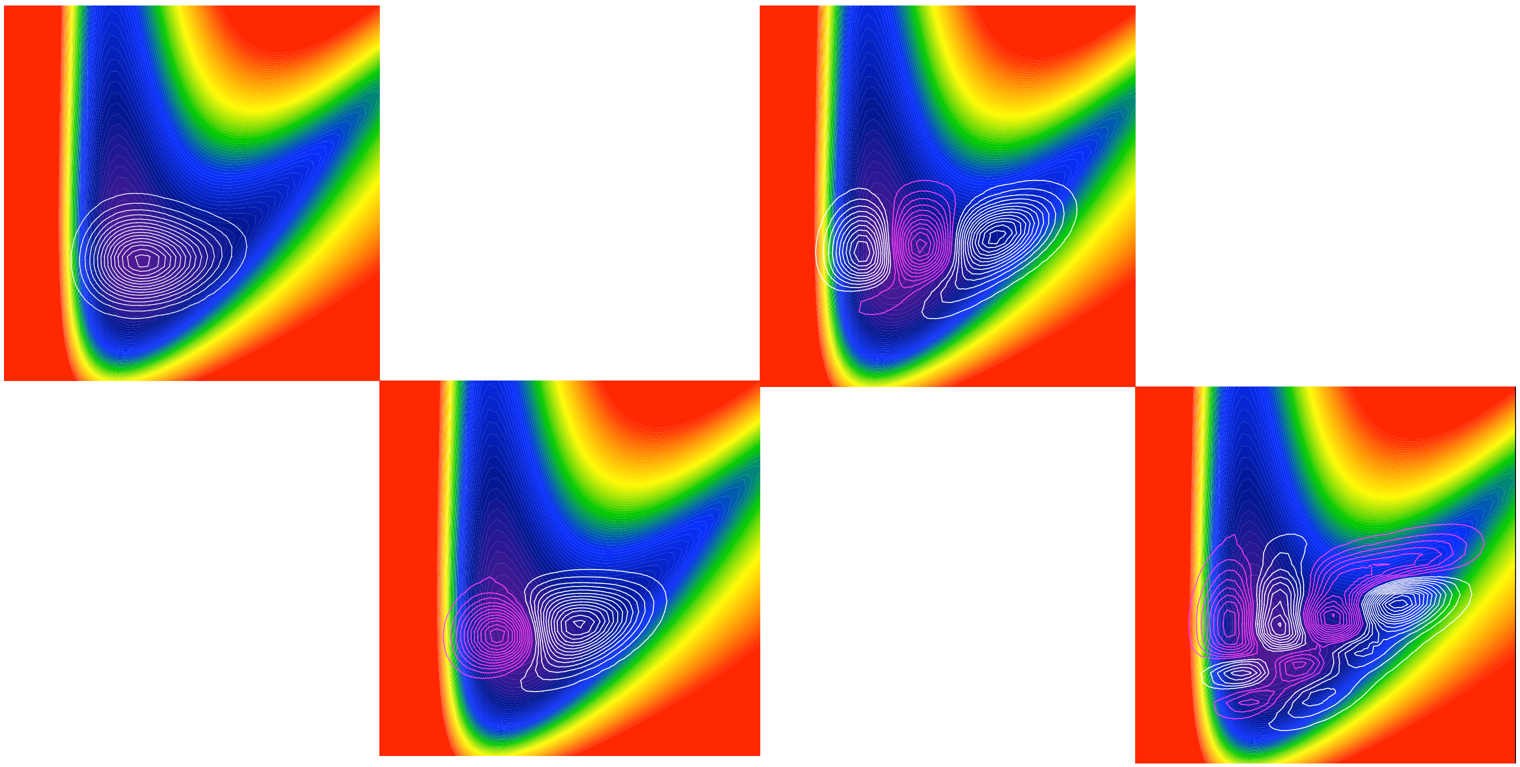
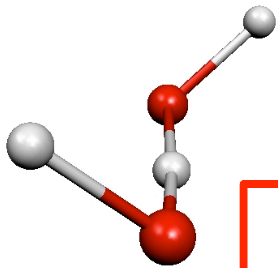
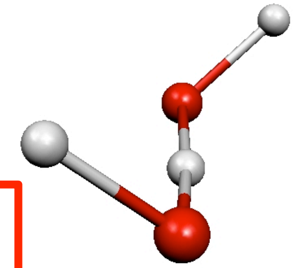
Progress Towards the Accurate Calculation of Anharmonic Vibrational States of Fluxional Molecules and Clusters Without a Potential Energy Surface



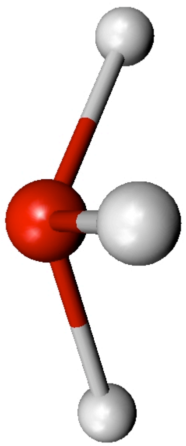
Andrew S. Petit and Anne B. McCoy
The Ohio State University

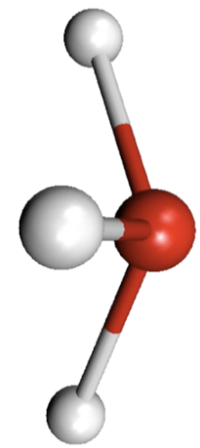
What Are the Challenges???

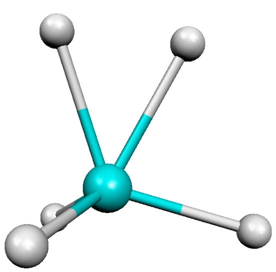


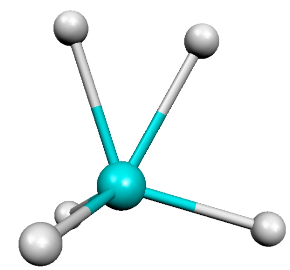


Harmonic analysis pathologically fails









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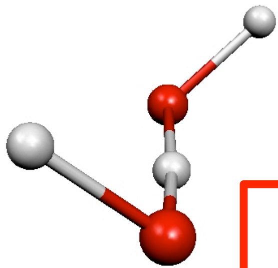

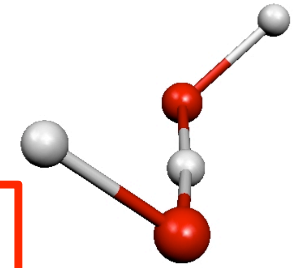

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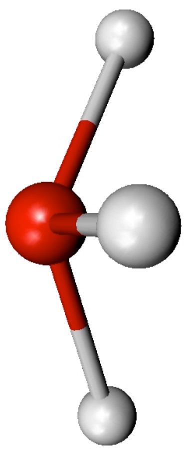

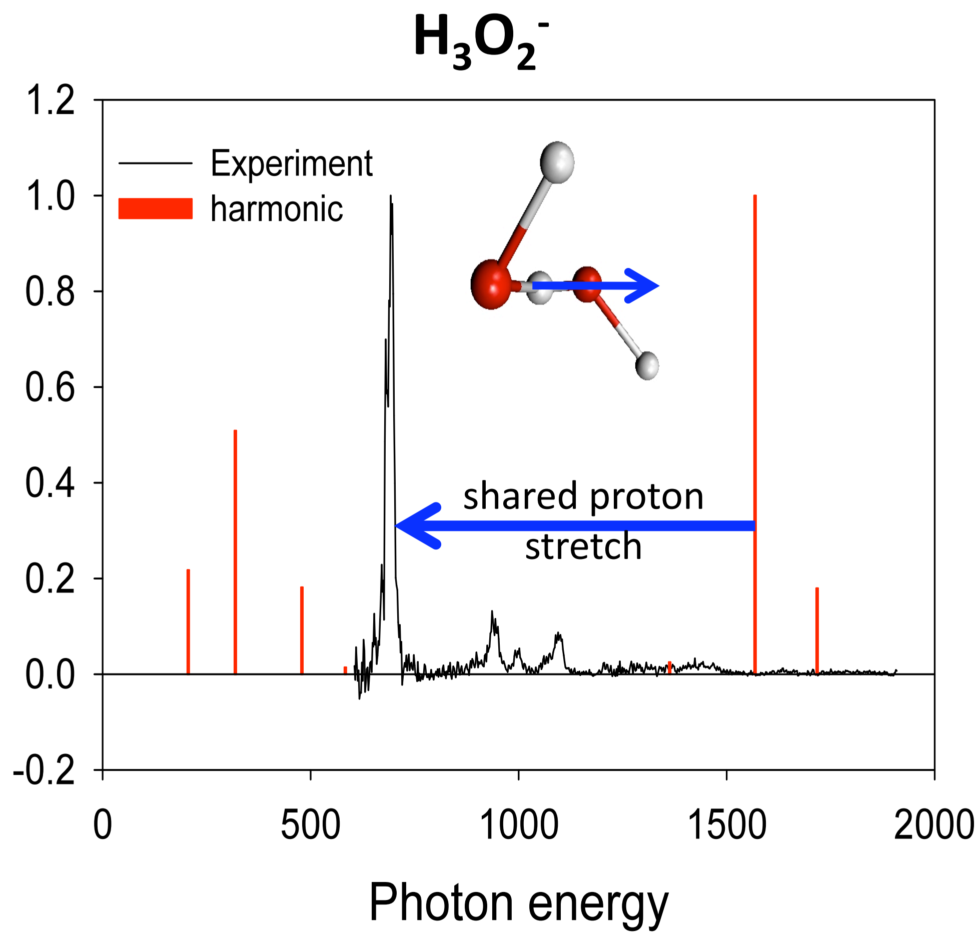

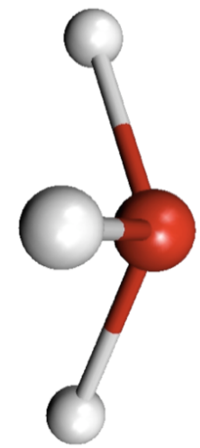

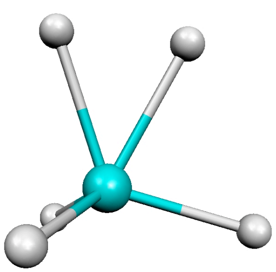

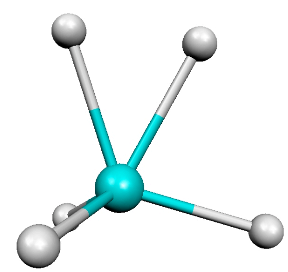

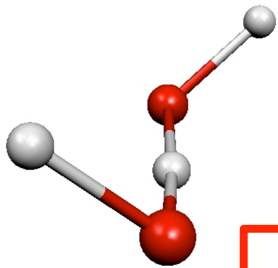

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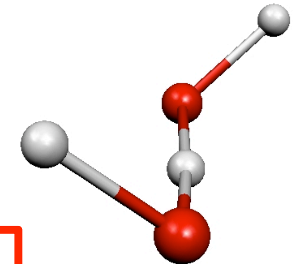

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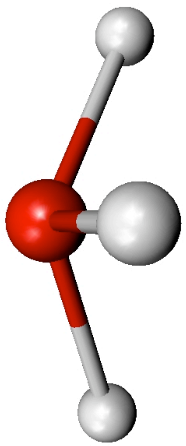
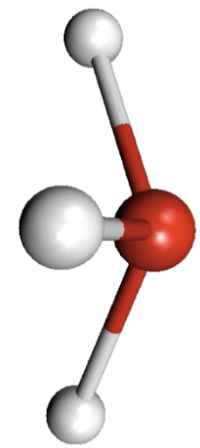
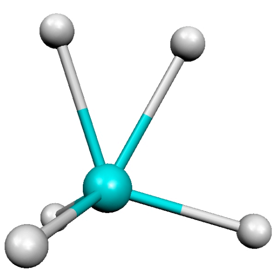
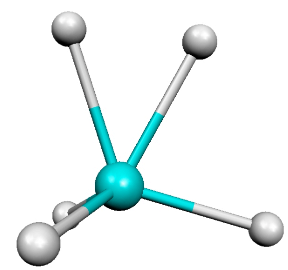


An accurate and general treatment of these highly fluxional systems requires either a global PES or a grid-based sampling of configuration space







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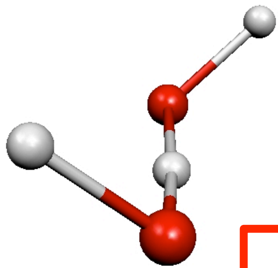

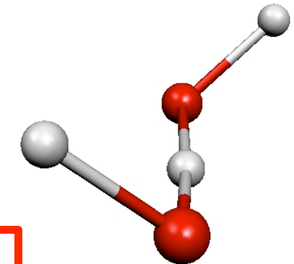

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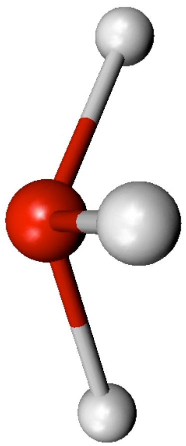
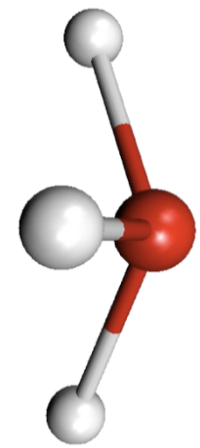
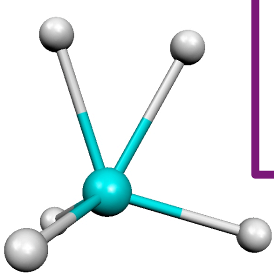
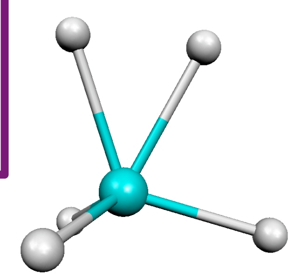


An accurate and general treatment of these highly fluxional systems requires either a global PES or a grid-based sampling of configuration space





Large basis set expansions required to fully capture the anharmoncity of these systems



