Wigner function quantum molecular dynamics

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Table of contents

Methods for time-dependent quantum problems

- Direct “exact” solution: Few-particle systems
  1. Schrödinger equation (2-3 particles)
  2. Time-dependent Green’s function (up to 20 particles)
- “Ab initio” molecular dynamics: Moderate system size
  1. R. Carr, M. Parrinello molecular dynamics (separation of fast and slow degrees of freedom) MD for nuclei + electron orbitals $\{\Psi_i(x,t)\}$
  2. Methods of quantum trajectories:
     Bohm trajectories, Wigner trajectories, etc.
- Time-dependent statistical approaches: Large systems
  1. Time-dependent DFT
  2. Quantum kinetic theory

Classical Molecular Dynamics

N classical interacting particles

$$\begin{aligned} \dot{\mathbf{p}}_i(t) &= \mathbf{F}_i = -\nabla U, \qquad i = 1, \dots N \qquad (1) \\ \mathbf{r}_i(0) &= \mathbf{r}_i^0 \\ \mathbf{p}_i(0) &= \mathbf{p}_i^0 \end{aligned}$$

Numerical solution for $1000 \dots 10^6$ particles: (in principle) exact treatment of classical systems

Problems: not applicable to quantum particles
Quantum generalizations (we discuss b and c):

a) Wave packet MD: phenomenological approach

b) Semiclassical MD (effective quantum potentials):
good results for weakly degenerate system.
Requires input of quantum potentials

c) Wigner function QMD

d) Many other methods ...

Classical Liouville Equation

Statistical approach to classical N-particle system:

N-particle phase space distribution $f(x_1, \dots x_N, t), \quad x_i = (\mathbf{r}_i, \mathbf{p}_i)$

Probability density, normalized $\int d^6x_1 \dots d^6x_N \, f(x_1, \dots x_N) = 1$

$$\boxed{0 = \frac{df}{dt} = \left\{ \frac{\partial f}{\partial t} + \sum_{i=1}^{N} \left(\frac{\partial f}{\partial \mathbf{r}_i} \dot{\mathbf{r}}_i + \frac{\partial f}{\partial \mathbf{p}_i} \dot{\mathbf{p}}_i \right) \right\}} \qquad (2)$$

Characteristics $\dot{\mathbf{r}}_i(t), \dot{\mathbf{p}}_i(t)$: Given by Hamilton's or Newton's equations.

→ solution of Newton's equations by classical MD $\hat{=}$ Solving (2)

Idea: Quantum generalization of (2) → quantum generalization of MD.

Density operator[1]

N particles, external potential $\mathcal{U}$, pair-wise potentials V_{ij}

Hamiltonian:

$$H_{1\dots N} = \sum_{i=1}^{N} H_i + \sum_{1\le i<j\le N} V_{ij}(|r_i - r_j|) \tag{3}$$

$$H_i(t) = \frac{p_i^2}{2\, m_i} + \mathcal{U}_i(t) \tag{4}$$

M possible quantum states $|\psi^{(1)}_{1\dots N}\rangle, |\psi^{(2)}_{1\dots N}\rangle \dots |\psi^{(M)}_{1\dots N}\rangle$

Orthonormal basis:

$$\langle\psi^{(k)}_{1\dots N}|\psi^{(l)}_{1\dots N}\rangle = \delta_{k,l}, \tag{5}$$

$$\sum_{k=1}^{M} |\psi^{(k)}_{1\dots N}\rangle\langle\psi^{(k)}_{1\dots N}| = 1. \tag{6}$$

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[1] For details see M. Bonitz, *Quantum Kinetic Theory*, Teubner 1998

Density operator II

Mixed state:

Micro-states with probability W_k ($W_k \geq 0$ and $\sum_{k=1}^{M} W_k = 1$)

***N*-particle density operator in nonequilibrium:**

$$\boxed{\rho_{1\ldots N}(t) = \sum_{k=1}^{M} W_k \, |\psi^{(k)}_{1\ldots N}(t)\rangle\langle\psi^{(k)}_{1\ldots N}(t)|} \tag{7}$$

Main properties of $\rho(t)$:

1. $\rho(t)$ generalizes thermodynamic result to nonequilibrium.
2. $\mathrm{Tr}_{1\ldots N}\, \rho_{1\ldots N} = 1$
3. ρ has statistical meaning, due to probabilities W_k.
4. For pure quantum state "k_0", $W_k = \delta_{k,k_0}$
5. $\rho^{\dagger}_{1\ldots N} = \rho_{1\ldots N}$
6. Average of a quantity A: $\langle A\rangle(t) = \mathrm{Tr}_{1\ldots N}\, A\, \rho_{1\ldots N}(t)$

Density operator III

Matrix representation of ρ:

Representation *b* of quantum states with $N-$particle basis states, $|b_{1\ldots N}\rangle = |b_1 \ldots b_N\rangle$,

Density operator becomes matrix $\langle b_N \ldots b_1|\rho_{1\ldots N}|b'_1 \ldots b'_N\rangle$.

