

# Quantum Virial Coefficients via Path Integral Monte Carlo: Theory and Development of Novel Algorithms

PhD dissertation defense by: Ramachandran Subramanian

Committee: Prof. David A. Kofke (Chair),  
Prof. Jeffrey R. Errington, Prof. Johannes Hachmann, Dr. Andrew J. Schultz

May 9, 2016

# Overview

- 1 Introduction
  - Viral coefficients
  - *Ab initio* potentials
- 2 Objectives
- 3 Methods
  - Mayer Sampling Monte Carlo
  - Path Integral Monte Carlo
  - Novel algorithms
- 4 Results
- 5 Summary

# Virial equation of state (VEOS)

$$\frac{P}{\rho k T} = 1 + B_2(T)\rho + B_3(T)\rho^2 + \dots$$

- $B_n$  -  $n^{th}$  order virial coefficient represents the effect of interaction of  $n$  molecules.
- Depends only on temperature.
- Works well for systems with low density (typically gases).

# Expressions for the virial coefficients

- Second and third order virial coefficients are given by:

$$\begin{aligned} B_2(T) &= -\frac{1}{2} \int d1 f(0, 1) \\ B_3(T) &= -\frac{1}{3} \int \int d1 d2 f(0, 1) f(0, 2) f(1, 2) \end{aligned} \quad (1)$$

where  $f(0, 1) = \left( \exp \left[ -\beta U_2(\mathbf{r}) \right] - 1 \right)$  and indices '1' and '2' denote the position and orientational degrees of freedom of molecules 1 and 2, respectively, with respect to molecule '0' at the origin.

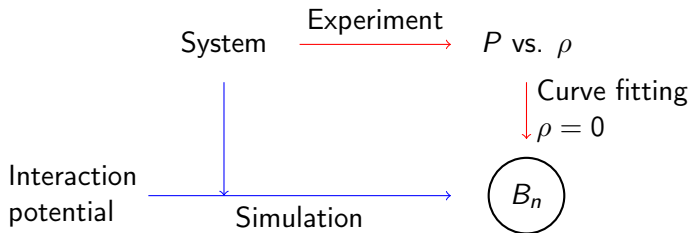
- The number of such integrals to be summed<sup>1</sup> is: 3 for  $B_4$ , 10 for  $B_5$ , 56 for  $B_6$ , 468 for  $B_7$ .

---

<sup>1</sup> J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (2006).

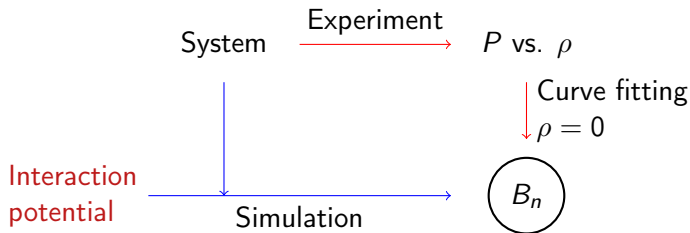
# Main uses:

- To compute other thermodynamic properties like the joules-thomson coefficient, critical point etc.
- To rank different potential models by comparing their virial coefficients to experimental results



## Main uses:

- To compute other thermodynamic properties like the joules-thomson coefficient, critical point etc.
- To rank different potential models by comparing their virial coefficients to experimental results



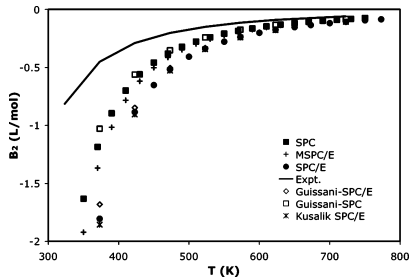
- To systematically tune and improve potentials as a result.

# Empirical potential models

- Usually functions fitted to experimental data of bulk property measurement.
- Represent the net effect of a variety of phenomenon taking place including 2 body interactions, multi-body interactions, nuclear quantum effects etc.
- As a result, fail to accurately represent interaction potential.
- Interaction potentials that better represent condensed (high density) phase fail to predict accurate virial coefficients for the gas (low density) phase.

# Example - different empirical models of water

- Importance of the accuracy of interaction potential<sup>2</sup>:



<sup>2</sup> K. M. Benjamin et al., J. Phys. Chem. B (2007).



# Ab initio potential models

- Fundamentally different from empirical models as they focus only on two or three molecules at a time
- Solve for the interaction energies starting with the Schrödinger equation and involve many approximations:

$$\mathcal{H} \Psi = E \Psi,$$

$$\mathcal{H} = \mathcal{T}_e + \mathcal{T}_N + \mathcal{V}_{ee} + \mathcal{V}_{eN} + \mathcal{V}_{NN}$$

- Account for electronic structure using different levels of theory and different basis sets
- We use potentials fitted to *ab initio* data rather than compute it on-the-fly (expensive)

# Nuclear quantum effects

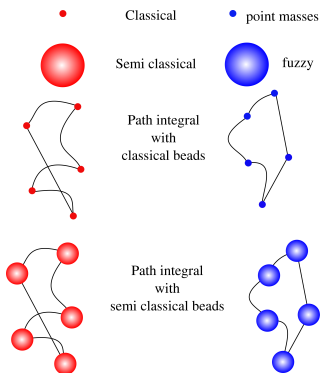
- Consequence of uncertainty in the positions of atoms at low temperatures (Zero-point vibrational energy).
- Have to be explicitly included in virial coefficient calculations as they are ignored in the development of *ab initio* potentials.
- Semi-classical routes to include quantum effects:
  1. Computing first order quantum corrections.
  2. Using an effective potential like the Quadratic Feynman-Hibbs<sup>3</sup>.
- Quantum route: path integral Monte Carlo (PIMC) (will be explained in detail later).

---

<sup>3</sup> R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (1965).

