Computational Material Chemistry

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Aim

- Understand the basic theory behind quantum chemistry calculation
- Learn running quantum chemistry program
- Understand what the output is saying
- Get a feeling of what method to use for what problem

Grading

- Oral Presentation (10-15 minutes) by students in class: 50% (of which class evaluation is half);
- Report on the calculation that they performed and compare with experiment if available 25%
- Quiz/Homework :25%

Schedule

1. Born Oppenheimer Approximation, LCAO H_2^+ calculation
2. $H_{2,}$ homonuclear and heteronuclear diatomic molecule, Restricted Hartree Fock.
3. Unrestricted Hartree Fock, Roothan Equation, Basis Set Gaussian Calculation Input/structure optimization.
4. Potential Energy Surface, Barrier Transition State.

Schedule

5. Electron correlation (DFT, MP2, QCISD, CCSD, CASSCF, MRCI, G2 G3)
6. Vibrational Spectroscopy, Electronic Spectroscopy
7. Force field parametrization, intermolecular potential
8. Molecular dynamics simulation of liquid

Questions?

- What grade are you in, and what lab are you in.
- Why did you take this class.

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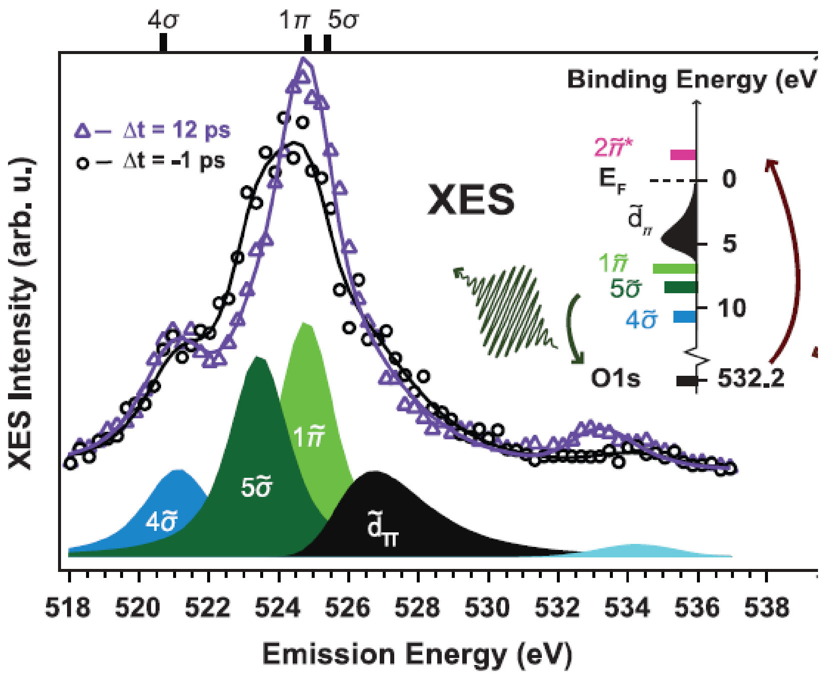
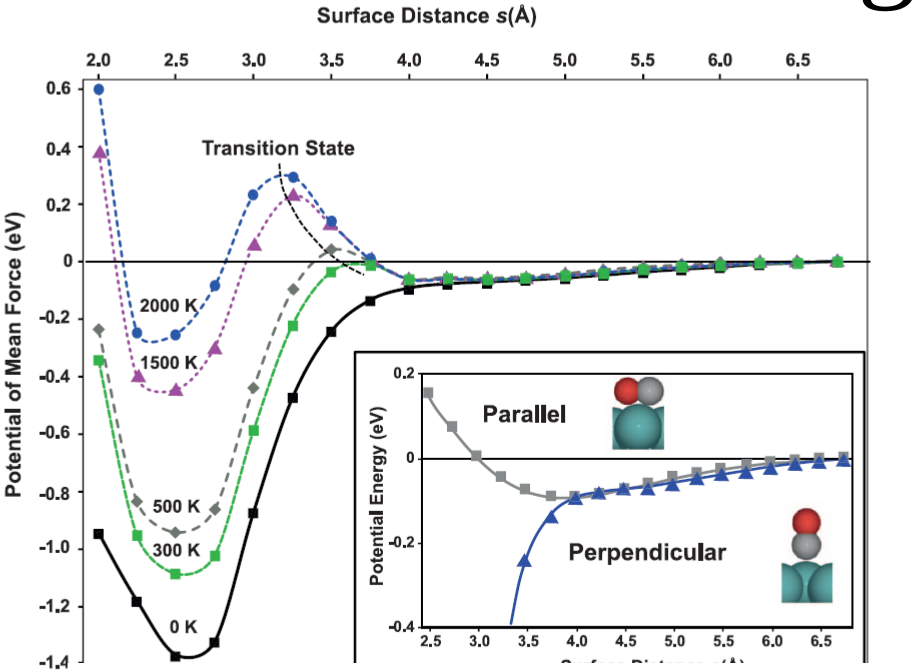
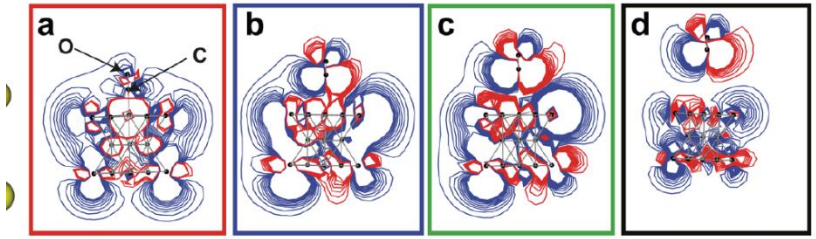
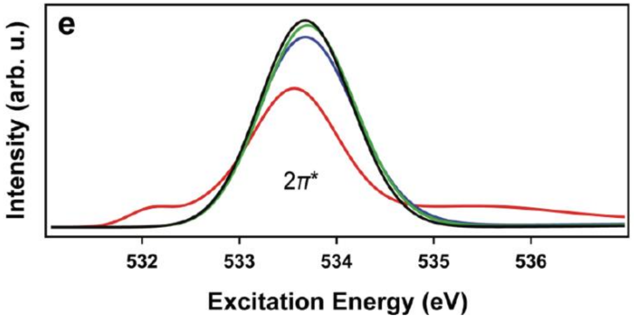
What can we calculate with quantum chemistry packages?