Physical meaning:

i-th *diagonal* matrix element: probability of finding system in state $|b^i_{1\ldots N}\rangle$, where $\langle b^i_{1\ldots N}|\rho_{1\ldots N}|b^i_{1\ldots N}\rangle \geq 0$,

off-diagonal elements correspond to the probability of transitions between two different states.

Von Neumann equation

Equation of motion of $\rho(t)$ follows from N-particle Schrödinger equation for $|\psi^{(k)}_{1\ldots N}\rangle$, with initial conditions $|\psi^{(k)}_{1\ldots N}(t_0)\rangle = |\psi^{(0k)}_{1\ldots N}\rangle$
von Neumann equation: (quantum Liouville equation)

$$\boxed{i\hbar\frac{\partial}{\partial t}\rho_{1\ldots N} - [H_{1\ldots N}, \rho_{1\ldots N}] = 0} \tag{8}$$

with initial condition $\rho_{1\ldots N}(t_0) = \rho^{(0)}_{1\ldots N} = \sum_{k=1}^{M} W_k\, |\psi^{(0k)}_{1\ldots N}\rangle\langle\psi^{(0k)}_{1\ldots N}|$.

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Further (dynamical) properties of ρ:

7. Total energy conservation:

$$\begin{aligned} E(t) = \langle H_{1\dots N}\rangle &= \mathrm{Tr}_{1\dots N} H_{1\dots N}\, \rho_{1\dots N}(t) = \\ &= \mathrm{Tr}_{1\dots N} H_{1\dots N}\, \rho^{(0)}_{1\dots N} = E(t_0). \end{aligned}$$

8. The evolution of $\rho_{1\dots N}$ is time reversible.

Reduced density operators

Instead of $\rho_{1\ldots N}$: **reduced density operators** F_1, $F_{12} \ldots F_{1\ldots s}$,

$$\boxed{F_{1\ldots s} = \mathcal{V}^s \,\mathrm{Tr}_{s+1\ldots N}\, \rho_{1\ldots N}, \quad \frac{1}{\mathcal{V}^s}\mathrm{Tr}_{1\ldots s} F_{1\ldots s} = 1} \tag{9}$$

($\mathcal{V}$ is volume)

Consistency property:

$$F_{1\ldots s} = \mathcal{V}^{-k}\,\mathrm{Tr}_{s+1\ldots s+k}\, F_{1\ldots s+k} \tag{10}$$

$F_{1\ldots s}$ allow for simpler calculation of averages of s-particle quantities:

$$\langle A_{1\ldots s}\rangle = \frac{n^s}{s!}\mathrm{Tr}_{1\ldots s} A_{1\ldots s} F_{1\ldots s} \tag{11}$$

(Spin effects neglected)

BBGKY-hierarchy

Equations of motion for$F_{1\dots s}$, **BBGKY-hierarchy**

$$\boxed{i\hbar\frac{\partial}{\partial t}F_{1\dots s}-[H_{1\dots s},F_{1\dots s}]=n\mathrm{Tr}_{s+1}\sum_{i=1}^{s}[V_{i,s+1},F_{1\dots s+1}]} \tag{12}$$

Formal solution.

$$\begin{aligned}F_{1\dots s}(t) &= U_{1\dots s}(t-t_0)\,F^{(0)}_{1\dots s}\,U^{\dagger}_{1\dots s}(t-t_0)\\ &+ \frac{n}{i\hbar}\int_0^{t-t_0}d\tau U_{1\dots s}(\tau)\,\mathrm{Tr}_{s+1}\sum_{i=1}^{s}[V_{i,s+1},F_{1\dots s+1}(t-\tau)]\,U^{\dagger}_{1\dots s}(\tau).\end{aligned}$$

First term: evolution of the $s-$particle complex, starting from initial state $F^{(0)}_{1\dots s}$.
Second term: contains influence of remaining part of the system.

$U_{1\dots s}$: time-evolution operator (solution of the homogeneous equation)

BBGKY-hierarchy II

Advantage of using the hierarchy:

Often decoupling at low level $s \leq 3$ possible.
Remaining equations:

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}F_1 - [H_1, F_1] &= n\mathrm{Tr}_2[V_{12}, F_{12}], \\ i\hbar\frac{\partial}{\partial t}F_{12} - [H_{12}, F_{12}] &= n\mathrm{Tr}_3[V_{13} + V_{23}, F_{123}], \end{aligned}$$

$\boxed{\text{Requires approximation } F_{123} = F_{123}[F_1, F_{12}].}$

Properties of the BBGKY hierarchy:

1. time reversible
2. Total particle number balance $N(t) = n\mathcal{V}(t) = n\mathrm{Tr}_1\, F_1(t) = \mathrm{const.}$

BBGKY-hierarchy III

3. Total energy balance.

Mean kinetic and potential energy:

$$\begin{aligned}\langle T\rangle &= n\mathrm{Tr}_1\,\frac{p_1^2}{2m}F_1\\ \langle V\rangle &= \frac{n^2}{2}\mathrm{Tr}_{12}\,V_{12}F_{12},\end{aligned}$$

Final result of a (lengthy) calculation:

$$\boxed{\frac{d}{dt}\langle T+V\rangle = \frac{n^3}{2\,i\hbar}\mathrm{Tr}_{123}\,V_{12}[V_{13}+V_{23},F_{123}] + \left\langle\frac{\partial\mathcal{U}(t)}{\partial t}\right\rangle - \frac{d}{dt}\,\langle\mathcal{U}(t)\rangle}$$

Last two terms: energy gain or loss due to external fields.

