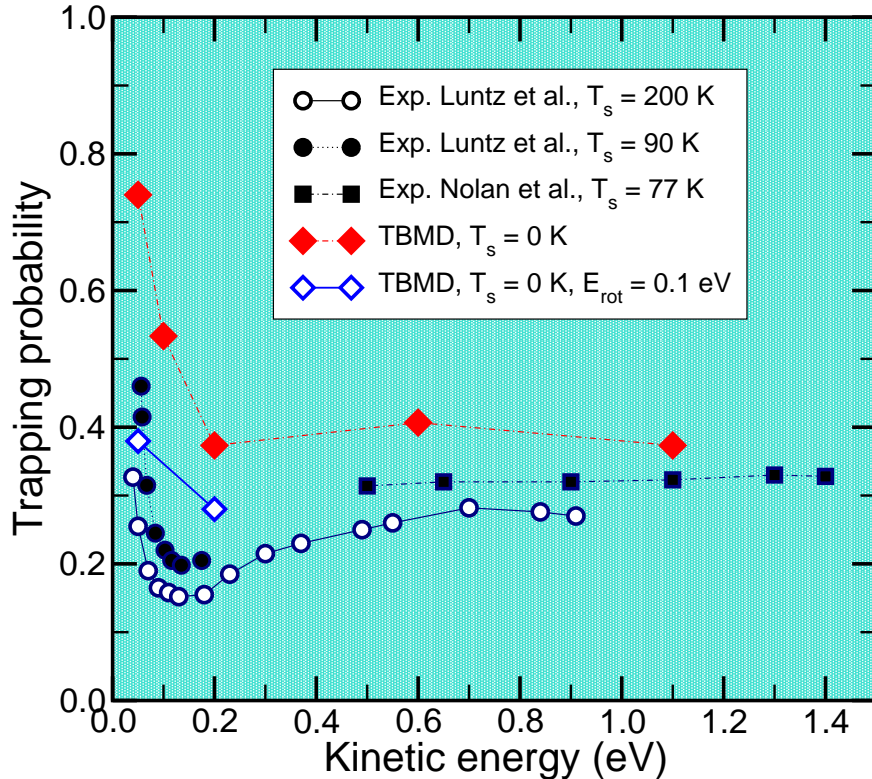
Steering effect



Tight-binding molecular dynamics simulations: O₂/Pt(111)

A. Groß, A. Eichler, J. Hafner, M.J. Mehl, and D.A. Papaconstantopoulos, Surf. Sci. Lett. **539**, L542-L548 (2003).

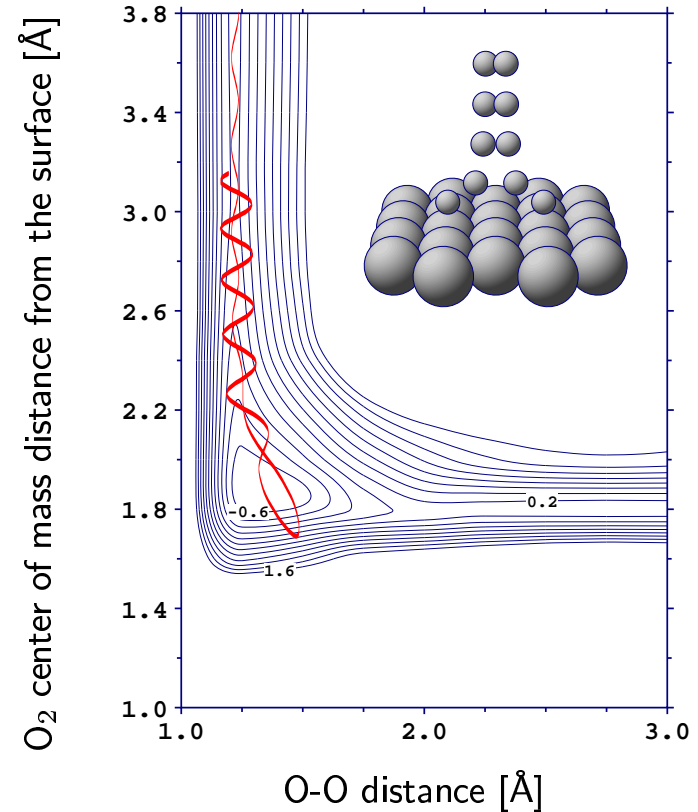
Sticking probability



Comparison of calculated and measured sticking probability as a function of the kinetic energy

Over the whole energy range sticking probability is determined by the trapping into the molecular chemisorption states

Dissociation?