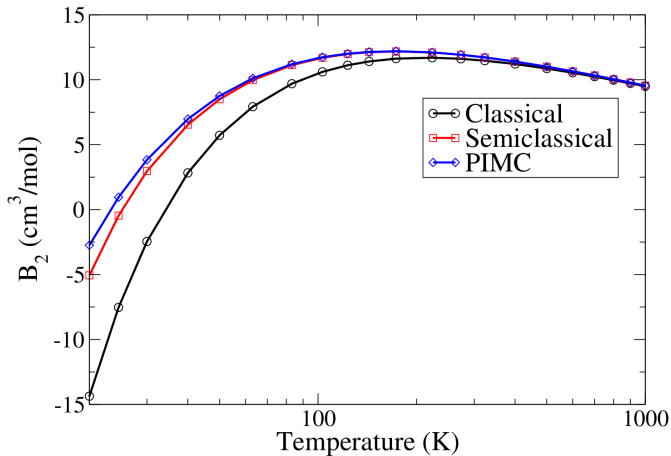
# Classification of virial coefficients

- Different levels of “quantumness”, using  $B_2$  as an example:



# Nuclear quantum effects

- Importance of nuclear quantum effects<sup>4</sup>



<sup>4</sup> K. R. S. Shaul, A. J. Schultz, and D. A. Kofke, J. Chem. Phys. (2012).

# Overview

- 1 Introduction
  - Viral coefficients
  - *Ab initio* potentials
- 2 Objectives
- 3 Methods
  - Mayer Sampling Monte Carlo
  - Path Integral Monte Carlo
  - Novel algorithms
- 4 Results
- 5 Summary

# Objective

## Diatomic molecules

Compute accurate virial coefficients using state-of-the-art *ab initio* potentials and PIMC method.

# Overview

- 1 Introduction
  - Viral coefficients
  - *Ab initio* potentials
- 2 Objectives
- 3 **Methods**
  - Mayer Sampling Monte Carlo
  - Path Integral Monte Carlo
  - Novel algorithms
- 4 Results
- 5 Summary

# Mayer Sampling Monte Carlo

- Second and third order virial coefficients are given by:

$$B_2(T) = -\frac{1}{2} \int d1 f(0,1)$$

$$B_3(T) = -\frac{1}{3} \int \int d1 d2 f(0,1) f(0,2) f(1,2)$$

- MSMC<sup>5</sup> is a free energy perturbation technique to evaluate the integrals in the above equations indirectly.

$$\Gamma(T) = \Gamma_o \frac{\langle \gamma/\pi \rangle_\pi / \langle \gamma_{os}/\pi \rangle_\pi}{\langle \gamma_o/\pi \rangle_{\pi_o} / \langle \gamma_{os}/\pi_o \rangle_{\pi_o}}$$

$$\gamma_{os} = \frac{|\gamma_o||\gamma|}{\alpha|\gamma_o| + |\gamma|}$$

---

<sup>5</sup> J. K. Singh and D. A. Kofke, Phys. Rev. Lett. (2004).



## PIMC - thermal density matrix

- The partition function is an important property in statistical mechanics:

$$P(x) = \frac{1}{Z} \rho(x, x),$$
$$Z = \int \rho(x, x) dx \equiv \text{trace}\{\rho\}.$$

where  $\rho(x', x)$  is the statistical thermal density matrix at temperature  $T$ .

- Richard Feynman<sup>6</sup> was able to connect it with quantum mechanics:

$$\rho(R, R'; \beta) = \langle R | e^{-\beta \mathcal{H}} | R' \rangle$$

where  $R = \{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n\}$  and  $\beta = 1/k_B T$ , with  $k_B$  Boltzmann's constant and  $T$  the temperature.

---

<sup>6</sup> R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (1965).

## Important equations

- A key property of the density matrix is that the product of two density matrices is also a density matrix. Hence the convolution<sup>7</sup>:

$$\rho(R_1, R_3; \beta_1 + \beta_2) = \int dR_2 \rho(R_1, R_2; \beta_1) \rho(R_2, R_3; \beta_2)$$

---

<sup>7</sup> D. M. Ceperley, Rev. Mod. Phys. (1995).

<sup>8</sup> T. Cui et al., Phys. Rev. B (1997).

# Important equations

- A key property of the density matrix is that the product of two density matrices is also a density matrix. Hence the convolution<sup>7</sup>:

$$\rho(R_1, R_3; \beta_1 + \beta_2) = \int dR_2 \rho(R_1, R_2; \beta_1) \rho(R_2, R_3; \beta_2)$$

- As  $\frac{\beta}{P} \rightarrow 0$  or equivalently as  $PT \rightarrow \infty$ , the “primitive approximation” is given by<sup>8</sup>:

$$e^{-\frac{\beta}{P}(\mathcal{T}+\mathcal{V})} \approx e^{-\frac{\beta}{P}\mathcal{T}} e^{-\frac{\beta}{P}\mathcal{V}}$$

---

<sup>7</sup> D. M. Ceperley, Rev. Mod. Phys. (1995).

<sup>8</sup> T. Cui et al., Phys. Rev. B (1997).

## Important equations

- A key property of the density matrix is that the product of two density matrices is also a density matrix. Hence the convolution<sup>7</sup>:

$$\rho(R_1, R_3; \beta_1 + \beta_2) = \int dR_2 \rho(R_1, R_2; \beta_1) \rho(R_2, R_3; \beta_2)$$

- As  $\frac{\beta}{P} \rightarrow 0$  or equivalently as  $PT \rightarrow \infty$ , the “primitive approximation” is given by<sup>8</sup>:

$$e^{-\frac{\beta}{P}(\mathcal{T}+\mathcal{V})} \approx e^{-\frac{\beta}{P}\mathcal{T}} e^{-\frac{\beta}{P}\mathcal{V}}$$

- The Trotter formula proves that this approximation does converge to the right result in the  $P \rightarrow \infty$  limit and is given by:

$$e^{-\beta(\mathcal{T}+\mathcal{V})} = \lim_{P \rightarrow \infty} \left[ e^{-\frac{\beta}{P}\mathcal{T}} e^{-\frac{\beta}{P}\mathcal{V}} \right]^P$$

---

<sup>7</sup> D. M. Ceperley, Rev. Mod. Phys. (1995).

<sup>8</sup> T. Cui et al., Phys. Rev. B (1997).

# Diatomic molecule - rigid rotor<sup>9</sup>

- Let  $m$  and  $I$  denote the mass of the atom and moment of inertia of the rigid rotor respectively with  $\Lambda_m = h/\sqrt{2\pi mk_B T}$ . Its Hamiltonian is given by:

$$\hat{h}_2 = \frac{\hat{\mathbf{p}}^2}{2m} + \frac{\hat{\mathbf{J}}_1^2}{2I} + \frac{\hat{\mathbf{J}}_2^2}{2I} + \hat{U}(r, \Omega_1, \Omega_2)$$

where  $\hat{\mathbf{p}}$  is the momentum operator conjugated to the COM separation,  $\hat{\mathbf{J}}_1$  and  $\hat{\mathbf{J}}_2$  are the angular momentum operators,  $\hat{U}(r, \Omega_1, \Omega_2)$  is the intermolecular potential function in terms of the COM distance  $r$  and the orientation vectors  $\Omega_1$  and  $\Omega_2$ .

