

CHEM3023: Spins, Atoms and Molecules

Lecture 9

Electronic correlation / Potential energy surfaces

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Learning outcomes

- Be able to describe the limitations of mean-field approaches such as Hartree-Fock theory
- Be able to predict the structure (geometry) and vibrational frequencies of molecules using Hartree-Fock calculations

Electron correlation

- Hartree-Fock theory is a “mean field” theory: each electron moves in an average field caused by all the other electrons and the nuclei
- Reasonably accurate but can not provide the exact many-electron wavefunction
- Hartree-Fock probability density for two electrons of opposite spin to be at the same point in space is nonzero – this is wrong!
- In reality each electron instantaneously responds to the positions of all other electrons and they can never coincide
- We say that the motions of the electrons are correlated

The exact electronic wavefunction....

- The exact wavefunction can be written as a linear combination of **all possible Slater determinants** for N_{elec} electrons that we can form from the occupied and unoccupied spin orbitals (explain why)
- Such a calculation is called configuration interaction (CI) and is extremely demanding computationally

A Slater determinant for N electrons

$$\Psi_{SD}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = |\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) \dots \chi_N(\mathbf{x}_N)\rangle$$

Exact wavefunction

$$|\Phi\rangle = c_0|\Psi_0\rangle + \sum_r \sum_a c_a^r |\Psi_a^r\rangle + \sum_{a < b} \sum_{r < s} c_{ab}^{rs} |\Psi_{ab}^{rs}\rangle + \dots$$