The General Scheme

The General Scheme

Monte Carlo Sample
Configuration Space

Monte Carlo Sample Configuration Space

Use importance sampling Monte Carlo

Monte Carlo Sample Configuration Space

Use importance sampling Monte Carlo

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

Monte Carlo Sample Configuration Space

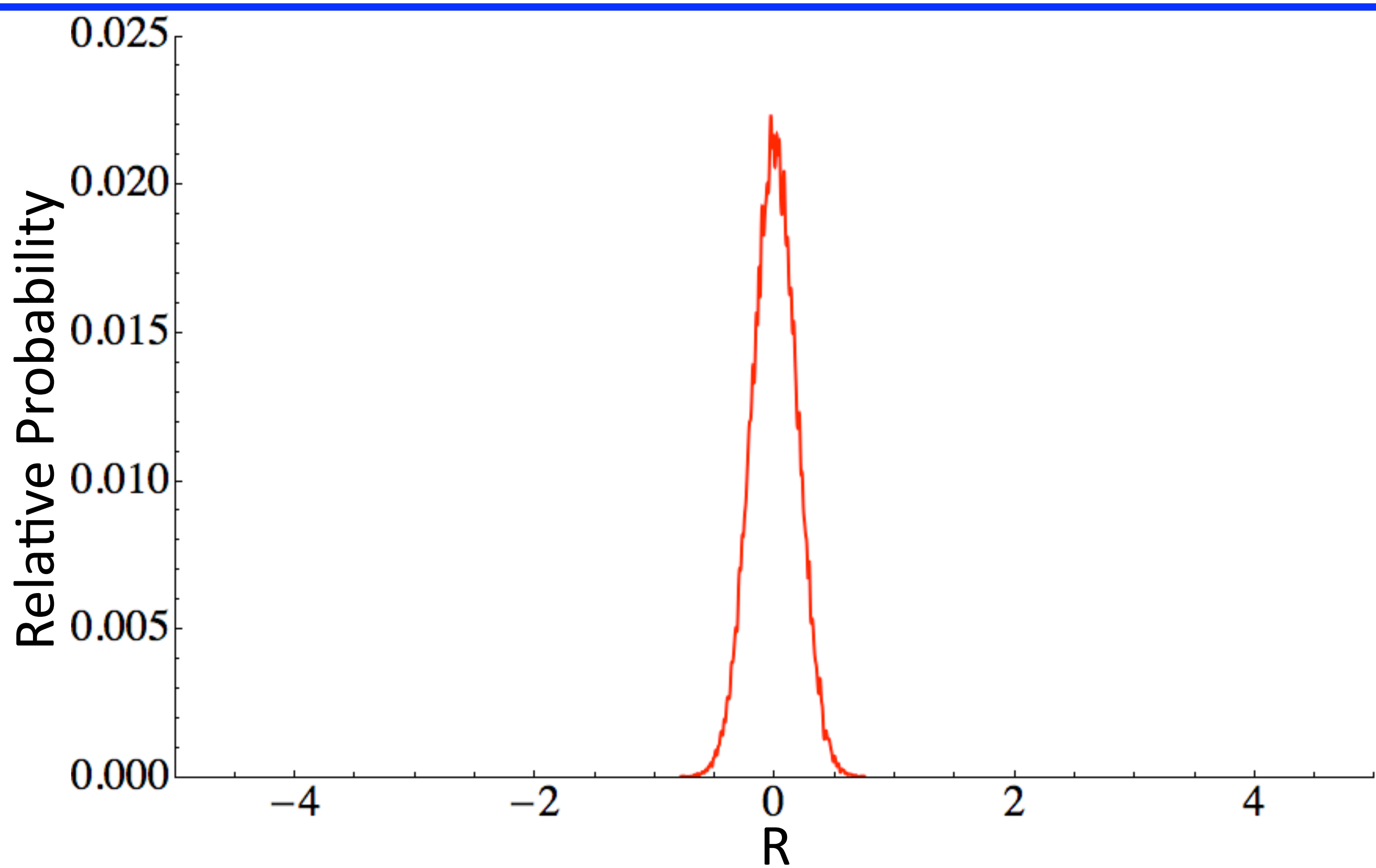
Use importance sampling Monte Carlo

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

Normalized probability distribution that is peaked, ideally, where the function of interest, f, is peaked.

Monte Carlo Sample Configuration Space

Sampling function based on harmonic ground state



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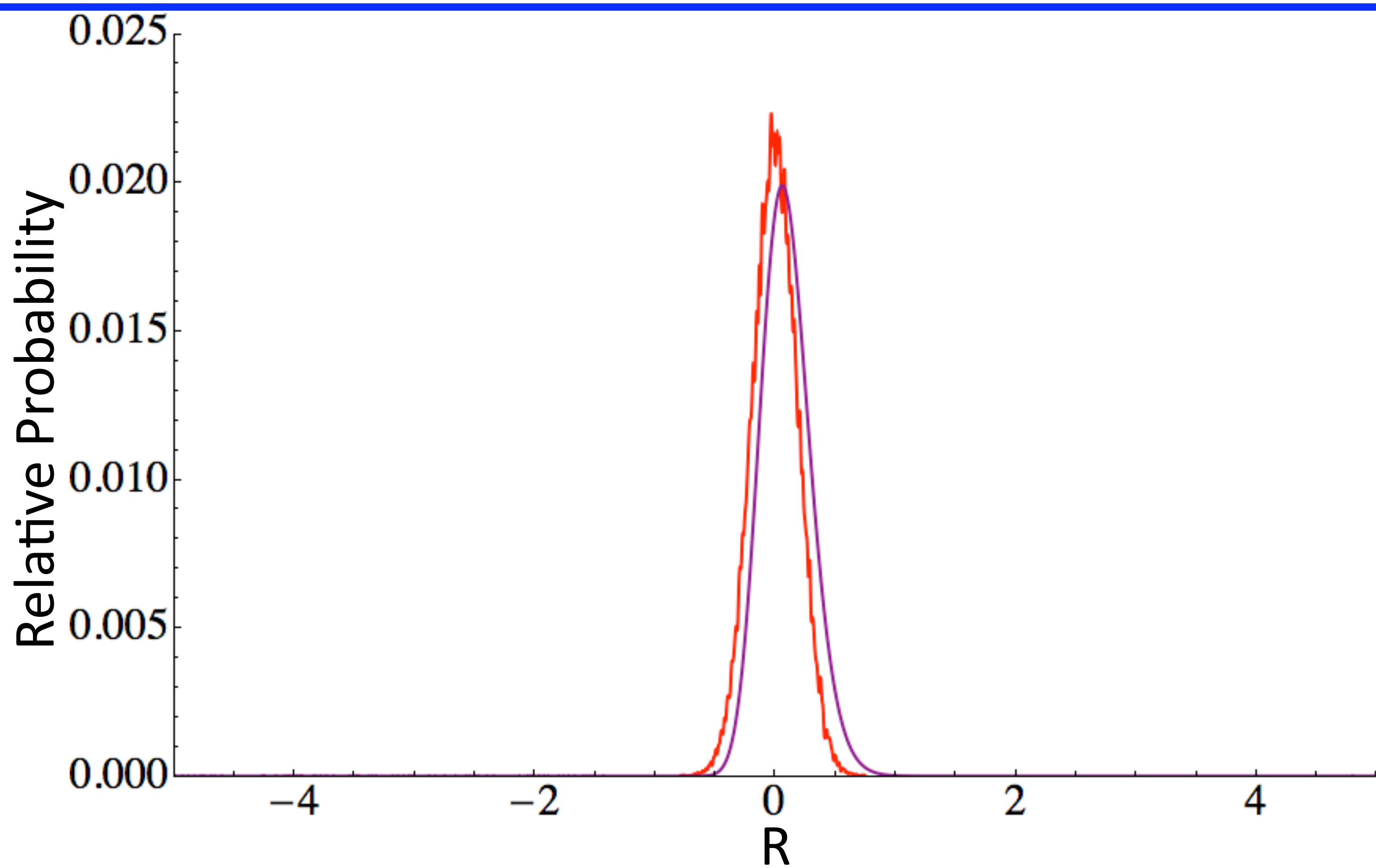

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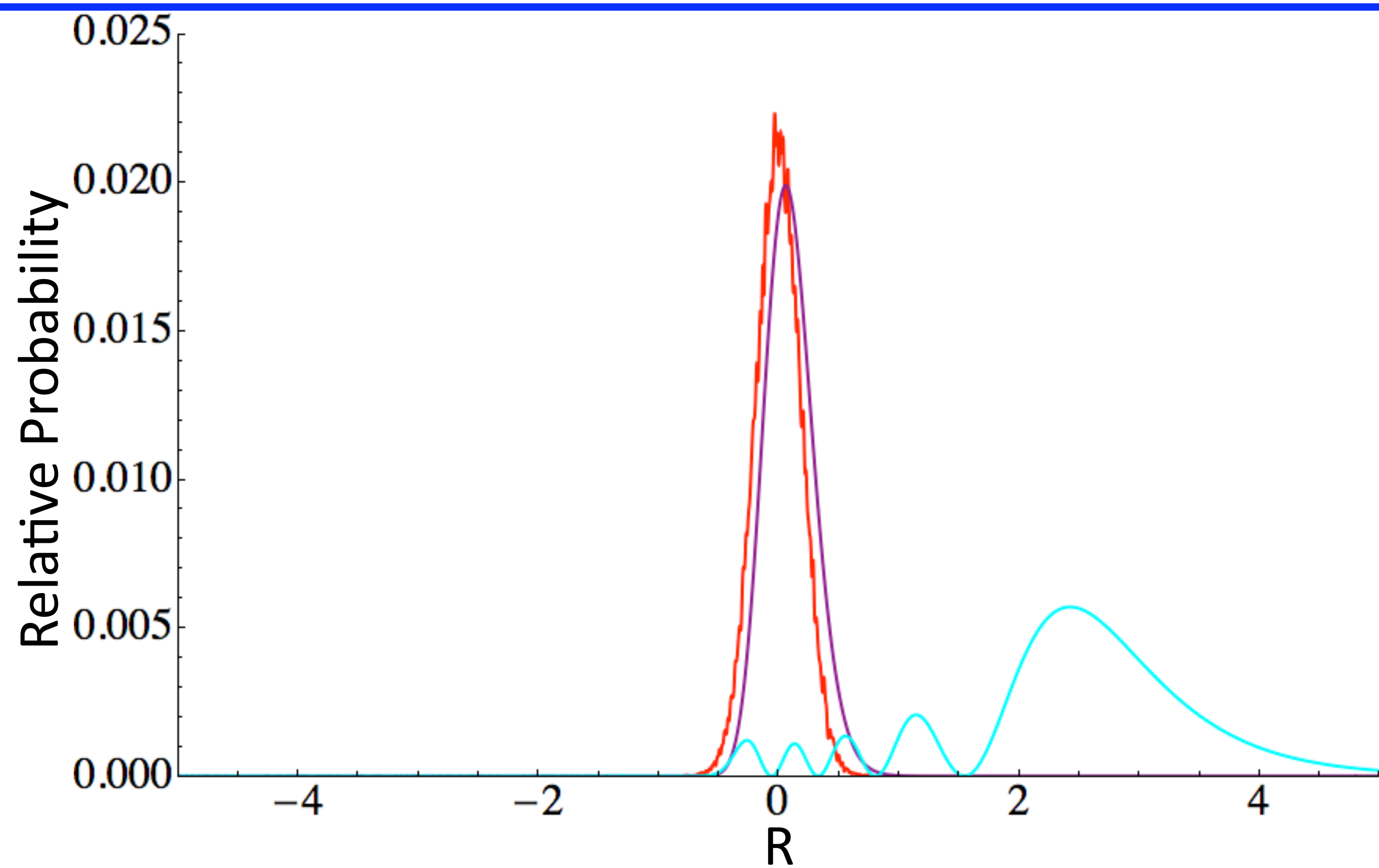

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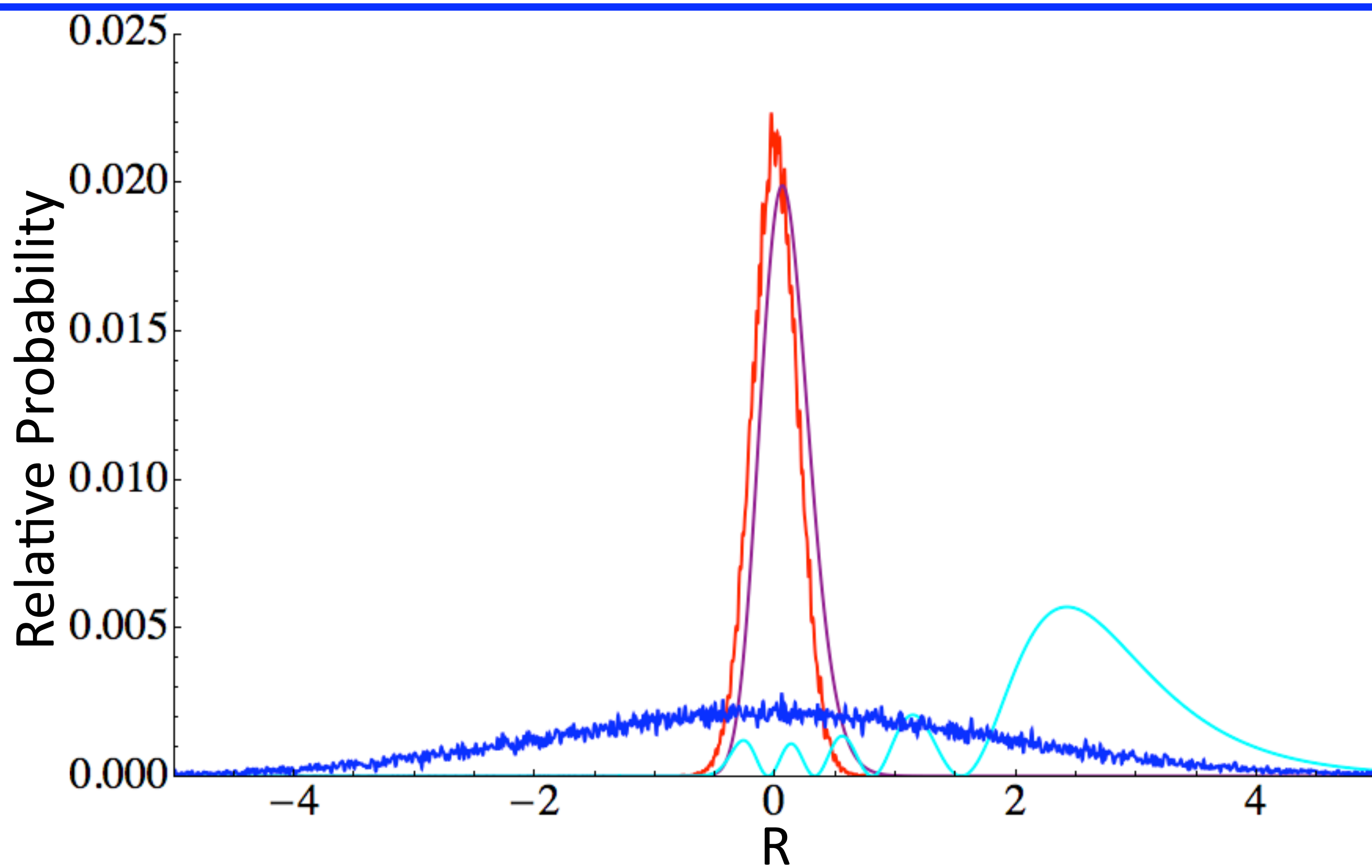

