1. Today

→ Dirac Notation
→ Exploring PES
→ Algorithms 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.
BO approximation (atoms are fixed, nuclei mass is infinite).

4. Method

\[ H_{i}^{method} \Psi_i = \epsilon_i \Psi_i \]
\[ H_{i}^{method} = \frac{-1}{2} \nabla^2 - \sum_{i,k}^{N} \frac{Z_k}{r_{ik}} + V_{i}^{method} \]

Where \( V_1 \) varies depending on the method we are using.

Examples of Methods: Molecular orbital vs Density functional theory.

\[ V_{i}^{method} = \sum_{j=2}^{N} \int \frac{\rho(r_j)}{r_{i-j}} dr_j^2 + V_{i}^{\text{exchange}} + V_{i}^{\text{correlation}} \]

Where \( \sum_{j=2}^{N} \int \frac{\rho(r_j)}{r_{i-j}} dr_j^2 \) is the mean field term.

\[ V_{i}^{\text{exchange}} \] exchange term (pauli exchange)

\[ V_{i}^{\text{correlation}} \] correlation term.

Use a trial basis set \( \Psi_i = \sum c_{ij} g_j \)

SOLVE \( E_0 = \sum_i^{N} \int \Psi_i^* H_{i}^{method} \Phi_i dr^2 + \text{Nuc} - \text{Nuc terms} \).

5. Solving

Need to find \( c_{ij} \)'s which minimize \( E_0 \). 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 \( \text{force} < \text{force}_{ATOL} \)? If yes, finished.
9) If not, update geometry, goto step 4.
6. Details

\[ E_{\text{elecc}} = V^{\text{nucleus}} = E(\vec{x}) \] meaning the energy of the electron is dependent on the potential of the nuclei.

\[ \vec{x} = 3N = (R_{1x}, R_{1y}, R_{1z}, R_{2x}, R_{2y}, \ldots) \]

In the geometry optimization, we want to minimize such that

\[ \frac{dE}{dx} = 0 \text{ or } \Delta \text{ATOL}. \]

expand \( E_{k+1}(\vec{x}_{k+1}) = E_k + g_k^T(\vec{x}_{k+1} - \vec{x}_k) + 1/2(\vec{x}_{k+1} - \vec{x}_k)^T \beta_k(\vec{x}_{k+1} - \vec{x}_k) \)

Where: \( k \) is the step

\( g_k \) are the gradient forces

\( \beta_k \) is the Hessian Matrix.

SCF gives us \( E_o, g \). Then, update \( \tilde{\beta}_k \) and it’s inverse \( \tilde{H}_k \)

\[ \frac{dE_{k+1}}{dx_{k+1}} = \tilde{g}_{k+1} + \tilde{\beta}_k(\vec{x}_{k+1} - \vec{x}_k) = 0 \]

→ \( \tilde{\beta} \) step size to move atoms to next position.

\[ \vec{P}_k = \vec{x}_{k+1} - \vec{v}ex_k = \tilde{\beta}_k^{-1}\tilde{g}_k = -\tilde{H}_k\tilde{g}_k \]

7. Updating \( \tilde{\beta}_k \)

Method → steepest descent.

\[ \tilde{\beta} = c \]

\[ \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ \vdots & \vdots & \vdots & \vdots \end{pmatrix} \]

\( c=1 \) or \( \neq 1 \)

Newton’s Method

\( \tilde{\beta} \rightarrow \) calculated explicitly (great for transition states)

\[ \tilde{H}_k\tilde{H}_{k-1} - \frac{\tilde{H}_{k-1}\Delta \tilde{g}_k\Delta \tilde{g}_k^T\tilde{H}_{k-1}}{\Delta \tilde{g}_k^T\tilde{H}_{k-1}\Delta \tilde{g}_k} \]