First term: should vanish for proper approximation for F_{123} ("conserving approximation").

Coordinate representation

Basis vectors in the coordinate representation:

$$|\psi_{1\ldots N}\rangle \longrightarrow |x_1 \ldots x_N\rangle, \qquad x_i = \mathbf{r}_i\, s_i,$$

(s_i: spin projection of particle i)

Matrix elements of $F_{1\ldots s}$:

$$\langle x_1 \ldots x_s | F_{1\ldots s} | x_s' \ldots x_1' \rangle = F_{1\ldots s}(x_1, \ldots ; x_s, x_1', \ldots, x_s'),$$

Matrix elements of the Hamilton operator:

$$\begin{aligned} \langle x_i | H_i | x_i' \rangle &= \left\{ -\frac{\hbar^2}{2\, m_i} \nabla_i^2 + \mathcal{U}(x_i) \right\} \delta(x_i - x_i'), \\ \langle x_j x_i | V_{ij} | x_j' x_i' \rangle &= V(\mathbf{r}_i - \mathbf{r}_j)\, \delta(x_i - x_i')\, \delta(x_j - x_j'), \end{aligned}$$

where $\delta(x_m - x_m') = \delta(\mathbf{r}_m - \mathbf{r}_m')\, \delta_{s_m, s_m'}$.

In coordinate representation one-particle operators and binary interaction potential are diagonal.

Coordinate representation of BBGKY

$$\boxed{\begin{aligned} &\left\{ i\hbar\frac{\partial}{\partial t} - H_{1\ldots k}(x_1,\ldots,x_k) + H_{1\ldots k}(x_1',\ldots,x_k') \right\} \\ &\qquad\qquad F_{1\ldots k}(x_1\ldots x_k; x_1'\ldots x_k', t) \\ &= n\sum_{i=1}^{k}\sum_{s_{k+1}} \int d\mathbf{r}_{k+1} \left\{ V(\mathbf{r}_i - \mathbf{r}_{k+1}) - V(\mathbf{r}_i' - \mathbf{r}_{k+1}) \right\} \\ &\qquad\qquad \times F_{k+1}(x_1,\ldots,x_{k+1}; x_1',\ldots,x_k', x_{k+1}, t) \end{aligned}}$$

Note: $x_{k+1}' = x_{k+1}$, due to trace over $k+1$.

Example: first hierarchy equation

$$\left\{ i\hbar\frac{\partial}{\partial t} + \frac{\hbar^2}{2\,m_1}(\nabla_1^2 - \nabla_{1'}^2) - \mathcal{U}(x_1,t) + \mathcal{U}(x_1',t) \right\} F_1(x_1; x_1', t)$$

$$= n\sum_{s_2}\int d\mathbf{r}_2 \left\{ V(\mathbf{r}_1 - \mathbf{r}_2) - V(\mathbf{r}_1' - \mathbf{r}_2) \right\} F_{12}(x_1, x_2; x_1', x_2, t).$$

Wigner representation

Center of mass and relative coordinates, R_i and r_i for each particle:

$$r_i' = R_i + \frac{r_i}{2}, \quad r_i^{''} = R_i - \frac{r_i}{2}, \quad \text{or, vice versa,} \tag{13}$$

$$R_i = \frac{r_i' + r_i''}{2}, \quad r_i = r_i' - r_i^{''}. \tag{14}$$

So, for example $F_1(r_1'; r_1^{''}, t) \longrightarrow F_1(R_1 + \frac{r_1}{2}; R_1 - \frac{r_1}{2}, t)$.

Introduce the new variables into the coordinate representation of the hierarchy and denote

$$F_{1\ldots s}(R_1 + \frac{r_1}{2}, \ldots, R_s + \frac{r_s}{2}; R_1' - \frac{r_1}{2}, \ldots, R_s' - \frac{r_s'}{2}, t) \doteq \tilde{F}_{1\ldots s}(R_1, r_1, \ldots, R_s, r_s, t)$$

Further take into account that

$$\nabla^2_{r_1'} - \nabla^2_{r_1''} = 2\,\nabla_{R_1}\nabla_{r_1}.$$

Wigner transform

In 1932 Wigner proposed a new representation of quantum mechanics based on the quasi-distribution function $f_N(R, p, t)$ depending on coordinate $R = \{R_1, \ldots, R_s\}$ and momenta $p = \{p_1, \ldots, p_s\}$. This idea stimulated development of quantum theories in a *extended phase space*.

