

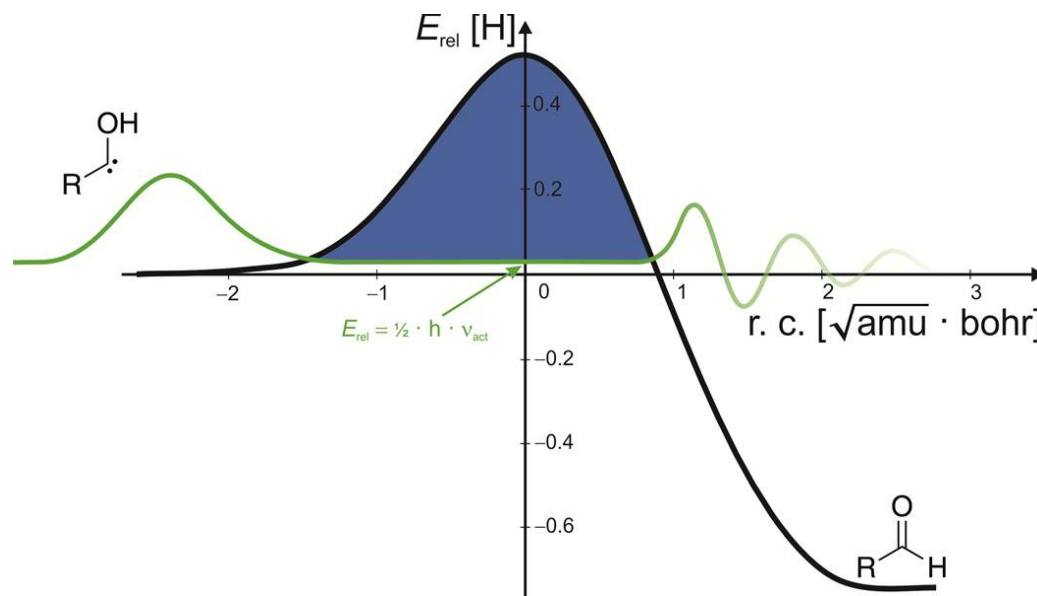


Presented by

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February 21th, 2014

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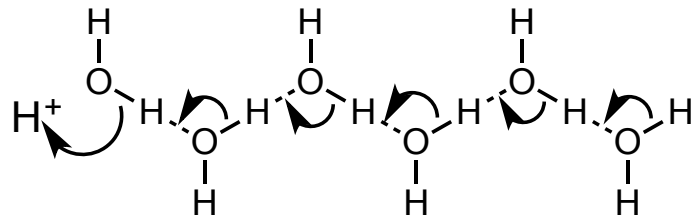




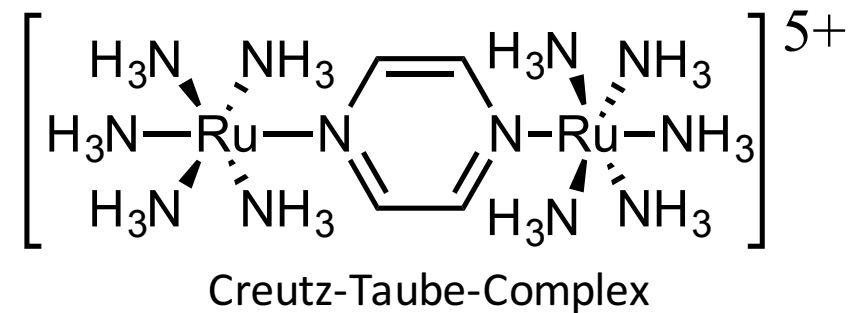
1. Tunneling processes
 2. WKB: Semiclassical approximation
 3. Tunneling approximation
 4. Workflow
 5. Program structure and algorithms
 6. Demo
 7. Future prospects
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- Examples in chemistry
 - Grotthuß mechanism



