# Approximation of quantum observables by molecular dynamics.

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- Observables of interest – dynamical properties at thermal equilibrium (quantum canonical ensemble)
  - diffusion coefficients
  - chemical reaction rates
  - scattering spectra

Canonical equilibrium density matrix operator $\widehat{\rho} = e^{-\beta \widehat{H}}$

equilibrium observables $$\langle \hat{A} \rangle_\beta \equiv \frac{\mathrm{Tr}\, \hat{\rho} \hat{A}}{\mathrm{Tr}\, \hat{\rho}}\,,$$

time-correlated observables $$\langle \hat{A}_\tau \hat{B}_0 \rangle_\beta \equiv \frac{\mathrm{Tr}\,(\hat{\rho} \hat{A}_\tau \hat{B}_0)}{\mathrm{Tr}\, \hat{\rho}}\,, \quad \text{or}$$

$$\frac{\frac{1}{2} \mathrm{Tr}\,(\hat{A}_\tau (\hat{B}_0 \hat{\rho} + \hat{\rho} \hat{B}_0))}{\mathrm{Tr}\, \hat{\rho}}$$

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time-correlated observables $\langle \hat{A}_\tau \hat{B}_0 \rangle_\beta \equiv \dfrac{\mathrm{Tr}\, (\hat{\rho} \hat{A}_\tau \hat{B}_0)}{\mathrm{Tr}\, \hat{\rho}}$, or

$$\frac{\frac{1}{2}\mathrm{Tr}\, (\hat{A}_\tau (\hat{B}_0 \hat{\rho} + \hat{\rho} \hat{B}_0))}{\mathrm{Tr}\, \hat{\rho}}$$

- Employ classical trajectories to approximate quantum observables at canonical ensemble

$$\langle \hat{A} \rangle_\beta = \frac{\mathrm{Tr}\, \hat{\rho} \hat{A}}{\mathrm{Tr}\, \hat{\rho}}, \quad \text{by} \quad \frac{1}{Z} \int_{\mathbb{R}^{2N}} \rho(x,p) A(x,p)\, dx\, dp$$

specifically the density matrix operator: $\hat{\rho} = e^{-\beta \hat{H}}$

## Nuclei-electron systems & Born-Oppenheimer Hamiltonian

- Many-body Hamiltonian $x \in \mathbb{R}^N$ – nuclei coordinates, $x_e \in \mathbb{R}^n$ – electron coordinates

$$\hat{H}(x_e, x) = -\frac{1}{2M} \sum_{i=1}^{N} \Delta_{x^i} + \hat{V}(x_e, x)$$

$$\hat{V}(x_e, x) = -\frac{1}{2} \sum_{i=1}^{n} \Delta_{x_e^i} + \sum_{1 \le i < j \le n} \frac{1}{|x_e^i - x_e^j|} - \sum_{i=1}^{n} \sum_{j=1}^{N} \frac{Z_j}{|x_e^i - x^j|} + \sum_{1 \le i < j \le N} \frac{Z_i Z_j}{|x^i - x^j|}$$

- Approximation in a basis $\{\psi_i\}$ of el. space the electronic operator $\hat{V}_e(x, x_e)$ becomes a matrix valued $\hat{V}(x) \in \mathbb{C}^{d \times d}$
- Born-Oppenheimer Hamiltonian

$$\hat{H} = -\frac{1}{2M} \mathrm{I}\Delta + \hat{V}\,, \quad \text{Weyl symbol: } H_{ij}(x,p) = \frac{1}{2}|p|^2 \delta_{ij} + V_{ij}(x)$$

wave functions $\Phi_n \in \mathcal{H} \equiv L^2(\mathbb{R}^N, \mathbb{C}^d)$

$$\hat{H}\Phi_n(x) = E_n \Phi_n(x)$$

semiclassical parameter: $\epsilon = 1/\sqrt{M}$

## Adiabatic approximations

- Quantum system with ”fast” degrees of freedom

$$i\hbar\partial_t\Phi_t(x,x_f) = \widehat{\mathbf{H}}\Phi_t(x,x_f)\,, \quad \Phi \in L^2(\mathbb{R}^N \times \mathbb{R}^n)$$

- Semi-classical degrees of freedom

$$i\epsilon\partial_t\Psi_t(x) = \widehat{H}\Psi_t(x)$$

  - $\widehat{H} = H(x, i\epsilon\nabla_x)$ is Weyl quantization of $H(x,p)$

    $H : \mathbb{R}^N \times \mathbb{R}^N \to \mathcal{H}_f$ operator-valued/matrix-valued function