Wigner transform of the $s-$particle density matrix $\tilde{F}_{1\ldots s}$ yields the quasiclassical $s-$particle phase space distribution:

$$
\begin{aligned}
& F_{1\ldots s}(R_1, p_1, \ldots, R_s, p_s, t) = \qquad (15)\\
& \int \frac{dr_1}{(2\pi\hbar)^3} \cdots \frac{dr_s}{(2\pi\hbar)^3} \exp\{-i\left(p_1 r_1 + \ldots p_s r_s\right)/\hbar\} \\
\times \quad & \tilde{F}_{1\ldots s}(R_1, r_1, \ldots, R_s, r_s, t).
\end{aligned}
$$

Common phase space distribution $f(r, p)$:

$$
f_{1\ldots s}(R_1, p_1, \ldots, R_s, p_s, t) = n^s\, F_{1\ldots s}(R_1, p_1, \ldots, R_s, p_s, t) \qquad (16)
$$

Normalization of f (we skip the spin summations $\sum_{s_1} \cdots \sum_{s_s}$):

$$
\int \frac{dr_1\, dp_1}{(2\pi\hbar)^3} \cdots \frac{dr_s dp_s}{(2\pi\hbar)^3}\, f_{1\ldots s}(R_1, p_1, \ldots, R_s, p_s, t) = N^s(t). \qquad (17)
$$

Properties of the Wigner function

1. Wigner function is real: $Im[f(R,p,t)] = 0$, may be negative (due to non-commutation of the arguments, $[\hat{\boldsymbol{r}}, \hat{\boldsymbol{p}}] \neq 0$)
2. Integration over one of the arguments gives a coordinate or momentum probability density (last equalities refer to pure state)

$$\int dp\, f(R,p) = \langle R|\hat{\rho}|R\rangle = |\Psi(R)|^2$$

$$\int dR\, f(R,p) = \langle p|\hat{\rho}|p\rangle = |\Phi(p)|^2$$

3. Expectation values:

$$\langle \hat{A} \rangle = \frac{1}{Z}\mathrm{Tr}[\hat{A}\hat{\rho}] = \int dR \int dr \left\langle R - \frac{r}{2}|\hat{A}|R + \frac{r}{2}\right\rangle \left\langle R + \frac{r}{2}|\hat{\rho}|R - \frac{r}{2}\right\rangle$$

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$$\langle \hat{A}(t)\rangle = \frac{1}{Z}\int dp \int dR\, A_N(R,p)\, f(R,p,t)$$

$$\text{Weyl symbol:}\quad A_N(R,p) = \int dr\, \left\langle R - \frac{r}{2}|\hat{A}|R + \frac{r}{2}\right\rangle\, e^{irp}$$

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4. Function $A(\hat{R},\hat{p})$ may depend on order of arguments. Example:

$$\hat{A}_1 = (\hat{R}\hat{p}) \neq (\hat{p}\hat{R})$$

BBGKY-hierarchy in Wigner representation

$$\left\{ \frac{\partial}{\partial t} + \sum_{i=1}^{k} \frac{p_i}{m_i} \nabla_{R_i} \right\} f(R_1 p_1, \ldots, R_k p_k, t) \tag{18}$$

$$- \quad \frac{1}{i\hbar} \sum_{1 \le i < j \le k} V_k^{(ij)} - \frac{1}{i\hbar} \sum_i U_k^{(i)} = \frac{1}{i\hbar} \sum_{i=1}^{k} F_{k+1}^{(i)}, \qquad \text{with}$$

$$\begin{aligned}
V_k^{(ij)} \quad &= \quad \int \frac{dr_{ij} d\bar{p}_i}{(2\pi\hbar)^3} \exp\{-i\,(p_i - \bar{p}_i)\, r_{ij}/\hbar\} \times \left\{ V\left(R_i - R_j + \frac{r_{ij}}{2}\right) - V\left(R_i - R_j - \frac{r_{ij}}{2}\right) \right\} \\
&\times \quad f_{1\ldots k}(R_1, p_1, \ldots, R_i, \bar{p}_i, \ldots, R_j, p_i - \bar{p}_i + p_j, \ldots, R_k, p_k, t),
\end{aligned}$$

$$\begin{aligned}
U_k^{(i)} \quad &= \quad \int \frac{dr_i d\bar{p}_i}{(2\pi\hbar)^3} \exp\{-i\,(p_i - \bar{p}_i)\, r_i/\hbar\} \times \left\{ \mathcal{U}\left(R_i + \frac{r_i}{2}\right) - \mathcal{U}\left(R_i - \frac{r_i}{2}\right) \right\} \\
&\times \quad f_{1\ldots k}(R_1, p_1, \ldots, R_{i-1}, p_{i-1} R_i, \bar{p}_i, R_{i+1}, p_{i+1}, \ldots, R_k, p_k, t),
\end{aligned}$$