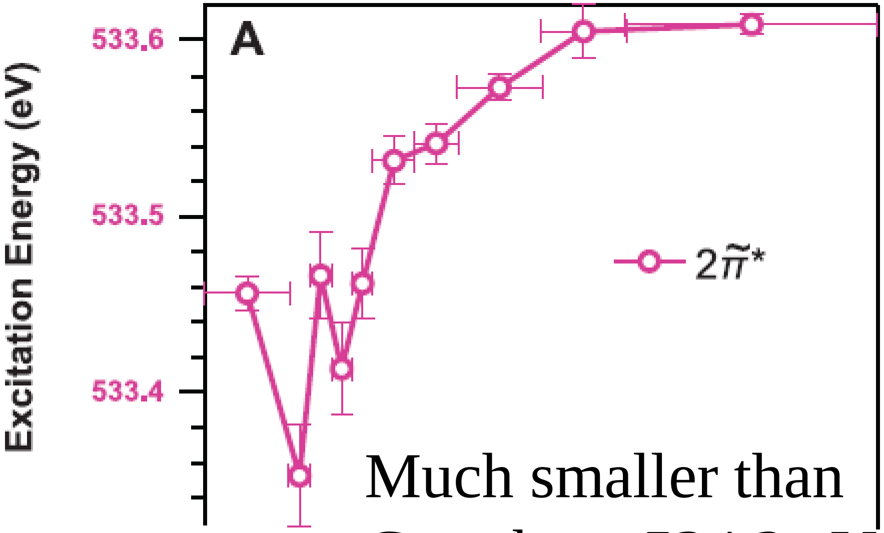
Understanding Metal Surface Binding











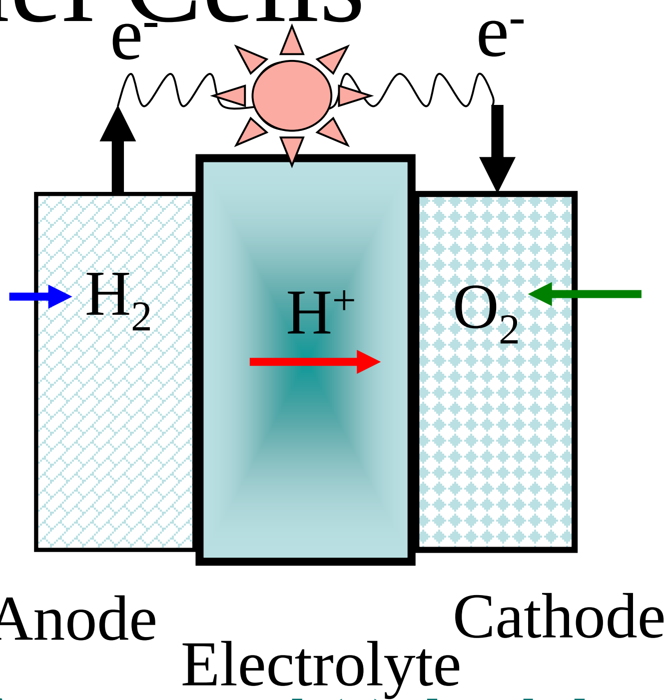
Much smaller than
Gas phase 534.2 eV

Nilsson et al. Science, 339, 1302 (2013)

Oxygen Reduction Reaction (ORR) in Hydrogen Fuel Cells

Anode: $H_2 = 2(H^+ + e^-)$

Cathode: $2(H^+ + e^-) + ½\ O_2 = H_2O$



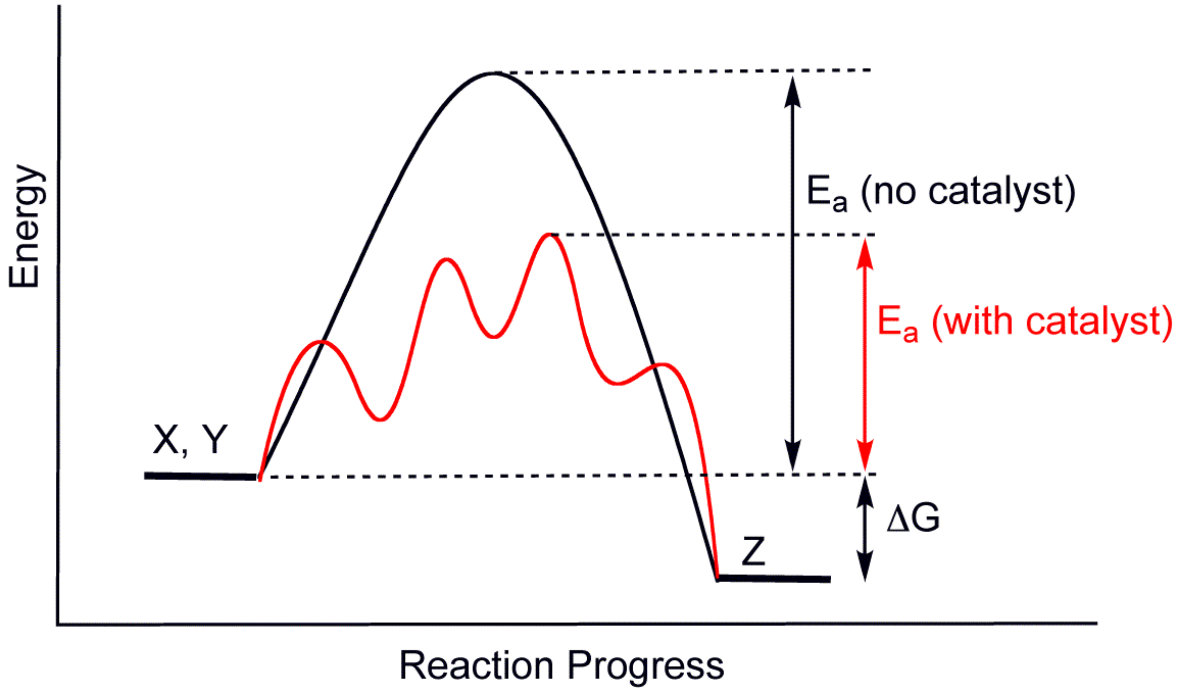
★ Slow kinetics of the ORR occuring at the cathode. Need a better metal than Pt

Is alloying the answer?

★Requirements: (a) low cost, (b) high efficiency, and (c) durability.

Why metal surfaces?

- Metal surfaces function as catalysts

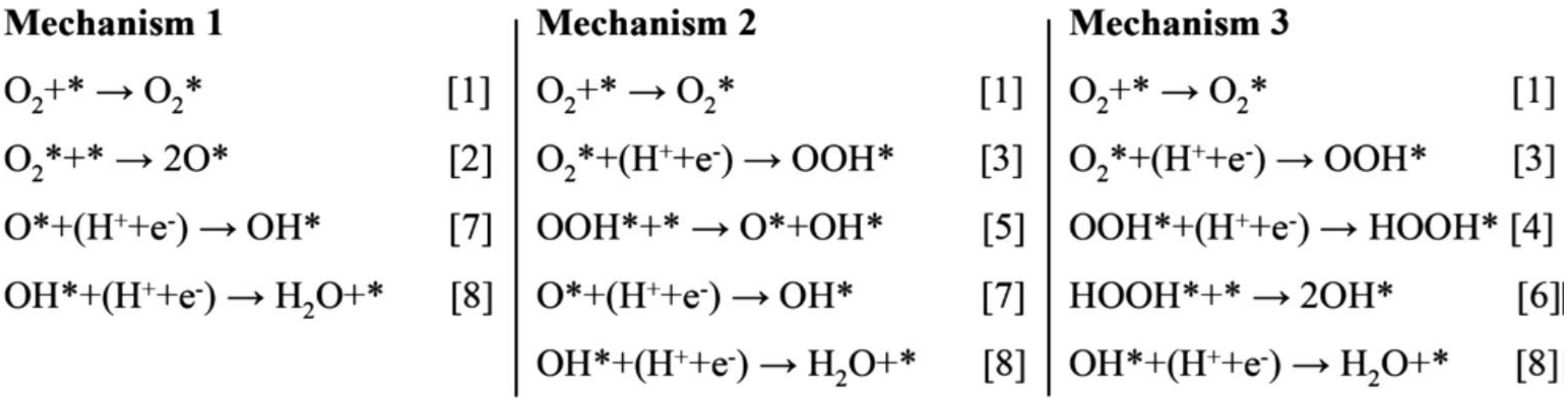


- Sabatier principle: optimum catalyst must have intermediate affinity for reactants

Oxygen Reduction Reaction (ORR)

$$2(H^+ + e^-) + \frac{1}{2} O_2 \rightarrow H_2O$$

- Mechanism (Intermediates, Rate Determining Steps), Surf. Sci. 602 (2008) L89-L94, On pure metals (Pt):