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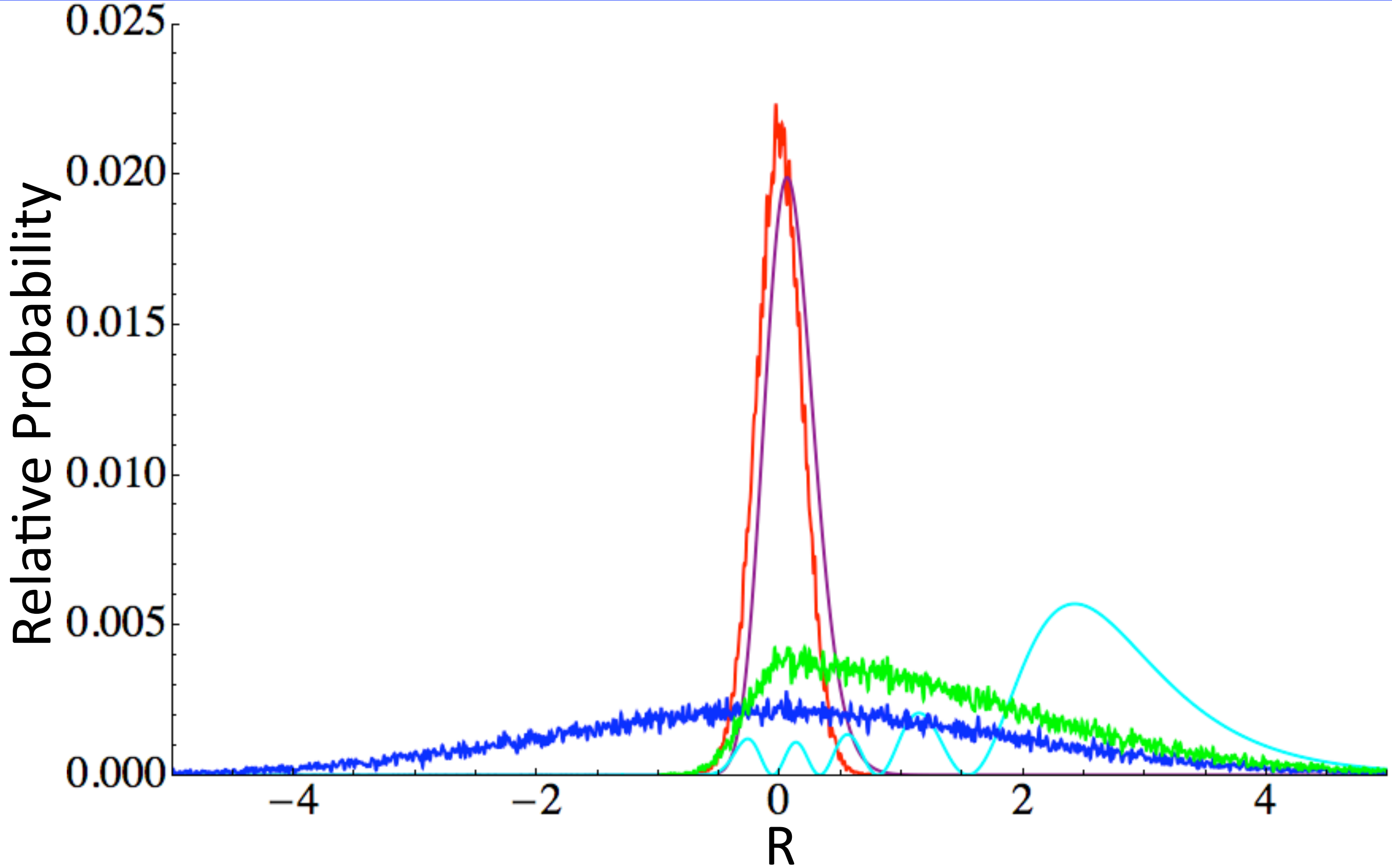
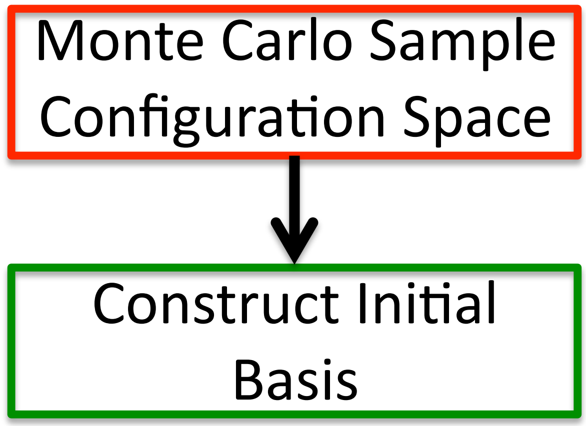


The General Scheme



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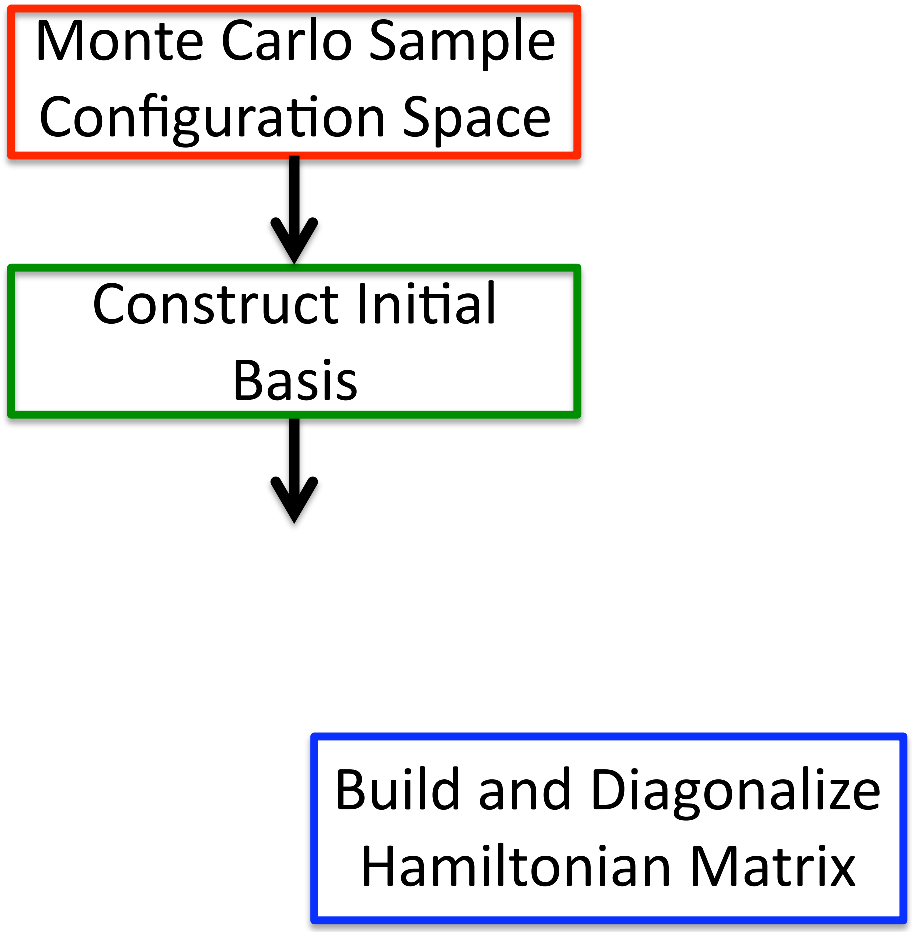

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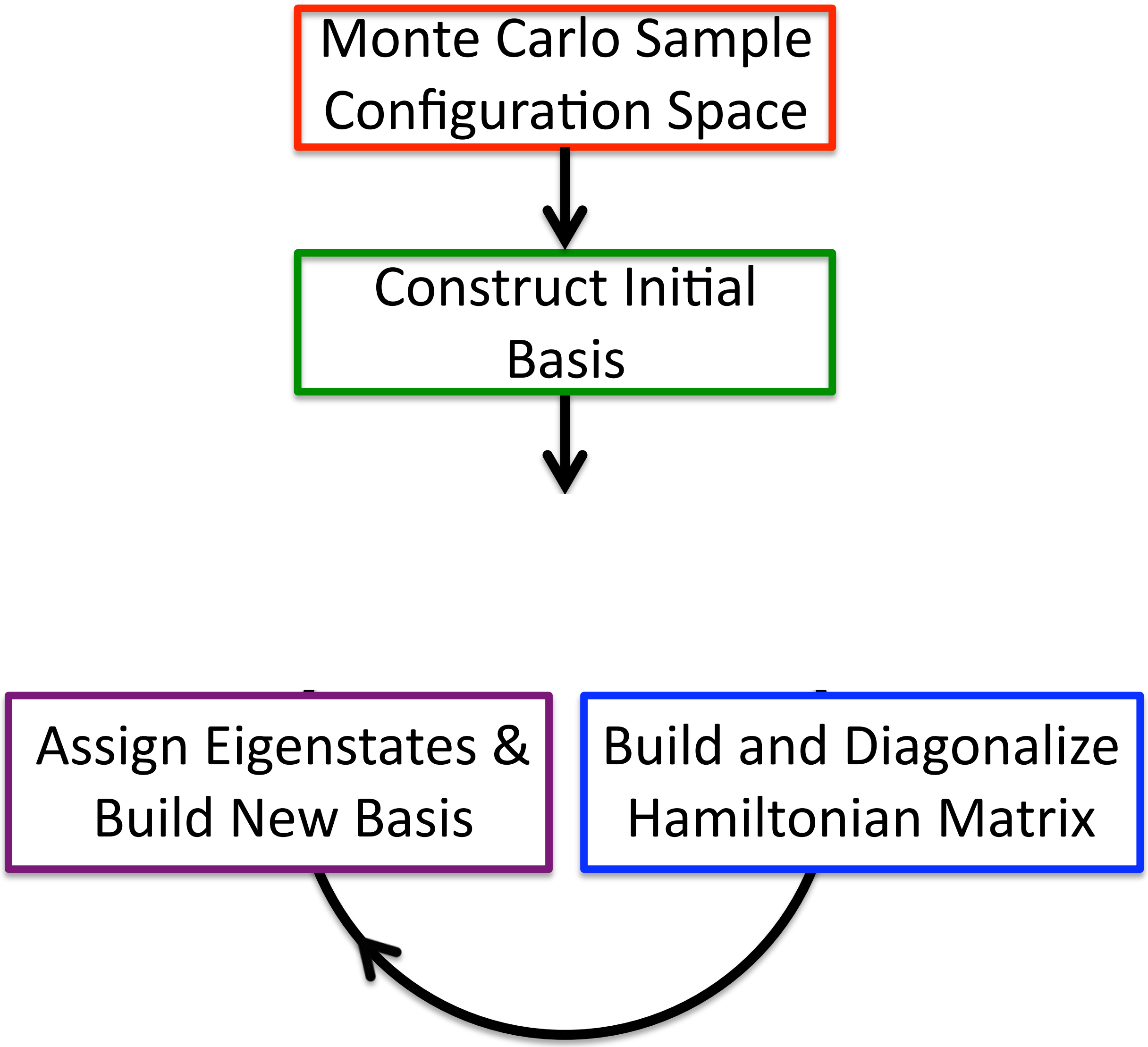

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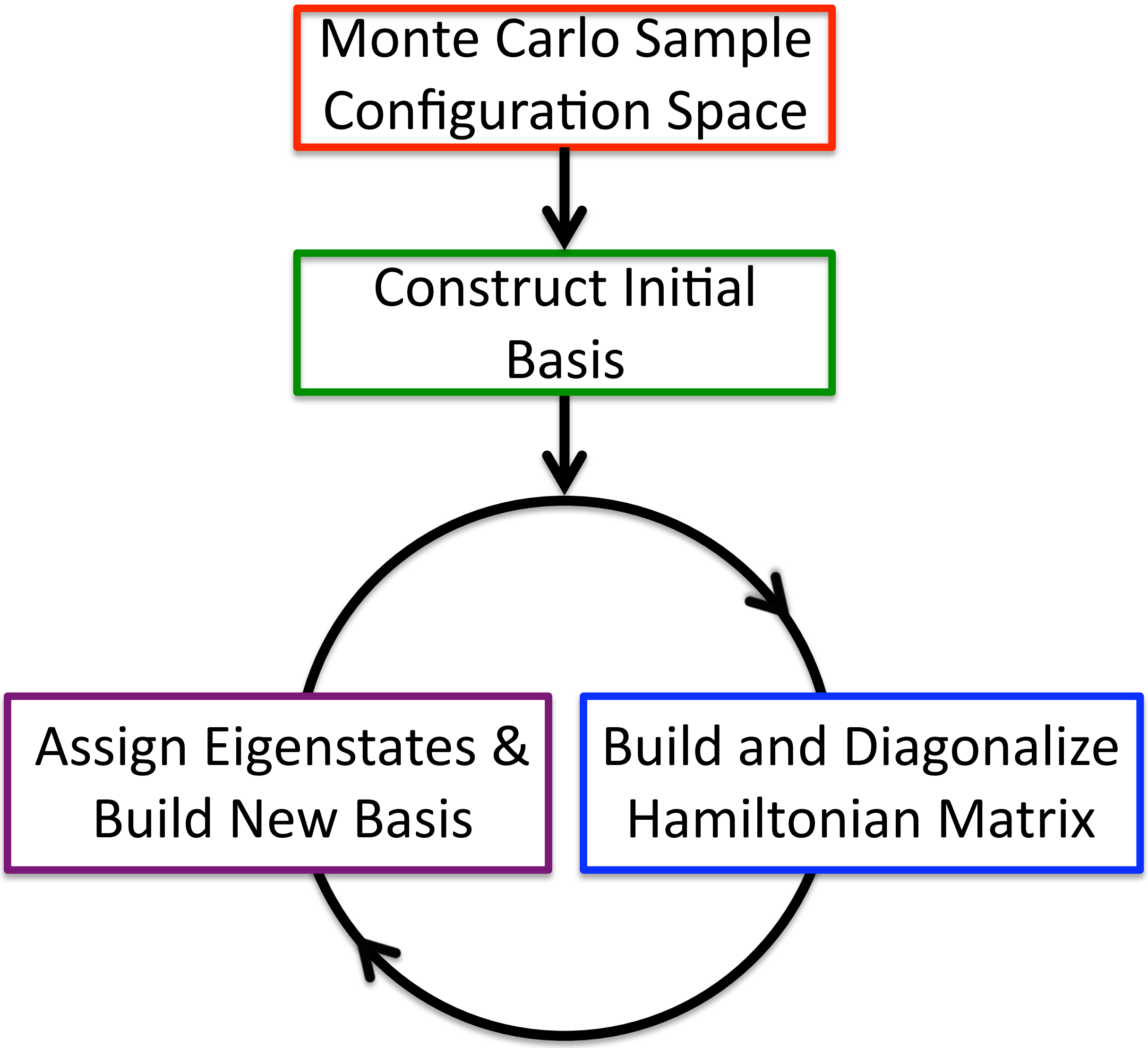

