Introduction to Imaginary-Time Path Integrals

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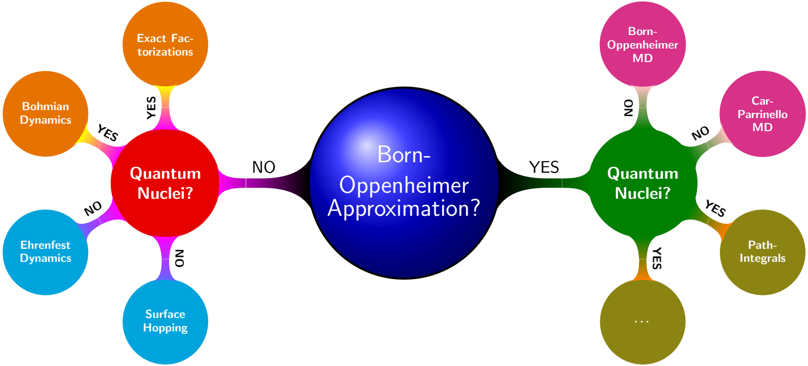
2019/10/09

Outline

The time-dependent Schrödinger equation:

$$i\hbar\frac{\partial\Psi(\mathbf{r},\mathbf{R},t)}{\partial t} = \hat{\mathcal{H}}(\mathbf{r},\mathbf{R})\Psi(\mathbf{r},\mathbf{R},t)$$

In practice, *approximations* have to be made! [1]

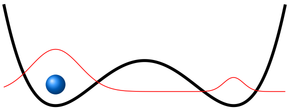


[1] "*Ab initio* molecular dynamics", Mariana Rossi, DFT Workshop 2017

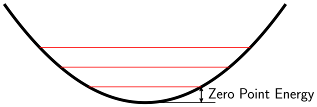
The *thermal* de Broglie wavelength of a particle:

$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

for a hydrogen atom at 300 K, $\Lambda \approx 1.0\,\text{Å}$.



Quantum Tunneling



Zero Point Motion

other nuclear quantum effects: exchange effects, quantum coherence...

- NQEs are important for any vibrational mode for which $\hbar\omega/k_B T > 1$. If $T = 300\,\text{K}$, $\omega \approx 208\,\text{cm}^{-1}$.

Outline

For a single particle moving in one spatial dimension potential [2]

$$\hat{\mathcal{H}} = \frac{\hat{p}^2}{2m} + \hat{V}(\hat{x}) \equiv \hat{T} + \hat{V}$$

The quantum partition function

$$\begin{aligned} Z &= \mathrm{tr}\left[e^{-\beta\hat{\mathcal{H}}}\right] = \mathrm{tr}\left[(e^{-\frac{\beta}{P}\hat{\mathcal{H}}})^P\right] = \mathrm{tr}\left[(e^{-\beta_P\hat{\mathcal{H}}})^P\right] \\ &= \int \mathrm{d}x_1 \, \langle x_1|(e^{-\beta_P\hat{\mathcal{H}}})^P|x_1\rangle \\ &= \int \mathrm{d}x_1 \ldots \int \mathrm{d}x_P \, \langle x_1|e^{-\beta_P\hat{\mathcal{H}}}|x_2\rangle \ldots \langle x_P|e^{-\beta_P\hat{\mathcal{H}}}|x_1\rangle \end{aligned}$$

Note the connection between the quantum propagator and the density matrix,

$$\langle x'|e^{-i\hat{\mathcal{H}}t/\hbar}|x\rangle \qquad \Rightarrow \qquad \langle x'|e^{-\beta\hat{\mathcal{H}}}|x\rangle; \quad t = -i\beta\hbar$$