- Coordination chemistry





$$\varphi''(x) + \frac{4 \cdot \pi^2}{\hbar^2} \cdot k^2 \varphi(x) = 0$$

$$k^2 = 2 \cdot m[E - V(x)]$$

$$\varphi(x) = \exp\left(\frac{2 \cdot \pi \cdot i}{h}\right) \int y(x) dx$$

$$\frac{h}{2 \cdot \pi \cdot i} \cdot y' = k^2 - y^2$$

$$\lim_{h \rightarrow 0} y = y_0 = \frac{dS}{dx}$$



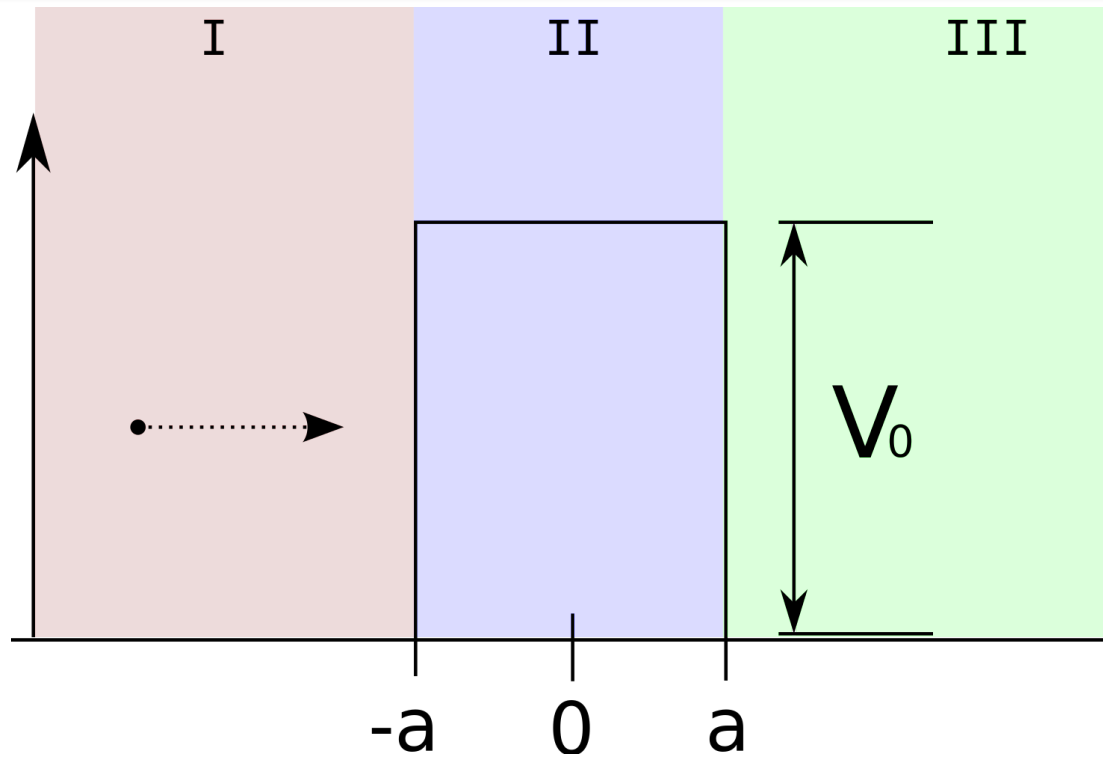
$$\left(\frac{d S}{d x}\right)^2 = y_0^2 = p^2$$

$$y = \sum_{v=0}^{\infty} \left(\frac{h}{2 \cdot \pi \cdot i}\right)^v \cdot y_v$$

$$y'_{v-1} + \sum_{\alpha=0}^v y_{\alpha} \cdot y_{v-\alpha} = 0$$

$$y(x) = \pm \int \sqrt{2 \cdot m \cdot (E - V'(x'))} dx'$$

$$\phi(x) = A \cdot \exp \left(\pm \frac{i}{\hbar} \int \sqrt{2 \cdot m \cdot (E - V'(x'))} dx' \right)$$