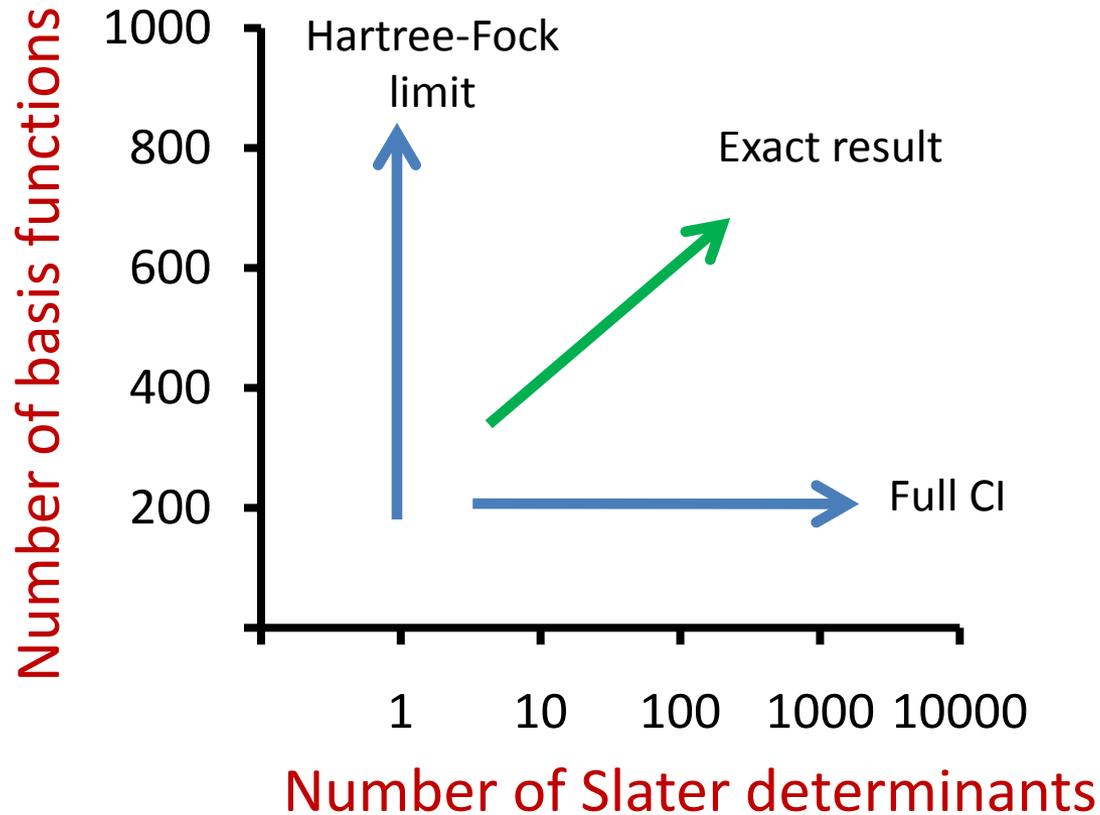
Ground-state Slater determinant

Slater determinant with a single excitation

Slater determinant with a double excitation

Correlation Energy

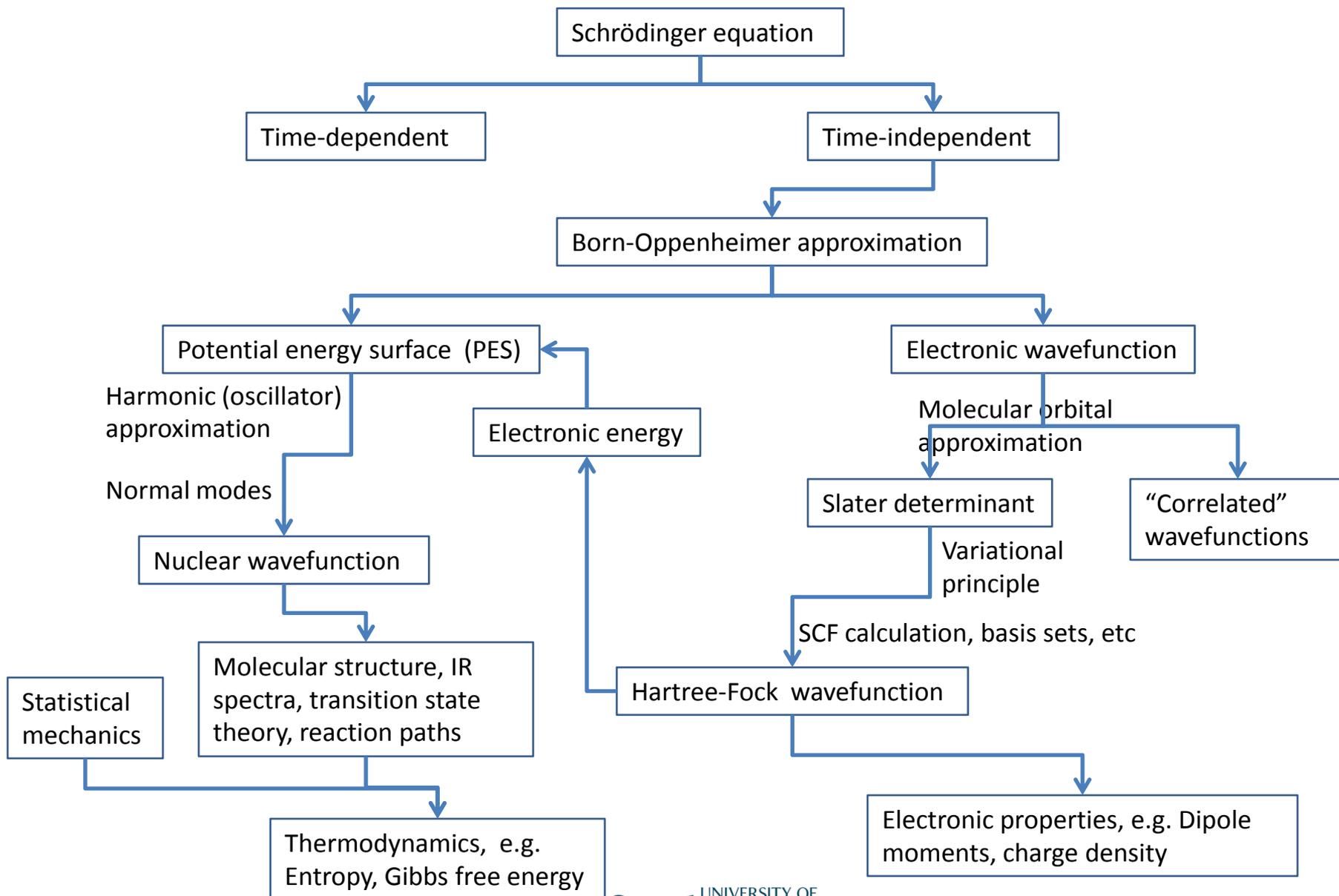
$$E_{\text{correlation}} = E_{\text{exact}} - E_{\text{Hartree-Fock limit}}$$