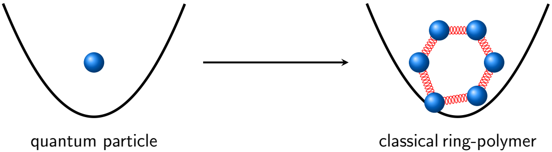
Hence the name *imaginary-time path integral*. By using the Trotter splitting[3]

$$e^{-\beta_P\hat{\mathcal{H}}} = e^{-\beta_p\hat{V}/2}e^{-\beta_p\hat{T}}e^{-\beta_p\hat{V}/2} + \mathcal{O}(\beta_P^3)$$

$$\Rightarrow \quad \langle x_i|e^{-\beta_P\hat{\mathcal{H}}}|x_j\rangle \approx \left(\frac{m}{2\pi\beta_P\hbar^2}\right)^{1/2} e^{-\beta_P\left[\frac{m}{2(\beta_P\hbar)^2}(x_i-x_j)^2+\frac{1}{2}\left(V(x_i)+V(x_j)\right)\right]}$$

Path Integral Isomorphism II

$$Z = \mathrm{tr}\left[e^{-\beta\hat{\mathcal{H}}}\right]$$
$$= \lim_{P\to\infty}\int \mathrm{d}x_1 \ldots \int \mathrm{d}x_P \left(\frac{m}{2\pi\beta_P\hbar^2}\right)^{P/2} \exp\left\{-\beta_P \underbrace{\sum_{i=1}^{P}\left[\frac{m}{2(\beta_P\hbar)^2}(x_{i+1}-x_i)^2 + V(x_i)\right]}_{V_{\mathrm{eff}}(x_1,\ldots,x_P)}\right\}\Bigg|_{x_{P+1}=x_1}$$



- Maps the *quantum partition function* to the *configuration integral* of classical ring-polymers.
- *EXACT* when $P \to \infty$. Reduce to classical partition function when $P = 1$.
- The integral can be sampled with Monte Carlo method (PIMC, not covered in this talk), but for MD we need *momenta*!

[2] "Statistical Mechanics: Theory and Molecular Simulation", Mark E. Tuckerman

[3] There are higher-order splitting techniques.

For a Hermitian operator $\hat{A}$, the expectation value follows,

$$\langle \hat{A} \rangle = \frac{1}{Z} \operatorname{tr}\left[\hat{A} e^{-\beta \hat{\mathcal{H}}}\right] = \frac{1}{Z} \operatorname{tr}\left[\hat{A} (e^{-\beta_P \hat{\mathcal{H}}})^P\right]$$

if $\hat{A}$ is purely a function of $\hat{x}$, i.e. $\hat{A}(\hat{x}) |x\rangle = a(x) |x\rangle$, then [4]

$$\langle \hat{A} \rangle = \frac{1}{Z} \lim_{P\to\infty} \int \mathrm{d}x_1 \ldots \int \mathrm{d}x_P \left(\frac{m}{2\pi\beta_P \hbar^2}\right)^{P/2} \left(\frac{1}{P}\sum_{i=1}^{P} a(x_i)\right) \exp\left\{-\beta_P \sum_{i=1}^{P} \left[\frac{m}{2(\beta_P \hbar)^2}(x_{i+1} - x_i)^2 + V(x_i)\right]\right\}\Bigg|_{x_{P+1}=x_1}$$

- If $\hat{A}$ is a function of momentum opeator $\hat{p}$, then the *cyclic-path* condition $x_{P+1} = x_1$ is released, in which case one should resort to the so-called *open-path* path integral method.
- The thermodynamic functions, which may depend on both $\hat{x}$ and $\hat{p}$, are exceptional because thermodynamic relations can be used. For example

$$E = \langle \hat{\mathcal{H}} \rangle = \langle \frac{\hat{p}^2}{2m} + V(\hat{x}) \rangle = -\frac{\partial}{\partial \beta} \ln Z = \frac{1}{Z}\frac{\partial Z}{\partial \beta}$$

[4] "Statistical Mechanics: Theory and Molecular Simulation", Mark E. Tuckerman

Insert P Gaussian integral into Z: $\left(\frac{\beta}{2\pi\tilde{m}}\right)^{1/2}\int \mathrm{d}p\, e^{-\beta p^2/2\tilde{m}} = 1$

$$Z = \left(\frac{1}{2\pi\hbar}\right)^P \prod_{i=1}^{P}\sqrt{\frac{m}{\tilde{m}_i}} \lim_{P\to\infty}\int \mathrm{d}x_1 \ldots \int \mathrm{d}x_P \int \mathrm{d}p_1 \ldots \int \mathrm{d}p_P$$

$$\exp\left\{-\beta_P \sum_{i=1}^{P}\left[\frac{p_i^2}{2\tilde{m}_i} + \frac{m}{2(\beta_P\hbar)^2}(x_{i+1}-x_i)^2 + V(x_i)\right]\right\}$$

$$= \mathcal{C}\lim_{P\to\infty}\int \mathrm{d}\mathbf{x}^P \int \mathrm{d}\mathbf{p}^P \exp\left[-\beta_P H_P(\mathbf{x},\mathbf{p})\right]$$