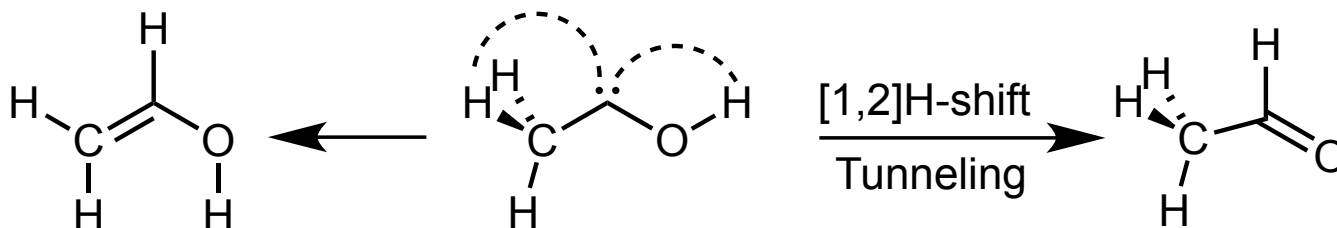


$$\ln |T|^2 \approx -2 \int_{\text{barrier}} \kappa(x) dx$$

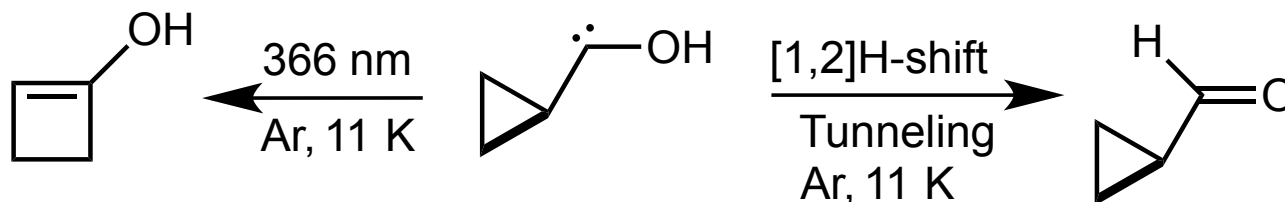
$$\kappa(x) = \sqrt{\frac{2m(V(x) - E)}{\hbar^2}}$$



- Tunneling in carbenes



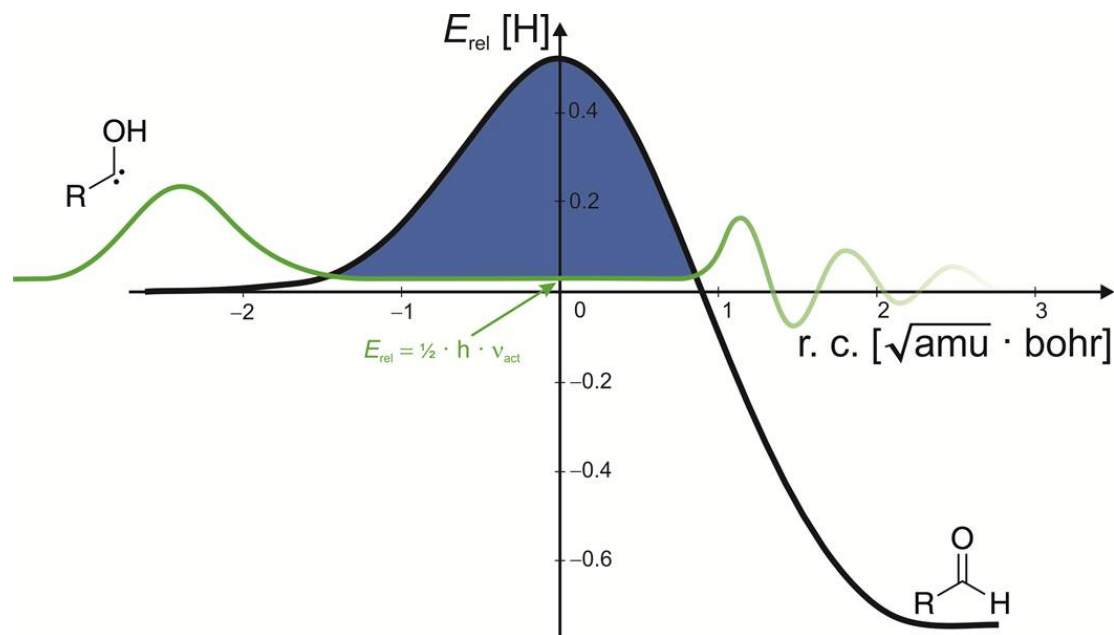
- Barrier of 28 kcal mol^{-1} vs. $22.6 \text{ kcal mol}^{-1}$



- Barrier of $21.9 \text{ kcal mol}^{-1}$ vs. $30.4 \text{ kcal mol}^{-1}$
- Tunneling Control

