Transition State Searching with Vibronic Model

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Outline

• Introduction

- Vibronic model
- Potential energy surface and transition state
- Goal: A fast method of finding the transition state.
- Current project
 - Examples
 - Interesting cases

Introduction

- Born-Oppenheimer Approximation
- Potential Energy Surface
- Vibronic Model
- Transition State

Born-Oppenheimer (BO) Approximation

• Full Hamiltonian

$$\hat{H} = \hat{T}_N + \hat{H}_{el}$$

• Full Schrodinger Equation

 $\hat{H}(\stackrel{f}{r},\stackrel{i}{R})\Psi(\stackrel{f}{r},\stackrel{i}{R}) = E\Psi(\stackrel{f}{r},\stackrel{i}{R})$

• Electronic Schrodinger Equation at fixed R

$$\hat{H}_{el}(\vec{r};\vec{R})\Psi(\vec{r};\vec{R}) = E_{el}(\vec{R})\Psi(\vec{r};\vec{R})$$

Potential Energy Surface (PES)

• A potential energy surface (PES) is the function of the energy of a system with parameters (in this case, it's defined as nuclear coordinates).

$$E_{el}(\dot{R})$$

• Calculating PES is time-consuming

Vibronic Model

- Potential energy surface can be obtained by diagonalize the at many R
- Only the lower surface (smaller Eigenvalue) is important

$$V(R) = \begin{pmatrix} V_{A}(R) & V_{AB}(R) \\ \Gamma & \Gamma & \Gamma \\ V_{AB}(R) & V_{B}(R) \end{pmatrix} \qquad \begin{array}{c} V_{1}(R) \\ V_{1}(R) \\ V_{2}(R) \\ \end{array}$$

•Near the minima, the energy is parabolic; so we use a harmonic approximation

$$V_A(R) = V_A(0) + g^{\dagger}(R - R_A) + \frac{1}{2}(R - R_A)^{\dagger}K(R - R_A)$$

Vibronic Model





Vibronic Model

•Modeling of off-diagonal terms $V_{AB}(R)$ to make a smooth and coherent PES

$$V_{AB}(\dot{R}) = V_{AB}^{Harmonic}(\dot{R}) \cdot W(\dot{R})$$

•Widow function

$$\dot{W}(\dot{R}) = \exp(-\alpha(R - R_{TS})^{\dagger}(R - R_{TS}))$$



Goal for Constructing PES

- Capture transition state properties correctly.
 - Barrier Height $V_i(0)$
 - Gradient

fix the linear coupling constant gi (in VA)
$$g_i = \frac{\partial E}{\partial R_i}$$

• Hessian K)

$$H_{i,j} = \frac{\partial^2 E}{\partial R_i \partial R_j}$$

fix the curvature (the quadratic parameters

Transition state

- Stationary point on PES
- Highest point along the reaction coordinate
- Why TS is important
 - Reaction rates
 - Enzymatic reactions
- Common issues of transition state searching
 - Fail to converge
 - Robust methods are always expensive

Intrinsic Reaction Coordinate (IRC)

 Connecting the empirical concept of a reaction path to a model relevant to theoretical treatment is of interest in computational chemistry. IRC approach can connect the transition state and two stationary points on the PES.

Transition state searching with vibronic model



TS searching failed to converge



Current Status of the Project

- Gaussian
 - Geometry optimization and force constant calculations
 - For Minima and TS
 - IRC
- Testing several examples on the vibronic model
 - Geometry optimization (TS, done by Marcel)
 - IRC comparison (with Prateek)
- Some interesting cases

 $H_2CNH \leftrightarrow HCNH_2$







Reactant

TS

Product

 $H_2CNH \leftrightarrow HCNH_2$





 $H_2CNH \leftrightarrow HCNH_2$

Comparison of IRC Energies (ATAN)



Figure made by Prateek

 $H_2CNH \leftrightarrow HCNH_2$



Figure made by Prateek

$HCONHON \longleftrightarrow HCOHNHO$



Reactant

TS

Product

$HCONHON \longleftrightarrow HCOHNHO$







Figure made by Prateek





Reactant





Product









 $CH_2CHOH \longleftrightarrow CH_3CHO$

Comparison of IRC Energies (ATAN)



Figure made by Prateek













В





 CH_3O









CH_3O with Reference as TS1



CH_3O with Reference as TS1



 CH_3O



Figures made by Prateek

Thank you for listening!