More general: $\prod_i \tilde{m}_i \Rightarrow \det[\mathrm{M}]$

real physical mass

$\tilde{m}_i$ need *not* be physical. More general form: $\frac{1}{2}\mathbf{p}^T\mathrm{M}^{-1}\mathbf{p}$, where M is the mass matrix, and $\mathbf{p} = (p_1, \ldots, p_P)$.

- PIMD trajectories are obtained by integrating Hamilton's classical equaiton of motion

$$\frac{\mathrm{d}p_i}{\mathrm{d}t} = +\frac{\partial H_P(\mathbf{x},\mathbf{p})}{\partial x_i}; \qquad \frac{\mathrm{d}x_i}{\mathrm{d}t} = -\frac{\partial H_P(\mathbf{x},\mathbf{p})}{\partial p_i}$$

- $\beta_P H_P(\mathbf{x},\mathbf{p}) \Rightarrow \beta\left(H_P(\mathbf{x},\mathbf{p})/P\right)$, which affects the dynamics but not the statistics.
- Different mass matrices give the same static average, only dynamics will be changed.
- Mathematically, the main difference between PIMD, PACMD and RPMD is the choice of the mass matrix. Physically, they differ dramatically!

Multiparticle Generalization

For a system of N *distinguishable* nuclei, [5]

$$\hat{\mathcal{H}}_P = \sum_I^N \frac{\mathbf{p}_I^2}{2m_I} + \underline{\hat{V}(\mathbf{x}_1, \ldots, \mathbf{x}_N)},$$

Potential energy: could be from emperical potential or from *ab initio* calculations. *Born-Oppenheimer approximation* implicitly implied.

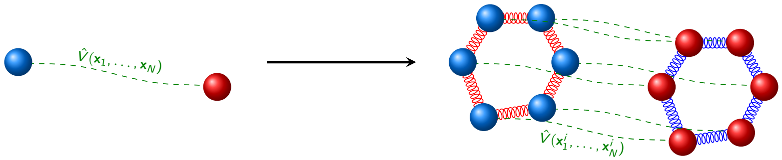
The PIMD Hamiltonian is

$$H_P(\{\mathbf{x}\}, \{\mathbf{p}\}) = \sum_{I=1}^{N} \sum_{i=1}^{P} \left[\frac{(\mathbf{p}_I^i)^2}{2\tilde{m}_I^i} + \frac{1}{2} m_I \omega_P^2 (\mathbf{x}_I^{i+1} - \mathbf{x}_I^i)^2 \right] + \sum_{i=1}^{P} \hat{V}(\mathbf{x}_1^i, \ldots, \mathbf{x}_N^i)$$

sum over nuclei index

sum over bead index

$\omega_P = P k_B T / \hbar$



quantum particle

classical ring-polymers

[5] We are neglecting the exchange effect, which is generally fine for nuclei (unless treating 4 K Helium) but not for electrons.

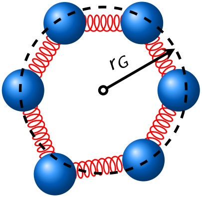
- **Radius of Gyration** – the spread in imaginary time. For a free particle the root mean square radius of gyration is:

$$\langle r_G^2(T)\rangle^{1/2} = \frac{\Lambda(T)}{\sqrt{8\pi}} \qquad \Lambda(T) = \frac{h}{\sqrt{2\pi m k_B T}}$$

- **Bead to bead distance** – For a free particle the average is:

$$\sqrt{\frac{\beta\hbar^2}{Pm}}$$

Note the distance decreases as P increases.