---

<sup>9</sup> K. Patkowski et al., J. Chem. Phys. (2008).

# Diatomic molecule - rigid rotor<sup>10</sup>

- Use  $\mathbf{x}^i, \Omega_1^i, \Omega_2^i$  to denote the configuration of the  $i^{\text{th}}$  rigid rotors,

## Matrix elements

$$\begin{aligned}\mathcal{T}_{\text{tra}}^{i,i+1} &= \left\langle \mathbf{x}^i \left| \exp \left( -\frac{\beta \hat{\mathbf{p}}^2}{2mP} \right) \right| \mathbf{x}^{i+1} \right\rangle = \frac{P^{3/2}}{\Lambda_m^3} \exp \left( -\frac{\pi P (\mathbf{x}^i - \mathbf{x}^{i+1})^2}{\Lambda_m^2} \right) \\ \mathcal{T}_{\text{rot}}^{i,i+1} &= \left\langle \Omega^i \left| \exp \left( -\frac{\beta \hat{\mathbf{J}}^2}{2IP} \right) \right| \Omega^{i+1} \right\rangle = \sum_{j=0}^{\infty} \frac{2j+1}{4\pi} \mathcal{P}_j(\cos(\theta_{i,i+1})) \\ &\quad \times \exp[-\beta j(j+1)\Upsilon/P]\end{aligned}$$

where  $j$  is the angular quantum number,  $\theta_{i,i+1}$  is the angle between bead orientation vectors  $\Omega_i, \Omega_{i+1}$ ,  $\mathcal{P}_j$  is the Legendre polynomial of order  $j$  and  $\Upsilon = \hbar^2/(2I)$ .

<sup>10</sup> K. Patkowski et al., J. Chem. Phys. (2008).

# Diatomic molecule - rigid rotor<sup>10</sup>

- Use  $\mathbf{x}^i, \Omega_1^i, \Omega_2^i$  to denote the configuration of the  $i^{\text{th}}$  rigid rotors,

## Matrix elements

$$\begin{aligned}\mathcal{T}_{\text{tra}}^{i,i+1} &= \left\langle \mathbf{x}^i \left| \exp \left( -\frac{\beta \hat{\mathbf{p}}^2}{2mP} \right) \right| \mathbf{x}^{i+1} \right\rangle = \frac{P^{3/2}}{\Lambda_m^3} \exp \left( -\frac{\pi P (\mathbf{x}^i - \mathbf{x}^{i+1})^2}{\Lambda_m^2} \right) \\ \mathcal{T}_{\text{rot}}^{i,i+1} &= \left\langle \Omega^i \left| \exp \left( -\frac{\beta \hat{\mathbf{J}}^2}{2IP} \right) \right| \Omega^{i+1} \right\rangle = \sum_{j=0}^{\infty} \frac{2j+1}{4\pi} \mathcal{P}_j(\cos(\theta_{i,i+1})) \\ &\quad \times \exp[-\beta j(j+1)\Upsilon/P]\end{aligned}$$

where  $j$  is the angular quantum number,  $\theta_{i,i+1}$  is the angle between bead orientation vectors  $\Omega_i, \Omega_{i+1}$ ,  $\mathcal{P}_j$  is the Legendre polynomial of order  $j$  and  $\Upsilon = \hbar^2/(2I)$ .

<sup>10</sup> K. Patkowski et al., J. Chem. Phys. (2008).

# Diatomic molecule - rigid rotor<sup>10</sup>

- Use  $\mathbf{x}^i, \Omega_1^i, \Omega_2^i$  to denote the configuration of the  $i^{\text{th}}$  rigid rotors,

## Matrix elements

$$\begin{aligned}\mathcal{T}_{\text{tra}}^{i,i+1} &= \left\langle \mathbf{x}^i \left| \exp \left( -\frac{\beta \hat{\mathbf{p}}^2}{2mP} \right) \right| \mathbf{x}^{i+1} \right\rangle = \frac{P^{3/2}}{\Lambda_m^3} \exp \left( -\frac{\pi P (\mathbf{x}^i - \mathbf{x}^{i+1})^2}{\Lambda_m^2} \right) \\ \mathcal{T}_{\text{rot}}^{i,i+1} &= \left\langle \Omega^i \left| \exp \left( -\frac{\beta \hat{\mathbf{J}}^2}{2IP} \right) \right| \Omega^{i+1} \right\rangle = \sum_{j=0}^{\infty} \frac{2j+1}{4\pi} \mathcal{P}_j(\cos(\theta_{i,i+1})) \\ &\quad \times \exp[-\beta j(j+1)\Upsilon/P]\end{aligned}$$

where  $j$  is the angular quantum number,  $\theta_{i,i+1}$  is the angle between bead orientation vectors  $\Omega_i, \Omega_{i+1}$ ,  $\mathcal{P}_j$  is the Legendre polynomial of order  $j$  and  $\Upsilon = \hbar^2/(2I)$ .

<sup>10</sup> K. Patkowski et al., J. Chem. Phys. (2008).



# Diatomic molecule - rigid rotor<sup>11</sup>

- Defining  $\mathbf{r} \equiv \mathbf{x}^{(1)}$ ,  $\Delta^{(i)} \equiv \mathbf{x}^{(i+1)} - \mathbf{x}^{(i)}$ ,

$$\exp[-\beta \bar{U}(|\mathbf{r}|)] = \left\langle \exp \left[ -\frac{\beta}{P} \sum_{i=1}^P U(|\mathbf{x}^i|, \Omega_1^i, \Omega_2^i) \right] \right\rangle_{F, \varrho}$$

- Probability distributions:

$$\varrho(\Omega) = \frac{1}{q_{\text{rot}}} \prod_{i=1}^P \mathcal{T}_{\text{rot}}^{i,i+1}, \quad F(\Delta) = \Lambda_m^3 \prod_{i=1}^P \mathcal{T}_{\text{tra}}^{i,i+1}$$

$$q_{\text{rot}} = \sum_{j'} (2j' + 1) \exp[-\beta \Upsilon j'(j' + 1)]$$

## Fully quantum second virial coefficient

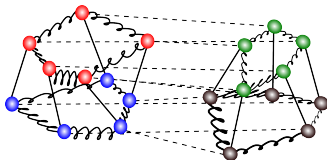
$$B_2(T) = -2\pi \int dr r^2 (e^{-\beta \bar{U}(r)} - 1)$$

<sup>11</sup> K. Patkowski et al., J. Chem. Phys. (2008).