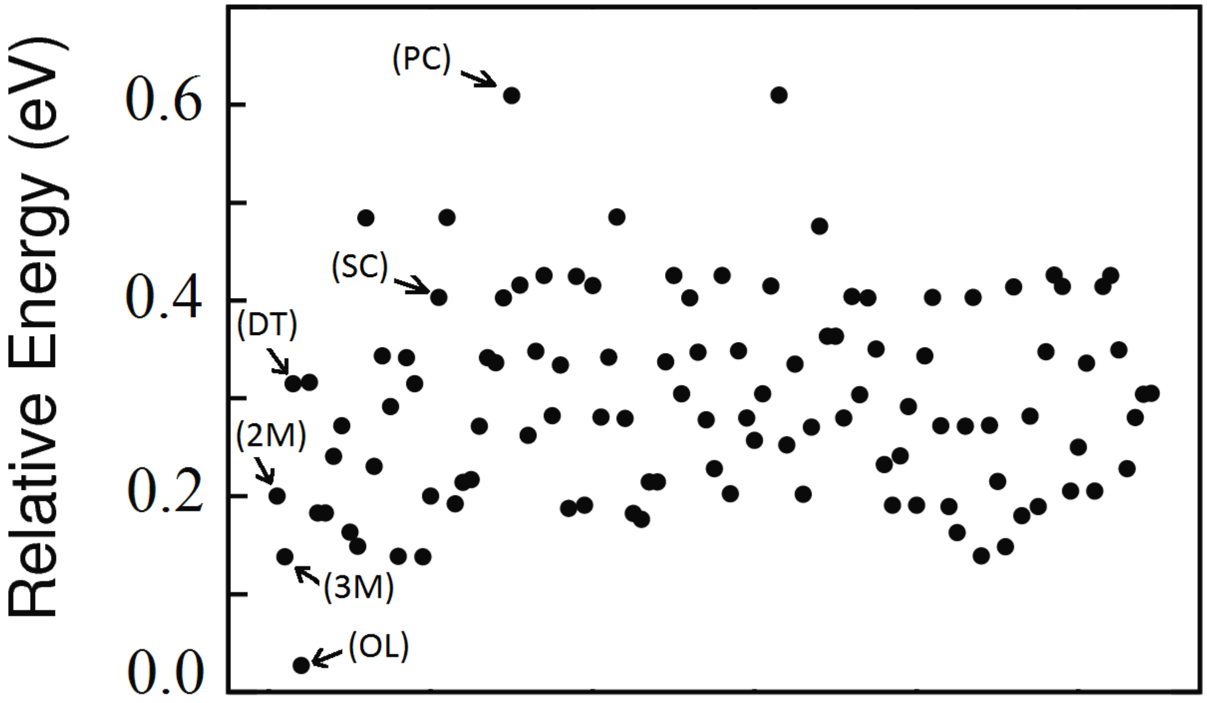


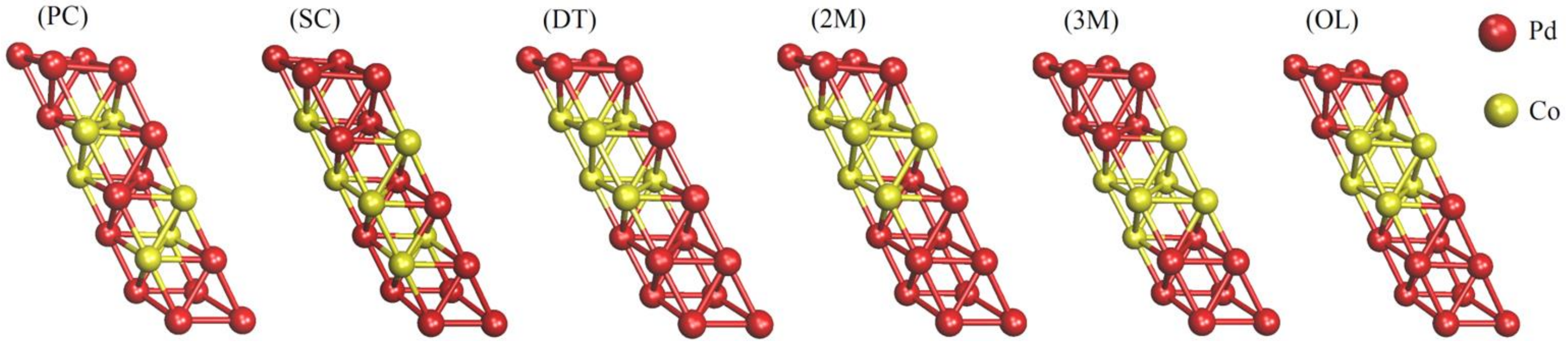
Mechanism 1		**Mechanism 2**		**Mechanism 3**	
$O_2 + * \rightarrow O_2*$	[1]	$O_2 + * \rightarrow O_2*$	[1]	$O_2 + * \rightarrow O_2*$	[1]
$O_2* + * \rightarrow 2O*$	[2]	$O_2* + (H^+ + e^-) \rightarrow OOH*$	[3]	$O_2* + (H^+ + e^-) \rightarrow OOH*$	[3]
$O* + (H^+ + e^-) \rightarrow OH*$	[7]	$OOH* + * \rightarrow O* + OH*$	[5]	$OOH* + (H^+ + e^-) \rightarrow HOOH*$	[4]
$OH* + (H^+ + e^-) \rightarrow H_2O + *$	[8]	$O* + (H^+ + e^-) \rightarrow OH*$	[7]	$HOOH* + * \rightarrow 2OH*$	[6]
		$OH* + (H^+ + e^-) \rightarrow H_2O + *$	[8]	$OH* + (H^+ + e^-) \rightarrow H_2O + *$	[8]

