Progress Towards the Calculation of Anharmonic Vibrational States Without a Pre-Existing Potential Energy Surface

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What Systems Are We Trying to Understand???

Highly fluxional molecules and clusters
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Very challenging to accurately model:
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Grid based methodologies scale poorly with system size
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  - Implementation and viability of reduced dimensional approaches highly system dependent
What Systems Are We Trying to Understand???

Highly fluxional molecules and clusters

Very challenging to accurately model:

Grid based methodologies scale poorly with system size

Implementation and viability of reduced dimensional approaches highly system dependent

Construction of global potential energy surfaces very challenging
The General Scheme
The General Scheme

Monte Carlo Sample
Configuration Space
An Intelligent Way to Sample Configuration Space
An Intelligent Way to Sample Configuration Space

Use importance sampling Monte Carlo
An Intelligent Way to Sample Configuration Space

Use importance sampling Monte Carlo

\[
\int_V f(\vec{x})dV = \int_L f(\vec{x}) \frac{g(\vec{x})}{g(\vec{x})} dV \approx \frac{V}{N} \sum_{i=1}^{N} \frac{f(\vec{x}_i)}{g(\vec{x}_i)}
\]
An Intelligent Way to Sample Configuration Space

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\[
\alpha \text{ from } \left. \frac{\partial^2 V}{\partial r^2} \right|_{r=r_{eq}}
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\[\alpha_{samp} = \beta_{fat} \alpha\]

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|\Psi_0|^2 \propto e^{-\alpha r^2}
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\[
\left. \frac{\partial^2 V}{\partial r^2} \right|_{r=r_{eq}}
\]

\[
\frac{\partial V}{\partial r}
\]
The General Scheme

Monte Carlo Sample Configuration Space

Construct Initial Basis
The Initial Basis (2D Example)
The Initial Basis (2D Example)

\[ \Psi_{0,0}^{(1)} \propto e^{-\frac{\alpha_1 r^2}{2}} e^{-\frac{\alpha_2 R^2}{2}} \]
The Initial Basis (2D Example)

\[ \psi_{0,0}^{(1)} \propto e^{-\frac{\alpha_1 r^2}{2}} e^{-\frac{\alpha_2 R^2}{2}} \]

Basis functions change each iteration
The Initial Basis (2D Example)

\[ \Psi^{(1)}_{0,0} \propto e^{-\frac{\alpha_1 r^2}{2}} e^{-\frac{\alpha_2 R^2}{2}} \]

Basis functions change each iteration

\[ \Psi^{(1)}_{m,n} = \sum_{j=1}^{m} K^{(1)}_{m,n;m-j,n} r^j \Psi^{(1)}_{m-j,n} + \sum_{j=1}^{n} K^{(1)}_{m,n;m,n-j} R^j \Psi^{(1)}_{m,n-j} \]
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\]

Phase factors
The Initial Basis (2D Example)

\[ \Psi_{0,0}^{(1)} \propto e^{-\frac{\alpha_1 r^2}{2}} e^{-\frac{\alpha_2 R^2}{2}} \]

Basis functions change each iteration

\[ \Psi_{m,n}^{(1)} = \sum_{j=1}^{m} K_{m,n;m-j,n}^{(1)} r_j \Psi_{m-j,n}^{(1)} + \sum_{j=1}^{n} K_{m,n;m,n-j}^{(1)} R_j \Psi_{m,n-j}^{(1)} \]

Phase factors

Will be made orthogonal to all previously built states and normalized
The Initial Basis (2D Example)

