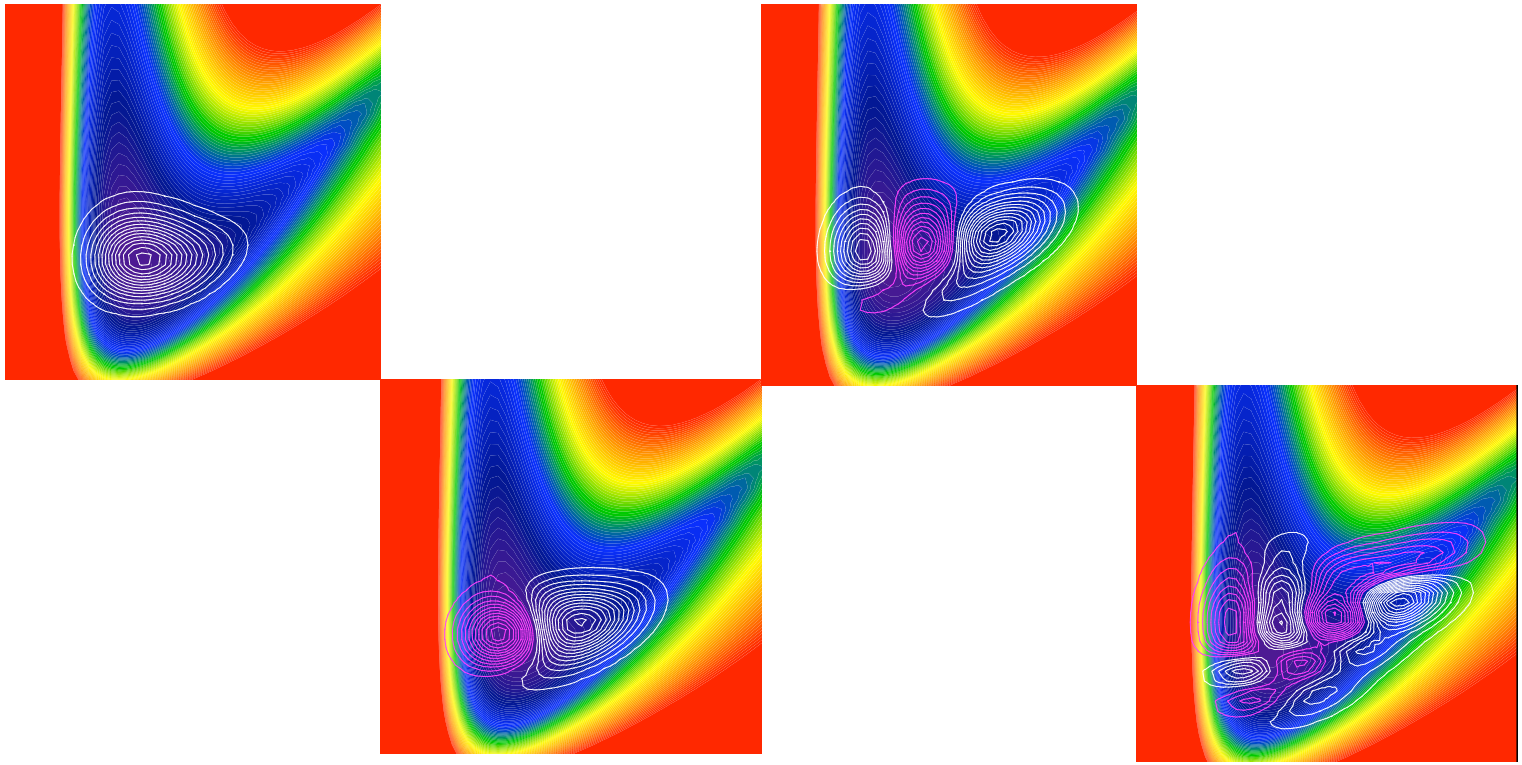
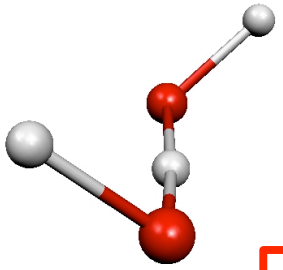
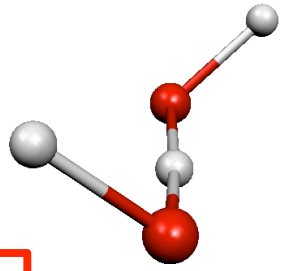
Progress Towards the Calculation of Anharmonic Vibrational States Without a Pre-Existing Potential Energy Surface



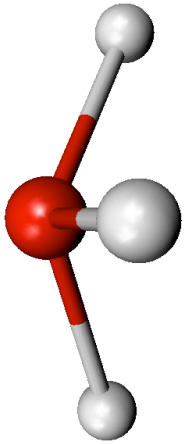
Andrew S. Petit and Anne B. McCoy
The Ohio State University

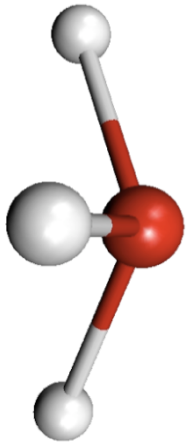
What Systems Are We Trying to Understand???

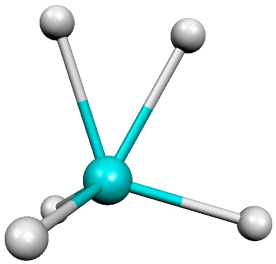


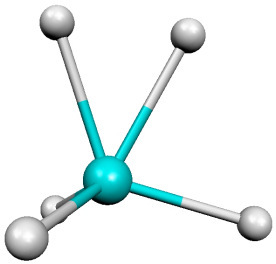


Highly fluxional molecules and clusters









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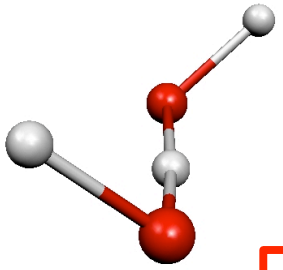

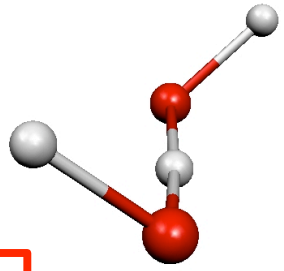

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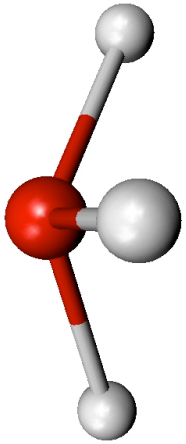

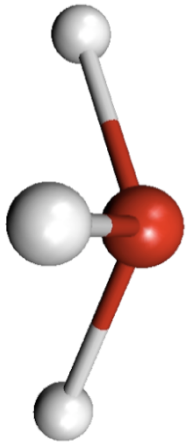

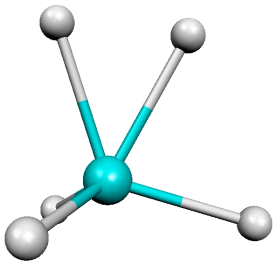

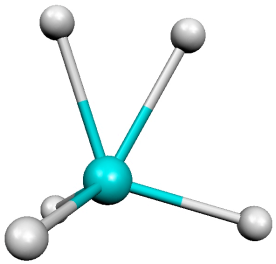

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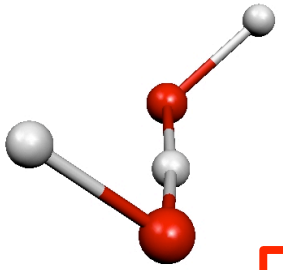

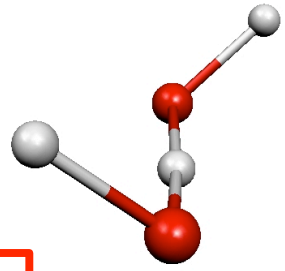

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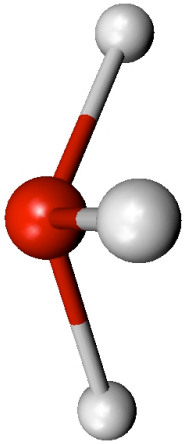

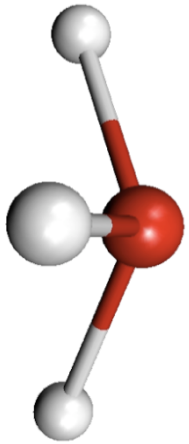

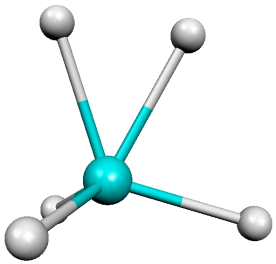

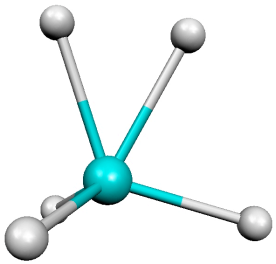

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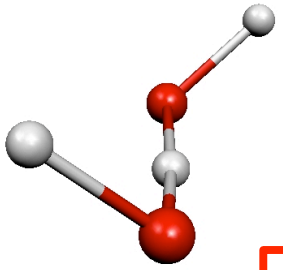

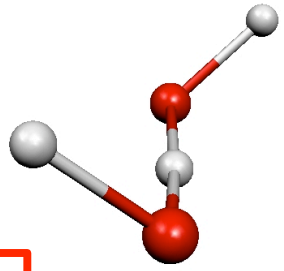

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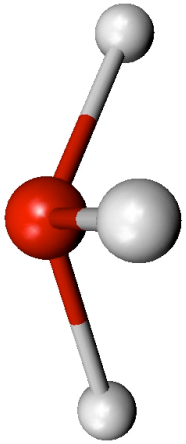

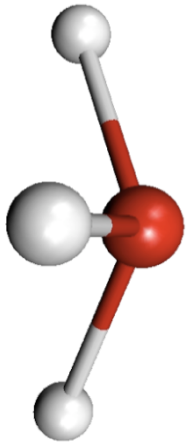

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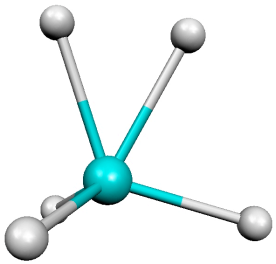

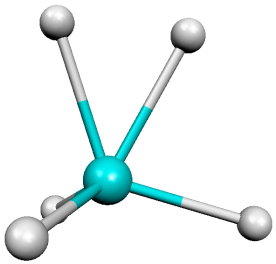

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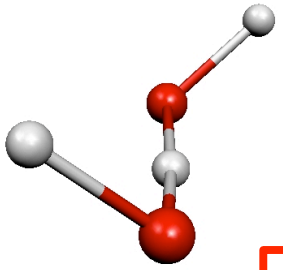

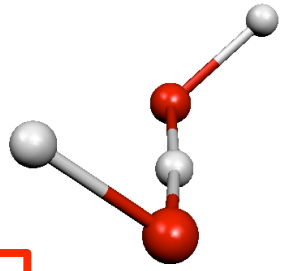

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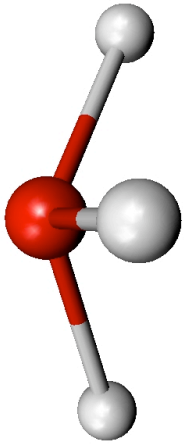

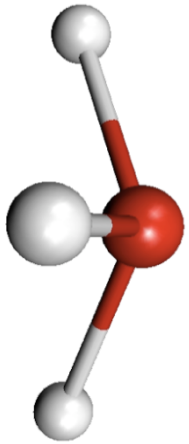

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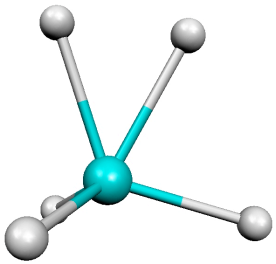

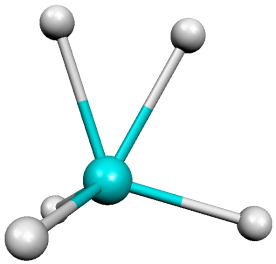

Construction of global potential energy surfaces very challenging

The General Scheme

The General Scheme

Monte Carlo Sample
Configuration Space

An Intelligent Way to Sample Configuration Space

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Use importance sampling Monte Carlo

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$$\int_V f(\vec{x})dV = \int_L \frac{f(\vec{x})}{g(\vec{x})} g(\vec{x})dV \approx \frac{V}{N}\sum_{i=1}^{N} \frac{f(\vec{x}_i)}{g(\vec{x}_i)}$$

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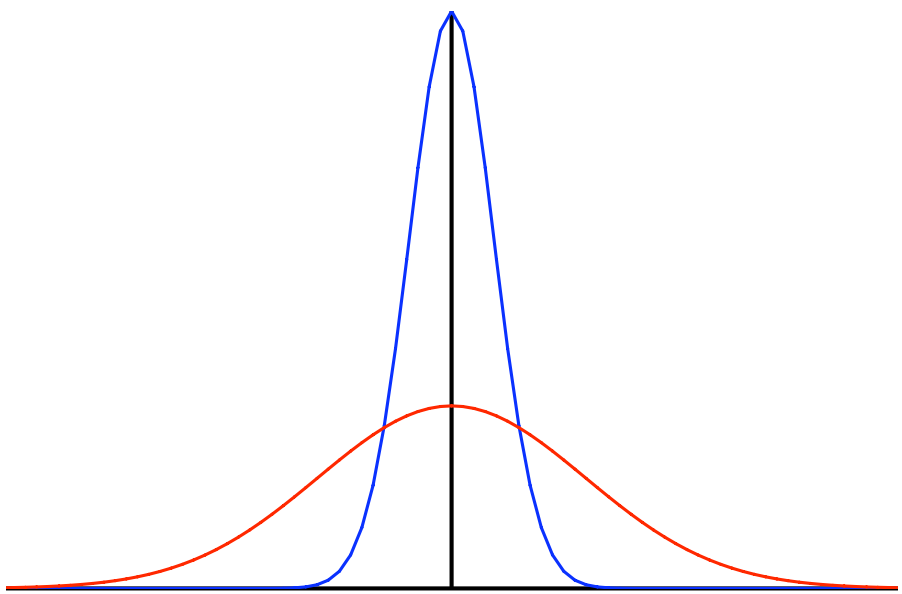