*: binding to surface

Depending on the condition different mechanisms dominate

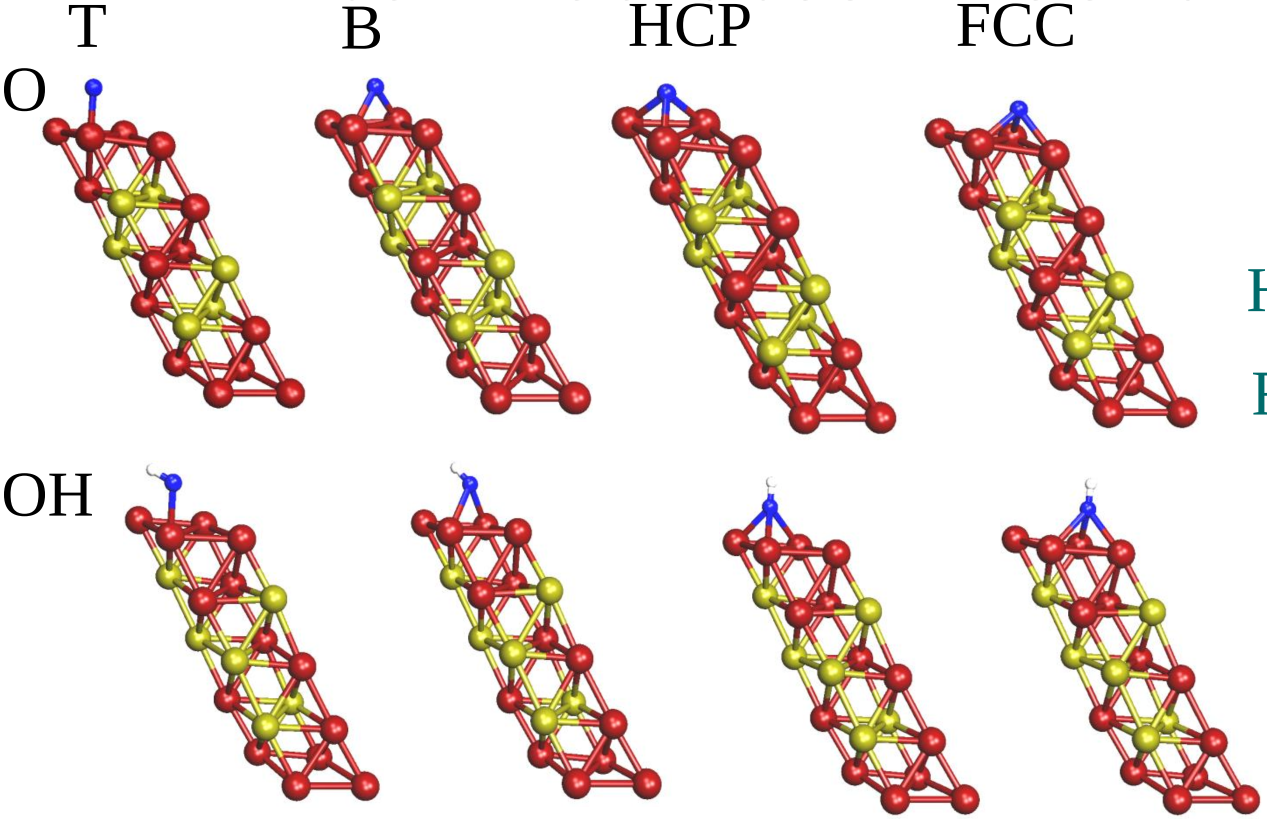
Co 30% Example





PC: Partially clustering
SC: Scattered
DT: Double-triangle
2M: 2nd-layer monolayer
3M: 3rd-layer monolayer
OL: Octahedral-like

Intermediates Mechanism 1



Top: T

Bridge: B

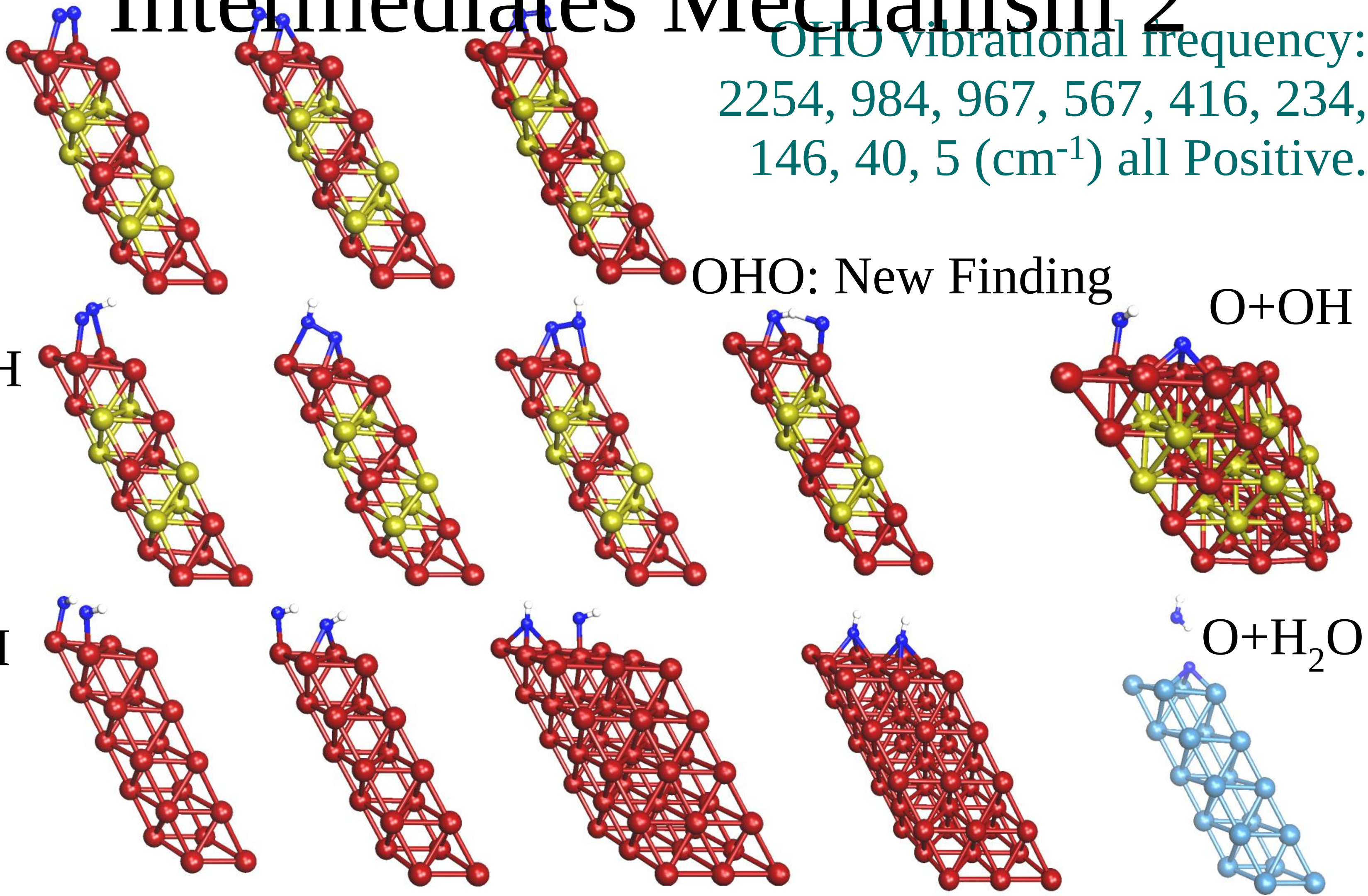
HCP Hollow: HCP

FCC Hollow: FCC

There are two intermediates: O and OH.

Intermediates Mechanism 2

OHO vibrational frequency:
2254, 984, 967, 567, 416, 234, 146, 40, 5 (cm^{-1}) all Positive.