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\[
\overline{\Psi}^{(1)}_{m,n} = \sum_{j=1}^{m} K^{(1)}_{m,n;m-j,n} r^j \Psi^{(1)}_{m-j,n} + \sum_{j=1}^{n} K^{(1)}_{m,n;m,n-j} R^j \Psi^{(1)}_{m,n-j}
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\]

\[
\begin{align*}
\Psi_{0,0} & \quad \Psi_{1,0} & \quad \Psi_{0,1} \\
\Psi_{2,0} & \quad \Psi_{1,1} & \quad \Psi_{0,2} \\
\Psi_{3,0} & \quad \Psi_{2,1} & \quad \Psi_{1,2} & \quad \Psi_{0,3}
\end{align*}
\]
The Initial Basis (2D Example)

\[
\overline{\Psi}_{m,n}^{(1)} = \sum_{j=1}^{m} K_{m,n;m-j,n}^{(1)} r^j \Psi_{m-j,n}^{(1)} + \sum_{j=1}^{n} K_{m,n;m,n-j}^{(1)} R^j \Psi_{m,n-j}^{(1)}
\]

\[
\overline{\Psi}_{2,1}^{(1)} = K_{2,1;2,0}^{(1)} R \Psi_{2,0}^{(1)} + K_{2,1;1,1}^{(1)} r \Psi_{1,1}^{(1)} + K_{2,1;0,1}^{(1)} r^2 \Psi_{0,1}^{(1)}
\]
The Initial Basis (2D Example)

\[ \Psi^{(1)}_{m,n} = \sum_{j=1}^{m} K_{m,n;m-j,n}^{(1)} r^j \Psi^{(1)}_{m-j,n} + \sum_{j=1}^{n} K_{m,n;m,n-j}^{(1)} R^j \Psi^{(1)}_{m,n-j} \]
The Initial Basis (2D Example)

The initial basis for a 2D example is given by:

\[
\overline{\Psi}_{m,n}^{(1)} = \sum_{j=1}^{m} K_{m,n;m-j,n}^{(1)} R^j \Psi_{m-j,n}^{(1)} + \sum_{j=1}^{n} K_{m,n;m,n-j}^{(1)} R^j \Psi_{m,n-j}^{(1)}
\]

The initial basis functions are shown graphically with labels for indices and coefficients.
The Initial Basis (2D Example)

\[ \overline{\Psi}^{(1)}_{m,n} = \sum_{j=1}^{m} K^{(1)}_{m,n;m-j,n} r_j \Psi^{(1)}_{m-j,n} + \sum_{j=1}^{n} K^{(1)}_{m,n;m,n-j} R_j \Psi^{(1)}_{m,n-j} \]
The General Scheme

Monte Carlo Sample Configuration Space

Construct Initial Basis

Build and Diagonalize Hamiltonian Matrix
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New Basis Set Construction in 1D

\[ H_{mn}^{(j)} = \langle \Psi_m^{(j)} | \hat{H} | \Psi_n^{(j)} \rangle \]
New Basis Set Construction in 1D

\[ H^{(j)}_{mn} = \langle \Psi_m^{(j)} | \hat{H} | \Psi_n^{(j)} \rangle \]

Iteration Number
New Basis Set Construction in 1D

\[ H_{mn}^{(j)} = \langle \Psi_m^{(j)} | \hat{H} | \Psi_n^{(j)} \rangle \]

\[ \{ \tilde{\Psi}^{(j)} \}, \{ E^{(j)} \} \]

Diagonalization
New Basis Set Construction in 1D

\[ H_{mn}^{(j)} = \langle \Psi_m^{(j)} | \hat{H} | \Psi_n^{(j)} \rangle \]

Diagonalization

\[ \{ \tilde{\Psi}^{(j)} \}, \{ E^{(j)} \} \]

Eigenstates used to construct next generation of basis functions
New Basis Set Construction in 1D

\[ H_{mn}^{(j)} = \langle \Psi_m^{(j)} | \hat{H} | \Psi_n^{(j)} \rangle \]

Diagonalization

\[ \{ \tilde{\Psi}^{(j)} \}, \{ E^{(j)} \} \]