    $x$ – position-type degrees of freedom
    $p$ – momenta-like degrees of freedom
  - $H$ is self-adjoint on the Hilbert space $\mathcal{H}_f$
  - $\Psi_t \in \mathcal{H} = L^2(\mathbb{R}^N, \mathcal{H}_f)$
  - Small parameter $\epsilon \ll 1$ – separation of scales, e.g., slow/fast degrees of freedom

[1] Littlejohn & Weigert (1993), Martinez&Sordoni (2002), Panati, Spohn & Teufel (2007)

Examples:

- Born-Oppenheimer approximation for a nuclei-electron system
  $x$ – positions of nuclei
  $p$ – momenta of nuclei
  $\epsilon = M^{-1/2}$
  $\mathcal{H}_f = \mathbb{C}^d$ – approximation of electronic space $L^2(\mathbb{R}^n)$
  $H(x,p) = \frac{1}{2}\mathrm{I}|p|^2 + V(x)$ – Weyl symbol of Born-Oppenheimer Hamiltonian

$$\dot{x} = \frac{1}{M} p\,, \quad \dot{p} = -\nabla_x \lambda_0(x)$$

- Electron in a crystal subject to slowly varying fields

$$i\epsilon\partial_t\phi = [\frac{1}{2}(-i\nabla_x - A(\epsilon x))^2 + V_\Gamma(x) + \phi(\epsilon x)]\phi$$

  Semiclassical equations of motion ($\epsilon \to 0$)
  $x \in \mathbb{R}^d$ – position of electron
  $\kappa = k - A(r)$ – kinetic momentum
  $\mathcal{H}_f = L^2(\mathbb{T}^d)$
  $H(r,k) = \frac{1}{2}(-i\nabla_x + k - A(r))^2 + V_\Gamma(x) + \phi(r)$

$$\dot{r} = \nabla E_n(\kappa)\,, \qquad \dot{\kappa} = -\nabla\phi(r) + \dot{r} \times B$$

  corrections in $\epsilon$: Panati, Spohn, Teufel (2003)

## Quantum canonical ensemble

- If the potential $V$ scalar the classical phase-space average [1]

$$\frac{\mathrm{Tr}\, e^{-\beta\hat{H}}\hat{A}}{\mathrm{Tr}\, e^{-\beta\hat{H}}} = \frac{\int_{\mathbb{R}^{2N}} A(x,p) e^{-\beta H(x,p)}\, dx\, dp}{\int_{\mathbb{R}^{2N}} e^{-\beta H(x,p)}\, dx\, dp} + \mathcal{O}(M^{-1})$$

  $A$, $H$ Weyl symbols of $\hat{A}$ and $\hat{H}$.

- Difficulty: $\hat{V}$ is matrix-valued and time-dependent $\hat{A}_t$
  Obstacle: approximation of Heissenberg equation

$$\frac{d\hat{A}_t}{dt} = iM^{1/2}[\hat{H}, \hat{A}_t], \quad \text{by} \quad \partial_t A_t = \{H, A_t\} \quad ?$$

[1] E. Wigner: On the quantum correction for thermodynamic equilibrium, Phys. Rev. (1932)

- Limit $1/M \to 0$ can be approximated by ab initio MD simulations for nuclei, with potential generated by electron eigenvalue problem [2].
- Using Born-Oppenheimer approximation [3] ab initio MD on the electron ground state can approximate quantum observables in the NVT ensemble provided:

  *temperature is low compared to the first electron eigenvalue gap*

  Limitations:

  1. low temperature compared to the spectral gap
  2. no excited states
  3. asymptotic expansions only, constants in $\mathcal{O}(M^{-1})$ error estimates potentially large (bounds on derivatives of order $N \gg 1$) not useful for computational approximations with realistic values of $M$.

[2] Stiepan & Teufel, (2013), Marx & Hutter (2009)

[3] Martinez& Sordoni (2002)

## Approximation of canonical quantum observables

**New results:**

- certain weighted average of the different ab initio dynamics approximates quantum observables at *any temperature*
- sharper error estimates with constants in $\mathcal{O}(M^{-1})$ independent of $N$
- use of non-linear eigenvalue problem to construct global projections $\Pi$ to the electronic states related to adiabatic approximation.
- Useful in further studies of situations with avoided crossings, degenerate and crossing electron eigenvalues or vanishing temperature.