The Evolving Basis

The Evolving Basis

Harmonic oscillator basis

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Harmonic oscillator basis

$$\underline{\underline{H}}^{(1)}$$

The Evolving Basis

Harmonic oscillator basis

$$\underline{\underline{H}}^{(1)}$$

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

The Evolving Basis

Harmonic oscillator basis

↓

$$\underline{\underline{H}}^{(1)}$$

↘

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

Eigenstates used to construct new basis

Assignment via:

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

The Evolving Basis

Harmonic oscillator basis

$$\underline{\underline{H}}^{(1)}$$

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

$$\left\{\Psi^{(2)}\right\}$$

Eigenstates used to construct new basis

Assignment via:

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

The Evolving Basis

Harmonic oscillator basis

$$\underline{\underline{H}}^{(1)}$$

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

Eigenstates used to construct new basis

$$\left\{\Psi^{(2)}\right\}$$

Define an active space:

$$\left\{\Psi_m^{(2)}\right\}_{active} = \left\{\tilde{\Psi}_m^{(1)}\right\}_{active}$$

Assignment via:

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

The Evolving Basis

Harmonic oscillator basis

$\underline{\underline{H}}^{(1)}$

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

Eigenstates used to construct new basis

$\left\{\Psi^{(2)}\right\}$

Define an active space:

$$\left\{\Psi_m^{(2)}\right\}_{active} = \left\{\tilde{\Psi}_m^{(1)}\right\}_{active}$$

$$\overline{\Psi}^{(2)}_{m \notin active} = \sum_{k=1}^{m} \kappa^{(2)}_{m,m-k} r^k \Psi^{(2)}_{m-k}$$

Assignment via:

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The Evolving Basis

Harmonic oscillator basis

$$\underline{\underline{H}}^{(1)}$$

$$\left\{\Psi^{(2)}\right\}$$

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The Evolving Basis

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

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

Define an active space:

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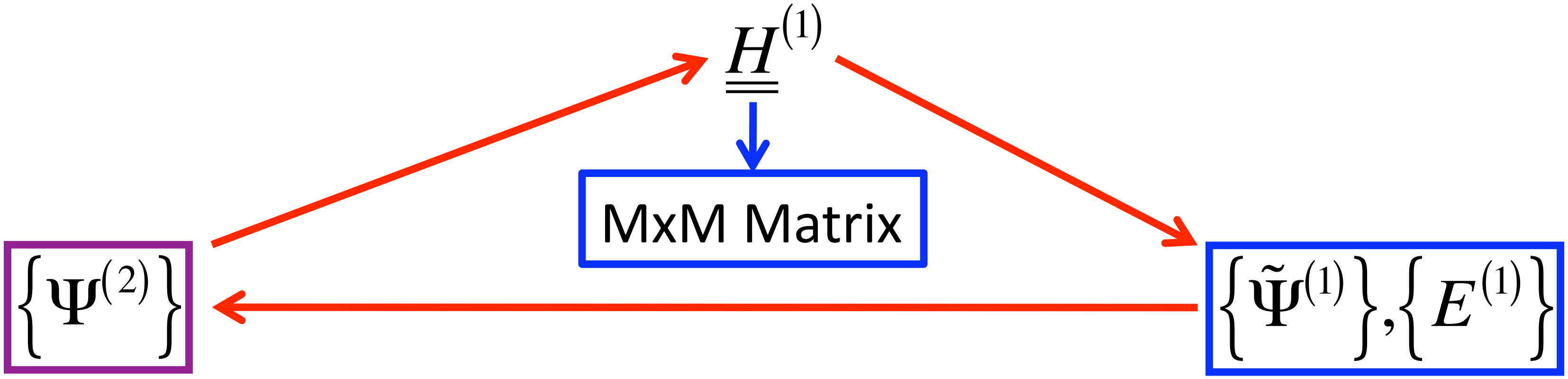
$$\overline{\Psi}^{(j+1)}_{m\notin active} = \sum_{k=1}^{m} \kappa^{(j+1)}_{m,m-k} r^k \Psi^{(j+1)}_{m-k}$$

Eigenstates used to construct new basis

Assignment via:

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

Construction of 2nd Iteration Basis



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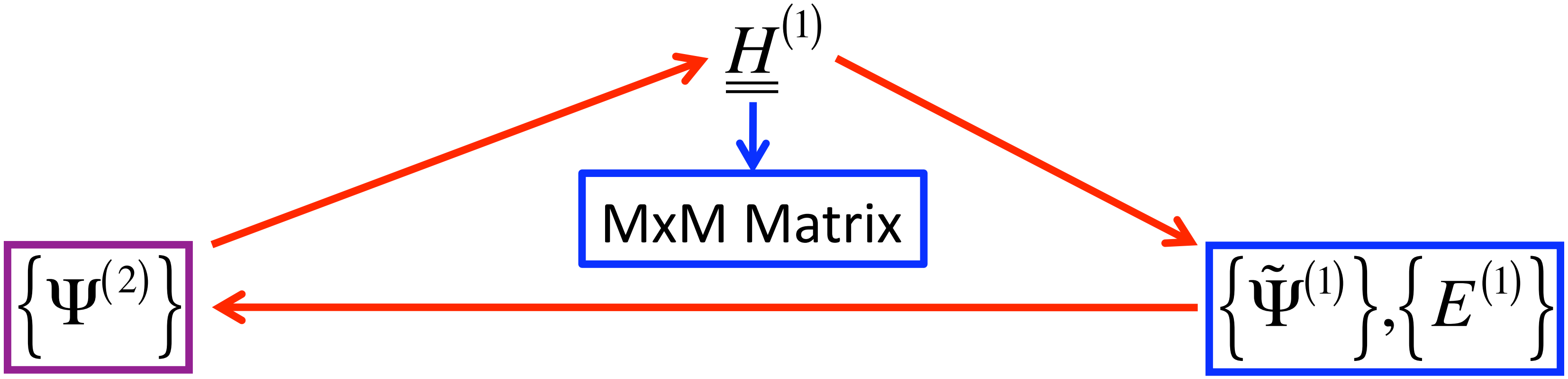
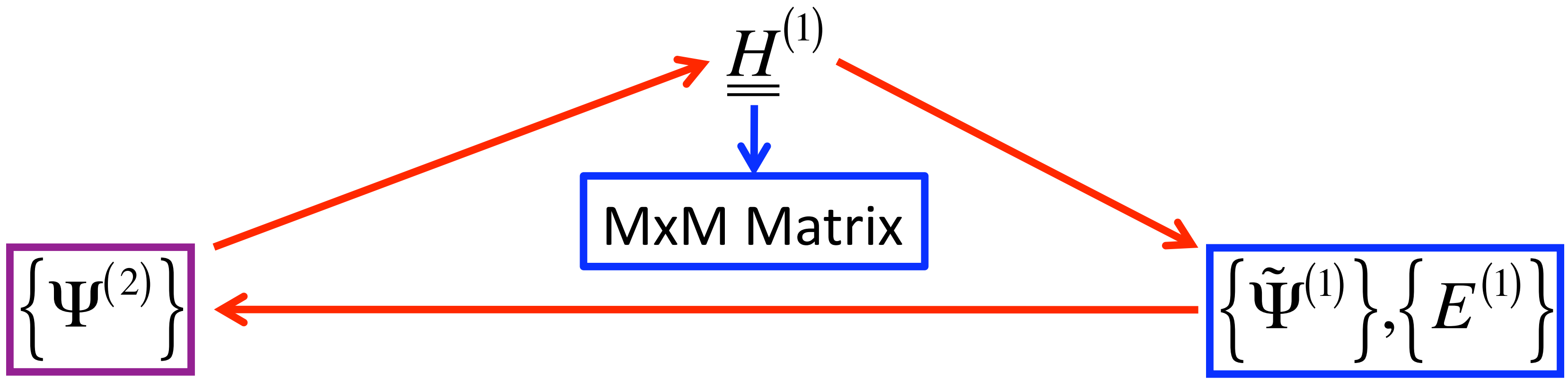


Suppose active space only contains ground state

Construction of 2nd Iteration Basis

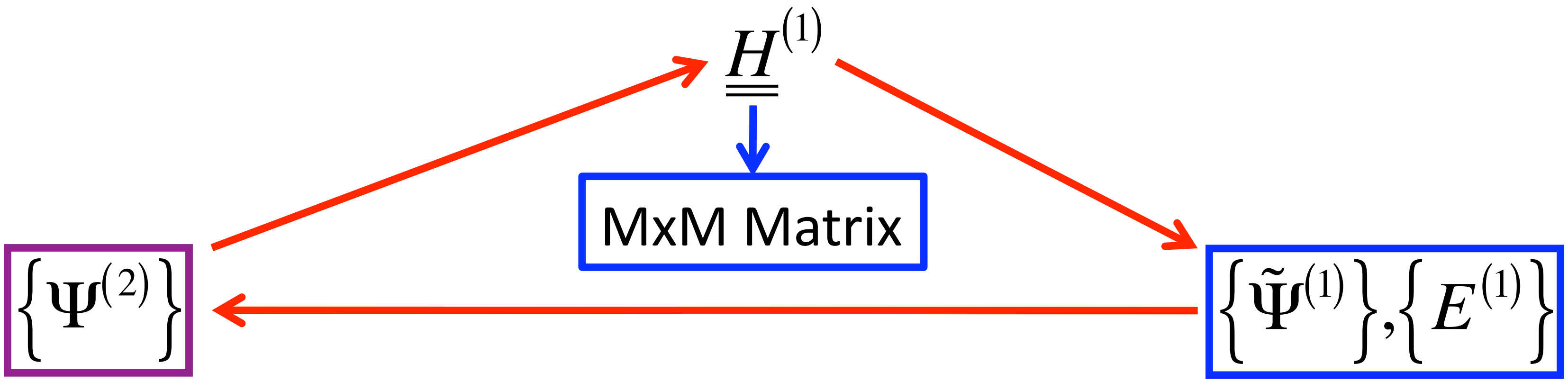


Suppose active space only contains ground state

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

Basis functions shown prior to orthonormalization

Construction of 2nd Iteration Basis



Suppose active space only contains ground state

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

$$\overline{\Psi}_0^{(2)} = \left(a_0^{(2)} + a_1^{(2)} r + a_2^{(2)} r^2 + \ldots + a_{M-1}^{(2)} r^{M-1}\right) e^{-\frac{\alpha r^2}{2}}$$

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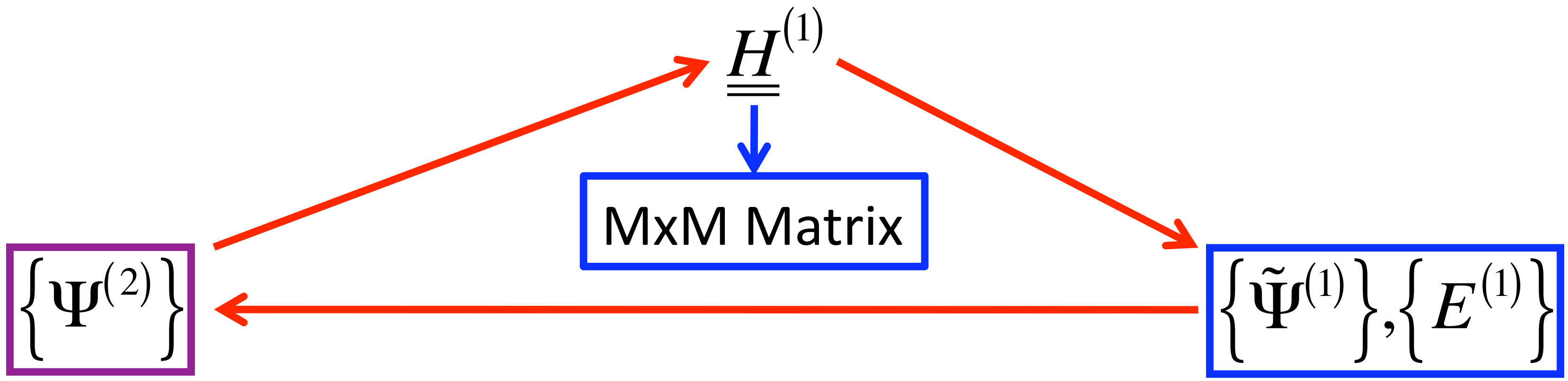
Construction of 2nd Iteration Basis