Eigenstates used to construct next generation of basis functions

Assignment via:

\[ \max \left( \left| \langle \tilde{\Psi}_k^{(j)} | \hat{r} | \Psi_{m-1}^{(j)} \rangle \right|^2 \right) \Rightarrow \tilde{\Psi}_m^{(j)} \]
New Basis Set Construction in 1D

\[ H_{mn}^{(j)} = \langle \Psi_{m}^{(j)} | \hat{H} | \Psi_{n}^{(j)} \rangle \]

\[ \{ \Psi^{(j+1)} \} \]

Eigenstates used to construct next generation of basis functions

Assignment via:

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\[ H_{mn}^{(j)} = \langle \Psi_m^{(j)} | \hat{H} | \Psi_n^{(j)} \rangle \]

Diagonalization

Define an active space:

\[ \{ \Psi^{(j+1)} \} \]

Eigenstates used to construct next generation of basis functions

Assignment via:

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New Basis Set Construction in 1D

\[ H_{mn}^{(j)} = \langle \Psi_m^{(j)} | \hat{H} | \Psi_n^{(j)} \rangle \]

Diagonalization

Define an active space:

\[ \{ \Psi_m^{(j+1)} \}_{\text{active}} = \{ \tilde{\Psi}_m^{(j)} \}_{\text{active}} \]

Eigenstates used to construct next generation of basis functions

Assignment via:

\[ \max \left( \left| \frac{\langle \tilde{\Psi}_k^{(j)} | \hat{r} | \Psi_m^{(j)} \rangle}{\langle \tilde{\Psi}_k^{(j)} | \tilde{\Psi}_m^{(j)} \rangle} \right|^2 \right) \Rightarrow \tilde{\Psi}_m^{(j)} \]
New Basis Set Construction in 1D

\[ H_{mn}^{(j)} = \langle \Psi_m^{(j)} | \hat{H} | \Psi_n^{(j)} \rangle \]

Define an active space:

\[ \{ \Psi_{m}^{(j+1)} \}_{active} = \{ \tilde{\Psi}_{m}^{(j)} \}_{active} \]

\[ \Psi_{m}^{(j+1)} \notin active \rightleftharpoons \sum_{k=1}^{m} \kappa_{m,m-k}^{(j+1)} r^k \Psi_{m-k}^{(j+1)} \]

Eigenstates used to construct next generation of basis functions

Assignment via:

\[ \text{max} \left( \left| \langle \tilde{\Psi}_k^{(j)} | \hat{r} | \Psi_{m-1}^{(j)} \rangle \right|^2 \right) \Rightarrow \tilde{\Psi}_m^{(j)} \]
New Basis Set Construction in 1D

$$H_{mn}^{(j)} = \langle \Psi_m^{(j)} | \hat{H} | \Psi_n^{(j)} \rangle$$

Eigenstates used to construct next generation of basis functions

Assignment via:

$$\max \left( \left| \langle \Psi_k^{(j)} | \hat{r} | \Psi_{m-1}^{(j)} \rangle \right|^2 \right) \Rightarrow \Psi_m^{(j)}$$

Define an active space:

$$\left\{ \Psi_m^{(j+1)} \right\}_{\text{active}} = \left\{ \tilde{\Psi}_m^{(j)} \right\}_{\text{active}}$$

$$\Psi_m^{(j+1)}_{m \notin \text{active}} = \sum_{k=1}^{m} \kappa_{m,m-k}^{(j+1)} r_k \Psi_{m-k}^{(j+1)}$$
New Basis Set Construction in 1D

\[ \left\{ \Psi^{(j+1)} \right\} \rightarrow H^{(j)} \rightarrow \left\{ \tilde{\Psi}^{(j)} \right\}, \left\{ E^{(j)} \right\} \rightarrow \left\{ \Psi^{(j)} \right\} {
New Basis Set Construction in 1D

\[
\begin{align*}
\{\Psi^{(j+1)}\} & \xrightarrow{\text{MxM Matrix}} \{\tilde{\Psi}^{(j)}\}, \{E^{(j)}\} \\
\{\Psi^{(j+1)}\} & \xrightarrow{H^{(j)}} \text{MxM Matrix} \\
\{\tilde{\Psi}^{(j)}\}, \{E^{(j)}\} & \xrightarrow{\text{MxM Matrix}} \{\Psi^{(j+1)}\}
\end{align*}
\]
New Basis Set Construction in 1D

\[ H^{(j)} \]