- **Centroid** – the center of the Ring-Polymer.

$$x_c = \frac{1}{P}\sum_{i=1}^{P} x_i$$

- **Bead spring constants** [6] – determined by $m\omega_P^2$

$$\omega_P = \frac{1}{\beta_P\hbar} = P k_B T/\hbar$$

The overall object is referred to as an *Imaginary Time Path* or a *Ring-Polymer*.

[6] In some textbooks, $\omega_P = \sqrt{P} k_B T/\hbar$ if the Hamiltonian is $H_P(\mathbf{x}, \mathbf{p})/P$

- **Normal Modes:** – the ring-polymer potential can be diagonalized

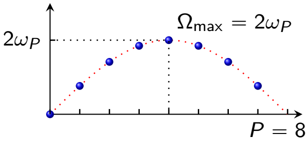
$$\sum_{i=1}^{P}\frac{1}{2}m\omega_P^2(x_{i+1}-x_i)^2 \quad\Longleftrightarrow\quad \begin{aligned}\tilde{\mathbf{x}} &= \mathbf{U}\cdot\mathbf{x}\\ \mathbf{x} &= \mathbf{U}^T\cdot\tilde{\mathbf{x}}\end{aligned} \quad\Longleftrightarrow\quad \sum_{j=1}^{P}\frac{1}{2}m\Omega_j^2\tilde{x}_j^2;$$

where $\mathbf{x}$ is the bead Cartesian coordinate and $\tilde{\mathbf{x}}$ is the normal mode coordinate.

- $\tilde{x}_1$ corresponds to the centroid motion and $\Omega_1 = 0$.
- The transformation $\tilde{\mathbf{x}} \Leftrightarrow \mathbf{x}$ can be done with FFT.[7]
- The normal mode frequencies [8]

$$\Omega_j = 2\omega_P \sin\left(\frac{(j-1)\pi}{P}\right)$$

e.g. $P = 8$



- The matrix element U_{kj} of the unitary transformation matrix $\mathbf{U}$ for even P

$$\begin{cases}\sqrt{1/P}, & k=1\\ \sqrt{2/P}\cos\left(\frac{2\pi}{P}(j-1)(k-1)\right), & 2\leqslant k\leqslant P/2\\ \sqrt{1/P}(-1)^j, & k=P/2+1\\ \sqrt{2/P}\sin\left(\frac{2\pi}{P}(j-1)(k-1)\right), & P/2+2\leqslant k\leqslant P\end{cases}$$

and $\tilde{x}_k = \sum_{j=1}^{P} U_{kj}x_j$.

- Note if we choose $\beta_P H_P \Rightarrow \beta(H_P/P)$, then

$$\tilde{\mathbf{x}} = \frac{1}{\sqrt{P}}\mathbf{U}\cdot\mathbf{x}$$
$$\mathbf{x} = \sqrt{P}\,\mathbf{U}^T\cdot\tilde{\mathbf{x}}$$

[7] *J. Chem. Phys.*, **104**, 2028(1996).

[8] This reminds me of the phonon dispersion of 1-D atomic chain.

$$H_P(\{\mathbf{x}\},\{\mathbf{p}\}) = \sum_{I=1}^{N}\sum_{i=1}^{P}\left[\frac{(\mathbf{p}_I^i)^2}{2\tilde{m}_I^i} + \frac{1}{2}m_I\omega_P^2(\mathbf{x}_I^{i+1}-\mathbf{x}_I^i)^2\right] + \sum_{i=1}^{P}\hat{V}(\mathbf{x}_1^i,\ldots,\mathbf{x}_N^i)$$

- To initialize PIMD requires specification of $3NP$ positions and $3NP$ momenta.