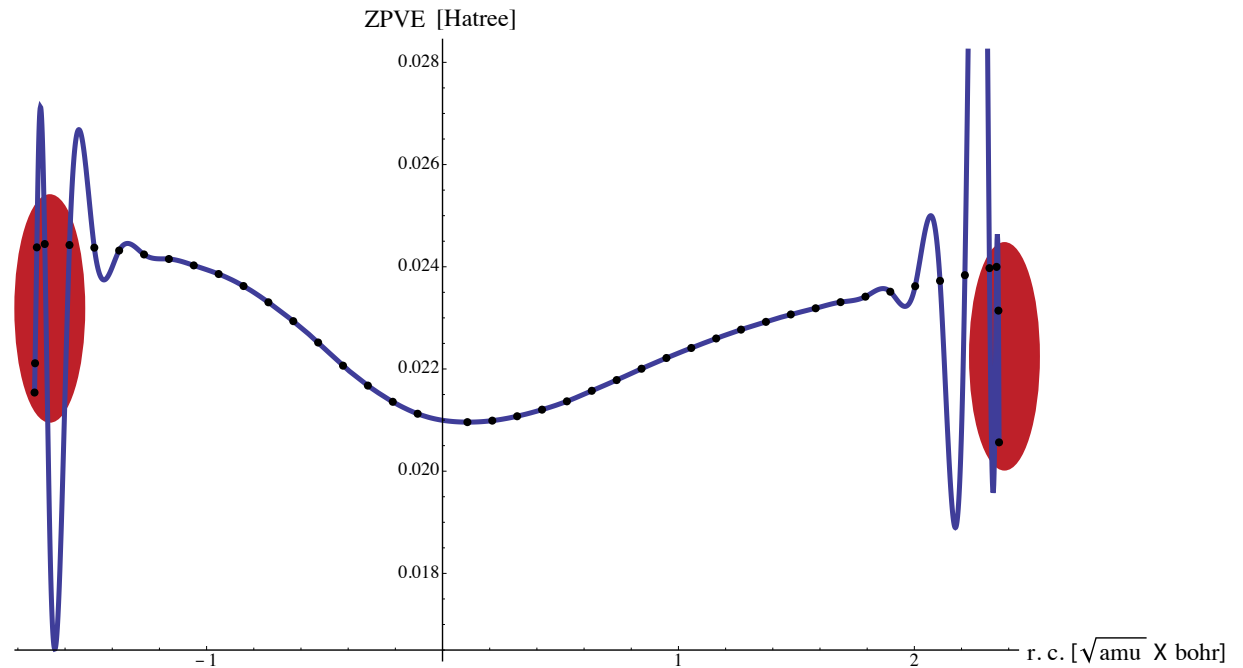


- Obtain transition state
- Compute IRC
- Compute ZPVE for each step
- Compute one-dimensional barrier action integrals
- Invoke WKB-Method





- Projected frequency
algorithm fails near minima
- Manual interpolation



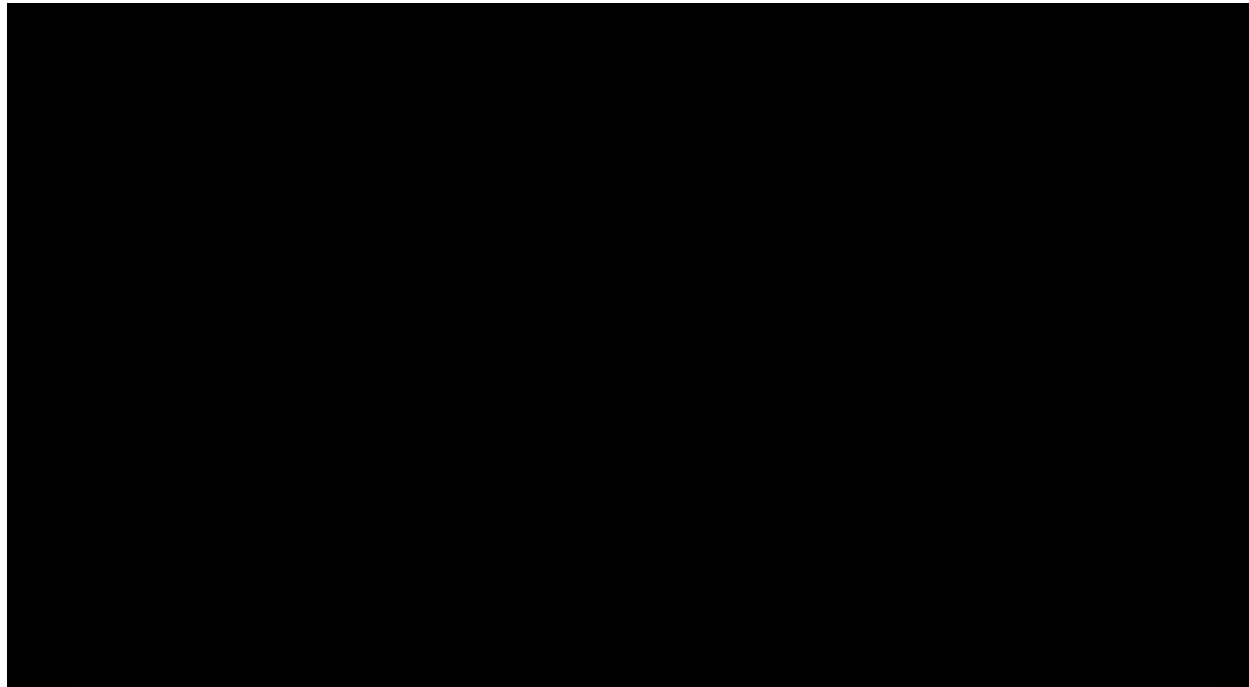


- Load IRC into program
- Load projected IRC into program
- Compute combined IRP
- Enter some parameters
- Compute half-lives
- Emphasis on reusable user friendly program
- Written entirely in C++ using Qt