$$\begin{aligned}
F_{k+1}^{(i)} \quad &= \quad \int \frac{dr_i d\bar{p}_i}{(2\pi\hbar)^3} dR_{k+1}\, dp_{k+1} \, \exp\{-i\,(p_i - \bar{p}_i)\, r_i/\hbar\} \\
&\times \quad \left\{ V\left(R_i - R_{k+1} + \frac{r_i}{2}\right) - V\left(R_i - R_{k+1} - \frac{r_i}{2}\right) \right\} \\
&\times \quad f_{1\ldots k+1}(R_1, p_1, \ldots, R_i, \bar{p}_i, \ldots, R_k, p_k, R_{k+1}, p_{k+1}, t).
\end{aligned}$$

First hierarchy equation in Wigner representation

$$
\boxed{
\begin{aligned}
& \left\{ \frac{\partial}{\partial t} + \frac{p_1}{m_1} \nabla_{R_1} \right\} f(R_1, p_1, t) \\
- \quad & \frac{1}{i\hbar} \int \frac{dr_1 \, d\bar{p}_1}{(2\pi\hbar)^3} \, \exp\{-i\,(p_1 - \bar{p}_1)\, r_1/\hbar\} \\
\times \quad & \left\{ \mathcal{U}\left(R_1 + \frac{r_1}{2}\right) - \mathcal{U}\left(R_1 - \frac{r_1}{2}\right) \right\} f(R_1, \bar{p}_1, t) \\
= \quad & \frac{1}{i\hbar} \int \frac{dr_1 \, d\bar{p}_1}{(2\pi\hbar)^3} \, dR_2 \, dp_2 \, \exp\{-i\,(p_1 - \bar{p}_1)\, r_1/\hbar\} \\
\times \quad & \left\{ V\left(R_1 - R_2 + \frac{r_1}{2}\right) - V\left(R_1 - R_2 - \frac{r_1}{2}\right) \right\} f_{12}(R_1, \bar{p}_1, R_2, p_2, t)
\end{aligned}
}
$$

Equation analogous to classical kinetic equation, except:.

1. f not confined to values between 0 and 1.

2. Potentials $\mathcal{U}$ and V appear not under gradient but as difference under integral (non-local form: different arguments compared to f).

Classical limit

Classical limit of the BBGKY-hierarchy: Taylor expansion of potentials V_{ij} and U_i with respect to the relative coordinates r_{ij} and r_i, respectively.

$$V\left(R_{ij} \pm \frac{r_{ij}}{2}\right) = \sum_{l=0}^{\infty} \frac{(\pm 1)^l}{l\,!} \frac{\partial^{(l)}}{\partial R_i^l} V(R_{ij}) \left(\frac{r_{ij}}{2}\right)^l , \tag{19}$$

$$U\left(R_i \pm \frac{r_i}{2}\right) = \sum_{l=0}^{\infty} \frac{(\pm 1)^l}{l\,!} \frac{\partial^{(l)}}{\partial R_i^l} U(R_i) \left(\frac{r_i}{2}\right)^l . \tag{20}$$

Note: to be understood as scalar products of two vectors, e.g.

$$\frac{\partial^{(2)}}{\partial R_i^2} U(R_i) \left(\frac{r_i}{2}\right)^2 = \frac{\partial^{(2)}}{\partial \boldsymbol{R}_i \partial \boldsymbol{R}_i'} U(R_i) \frac{\boldsymbol{r}_i}{2} \frac{\boldsymbol{r}_i'}{2} \tag{21}$$

Classical limit II

To the potential differences only the odd powers contribute:

$$
\begin{aligned}
V\left(R_{ij}+\frac{r_{ij}}{2}\right)-V\left(R_{ij}-\frac{r_{ij}}{2}\right) &= \sum_{l=0}^{\infty}\frac{2}{(2\,l+1)!}\,\frac{\partial^{(2\,l+1)}}{\partial R_i^{2\,l+1}}\,V(R_{ij})\left(\frac{r_{ij}}{2}\right)^{2\,l+1} \\
U\left(R_i+\frac{r_i}{2}\right)-U\left(R_i-\frac{r_i}{2}\right) &= \sum_{l=0}^{\infty}\frac{2}{(2\,l+1)!}\,\frac{\partial^{(2\,l+1)}}{\partial R_i^{2\,l+1}}\,U(R_i)\left(\frac{r_i}{2}\right)^{2\,l+1} \\
&= \frac{\partial U(R_i)}{\partial R_{i,\alpha}}r_{i,\alpha}+\frac{1}{24}\,\frac{\partial^3\,U(R_i)}{\partial R_{i,\alpha}\partial R_{i,\beta}\partial R_{i,\gamma}}r_{i,\alpha}r_{i,\beta}r_{i,\gamma} \\
&\quad +\dots \qquad (22)
\end{aligned}
$$

with summation over repeated indices α,β,γ.