Momenta

- We inserted P Gaussians when introducing momenta

$$\left(\frac{\beta}{2\pi\tilde{m}}\right)^{1/2}\int \mathrm{d}p\, e^{-\beta p^2/2\tilde{m}}$$

- We can then sample the momentum of each bead from a Gaussian distribution with

$$\bar{p} = 0$$

$$\sigma_p = \sqrt{\frac{\tilde{m}}{\beta_P}} = \sqrt{\tilde{m}k_B PT}$$

Positions

1. Start all beads at the same positions and equilibrate.
   - RP will expand under NVE, T will drop.
   - Strong Thermostatting is need!
2. Sample from the *free* ring-polymer distribution.
   - The only potential is the harmonic springs.
   - In normal mode coordinates

$$\sum_{j=1}^{P}\frac{1}{2}m\Omega_j^2\tilde{x}_j^2 \quad\Rightarrow\quad \int \mathrm{d}\tilde{x}_j\, e^{-\beta_P\left(\frac{1}{2}m\Omega_j^2\tilde{x}_j^2\right)}$$

   - $\bar{\tilde{x}}_j = 0$ and $\sigma_{\tilde{x}_j} = \sqrt{\frac{1}{\beta_P m\Omega_j^2}}$.
   - In practice, RP slightly too extended.

For the 1D harmonic oscillator: $V(x) = \frac{1}{2}m\omega x^2$, the RP potential in the normal-mode coordinates

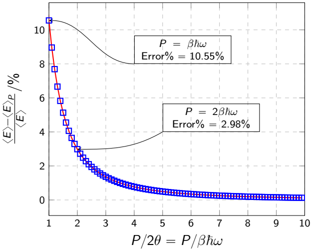
$$\sum_{i=1}^{P}\left[\frac{m}{2(\beta_P\hbar)^2}(x_{i+1}-x_i)^2 + V(x_i)\right] \quad\Rightarrow\quad \sum_{i=1}^{P}\frac{1}{2}m(\Omega_i^2+\omega^2)\tilde{x}_i^2$$

then $\langle\tilde{x}_i^2\rangle = 1/\beta_P m(\Omega_i^2+\omega^2)$, the energy of the harmonic oscillator $\langle E\rangle_P$

$$\langle E\rangle_P = \langle T\rangle_P + \langle V\rangle_P = 2\langle V\rangle_P = 2\cdot\frac{1}{2}m\omega^2\langle x^2\rangle = \frac{m\omega^2}{P}\sum_{i=1}^{P}\langle x_i^2\rangle = \frac{m\omega^2}{P}\sum_{i=1}^{P}\langle\tilde{x}_i^2\rangle$$

$$= \frac{\theta}{\beta}\sum_{i=1}^{P}\frac{\theta}{P^2\sin^2\left(\frac{(i-1)\pi}{P}\right)+\theta^2} \qquad (\theta = \beta\hbar\omega/2)$$

the exact solution is $\langle E\rangle = \frac{\theta}{\beta}\coth(\theta)$



- Commonly used convergence criteria: $P > \hbar\omega_{\max}/k_B T$
- Standard PIMD converges as $1/P^2$.
- Some properties converges faster, e.g. RDF converges fast but heat capacity very slowly.
- Methods exist to accelerate the convergence, e.g. PI + GLE.

For the 1D harmonic oscillator: $V(x) = \frac{1}{2}m\omega x^2$, the normal mode frequencies

$$\tilde{\Omega}_i = \sqrt{\Omega_i^2 + \omega^2}; \qquad \Omega_i = 2\omega_P \sin\left(\frac{(i-1)\pi}{P}\right)$$

Hence the highest frequency is

$$\tilde{\Omega}_{\text{max}} = \sqrt{\Omega_{\text{max}}^2 + \omega^2} = \sqrt{4\omega_P^2 + \omega^2}$$

If we use the typical convergence criteria: $P = \alpha\hbar\omega/k_B T$, where $\alpha > 1$ determines how accurate the calculation is.

$$\tilde{\Omega}_{\text{max}} = (4\alpha^2 + 1)^{\frac{1}{2}}\omega$$

- For $\alpha = 1$, the highest frequency in PIMD is $\sqrt{5}$ times larger than classical MD.
- For a *naive* implementation of PIMD, the time step should be $\sqrt{5}$ times smaller than classical MD.

- Methods to allow bigger time-steps:
  1. Scale the normal mode masses so they all oscillate at the same frequency.
  2. Multiple time-scale molecular dynamics: use smaller time-steps for bead forces.
  3. Use an integrator where the free ring polymer is evolved exactly.