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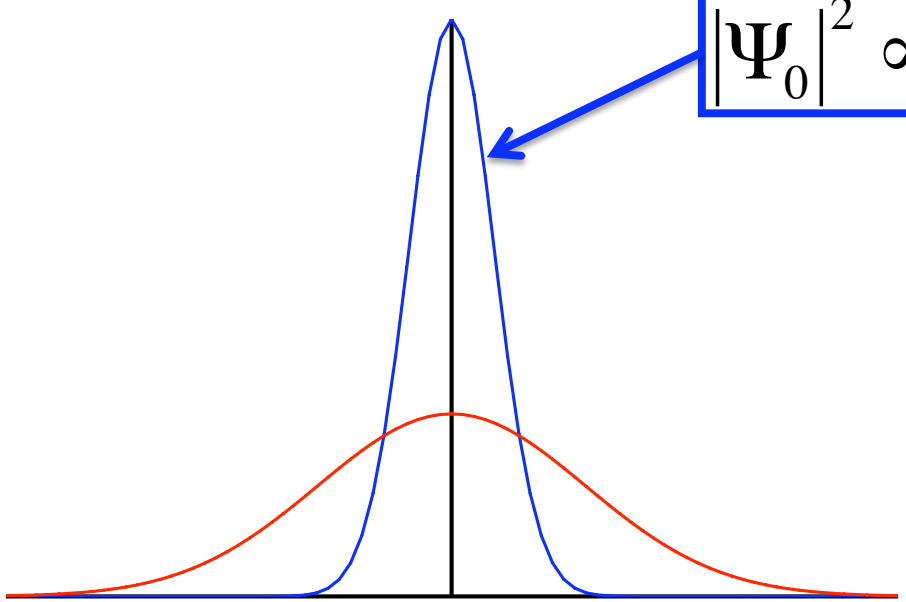
$$\boxed{|\Psi_0|^2 \propto e^{-\alpha r^2}}$$



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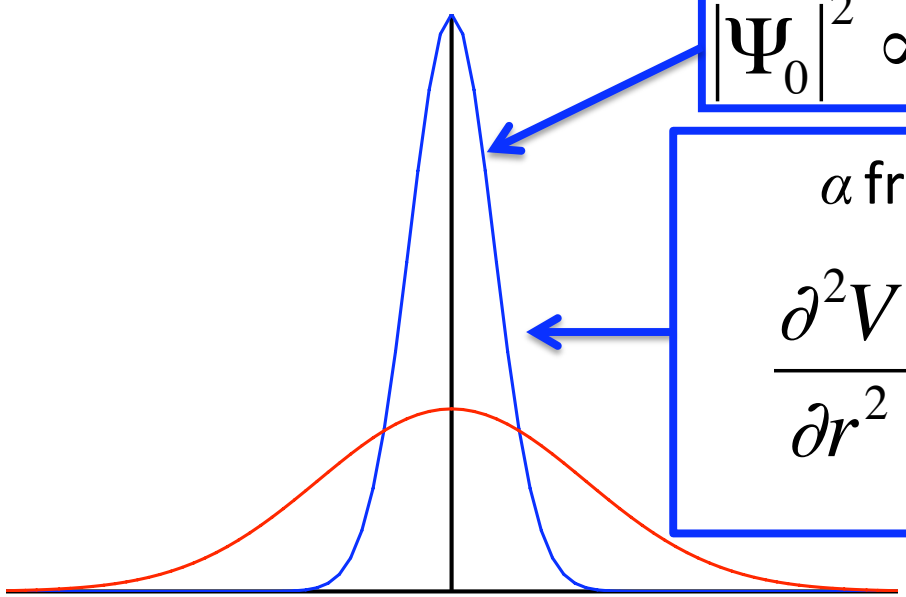

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α from

$$\left.\frac{\partial^2 V}{\partial r^2}\right|_{r=r_{eq}}$$

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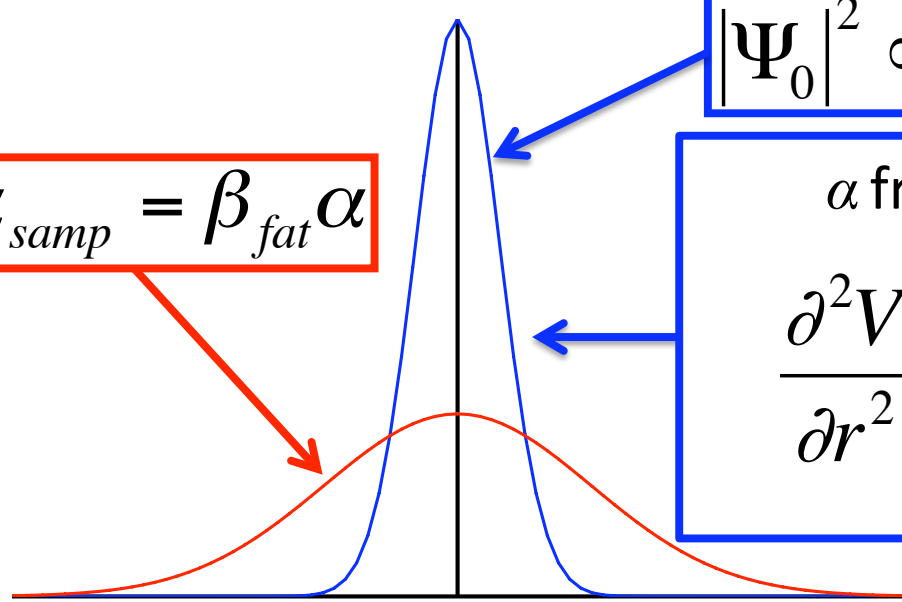

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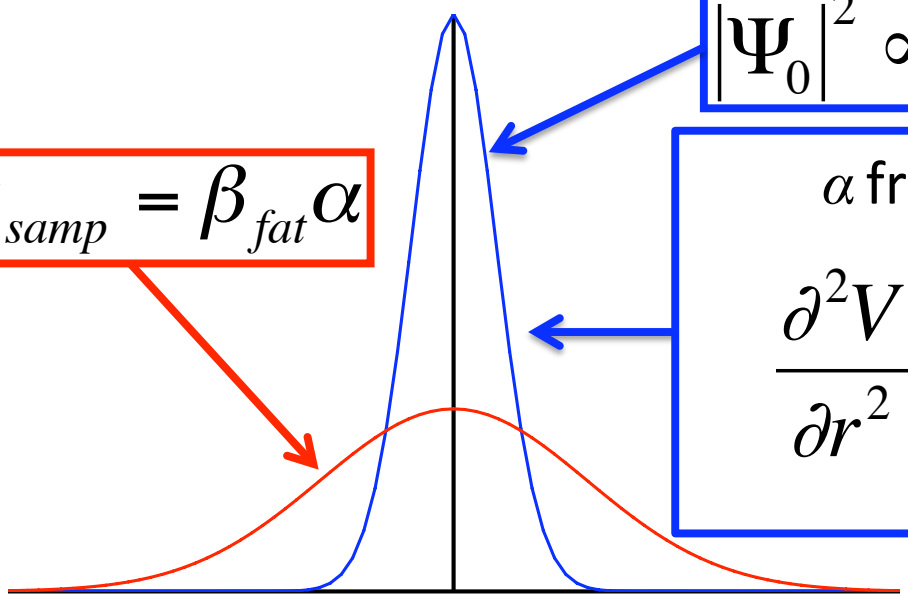

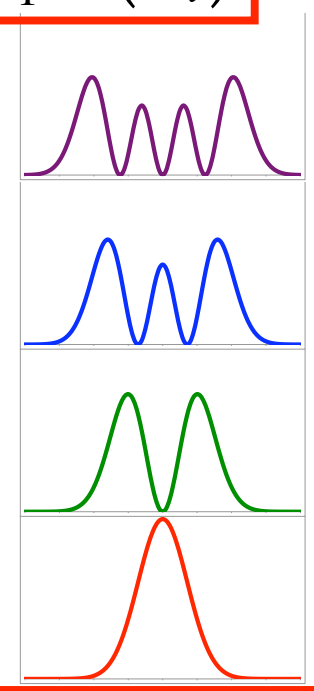

The General Scheme

Monte Carlo Sample Configuration Space

↓

Construct Initial Basis

The Initial Basis (2D Example)

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

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Basis functions change each iteration

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

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Phase factors

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Phase factors

Will be made orthogonal to all previously built states and normalized

The Initial Basis (2D Example)

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

$$\Psi_{0,0}$$

$$\Psi_{1,0} \qquad \Psi_{0,1}$$

$$\Psi_{2,0} \qquad \Psi_{1,1} \qquad \Psi_{0,2}$$

$$\Psi_{3,0} \qquad \Psi_{2,1} \qquad \Psi_{1,2} \qquad \Psi_{0,3}$$

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$$\begin{array}{ccccccc}
 & & & \Psi_{0,0} & & & \\
 & & \Psi_{1,0} & & \Psi_{0,1} & & \\
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\end{array}$$

$$\boxed{\overline{\Psi}^{(1)}_{3,0} = \kappa^{(1)}_{3,0;2,0} r \Psi^{(1)}_{2,0} + \kappa^{(1)}_{3,0;1,0} r^{2} \Psi^{(1)}_{1,0} + \kappa^{(1)}_{3,0;0,0} r^{3} \Psi^{(1)}_{0,0}}$$

The Initial Basis (2D Example)

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

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$$\boxed{\overline{\Psi}^{(1)}_{2,1} = \kappa^{(1)}_{2,1;2,0} R \Psi^{(1)}_{2,0} + \kappa^{(1)}_{2,1;1,1} r \Psi^{(1)}_{1,1} + \kappa^{(1)}_{2,1;0,1} r^{2} \Psi^{(1)}_{0,1}}$$

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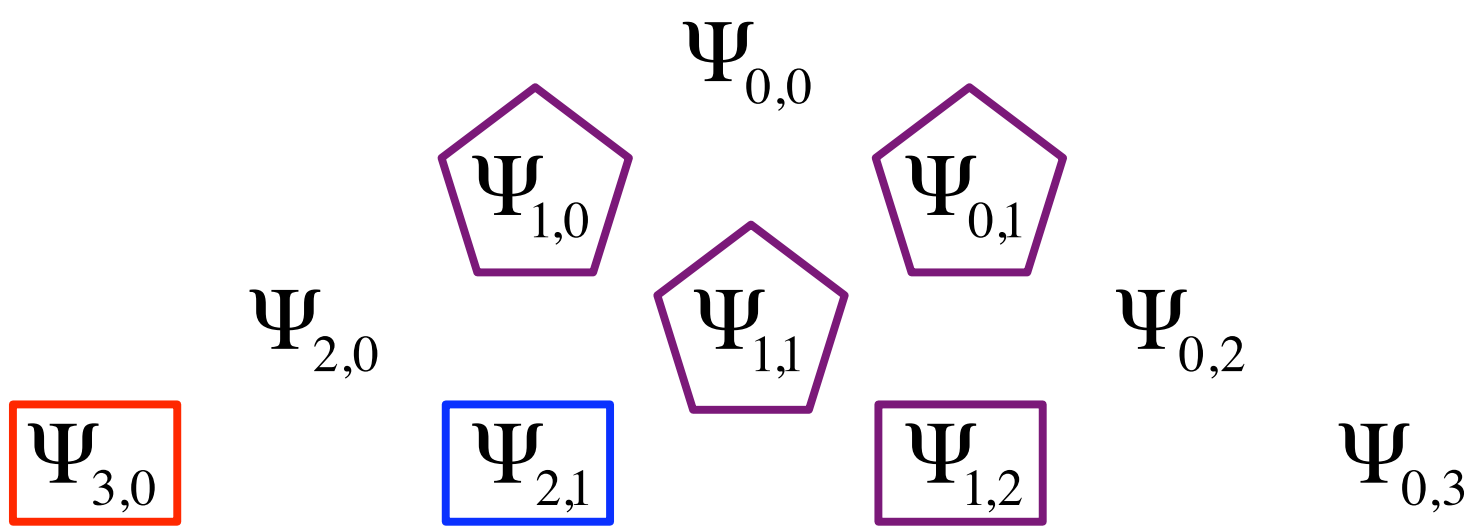


$$\boxed{\overline{\Psi}^{(1)}_{1,2} = \kappa^{(1)}_{1,2;1,1} R \Psi^{(1)}_{1,1} + \kappa^{(1)}_{1,2;1,0} R^{2} \Psi^{(1)}_{1,0} + \kappa^{(1)}_{1,2;0,2} r \Psi^{(1)}_{0,0}}$$

The Initial Basis (2D Example)