[1] A. Kammonen, P. Plechac, M. Sandberg, A. Szepessy, (2018)

## Weyl quantization

- matrix-valued symbol $A(x,p)$

$$\widehat{A}\Phi(x) = \int_{\mathbb{R}^N} \left[ \left(\frac{\sqrt{M}}{2\pi}\right)^N \int_{\mathbb{R}^N} e^{iM^{1/2}(x-y)\cdot p} A(\frac{1}{2}(x+y),p)\,dp \right] \Phi(y)\,dy$$

- Moyal product & Composition rule: $\widehat{A\#B} = \hat{A}\hat{B}$

$$[A\#B](x,p) = e^{\frac{\mathrm{i}}{2\sqrt{M}}(\nabla_{x'}\cdot\nabla_p - \nabla_x\cdot\nabla_{p'})} A(x,p)B(x',p')\Big|_{(x,p)=(x',p')}$$

- Trace

$$\operatorname{Tr}\widehat{A} = \int_{\mathbb{R}^N} \operatorname{Tr} K_A(x,x)\,dx = \left(\frac{\sqrt{M}}{2\pi}\right)^N \int_{\mathbb{R}^N}\int_{\mathbb{R}^N} \operatorname{Tr} A(x,p)\,\mathrm{d}p\,\mathrm{d}x$$

$$\operatorname{Tr}\hat{B} := \sum_{n=1}^{\infty} \langle \Phi_n, \hat{B}\Phi_n\rangle\,, \quad \text{for an operator } \hat{B} \text{ on } \mathcal{H},$$

$$\operatorname{Tr} B := \sum_{j=1}^{d} B_{jj}\,, \quad \text{for a } d\times d \text{ matrix } B$$

## Basic idea – equilibrium observables

- **Lemma:** $A(z)$, $B(z)$ Weyl symbols of the operators $\widehat{A}$, $\widehat{B}$

$$\mathrm{Tr}(\widehat{A}\widehat{B}) = \left(\frac{M^{1/2}}{2\pi}\right)^N \int_{\mathbb{R}^{2N}} \mathrm{Tr}(A(z)B(z))\,dz\,, \quad z \equiv (x,p),$$

- Replace $\widehat{\rho} = e^{-\beta\widehat{H}}$ with $\widehat{\tilde{\rho}} = \widehat{e^{-\beta H}}$:

$$\widehat{e^{-\beta H}} = e^{-\beta\hat{H}} + \mathcal{O}(M^{-1})$$

- Diagonalization transformation $\tilde{\Psi}(x)$ for the matrix potential $V(x)$

$$\begin{aligned} H(z) &= \tilde{\Psi}(x)\tilde{H}(z)\tilde{\Psi}^*(x), \;\; \text{where } \tilde{H}_{jk}(z) = \delta_{jk}\big(\frac{|p|^2}{2} + \tilde{\lambda}_j(x)\big)\,, \\ A(z) &= \tilde{\Psi}(x)\tilde{A}(z)\tilde{\Psi}^*(x), \;\; \text{where } \tilde{A}(z) = \tilde{\Psi}^*(x)A(z)\tilde{\Psi}(x) \end{aligned}$$

Then the trace

$$\mathrm{Tr}\left(A(z)e^{-\beta H(z)}\right) = \mathrm{Tr}\left(\tilde{A}(z)e^{-\beta\tilde{H}(z)}\right) = \sum_{j=1}^{d} \tilde{A}_{jj}(z)e^{-\beta\tilde{H}_{jj}(z)}$$

## Equilibrium observables

### Theorem

The approximate canonical ensemble average satisfies, for $\beta > 0$,

$$\frac{\mathrm{Tr}\,(\widehat{e^{-\beta H}}\,\hat{A})}{\mathrm{Tr}\,(\widehat{e^{-\beta H}})} = \sum_{j=1}^{d} q_j \int_{\mathbb{R}^{2N}} \tilde{A}_{jj}(z) \frac{e^{-\beta \tilde{H}_{jj}(z)}}{\int_{\mathbb{R}^{2N}} e^{-\beta \tilde{H}_{jj}(z')}\,\mathrm{d}z'}\,\mathrm{d}z$$

with the weights given by respective probability to be in the state $j$

$$q_j = q_j(\tilde{H}) := \frac{\int_{\mathbb{R}^{2N}} e^{-\beta \tilde{H}_{jj}(z)}\,\mathrm{d}z}{\sum_{k=1}^{d} \int_{\mathbb{R}^{2N}} e^{-\beta \tilde{H}_{kk}(z')}\,\mathrm{d}z'}\,, \quad j = 1, \ldots, d\,.$$

$$\frac{\mathrm{Tr}\,(e^{-\beta \hat{H}}\,\hat{A})}{\mathrm{Tr}\,(e^{-\beta \hat{H}})} = \frac{\mathrm{Tr}\,(\widehat{e^{-\beta H}}\,\hat{A})}{\mathrm{Tr}\,(\widehat{e^{-\beta H}})} + \mathcal{O}(M^{-1})$$