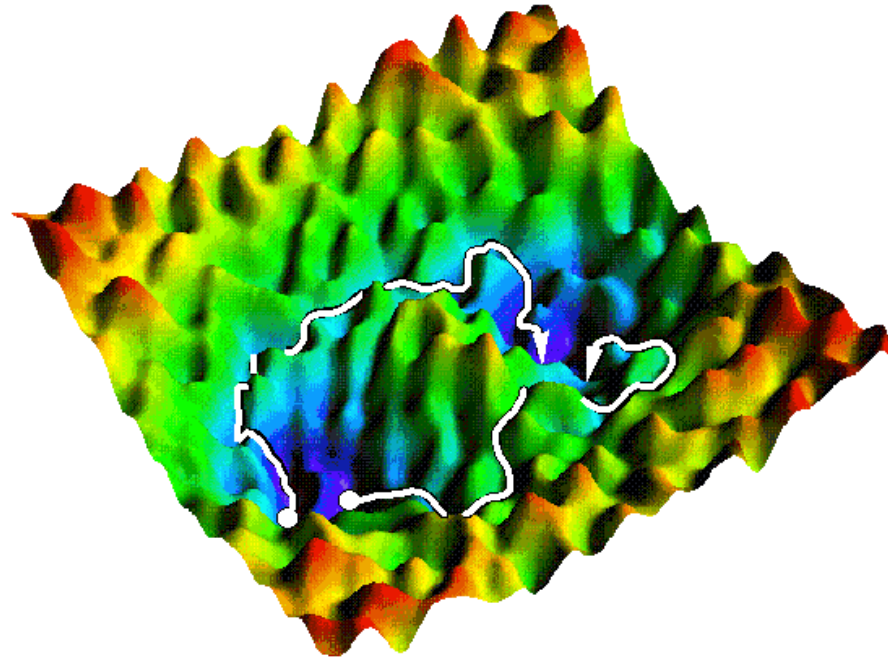


Initial O₂ kinetic energy $E_{\text{kin}} = 0.6$ eV

O₂ does not directly dissociate on Pt(111)
→ dissociation of O₂/Pt(111) is a two-step process involving thermalisation

Potential energy surfaces

Complex PES, for example describing a polymer or protein



UC Berkeley

Finding minima and saddle points of potential energy surfaces is crucial for the determination of energy minimum structures and reaction barriers

Characterization of potential energy surfaces

$p = 3n - 6$ degrees of freedom, Coordinates \mathbf{q} and gradient \mathbf{g} :

$$\mathbf{q} = \begin{pmatrix} q_1 \\ q_2 \\ \vdots \\ q_p \end{pmatrix}, \quad \mathbf{g} = \begin{pmatrix} \frac{\partial U}{\partial q_1} \\ \frac{\partial U}{\partial q_2} \\ \vdots \\ \frac{\partial U}{\partial q_p} \end{pmatrix}. \quad (32)$$

At stationary points, the gradient is zero

Characterization of stationary points: Calculate Hesse matrix at that points:

$$\mathbf{H} = \begin{pmatrix} \frac{\partial^2 U}{\partial q_1^2} & \cdots & \frac{\partial^2 U}{\partial q_1 \partial q_p} \\ \vdots & \ddots & \vdots \\ \frac{\partial^2 U}{\partial q_p \partial q_1} & \cdots & \frac{\partial^2 U}{\partial q_p^2} \end{pmatrix}. \quad (33)$$

