Path-Integral Molecular Dynamics
Turning Nuclei Quantum

George Trenins, Hannah Bertschi, Jorge Castro, and Mariana Rossi

MPI for the Structure and Dynamics of Matter, Hamburg

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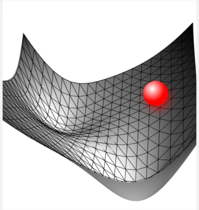
Outline

Born–Oppenheimer



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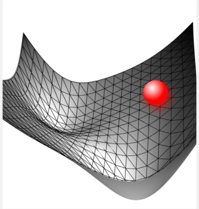
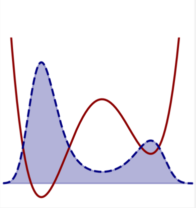


thermal equilibrium



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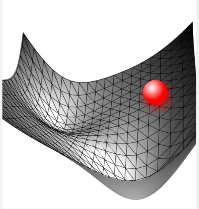

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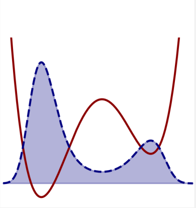
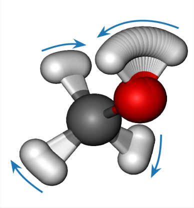


distinguishable particles



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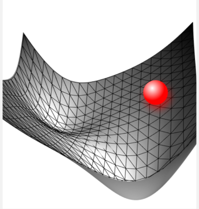

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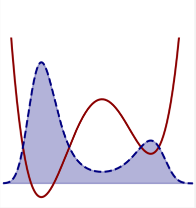

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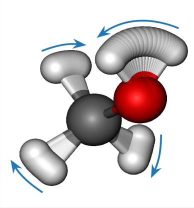
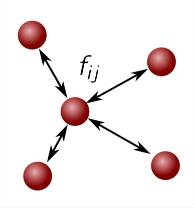


static properties



The partition function

$$Z = \mathrm{Tr}\left[\mathrm{e}^{-\beta \hat{H}}\right]$$

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$$\begin{array}{c|cccc}
\hat{\rho} & |\psi_0\rangle & |\psi_1\rangle & |\psi_2\rangle & \cdots \\
\hline
\langle\psi_0| & \boldsymbol{\rho_{0,0}} & \boldsymbol{\rho_{0,1}} & \boldsymbol{\rho_{0,2}} & \cdots \\
\langle\psi_1| & \boldsymbol{\rho_{1,0}} & \boldsymbol{\rho_{1,1}} & & \\
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\vdots & \vdots & & & \ddots
\end{array}$$

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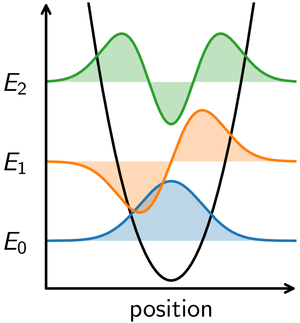
$\hat{\rho}$	$\lvert\psi_0\rangle$	$\lvert\psi_1\rangle$	$\lvert\psi_2\rangle$	$\cdots$
$\langle\psi_0\rvert$	$\boldsymbol{\rho_{0,0}}$	$\boldsymbol{\rho_{0,1}}$	$\boldsymbol{\rho_{0,2}}$	$\cdots$
$\langle\psi_1\rvert$	$\boldsymbol{\rho_{1,0}}$	$\boldsymbol{\rho_{1,1}}$		
$\langle\psi_2\rvert$	$\boldsymbol{\rho_{2,0}}$		$\boldsymbol{\rho_{2,2}}$	
$\vdots$	$\vdots$			$\ddots$



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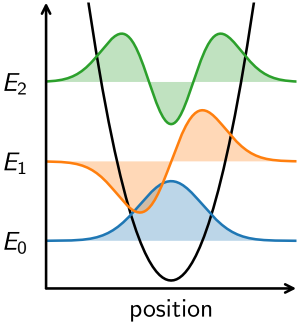

