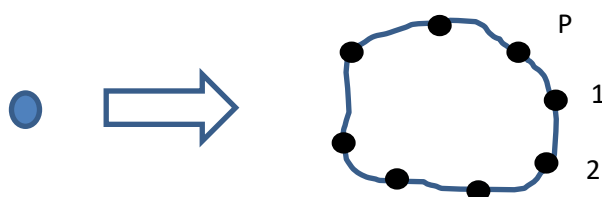


## Atoms quantum motion

So far we have ignored the quantum movement of atoms. At room temperature the effect is not very large. The atom that have largest quantum movement is hydrogen. In chemistry we can ignore the other atoms. Naturally there are several interesting quantum effects at low temperatures (below ca. 10 K). These are superfluidity, Bose-Einstein condensate.

The atomic quantum movements can be modelled with path-intergral (PI) method. In the PI method a classical particle is expressed with many fictitious particles (beads) that are connected with harmonic springs. The mass of each bead is  $M/P$ . (Note this has nothing to do with the NEB method.) The PI methods is in fact an alternative methods to write the quantum mechanics. (There is a good but very technical paper of the PIMD by Mark Tuckerman.)

So a particle become a ring of particles



We can then write this systems partition function

$$Z_P(T) = \left( \frac{mP}{2\pi\beta\hbar^2} \right) \int dx_1 dx_2 \dots dx_P \exp \left( - \sum_{i=1}^P \left[ \frac{mP}{2\beta\hbar^2} (x_{i+1} - x_i)^2 + \frac{\beta}{P} \varphi(x_i) \right] \right)_{x_P=x_1}, \beta = \frac{1}{kT}$$

Here we integrate over all the bead positions. This integration is not practical but the molecular dynamics (or Monte Carlo) can be used to compute relevant quantities from this system. Note that the bead are in a potential  $\varphi(x)$ .

The general partition functions is

$$Z(T) = \int dx dp \exp(-\beta H(x,p)), \quad H = T(p) + V(x)$$

And here the T is the kinetic energy and V is the potential energy. If we want to obtain an average of some atomic position dependent function it can be obtained as an integral.

$$\langle A \rangle = \frac{1}{Z} \int dx_1 dx_2 \dots dx_N A(x) \exp(-\beta V(x))$$

And general position and momentum dependent function

$$\langle A \rangle = \frac{1}{Z} \int dx_1 \dots dx_N dp_1 \dots dp_N A(x, p) \exp(-\beta H)$$

The position dependent function can be computer using an atomic positions from a MD simulation with potential V(x)

$$\langle A \rangle = \lim_{\Delta t \rightarrow \infty} \frac{1}{\Delta t} \int_0^{\Delta t} dt A(x(t))$$

Note that there is no  $\exp(-\beta H)$  term in this intregal. The reason is that MD the stomic positions will follow the  $\exp(-\beta V)$  distribution (providing the MD simulation is long enough).

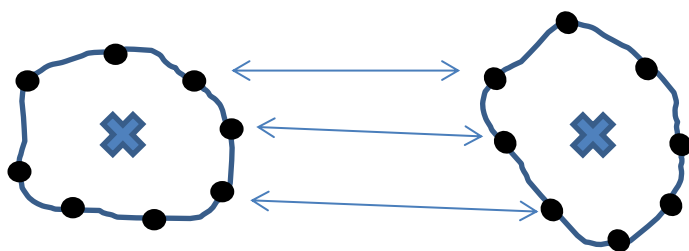
In the case of the Path Integral the relevant potential is

$$V(x) = \sum_{i=1}^P \left[ \frac{mP}{2\beta\hbar^2} (x_{i+1} - x_i)^2 + \frac{\beta}{P} \varphi(x_i) \right] \quad (\text{PI potential})$$

This equation looks simple and it is easy to be used with low values of P but as the P increaces the harmonic term increaces and the potential will reduce. This cause the potential sampling to become inefficient. This can be overcome with new variables (see details from Tuckerman page 286.)

So the quantum effect of the atoms can be simulated using classical MD with the (PI potential). So far the simulation do not take into account several beads of the atomic motion or in this picture the centre of mass movement of the bead. The derivation of the Centroid-PI-MD is rather tricky but the result is very simple. We can compute all forces between SAME beads and let the centroids (centre of masses) to move. There is the spring between the beads. The centroid mass is the same as the mass of the atom.

$$Z_P(T) = \prod_I^N \left( \frac{M_I P}{2\pi\beta\hbar^2} \right) \int dR_1 dR_2 \dots dR_P \exp \left( - \sum_{I=1}^N \sum_{i=1}^P \left[ \frac{M_I \omega_P^2}{2} (R_i^{(i+1)} - R_i^{(i)})^2 + \frac{1}{P} \varphi(R_1^{(i)} \dots R_N^{(i)}) \right] \right)_{x_P=x_1}$$