Eigenvalues all positive \Rightarrow Minimum, Eigenvalues all negative \Rightarrow Maximum, \Rightarrow Maximum
otherwise \Rightarrow Saddle point

Transition state (barrier): Hesse matrix has exactly one negative eigenvalue

Finding minima

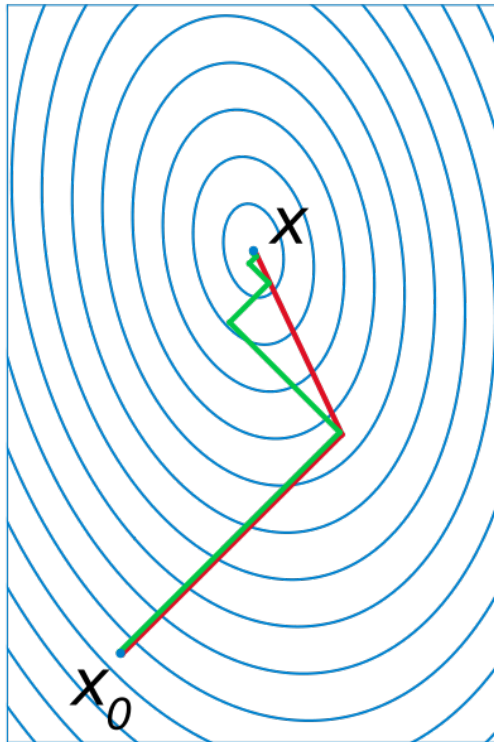
Finding minima = Optimization problem

Grid methods: multivariate and univariate grid search

Finding minima

Finding minima = Optimization problem

Grid methods: multivariate and univariate grid search



Green: steepest descent

Red: conjugate gradient

Derivative methods

First-order methods

Steepest descent: Search minima along the negative of the gradient
Problem: many perpendicular steps

Solution: Conjugate gradient method:

In k-th iteration, move in direction given by

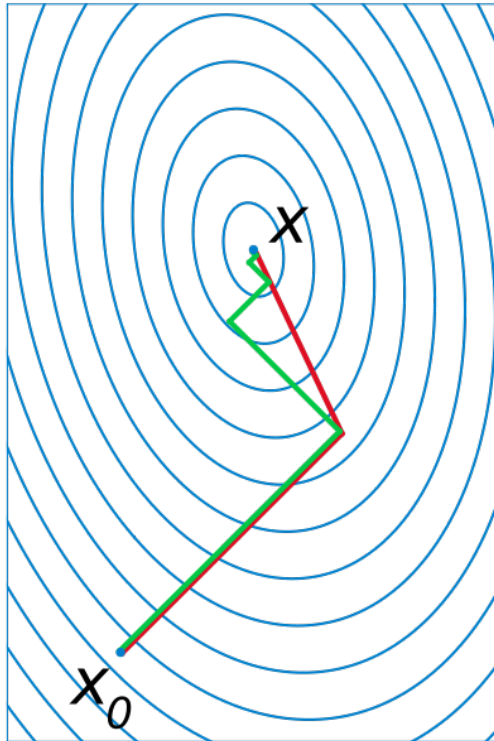
$$\mathbf{v}^{(k)} = -\mathbf{g}^{(k)} + \gamma^{(k)}\mathbf{v}^{(k-1)}, \quad \gamma^{(k)} = \frac{(\mathbf{g}^{(k)})^T \mathbf{g}^{(k)}}{((\mathbf{g}^{(k-1)})^T \mathbf{g}^{(k-1)})} \quad (34)$$

Conjugate directions: perpendicular in isotropic configuration space

Finding minima

Finding minima = Optimization problem

Grid methods: multivariate and univariate grid search



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Conjugate directions: perpendicular in isotropic configuration space

Second-order methods

Computationally more expansive since second derivative is required

Further methods: Simulated annealing, Monte Carlo methods, generic algorithms, . . .