Transform of the external potential U

use: $r_1 = \frac{\hbar}{i}\frac{d}{d\bar{p}_1}\exp\{-i\,(p_1-\bar{p}_1)\,r_1/\hbar\}$

r_1 integral yields $\delta(p_1-\bar{p}_1)$, perform partial integration over $\bar{p}_1$:

$$\begin{aligned}
- \quad & \frac{1}{i\hbar}\int \frac{dr_1\,d\bar{p}_1}{(2\pi\hbar)^3}\,\exp\{-i\,(p_1-\bar{p}_1)\,r_1/\hbar\} \\
\times \quad & \left\{\frac{\partial U(R_1)}{\partial R_{1,\alpha}}r_{1,\alpha} + \frac{1}{24}\frac{\partial^3 U(R_1)}{\partial R_{1,\alpha}\partial R_{1,\beta}\partial R_{1,\gamma}}r_{1,\alpha}r_{1,\beta}r_{1,\gamma} + \dots\right\} f(R_1,\bar{p}_1,t) \\
= \quad & -\frac{dU(R_1)}{d\boldsymbol{R}_1}\,\frac{\partial f(R_1,p_1,t)}{\partial \boldsymbol{p}_1} \qquad \text{Classical result} \\
& +\frac{\hbar^2}{24}\frac{\partial^3 U(R_1)}{\partial R_{1,\alpha}\partial R_{1,\beta}\partial R_{1,\gamma}}\,\frac{\partial^3 f(R_1,p_1,t)}{\partial p_{1,\alpha}\partial p_{1,\beta}\partial p_{1,\gamma}} \qquad \text{First quantum correction}
\end{aligned}$$

Analogous transform of the interaction potential contributions

Transform of the external potential U

use: $r_1 = \frac{\hbar}{i}\frac{d}{d\bar{p}_1}\exp\{-i\,(p_1 - \bar{p}_1)\,r_1/\hbar\}$

r_1 integral yields $\delta(p_1 - \bar{p}_1)$, perform partial integration over $\bar{p}_1$:

$$\begin{aligned} - \quad & \frac{1}{i\hbar}\int \frac{dr_1\, d\bar{p}_1}{(2\pi\hbar)^3}\exp\{-i\,(p_1 - \bar{p}_1)\,r_1/\hbar\} \\ \times \quad & \left\{ \frac{\partial U(R_1)}{\partial R_{1,\alpha}} r_{1,\alpha} + \frac{1}{24}\frac{\partial^3\, U(R_1)}{\partial R_{1,\alpha}\partial R_{1,\beta}\partial R_{1,\gamma}} r_{1,\alpha} r_{1,\beta} r_{1,\gamma} + \ldots \right\} f(R_1, \bar{p}_1, t) \end{aligned}$$

$$\begin{aligned} = \quad & -\frac{dU(R_1)}{d\boldsymbol{R}_1}\,\frac{\partial f(R_1, p_1, t)}{\partial \boldsymbol{p}_1} && \text{Classical result} \\ & +\frac{\hbar^2}{24}\frac{\partial^3\, U(R_1)}{\partial R_{1,\alpha}\partial R_{1,\beta}\partial R_{1,\gamma}}\,\frac{\partial^3\, f(R_1, p_1, t)}{\partial p_{1,\alpha}\partial p_{1,\beta}\partial p_{1,\gamma}} && \text{First quantum correction} \end{aligned}$$

$$\equiv \quad -\frac{dU^{\text{eff}}(R_1)}{d\boldsymbol{R}_1}\,\frac{\partial f(R_1, p_1, t)}{\partial \boldsymbol{p}_1} \qquad \text{Effective quantum potential}$$

Analogous transform of the interaction potential contributions

Result for $k-$th equation of BBGKY-Hierarchy

$$\left\{ \frac{\partial}{\partial t} + \sum_{i=1}^{k} \frac{p_i}{m_i} \nabla_{R_i} \right\} f(R_1 p_1, \dots, R_k p_k, t) \tag{23}$$

$$- \quad \frac{1}{i\hbar} \sum_{1 \le i < j \le k} V_{cl,k}^{(ij)} - \frac{1}{i\hbar} \sum_{i} U_{cl,k}^{(i)} = \frac{1}{i\hbar} \sum_{i=1}^{k} F_{cl,k+1}^{(i)} + O(\hbar^4), \qquad \text{with}$$