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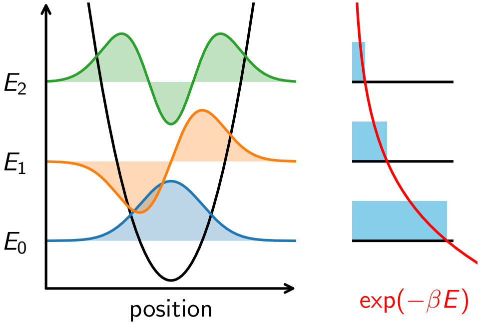

Splitting up

$$Z = \mathrm{Tr}\left[\mathrm{e}^{-\beta \hat{H}}\right]$$

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Trotter formula

$$\mathrm{e}^{-\beta(\hat{K}+\hat{U})} \sim \mathrm{e}^{-\beta\hat{K}}\mathrm{e}^{-\beta\hat{U}}\left(1 - \frac{\beta^2}{2}[\hat{K}, \hat{U}]\right)$$

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Eigenvalue equation

$$\hat{X}\,|X\rangle = X\,|X\rangle \quad \Rightarrow \quad \mathrm{e}^{-\beta U(\hat{X})}\,|X\rangle = \mathrm{e}^{-\beta U(X)}\,|X\rangle$$

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Gaining momentum

$$Z \sim Z_{\text{cl}} = \int_{-\infty}^{\infty} \mathrm{d}X \; \langle X | \mathrm{e}^{-\beta \hat{K}} | X \rangle \, \mathrm{e}^{-\beta U(X)}$$

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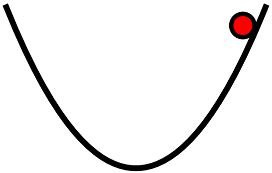

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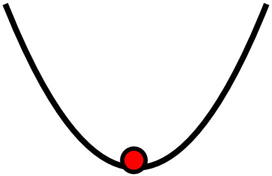

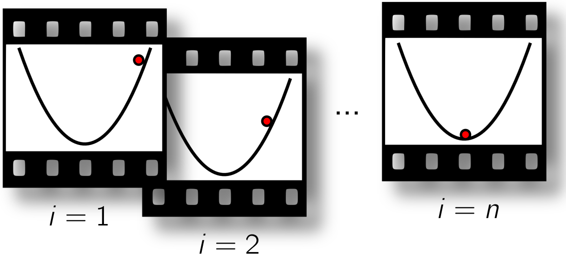

Divide and conquer

$$Z = \mathrm{Tr}\left[\mathrm{e}^{-\beta(\hat{K}+\hat{U})}\right] \sim \mathrm{Tr}\left[\mathrm{e}^{-\beta\hat{K}}\mathrm{e}^{-\beta\hat{U}}\right] \qquad (\beta \to 0)$$

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$$\mathrm{e}^{-\epsilon(\hat{K}+\hat{U})} \sim \mathrm{e}^{-\epsilon\hat{K}}\mathrm{e}^{-\epsilon\hat{U}}\left(1 - \tfrac{\epsilon^2}{2}[\hat{K},\hat{U}]\right)$$

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$$= \mathrm{Tr}\left[\left(\mathrm{e}^{-\frac{\beta}{N}(\hat{K}+\hat{U})}\right)^{N}\right]$$

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$$= \mathrm{Tr}\left[\left(e^{-\frac{\beta}{N}(\hat{K}+\hat{U})}\right)^N\right] \sim \mathrm{Tr}\left[\left(e^{-\frac{\beta}{N}\hat{K}}e^{-\frac{\beta}{N}\hat{U}}\right)^N\right] \qquad \left(\frac{\beta}{N} \to 0\right)$$

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$$e^{-\epsilon(\hat{K}+\hat{U})} \sim e^{-\epsilon\hat{K}}e^{-\epsilon\hat{U}}\left(1 - \frac{\epsilon^2}{2}[\hat{K}, \hat{U}]\right)$$