MxM Matrix

\[ \{ \Psi^{(j+1)} \} \]

\[ \{ \tilde{\Psi}^{(j)}, \{ E^{(j)} \} \} \]

Suppose active space only contains ground state
New Basis Set Construction in 1D

\[ H^{(j)} \]

Suppose active space only contains ground state

\[ \Psi^{(1)}_1 = r d_0^{(1)} e^{-\frac{\alpha r^2}{2}} \]
New Basis Set Construction in 1D

Suppose active space only contains ground state

\[ \overline{\Psi}_1^{(1)} = r a_0^{(1)} e^{-\frac{\alpha r^2}{2}} \]

\[ \overline{\Psi}_1^{(2)} = r \left( a_0^{(2)} + a_1^{(2)} r + a_2^{(2)} r^2 + \ldots + a_{M-1}^{(2)} r^{M-1} \right) e^{-\frac{\alpha r^2}{2}} \]
New Basis Set Construction in 1D

\[
\begin{align*}
\{\Psi^{(j+1)}\} & \xrightarrow{H^{(j)}} \text{MxM Matrix} \\
\{\Psi^{(j)}\}, \{E^{(j)}\} & \xrightarrow{H^{(j)}} \\{\Psi^{(j+1)}\}
\end{align*}
\]

Suppose active space only contains ground state

\[
\Psi_1^{(1)} = r a_0^{(1)} e^{-\alpha r^2 / 2}
\]

\[
\Psi_1^{(2)} = \left( a_0^{(2)} r + a_1^{(2)} r^2 + a_2^{(2)} r^3 + \ldots + a_M^{(2)} r^M \right) e^{-\alpha r^2 / 2}
\]
New Basis Set Construction in 1D

\[
H^{(j)} \rightarrow \{ \Psi^{(j+1)} \} \rightarrow \text{MxM Matrix} \rightarrow \{ \tilde{\Psi}^{(j)} \}, \{ E^{(j)} \}
\]

Suppose active space only contains ground state

\[
\Psi^{(1)}_1 = ra_0^{(1)} e^{-\frac{\alpha r^2}{2}}
\]

\[
\Psi^{(2)}_1 = \left( a_0^{(2)} r + a_1^{(2)} r^2 + a_2^{(2)} r^3 + \ldots + a_{M-1}^{(2)} r^M \right) e^{-\frac{\alpha r^2}{2}}
\]

\[
\Psi^{(3)}_1 = r \left( a_0^{(3)} + a_1^{(3)} r + a_2^{(3)} r^2 + \ldots + a_M^{(3)} r^M \right) e^{-\frac{\alpha r^2}{2}}
\]
New Basis Set Construction in 1D

\[ H^{(j)} \]

\[ \{\Psi^{(j+1)}\} \leftarrow \text{MxM Matrix} \rightarrow \{\tilde{\Psi}^{(j)}\},\{E^{(j)}\} \]

Suppose active space only contains ground state

\[ \overline{\Psi}_1^{(1)} = r a_0^{(1)} e^{-\frac{\alpha r^2}{2}} \]

\[ \overline{\Psi}_1^{(2)} = \left( a_0^{(2)} r + a_1^{(2)} r^2 + a_2^{(2)} r^3 + \ldots + a_{M-1}^{(2)} r^M \right) e^{-\frac{\alpha r^2}{2}} \]

\[ \overline{\Psi}_1^{(3)} = \left( a_0^{(3)} r + a_1^{(3)} r^2 + a_2^{(3)} r^3 + \ldots + a_{M}^{(3)} r^{M+1} \right) e^{-\frac{\alpha r^2}{2}} \]
New Basis Set Construction in 1D

\[ H^{(j)} \]

\[ \{ \Psi^{(j+1)} \} \]

\[ \{ \tilde{\Psi}^{(j)} \}, \{ E^{(j)} \} \]