# Diatomic molecule - rigid rotor<sup>12</sup>

- A closer look at the effective potential:

$$\exp[-\beta \bar{U}(|\mathbf{r}|)] = \left\langle \exp \left[ -\frac{\beta}{P} \sum_{i=1}^P U(|\mathbf{x}^i|, \Omega_1^i, \Omega_2^i) \right] \right\rangle_{F, \varrho}$$



<sup>12</sup> K. Patkowski et al., J. Chem. Phys. (2008).

# Objectives

## Diatomic molecules

Compute accurate virial coefficients using state-of-the-art *ab initio* potentials, MSMC and PIMC methods for the rigid case.

## Challenges

Lack of efficient an sampling algorithm for orientations.

# Orientation sampling

- Idea proposed by Garberoglio et al.<sup>13</sup>: two independent atoms (vs. one rigid rotor previously)
- Leads to possibility of avoiding quantum chemistry calculations
- Look at the sampling more mathematically, without having to worry about the physics of the rigid rotor

---

<sup>13</sup> G. Garberoglio et al., J. Chem. Phys. (2014).

## Orientation sampling

- Instead of using Cartesian coordinates, we use the  $P$  COM position vectors  $\mathbf{R}_i$  and the  $P$  bead (or image) vectors  $\mathbf{b}_i$ .
- We consider both Boltzmann type as well as exchange type configurations.
- Probability associated with a configuration  $\mathbf{Z} \equiv (\mathbf{R}, \mathbf{b})$  is given as:

$$P_{\sigma}(\mathbf{Z}) = \frac{1}{Q_1^{(\sigma)}} F(\mathbf{R}; 2m) F(\mathbf{b}^{(\sigma)}; m/2) e^{-\beta \bar{u}(\mathbf{b})}$$

where  $F$  is the path-integral weight, and  $\bar{u}$  is the intramolecular potential energy averaged over all images:

$$F(\mathbf{x}; m) = \left( \frac{P^{3/2}}{\Lambda_m^3} \right)^P \exp \left[ -\frac{\pi P}{\Lambda_m^2} \sum_{i=0}^{P-1} |\mathbf{x}_{i+1} - \mathbf{x}_i|^2 \right]$$
$$\bar{u}(\mathbf{b}) = \frac{1}{P} \sum_{i=0}^{P-1} u(b_i)$$

# Orientation sampling

- Define  $\pi$  to be the  **$b$** -dependent terms of the probability distribution  $F$ .
- We sample from an approximate distribution  $\tau(o \rightarrow n)$  and accept or reject based on:

$$P_{\text{acc}} = \text{Min} \left[ 1, \frac{\pi(n)/\pi(o)}{\tau(o \rightarrow n)/\tau(n \rightarrow o)} \right]$$

where ' $o$ ' and ' $n$ ' denote the old and new configurations respectively.

- We derive a simple and analytic expression for  $\tau(o \rightarrow n)$

# Orientation sampling - bisection algorithm

- Image 0  $\parallel$  image P and the angle between them is 0 for Boltzmann type and  $\pi$  for exchange type. The choice of orientation of image 0 is arbitrary
- At every stage, we are given two images  $\mathbf{b}_i, \mathbf{b}_k$  and we choose the orientation of image  $j = (i + k)/2$ .
- We note that  $\tau(o \rightarrow n)$  is exact for the last step of the algorithm.



Figure 1: Example for  $P = 8$

# Orientation sampling - bisection algorithm

- Image 0  $\parallel$  image P and the angle between them is 0 for Boltzmann type and  $\pi$  for exchange type. The choice of orientation of image 0 is arbitrary
- At every stage, we are given two images  $\mathbf{b}_i, \mathbf{b}_k$  and we choose the orientation of image  $j = (i + k)/2$ .
- We note that  $\tau(o \rightarrow n)$  is exact for the last step of the algorithm.



Figure 1: Example for  $P = 8$



# Orientation sampling - bisection algorithm

- Image 0  $\parallel$  image P and the angle between them is 0 for Boltzmann type and  $\pi$  for exchange type. The choice of orientation of image 0 is arbitrary
- At every stage, we are given two images  $\mathbf{b}_i, \mathbf{b}_k$  and we choose the orientation of image  $j = (i + k)/2$ .
- We note that  $\tau(o \rightarrow n)$  is exact for the last step of the algorithm.

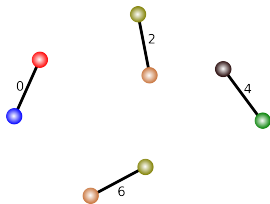


Figure 1: Example for  $P = 8$

# Orientation sampling - bisection algorithm

- Image 0  $\parallel$  image P and the angle between them is 0 for Boltzmann type and  $\pi$  for exchange type. The choice of orientation of image 0 is arbitrary
- At every stage, we are given two images  $\mathbf{b}_i, \mathbf{b}_k$  and we choose the orientation of image  $j = (i + k)/2$ .
- We note that  $\tau(o \rightarrow n)$  is exact for the last step of the algorithm.

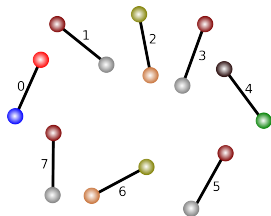


Figure 1: Example for  $P = 8$

# Orientation sampling

- Adjacent image probability distribution:

$$\begin{aligned}
 \tau^{\text{adj}}(\mathbf{b}_j(\alpha, \beta) : \mathbf{a}_j, \psi_{i,k}) \\
 &= \pi(\mathbf{b}_i, \mathbf{b}_j) \pi(\mathbf{b}_j, \mathbf{b}_k) \\
 &= \exp(-4k_h[d_{AC}^2 + d_{BC}^2]/b^2) \\
 &= \exp(-4k_h[1 - \cos(\psi_{i,k}/2) \cos(\alpha)])
 \end{aligned}$$

- The angle  $\alpha$  can be calculated by choosing  $C$  at random, uniformly on  $[0, 1]$ .

$$\begin{aligned}
 \alpha &= \cos^{-1} \left[ 1 + (1/\kappa) \right. \\
 &\quad \left. \times \ln(1 - C(1 - \exp[-2\kappa])) \right], \\
 \kappa &= 4 \cos(\psi_{i,k}/2) k_h b^2
 \end{aligned}$$

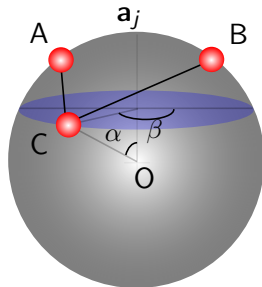


Figure 2: Simplified picture

# Objectives

## Diatomic molecules

Compute accurate virial coefficients using state-of-the-art *ab initio* potentials, MSMC and PIMC methods for the flexible case.