Identity crisis

$$\mathrm{Tr}\left[\left(e^{-\frac{\beta}{N}\hat{K}}e^{-\frac{\beta}{N}\hat{U}}\right)^N\right] = \mathrm{Tr}\Bigg[\underbrace{\left(e^{-\frac{\beta}{N}\hat{K}}e^{-\frac{\beta}{N}\hat{U}}\right)\cdots\left(e^{-\frac{\beta}{N}\hat{K}}e^{-\frac{\beta}{N}\hat{U}}\right)\cdot\left(e^{-\frac{\beta}{N}\hat{K}}e^{-\frac{\beta}{N}\hat{U}}\right)}_{N\text{ times}}\Bigg]$$

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Trace formula

$$\mathrm{Tr}\,\hat{O} = \int_{-\infty}^{\infty} \mathrm{d}X_I \,\langle X_I|\hat{O}|X_I\rangle$$

Identity crisis

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Resolution of the identity

$$\hat{I} = \int_{-\infty}^{\infty} \mathrm{d}X_I\, |X_I\rangle\langle X_I|$$

Identity crisis

$$\mathrm{Tr}\left[\left(\mathrm{e}^{-\frac{\beta}{N}\hat{K}}\mathrm{e}^{-\frac{\beta}{N}\hat{U}}\right)^{N}\right] = \left[\prod_{l=1}^{N}\int \mathrm{d}X_l\ \langle X_{l+1}|\mathrm{e}^{-\frac{\beta}{N}\hat{K}}|X_l\rangle\ \mathrm{e}^{-\frac{\beta}{N}U(X_l)}\right], \qquad X_{N+1} \equiv X_1$$

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Element of surprise

$$Z \sim \left[\prod_{l=1}^{N} \int \mathrm{d}X_l \; \langle X_{l+1} | \mathrm{e}^{-\beta_N \hat{K}} | X_l \rangle \, \mathrm{e}^{-\beta_N U(X_l)} \right]$$

$$\beta_N \equiv \beta / N$$

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$$\beta_N \equiv \beta / N \qquad \omega_N \equiv 1/\beta_N \hbar$$

Trickery

Derivation

$$\langle X_{l+1} | \mathrm{e}^{-\frac{\beta}{N}\hat{K}} | X_l \rangle = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \mathrm{d}P_l \exp\left[-\frac{\beta_N P_l^2}{2M} \right] \cdot \exp\left[-\beta_N \frac{M\omega_N^2 (X_{l+1} - X_l)^2}{2} \right]$$

What's an isomorphism?

$$Z_{\mathrm{cl}} = \iint \frac{\mathrm{d}P_I\,\mathrm{d}X_I}{2\pi\hbar} \exp\left(-\beta\left[\frac{P^2}{2M} + U(X)\right]\right)$$

$$Z_{\mathrm{qm}} = \left[\prod_{I=1}^{N} \iint \frac{\mathrm{d}P_I\,\mathrm{d}X_I}{2\pi\hbar}\right] \exp\left(-\beta_N \sum_{I=1}^{N} \left[\frac{P_I^2}{2M} + U(X_I) + \frac{M\omega_N^2 (X_{I+1} - X_I)^2}{2}\right]\right)$$

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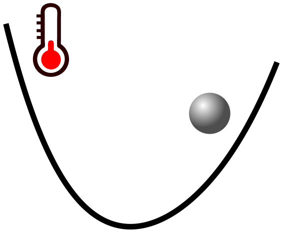

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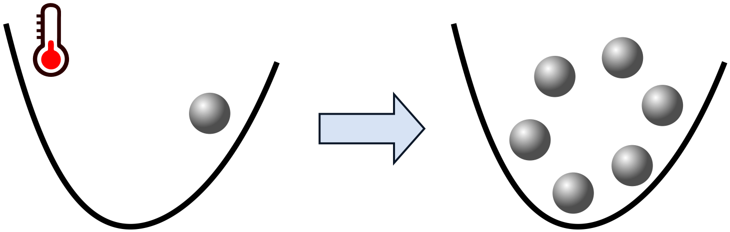