The centroid position and force are

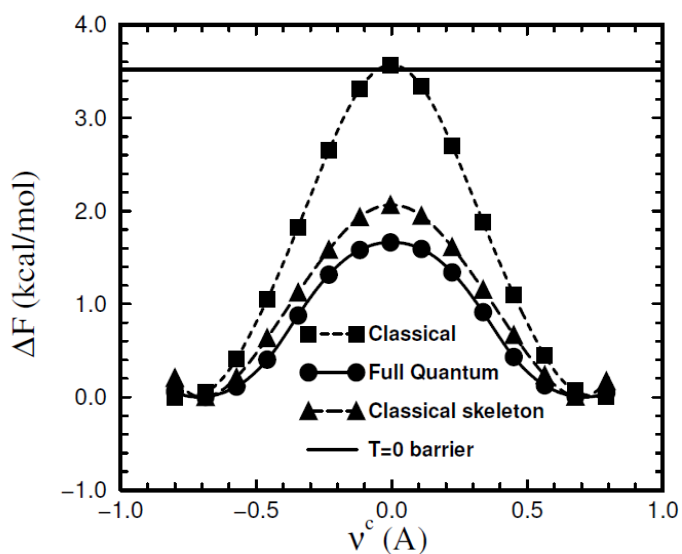
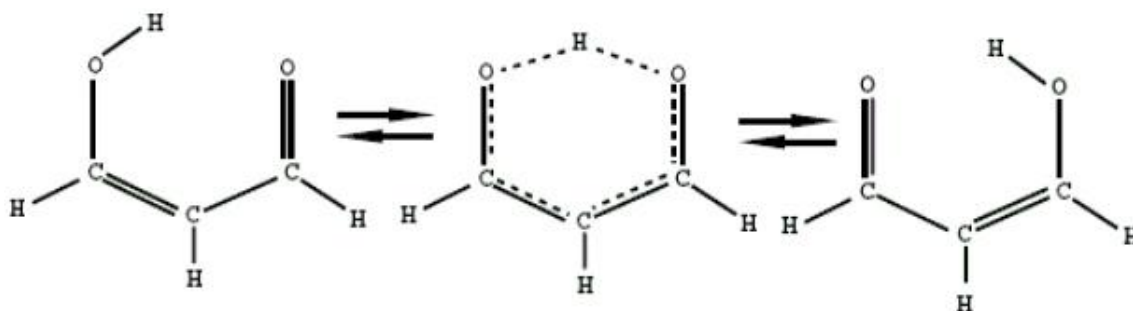
$$x_{cent} = \frac{1}{P} \sum_{i=1}^P x_i, \quad F_{cent} = \frac{1}{P} \sum_{i=1}^P F_i,$$

How about PI-AIMD. So coupling the AIMD to PI methods. That is easy. Now each bead with the same index will have its own KS-wave function. So with 8 bead there will be 8 parallel wave functions.

$$\varphi_n(r) \rightarrow \varphi_{n,i}(r_i)$$

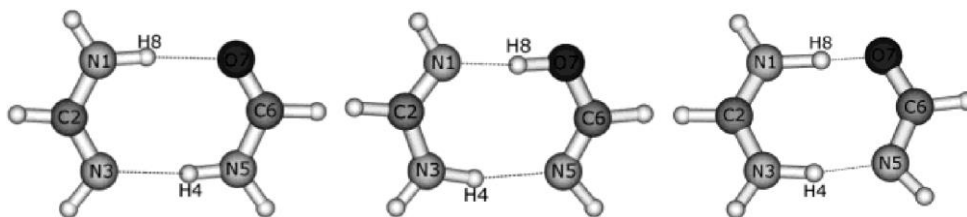
How many bead are needed ? At room temperature 8 (or 16) is OK.

Example. Proton barrier in Malonaldehyde

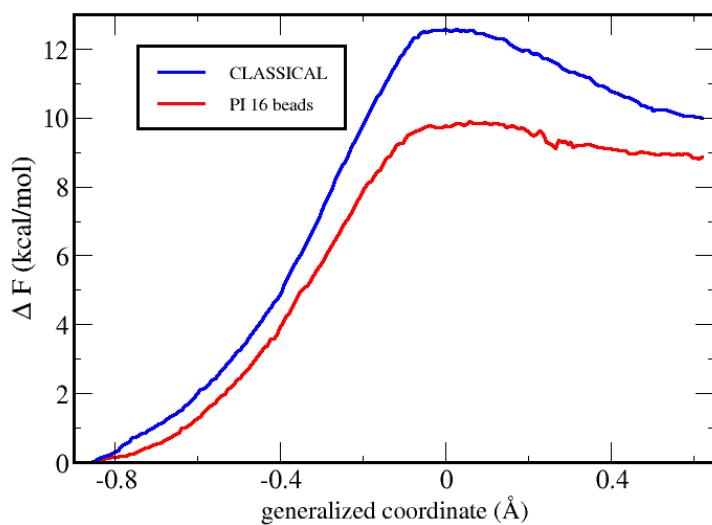


From: Tuckerman & Marx, PRL **86** 4946 (2001))

Similar effect on



Free Energy Profile FIFA 300 K



Videos of PI-AIMD

[http://www.youtube.com/watch?v=Y1Ng\\_e5CxGQ&feature=player\\_detailpage](http://www.youtube.com/watch?v=Y1Ng_e5CxGQ&feature=player_detailpage)

[http://www.youtube.com/watch?feature=player\\_detailpage&v=FlTjyl0WLb0](http://www.youtube.com/watch?feature=player_detailpage&v=FlTjyl0WLb0)

A similar lecture:

[http://www.fhi-berlin.mpg.de/~luca/Course\\_TU/05\\_PathIntegralMolecularDynamics.pdf](http://www.fhi-berlin.mpg.de/~luca/Course_TU/05_PathIntegralMolecularDynamics.pdf)