CMD

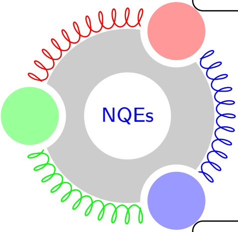
- Approximate quantum dynamics
- Path centroid idea

$$m\ddot{x}_c = \langle \delta(x_0 - x_c) \frac{1}{P} \sum_{i=1}^{P} \frac{\partial V(x_i)}{\partial x_i} \rangle$$

- Sample the whole configuration space available to the non-centroid modes at each given position of centroid.

(PA)CMD

- PIMD with *adiabatic decoupling* of centroid and non-centroid motions.
- *No* thermostat for the centroid mode.
- Thermostatting for noncentroid mode as in PIMD.
- Must sample initial conditions.



PIMD

- Static equilibrium properties.
- Need to efficiently and ergodically sample the phase surface.
  - Thermostatting
  - Coordinate transformation and bead masses scaling

RPMD

- Approximate quantum dynamics
- PIMD with *physical* bead masses.
- Thermostats should *not* be used.
- Must sample initial conditions.

[9] *J. Chem. Phys.*, **130**, 194510(2009); *J. Chem. Phys.*, **129**, 074501(2009);

PIMD, (PA)CMD and RPMD — Fictitious Masses

The RP Hamiltonian in the normal-mode coordinates

$$H_P(\{\tilde{\mathbf{x}}\},\{\tilde{\mathbf{p}}\}) = \sum_{i=1}^{P}\left[\frac{\tilde{p}_i^2}{2\tilde{m}_i} + \frac{1}{2}m\Omega_i^2\tilde{x}_i^2\right] + \sum_{i=1}^{P} V\left(x_i(\tilde{x}_1,\ldots,\tilde{x}_P)\right)$$

$$\Rightarrow \quad \tilde{m}_i\ddot{\tilde{x}}_i = -m\Omega_i^2\tilde{x}_i - \sum_{j=1}^{P}\frac{\partial V\left(x_j(\tilde{x}_1,\ldots,\tilde{x}_P)\right)}{\partial \tilde{x}_i}$$

$$\boxed{\sum_{j=1}^{P}\frac{\partial V(x_j)}{\partial x_j}U_{ji}^T}$$

Note that $\tilde{x}_1 = 1/\sqrt{U}\sum_{j=1}^{P} x_j$ and $\Omega_1 = 0$, we have

$$\tilde{m}_1\ddot{\tilde{x}}_1 = -\frac{1}{\sqrt{P}}\sum_{j=1}^{P}\frac{\partial V(x_j)}{\partial x_j}$$

- PIMD — scale the mass to bring all the frequencies to the same value.

$$\tilde{m}_1 = m, \qquad \tilde{m}_i = 4\sin^2\left(\frac{(i-1)\pi}{P}\right)m \quad (2 \leqslant i \leqslant P)$$

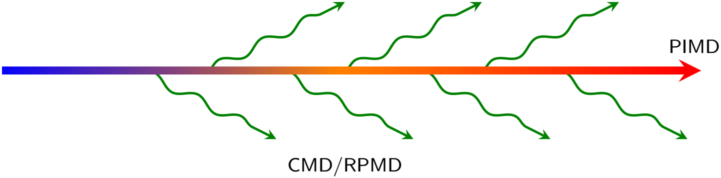
- (PA)CMD — adiabatic parameter $\gamma > 1$, accelerating the dynamics of the non-centroid modes.

$$\tilde{m}_1 = m, \qquad \tilde{m}_i = 4\sin^2\left(\frac{(i-1)\pi}{P}\right)m/\gamma^2 \quad (2 \leqslant i \leqslant P)$$

- RPMD — Use real masses for all the beads.

$$\tilde{m}_i = m, \quad (1 \leqslant i \leqslant P)$$

- CMD and RPMD are intended to provide approximations to quantum dynamics and not to efficiently sample the quantum phase space.
- The ergodicity problem can be circumvented by launching trajectories from many different choice of configurations and momenta.



1. Run a PIMD trajectory using an efficient thermostat scheme.
2. Pick configurations and momenta from the thermostatted trajectory and launch RPMD or CMD trajectories from them.
3. Ideally the separation in time between each should be determined by the correlation time of the properties in the system.

Thank you!