## Challenges

To include vibrational degrees of freedom.

# Bond-length sampling

- Define  $\pi$  in a similar fashion to the orientation sampling algorithm:

$$\pi(\mathbf{b}) = \prod_{i=0}^{P-1} b_i^2 e^{-\beta u(b_i)/P} \pi(b_i, b_{i+1}, \theta_{i,i+1})$$

$$\pi(b_i, b_j, \theta_{i,j}) = \exp\left(-\frac{1}{2}k_h(b_i^2 + b_j^2 - 2b_i b_j \cos(\theta_{i,j}))\right)$$

where  $\theta_{i,j}$  is the angle between orientations of images  $i$  and  $j$ .

## Bond-length sampling

- Let  $\pi(\mathbf{b}) = \exp(-y)$ , where  $y$  can be defined as follows:-

$$y = \sum_{i=0}^{P-1} \left\{ k_h \left( b_i^2 - b_i b_j \cos(\theta_{ij}) \right) - 2 \log b_i + \frac{\beta u(b_i)}{P} \right\}$$

- We define  $\tilde{y} \approx y$  such that:

$$\tilde{y} = \sum_{i=0}^{P-1} \left\{ k_h \left( b_i^2 - b_i b_j \right) - \frac{2 \log b_i}{P} + \frac{\beta u(b_i)}{P} \right\}$$

- We solve for the nominal  $\cos(\hat{\theta})$  value by:

$$\frac{\partial y}{\partial b_i} = \frac{\partial \tilde{y}}{\partial b_i} \Rightarrow \cos(\hat{\theta}) = 1 - \frac{P-1}{P k_h b_i^2}$$

- Using this nominal value in the expression for  $y$ , we find  $b_m$  such that:

$$\left. \frac{\partial y}{\partial b_i} \right|_{b_i=b_m} = 0 \quad \forall i$$

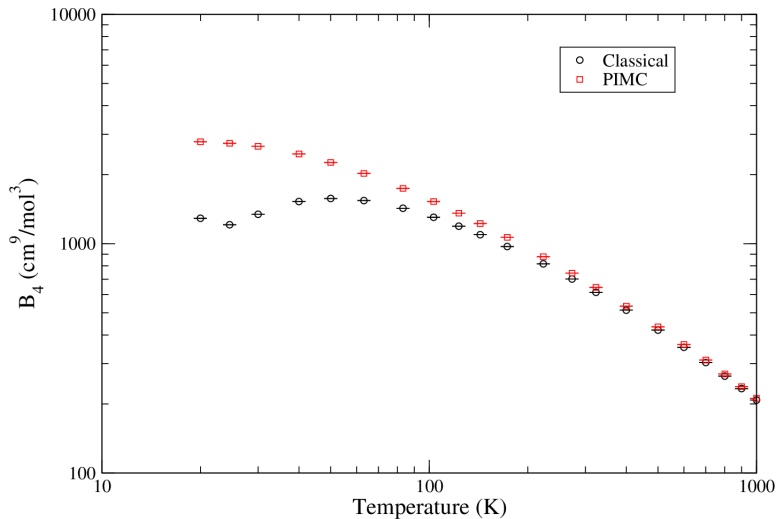
# Overview

- 1 Introduction
  - Viral coefficients
  - *Ab initio* potentials
- 2 Objectives
- 3 Methods
  - Mayer Sampling Monte Carlo
  - Path Integral Monte Carlo
  - Novel algorithms
- 4 Results
- 5 Summary

# Overview

- 1 Introduction
  - Viral coefficients
  - *Ab initio* potentials
- 2 Objectives
- 3 Methods
  - Mayer Sampling Monte Carlo
  - Path Integral Monte Carlo
  - Novel algorithms
- 4 Results
- 5 Summary



PIMC results for Helium-4<sup>14</sup>

<sup>14</sup> K. R. S. Shaul, A. J. Schultz, and D. A. Kofke, J. Chem. Phys. (2012).

# A new orientational sampling algorithm

- What if we don't model using the quantum rigid rotor approximation?
- The only factor that affects the probability of any configuration is the **harmonic spring-like interaction** between adjacent beads
- $U_h = \sum_{\#rings} \sum_i k_h |\mathbf{x}_i - \mathbf{x}_{i-1}|^2$ , with  $k_h = \frac{\pi P}{\Lambda^2}$  where  $\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$   
and  $\mathbf{x}_i$  denotes position of the bead  $i$
- The actual probability of any configuration is given by  
 $P_{act} = \exp(-U_h)$

## Growing the ring

- Tight coupling between adjacent beads makes it difficult to sample orientations that are different, thus lowering the sampling efficiency
- We always **grow the complete ring each time** and we do so **non-sequentially**

# Non-sequential algorithm

- Image 0 and image P are one and the same. The choice of orientation of image 0 is arbitrary
- Each image(child) has a set of two(parent) orientations which affect where it is placed
- For each pass, we need a probability distribution of the child image that depends on the orientations of both the parent images



Figure 3: Example for  $P = 8$

# Non-sequential algorithm

- Image 0 and image P are one and the same. The choice of orientation of image 0 is arbitrary
- Each image(child) has a set of two(parent) orientations which affect where it is placed
- For each pass, we need a probability distribution of the child image that depends on the orientations of both the parent images

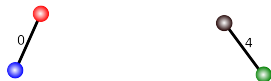


Figure 3: Example for  $P = 8$

# Non-sequential algorithm

- Image 0 and image P are one and the same. The choice of orientation of image 0 is arbitrary
- Each image(child) has a set of two(parent) orientations which affect where it is placed
- For each pass, we need a probability distribution of the child image that depends on the orientations of both the parent images