Ab initio and semiempirical methods

- In between Hartree-Fock and Configuration Interaction there are many other computational approaches such as Perturbation Theory, Coupled-Cluster theory and Density Functional theory
- Density Functional theory (W. Kohn, Chemistry Nobel prize 1998) stands out: It is able to include electronic correlation at a computational cost similar to Hartree-Fock theory – Fundamentally different as it is based on the electronic density instead of the wavefunction
- All these methods are called “*ab initio*” or “first principles” because they solve the electronic problem using only physical constants (e.g. the charge and mass of the electron) and no adjustable parameters
- In contrast “semiempirical” methods (such as the Huckel theory that you saw in CHEM3006) depend on parameters fitted to experiment or *ab initio* calculations
- Semiempirical methods are computationally less demanding but also much less accurate than *ab initio* methods

From molecular quantum theory to chemical predictions



Potential Energy Surface (PES)

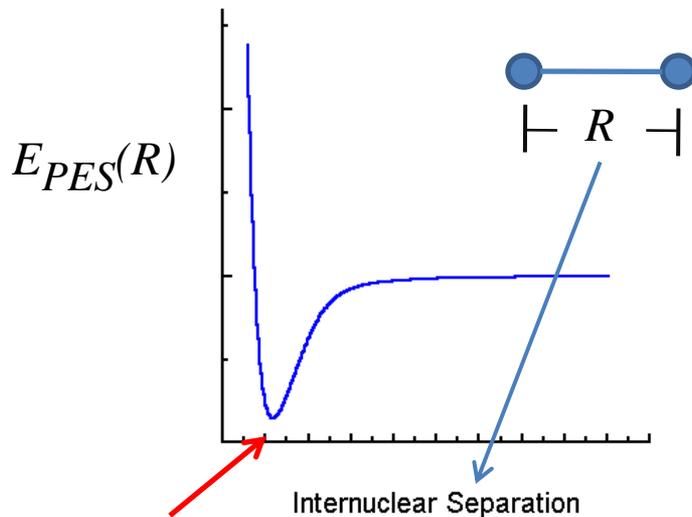
- The electronic energy is a function of the nuclear positions. So is the internuclear repulsion energy
- Their sum is called the Potential Energy Surface (PES). It is a function of $3 \times N_{\text{atoms}}$ variables that represents a “surface” in $(3 \times N_{\text{atoms}} + 1)$ dimensions

$$E_{PES}(\{\mathbf{R}_I\}) = E_{elec}(\{\mathbf{R}_I\}) + \sum_I \sum_{J>I} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$