Recall

$$\widetilde{H}_{jk}(z) = \delta_{jk}\left(\frac{1}{2}|p|^2 + \widetilde{\lambda}_j(x)\right), \quad \widetilde{A}(z) = \widetilde{\Psi}^* A(z) \widetilde{\Psi}$$

## Is it useful ?

$$\langle \widehat{A} \rangle_\beta = \sum_{j=1}^{d} q_j \, \mathbb{E}[\widetilde{A}_{jj}] + \mathcal{O}(M^{-1})$$

**(I)** Run Langevin dynamics to obtain $z_t^{(j)} = (x_t^{(j)}, p_t^{(j)})$

$$\begin{aligned} dx_t^{(j)} &= p_t^{(j)} \, dt \\ dp_t^{(j)} &= -\nabla \widetilde{\lambda}_j(x_t^{(j)}) \, dt - \gamma p_t^{(j)} \, dt + \sqrt{2\gamma/\beta} \, dW_t \end{aligned}$$

**(II)** Approximate $\mathbb{E}[\widetilde{A}_{jj}]$, $q_j$ from time-averaging

$$\mathbb{E}[\widetilde{A}_{jj}] := \int_{\mathbb{R}^{2N}} \widetilde{A}_{jj}(z) \frac{e^{-\beta \widetilde{H}_{jj}(z)}}{\int_{\mathbb{R}^{2N}} e^{-\beta \widetilde{H}_{jj}(z')} \, dz'} \, dz = \lim_{T \to \infty} \frac{1}{T} \int_0^T \widetilde{A}_{jj}(z_t^{(j)}) \, dt$$

$$q_j = \frac{\bar{q}_j}{\sum_k \bar{q}_k} \qquad \bar{q}_j = \int_{R^N} e^{-\beta(\widetilde{\lambda}_j - \widetilde{\lambda}_1)} \frac{e^{-\beta \widetilde{\lambda}_1(x)}}{\int_{\mathbb{R}^N} e^{-\beta \widetilde{\lambda}_1(x')} \, dx'}$$

$$\bar{q}_j = \lim_{T \to \infty} \frac{1}{T} \int_0^T e^{-\beta(\widetilde{\lambda}_j(x_t^{(1)}) - \widetilde{\lambda}_1(x_t^{(1)}))} \, dt$$

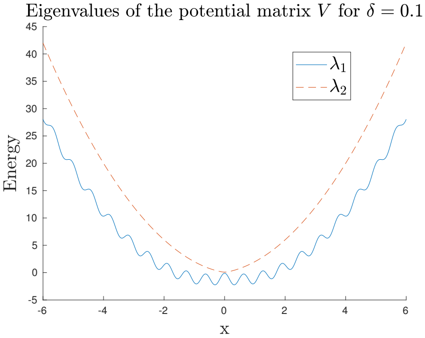
## Computational example

- Hamiltonian:

$$\hat{H} = -\frac{1}{2M}\mathrm{I}\,\Delta + V(x)\,, \quad \text{with } V : \mathbb{R} \to \mathbb{R}^{2\times 2}$$

,

- Ground-state and excited state




The eigenvalue functions $\lambda_1(x)$ and $\lambda_2(x)$ of $V(x)$.