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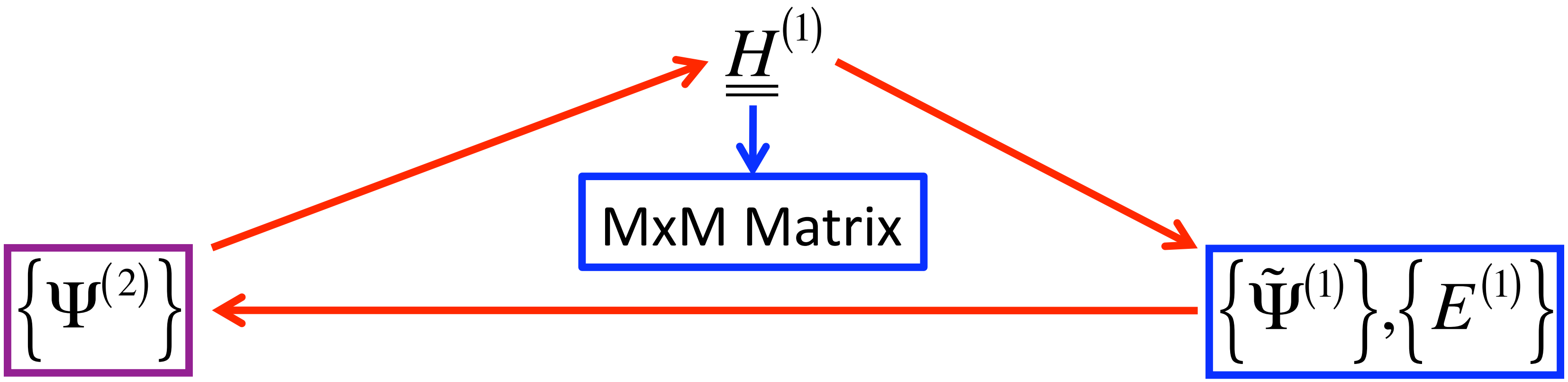

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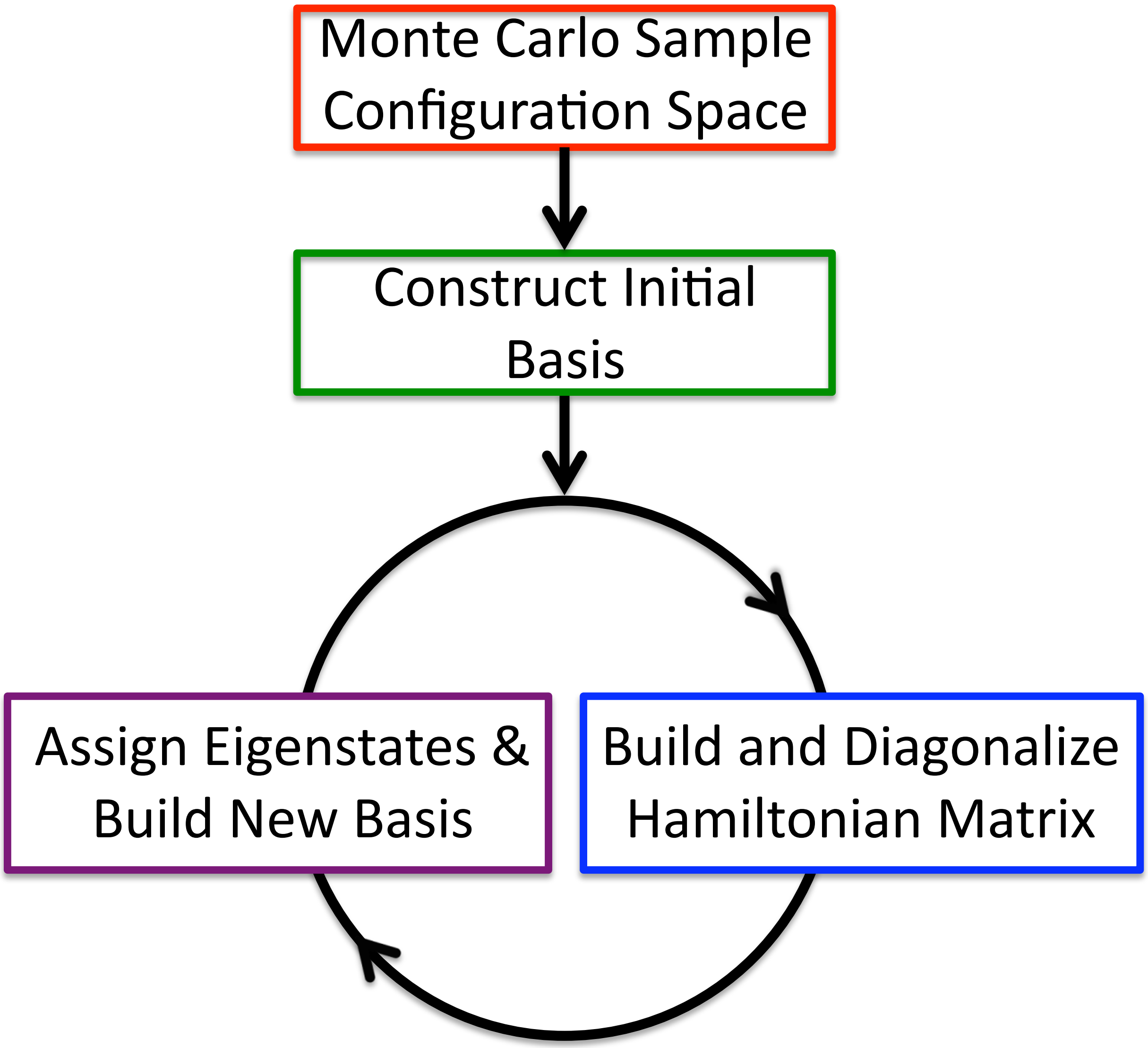
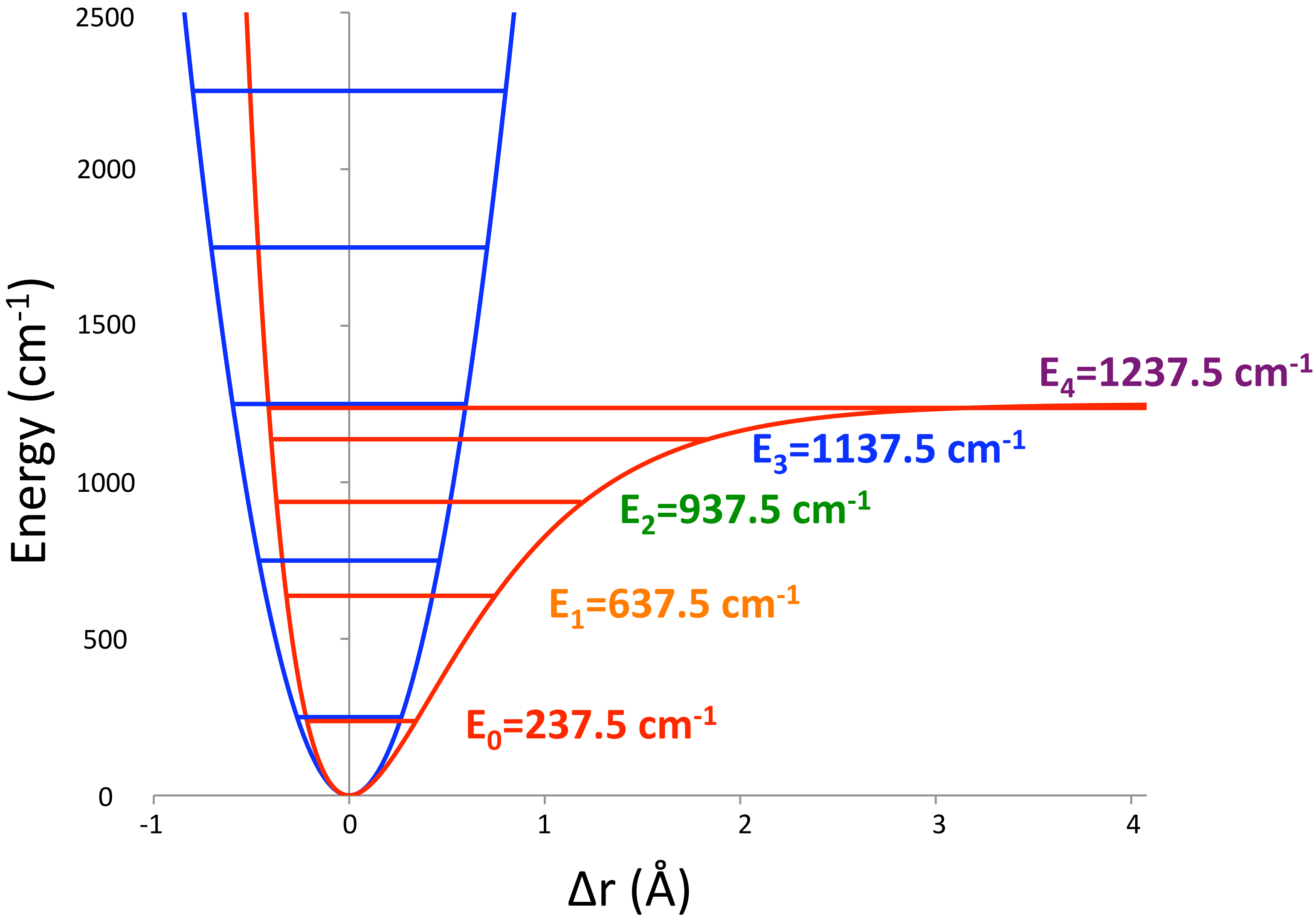
Effective size of basis grows each iteration

Basis functions shown prior to orthonormalization

The General Scheme



Testing the Method



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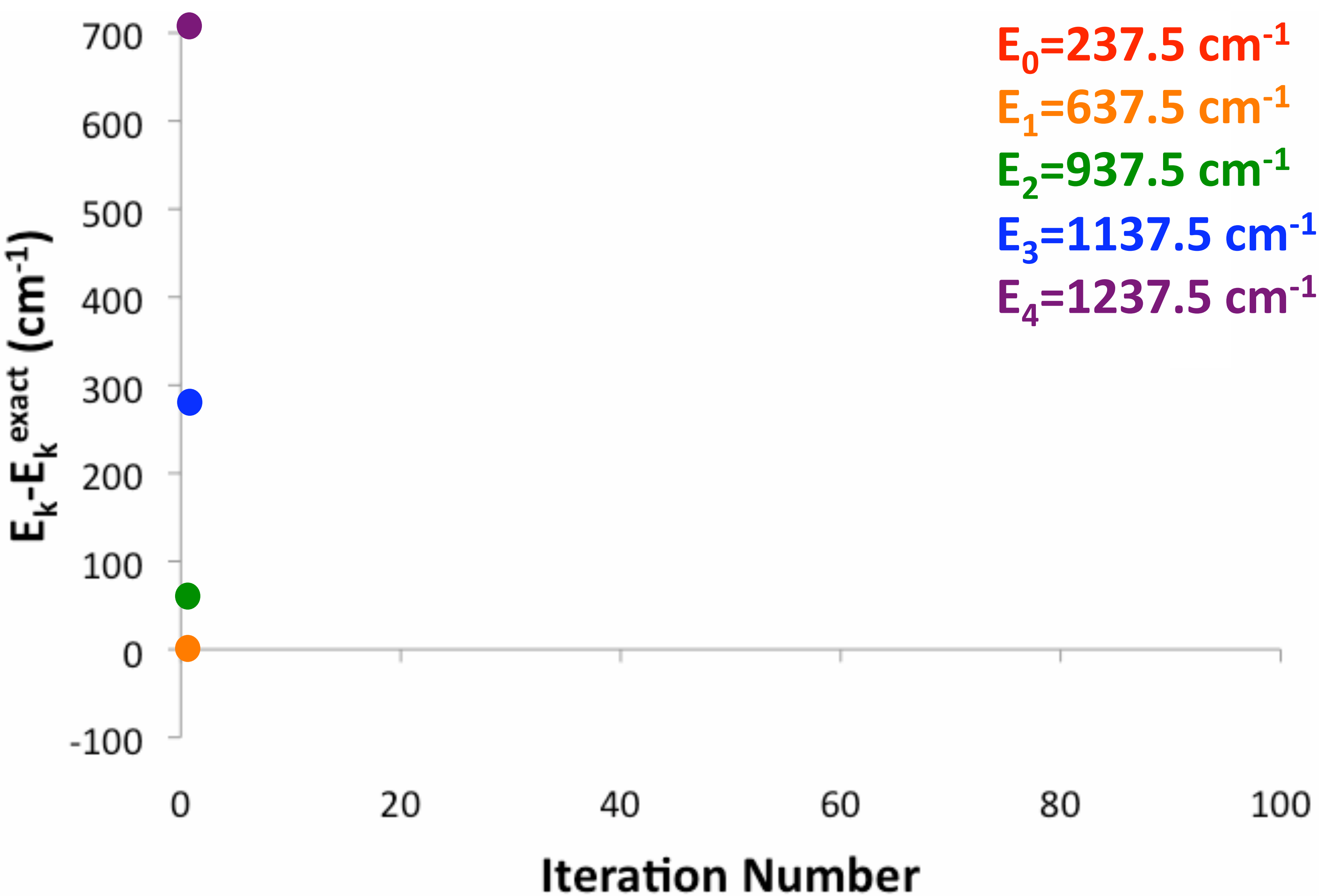

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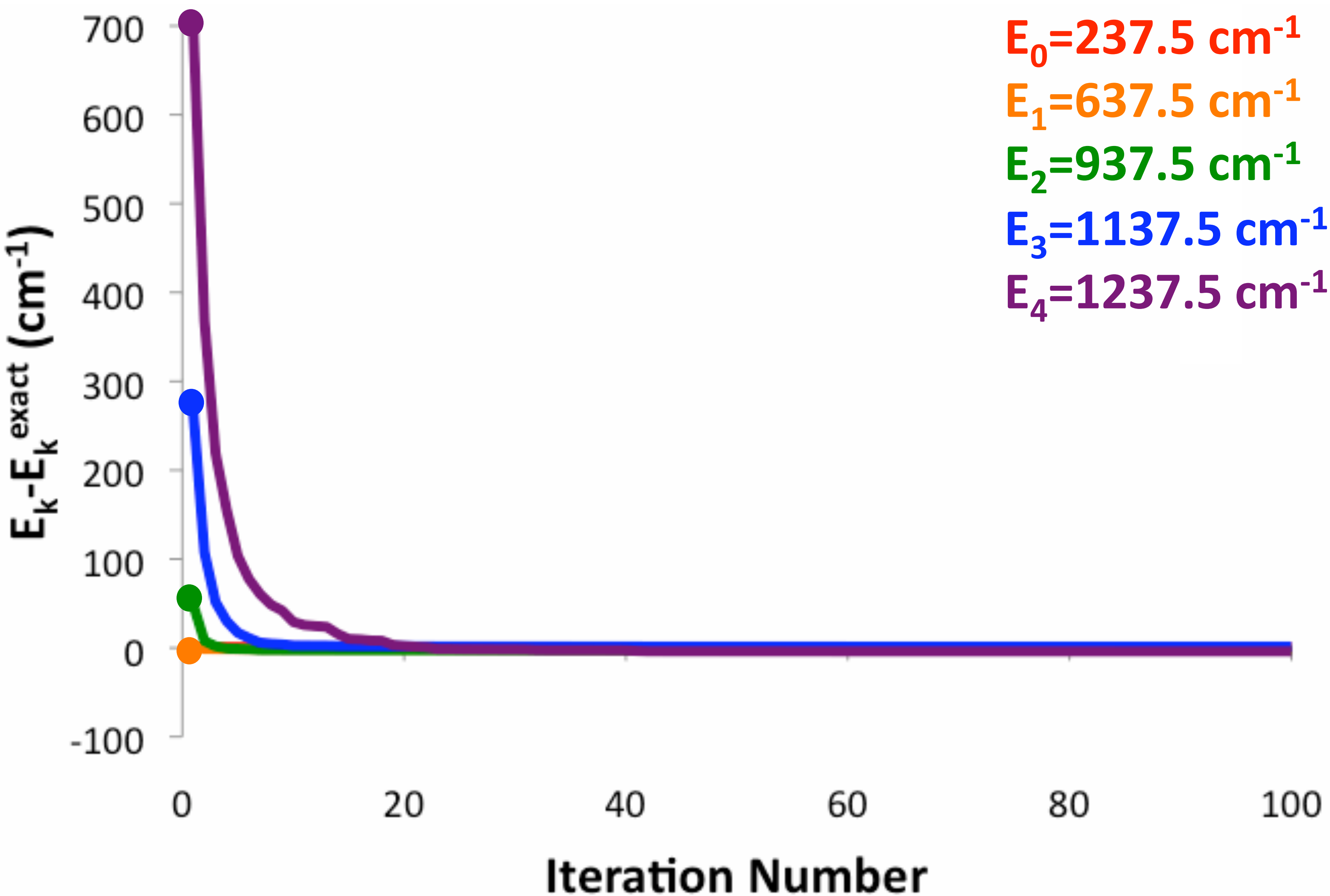