Electronic energy

Repulsion energy between nuclei I and J

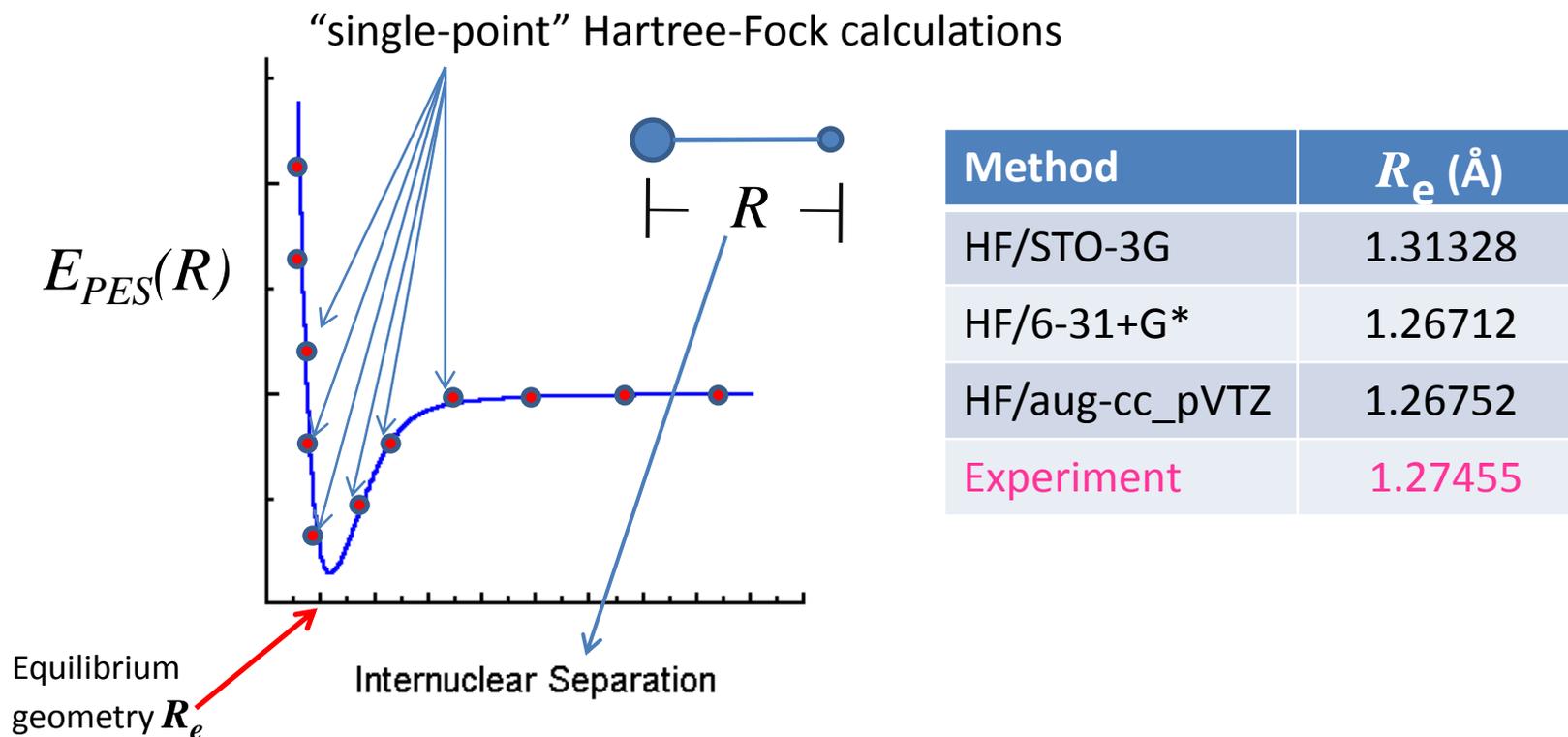
Example: PES of a diatomic



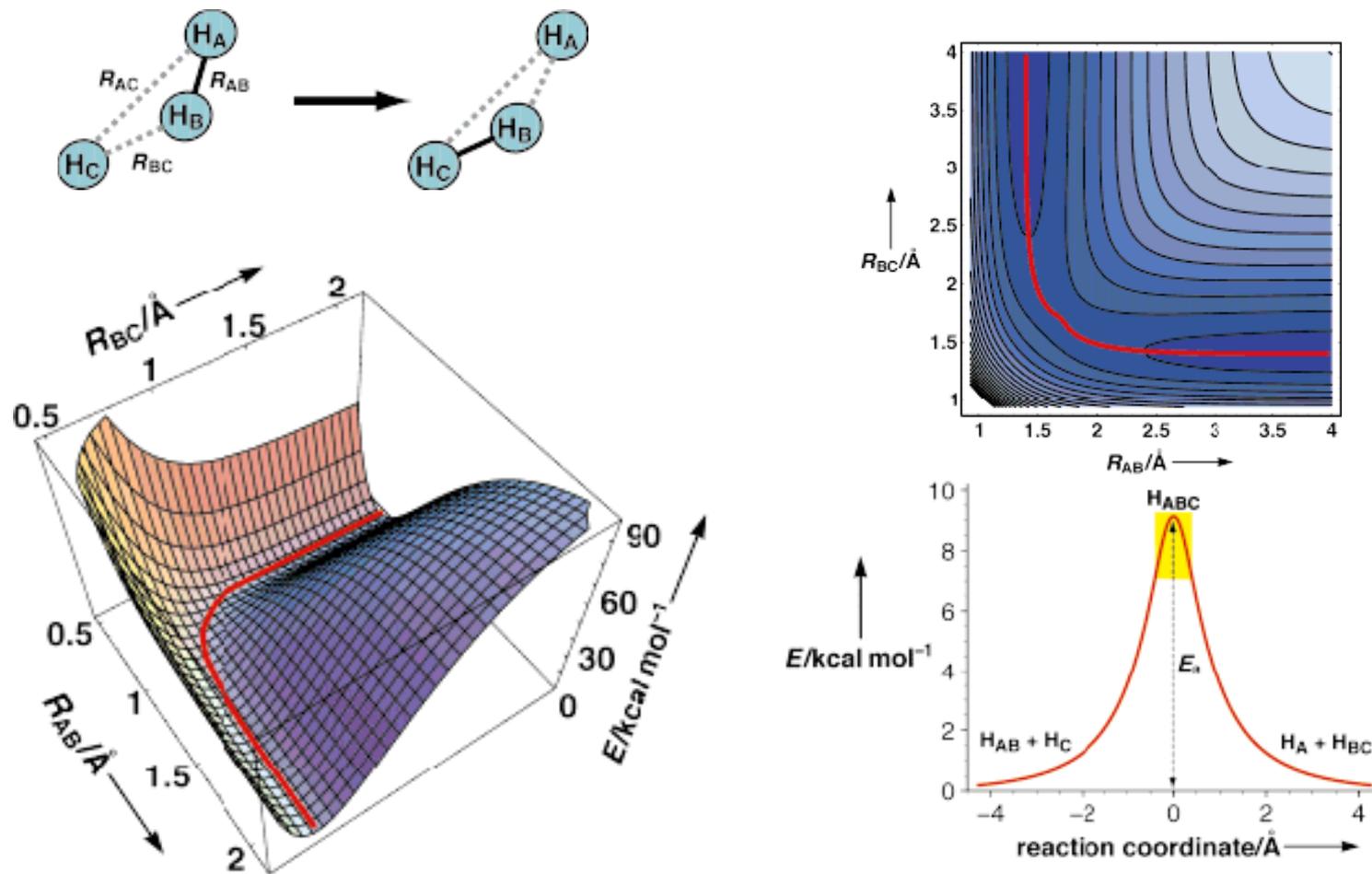
Equilibrium geometry R_e

Example: PES of HCl

- The PES is a function of 6 coordinates
- 5 of these can be removed as they correspond to entire-molecule translation (3 coordinates) and rotation (2 coordinates)
- So in practice the PES depends only on 1 coordinate (the H-Cl distance)