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

$$\Psi_{0,0}$$

$$\Psi_{1,0} \qquad \Psi_{0,1}$$

$$\Psi_{2,0} \qquad \Psi_{1,1} \qquad \Psi_{0,2}$$

$$\Psi_{3,0} \qquad \Psi_{2,1} \qquad \Psi_{1,2} \qquad \Psi_{0,3}$$

The General Scheme

Monte Carlo Sample Configuration Space

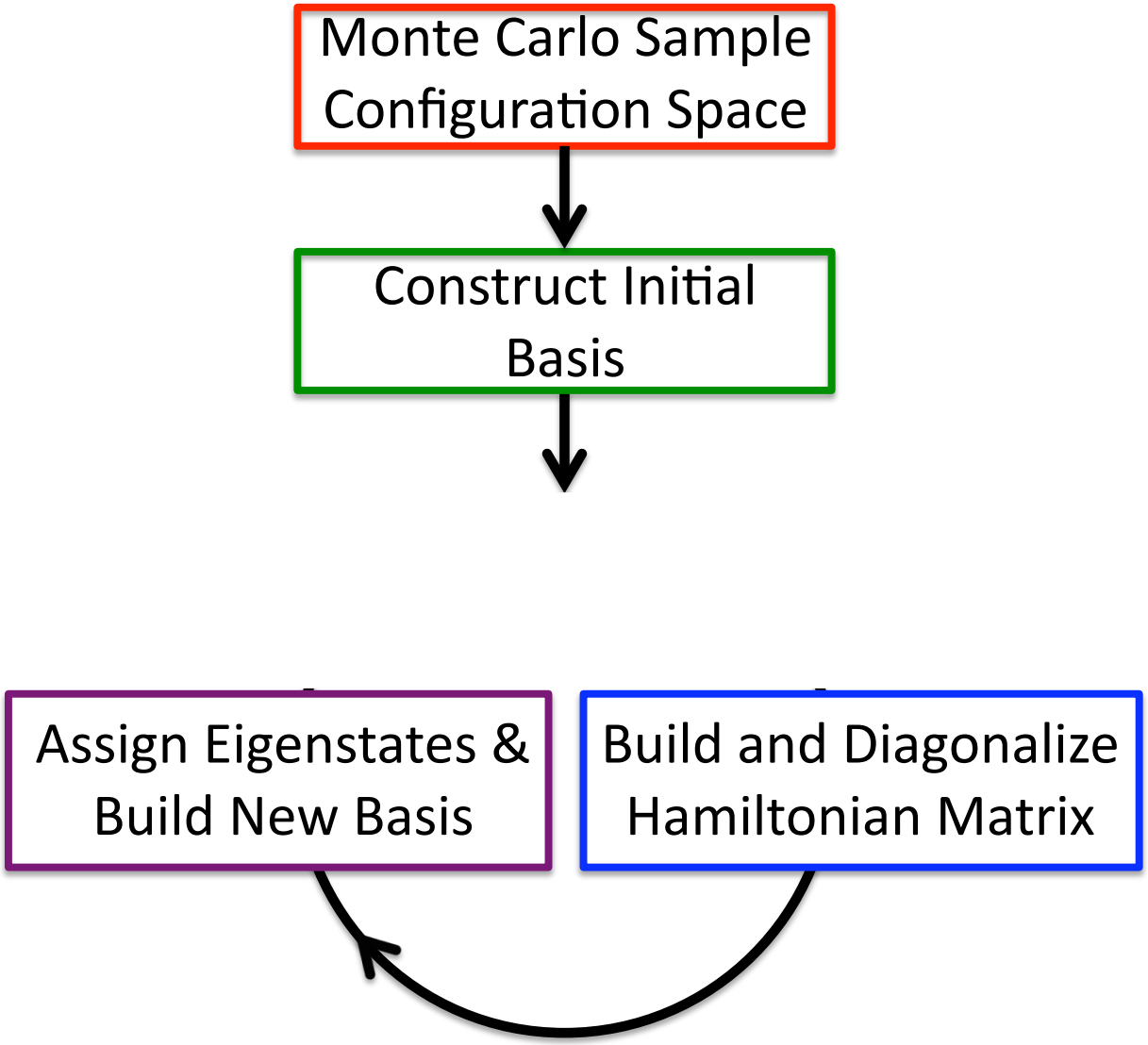
↓

Construct Initial Basis

↓

Build and Diagonalize Hamiltonian Matrix

The General Scheme



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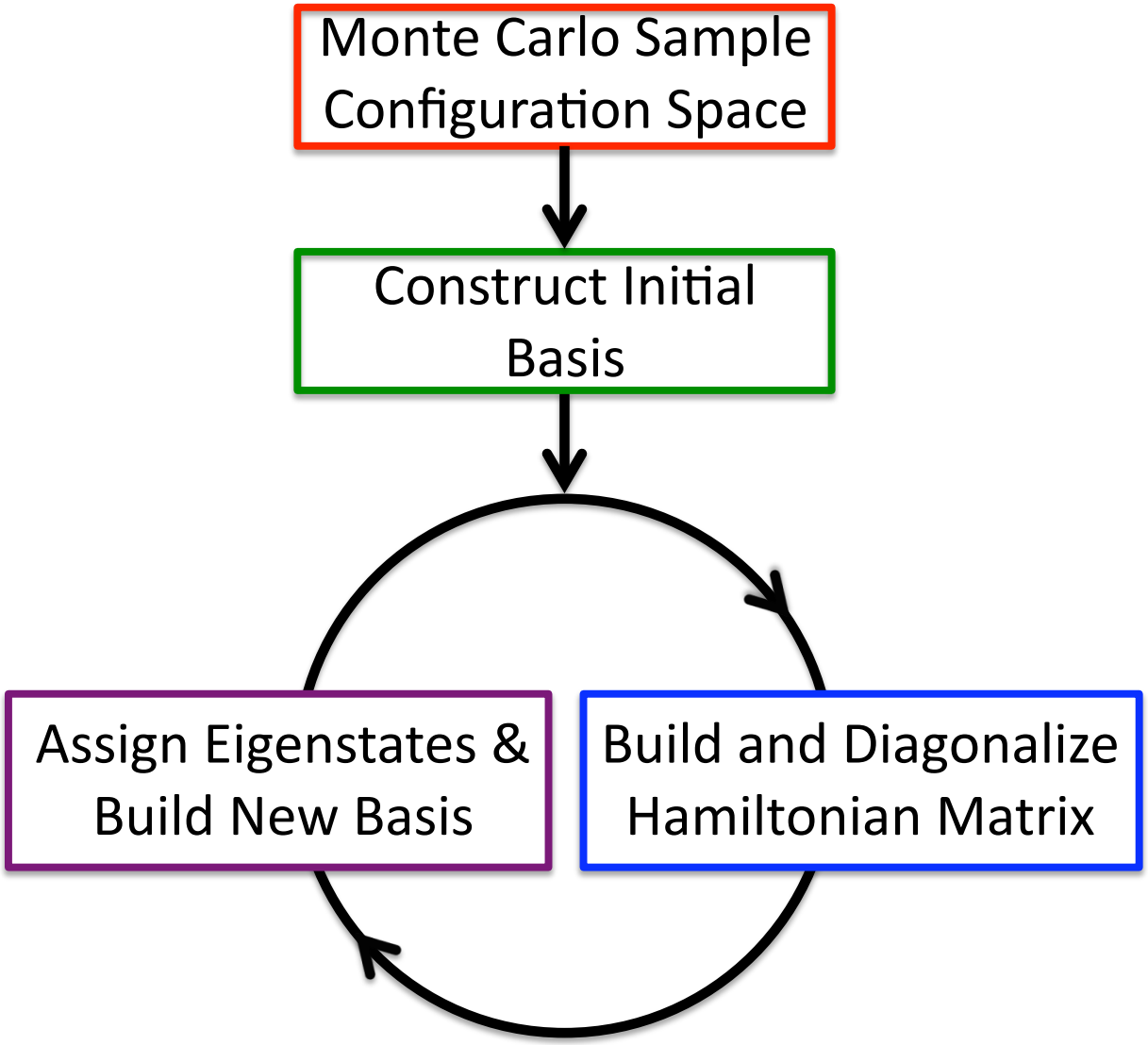

New Basis Set Construction in 1D

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

New Basis Set Construction in 1D

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

Iteration Number

New Basis Set Construction in 1D

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

Diagonalization

$$\left\{ \tilde{\Psi}^{(j)} \right\}, \left\{ E^{(j)} \right\}$$

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Eigenstates used to construct next generation of basis functions

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Eigenstates used to construct next generation of basis functions

Assignment via:

$$\max\left(\left| \left\langle \tilde{\Psi}_k^{(j)} \middle| \hat{r} \middle| \Psi_{m-1}^{(j)} \right\rangle \right|^2 \right) \Rightarrow \tilde{\Psi}_m^{(j)}$$

New Basis Set Construction in 1D

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

Diagonalization

$$\left\{ \Psi^{(j+1)} \right\} \leftarrow \boxed{\left\{ \tilde{\Psi}^{(j)} \right\}}, \left\{ E^{(j)} \right\}$$

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$$\left\{ \Psi^{(j+1)} \right\}$$

Define an active space:

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Define an active space:

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

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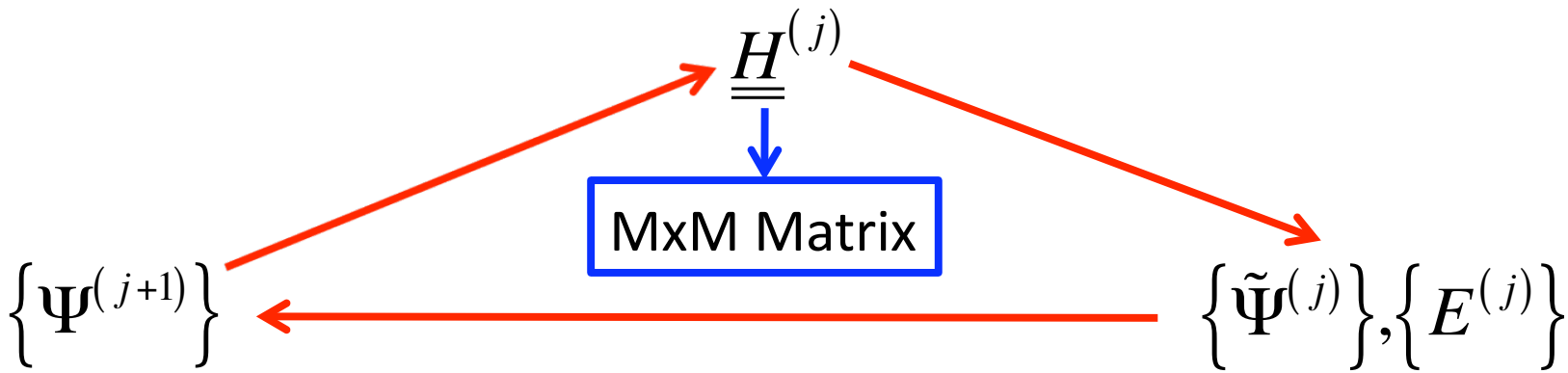
New Basis Set Construction in 1D

$$\underline{\underline{H}}^{(j)}$$

$$\left\{\Psi^{(j+1)}\right\} \longrightarrow \underline{\underline{H}}^{(j)} \longrightarrow \left\{\tilde{\Psi}^{(j)}\right\},\left\{E^{(j)}\right\} \longrightarrow \left\{\Psi^{(j+1)}\right\}$$

New Basis Set Construction in 1D



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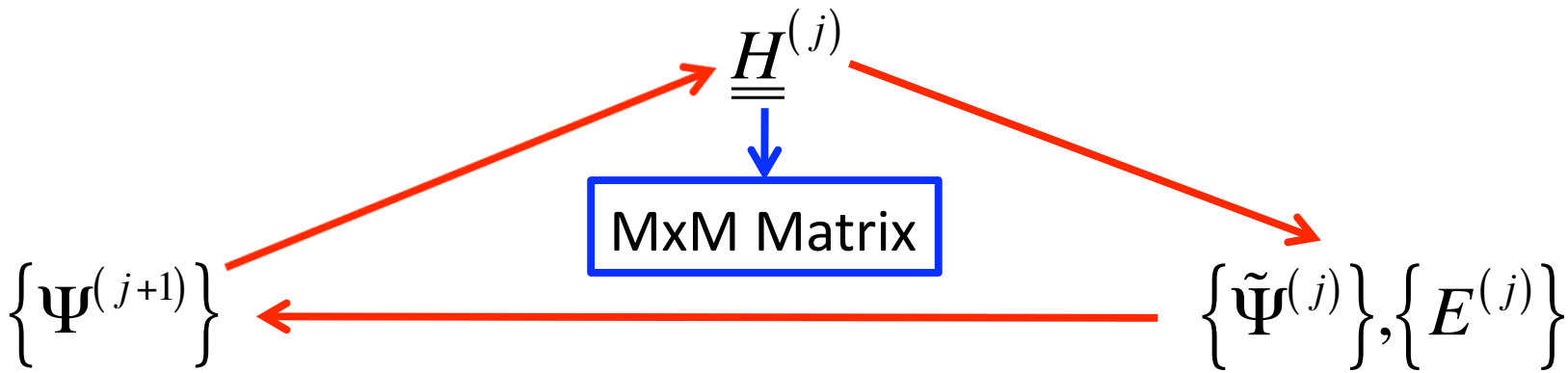

Suppose active space only contains ground state

New Basis Set Construction in 1D

$$\underline{\underline{H}}^{(j)}$$

MxM Matrix

$$\left\{\Psi^{(j+1)}\right\} \qquad \left\{\tilde{\Psi}^{(j)}\right\}, \left\{E^{(j)}\right\}$$

Suppose active space only contains ground state

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

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$$\left\{\Psi^{(j+1)}\right\} \longleftarrow \left\{\tilde{\Psi}^{(j)}\right\},\left\{E^{(j)}\right\}$$

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

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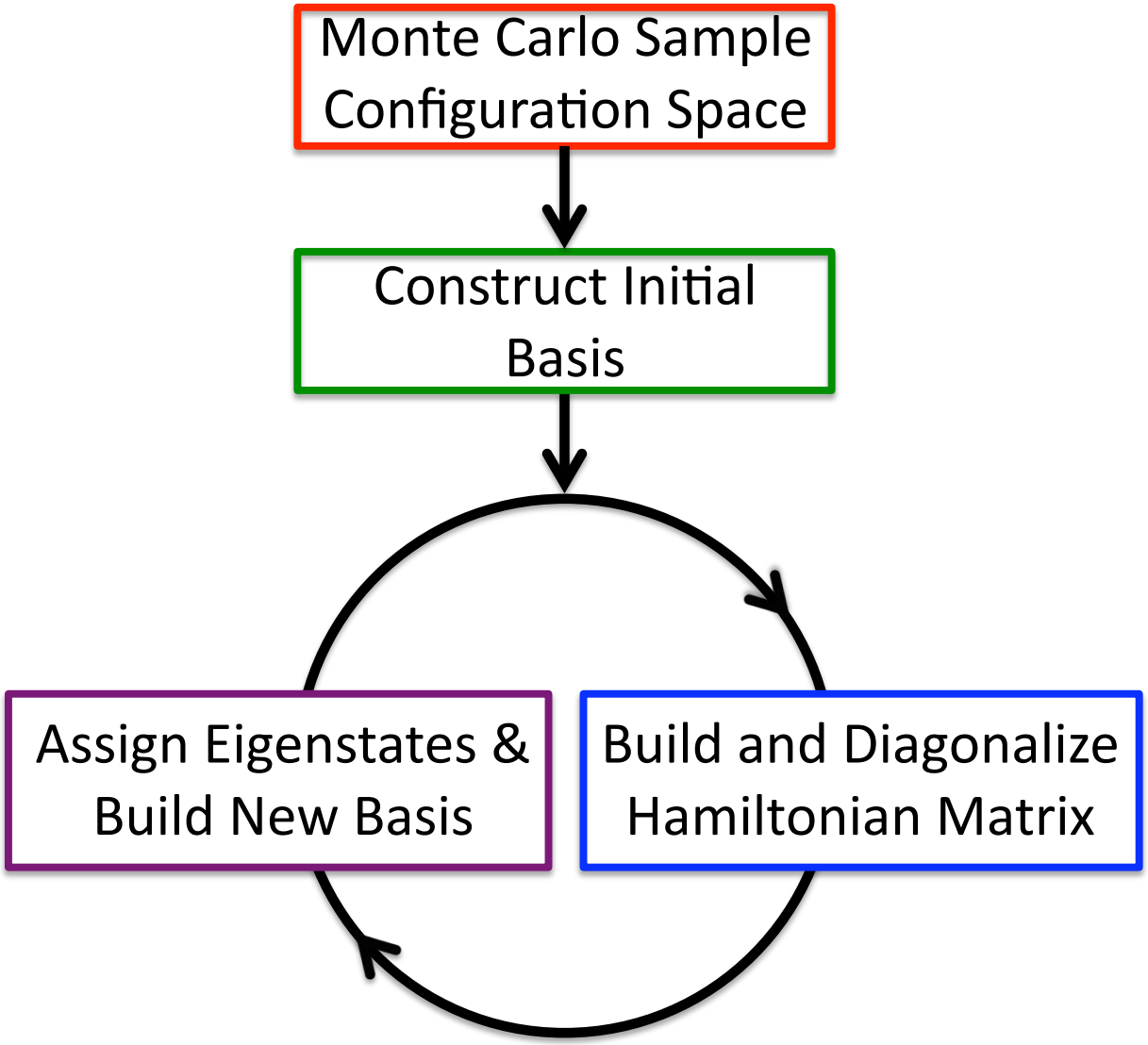
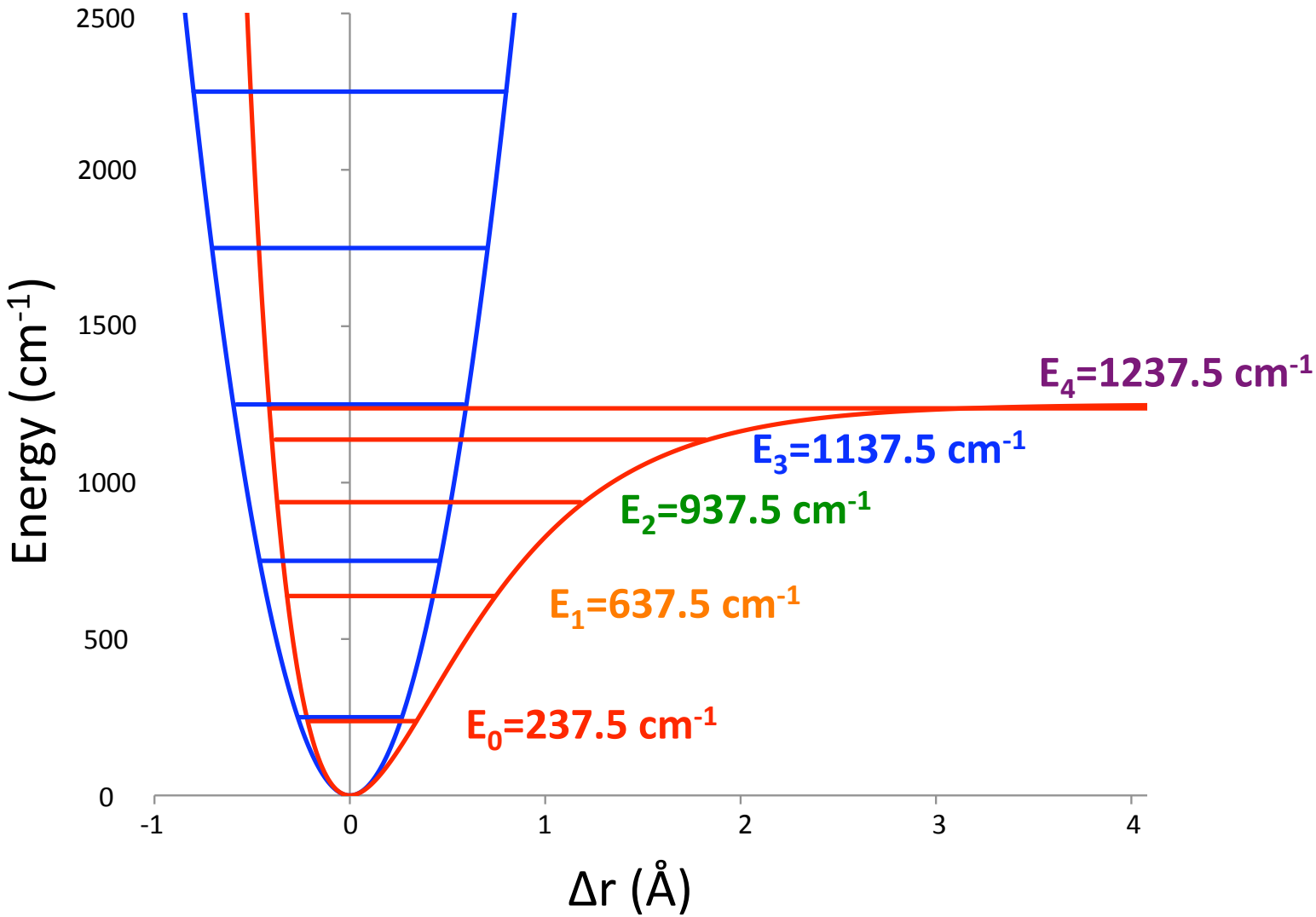
Effective size of basis grows each iteration