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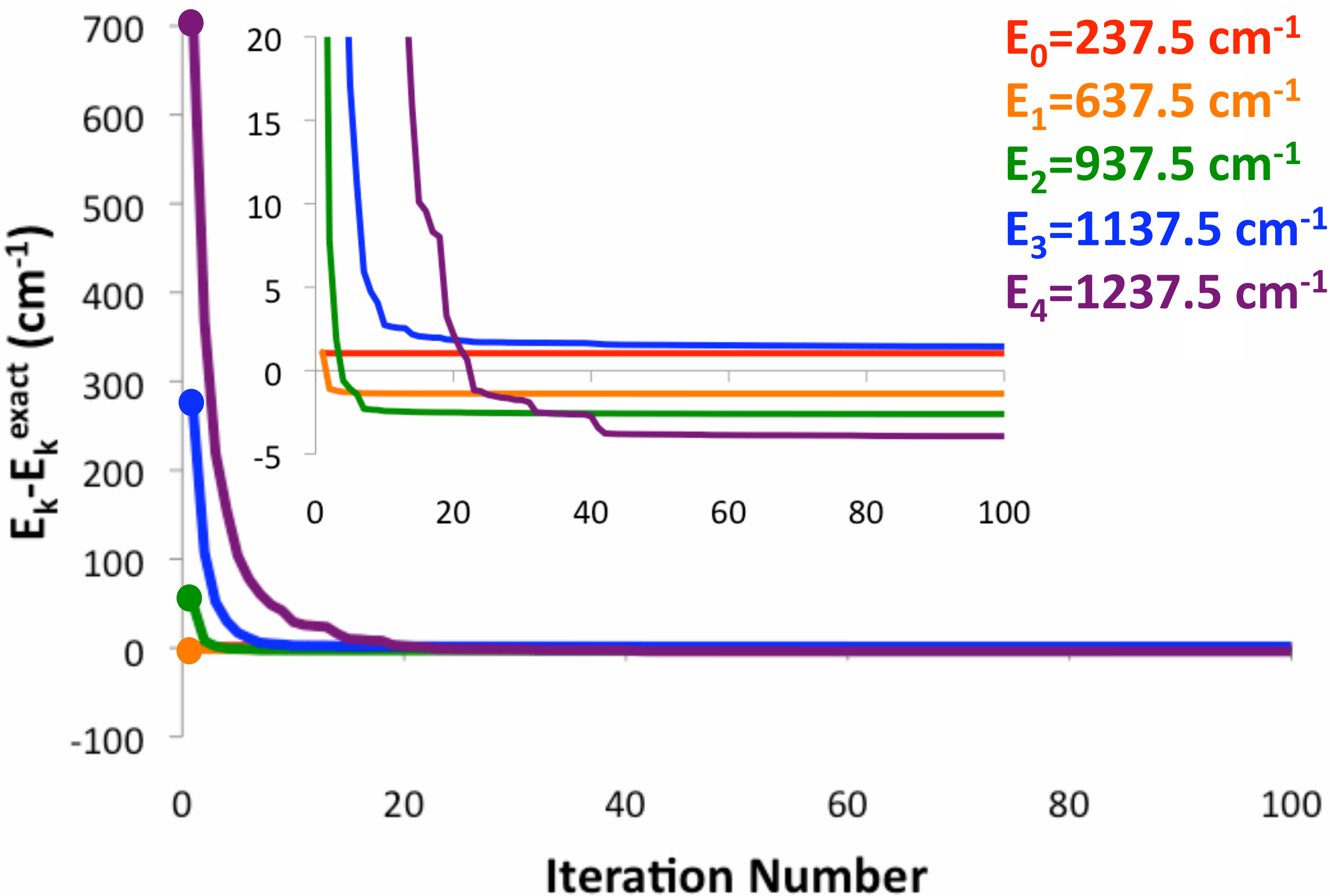


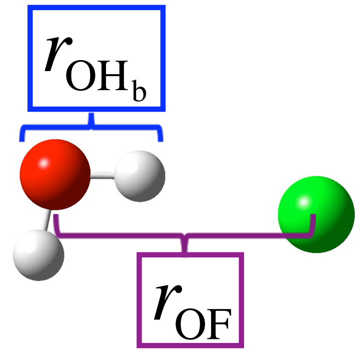
Moving on to 2D

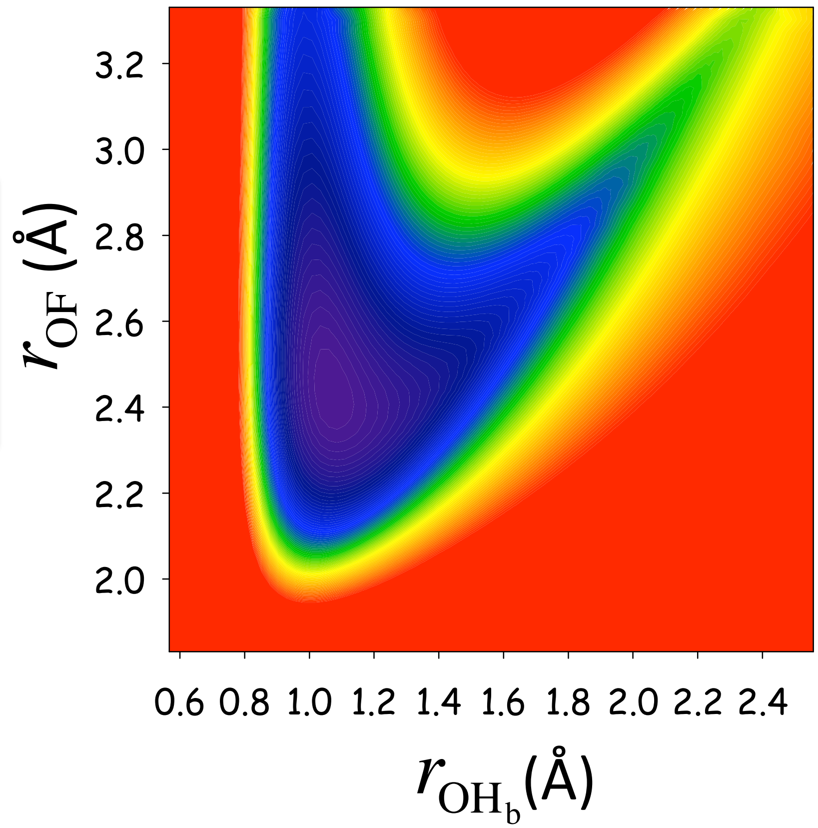
2D PES and G matrix elements constructed by S. Horvath from a bicubic spline interpolation of a grid of points on which MP2/aug-cc-pVTZ calculations were performed.

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

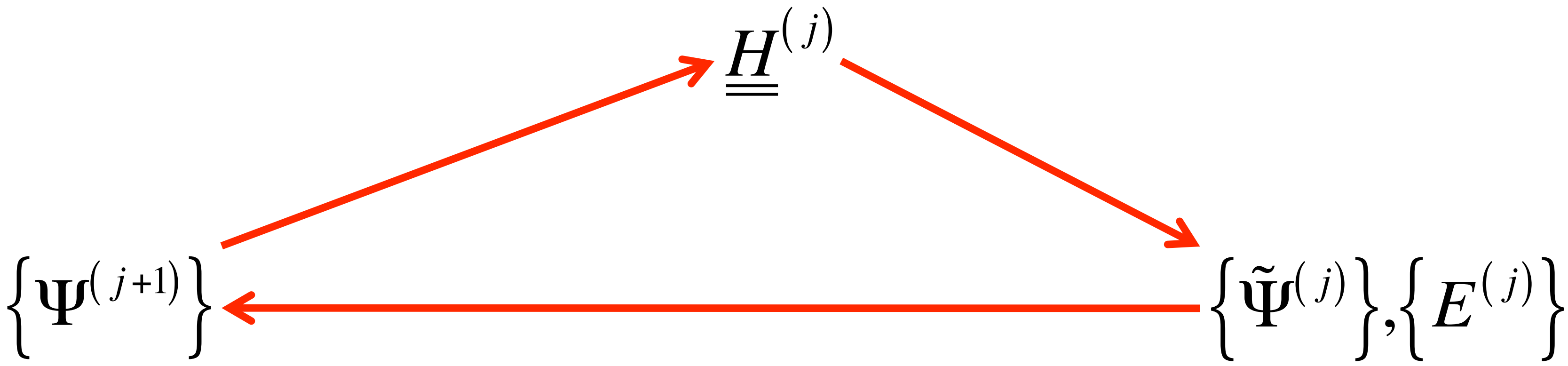
Our goal is to accurately capture all states with up to 3 total quanta of excitation.

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





The Problem of Assignment

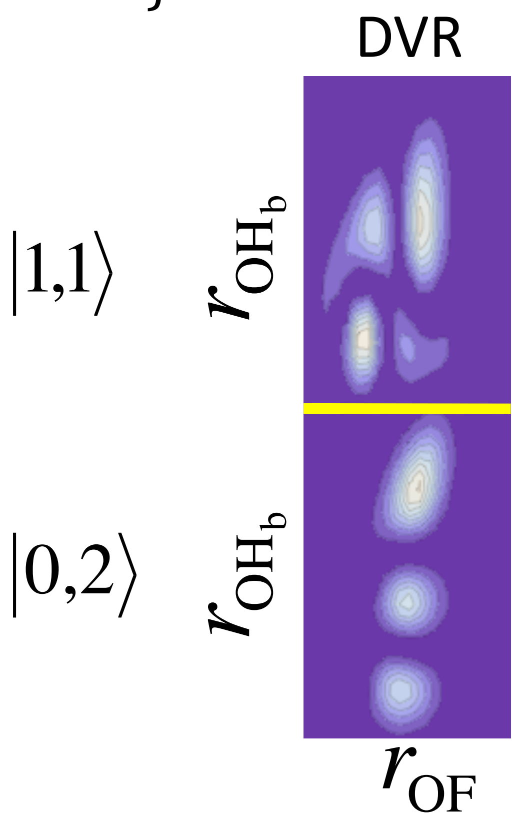


Eigenstates used to construct new basis

The Problem of Assignment

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

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



Eigenstates used to construct new basis

The Problem of Assignment

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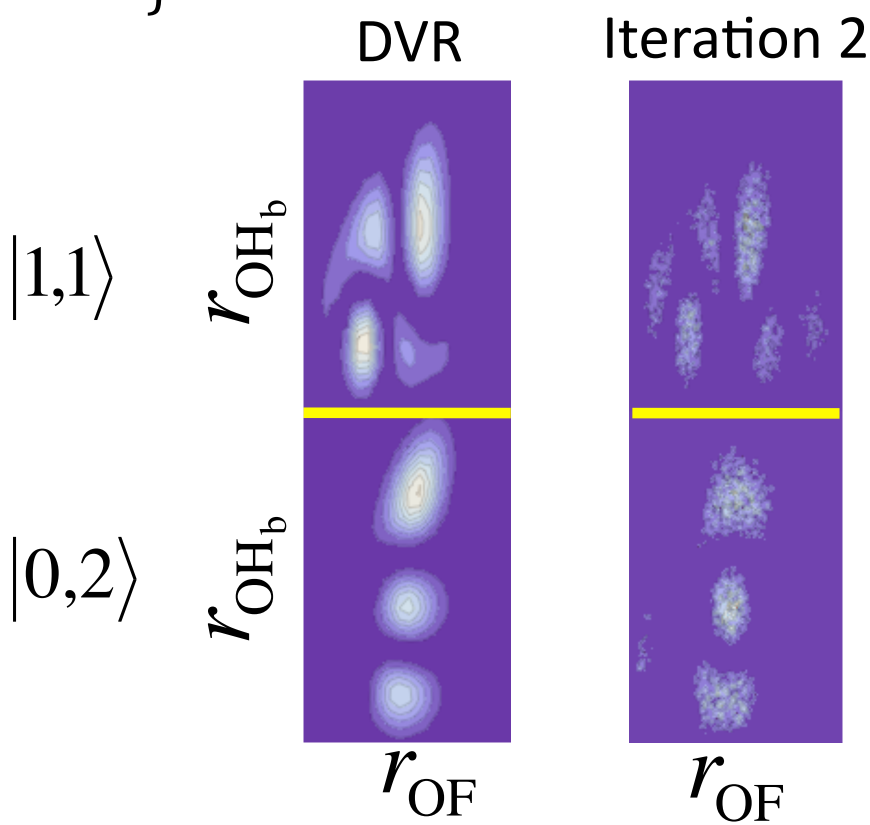
$$\left\{\Psi^{(j+1)}\right\} \longleftarrow \left\{\tilde{\Psi}^{(j)}\right\},\left\{E^{(j)}\right\}$$