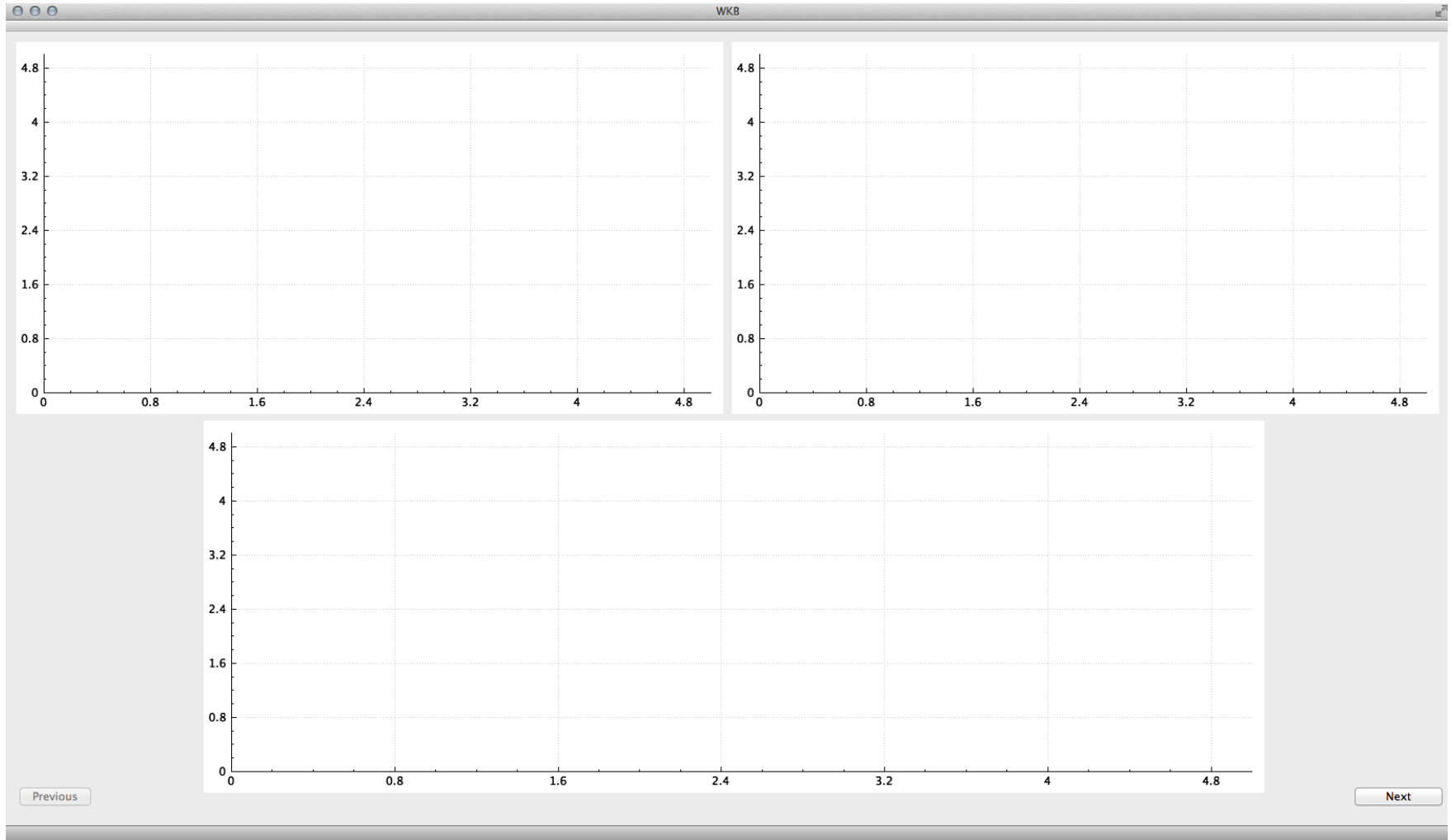


- ALGLIB
 - used for spline interpolation
- Qt
 - A c++ GUI library
- Root finding algorithm
- Integration