O_2

OHO: New Finding

OOH

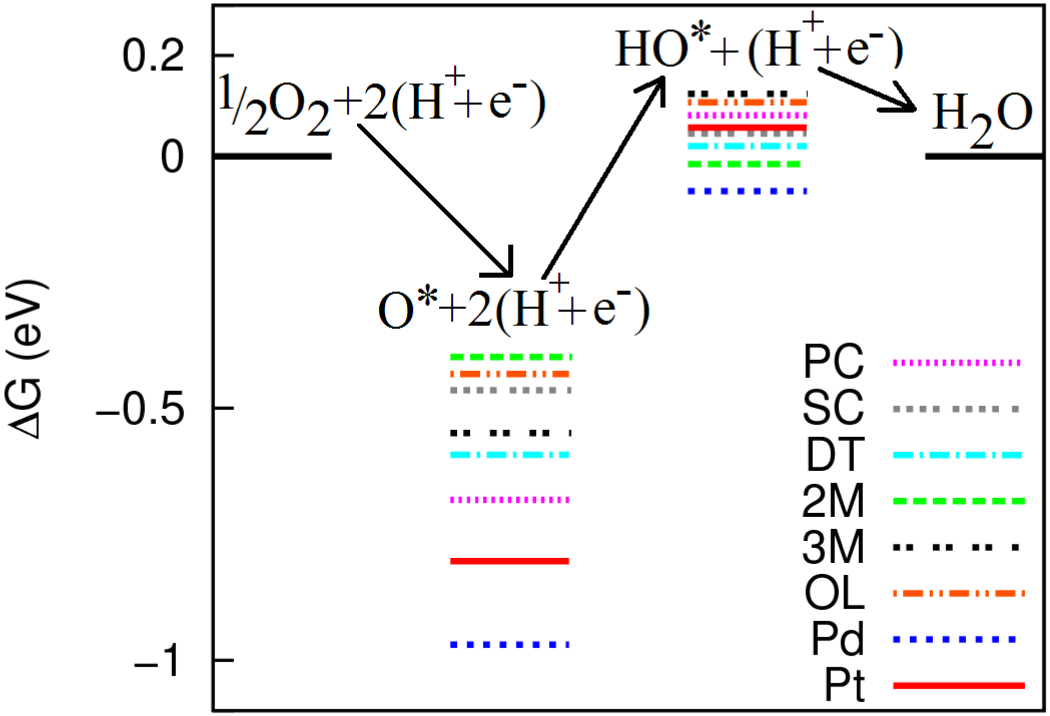
O+OH

2OH

$O+H_2O$

Free Energy Diagram path 1

At equilibrium potential *U* = 1.23 (V), *T* = 300 (K), pressure *P* = 1 (bar), pH = 0. Free energy ΔG calculations take into account reaction energy, zero point energy, and entropy change from DFT results (Computational Methods).



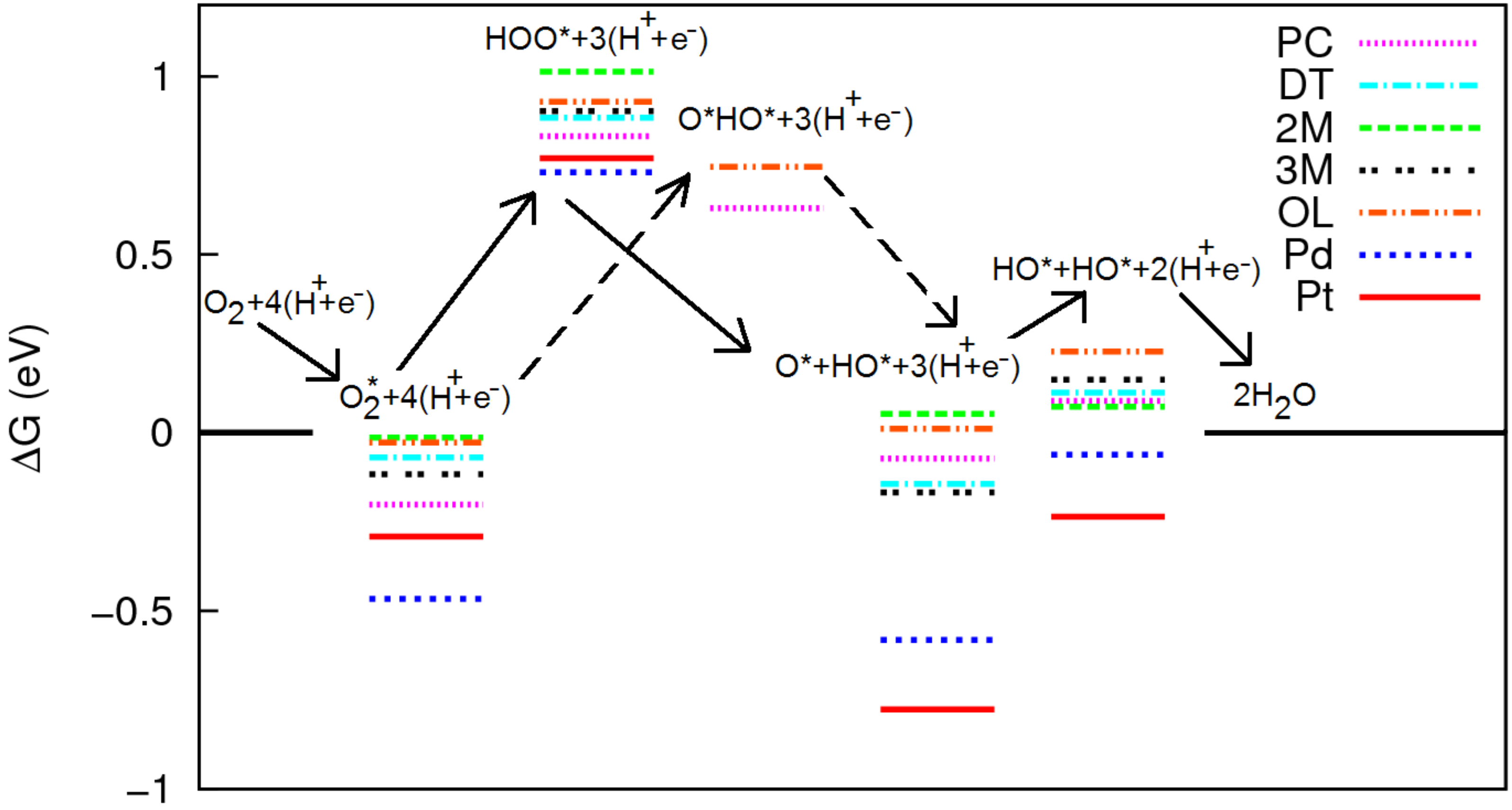
Path 1

Highest thermodynamic barrier locates in the first hydrogenation.

Reference for Pt and Pd:

J. Chem. Theory Comput. 2 (2006) 1388.

Free Energy Diagram path 2,3



Reference for Pt, Pd: *Surf. Sci. 602 (2008) L89-L94.*

Highest thermodynamic barrier also locates in the first hydrogenation.

Born-Oppenheimer Approximation

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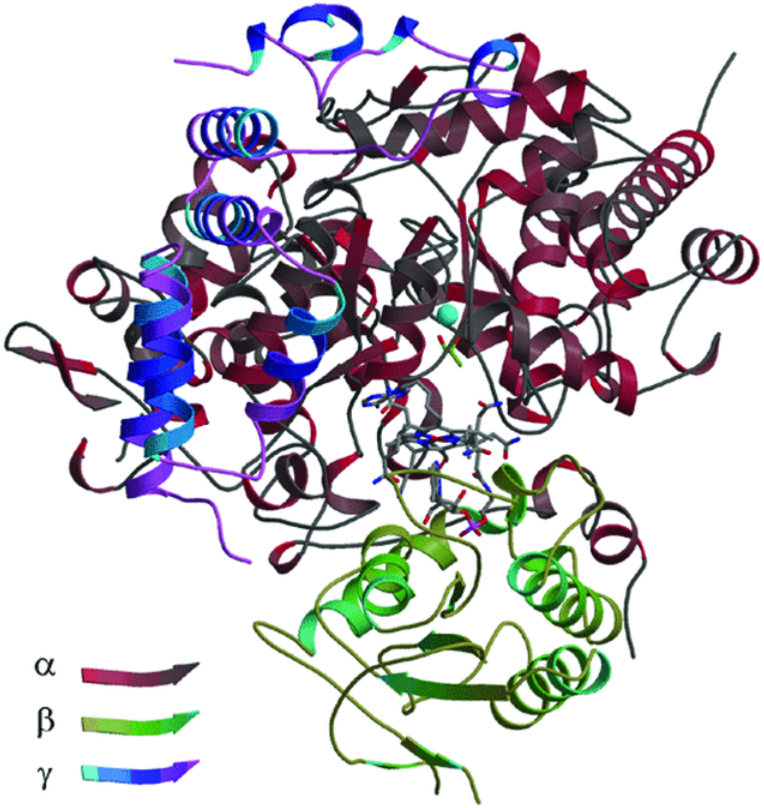
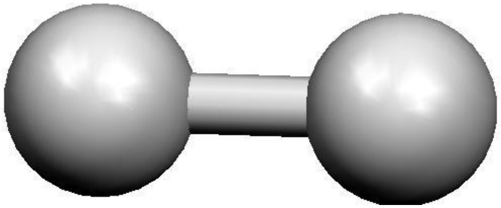
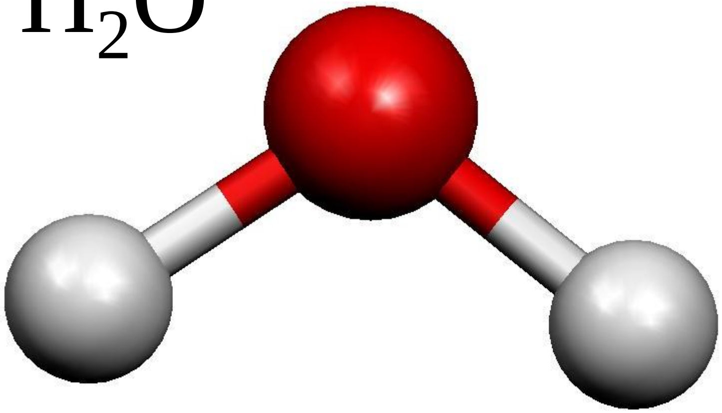
Proteins, Molecules