Finding transition states

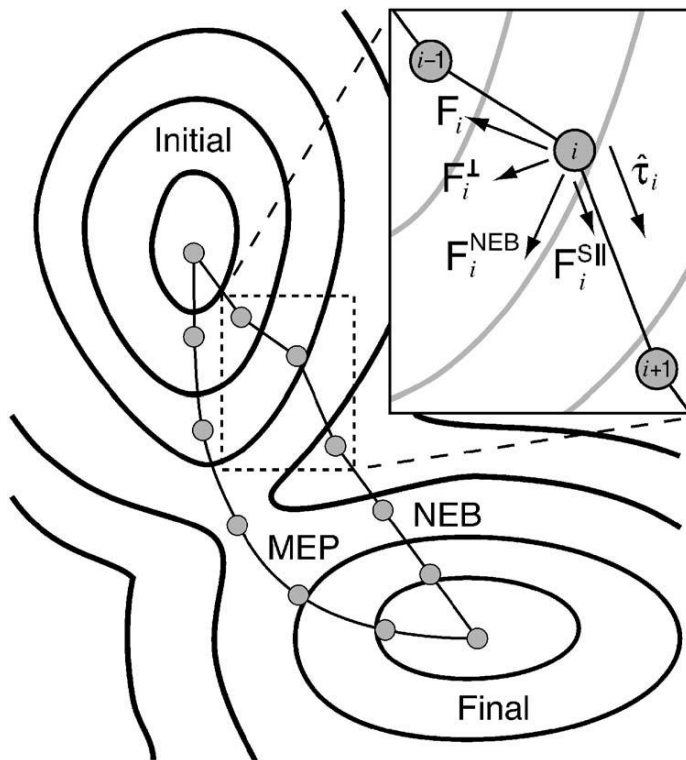
There is no analytical method that guarantees to find the nearest transition states \Rightarrow
approximate schemes

Finding transition states

There is no analytical method that guarantees to find the nearest transition states \Rightarrow approximate schemes

Nudged elastic band method

<http://theory.cm.utexas.edu/henkelman/research/saddle/>



The Nudged Elastic Band (NEB) method is used to find minimum energy path (NEB) when both the initial and final states are known.

G. Henkelman and H. Jonsson, J. Chem. Phys. **113**, 9978 (2000).

The code works by linearly interpolating a set of images between the initial and final states (as a "guess" at the MEP), and then minimizes the energy of this string of images connected by springs.

Each "image" corresponds to a specific geometry of the atoms on their way from the initial to the final state.

Once the energy of this string of images has been minimized, the true MEP is revealed.

Further methods: Dimer method

Molecular Mechanics (MM)