Suppose active space only contains ground state

\[ \Psi^{(2)}_1 = (a_0^{(2)} r + a_1^{(2)} r^2 + a_2^{(2)} r^3 + \ldots + a_{M-1}^{(2)} r^M)e^{-\alpha r^2/2} \]

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New Basis Set Construction in 1D

\[ \{ \Psi^{(j+1)} \} \rightarrow \frac{H^{(j)}}{\text{MxM Matrix}} \rightarrow \{ \tilde{\Psi}^{(j)} \}, \{ E^{(j)} \} \]

Suppose active space only contains ground state

\[ \Psi^{(2)}_1 = \left( a_0^{(2)} r + a_1^{(2)} r^2 + a_2^{(2)} r^3 + \ldots + a_{M-1}^{(2)} r^M \right) e^{-\frac{\alpha r^2}{2}} \]

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Effective size of basis grows each iteration
The General Scheme

1. Monte Carlo Sample Configuration Space
2. Construct Initial Basis
3. Assign Eigenstates & Build New Basis
4. Build and Diagonalize Hamiltonian Matrix

The process is cyclic, starting with Monte Carlo sampling and repeating the steps until convergence.
Testing the Method

\[ \Delta r (\text{Å}) \]

Energy (cm\(^{-1}\))

- \( E_0 = 237.5 \text{ cm}^{-1} \)
- \( E_1 = 637.5 \text{ cm}^{-1} \)
- \( E_2 = 937.5 \text{ cm}^{-1} \)
- \( E_3 = 1137.5 \text{ cm}^{-1} \)
- \( E_4 = 1237.5 \text{ cm}^{-1} \)
Testing the Method

\[ E(k) = \hbar \omega_0 \left( k + \frac{1}{2} \right) - \hbar \omega_e x_e \left( k + \frac{1}{2} \right)^2 \]

\[ \frac{\hbar \omega_e x_e}{\hbar \omega_0} = 0.1 \]

\[ E_0 = 237.5 \text{ cm}^{-1} \]
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Testing the Method

20,000 sampling points

$E_0 = 237.5\text{ cm}^{-1}$

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Testing the Method

20,000 sampling points
Active space consists of all bound states

\( E_0 = 237.5 \text{ cm}^{-1} \)
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Testing the Method

20,000 sampling points

Active space consists of all bound states

Total of 10 basis functions used

$E_0 = 237.5 \text{ cm}^{-1}$

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Moving on to 2D
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2D PES and G matrix elements constructed by S. Horvath from a bicubic spline interpolation of a grid of points on which MP2/aug-cc-pVTZ calculations were performed.

Moving on to 2D

2D PES and G matrix elements constructed by S. Horvath from a bicubic spline interpolation of a grid of points on which MP2/aug-cc-pVTZ calculations were performed.

Highly anharmonic system with a strong coupling observed between $r_{OH_b}$ and $r_{OF}$.

Moving on to 2D

2D PES and G matrix elements constructed by S. Horvath from a bicubic spline interpolation of a grid of points on which MP2/aug-cc-pVTZ calculations were performed.

Highly anharmonic system with a strong coupling observed between $r_{\text{OH}_b}$ and $r_{\text{OF}}$.

Our goal is to accurately capture all states with up to 3 total quanta of excitation.