$$\begin{aligned}
\frac{1}{i\hbar} V_{cl,k}^{(ij)} &= \left\{ \nabla_{R_i} V(R_i - R_j) \nabla_{p_i} + \frac{(i\hbar)^2}{24} \nabla_{R_i}^3 V(R_i - R_j) \nabla_{p_i}^3 \right\} \\
&\times \quad f_{1\dots k}(R_1, p_1, \dots, R_k, p_k, t), && (24) \\
\frac{1}{i\hbar} U_{cl,k}^{(i)} &= \left\{ \nabla_{R_i} \mathcal{U}(R_i) \nabla_{p_i} + \frac{(i\hbar)^2}{24} \nabla_{R_i}^3 \mathcal{U}(R_i) \nabla_{p_i}^3 \right\} \\
&\times \quad f_{1\dots k}(R_1, p_1, \dots, R_k, p_k, t), && (25) \\
\frac{1}{i\hbar} F_{cl,k+1}^{(i)} &= \int dR_{k+1}\, dp_{k+1} \\
&\times \left\{ \nabla_{R_i} V(R_i - R_j) \nabla_{p_i} + \frac{(i\hbar)^2}{24} \nabla_{R_i}^3 V(R_i - R_j) \nabla_{p_i}^3 \right\} \\
&\times \quad f_{1\dots k+1}(R_1, p_1, \dots, R_{k+1}, p_{k+1}, t), && (26)
\end{aligned}$$

Liouville equation with first quantum correction

$$
\begin{aligned}
0 \quad = \quad & \left\{ \frac{\partial}{\partial t} + \sum_{i=1}^{N} \frac{p_i}{m_i} \nabla_{R_i} - \sum_{i=1}^{N} \frac{d}{dR_i} \left[U^{\mathrm{eff}}(R_i) + \sum_{j \neq i}^{N} V^{\mathrm{eff}}(R_i - R_j) \right] \nabla_{p_i} \right\} \\
& \times f_N(R_1 p_1, \ldots, R_N p_N, t)
\end{aligned}
$$

with

$$
U^{\mathrm{eff}}(R_i) = \mathcal{U}(R_i) - \frac{\hbar^2}{24} \nabla^2_{R_i} \mathcal{U}(R_i) \nabla^2_{p_i} + O(\hbar^4)
$$

$$
V^{\mathrm{eff}}(R_i - R_j) = V(R_i - R_j) - \frac{\hbar^2}{24} \nabla^2_{R_i} V(R_i - R_j) \nabla^2_{p_i} + O(\hbar^4)
$$

Liouville equation with first quantum correction

$$0 = \frac{\partial f_N}{\partial t} + \frac{p}{m}\frac{\partial f_N}{\partial R} - \frac{\partial V_{eff}}{\partial R}\frac{\partial f_N}{\partial p}$$

Liouville equation with first quantum correction

$$0 = \frac{\partial f_N}{\partial t} + \frac{p}{m}\frac{\partial f_N}{\partial R} - \frac{\partial V_{eff}}{\partial R}\frac{\partial f_N}{\partial p}$$

- Introduce time-dependent trajectories $\{\bar{q} = q(t), \bar{p} = p(t)\}$ given by "classical" equations of motion

$$\frac{\partial \bar{R}}{\partial t} = \dot{\bar{R}} = \frac{\bar{p}}{m}, \quad \frac{\partial \bar{p}}{\partial t} = \dot{\bar{p}} = -\frac{\partial V_{eff}(\bar{p}, \bar{R}, t)}{\partial R} \tag{27}$$

- Substitute (27) in Wigner-Liouville equation: Wigner function is conserved along *Wigner trajectories* (27)

$$\frac{\partial f_N}{\partial t} + \dot{R}\frac{\partial f_N}{\partial R} + \dot{p}\frac{\partial f_N}{\partial p} = \frac{df_N}{dt} = 0$$

- Time-dependence given by propagation of initial function

$$f_N(R, p, t) = f_N[R(t), p(t), t] = f_N[R(0), p(0), 0] = f_N^0(R_0, p_0)$$

  - "Recipe": for arbitrary phase-space point $\{R, p\}$ solve Eq. (27) backward in time to find $\{R_0, p_0\}$.
  - Initial Wigner function specified by initial system state

$$\Psi(R, 0), \ \rho(R, R', 0) \ \ f_N^0(R, p).$$

Wigner trajectories: “quantum” force

- Effective potential V_{eff} given by infinite series in powers of $\hbar$

$$\frac{\partial V_{eff}}{\partial R}\frac{\partial f_N}{\partial p} = \frac{\partial V}{\partial R}\frac{\partial f_N}{\partial p} - \frac{\hbar^2}{24}\frac{\partial^3 V}{\partial R^3}\frac{\partial^3 f_N}{\partial p^3} + \cdots$$

- The method works only if the series is rapidly converging.
- First order perturbation theory in $\hbar$:

$$-\frac{\partial V_{eff}}{\partial R_k} = F_k^{eff} = F_k^{class} + F_k^{quan}, \quad F_k^{quan} = \frac{\hbar^2}{24}\sum_{i,l}\frac{\partial^3 V}{\partial R_i \partial R_l \partial R_k}\frac{\partial^2 f_N}{\partial p_i \partial p_l}$$

- Principle problems with unbounded potentials like, $\sim 1/r^n$, or with diverging derivatives: hard wall, hard sphere, etc.