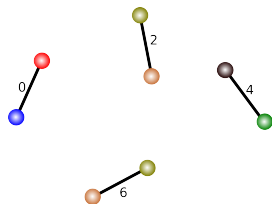


Figure 3: Example for  $P = 8$

# Non-sequential algorithm

- Image 0 and image P are one and the same. The choice of orientation of image 0 is arbitrary
- Each image(child) has a set of two(parent) orientations which affect where it is placed
- For each pass, we need a probability distribution of the child image that depends on the orientations of both the parent images

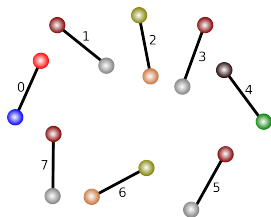


Figure 3: Example for  $P = 8$

## Adjacent image probability $P_{01}$

- Consider a sphere with diameter = bond length of the molecule i.e.  $r = b/2$
- Let image '0' be oriented along the z-axis and image '1', at angle  $\phi_1$  away from it
- Distance 'x' between beads of adjacent images is given by  $x^2 = 2r^2(1 - \cos\phi_1)$
- The harmonic interaction energy is given by,  $U_h = 4k_h r^2(1 - \cos\phi_1)$
- $P_{01}$  is given by:

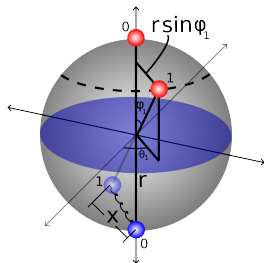


Figure 4:  $P = 2$  case

$$P_{01}(\phi_1) = \exp[-4k_h r^2(1 - \cos\phi_1)] \quad (2)$$



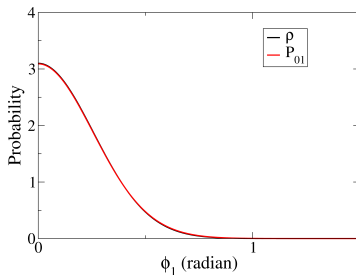
# Comparison between algorithms<sup>15</sup>

Normalize these the two functions  $P_{01}, \rho$  :

$$P_{01}(\phi_1) = \exp[-4k_h r^2(1 - \cos\phi_1)]$$

$$\rho(\phi_1) = \frac{1}{q_{rot}} \sum_{j=0}^{100} \frac{2j+1}{4\pi} P_j(\cos\phi_1) \times \exp[-\beta j(j+1)\Upsilon/P]$$

Comparison of probabilities

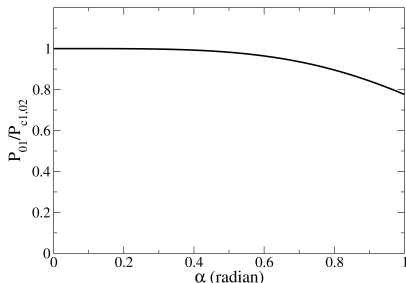


<sup>15</sup> K. Patkowski et al., J. Chem. Phys. (2008).

# Parent $\rightarrow$ child

- Given two parent images  $I_1, I_2$ , the harmonically most favorable orientation for the child image is the average of the their orientations
- Let  $c_n$  denote the average orientation of the two parents for image  $n$  and  $P_{c_n, I_1 I_2}$  denote the probability distribution centered around  $c_n$
- For the case of  $n = 1$ ,  $P_{c_1, 02}$  can be computed analytically

Ratio of probabilities



# Parent → child

- We performed MC simulations and collected histograms of angles  $\phi_2, \phi_4, \phi_8 \dots$  and observed that:

$$P_{c_n, l_1 l_2}(\phi_n) \approx P_{01}(k_n^{eff}, \phi_n)$$

$$k_n^{eff} \propto k_h \cos(\psi_n/2)$$

where  $\psi_n$  is the angle between the orientations of  $l_1, l_2$

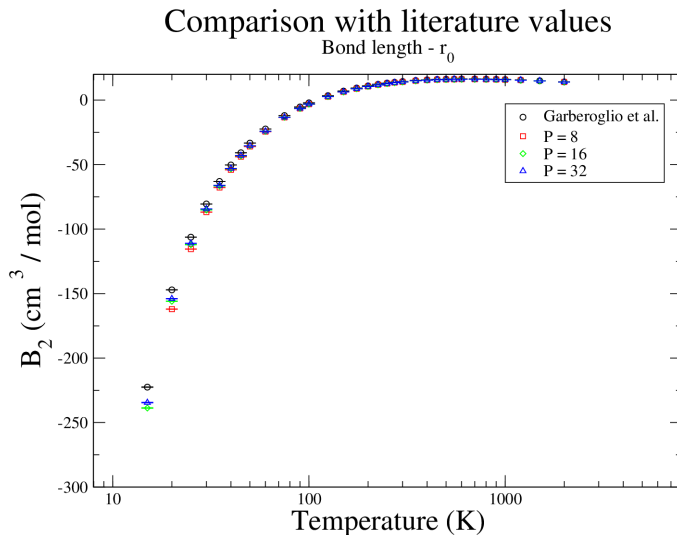
- For the first pass alone, set  $l_1 = 0, l_2 = 0$  and subsequent passes will have different sets of parents
- Cumulative distribution function:

$$C(\alpha) = \frac{e^{2k_n^{eff}} - e^{k_n^{eff}(1+\cos\alpha)}}{e^{2k_n^{eff}} - 1} \quad (3)$$

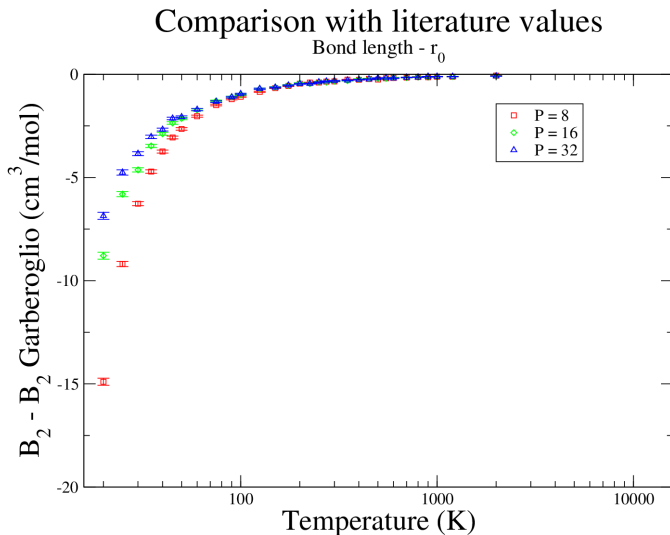
- Simple and computationally inexpensive