A Taste of the Preliminary Results

<table>
<thead>
<tr>
<th>$r_{\text{OF}}$ (Å)</th>
<th>$r_{\text{OH}_b}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1149.66 (cm$^{-1}$)</td>
<td>$\pm$7.12</td>
</tr>
<tr>
<td>1136.08</td>
<td>$\pm$8.66</td>
</tr>
<tr>
<td>1533.04</td>
<td>$\pm$32.39</td>
</tr>
<tr>
<td>898.25</td>
<td>$\pm$11.86</td>
</tr>
<tr>
<td>2111.92</td>
<td>$\pm$36.39</td>
</tr>
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Active space and basis contain all states with up to 3 and 6 quanta respectively.

50,000 sampling points

$\beta_{fat} = 0.01, 0.01$

Statistics from 4 calculations
A Taste of the Preliminary Results

$\begin{array}{cccc}
2933.67 & 1308.01 & 2668.11 & 3445.36 & 4469.33 \\
2930.23 & 1347.58 & 2692.54 & 3496.77 & 4565.43 \\
\pm16.17 & \pm35.42 & \pm34.04 & \pm67.19 & \pm55.85 \\
\end{array}$

$r_{OH_b}$ (Å)  $r_{OF}$ (Å)  Active space and basis contain all states with up to 3 and 6 quanta respectively

50,000 sampling points  $eta_{fat}=0.01, 0.01$

Statistics from 4 calculations
Conclusions and Future Work

Developed a methodology that uses importance sampling Monte Carlo and evolving basis to intelligently sample configuration space and minimize size of basis required.
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The method has been shown to be able to accurately describe a highly anharmonic Morse oscillator.
**Conclusions and Future Work**

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Conclusions and Future Work

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The method has been shown to be able to accurately describe a highly anharmonic Morse oscillator.

Promising preliminary proof of principle calculations on $F^-(H_2O)$.

Complete testing with $F^-(H_2O)$ and perform benchmarking calculations on higher dimensional systems to further test method and explore its scaling.
Conclusions and Future Work

Developed a methodology that uses importance sampling Monte Carlo and evolving basis to intelligently sample configuration space and minimize size of basis required.

The method has been shown to be able to accurately describe a highly anharmonic Morse oscillator.

Promising preliminary proof of principle calculations on F⁻(H₂O).

Complete testing with F⁻(H₂O) and perform benchmarking calculations on higher dimensional systems to further test method and explore its scaling.

Couple algorithm with ab initio electronic structure calculations.
Acknowledgements

Dr. Anne B. McCoy (RB03)  Bethany A. Wellen  Annie L. Lesiak (RB02)  Dr. Samantha Horvath (RA06, FE07)

Dr. Sara E. Ray (FE08)  Andrew S. Petit  Charlotte E. Hinkle (RA05)
Effect of $\beta_{\text{fat}}$

- $\beta_{\text{fat}} = 0.01$
- $\beta_{\text{fat}} = 0.02$
- $\beta_{\text{fat}} = 0.05$
- $\beta_{\text{fat}} = 0.1$

$|\psi_0|^2$

50,000 sampling points
10 basis functions
5 states in active space
Effect of $\beta_{\text{fat}}$

$\beta_{\text{fat}} = 0.01$
$\beta_{\text{fat}} = 0.02$
$\beta_{\text{fat}} = 0.05$
$\beta_{\text{fat}} = 0.1$

$|\psi_0|^2$

50,000 sampling points
10 basis functions
5 states in active space
Effect of $\beta_{\text{fat}}$

- 50,000 sampling points
- 10 basis functions
- 5 states in active space
- 5 statistically independent calculations

$E_k - E_{\text{exact}}$ (cm$^{-1}$)

$k$

$\beta_{\text{fat}}$

- $0.01$
- $0.02$
- $0.05$
- $0.1$
Effect of $\beta_{\text{fat}}$

\[
E_4 - E_4^{\text{exact}}
\]