The General Scheme



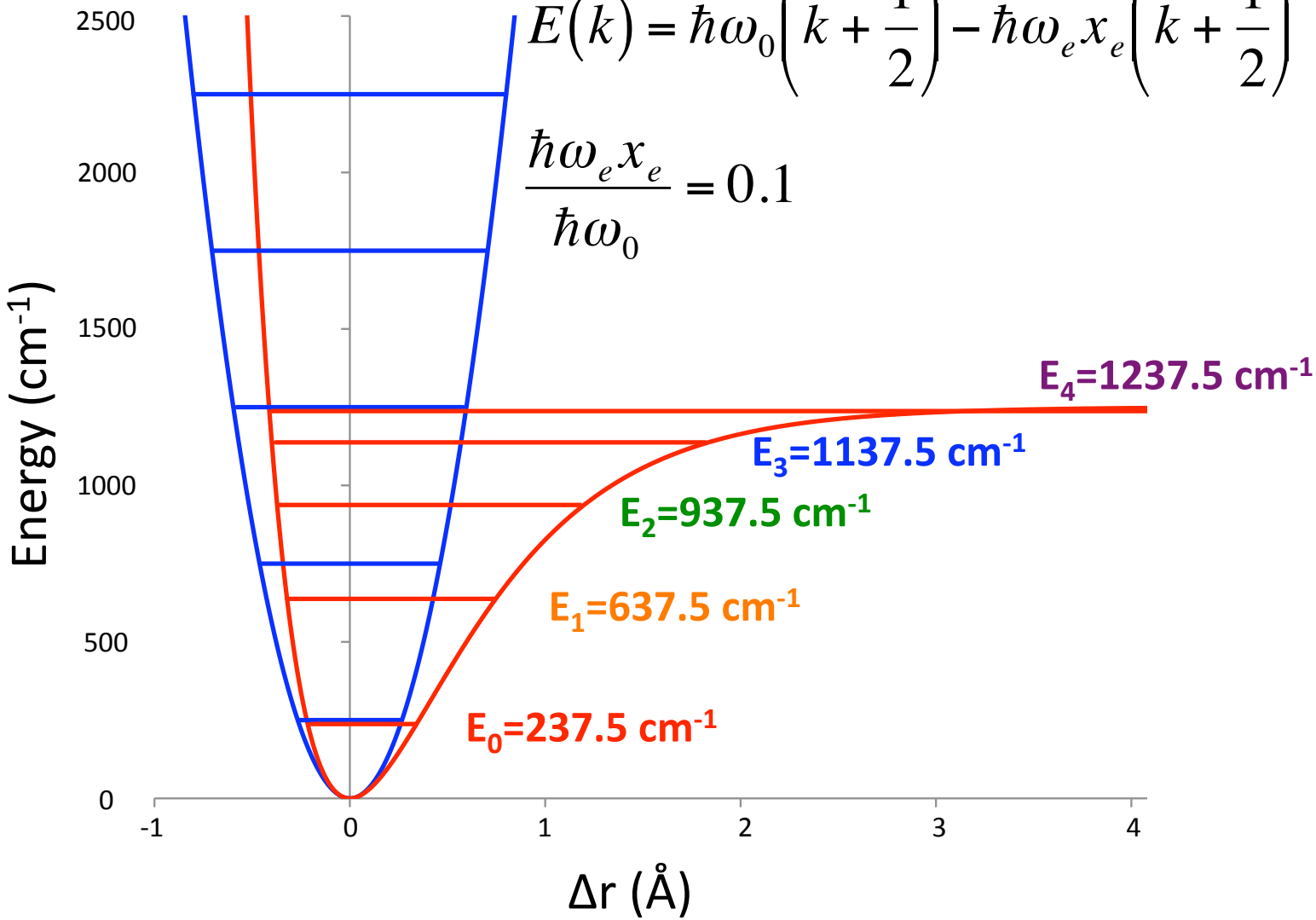
Testing the Method



Testing the Method

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

$$\frac{\hbar\omega_e x_e}{\hbar\omega_0} = 0.1$$



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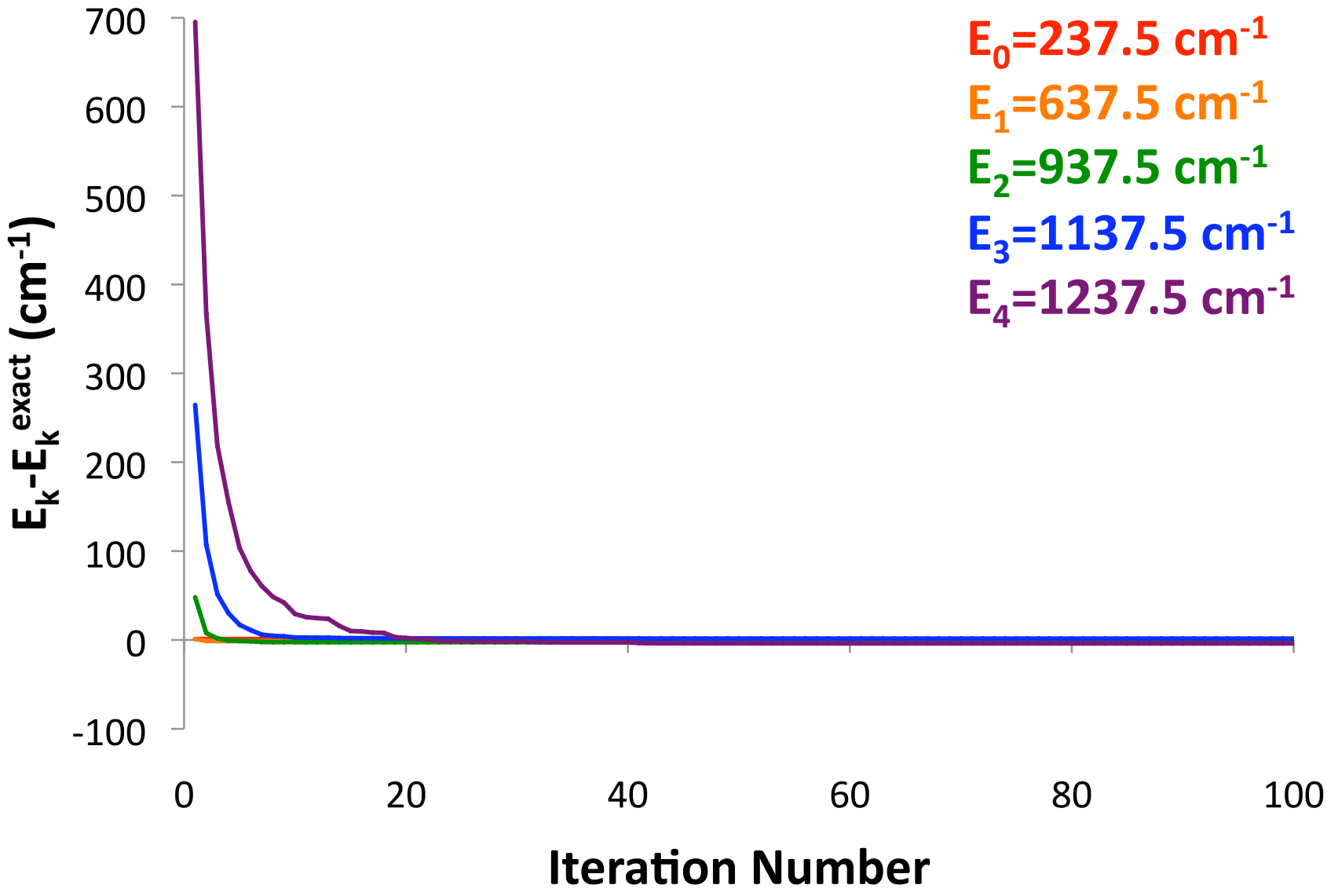

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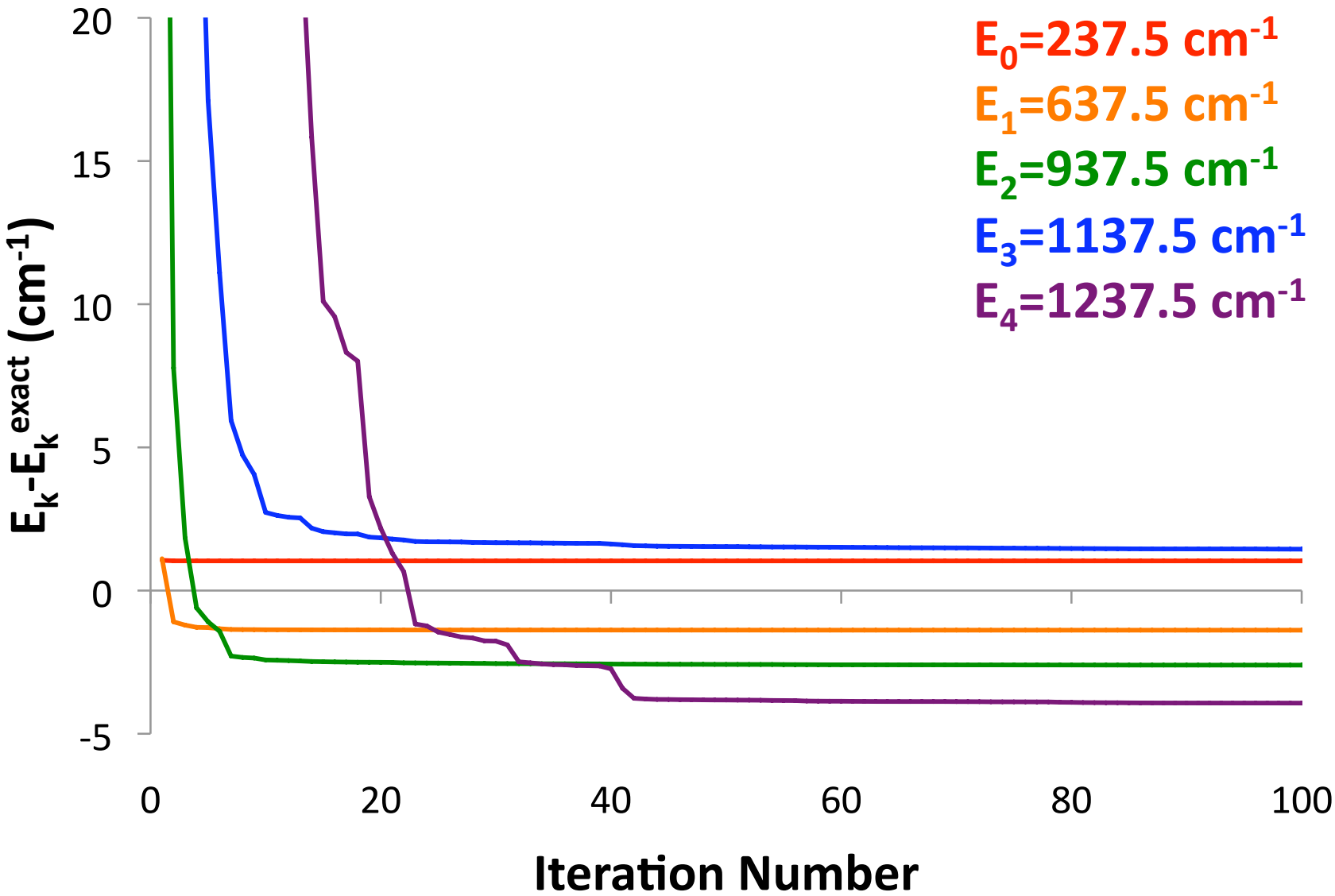