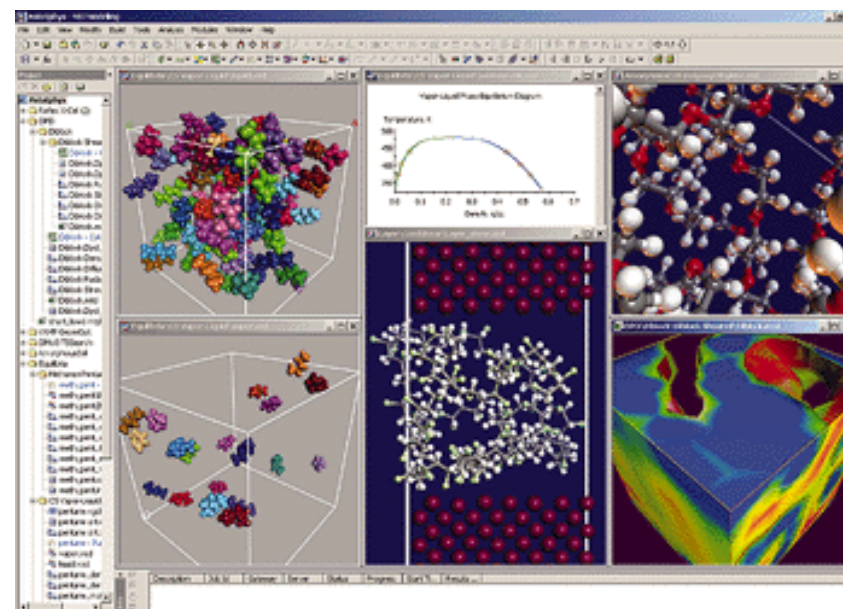
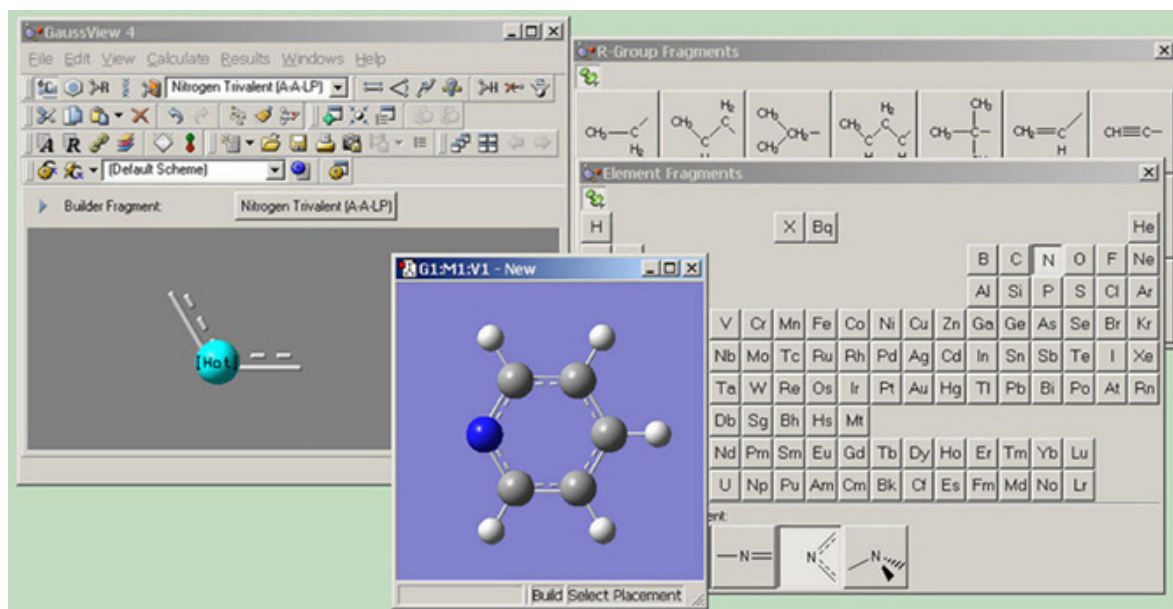
Molecular Mechanics (MM) useful for the determination of possible equilibrium properties of molecules

Many software packages available

Commercial products often offer convenient graphical user interfaces (GUI)

GaussView (GAUSSIAN)

Materials Visualizer (Materials Studio)



Besides MM programmes, often quantum chemistry codes included in the packages

Statistical Mechanics

Statistical mechanics provides a relation between microscopic (atomistic) and macroscopic description of matter using mean values and deviations

Statistical description \Rightarrow Mean values of significant importance

Mean value $\langle x \rangle$:

$$\langle x \rangle = \frac{1}{n} \sum_{i=1}^n x_i \quad (35)$$

Root mean square deviations (fluctuations):

$$\sigma_n = \sqrt{\frac{1}{n} \sum_{i=1}^n (x_i - \langle x \rangle)^2} \quad (36)$$

Central entity in statistical mechanics: **ensemble**

Self-consistent field (SCF) solution

Effective one-particle Hartree-Fock Hamiltonians contain solution: \Rightarrow SCF iteration scheme