$\beta_{\text{fat}} = 0.01; \ 5.62 \ \text{cm}^{-1}$

$\beta_{\text{fat}} = 0.02; \ 6.53 \ \text{cm}^{-1}$

$\beta_{\text{fat}} = 0.05; \ -3.81 \ \text{cm}^{-1}$

$\beta_{\text{fat}} = 0.1; \ 16.52 \ \text{cm}^{-1}$

DVR

\[
\frac{\hat{H}\psi}{\psi} = E
\]
Effect of $\beta_{\text{fat}}$

$E_4 - E_4^{\text{exact}}$

$\beta_{\text{fat}} = 0.01; \ 5.62 \ \text{cm}^{-1}$

$\beta_{\text{fat}} = 0.02; \ 6.53 \ \text{cm}^{-1}$

$\beta_{\text{fat}} = 0.05; \ -3.81 \ \text{cm}^{-1}$

$\beta_{\text{fat}} = 0.1; \ 16.52 \ \text{cm}^{-1}$

DVR

$\frac{\hat{H}\Psi}{\Psi} = E$
Effect of Size of Active Space

![Graph showing the effect of size of active space on energy difference](image)
Effect of Size of Active Space

\[ |\Psi_4(r)|^2 \] 

\[ |\Psi_0(r)|^2 \]
Effect of Number of Sampling Points

$E_4 - E_4^{\text{exact}} \text{ (cm}^{-1}\text{)}$ vs. Number of Sampling Points

- Red diamonds: 0.01
- Green squares: 0.02
- Blue triangles: 0.05
- Purple circles: 0.1
Improving Methodology

Assignment Scheme

\[ \langle \tilde{\Psi}_m^n(j) | \Psi_{o,p}^{(j)} \rangle^2 \]

Eigenstate  \quad Basis function

\[ \langle \tilde{\Psi}_m^n(j) | \Psi_{\text{trial}}^{(j)} \rangle^2 \]

Trial function with proper nodal structure built out of previously assigned states

Take linear combination of 2 eigenstates which maximally overlap \( \Psi_{\text{trial}}^{(j)} \).
Improving Methodology

Active Space Evolution

\[ \{ \Psi^{(j+1)} \} \xrightarrow{H^{(j)}} \{ \tilde{\Psi}^{(j)} \}, \{ E^{(j)} \} \]

Define an active space:

\[ \left\{ \Psi_{m}^{(j+1)} \right\}_{active} = \left\{ \tilde{\Psi}_{m}^{(j)} \right\}_{active} \]

\[ \left\{ \Psi_{m}^{(j+1)} \right\}_{active} \Rightarrow \varphi_{m \notin \text{active}}^{(j+1)} \]

Labeling based on order in which state is constructed

Basis functions outside of active space built out of active space
Improving Methodology

Active Space Evolution

$\{\Psi^{(j+1)}\} \overset{H^{(j)}}{\rightarrow} \{\tilde{\Psi}^{(j)}\}, \{E^{(j)}\}$

These basis functions are fixed for a series of $N$ iterations

$\Psi^{(j+1)}_{m<nactive} = \Psi^{(j)}_{m<nactive}$

$\Psi^{(j+1)}_{nactive} = \tilde{\Psi}^{(j)}_{nactive}$

$\{\Psi^{(j+1)}_m\}_{active} \Rightarrow \varphi^{(j+1)}_m \notin active$
Improving Methodology

Active Space Evolution

After N iterations:

- Size of active space grows by 1
- Members of new active space allowed to mix via diagonalization of active space only $H$. 

$\Psi^{(j+1)}_{m<n\text{active}} = \Psi^{(j)}_{m<n\text{active}}$

$\Psi^{(j+1)}_{n\text{active}} = \tilde{\Psi}^{(j)}_{n\text{active}}$

$\{\Psi^{(j+1)}_m\}_{\text{active}} \Rightarrow \varphi^{(j+1)}_m \notin \text{active}$