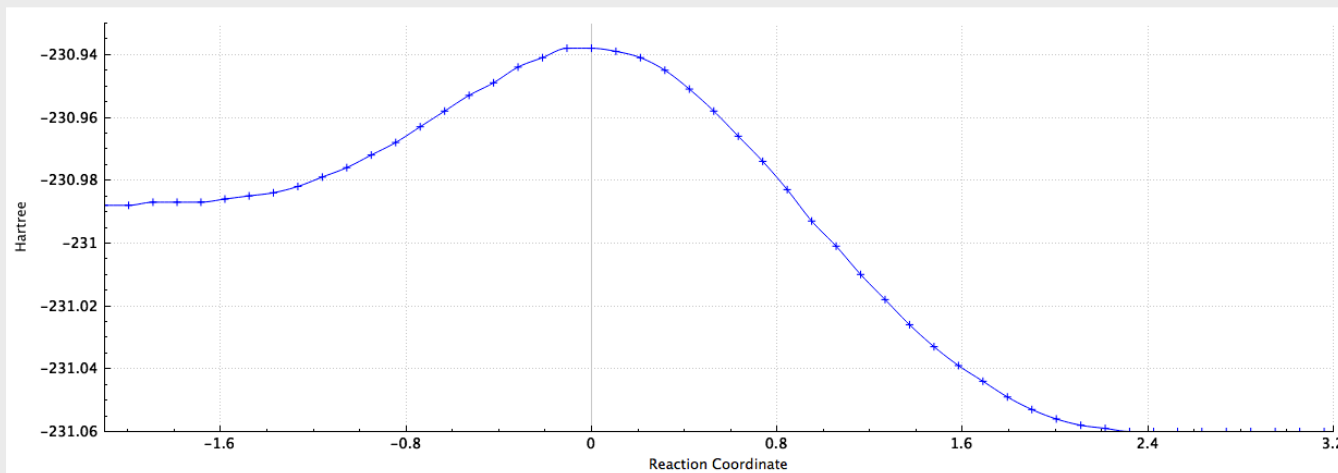
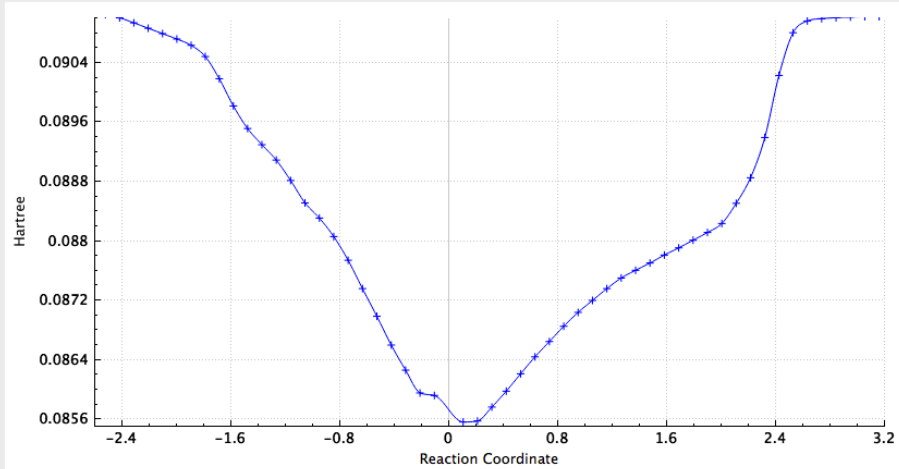
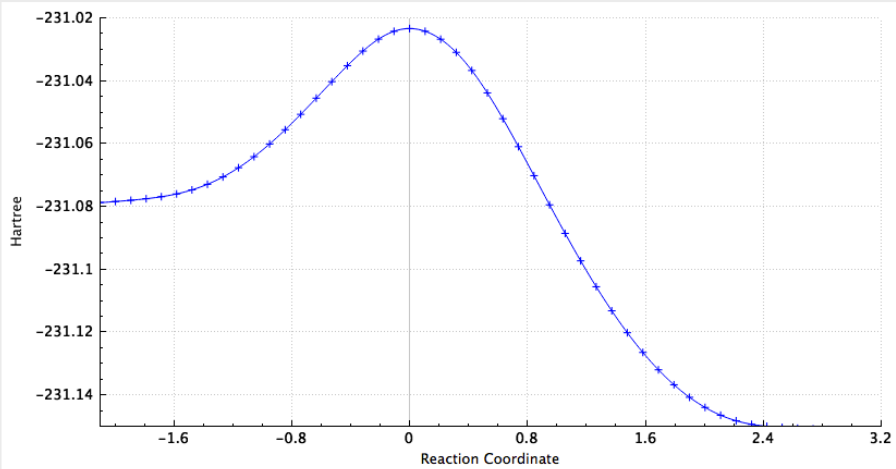