Initial guess:

$$n^0(\vec{r}) \longrightarrow v_{\text{eff}}^0(\vec{r})$$

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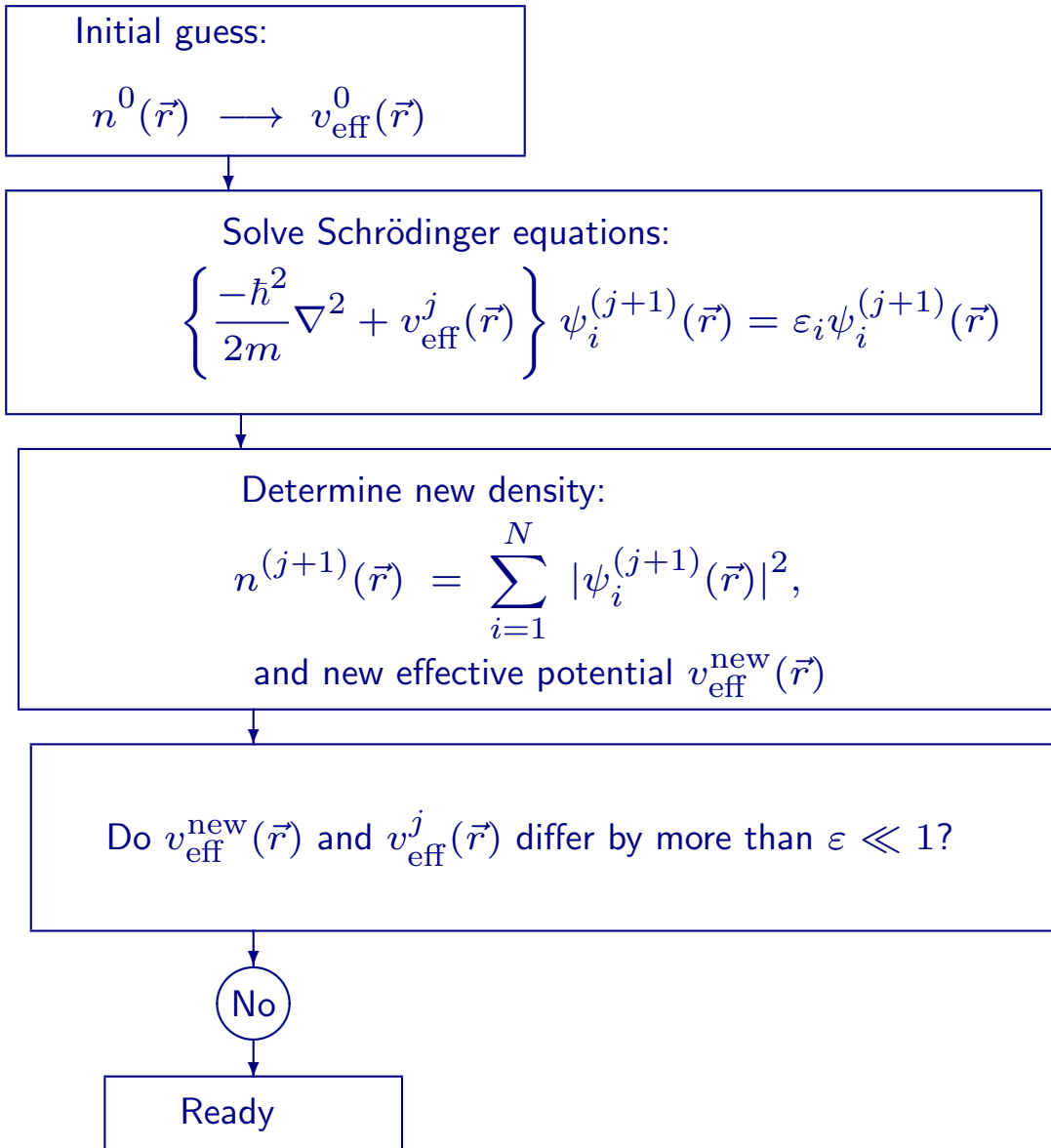
Determine new density:

$$n^{(j+1)}(\vec{r}) = \sum_{i=1}^N |\psi_i^{(j+1)}(\vec{r})|^2,$$

and new effective potential $v_{\text{eff}}^{\text{new}}(\vec{r})$

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