## Equilibrium observables

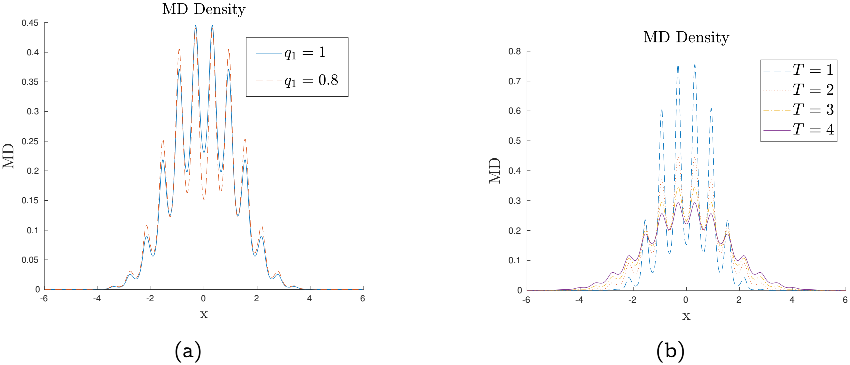
- Observable: $g : \mathbb{R} \to \mathbb{R}$ depending only on the position.
- Quantum observable
$$\langle \hat{g} \rangle = \int_{\mathbb{R}} g(x)\, \mu_{\mathrm{qc}}(x)\, \mathrm{d}x$$
- Observable in MD
$$\langle g \rangle = \int_{\mathbb{R}} g(x)\, \mu_{\mathrm{cl}}(x)\, \mathrm{d}x$$

Spectrum of $\hat{H}$

$$\hat{H}\Phi_n(x) = E_n \Phi_n(x)$$

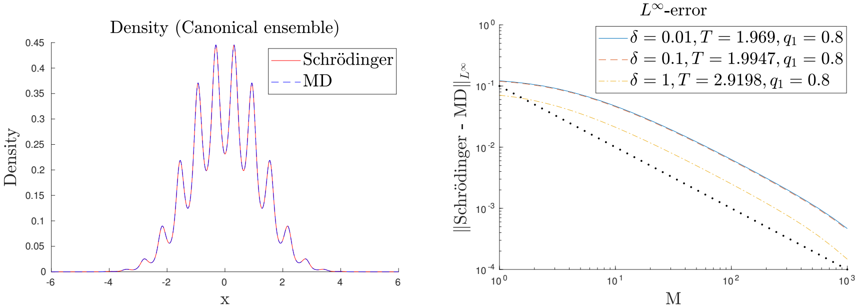
$$\begin{aligned} \mu_{\mathrm{qc}}(x) &= \frac{\sum_n |\Phi_n(x)|^2 e^{-\beta E_n}}{\int_{\mathbb{R}} \sum_n |\Phi_n(x')|^2 e^{-\beta E_n}\, \mathrm{d}x'}\,, \\ \mu_{\mathrm{cl}}(x) &= \sum_{k=1}^{2} q_k \frac{e^{-\beta \lambda_k(x)}}{\int_{\mathbb{R}} e^{-\beta\lambda_k(x')}\, \mathrm{d}x'}\,, \quad q_k = \frac{\int_{\mathbb{R}} e^{-\beta\lambda_k(x)}\, \mathrm{d}x}{\sum_{j=1}^{2} \int_{\mathbb{R}} e^{-\beta\lambda_j(x)}\, \mathrm{d}x}\,. \end{aligned}$$

# Quantum vs Molecular density




(a) The classical density $\mu_{\mathrm{cl}}$ using $q_1 = 1$, corresponding to molecular dynamics on the canonical ground state compared to the classical density with $q_1 = 0.8$. (b) Molecular dynamics density for different temperatures $T$ and $M = 1000$

# Comparison of quantum and molecular density




Dependence on the mass $M$ of the error between quantum and molecular dynamics densities $\mu_{\mathrm{qc}}$ and $\mu_{\mathrm{cl}}$ respectively, shown in log-log scale. The dotted lines show the reference slope $-1$.

## Example: time-correlated observables

- the position observable operator in Heisenberg representation

$$\hat{x}_\tau := e^{\mathrm{i}\tau\sqrt{M}\hat{H}}\,\hat{x}_0\,e^{-\mathrm{i}\tau\sqrt{M}\hat{H}}.$$

- Approximate the position correlation observable

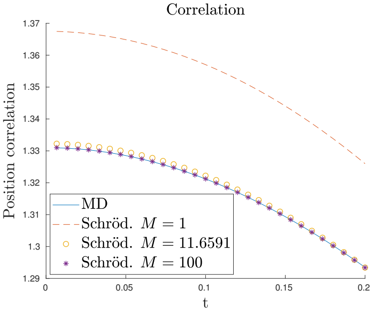
$$= \sum_{j=1}^{2} q_j \int_{\mathbb{R}^2} x_\tau^j(z_0) x_0^j(z_0) \frac{e^{-\beta(\frac{|p_0|^2}{2}+\lambda_j(x_0))}}{\int_{\mathbb{R}^2} e^{-\beta(\frac{|p|^2}{2}+\lambda_j(x))}\,\mathrm{d}z}\,\mathrm{d}z_0\,,$$

where $z_\tau^j = (x_\tau^j, p_\tau^j)$, $j = 1, 2$ solve the Hamiltonian dynamics