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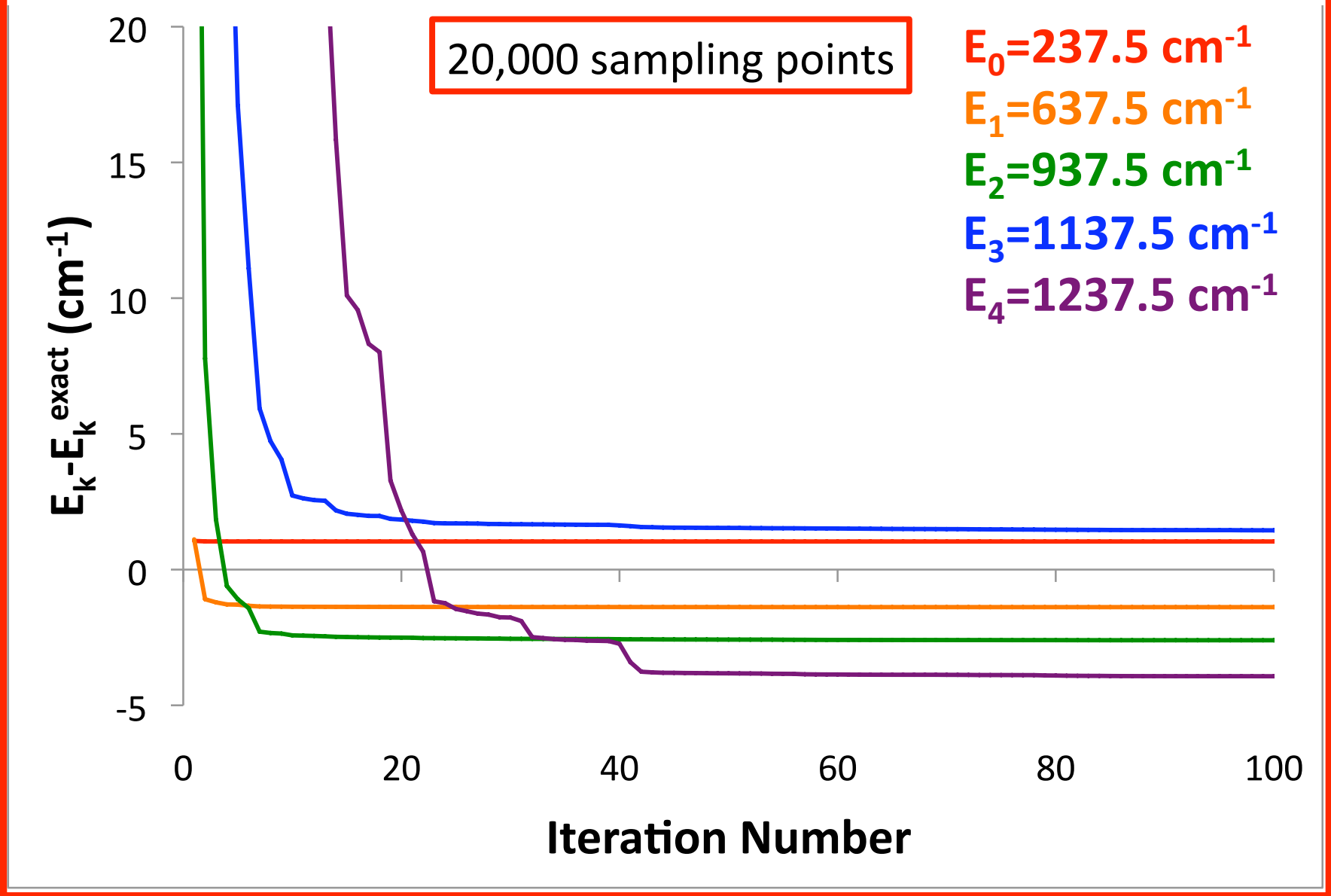

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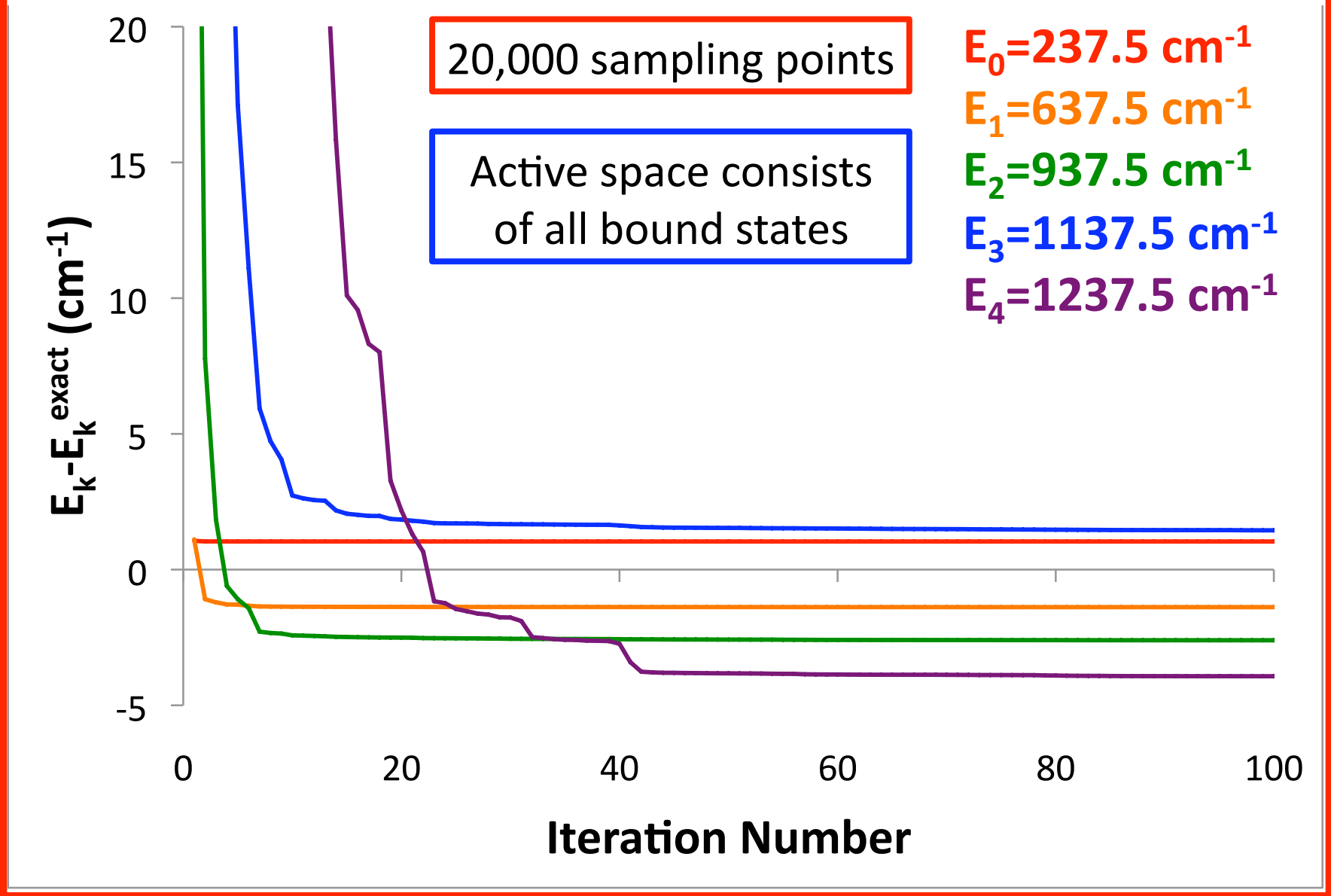

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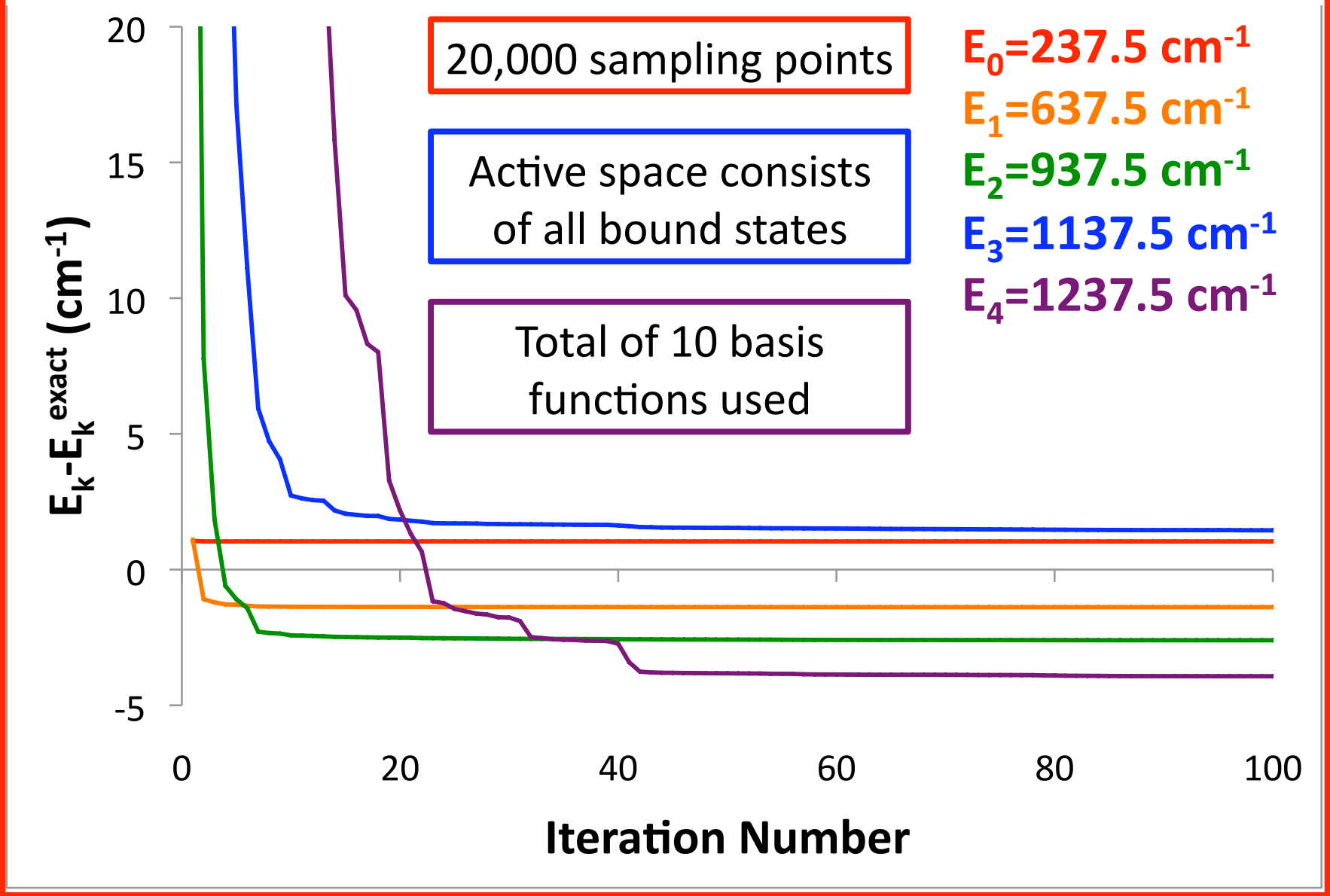

Moving on to 2D

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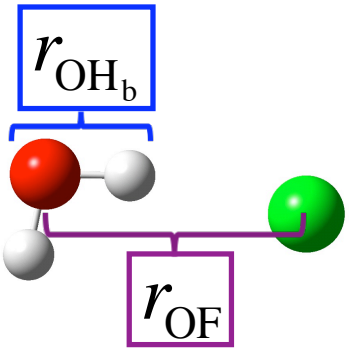
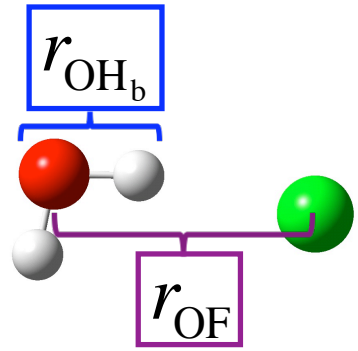
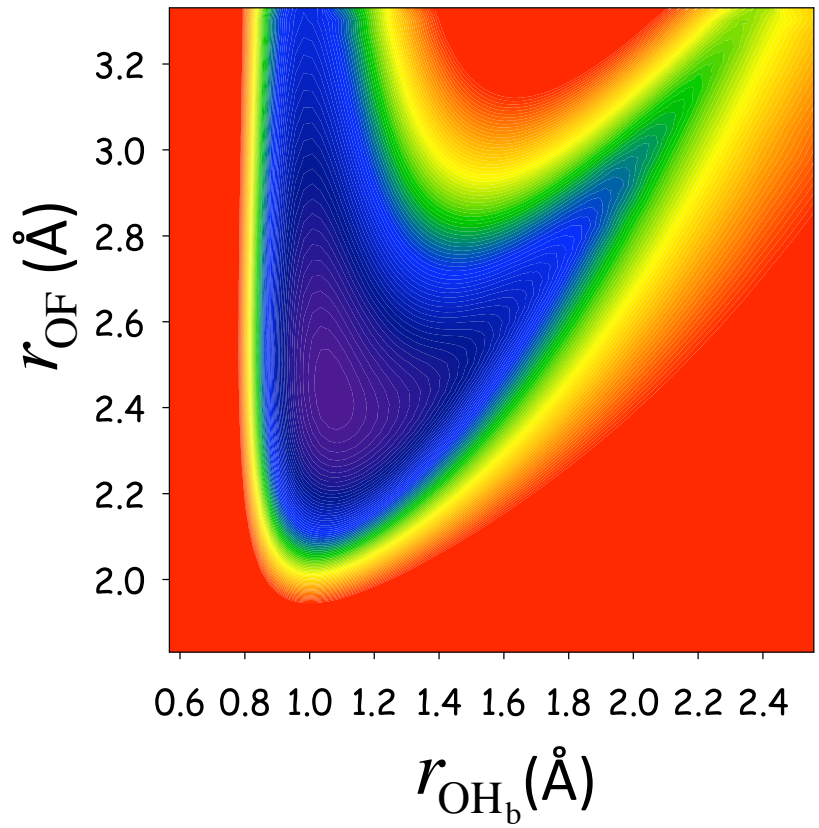


Moving on to 2D

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.





Horvath *et al. J. Phys. Chem. A* **2008**, *112*, 12337-12344.