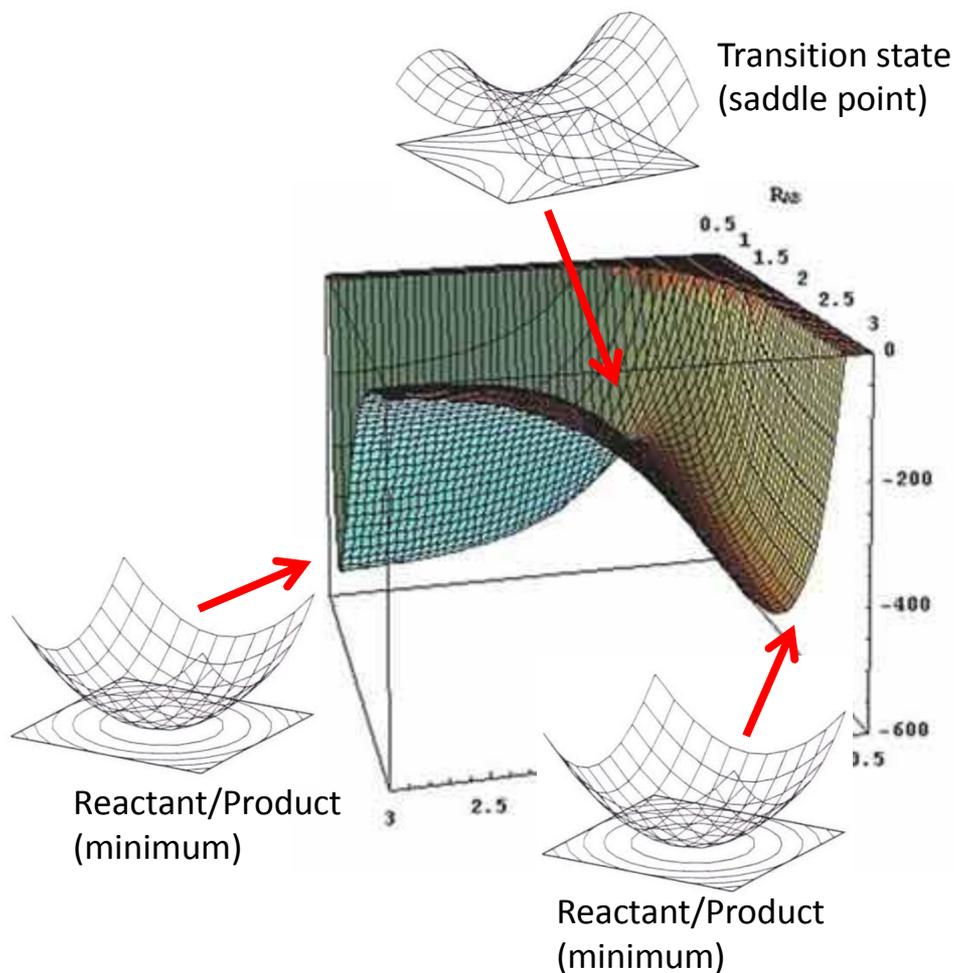


PES for $\text{H}_2 + \text{H} \rightarrow \text{H} + \text{H}_2$



This PES represents chemical interactions that can take place between 3 H atoms

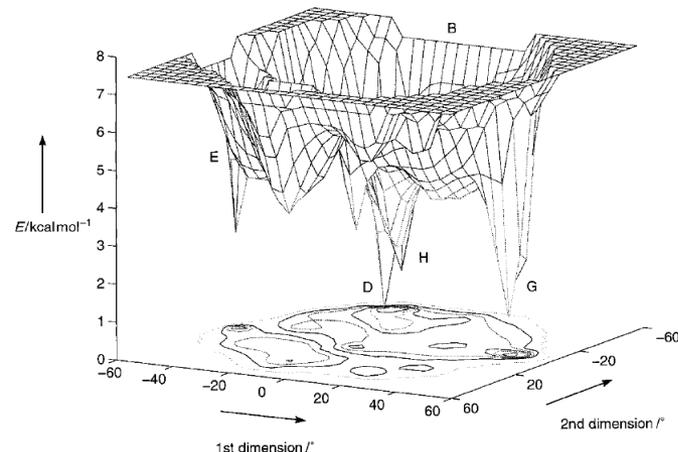
Minima and saddle points



Products, reactants and transition states are **stationary points**, i.e. they are points on the PES where the derivative of E_{PES} with respect to all nuclear coordinates is zero

$$\frac{\partial E_{PES}}{\partial R_{I\gamma}} = 0, \quad \gamma = x, y, z$$

A more complicated PES...