H_2



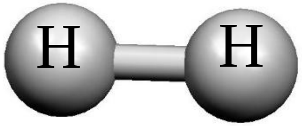
H_2O

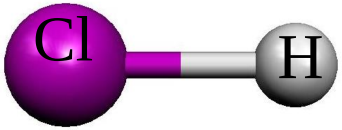


You always write where the nucleus is but you never write the electrons or the electrons are written as a line!!!
YOU ARE ALREADY ASSUMING BORN-OPPENHEIMER APPROXIMATION

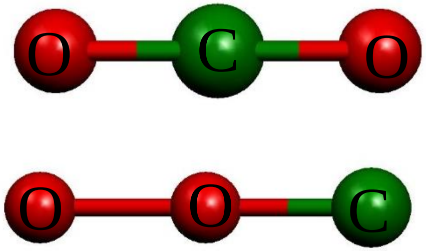
Atoms vs Molecules

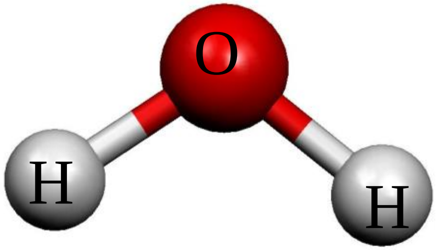
- Simple case : Diatomic Molecules
  - H_2, O_2, F_2,HCl

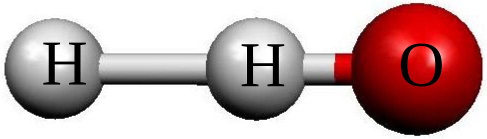




- More Complex: Triatomic Molecules
  - H_2O, CO_2







Why graphene like structure is seen for carbon but not nitrogen?

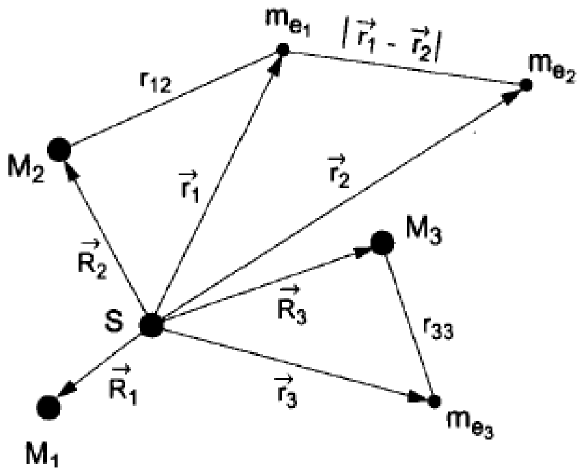
Which structure is the most likely?

Full Problem

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\nabla_i^2 - \frac{\hbar^2}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2 + V(\mathbf{r},\mathbf{R})$$

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \qquad \nabla_I^2 = \frac{\partial^2}{\partial X_I^2} + \frac{\partial^2}{\partial Y_I^2} + \frac{\partial^2}{\partial Z_I^2}$$

$$V(\mathbf{r},\mathbf{R}) = \frac{e^2}{4\pi\varepsilon_0}\left[\sum_{I=1}^{N}\sum_{J\neq I}^{N}\frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} - \sum_{I=1}^{N}\sum_{i=1}^{n}\frac{Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} + \sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right]$$



$$\mathbf{R}_I = \vec{R}_I = X_I\vec{e}_x + Y_I\vec{e}_y + Z_I\vec{e}_z$$

$$\mathbf{r}_i = \vec{r}_i = x_i\vec{e}_x + y_i\vec{e}_y + z_i\vec{e}_z$$

$$\hat{H}\Psi(\mathbf{r},\mathbf{R}) = E_{el,NU}\Psi(\mathbf{r},\mathbf{R})$$

Atomic Units

For quantum systems such as electrons and molecules it is easier to use units that fit them=ATOMIC UNIT

Use mass of electron (not kg)
Use charge of electron (not coulomb)
Use hbar for angular momentum (not kg m^2 s^{-1})
Use $4\pi\varepsilon_0$ for permittivity (not C^2 s^2 kg^{-1} m^{-3})

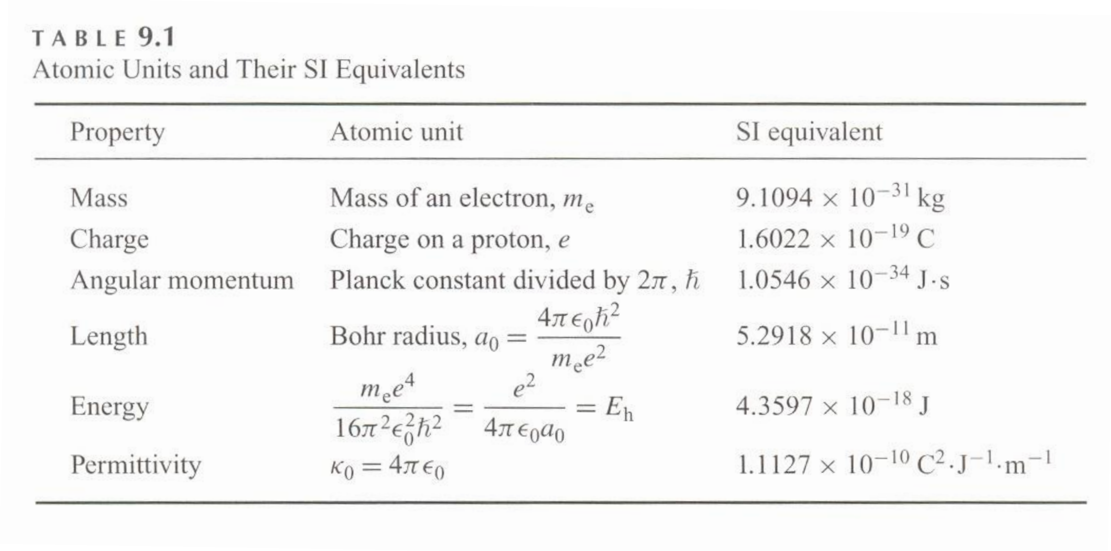


TABLE 9.1
Atomic Units and Their SI Equivalents

Property	Atomic unit	SI equivalent
Mass	Mass of an electron, m_e	9.1094×10^{-31} kg
Charge	Charge on a proton, e	1.6022×10^{-19} C
Angular momentum	Planck constant divided by 2π, $\hbar$	1.0546×10^{-34} J·s
Length	Bohr radius, $a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$	5.2918×10^{-11} m
Energy	$\frac{m_e e^4}{16\pi^2\epsilon_0^2\hbar^2} = \frac{e^2}{4\pi\epsilon_0 a_0} = E_h$	4.3597×10^{-18} J
Permittivity	$\kappa_0 = 4\pi\epsilon_0$	1.1127×10^{-10} $C^2 \cdot J^{-1} \cdot m^{-1}$

