Quantum Nuclei

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Static and dynamic properties

Physical observables are associated to static and dynamic correlation functions, such as:

\[ \langle n(r)n(r') \rangle \quad \langle n(r,t)n(r',t') \rangle \]

Here I will focus mostly on static properties.

Computer simulations such as MD (MC) allow us to compute correlation functions. In these simulations the nuclei are treated as classical particles: is this adequate?

In presence of light atoms (such as H) quantum effects are not negligible even at room temperature and above.
Do nuclei really behave classically?

Isotopic effects on thermodynamic equilibrium properties would not occur in classical water.
Why does QM lead to mass dependence

Configurations are weighted by a Boltzmann factor
\[ \exp\left(-\frac{E}{k_B T}\right) \]

\(E\) include kinetic (depending on mass and momentum) and potential (depending on position) contributions.

In classical mechanics kinetic and potential contributions to the Boltzmann weight factorize, leading to a partition function that is the product of an *ideal* and an *excess (configurational)* part.

In quantum mechanics kinetic and potential contributions do **not** factorize (uncertainty principle).
Protons in water and ice: their momentum distribution deviates substantially from the classical Maxwell-Boltzmann distribution

Classical Distribution: \( n(p) \propto e^{-p^2/(2mk_BT)} \)


Experiment: deep inelastic neutron scattering (DINS), G. Reiter et al., Braz. J. Phys 2004
Quantum statistical averages

\[ Z = \text{Tr} \left[ e^{-\beta H} \right] \quad \langle A \rangle = Z^{-1} \text{Tr} \left[ A e^{-\beta H} \right] \]

\( A \) and \( H \) are quantum-mechanical operators

\[ \langle A \rangle = \sum_n \frac{e^{-\beta E_n}}{Z} \langle \psi_n | A | \psi_n \rangle \quad \langle A \rangle = Z^{-1} \int dx dx' \langle x | A | x' \rangle \rho(x',x) \]

\( \rho(x',x) = \langle x' | e^{-\beta H} | x \rangle \quad \rho = e^{-\beta H} \) is the density operator

Can we compute the averages without dealing with operators?
Feynman path integral formulation of quantum statistical mechanics

\[ e^{-\beta H} = \left( e^{\frac{-\beta H}{P}} \right)^P \equiv e^{\frac{-\beta H}{P}} e^{\frac{-\beta H}{P}} ... e^{\frac{-\beta H}{P}} \]

\[ \rho(x', x) = \lim_{P \to \infty} \int dx_1 ... dx_{P-1} \langle x' | e^{\frac{-\beta H}{P}} | x_{P-1} \rangle \langle x_{P-1} | e^{\frac{-\beta H}{P}} | x_{P-2} \rangle ... \langle x_1 | e^{\frac{-\beta H}{P}} | x \rangle \]

\[ x, x_1, x_2, ..., x_{P-1}, x' \] constitutes a path \( x(\tau) \) where the label \( \tau \in (0, \beta) \)

The product \( \langle x' | e^{\frac{-\beta H}{P}} | x_{P-1} \rangle ... \langle x_1 | e^{\frac{-\beta H}{P}} | x \rangle \) takes a value \( W[\{x(\tau)\}] \)

\( W[\{x(\tau)\}] \) is a functional of the path \( x(\tau) \)

\[ \rho(x', x) = \int_{x(0)=x; x(\beta)=x'} \mathcal{D}[x(\tau)] W[\{x(\tau)\}] \quad \text{a sum (integral) over open paths} \]

\[ \rho(x, x) = \int_{x(0)=x(\beta)=x} \mathcal{D}[x(\tau)] W[\{x(\tau)\}] \quad \text{a sum (integral) over close paths} \]
Computing statistical averages

Let's consider an observable $A$ diagonal in the coordinate representation and consider discretized paths $(x, x_1, ..., x)$. Then:
\[
\langle A \rangle = Z^{-1} \int dx_1 dx_2 ... dx_{p-1} dx_p A(x_p) W(x_1, x_2, ..., x_p) \quad (x_p = x)
\]

If $W$ is positive definite: $W(x_1, ..., x_p) = e^{-\Phi(x_1, ..., x_p)}$ where $\Phi$ plays the role of potential energy. Then $\langle A \rangle$ is like a classical configuration average. Since all points in a close path are topologically equivalent we can write:
\[
\langle A \rangle = Z^{-1} \int dx_1 ... dx_p \left( \frac{1}{P} \sum_{i=1,P} A(x_i) \right) W(x_1, ..., x_p)
\]

$E_A \equiv \frac{1}{P} \sum_{i=1,P} A(x_i)$ is the estimator of $A$ \quad $Z^{-1}W$ is the weight of the configuration