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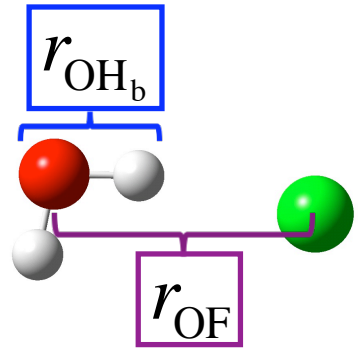
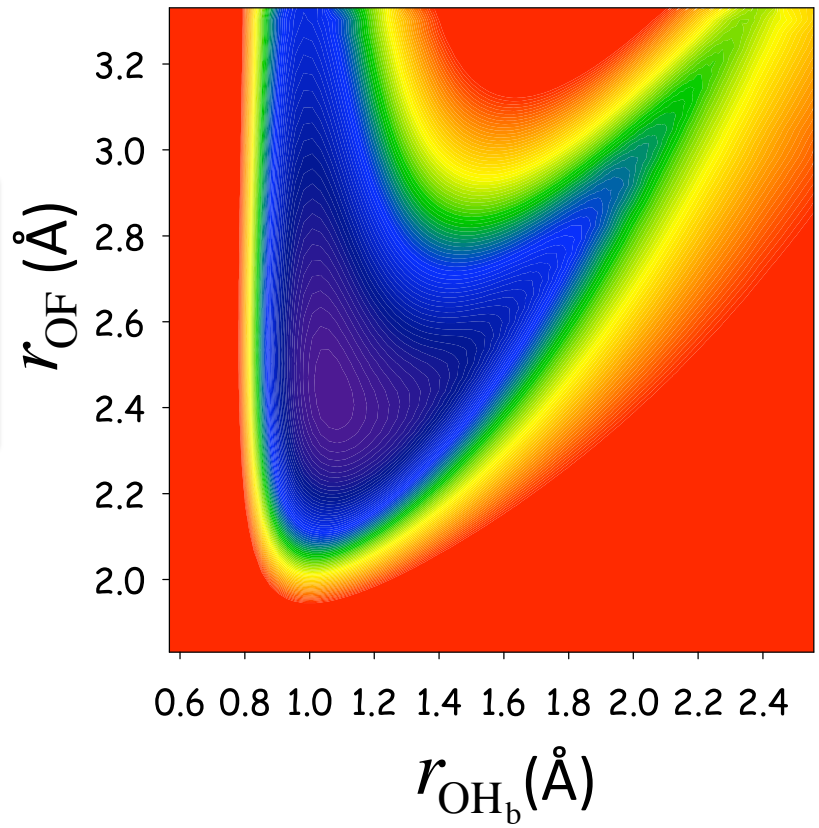
Highly anharmonic system with a strong coupling observed between r_{OH_b} and r_{OF}.





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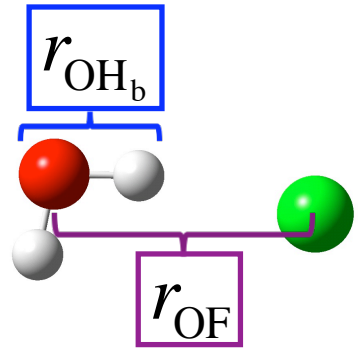
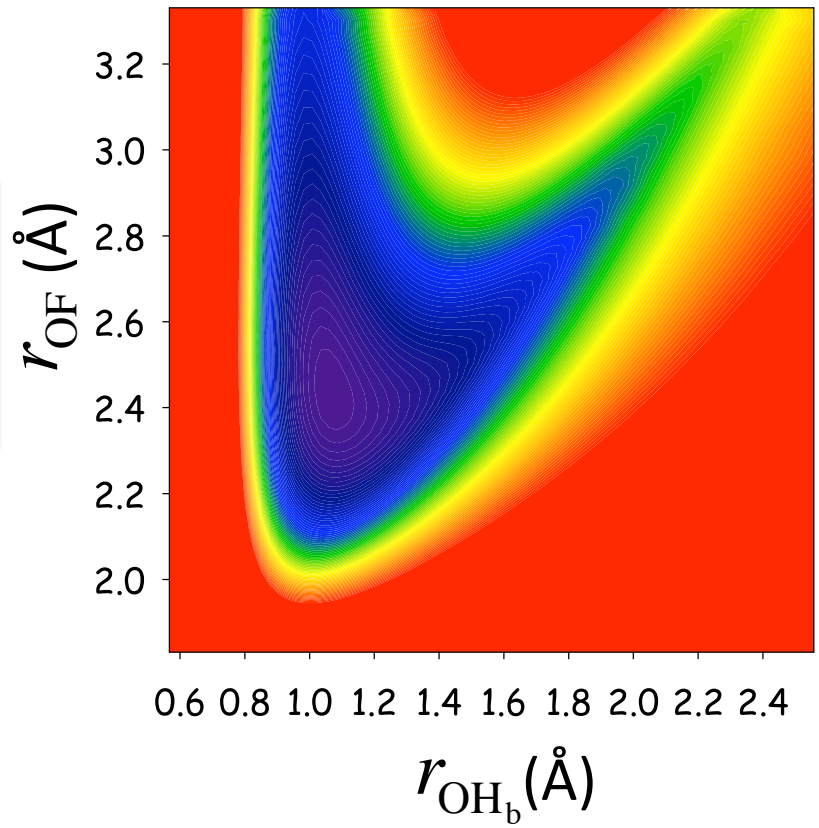
Our goal is to accurately capture all states with up to 3 total quanta of excitation.





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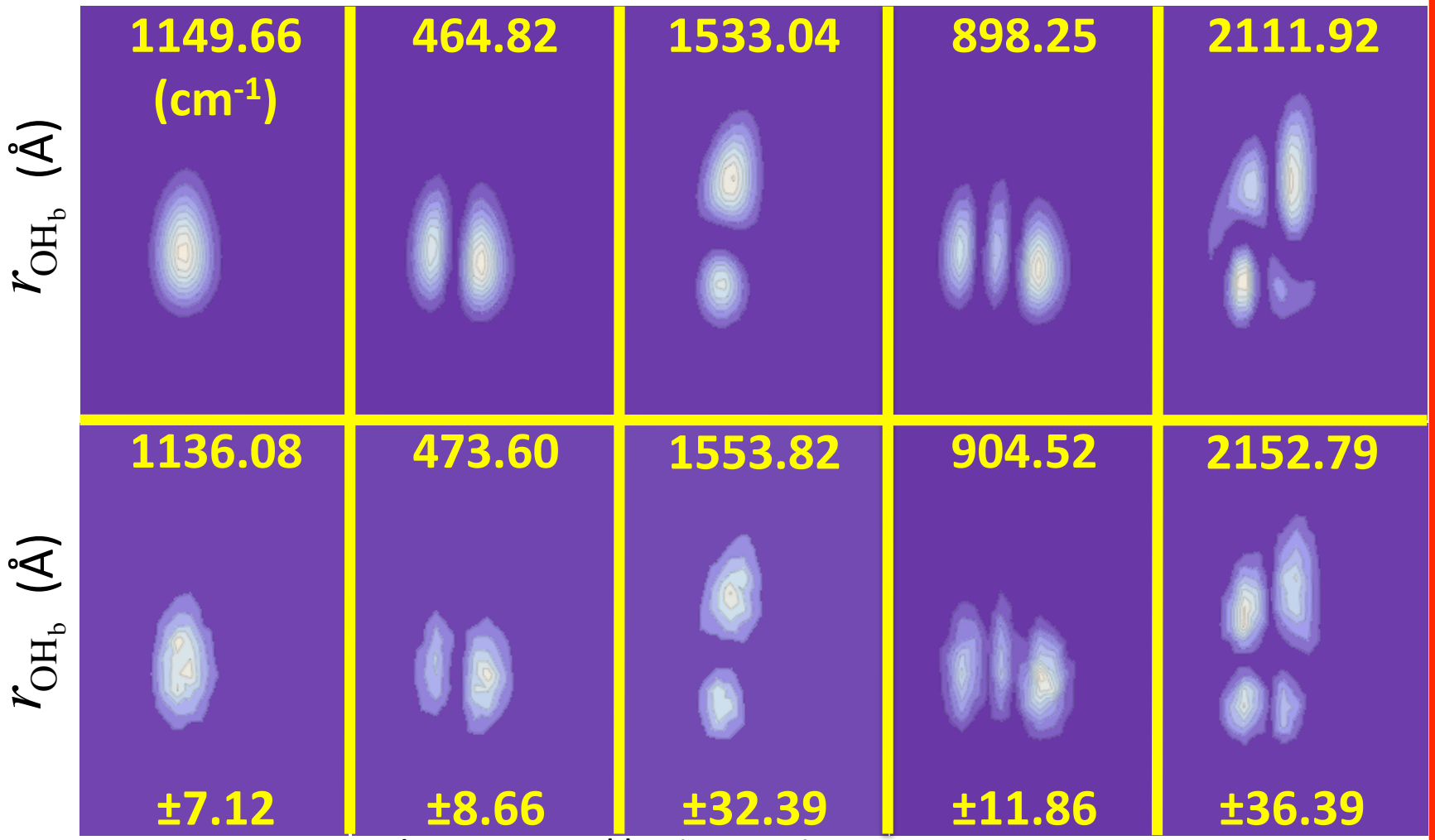
A Taste of the Preliminary Results



Active space and basis contain all states with up to 3 and 6 quanta respectively

50,000 sampling points
β_{fat}=0.01,0.01
Statistics from 4 calculations

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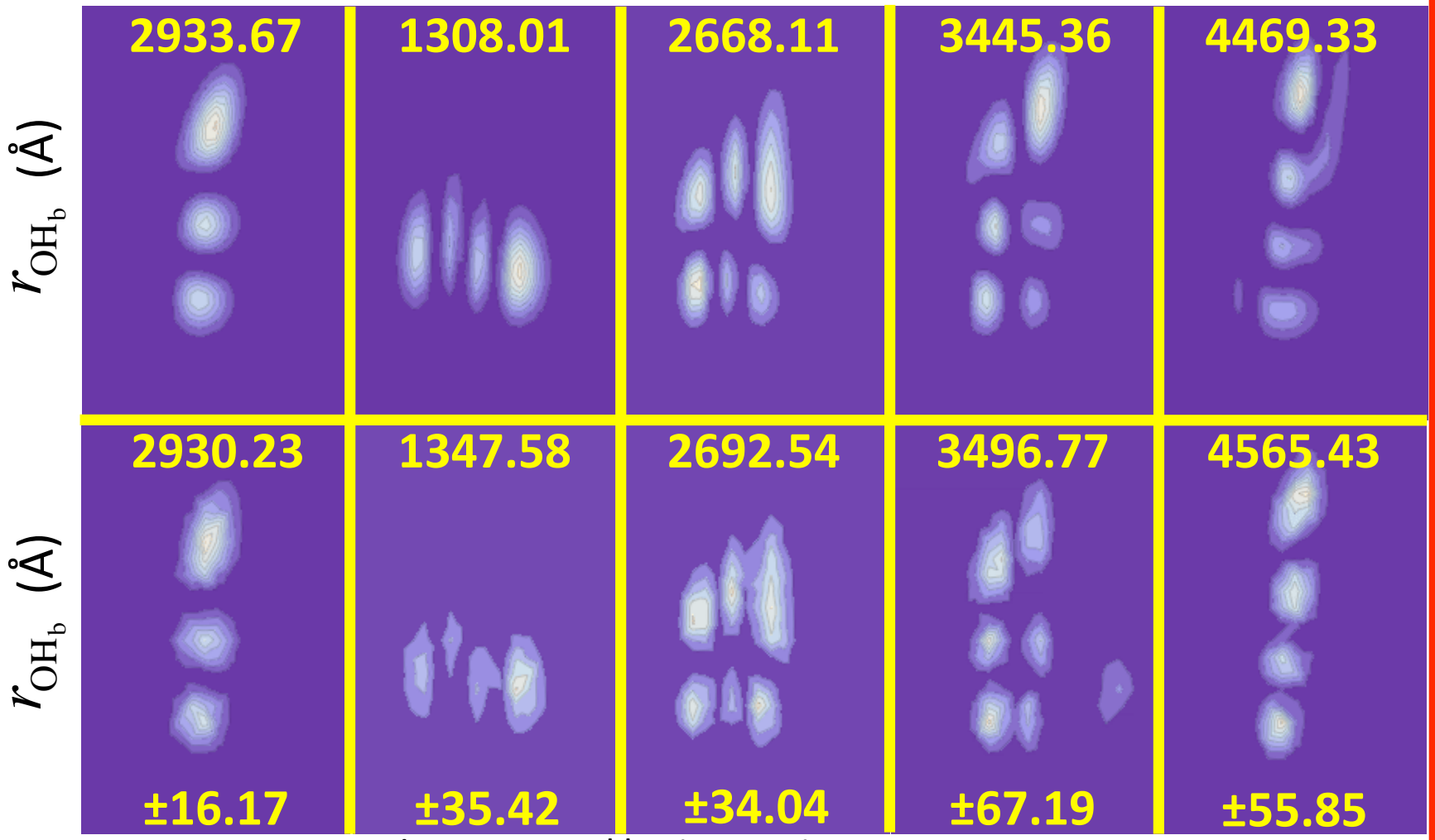

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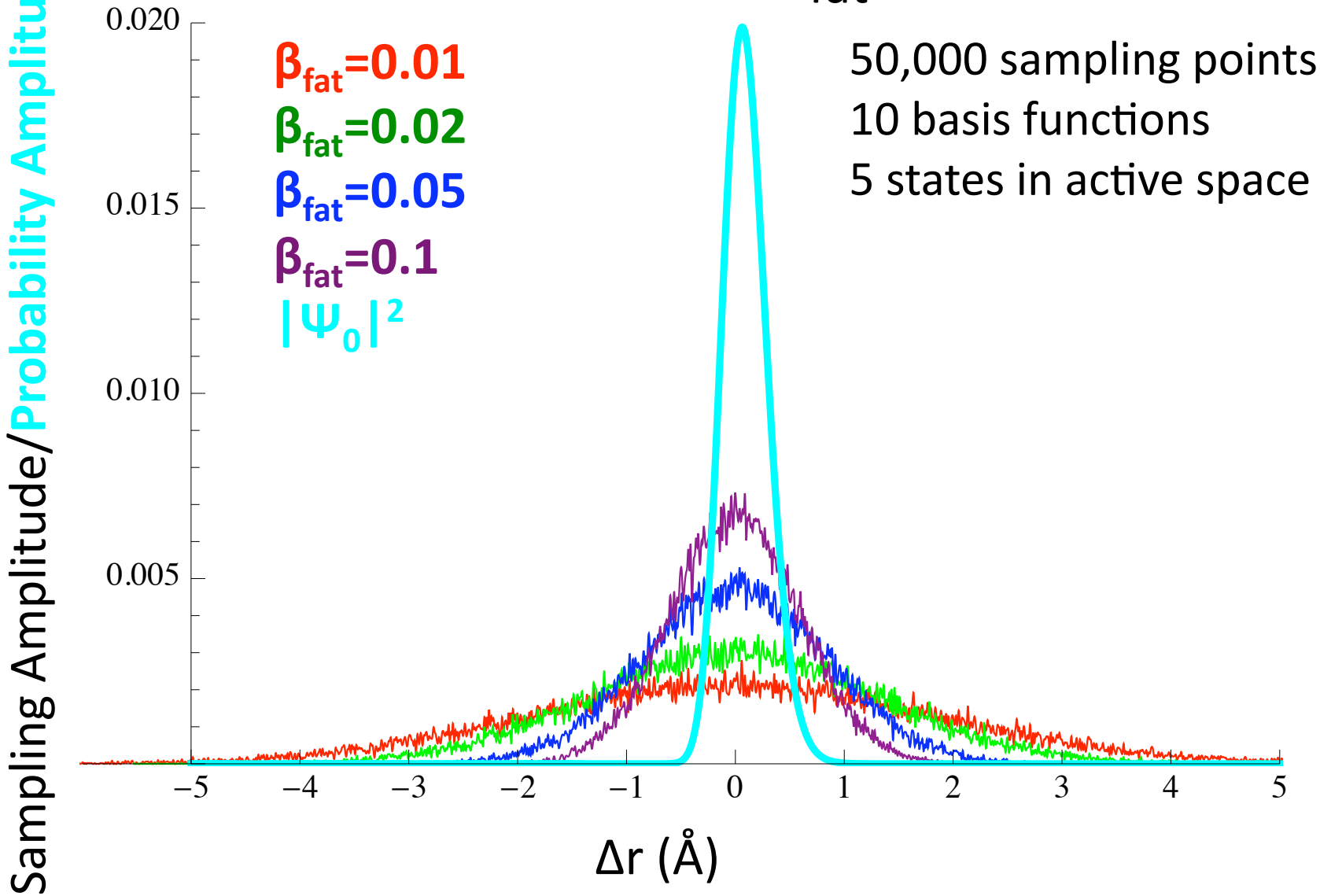
Couple algorithm with ab initio electronic structure calculations