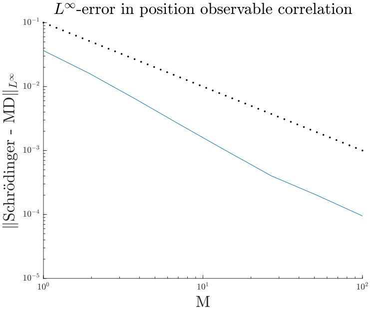
$$\begin{cases} \dot{x}_\tau^j = p_\tau^j \\ \dot{p}_\tau^j = -\frac{\mathrm{d}}{\mathrm{d}x_\tau^j}\lambda_j(x_\tau^j), \quad \tau > 0 \end{cases}$$

and $z_0^j = (x_0, p_0) = z_0$

# Example: time-correlation observables




(a) Correlation observable




(b) Error in correlation observable

(a) Molecular dynamics position correlation observable shown together with its Schrödinger counterpart. (b) The $L^\infty$-error in the molecular dynamics position correlation observable approximation.

## Time correlated observables

### Theorem

Assume that $\bar{A}_0$ and $\bar{B}_0$ are diagonal, the $d \times d$ matrix valued Hamiltonian $H$ has distinct eigenvalues, and regularity assumptions then the canonical ensemble average satisfies

$$\frac{\frac{1}{2}\mathrm{Tr}\left(\hat{A}_\tau(\hat{B}_0 e^{-\beta\hat{H}} + e^{-\beta\hat{H}}\hat{B}_0)\right)}{\mathrm{Tr}\left(e^{-\beta\hat{H}}\right)}$$

$$= \sum_{j=1}^{d} \int_{\mathbb{R}^{2N}} q_j \bar{A}_{jj}(0, z_\tau^j(z_0)) \bar{B}_{jj}(z_0) \frac{e^{-\beta\tilde{H}_{jj}(z_0)}}{\int_{\mathbb{R}^{2N}} e^{-\beta\tilde{H}_{jj}(z)}\,\mathrm{d}z}\,\mathrm{d}z_0 + \mathcal{O}(M^{-1/2}),$$

where $z_\tau^j = (x_\tau, p_\tau)$ solves

$$\dot{x}_t = p_t\,, \quad \dot{p}_t = -\nabla\tilde{\lambda}_j(x_t), \quad t > 0,$$

and $q_j = q_j(\tilde{H})$ as before.

Under additional regularity the estimate holds with the bound $\mathcal{O}(M^{-1})$ replacing $\mathcal{O}(M^{-1/2})$.

## Time correlated observables

### Theorem

Assume that $\bar{A}_0$ and $\bar{B}_0$ are diagonal, the $d \times d$ matrix valued Hamiltonian $\hat{H}$ has distinct eigenvalues and $\bar{H} = \bar{H}_0 + \mathcal{O}(M^{-1})$, then the canonical ensemble average satisfies

$$\frac{\mathrm{Tr}\left(\hat{\bar{A}}_\tau (\bar{B}_0 e^{-\beta \bar{H}_0}\widehat{)}\right)}{\mathrm{Tr}\,(\widehat{e^{-\beta \bar{H}_0}})}$$

$$= \sum_{j=1}^{d} q_j \int_{\mathbb{R}^{2N}} \bar{A}_{jj}(0, z_\tau^j(z_0))\bar{B}_{jj}(z_0)\frac{e^{-\beta(\bar{H}_0)_{jj}(z_0)}}{\int_{\mathbb{R}^{2N}} e^{-\beta(\bar{H}_0)_{jj}(z)}\,\mathrm{d}z}\,\mathrm{d}z_0 + \mathcal{O}(M^{-1}),$$

where $z_\tau^j$ solves

$$\dot{x}_t = p_t\,, \quad \dot{p}_t = -\nabla\lambda_j(x_t), \quad t > 0,$$

and $q_j = q_j(\bar{H}_0)$.