Born-Oppenheimer Approximation in words

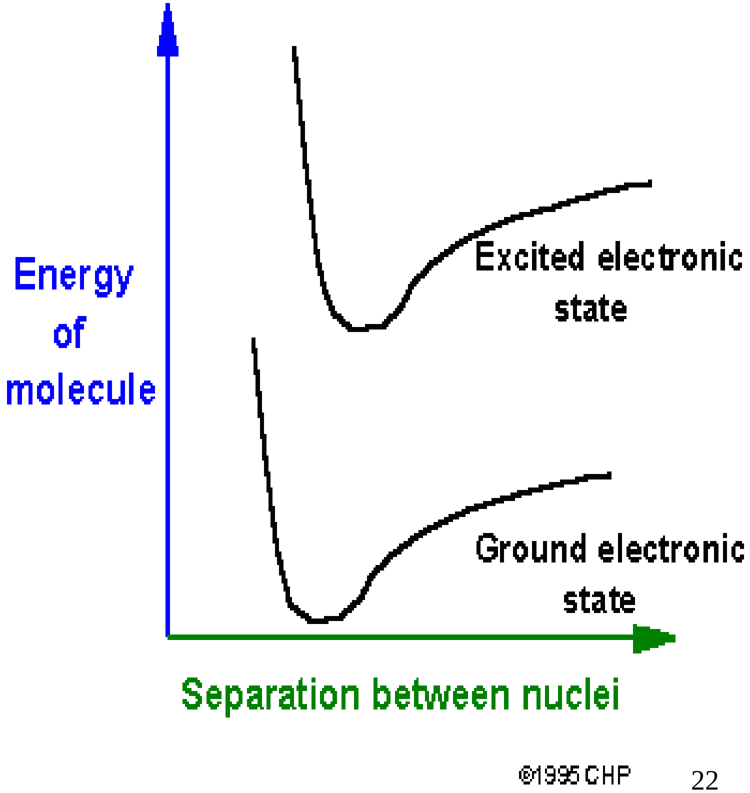
Mass of electron versus mass of nucleus

1 <<< 1830 (at least)

electron moves much faster than nucleus, so electron can instantly adjust to change in nuclear coordinate, so nucleus moves in an average field made up by the electrons

At a given value for the nuclear geometry **R,** there exist a well defined electronic state distribution and Energy

$$\phi_n^{el}(\mathbf{r};\mathbf{R}); E_n(\mathbf{R})$$



This electronic state depends on position of nucleus, ***but not on the momentum***

BO Approximation

Real problem: N nucleus n electron problem

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\nabla_i^2 - \frac{\hbar^2}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2 + V(\mathbf{r},\mathbf{R}) = -\frac{\hbar^2}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2 + \hat{H}^0$$

Born-Oppenheimer Approximation ignore nonadiabatic coupling

Solve the electronic state at fixed nuclear geometry,

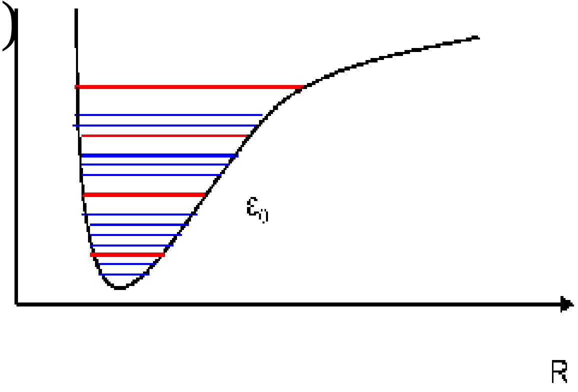
$$\hat{H}^0(\mathbf{r};\mathbf{R})\phi_n^{el}(\mathbf{r};\mathbf{R}) = E_n(\mathbf{R})\phi_n^{el}(\mathbf{r};\mathbf{R})$$

Quantum chemistry

many nuclear geometries: **adiabatic potential energy surface**

$$\left(-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2 + E_n(\mathbf{R})\right)\chi_n(\mathbf{R}) = E_{el,NU}\chi_n(\mathbf{R})$$

Quantum Dynamics
(Vibrational Schroedinger Eq)



Classical Molecular Dynamics,
Statistical Modeling

BO Approximation in equation 1

$$\hat{H}=\hat{T}+\hat{V}=-\frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\nabla_i^2-\frac{\hbar^2}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2+V(\mathbf{r},\mathbf{R})$$

$$=\hat{T}_{el}+\hat{T}_{NU}+\hat{V}=\hat{T}_{el}+\hat{V}+\hat{T}_{NU}=\hat{H}^0+\hat{T}_{NU}$$

$$\hat{H}^0(\mathbf{r};\mathbf{R})=-\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2+V(\mathbf{r},\mathbf{R}) \qquad \hat{T}_{NU}=-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2$$

$$\hat{H}^0(\mathbf{r};\mathbf{R})\phi_n^{el}(\mathbf{r};\mathbf{R})=E_n(\mathbf{R})\phi_n^{el}(\mathbf{r};\mathbf{R})$$

$$\int\phi_n^{el*}(\mathbf{r};\mathbf{R})\phi_m^{el}(\mathbf{r};\mathbf{R})d\mathbf{r}=\delta_{mn}$$

$$\hat{H}\Psi(\mathbf{r},\mathbf{R})=E_{el,NU}\Psi(\mathbf{r},\mathbf{R})$$

$$\Psi(\mathbf{r},\mathbf{R})=\sum_{m}^{\infty}\chi_m(\mathbf{R})\phi_m^{el}(\mathbf{r};\mathbf{R})$$

$$\chi_m(\mathbf{R})=\text{Expansion Coefficient}$$

BO Approximation 2

$$\left(\hat{H} - E_{el,NU}\right)\Psi(\mathbf{r},\mathbf{R}) = 0$$

multiply ϕ_n
then integrate with r

$$\int \phi_n^{el*}(\mathbf{r};\mathbf{R})\left(\hat{H} - E_{el,NU}\right)\sum_m^{\infty}\chi_m(\mathbf{R})\phi_m^{el}(\mathbf{r};\mathbf{R})\,d\mathbf{r} = 0$$

$$\int \phi_n^{el*}(\mathbf{r};\mathbf{R})\left(\hat{H}^0 + \hat{T}_{NU} - E_{el,NU}\right)\sum_m^{\infty}\chi_m(\mathbf{R})\phi_m^{el}(\mathbf{r};\mathbf{R})\,d\mathbf{r} = 0$$

$$\int \phi_n^{el*}(\mathbf{r};\mathbf{R})\left(\hat{H}^0 - E_{el,NU} + \hat{T}_{NU}\right)\sum_m^{\infty}\chi_m(\mathbf{R})\phi_m^{el}(\mathbf{r};\mathbf{R})\,d\mathbf{r} = 0$$

$$\sum_m^{\infty}\chi_m(\mathbf{R})\left[\int \phi_n^{el*}(\mathbf{r};\mathbf{R})\left(\hat{H}^0 - E_{el,NU}\right)\phi_m^{el}(\mathbf{r};\mathbf{R})\,d\mathbf{r}\right]$$

$$+\int \phi_n^{el*}(\mathbf{r};\mathbf{R})\left(\hat{T}_{NU}\right)\sum_m^{\infty}\chi_m(\mathbf{R})\phi_m^{el}(\mathbf{r};\mathbf{R})\,d\mathbf{r} = 0$$