# Generating configurations

- Difficult to generate configurations based on the actual distribution that we desire
- Instead we can generate angles from an approximate distribution  $C(\alpha)$  much easily
- Need to account for it by computing the ratio of the actual and generating probabilities of a configuration
- Our acceptance probability is given as:  $P_{acc} = \frac{P_{act}^{new} / P_{act}^{old}}{P_{gen}^{new} / P_{gen}^{old}}$
- Accept/reject based on  $P_{acc}$  and we can sample the (desired) actual distribution more accurately and efficiently

Bond length<sup>16</sup> -  $r_0$ 

<sup>16</sup> G. Garberoglio et al., J. Chem. Phys. (2014).

Bond length<sup>17</sup> -  $r_0$ 

<sup>17</sup> G. Garberoglio et al., J. Chem. Phys. (2014).

## Methods to handle flexibility

- Instead of using ground state bond length ( $r_0$ ) use average bond length at each temperature ( $\langle r \rangle_T$ )
- Average the bond length values over internal degrees of freedom of each monomer, weighted by the appropriate wave function<sup>18</sup>

$$\langle r \rangle_T = \sum_{n,J} p(n, J : T) \langle \chi_{nJ} | r | \chi_{nJ} \rangle$$

where  $n$  and  $J$  are quantum numbers that define the vibrational and rotational state of  $H_2$ , respectively, while  $\chi_{nJ}$  denotes the corresponding wave-function and

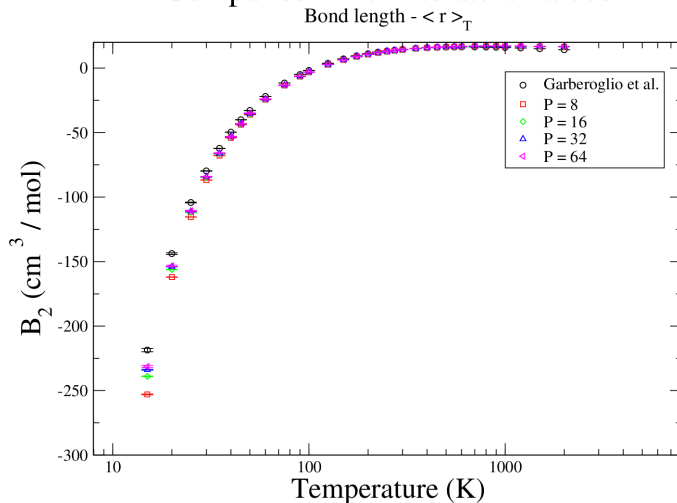
$$p(n, J : T) = \frac{(2J + 1) \exp(-E(n, J)/T)}{\sum_{n', J'} (2J' + 1) \exp(-E(n', J')/T)}$$

where  $E(n', J')$  is the energy of the  $(n', J')$  state

<sup>18</sup> G. Garberoglio et al., J. Chem. Phys. (2012).

Bond length<sup>19</sup> -  $\langle r \rangle_T$ 

## Comparison with literature values

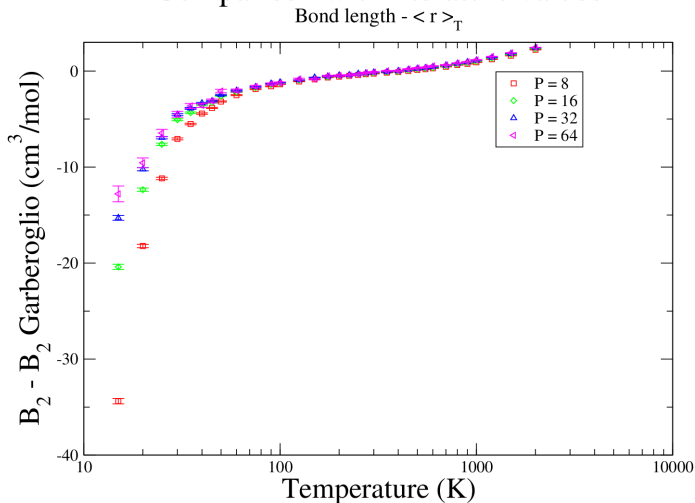


<sup>19</sup> G. Garberoglio et al., J. Chem. Phys. (2014).



Bond length<sup>20</sup> -  $\langle r \rangle_T$ 

## Comparison with literature values



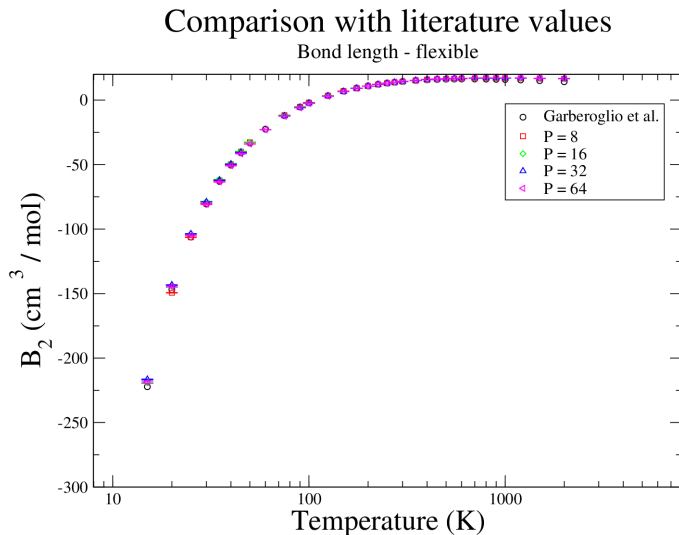
<sup>20</sup> G. Garberoglio et al., J. Chem. Phys. (2014).