GUI





WKB

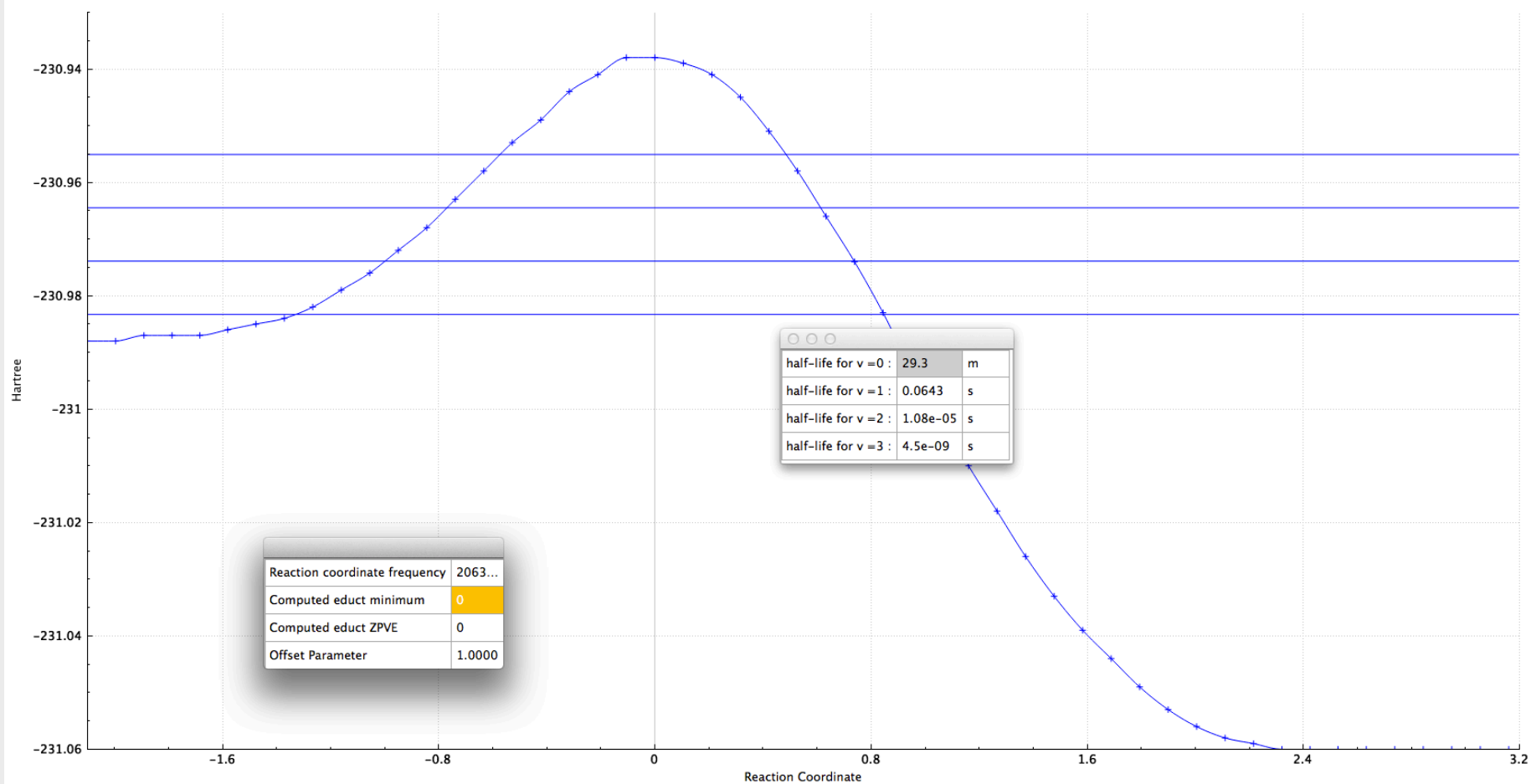


Previous

Next



WKB



Previous

Do the WKB!

