10.675 LECTURE 4

RICK RAJTER

1. Today

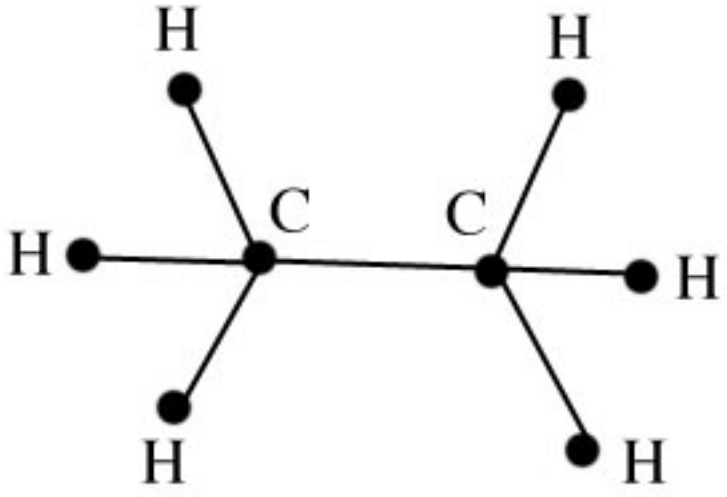
→ Dirac Notation
→ Exploring PES
→ Algorhythms for Geometry Optimization
→ Zero Point Energies and Stat Mech.

2. Concepts

minima and transition states.

3. PES - Potential Energy Surface

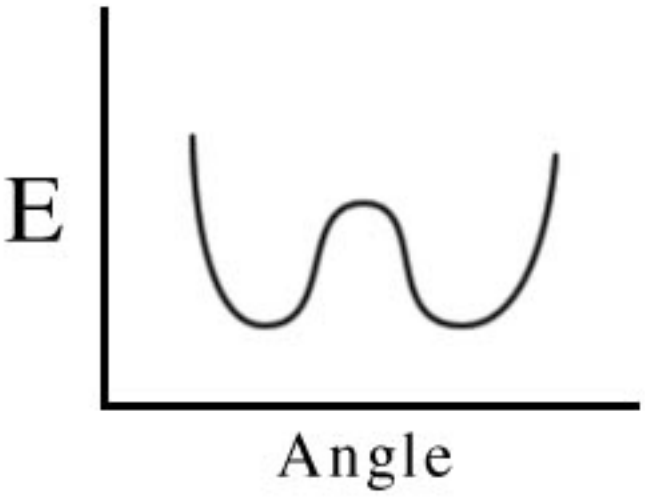
Example: Rotation of carbon-carbon bond in ethane (C_2H_6).



In general, one can look at E_o as a function of any parameter. In this example, we will use orientation.
3N - 6 degrees of freedom.

Date: Fall 2004.

BO approximation (atoms are fixed, nuclei mass is infinite).



4. Method

$H_i^{method}\Psi_i = \epsilon_i\Psi_i$
$H_i^{method} = \frac{-1}{2}\nabla^2 - \sum^N \frac{Z_k}{r_{1K}} + V_1^{method}$
Where V_1 varies depending on the method we are using.
Examples of Methods: Molecular obital vs Density functional theory.
$V_i^{method} = \sum_{j=2}^N \int \frac{\rho(r_j)}{\vec{r_i}-\vec{r_j}} d\vec{r_j} + V_i^{\chi method} + V_i^{Cmethod}$
Where $\sum_{j=2}^N \int \frac{\rho(r_j)}{\vec{r_i}-\vec{r_j}} d\vec{r_j}$ is the mean field term.
$V_i^{\chi method}$ exchange term (pauli exchange)
$V_i^{Cmethod}$ correlation term.
Use a trial basis set $\Psi_i = \sum c_{ij} g_j$
SOLVE $E_o = \sum_1^N \int \Psi_i^* H_i^{method} \Phi_i d\vec{r}$+ Nuc - Nuc terms.

5. Solving

Need to find c_{ij}'s which minimize E_o. Here's the detailed method.
1) Choose molecule nuclear positions + num of electrons
2) Choose method
3) Choose basis set
4) Choose initial guess for $c'_{ij}s$
5) Solve Eigenvalue equation for new c_ij's
6) Is $E_{old} - E_{new} < ATOL$?
7) If no, return to step 4 with new c_{ij}'s
7b) If yes, calculate the forces on the nuclei
8) Is the $force < force^{ATOL}$? If yes, finished.
9) If not, update geometry, goto step 4.

6. Details

$E_o^{elec} = V^{nucleous} = E(\vec{x})$ meaning the energy of the electron is dependent on the potential of the nuclei.
$\vec{x} = 3N = (R_{1x}, R_{1y}, R_{1z}, R_{2x}, R_{2y}, ...)$
In the geometry optimization, we want to minimize such that
$dE/dx = 0 or < ATOL.$
expand $E_{k+1}(\vec{x}_{k+1}) = E_k + \vec{g}_k^t \cdot (\vec{x}_{k+1} - \vec{x}_k) + 1/2(\vec{x}_{k+1} - \vec{x}_k)^T \bar{\bar{\beta}}_k (\vec{x}_{k+1} - \vec{x}_k)$
Where: k is the step
$\vec{g}_k^t$ are the gradient forces
$\bar{\bar{\beta}}_k$ is the Hessian Matrix.
SCF gives us $E_o, \vec{g}$. Then, update $\bar{\bar{\beta}}_k$ and it's inverse $\bar{\bar{H}}_k$
$\frac{dE_{k+1}}{dx_{k+1}} = \vec{g}_{k+1} g_k + \bar{\bar{\beta}}_k (\vec{x}_{k+1} - x_k) = 0$
$\rightarrow \vec{P}$ step size to move atoms to next position.
$\vec{P}_k = \vec{x}_{k+1} - vecx_k = \bar{\bar{\beta}}_k^{-1} \vec{g}_k = -\bar{\bar{H}}_k \vec{g}_k$

7. updating $\bar{\bar{\beta}}_k$

Method $\rightarrow$ steepest descent.

$$\bar{\bar{\beta}} = c \begin{pmatrix} 1 & 0 & 0 & 0 & . & . \\ 0 & 1 & 0 & 0 & . & . \\ 0 & 0 & 1 & 0 & . & . \\ 0 & 0 & 0 & 1 & . & . \\ . & . & . & . & . & . \\ . & . & . & . & . & . \end{pmatrix}$$

c=1 or $\neq 1$
Newton's Method
$\bar{\bar{\beta}} \rightarrow$ calculated explicitly (great for transition states)
$\bar{\bar{H}}_k \bar{\bar{H}}_{k-1} - \frac{\bar{\bar{H}}_{k-1} \Delta \vec{g}_k \Delta \vec{g}_k^T \bar{\bar{H}}_{k-1}}{\Delta \vec{g}_k^T \bar{\bar{H}}_{k-1} \Delta \vec{g}_k}$