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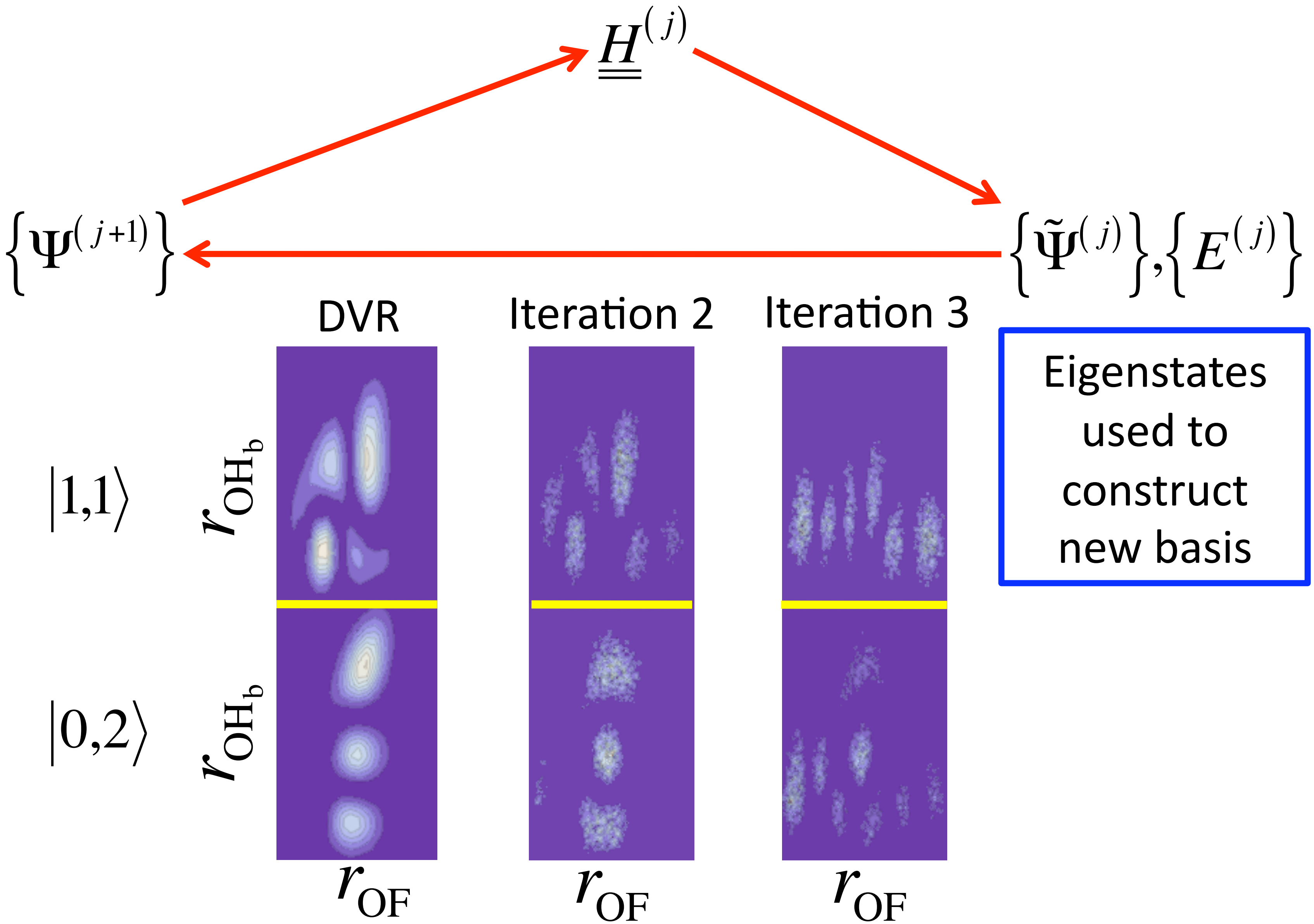
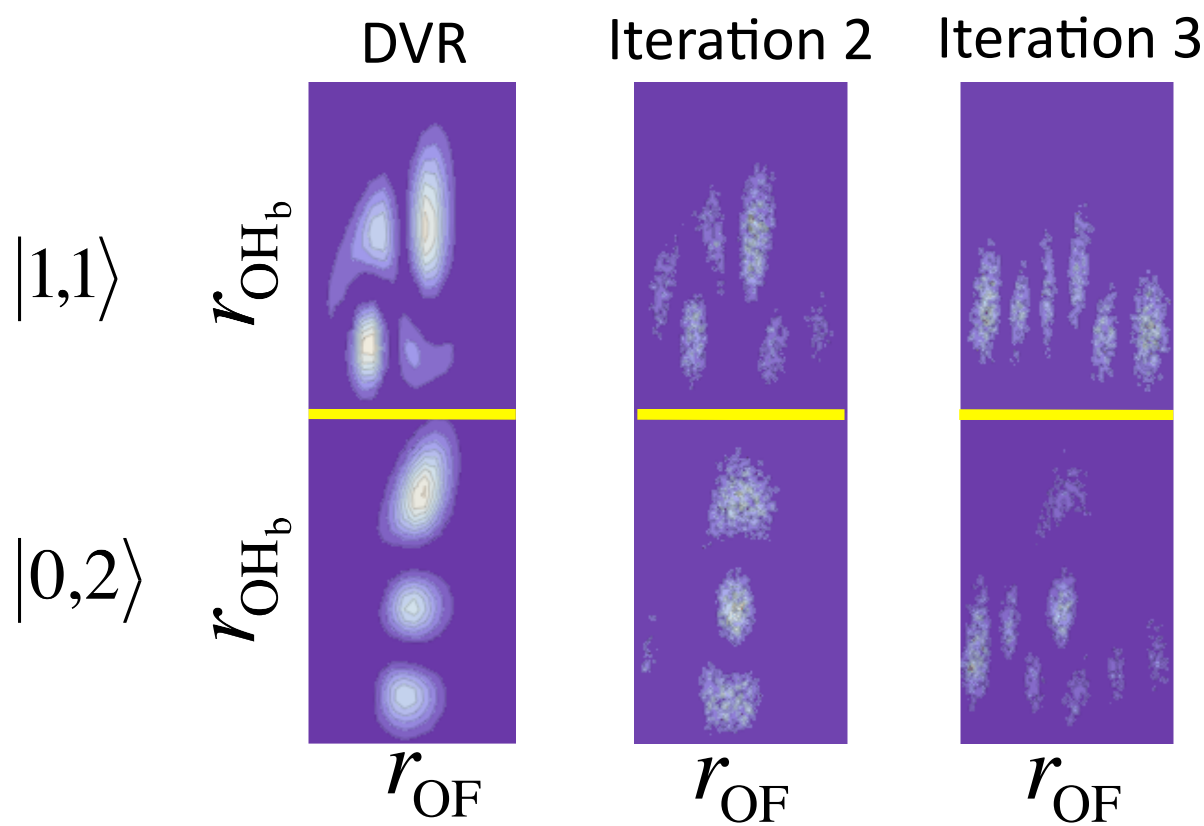


The Problem of Assignment

Identity of problem states dependent on parameters of algorithm AND exact distribution of Monte Carlo sampling points



The Hunt for an Effective Metric

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$\phi_k^{(j)}$ Un-assigned eigenstate

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Compare moments of the two sets of wavefunctions:

$$\left\{ \begin{array}{c} \left\langle \left(r_{OF} - \left\langle r_{OF} \right\rangle_k \right)^2 \right\rangle_k \\ \left\langle \left(r_{OF} - \left\langle r_{OF} \right\rangle_k \right) \left(r_{OH_b} - \left\langle r_{OH_b} \right\rangle_k \right) \right\rangle \\ \left\langle \left(r_{OH_b} - \left\langle r_{OH_b} \right\rangle_k \right)^2 \right\rangle_k \end{array} \right\}$$

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$$F_{k,l;m,n}^{(j)} = \frac{1}{\sqrt{1+\left(\frac{E_{k,l}^{(j)} - E_{m,n}^{(j)}}{H_{k,l;m,n}^{(j)}}\right)^2}}$$

Gruebele *et al. Int. Rev. Phys. Chem* **1998**, *17*, 91-145.

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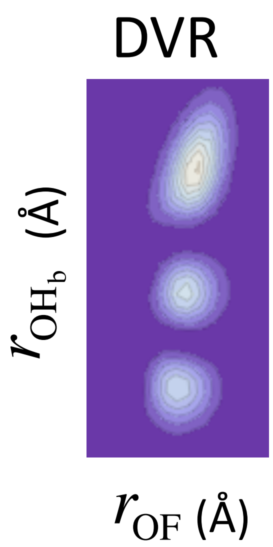

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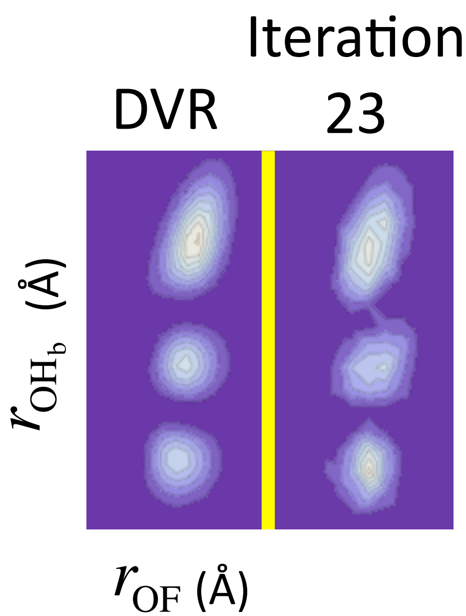

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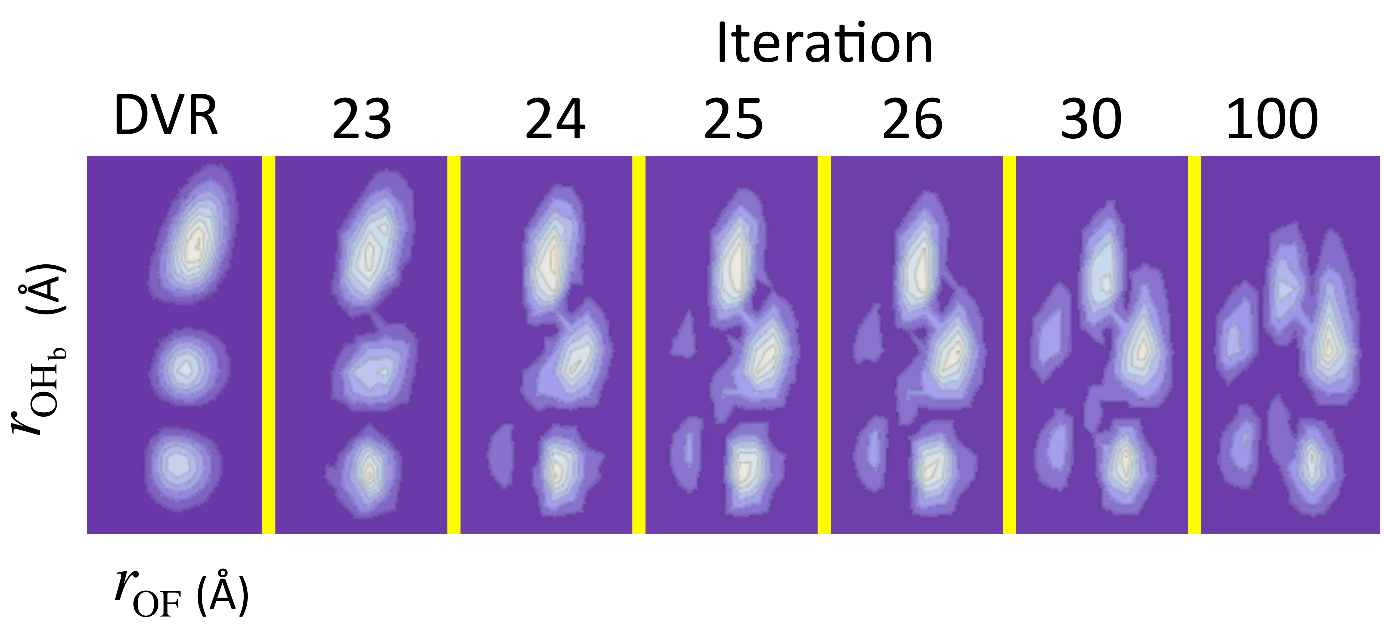

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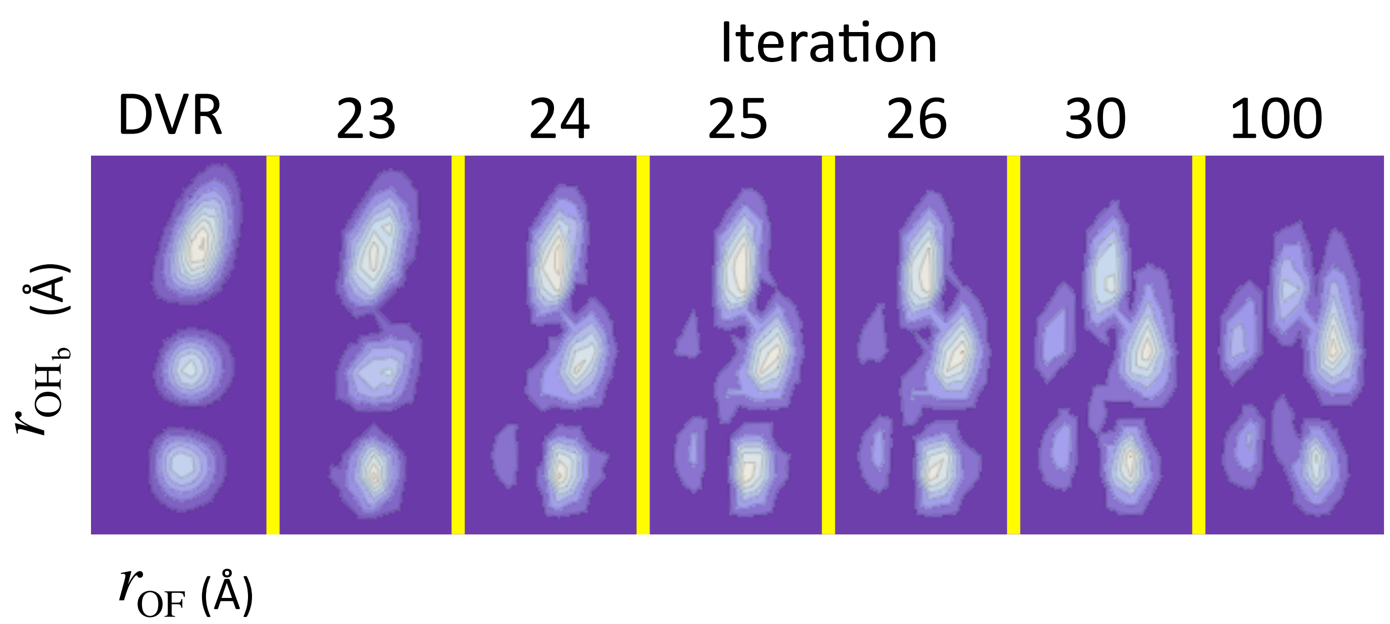