Next



Parameters

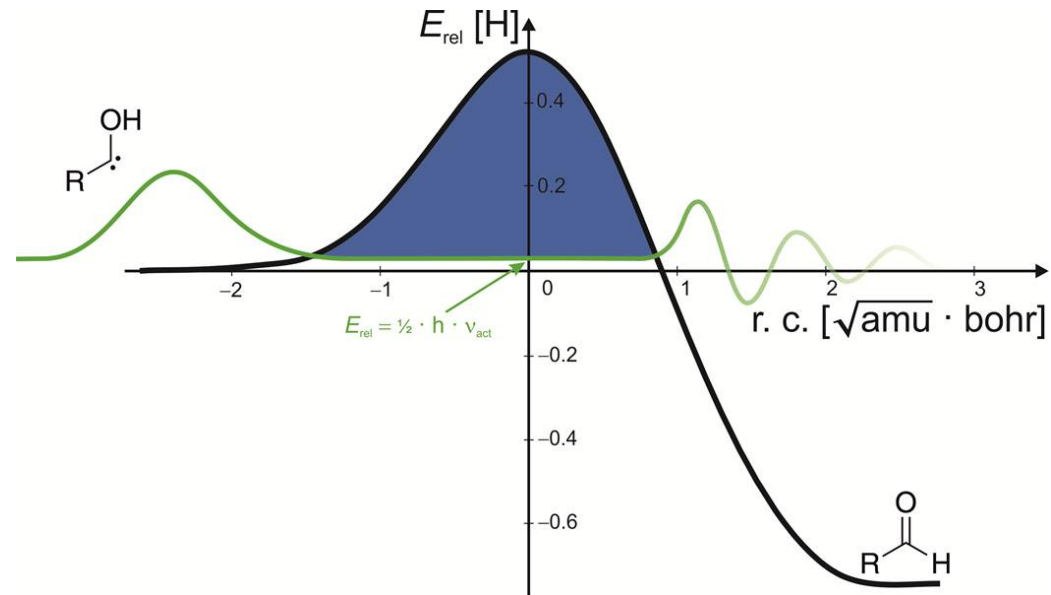
- Reaction coordinate frequency
 - The imaginary frequency from the TS
- Computed educt minimum
 - Can be zero
 - Left Value of curve is used
 - If not zero minimum will be used
- Computed educt ZPVE
 - ZPVE correction
- Scaling Parameter
 - factor that scales the function to be integrated

Reaction coordinate frequency	0.0
Computed educt minimum	0
Computed educt ZPVE	0
Offset Parameter	1.0000



WKB algorithm

- Calculate attempt energies
- Retrieve Parameters
- Sum educt energy with ZPVE
- Retrieve interpolation function
- Plot energy levels
- Find start points for integration
- Integration

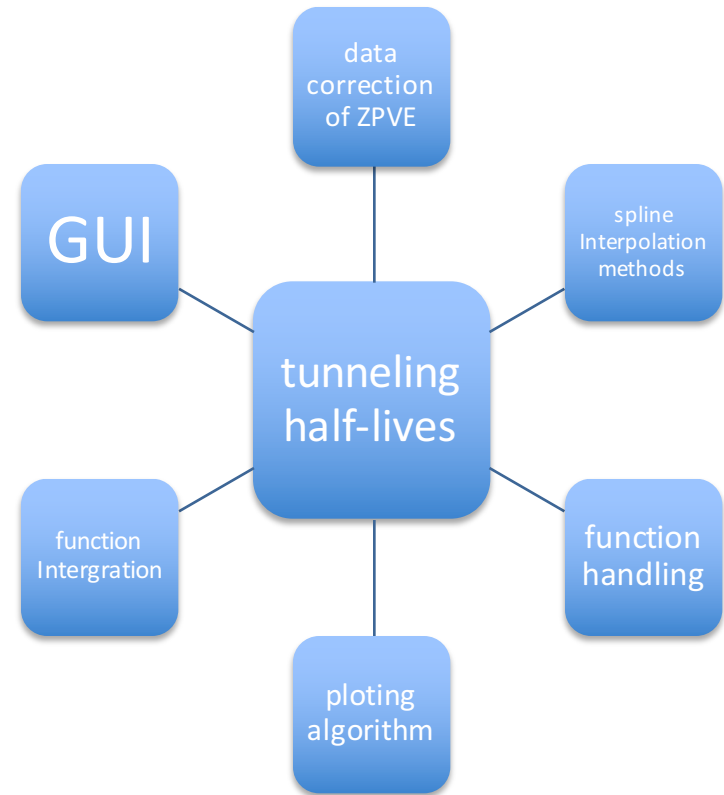




DEMO



- Redo, undo check
- ssh terminal for gaussian input
- project file format
- Advanced testing on every platform
- Own spline interpolation algorithm





- **Prof. Dr. Peter R. Schreiner, Ph.D.**, for allowing me to work on this current topic in his group at the Justus-Liebig Universität Gießen and for the possibility to continue my work here
- **Dr. Dennis Gerbig** and **Dr. David Ley** for their help and for leading my way through this project
- the whole **PRS Group** for cookies, great conversations and for highly enjoyable months