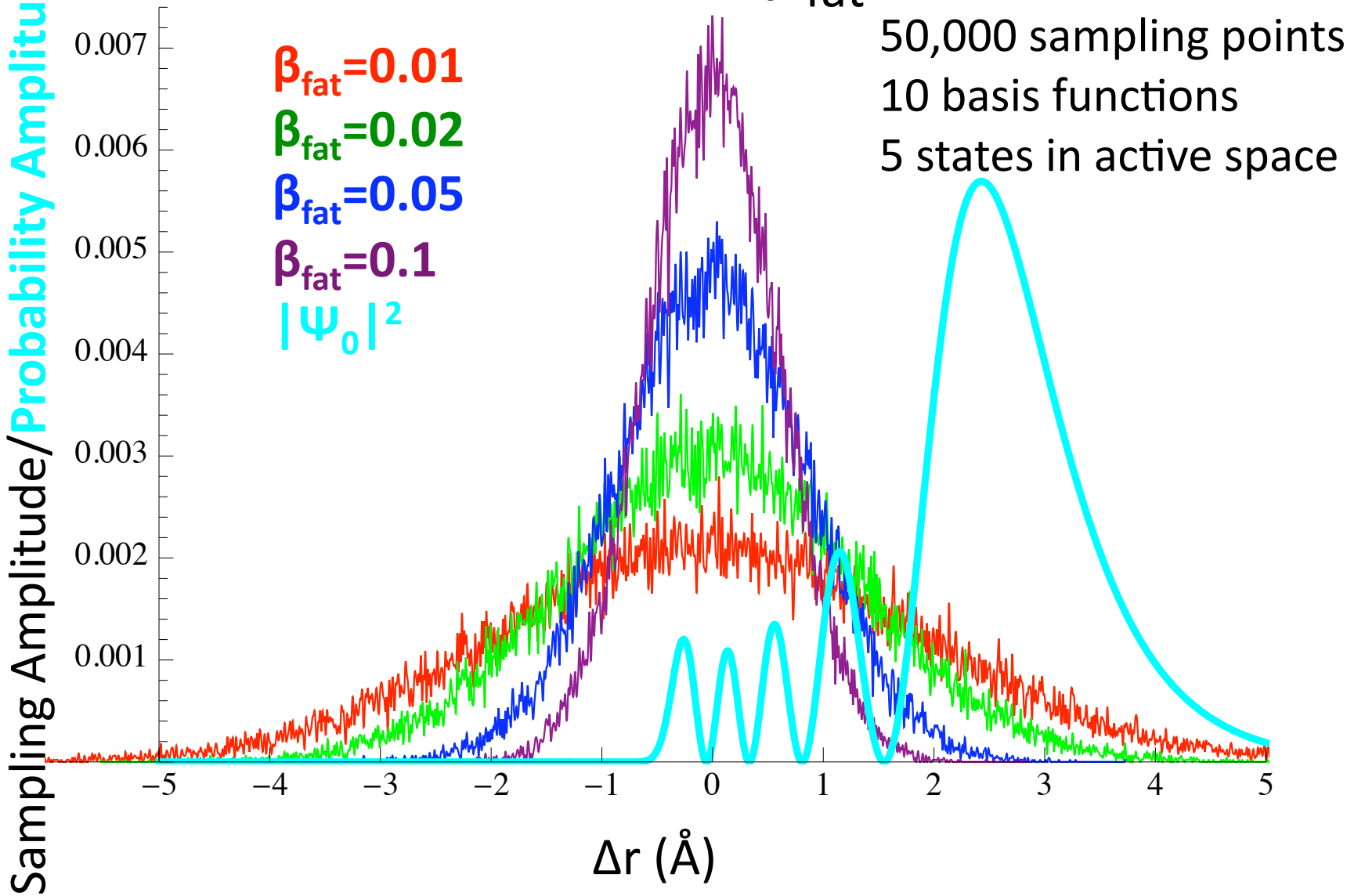
Acknowledgements

Effect of β_{fat}



50,000 sampling points
10 basis functions
5 states in active space

Effect of β_{fat}



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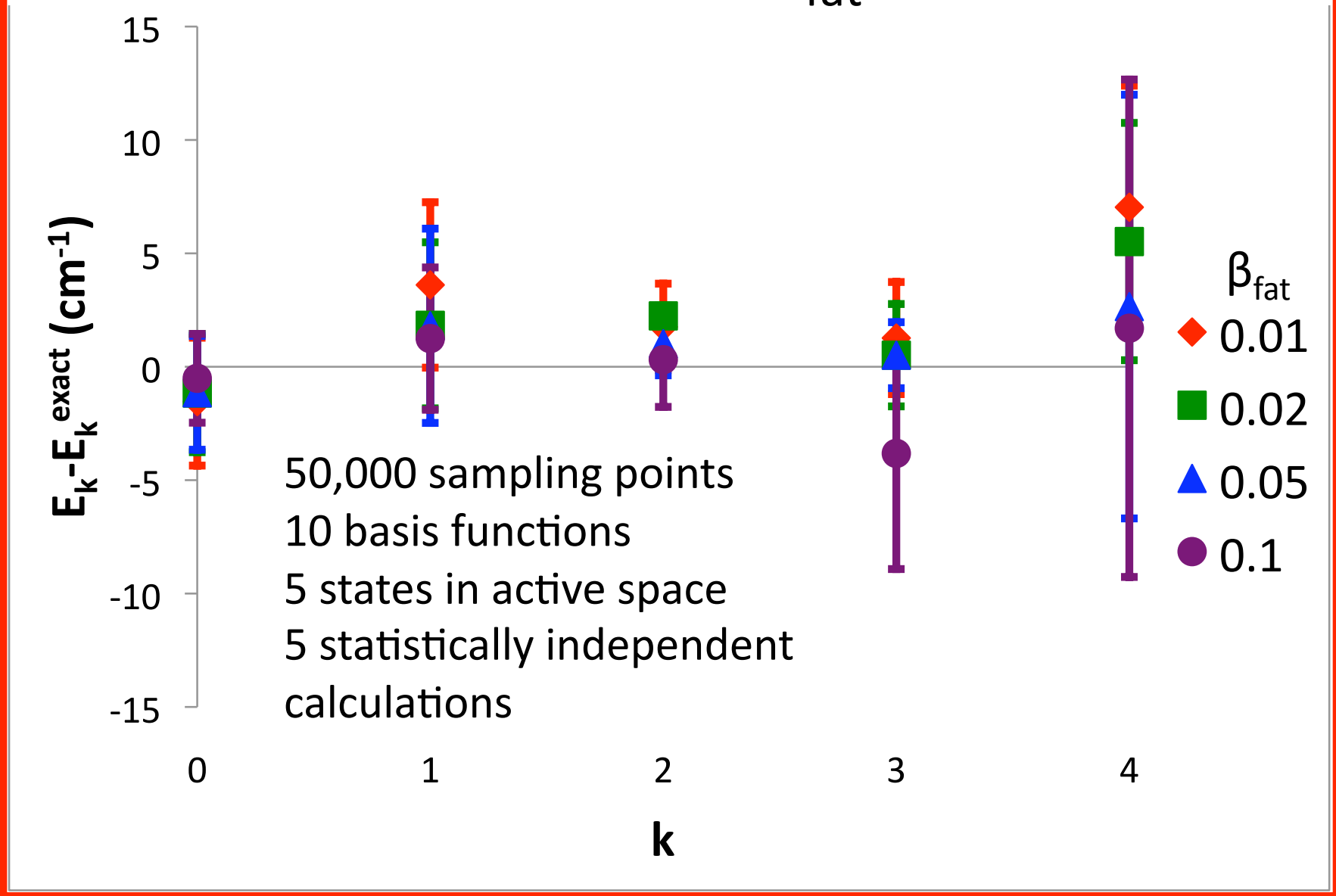

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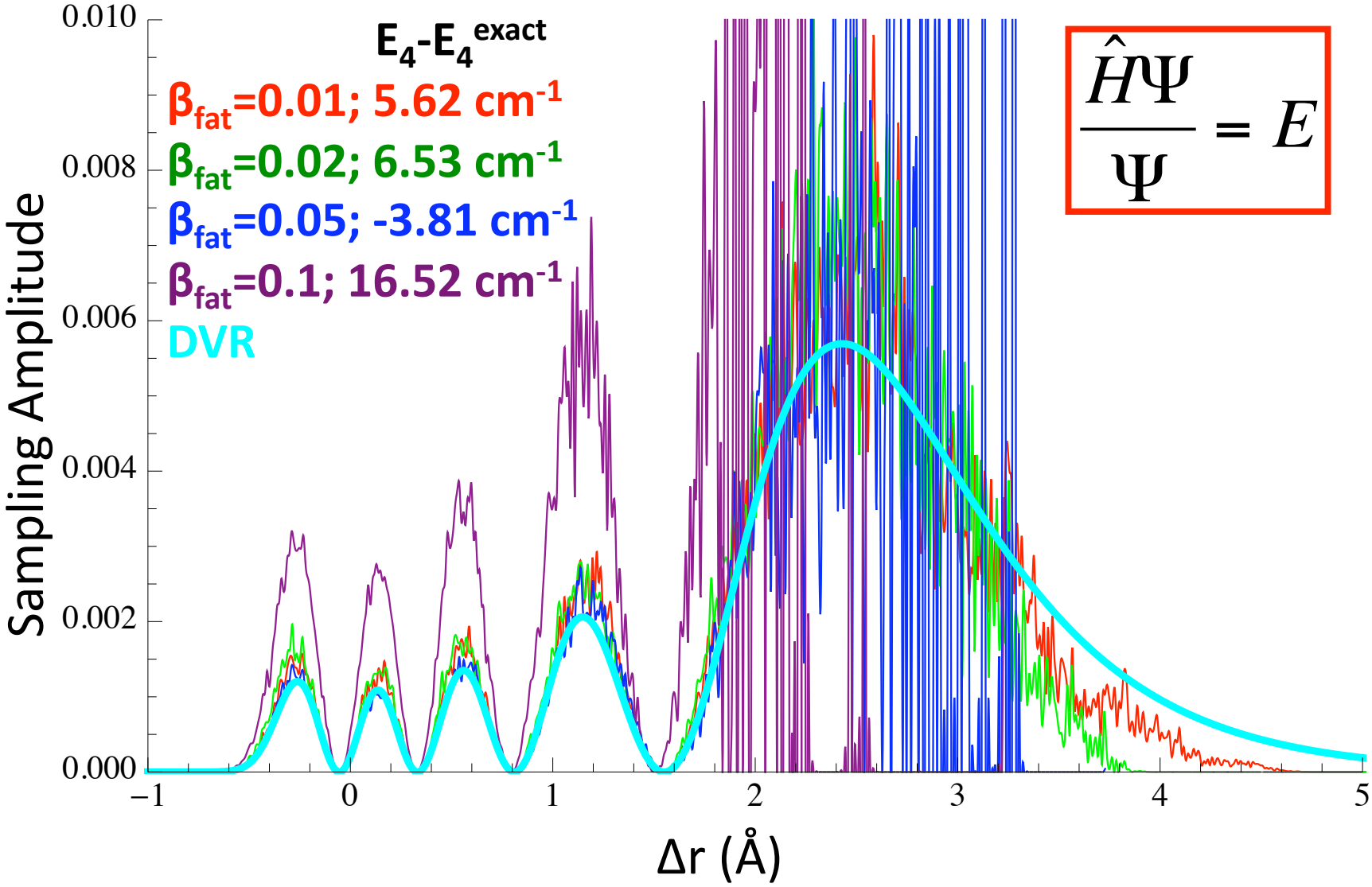
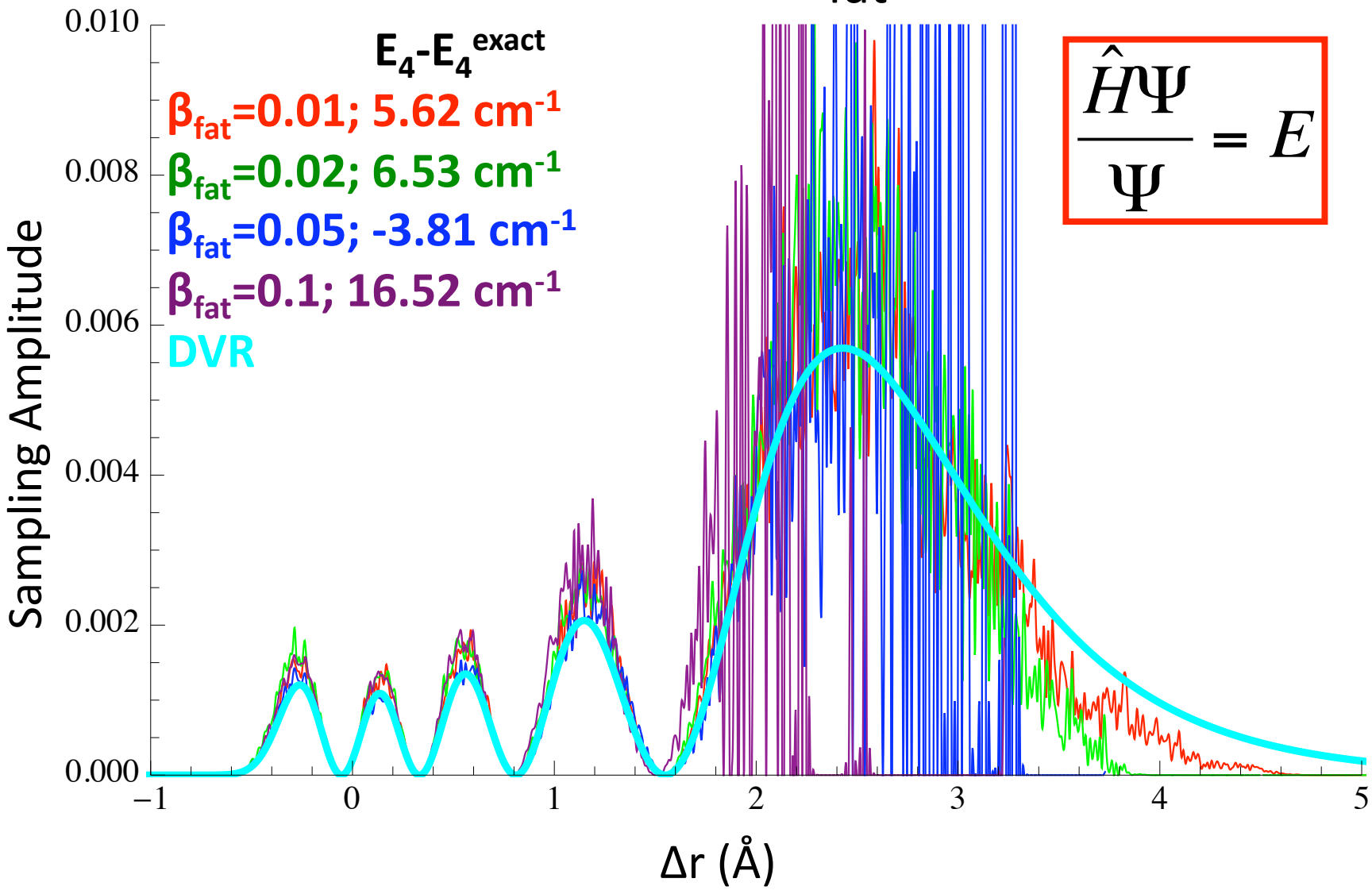


