

## 10.675 LECTURE 10

RICK RAJTER

### 1. TODAY

- MP2, 3, 4
- DFT Intro
- DFT Theorems
- DFT Functionals

### 2. METHODS

Car-Parrinello Molecular Dynamics - Works using plane waves.

CI, can only be used for small systems because it scales as  $N!$

Transition State Theory  $K_a = \frac{kt}{h} e^{-\frac{\Delta G}{RT}}$

### 3. PERTURBATION THEORY

Perturbation → needs normalization

$$\int \Psi_i^o \Phi_i dr = 1$$

$$\int \Psi_i^{*o} \Psi_i^n = 0 \quad n = 1, 2, 3, \dots$$

$$E_i^o = \int \Psi_i^{*o} H_o \Psi_i^o dr$$

$$E_i^1 = \int \Psi_i^{*o} V \Psi_i^o dr$$

$$E_i^2 = \int \Psi_i^{*o} V \Psi_i^1 dr$$

$$\text{let } \Psi_i^1 = \sum C_n' \Psi_m^o$$

But we know  $(E_i - H_o)\Psi_i^1 = (V - E_i^1)\Psi_i^o$  from first order expansion of  $\Psi_i^1$

Substitute into and multiply by  $\Psi_m^o$

$$\Rightarrow \int dr \Psi_m^o (E_i - H_o) \sum C_n' \Psi_n^o = \int dr \Psi_m^o (V - E_i^1) \Psi_i^o$$

$$= \int dr \Psi_m^o (E_i - \sum_n C_n' E_n^o) \Psi_n^o = \int dr \Psi_m^o V \Psi_i^o - E_i^1 \int \Psi_m^o \Psi_i^o dr$$

for  $m = n$  or terms = 0

Solve for  $C_n'$ 's

$$C_n' = \frac{\int \Psi_n^o V \Psi_i^o}{E_i^o - E_n^o}$$

Use to calculate first, second order calculations.

$$E_i^2 = \int \Psi_i^o V \Psi_i^1 dr = \int \Psi_i^o V \sum_n C_n' \Psi_n^o dr$$

$$= \sum \int \Psi_i^o V \frac{V(\int dr V_n^o V \Psi_i^o) \Psi_n^o dr}{E_i^o - E_n^o}$$

$$= \sum \frac{(\int \Psi_i^o V \Psi_n^o dr)^2}{E_i^o - E_n^o}$$

Now, we plug in V.

$$E_o^i = \int \Psi_o^i (\sum^N \sum^N \frac{1}{r_i - r_j} - \sum J_i - K_i) \Psi_o^i dr \Rightarrow \text{First order correction}$$

$$= \frac{1}{2} \sum_a \sum_b (J_{ab} - K_{ab}) - \sum_a \sum_b (J_{ab} - K_{ab})$$

$$= E_o + E_o^1 = \sum_a \epsilon_a - \frac{1}{2} \sum_a \sum_b (J_{ab} - K_{ab}) = E_o^{HF}$$

Where the coefficient of  $\frac{1}{2}$  is to eliminate double counting.

Date: Fall 2004.

This Mean's that the 2nd order term is actually a first order correction.

$$E_o^2 = \sum_a \sum_b b < a \sum_r \sum_{r < s} \frac{(\int \Psi_o \sum_i \sum_{j < i} \frac{1}{r_{12}} \Psi_{ab}^{rs} dr_i dr_j)^2}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s}$$

MP2, 2nd order comes from double excitations.

#### 4. MP VS. HF COMPARISONS

How does it stack up? Gaussian can do up to MP5

Relative Timing on methylammonium with (6-31G\* Basis Set)

HF 1.0 (reference state)

MP2 1.5

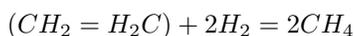
MP3 3.6

MP4 5.8

So, less than an order of magnitude difference in time scale.

Why is it not more expensive? Hartree mean field is essentially double counting, which MP eliminates.

#### 5. BOND ENERGY COMPARISONS - ETHYLENE 6-31G\*\* BASIS SET



<i>Method</i>	<i>CalculatedEnergies</i>	<i>RXNEnergy</i>
<i>HF</i>	-78.03884	-64
<i>MP2</i>	-78.31682	-60.9
<i>MP3</i>	-78.33998	-62.4
<i>MP4</i>	-78.344	-61.3
<i>MP5</i>	-78.35306	-59.7

All energies are in hartree's. Experimental zero point corrected energy is 57.2 hartree.

Need to subtract off zero point energy data from bond vibrations.

CO hartree theory completely messes up the dipole moment, even predicts the opposite sign!

#### 6. DENSITY FUNCTIONAL THEORY - DFT

In hartree theory, we have minimized the energy functional  $E[\Psi]$  if  $\rho(\vec{r})$  is the external potential (nuclei), it defines the hamiltonian for an N electron system.

Question, can we express E in terms of  $\rho(\vec{r})$  such that  $E = E[\rho]$ ?

First Theorem. (Hohenberg-Kohn, 1964)

$v(\vec{r})$ , and thus the many body ground state (no excited states) is determined uniquely by  $\rho(\vec{r})$  for an N-electron non-degenerate system (within a trivial additive constant).

If we know  $\rho(r)$  of the ground state, then we know  $v(r)$  and ground state energy, as well as all other measurable properties.

The proof is in the pudding... or in the first section of the paper.

Essentially, it's not possible to give 2 different  $v(r)$ 's for the same potential well.

$v(r) \rightarrow \rho(r)$  uniquely

$v'(r) \rightarrow \Psi'(r) \rightarrow \rho(r)$

$v(r) \rightarrow \Psi \rightarrow \rho(r)$

From variational principle, we know that  $\Psi' = \Psi$  unless  $v'(r) - v(r) = \text{constant}$  or 0. Assume it's not true for  $\rho$ .

$$E'[\Psi' H \Psi'] = \int \Psi' H \Psi' < \int \Psi H' \Psi$$

$$E' < E + \int (v'(r) - v(r)) \rho(r) dr$$

Do the same for E

$$E < E' + \int (v(r) - v'(r)) \rho(r) dr$$

Which results in  $E + E' < E + E'$  and that can't happen.

So, we can't get the same  $\rho$  from 2 different external potentials.