BO Approximation 3

$$\sum_m^\infty \chi_m(\mathbf{R})\left[\int \phi_n^{el*}(\mathbf{r};\mathbf{R})\left(\hat{H}^0 - E_{el,NU}\right)\phi_m^{el}(\mathbf{r};\mathbf{R})\,d\mathbf{r}\right]$$

Remember

$$\int \phi_n^{el*}(\mathbf{r};\mathbf{R})\phi_m^{el}(\mathbf{r};\mathbf{R})d\mathbf{r} = \delta_{mn}$$

$$= \sum_m^\infty \chi_m(\mathbf{R})\left[\left(E_m(\mathbf{R}) - E_{el,NU}\right)\delta_{nm}\right] = \left(E_n(\mathbf{R}) - E_{el,NU}\right)\chi_n(\mathbf{R})$$

$$\int \phi_n^{el*}(\mathbf{r};\mathbf{R})\left(\hat{T}_{NU}\right)\sum_m^\infty \chi_m(\mathbf{R})\phi_m^{el}(\mathbf{r};\mathbf{R})\,d\mathbf{r}$$

$$= \int \phi_n^{el*}(\mathbf{r};\mathbf{R})\left(-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2\right)\sum_m^\infty \chi_m(\mathbf{R})\phi_m^{el}(\mathbf{r};\mathbf{R})\,d\mathbf{r}$$

Using Bra-Ket Notation

$$|n\rangle = \psi_n(x) \qquad \langle m| = \psi_m{}^*(x)$$

$$\langle n|\hat{x}|m\rangle = \int_{-\infty}^{\infty} \psi_n{}^*(x)\,x\,\psi_m(x)\,dx$$

$$\langle n|\hat{1}|m\rangle = \langle n|m\rangle = \langle n\|m\rangle = \int^{\infty} \psi_n{}^*(x)\psi_m(x)\,dx$$

BO Approximation 4

$$\int \phi_n^{el*}(\mathbf{r};\mathbf{R})\left(-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2\right)\sum_{m}^{\infty}\chi_m(\mathbf{R})\phi_m^{el}(\mathbf{r};\mathbf{R})\,d\mathbf{r}$$

Divide integration to different parts

$$= \int \phi_n^{el*}(\mathbf{r};\mathbf{R})\sum_{m}^{\infty}\left(-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2\chi_m(\mathbf{R})\right)\phi_m^{el}(\mathbf{r};\mathbf{R})\,d\mathbf{r}$$

$$+\int \phi_n^{el*}(\mathbf{r};\mathbf{R})\sum_{m}^{\infty}\left(-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2\phi_m^{el}(\mathbf{r};\mathbf{R})\right)\chi_m(\mathbf{R})\,d\mathbf{r}$$

$$+\int \phi_n^{el*}(\mathbf{r};\mathbf{R})\sum_{m}^{\infty}\left(-\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I\phi_m^{el}(\mathbf{r};\mathbf{R})\right)\nabla_I\chi_m(\mathbf{R})\,d\mathbf{r}$$

$$= \sum_{m}^{\infty}-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2\chi_m(\mathbf{R})\langle n\|m\rangle_r = -\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2\chi_n(\mathbf{R})$$

$$+\sum_{m}^{\infty}\left\langle n\left|-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2\right|m\right\rangle\chi_m(\mathbf{R})+\sum_{m}^{\infty}\left\langle n\left|-\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I\right|m\right\rangle\nabla_I\chi_m(\mathbf{R})$$

BO Approximation 5

Bring all the things together

$$\int \phi_n^{el*}(\mathbf{r};\mathbf{R})\left(E_n(\mathbf{R})+\hat{T}_{NU}-E_{el,NU}\right)\sum_m^{\infty}\chi_m(\mathbf{R})\phi_m^{el}(\mathbf{r};\mathbf{R})\,d\mathbf{r}=0$$

$$=\left(E_n(\mathbf{R})-E_{el,NU}\right)\chi_n(\mathbf{R})-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2\chi_n(\mathbf{R})+\sum_m^{\infty}C_{nm}\chi_m(\mathbf{R})=0$$

$$\sum_m^{\infty}C_{nm}\chi_m(\mathbf{R})$$

$$\equiv\sum_m^{\infty}\left\langle n\left|-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2\right|m\right\rangle\chi_m(\mathbf{R})+\sum_m^{\infty}\left\langle n\left|-\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I\right|m\right\rangle\nabla_I\chi_m(\mathbf{R})$$

Collect the parts other than total energy

$$\left(-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2+E_n(\mathbf{R})\right)\chi_n(\mathbf{R})+\sum_m^{\infty}C_{nm}\chi_m(\mathbf{R})=E_{el,NU}\chi_n(\mathbf{R})$$

$$\hat{H}^0(\mathbf{r};\mathbf{R})\phi_n^{el}(\mathbf{r};\mathbf{R})=E_n(\mathbf{R})\phi_n^{el}(\mathbf{r};\mathbf{R})$$

BO Approximation 6

Born-Oppenheimer Approximation: **ignore all $\mathbf{C}_{\mathbf{nm}}$**

$$\left(-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2 + E_n(\mathbf{R})\right)\chi_n(\mathbf{R}) = E_{el,NU}\,\chi_n(\mathbf{R})$$

$$\hat{H}^0(\mathbf{r};\mathbf{R})\phi_n^{el}(\mathbf{r};\mathbf{R}) = E_n(\mathbf{R})\phi_n^{el}(\mathbf{r};\mathbf{R})$$

Nuclear wavefunction is given by the expansion coefficient!

$$\hat{H}_{NU}(\mathbf{R})\chi_{n,v_n}^{NU}(\mathbf{R}) = E_{el,NU}\,\chi_{n,v_n}^{NU}(\mathbf{R})$$

$$\hat{H}_{NU}(\mathbf{R}) = \left(-\frac{1}{2}\sum_{I=1}^{N}\frac{1}{M_I}\nabla_I^2 + V(\mathbf{R})\right)$$

The potential energy that the nucleus feels *V*(**R**) is the energy of the electron E_n(**R**) at that geometry **R**!

You have separated the motion of the electron and nucleus.

Conclusion of Born-Oppenheimer Approximation

$$\hat{H}^{0}(\mathbf{r};\mathbf{R})\phi_{n}^{el}(\mathbf{r};\mathbf{R}) = E_{n}(\mathbf{R})\phi_{n}^{el}(\mathbf{r};\mathbf{R})$$

$$\hat{H}_{NU}(\mathbf{R})\chi_{n,v_n}^{NU}(\mathbf{R}) = E_{el,NU}\,\chi_{n,v_n}^{NU}(\mathbf{R})$$

Now you can say nuclear wave function on the n-th electronic state

$$\Psi(\mathbf{r},\mathbf{R}) = \phi_{n}^{el}(\mathbf{r};\mathbf{R})\chi_{n,v_n}^{NU}(\mathbf{R})$$

Electron moves so fast that it does not care about **how "fast" (much slower compared to electron) the nucleus is moving**.

Another way to consider is when the electron goes from a certain state to another the nucleus does not move:
Franck-Condon principle.