All this is correct provided $W$ can be assimilated to a classical Boltzmann weight.
Evaluating $W$

\[
\Delta \equiv \frac{\beta}{P}, \quad H = T + V, \quad e^{-\Delta H} = e^{-\Delta T} e^{-\Delta V} + O(\Delta^2)
\]

\[
\langle x_i | e^{-\Delta H} | x_{i-1} \rangle = \langle x_i | e^{-\Delta T} | x_{i-1} \rangle e^{-\Delta V(x_{i-1})} + O(\Delta^2)
\]

\[
\langle x_i | e^{-\Delta T} | x_{i-1} \rangle = \int dp \langle x_i | e^{-\frac{p^2}{2M}\Delta} | p \rangle \langle p | x_{i-1} \rangle = \int dp \langle x_i | p \rangle \langle p | x_{i-1} \rangle e^{-\frac{p^2}{2M}\Delta}
\]

\[
= \frac{1}{2\pi \hbar} \int dp e^{ip(x_i-x_{i-1})/\hbar} e^{-\frac{p^2}{2M}\Delta} = \sqrt{\frac{M}{2\pi \Delta \hbar^2}} \exp\left[-\frac{M(x_i-x_{i-1})^2}{2\Delta \hbar^2}\right]
\]

\[
W = \left(\frac{M}{2\pi \Delta \hbar^2}\right)^{p/2} \exp\left[-\sum_{i=1,p} \left(\frac{M}{\hbar^2} \frac{(x(\tau_i) - x(\tau_{i-1}))^2}{2\Delta} + V(x(\tau_i))\Delta\right)\right]
\]

\[
= \left(\frac{M}{2\pi \Delta \hbar^2}\right)^{p/2} \exp[-\Phi(x_1,\ldots,x_p)]
\]

Notice: \( \frac{1}{2} \frac{M}{\hbar^2 \Delta} (x_i - x_{i-1})^2 \) is a harmonic interaction between neighboring points (beads) in a path.

The spring constant is \( k = \frac{M}{\hbar^2 \Delta} \)

When \( M \to \infty \) or \( \beta \to 0 \) or \( \hbar \to 0 \), \( k \to \infty \) and one recovers the *classical* limit.
Sampling the paths

\[ \langle A \rangle = Z^{-1} \int dxA(x) \langle x \, | \, e^{-\beta H} \, | \, x \rangle = \frac{\int dx_1...dx_p E_A(x_1,...,x_p) e^{-\Phi(x_1,...,x_p)}}{\int dx_1...dx_p e^{-\Phi(x_1,...,x_p)}} \]

Importance sampling can be achieved either by MC or by MD.
In the MD case, one introduces (fictitious) sampling masses \( M_i \):

\[ M_i \dot{x}_i = -\frac{\partial \Phi}{\partial x_i} \quad \text{with} \quad \sum_i \frac{1}{2} M_i \dot{x}_i^2 = \frac{1}{2} \quad \text{exploiting ergodicity} \quad (k_B T = 1) \]

Efficacious sampling is also achieved by Langevin dynamics (LD):

\[ \dot{x}_i = -\frac{\partial \Phi}{\partial x_i} + \delta F \quad \langle \delta F(t) \delta F(t') \rangle = 2\delta(t - t') \]

Here \( t \) is the sampling time.
Many distinguishable particles (Boltzmannions)

Consider 2 particle for example

\[ H = \sum_{i=1,2} \frac{p_i^2}{2M} + V(x_1,x_2) \]

\[ \langle x_1^1 x_1^2 \mid e^{-\left(\frac{p_1^2}{2M} + \frac{p_2^2}{2M}\right)\Delta} e^{-V(x_1,x_2)\Delta} \mid x_{n-1}^1 x_{n-1}^2 \rangle = \langle x_1^1 x_1^2 \mid e^{-\left(\frac{p_1^2}{2M} + \frac{p_2^2}{2M}\right)\Delta} \mid x_{n-1}^1 x_{n-1}^2 \rangle e^{-V(x_1,x_2)\Delta} \]

\[ = \langle x_1^1 \mid e^{-\left(\frac{p_1^2}{2M}\right)\Delta} \mid x_{n-1}^1 \rangle \langle x_1^2 \mid e^{-\left(\frac{p_2^2}{2M}\right)\Delta} \mid x_{n-1}^2 \rangle e^{-V(x_1,x_2)\Delta} \]

\[ = \left( \frac{M}{2\pi\Delta\hbar^2} \right) \exp \left[ - \sum_{i=1,2; n=1} \frac{M}{2\hbar^2 \Delta} \left( x_n^i - x_{n-1}^i \right)^2 - \Delta \sum_{n=1}^P V(x_n^1,x_n^2) \right] \]

The required amount of information is linear in \( N \) (no. of particles) and also linear in \( P \): it is a classical simulation of \( N \) ring polymers (with \( P \) beads each)
Some (important) formal matter

\[ Z = \text{Tr} \left[ e^{-\beta H} \right] = \int_{x(0)=x(\beta)} \mathcal{D}[x(\tau)] \exp \left\{ -\Phi[x(\tau)] \right\} \]

\[ \Phi = \lim_{P \to \infty} \sum_{n=1}^{P} \left( \frac{M}{\hbar^2} \left( \frac{x(\tau_n) - x(\tau_{n-1})}{2\Delta} \right)^2 + V(x(\tau_n))\Delta \right) \]