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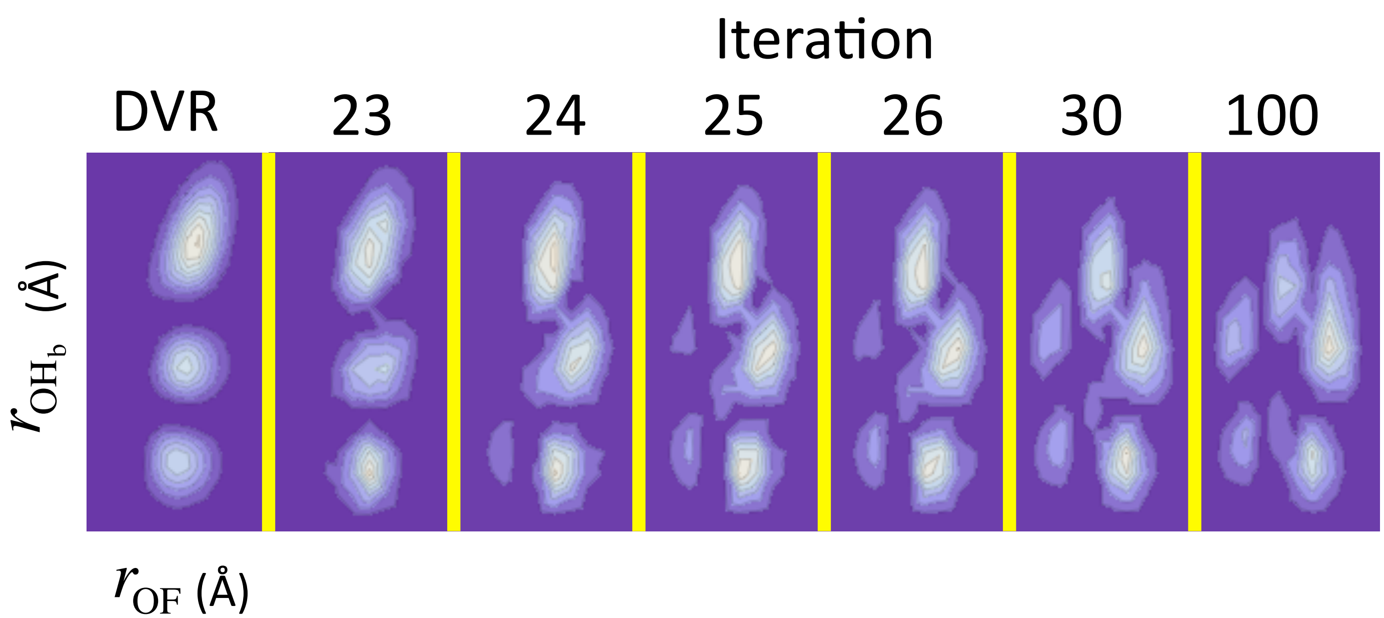

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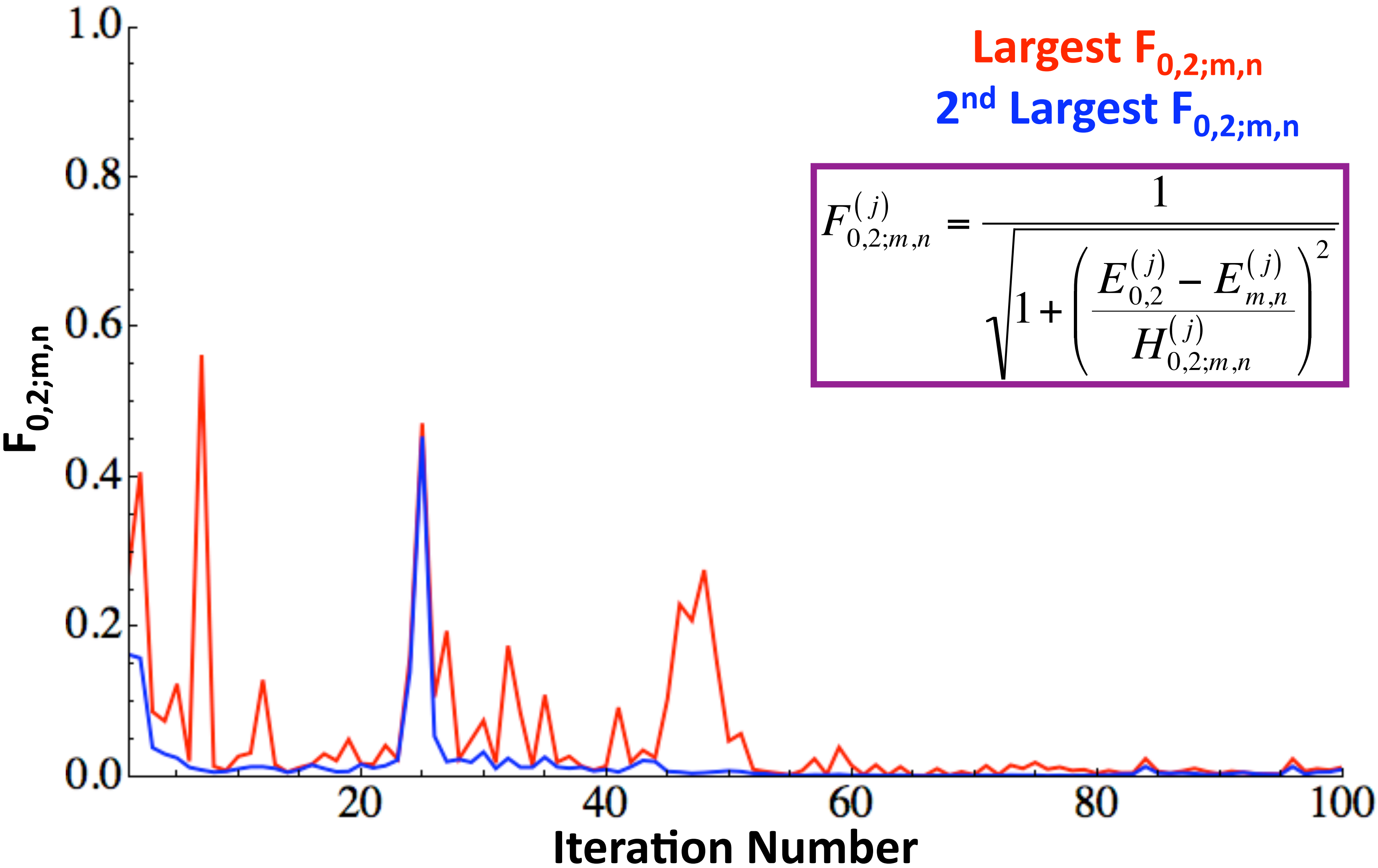

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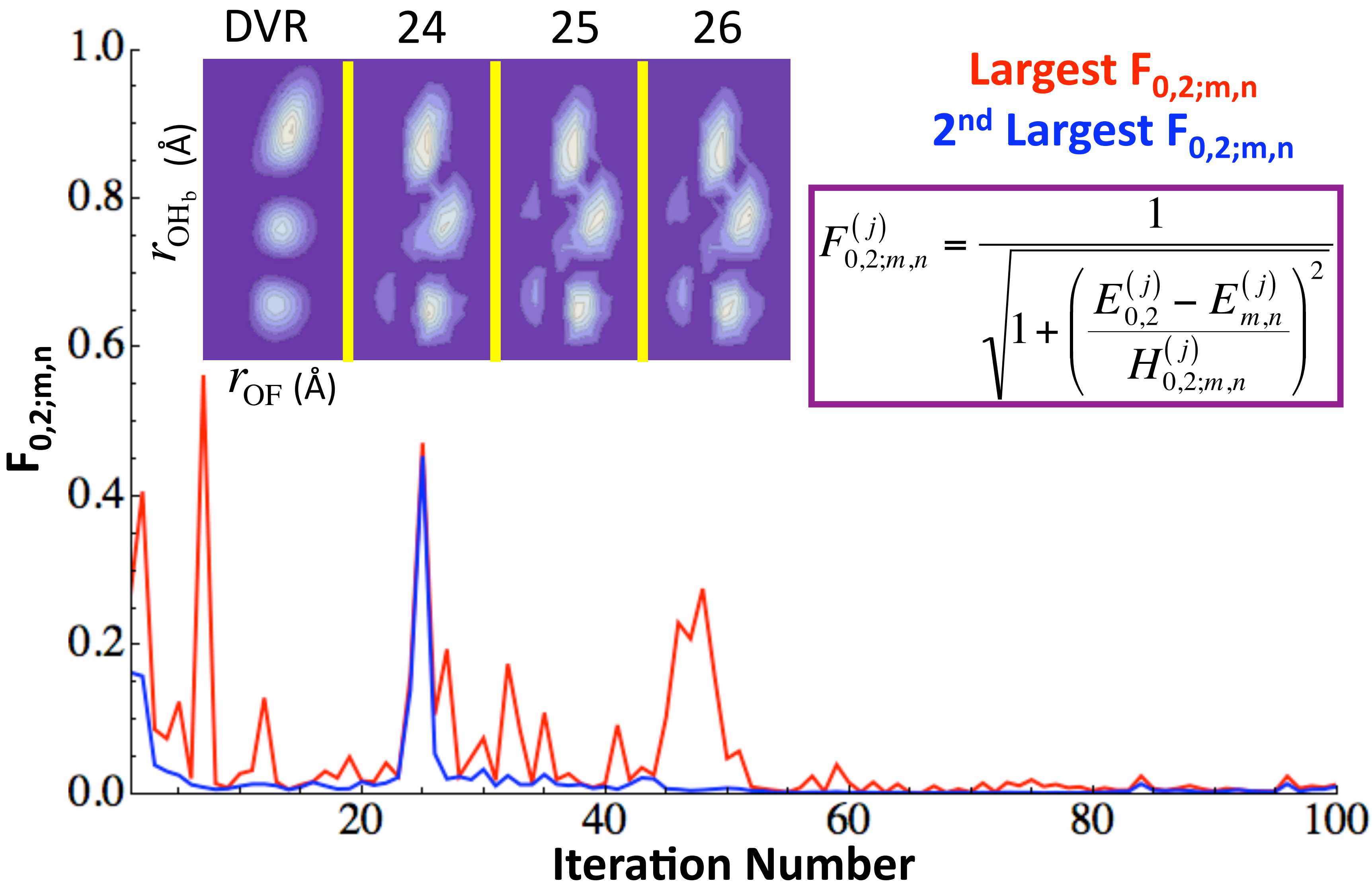

$$F_{0,2;m,n}^{(j)} = \frac{1}{\sqrt{1 + \left(\frac{E_{0,2}^{(j)} - E_{m,n}^{(j)}}{H_{0,2;m,n}^{(j)}} \right)^2}}$$

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Further multi-dimensional benchmarking

Couple algorithm with ab initio electronic structure calculations

Acknowledgements

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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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Phase factors

Will be made orthogonal to all previously built states and normalized

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

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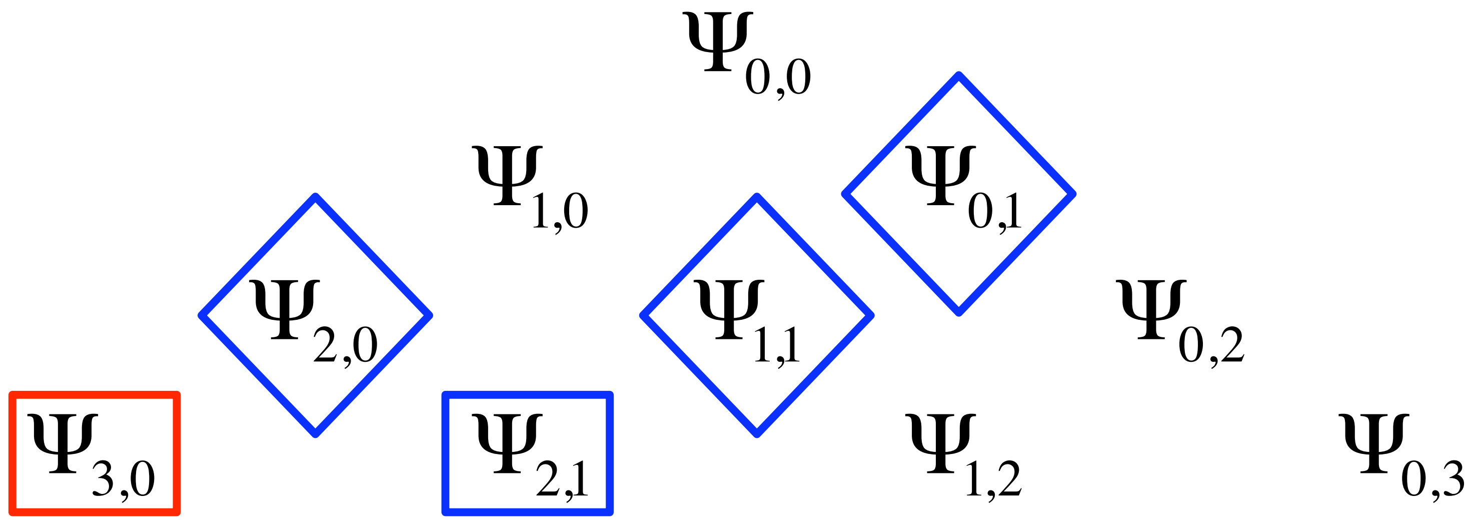

$$\overline{\Psi}^{(1)}_{2,1} = \kappa^{(1)}_{2,1;2,0} R \Psi^{(1)}_{2,0} + \kappa^{(1)}_{2,1;1,1} r \Psi^{(1)}_{1,1} + \kappa^{(1)}_{2,1;0,1} r^{2} \Psi^{(1)}_{0,1}$$