## Time-correlated observables

### Theorem

Assume that $V$ is real analytic, $\bar{A}_0$ and $\bar{B}_0$ are diagonal, the $d \times d$ matrix valued Hamiltonian $H$ has distinct eigenvalues, and regularity assumptions on eigenvalues and observables then there is a constant $c$, such that the canonical ensemble average satisfies

$$\Big|\frac{\mathrm{Tr}\,\big(\hat{A}_\tau(\widehat{\bar{B}_0\,e^{-\beta\bar{H}}})\big)}{\mathrm{Tr}\,\big(\widehat{e^{-\beta\bar{H}}}\big)} - \sum_{j=1}^{d}\int_{\mathbb{R}^{2N}} \frac{\bar{A}_{jj}(0, z_\tau^j(z_0))\,\bar{B}_{jj}(z_0)\,e^{-\beta\bar{H}_{jj}(z_0)}}{\sum_{k=1}^{d}\int_{\mathbb{R}^{2N}} e^{-\beta\bar{H}_{kk}(z)}\,\mathrm{d}z}\,\mathrm{d}z_0\Big| \leq cM^{-1}\,,$$

where $z_\tau^j$ solves

$$\dot{x}_t = p_t\,,\quad \dot{p}_t = -\nabla\lambda_j(x_t),\quad t > 0,$$

and $q_j = q_j(\bar{H}_0)$.

## Nonlinear eigenvalue problem

Comments on the operator $e^{t\alpha\hat{H}}$
Time-dependent operator $\hat{A}_t$

$$\hat{A}_t = e^{itM^{1/2}\hat{H}}\hat{A}_0 e^{-itM^{1/2}\hat{H}}$$

Construct unitary transformation $\Psi(x)$ such that

$$\widehat{\bar{A}_t(z)} = \hat{\Psi}^*(x)\hat{A}_t\hat{\Psi}(x)\,, \text{ and } \partial_t\hat{\bar{A}}_t = iM^{1/2}[\hat{\bar{H}}, \hat{\bar{A}}_t]$$

and define

$$\bar{H}(x,p) := \Psi^* \# H \# \Psi\,, \quad \text{thus} \quad \hat{\Psi}^*\hat{H}\hat{\Psi} = \hat{\bar{H}}$$

and

$$\hat{\Psi}^* e^{t\alpha\hat{H}}\hat{\Psi} = e^{t\alpha\hat{\bar{H}}}$$

Construct $\Psi$ such that $\bar{H}$ is diagonal (or approximately diagonal).

- Observation:
  Expansion of $A\#B$, due to special form of $H(x,p) = \frac{1}{2}|p|^2 \mathrm{I} + V(x)$ terminates at $M^{-1}$
- Lemma:

$$\bar{H}(x,p) \equiv \Psi^* \# H \# \Psi(x,p) = \Psi^*(x) H(x,p) \Psi(x) + \frac{1}{4M} \nabla \Psi^*(x) \cdot \nabla \Psi(x)$$

- Nonlinear eigenvalue problem

$$\left( V + \frac{1}{4M} \Psi \nabla \Psi^* \cdot \nabla \Psi \Psi^* \right) \Psi = \Psi \Lambda$$

  Solved by using Cauchy-Kovalevsky theorem
- $\Psi(x)$ is $\mathcal{O}(M^{-1})$ perturbation of $\tilde{\Psi}(x)$ provided $\tilde{\lambda}_j(x)$ do not cross

$$\lambda_j(x) - \tilde{\lambda}_j(x) = \mathcal{O}(M^{-1})$$

- $\bar{H}(x,p) = \frac{1}{2}|p|^2 + \Lambda(x) + \mathcal{O}(M^{-1}) \equiv \bar{H}_0 + \mathcal{O}(M^{-1})$

## Error representation

- Error estimation in two parts:
  "error of Gibbs density operator" + "error of dynamics of observable"

$$
\begin{aligned}
&\mathrm{Tr}\left(\hat{\bar{A}}_\tau\,\hat{\bar{B}}_0\,e^{-\beta\hat{\bar{H}}} - \widehat{A(\tau,z)}\,\widehat{\bar{B}_0\,e^{-\beta H_0}}\right)\\
&= \mathrm{Tr}\left(\hat{\bar{A}}_\tau\left(\hat{\bar{B}}_0\,e^{-\beta\hat{\bar{H}}} - (\bar{B}_0\,e^{-\beta H_0})\widehat{\ }\right)\right) + \mathrm{Tr}\left((\hat{\bar{A}}_\tau - \widehat{A(\tau,z)})(\bar{B}_0\,e^{-\beta H_0})\widehat{\ }\right)
\end{aligned}
$$