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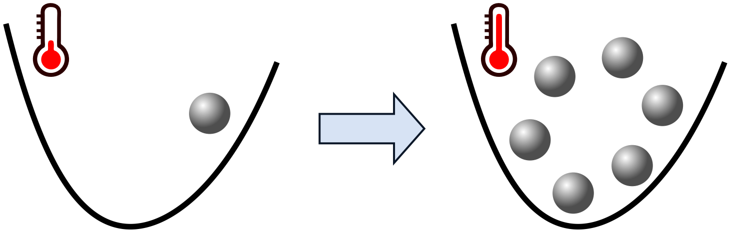

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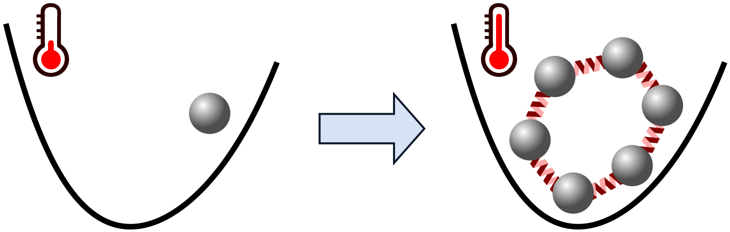

Thermal averages

$$\langle A \rangle_{\mathsf{qm}} = \frac{1}{Z}\,\mathsf{Tr}\left[\hat{A}\,\mathsf{e}^{-\beta \hat{H}}\right]$$

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Position estimators

$$A_N(\boldsymbol{X}) = \frac{1}{N} \sum_{I=1}^{N} A(X_I)$$

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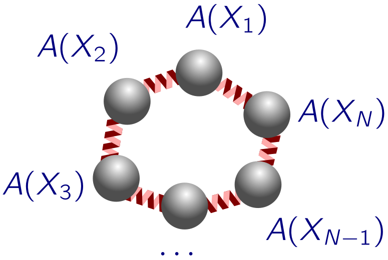
$$\langle A \rangle_{\mathrm{qm}} = \frac{1}{Z}\,\mathrm{Tr}\left[\hat{A}\,\mathrm{e}^{-\beta\hat{H}}\right] = \frac{1}{Z}\iint \mathrm{d}^N P\,\mathrm{d}^N X\, A_N(\boldsymbol{X})\,\mathrm{e}^{\beta_N H_N(\boldsymbol{P},\boldsymbol{X})}$$

Position estimators

$$A_N(\boldsymbol{X}) = \frac{1}{N}\sum_{l=1}^{N} A(X_l)$$



It's gone virial

$$K_N(\boldsymbol{P}) \stackrel{?}{=} \frac{1}{N}\sum_{I=1}^{N}\frac{P_I^2}{2M}$$

It's gone virial

$$K_N(\boldsymbol{P}) \stackrel{?}{=} \frac{1}{N} \sum_{I=1}^{N} \frac{P_I^2}{2M}$$

Trickery!

It's gone virial

Primitive estimator

$$K_N^{\mathrm{p}}(\boldsymbol{X}) = \frac{N}{2\beta} - \frac{1}{N}\sum_{l=1}^{N}\frac{M\omega_N^2(X_{l+1} - X_l)^2}{2}$$

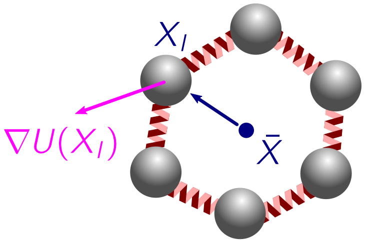
It's gone virial

Primitive estimator

$$K_N^{\mathrm{p}}(\boldsymbol{X}) = \frac{N}{2\beta} - \frac{1}{N}\sum_{l=1}^{N} \frac{M\omega_N^2 (X_{l+1} - X_l)^2}{2}$$

