

10.675 LECTURE 1

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1. TODAY

- Motivation
- Course Overview

2. MISC

- Books. Jensen - DFT. Szabo Modern Quantum Chemistry.
- Grading. Homework 30%, Participation 20%, Final Project 50%.
- Check out Gaussian Site <http://www.gaussian.com/> as well as CPMD <http://www.cpmc.org/> for information on software we will be using in the course.

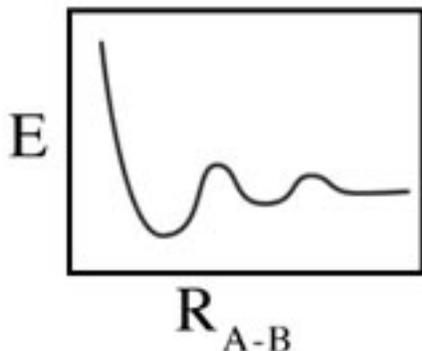
3. INTRO CONCEPTS

- Model electrons quantum mechanically (QM) while using classical mechanics (CM) for the nuclei.
- In today's research, 50 atom QM simulations is the high end.
- Goal: Solve for nuclear/electron interactions.
- Option 1: Nuclei with an electron cloud in a cluster model isolated system.
- Option 2: Physics approach → periodic structure in 3D.

4. SETUP

- Born-Oppenheimer (BO) Approximation... Important! Also called the adiabatic approximation. Essentially, the nuclei are far heavier and less mobile than electrons. Thus, we can decouple the motions of the electrons from that of the nuclei and solve independently.
- Because of BO approximation, we treat nuclei as point charges of zero volume.
- Typically, this means we're working in a $3N-6$ dimensional space, where N → # of Nuclei in our system.

→ We are trying to determine the potential energy surfaces.



5. NOTATION

Introducing the time-independent Schrödinger Equation (SE).

$$H\Psi_i = E_i\Psi_i$$

Where H is the Hamiltonian for the system, and E_i 's are the Eigenvalues.

6. HYDROGEN

The Hamiltonian is as follows.

$$\frac{-\hbar^2}{2m_e} \nabla^2 \Psi_i - \frac{e^2}{r} \Psi_i = E_i \Psi_i$$

$$e^2 = \frac{q^2}{4\pi\epsilon_0}$$

From now on, and for the rest of these lectures, we will be using atomic units to stop us from writing out all the miscellaneous constants each and every time.

→ length bohr $a_o = \frac{\hbar^2}{m_e} = 0.52918 \text{ \AA}$

→ energy hartree $E_h = e^2 = 27.21 \text{ eV}$

→ 1 eV = 23.06 Kcal/mol

The SE thus becomes

$$\frac{-1}{2} \nabla^2 \Psi_i - \frac{1}{r} \Psi_i = E_i \Psi_i$$

7. MANY BODY SCHRÖDINGER EQUATION - NO SPIN

$$H = \frac{-1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \sum_{k=1}^M \frac{Z_k}{r_i - \bar{R}_k} + \sum_{i=1}^N \sum_{j < i}^N \frac{Z_k}{r_i - \bar{R}_j}$$

First term is electron KE, second term elec/nuc interaction, last term is elec/elec interactions. Nuc/Nuc terms are ignored for the time being.

N → Electrons

M → Nuclei

The electron/electron interaction term is the hardest part as r_i and r_j are not separable.

8. SOLVING

Many different ways of going about it

Single particle equations, solve through self consistent field (SCF) "Mean Field Theory".

Molecular orbital theory. → Hartree-Fock Methods.

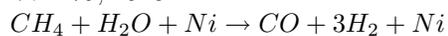
Density Functional Theory (DFT).

In all approaches, there are no adjustable parameters.

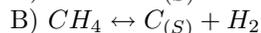
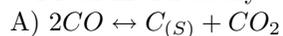
9. DEMOS/EXAMPLES

Gaussian Code Intro - Gaussview Display

Catalyst Design, paper → Steam Reforming Catalyst. Science, 20 March, 1998, Vol 279, 1913.



→ Problem: Ni catalyst "cokes", ie carbon deposits on the surface.



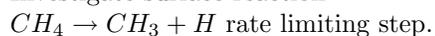
Coking Deactivates the process.

GOAL: Investigate the coking reactions with/without Au. Want to hinder nucleation of $\text{C}_{(s)}$.

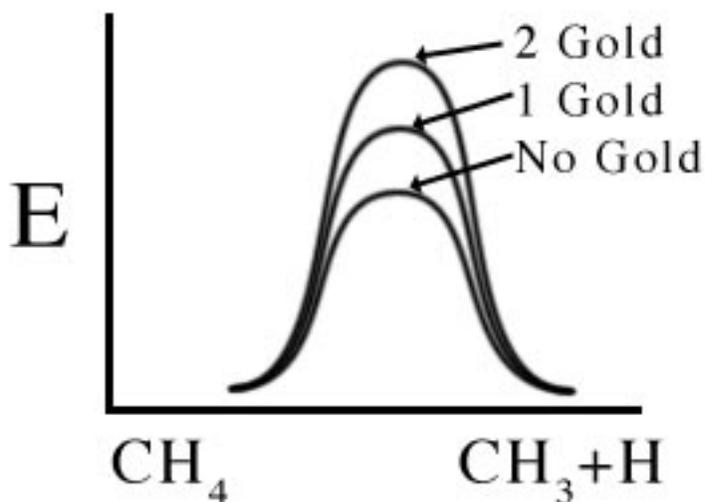
Objective: Have the catalyst selective for reaction A over B.

Choose the model surface (Ni 111 plane)

Investigate surface reaction



Add gold, how will it effect this rxn?



Compare with Experiment... which it all worked with almost NO coking.