$$\frac{\hat{H}\Psi}{\Psi} = E$$

Effect of β_{fat}



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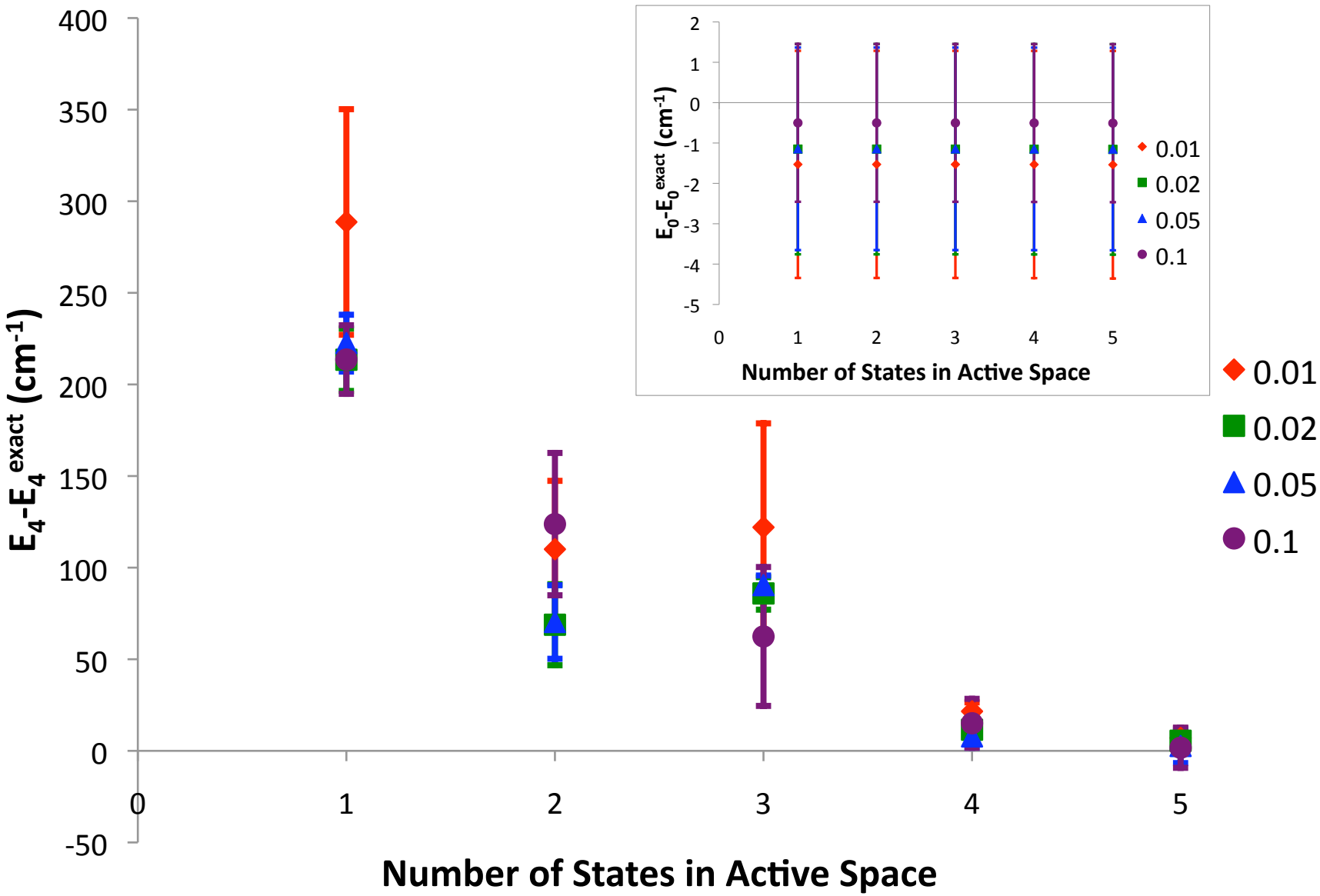
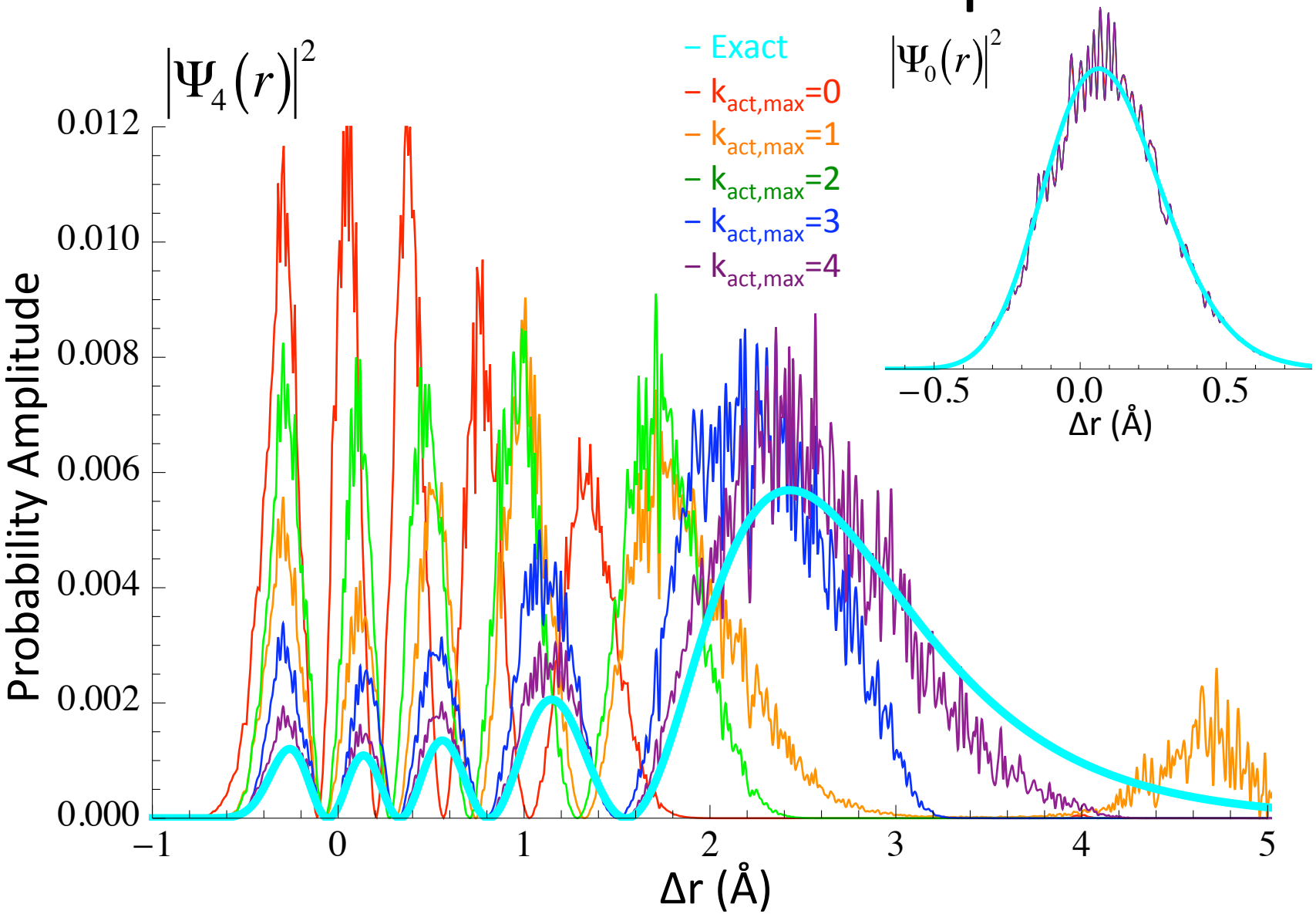
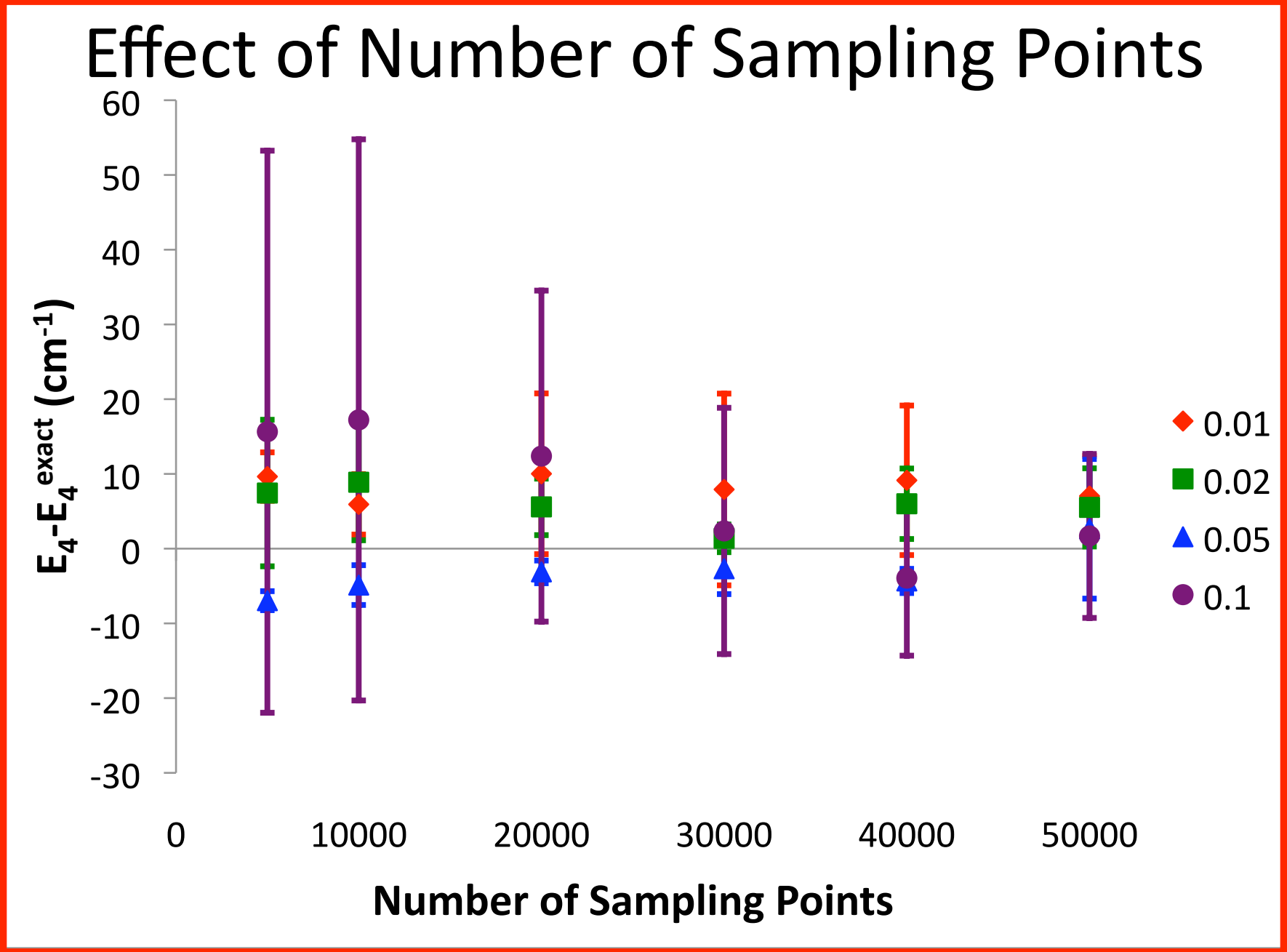
Effect of Size of Active Space



Effect of Size of Active Space




Effect of Number of Sampling Points
60
50
40
30
20
10
0
-10
-20
-30
E_4-E_4^{exact} (cm^{-1})
0
10000
20000
30000
40000
50000
Number of Sampling Points
0.01
0.02
0.05
0.1

Improving Methodology

Assignment Scheme

$$\left|\left\langle \tilde{\Psi}^{(j)}_{m,n} \middle| \Psi^{(j)}_{o,p} \right\rangle\right|^2$$

Eigenstate

Basis function

$$\left|\left\langle \tilde{\Psi}^{(j)}_{m,n} \middle| \Psi^{(j)}_{trial} \right\rangle\right|^2$$

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

Take linear combination of 2 eigenstates which maximally overlap $\Psi^{(j)}_{trial}$.

Improving Methodology

Active Space Evolution

$$\underline{\underline{H}}^{(j)}$$

$$\left\{\Psi^{(j+1)}\right\} \qquad \left\{\tilde{\Psi}^{(j)}\right\},\left\{E^{(j)}\right\}$$

Define an active space:

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

Labeling based on order in which state is constucted

$$\left\{\Psi_m^{(j+1)}\right\}_{active} \Rightarrow \varphi_{m\notin active}^{(j+1)}$$

Basis functions outside of active space built out of active space

Improving Methodology

Active Space Evolution

$$\underline{\underline{H}}^{(j)}$$

$$\left\{\Psi^{(j+1)}\right\} \qquad \left\{\tilde{\Psi}^{(j)}\right\}, \left\{E^{(j)}\right\}$$

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

These basis functions are fixed for a series of N iterations

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

$$\left\{\Psi^{(j+1)}_{m}\right\}_{active} \Rightarrow \varphi^{(j+1)}_{m\notin active}$$

Improving Methodology

Active Space Evolution

$$\underline{\underline{H}}^{(j)}$$

$$\left\{\Psi^{(j+1)}\right\} \qquad \left\{\tilde{\Psi}^{(j)}\right\}, \left\{E^{(j)}\right\}$$

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

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

$$\left\{\Psi^{(j+1)}_{m}\right\}_{active} \Rightarrow \varphi^{(j+1)}_{m\notin active}$$

After N iterations:

Size of active space grows by 1

Members of new active space allowed to mix via diagonalization of active space only $\underline{\underline{H}}$.