Centroid virial estimator

$$K_N^{\mathrm{cv}}(\boldsymbol{P}, \boldsymbol{X}) = \frac{1}{2\beta} + \frac{1}{2N}\sum_{l=1}^{N} (X_l - \bar{X}) \cdot \frac{\partial U(X_l)}{\partial X_l}$$



The i-PI code

RESEARCH ARTICLE | AUGUST 14 2024

i-PI 3.0: A flexible and efficient framework for advanced atomistic simulations

Special Collection: Modular and Interoperable Software for Chemical Physics

Yair Litman; Venkat Kapil; Yotam M. Y. Feldman; Davide Tisi; Tomislav Begušić; Karen Fidanyan; Guillaume Fraux; Jacob Higer; Matthias Kellner; Tao E. Li; Eszter S. Pós; Elia Stocco; George Trenins; Barak Hirshberg; Mariana Rossi; Michele Ceriotti

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J. Chem. Phys. 161, 062504 (2024)

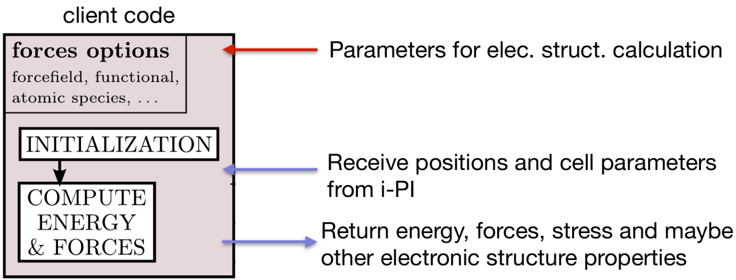
https://doi.org/10.1063/5.0215869 **Article history**

Connected Content

A companion article has been published: Updates to i-PI package improve performance in widely used atomistic simulation software

The i-PI code

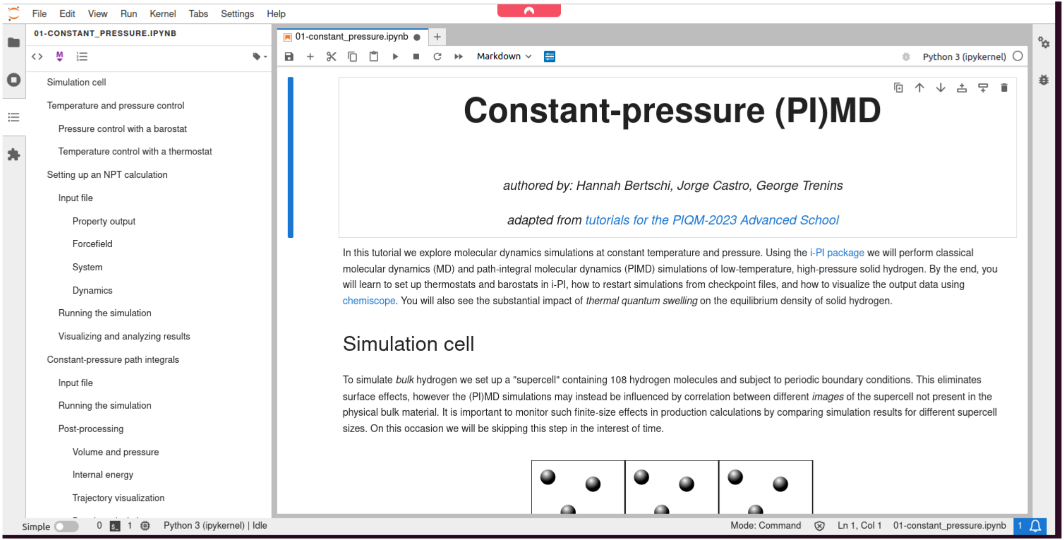
- The engine *receives forces* and *gives back positions*.
- Works for many kinds of "motion": dynamics, optimization, phonons, . . .
- Electronic structure or ML potential acts as a simple driver (client).