## $\mathcal{P}$ - actual probability of a configuration

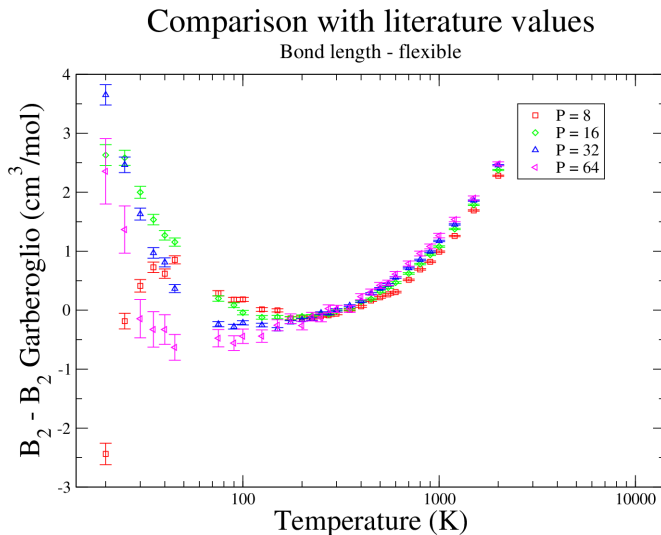
- Expression for  $\mathcal{P}$  is almost exponential
- Consider the argument of the exponential

$$-\log \mathcal{P} = \sum_{i=0}^P \left\{ k_h \cdot \left( b_i^2 - b_i \cdot b_j \cdot \cos(\theta_{ij}) \right) - 2 \cdot \log b_i + \frac{\beta \cdot U_i(b_i)}{P} \right\}$$

- We can clearly see that it is not quadratic due to the presence of  $U_i$
- Presence of cross terms such as  $b_i \cdot b_j$  makes the bond lengths non-independent of each other

Bond length<sup>21</sup> - flexible

<sup>21</sup> G. Garberoglio et al., J. Chem. Phys. (2014).

Bond length<sup>22</sup> - flexible

<sup>22</sup> G. Garberoglio et al., J. Chem. Phys. (2014).

## Summary and future work

- We have developed a bond length sampling algorithm that can be used to compute virial coefficients for flexible diatomic molecules
- We applied the algorithm for  $H_2$  molecule and the resulting second virial coefficients are not in perfect agreement with literature data
- Fix remaining issues and improve efficiency of the move
- Apply the algorithm for other diatomic systems like  $N_2$
- Extend the algorithm to other complicated systems like water

# Acknowledgment

- My advisor Dr. David Kofke
- Dr. Andrew Schultz
- Members of the Kofke group
- Funding:



National Science Foundation  
WHERE DISCOVERIES BEGIN

- Computational resources:



- We would like to thank Dr. Allan H. Harvey for insightful discussions

Thank you for your attention!

Questions???

$P_{act}$ 

- Let  $P_{act} = \exp(-z_{act})$  where  $z_{act}$  can be defined as follows:-

$$z_{act} = \sum_{i=0}^P \left\{ k_h \cdot \left( b_i^2 - b_i \cdot b_j \cdot \cos(\theta_{ij}) \right) - 2 \cdot \log b_i + \frac{\beta \cdot U_i(b_i)}{P} \right\}$$

- Since  $z_{act}$  is not quadratic, it is not easy to sample from
- All bond lengths not independent of each other



# Assumptions and modifications

- $z_{act}$  is given by:

$$z_{act} = \sum_{i=0}^P \left\{ k_h \cdot \left( b_i^2 - b_i \cdot b_j \cdot \cos(\theta_{ij}) \right) - 2 \cdot \log b_i + \frac{\beta \cdot U_i(b_i)}{P} \right\}$$

- Finding  $b_{min}$ , given as the solution of  $\left. \frac{\partial z_{act}}{\partial b_i} \right|_{b_i=b_{min}} = 0$ , before each move can be very inefficient
- Let  $z_{act}^*$  be given by:

$$z_{act}^* = \sum_{i=0}^P \left\{ k_h \cdot \left( b_i^2 - b_i \cdot b_j \right) - \frac{2 \cdot \log b_i}{P} + \frac{\beta \cdot U_i(b_i)}{P} \right\}$$

- Find  $b_{min}$  using  $\left. \frac{\partial z_{act}^*}{\partial b_i} \right|_{b_i=b_{min}} = 0$ , set  $\frac{\partial z_{act}}{\partial b_i} = \frac{\partial z_{act}^*}{\partial b_i}$  and solve for  $\theta_{ij}$

# Assumptions and modifications

- Let  $\frac{\partial z_{act}}{\partial b_i} = \frac{\partial z_{act}^*}{\partial b_i}$  solve for  $\cos(\theta_{ij})$
- $\cos(\theta_{ij}) = 1 - \frac{P-1}{P \cdot k_h \cdot b_i^2}$
- Compute  $b_{min}$  using  $\left. \frac{\partial z_{act}}{\partial b_i} \right|_{b_i=b_{min}} = \left. \frac{\partial z_{act}^*}{\partial b_i} \right|_{b_i=b_{min}} = 0$

# Conclusions

- Let  $\frac{\partial z_{act}}{\partial b_i} = \frac{\partial z_{act}^*}{\partial b_i}$  solve for  $\cos(\theta_{ij})$
- $\cos(\theta_{ij}) = 1 - \frac{P-1}{P \cdot k_h \cdot b_i^2}$
- Compute  $b_{min}$  using  $\left. \frac{\partial z_{act}}{\partial b_i} \right|_{b_i=b_{min}} = \left. \frac{\partial z_{act}^*}{\partial b_i} \right|_{b_i=b_{min}} = 0$

# Future work

- Let  $\frac{\partial z_{act}}{\partial b_i} = \frac{\partial z_{act}^*}{\partial b_i}$  solve for  $\cos(\theta_{ij})$
- $\cos(\theta_{ij}) = 1 - \frac{P-1}{P \cdot k_h \cdot b_i^2}$
- Compute  $b_{min}$  using  $\left. \frac{\partial z_{act}}{\partial b_i} \right|_{b_i=b_{min}} = \left. \frac{\partial z_{act}^*}{\partial b_i} \right|_{b_i=b_{min}} = 0$

# Future work

- Let  $\frac{\partial z_{act}}{\partial b_i} = \frac{\partial z_{act}^*}{\partial b_i}$  solve for  $\cos(\theta_{ij})$
- $\cos(\theta_{ij}) = 1 - \frac{P-1}{P \cdot k_h \cdot b_i^2}$
- Compute  $b_{min}$  using  $\left. \frac{\partial z_{act}}{\partial b_i} \right|_{b_i=b_{min}} = \left. \frac{\partial z_{act}^*}{\partial b_i} \right|_{b_i=b_{min}} = 0$