Taylor series expansion of functions

Any function (under certain conditions) can be expanded as a Taylor series about any point x_0 :

$$f(x) = f(x_0) + \left. \frac{df}{dx} \right|_{x_0} (x-x_0) + \frac{1}{2} \left. \frac{d^2f}{dx^2} \right|_{x_0} (x-x_0)^2 + \frac{1}{6} \left. \frac{d^3f}{dx^3} \right|_{x_0} (x-x_0)^3 + \dots = \sum_{n=0}^{\infty} \frac{1}{n!} \left. \frac{d^n f}{dx^n} \right|_{x_0} (x-x_0)^n$$

Expand some known functions in Taylor series and examine (numerically) their convergence as you add more terms in the series

The Taylor expansion can be generalised to functions of many variables (such as the PES) as follows:

$$f(\mathbf{x}) = f(\mathbf{x}_0) + (\mathbf{x} - \mathbf{x}_0)^\dagger \mathbf{g}(\mathbf{x}_0) + \frac{1}{2} (\mathbf{x} - \mathbf{x}_0)^\dagger \mathbf{H}(\mathbf{x}_0) (\mathbf{x} - \mathbf{x}_0) + \dots$$


$$g_i = \left. \frac{\partial f}{\partial x_i} \right|_{x_{i0}}$$

**Gradient
(vector)**


$$H_{ij} = \left. \frac{\partial^2 f}{\partial x_i \partial x_j} \right|_{x_{i0}, x_{j0}}$$

**Hessian
(matrix)**

Nuclear Schrödinger equation for diatomic (e.g. HCl)

- We will consider the Taylor expansion of the PES only up to the second derivative (“second order”)
- This is called the **harmonic approximation**
- We perform the Taylor expansion about the equilibrium bond length R_e (Why?)

$$\begin{aligned} E_{PES}(R) &\simeq E_{PES}(R_e) + \frac{dE_{PES}}{dR}(R-R_e) + \frac{1}{2} \frac{d^2 E_{PES}}{dR^2}(R-R_e)^2 \\ &= E_{PES}(R_e) + \frac{1}{2} \frac{d^2 E_{PES}}{dR^2}(R-R_e)^2 \end{aligned}$$

Nuclear Schrödinger equation for diatomic (e.g. HCl)

$$\left[-\frac{1}{2\mu} \frac{d^2}{dR^2} + E_{PES}(R) \right] \Psi_{nuc}(R) = E' \Psi_{nuc}(R)$$

“reduced mass”

$$\mu = \frac{M_1 M_2}{M_1 + M_2}$$

$$\left[-\frac{1}{2\mu} \frac{d^2}{dR^2} + E_{PES}(R_e) + \frac{1}{2} \frac{d^2 E_{PES}}{dR^2} (R - R_e)^2 \right] \Psi_{nuc}(R) = E' \Psi_{nuc}(R)$$

$$\left[-\frac{1}{2\mu} \frac{d^2}{dR^2} + \frac{1}{2} \frac{d^2 E_{PES}}{dR^2} (R - R_e)^2 \right] \Psi_{nuc}(R) = \underbrace{(E' - E_{PES}(R_e))}_{E} \Psi_{nuc}(R)$$

$$\left[-\frac{1}{2\mu} \frac{d^2}{dR^2} + \frac{1}{2} k (R - R_e)^2 \right] \Psi_{nuc}(R) = E \Psi_{nuc}(R)$$

This is just the Schrödinger equation for a harmonic oscillator (a spring) with force constant k and frequency:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

Example: IR bond stretching frequency of HCl

Run Hartree-Fock calculations to:

- 1) Locate R_e
- 2) Obtain k as the second derivative of the E_{PEs} at $R=R_e$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

Method	H-Cl stretch (cm ⁻¹)
HF/STO-3G	3373
HF/6-31+G*	3178
HF/aug_cc-pVTZ	3136
Experiment	2991

Summary / Reading assignment

- Electron correlation (Cramer, pages 203-207)
- Semiempirical methods (Cramer, pages 131-133)
- Vibrational Schrödinger equation for diatomic under the harmonic approximation (Cramer, pages 334 – 342)