Communication via sockets

- i-PI communicates via internet (or UNIX) sockets
- Interfaced to: CP2K, DFTB+, **LAMMPS**, Quantum ESPRESSO, **Siesta**, **FHI-aims**, Yaff, deMonNano, plumed, **ASE**, TBE, CASTEP, AMS, ...

Visit:
https://ipi-code.org/
https://github.com/i-pi/i-pi


File
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Tabs
Settings
Help
01-CONSTANT_PRESSURE.IPYNB
Simulation cell
Temperature and pressure control
Pressure control with a barostat
Temperature control with a thermostat
Setting up an NPT calculation
Input file
Property output
Forcefield
System
Dynamics
Running the simulation
Visualizing and analyzing results
Constant-pressure path integrals
Input file
Running the simulation
Post-processing
Volume and pressure
Internal energy
Trajectory visualization
01-constant_pressure.ipynb
Markdown
Python 3 (ipykernel)
Constant-pressure (PI)MD
authored by: Hannah Bertschi, Jorge Castro, George Trenins
adapted from tutorials for the PIQM-2023 Advanced School
In this tutorial we explore molecular dynamics simulations at constant temperature and pressure. Using the i-PI package we will perform classical molecular dynamics (MD) and path-integral molecular dynamics (PIMD) simulations of low-temperature, high-pressure solid hydrogen. By the end, you will learn to set up thermostats and barostats in i-PI, how to restart simulations from checkpoint files, and how to visualize the output data using chemiscope. You will also see the substantial impact of thermal quantum swelling on the equilibrium density of solid hydrogen.
Simulation cell
To simulate bulk hydrogen we set up a "supercell" containing 108 hydrogen molecules and subject to periodic boundary conditions. This eliminates surface effects, however the (PI)MD simulations may instead be influenced by correlation between different images of the supercell not present in the physical bulk material. It is important to monitor such finite-size effects in production calculations by comparing simulation results for different supercell sizes. On this occasion we will be skipping this step in the interest of time.
Simple
Python 3 (ipykernel) | Idle
Mode: Command
Ln 1, Col 1
01-constant_pressure.ipynb

“Kinetic” matrix element

1. **initial expression**

$$\langle X_{l+1}|e^{-\beta_N \hat{K}}|X_l\rangle = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dP_l' \exp\left[-\frac{\beta_N P_l'^2}{2M} + \frac{iP_l'}{\hbar}(X_{l+1}-X_l)\right]$$

2. **complete the square**

$$= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dP_l' \exp\left[-\frac{\beta_N}{2M}\left(P_l' - \frac{iM}{\beta_N\hbar}(X_{l+1}-X_l)\right)^2\right] \exp\left[-\beta_N \frac{M\omega_N^2(X_{l+1}-X_l)^2}{2}\right]$$

3. **change integration variable**

$$= \frac{1}{2\pi\hbar}\int_{-\infty-i\Delta_l}^{\infty-i\Delta_l} dP_l \exp\left[-\frac{\beta_N P_l^2}{2M}\right] \exp\left[-\beta_N \frac{M\omega_N^2(X_{l+1}-X_l)^2}{2}\right] \qquad \left\{\begin{array}{c}\Delta_l = \frac{M}{\beta_N\hbar}(X_{l+1}-X_l) \\ P_l = P_l' - i\Delta_l\end{array}\right\}$$

4. **deform integration contour**

$$= \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dP_l \exp\left[-\frac{\beta_N P_l^2}{2M}\right] \exp\left[-\beta_N \frac{M\omega_N^2(X_{l+1}-X_l)^2}{2}\right]$$

◂ Back to Main Slide