- Error representation
  Compare the classical dynamics

$$
\partial_t y(t,z) = \{\bar{H}_0(z), y(t,z)\}, \quad t>0\,, \quad y(0,\cdot) = \bar{A}_0\,,
$$

with the quantum dynamics that satisfies

$$
\partial_t \widehat{\bar{y}(t,z)} = \mathrm{i}M^{1/2}[\hat{\bar{H}}, \widehat{\bar{y}(t,z)}]\,, \quad t>0\,, \quad \widehat{\bar{y}(0,\cdot)} = \hat{\bar{A}}_0\,.
$$

$$
\partial_t \bar{y}(t,z) = \mathrm{i}M^{1/2}\big(\bar{H}(z)\#\bar{y}(t,z) - \bar{y}(t,z)\#\bar{H}(z)\big)\,, \quad t>0\,, \quad \bar{y}(0,\cdot) = \bar{A}_0\,,
$$

- Duhamel's principle applied to $\widehat{y(t,z)} - \widehat{\bar{y}(t,z)}$

$$\widehat{y(t,z)} - \widehat{\bar{y}(t,z)}$$
$$= \int_0^t e^{\mathrm{i}(t-s)M^{1/2}\hat{\bar{H}}} \widehat{\Big(\{\bar{H}_0(z), y(s,z)\} - \mathrm{i}M^{1/2}\big(\bar{H}\# y(s,z) - y(s,z)\#\bar{H}\big)\Big)}$$
$$\times\, e^{-\mathrm{i}(t-s)M^{1/2}\hat{\bar{H}}}\,\mathrm{d}s$$
$$= \int_0^t e^{\mathrm{i}(t-s)M^{1/2}\hat{\bar{H}}}\,\hat{R}_s\, e^{-\mathrm{i}(t-s)M^{1/2}\hat{\bar{H}}}\,\mathrm{d}s$$

- Estimates: Hilbert-Schmidt norms & Weyl's law

  Take $C(x,p) = \bar{B}(x,p)e^{-\beta\bar{H}(x,p)}$

$$|\mathrm{Tr}\,(\hat{C}(\widehat{y(t,z)} - \widehat{\bar{y}(t,z)}))| = \left|\int_0^t \mathrm{Tr}\left(e^{-\mathrm{i}(t-s)M^{1/2}\hat{\bar{H}}}\,\hat{C}\, e^{\mathrm{i}(t-s)M^{1/2}\hat{\bar{H}}}\,\hat{R}_s\right)\mathrm{d}s\right|$$
$$\le \int_0^t \Big(\mathrm{Tr}\,(\hat{C}^*\hat{C})\mathrm{Tr}\,(\hat{R}_s^*\hat{R}_s)\Big)^{1/2}\mathrm{d}s$$
$$= \left(\frac{M^{1/2}}{2\pi}\right)^N \int_0^t \left(\int_{\mathbb{R}^{2N}} \mathrm{Tr}\,(C^*C)\,dz \int_{\mathbb{R}^{2N}} \mathrm{Tr}\,(R_s^*R_s)\,dz\right)^{1/2}\mathrm{d}s$$

- Careful inspection of expansion of remainders in the Moyal product

$$
\begin{aligned}
A\#B &= AB - \frac{i}{2}M^{-1/2}\{A,B\} + \mathcal{O}(M^{-1}) \\
A\#B - B\#A &= [A,B] - \frac{i}{2}M^{-1/2}(\{A,B\} - \{B,A\}) + \mathcal{O}(M^{-1})
\end{aligned}
$$

- Lemma (Estimates):

$$
\mathrm{Tr}\left(\hat{A}_\tau(\hat{\bar{B}}_0 e^{-\beta\hat{\bar{H}}} - \widehat{(\bar{B}_0 e^{-\beta H_0})}\right) = \mathcal{O}(M^{-1})
$$

$$
\mathrm{Tr}\left((\hat{\bar{A}}_\tau - \widehat{A(\tau,z)})\widehat{(\bar{B}_0 e^{-\beta H_0})}\right) = \mathcal{O}(M^{-1})
$$

## Summary

1. approximation equilibrium and *time-correlation observables*
2. certain weighted average of the different ab initio dynamics approximates quantum observables at *any temperature*
3. new algorithm for computing canonical (Gibbs) observables by sampling classical trajectories
4. sharper error estimates with constants in $\mathcal{O}(M^{-1})$ independent of $N$
5. use of non-linear eigenvalue problem to construct global projections $\Pi_0$ to the electronic states related to adiabatic approximation.

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**Limitations and open problems**

1. Requires non-intersecting relevant bands (energy surfaces).
2. How to extend the analysis to more general Hamiltonians ?
3. Low temperature asymptotics ?
4. Crossing of electron eigenvalues and surface hopping type methods.