One can associate a time to \( \Delta \): \( \delta \tau \equiv \hbar \Delta = \frac{\hbar \beta}{P} \)

\[ \lim_{\delta \tau \to 0} \frac{x(\tau + \delta \tau) - x(\tau)}{\delta \tau} = \dot{x}(\tau) \]

\[ \Phi = \frac{1}{\hbar} \int_{0}^{\beta \hbar} d\tau \left\{ \frac{1}{2} M\dot{x}(\tau)^2 + V(x(\tau)) \right\} = \frac{1}{\hbar} S_E \left[ x(\tau) \right] \quad S_E \text{ is the Euclidean action} \]

\[ Z = \int_{x(0)=x(\beta \hbar)} \mathcal{D}[x(\tau)] \exp \left\{ -\frac{S_E[x(\tau)]}{\hbar} \right\} \quad \hbar \text{ sets the scale for the action } S_E \]

Path integral simulations

\[ \rho_i(r, r') = \frac{1}{Z} \int dr_1 \cdots dr_{i-1} dr_{i+1} \cdots dr_M \langle R | e^{-\beta \hat{H}} | R' \rangle \]

\[ \rho_i(r, r') = \frac{1}{Z} \int_{R(0) = R, R(\beta \hbar) = R'} DR(\tau) e^{-\frac{1}{\hbar} \int_0^{\beta \hbar} d\tau \frac{m \dot{R}^2(\tau)}{2} + V(R(\tau))} \]

\[ Z = \int_{R(0) = R, R(\beta \hbar) = R} DR(\tau) e^{-\frac{1}{\hbar} \int_0^{\beta \hbar} d\tau \frac{m \dot{R}^2(\tau)}{2} + V(R(\tau))} \]

\[ R = (r_1, \ldots, r_{i-1}, r, r_{i+1}, \ldots, r_M), \]
\[ R' = (r_1, \ldots, r_{i-1}, r', r_{i+1}, \ldots, r_M) \]

Feynman paths: closed and open
Quantal protons in water and ice

The momentum distribution differs considerably from the classical equilibrium distribution

Experiment: deep inelastic neutron scattering (DINS), G. Reiter et al., Braz. J. Phys 2004

L. Lin, J. Morrone, RC, M. Parrinello, PRB 2011

Quasi-harmonic model fits the ice data well: zero-point motion is large but still semi-classical in nature
How does the potential that the proton experiences look like?
Can the potential of mean force be reduced to a 1D potential?

In the cases considered so far, proton motion along a bond (H stretching) reduces to an effective single particle quantum problem, in spite of the many-body nature of the problem.

More interesting situations occur when the protons are allowed to tunnel.
Phase Diagram

M. Chaplin  [www.lsbu.ac.uk/water/phase.html](http://www.lsbu.ac.uk/water/phase.html)

Pruzan et al., *JCP* (1993)
Tunneling can drive phase transitions

Cartoon from J. Texeira, *Nature*
*N&V* commenting

Picture is suggestive but rooted in Mean Field Theory

ice VIII -> ice VII: *antiferroelectric* to *disordered* proton sublattice
Another transition driven by quantum fluctuations occurs in KDP: *ferroelectric* to *disordered*
Reduced longitudinal model

\[ \rho(r, r') \sim \rho(x, x') \rho(b, b') \]

L. Lin, J. A. Morrone, RC, JSP (2011)
Entangled protons

von Neumann entanglement entropy

\[ \rho = \sum_i |\phi(i)\rangle P(i) \langle \phi(i)| \]

\[ S = -\text{Tr}[\rho \log \rho] \]

What is the origin of the entanglement? Why does it occur in ice VII and X?
Spectrum of the longitudinal density matrix

Effective potential and tunnel splitting

The first 2 eigenstates in ice VII

Tunnel splitting $547K$  
$T$ of simulation $100K$

Entanglement is mostly due to correlations
Simulation versus Mean Field

The distribution of local charge fluctuations in a 3-state (spin 1) model with N, C, and F states.

MFA would need to a ionization catastrophe that would severely violate local charge neutrality.

Ring tunneling does occur but is not the only process as some ionized configurations exist.

Role of: small cell size, T of the simulation, chosen lattice parameter (applied pressure)
Tunneling in KDP

Is there a node in the proton momentum distribution of KDP in the paraelectric phase?

(from Reiter, Mayers, Platzman, PRL (2002))

(from Morrone, Lin, RC, JPC (2009))
Remarks

• ZPE and tunneling (Boltzmannions)

• Faster convergence with the number of beads ($P$): GLE thermostats (M. Ceriotti, G. Bussi, M. Parrinello, *PRL* 2009, M. Ceriotti, D. Manolopoulos, M. Parrinello, *JCP* 2011)

• Quantum statistics: Bosons and Fermions

• Dynamic properties: harmonic approximation, semiclassical approaches (Centroid MD, Ring Polymer MD); analytic continuation from imaginary to real time correlation functions

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