Wigner trajectories: "quantum" force

- Effective potential V_{eff} given by infinite series in powers of $\hbar$

$$\frac{\partial V_{eff}}{\partial R}\frac{\partial f_N}{\partial p} = \frac{\partial V}{\partial R}\frac{\partial f_N}{\partial p} - \frac{\hbar^2}{24}\frac{\partial^3 V}{\partial R^3}\frac{\partial^3 f_N}{\partial p^3} + \cdots$$

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- Principle problems with unbounded potentials like, $\sim 1/r^n$, or with diverging derivatives: hard wall, hard sphere, etc.
  – Partial solution: replace the original potential with a model potential which is more smooth and captures similar physics.

Wigner trajectories: “quantum” force

- Effective potential V_{eff} given by infinite series in powers of $\hbar$

$$\frac{\partial V_{eff}}{\partial R}\frac{\partial f_N}{\partial p} = \frac{\partial V}{\partial R}\frac{\partial f_N}{\partial p} - \frac{\hbar^2}{24}\frac{\partial^3 V}{\partial R^3}\frac{\partial^3 f_N}{\partial p^3} + \cdots$$

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- Principle problems with unbounded potentials like, $\sim 1/r^n$, or with diverging derivatives: hard wall, hard sphere, etc.
  Example: electrons in a quantum wire. The problem becomes quasi one-dimensional when $\Delta E_x \ll \Delta E_{yz}$: transverse quantization is much larger than the energy of the longitudinal motion. Integration over the transverse motion reduces the Coulomb potential

$$U(r) \sim \frac{1}{a^2}\int_0^\infty \frac{e^{-\rho^2/a^2}\rho}{\sqrt{r^2+\rho^2}}d\rho = \frac{\sqrt{\pi}}{a}e^{r^2/a^2}\left[1 - \operatorname{erf}\left(\frac{r}{a}\right)\right],$$

with a being the characteristic width of the quantum wire.

Wigner trajectories: “quantum” force

- Effective potential V_{eff} given by infinite series in powers of $\hbar$

$$\frac{\partial V_{eff}}{\partial R}\frac{\partial f_N}{\partial p} = \frac{\partial V}{\partial R}\frac{\partial f_N}{\partial p} - \frac{\hbar^2}{24}\frac{\partial^3 V}{\partial R^3}\frac{\partial^3 f_N}{\partial p^3} + \cdots$$

- The method works only if the series is rapidly converging.
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- Principle problems with unbounded potentials like, $\sim 1/r^n$, or with diverging derivatives: hard wall, hard sphere, etc.
- “Quantum force” depends on the partial derivatives of the Wigner function which itself is unknown. Then use approximations:

$$f_N(R, p, t_i) \to f_N(R, p, t_{i-1}), \quad \text{or}$$

$$f_N(R, p, t_i) \approx \frac{1}{K}\sum_{k=1}^{K}\delta\{R - R_k(t_i)\}\,\delta\{p - p_k(t_i)\},$$

Wigner function determined through density of trajectories.

Example: Tunneling - transmission and reflection

$t = 0$: Gaussian wavepacket
(minimum position uncertainty)

$$\Psi(x,0) = \frac{1}{(\pi\sigma_x^2)^{1/4}} \exp\left(-\frac{(x-x_c)^2}{2\sigma_x^2} + ik_c x\right)$$

Initial Wigner function reflects QM uncertainty principle

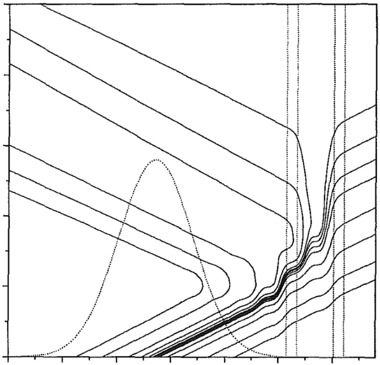
$$f_1(x,p,0) =$$

$$\frac{1}{2\pi\hbar}\int dr\, \Psi^*\left(x+\frac{r}{2},0\right)\Psi\left(x-\frac{r}{2},0\right)\, e^{-irp} =$$

$$2\exp\left[-\frac{(x-x_c)^2}{2\sigma_x^2}\right]\cdot\exp\left[-\frac{(p-\hbar k_c)^2}{2\sigma_p^2}\right]$$

where

$$\sigma_p^2 = \frac{\hbar^2}{4\sigma_x^2} \;\Rightarrow\; \sigma_x\cdot\sigma_p = \frac{\hbar}{2}$$



Wigner trajectories for Gaussian wavepacket during tunneling through finite height double barrier.

Quantum statistics

- Exchange requires (anti-)symmetrization of N-particle wavefunction. Two-particle (anti-)symmetrical wavefunction

$$|\Psi(1,2)\rangle = \frac{|\phi_1(1)\rangle\,|\phi_2(2)\rangle \pm |\phi_1(2)\rangle\,|\phi_2(1)\rangle}{\sqrt{2(1 \pm |\langle\phi_1|\,\phi_2\rangle|^2)}},$$

- (Anti-)Symmetrical two-particle Wigner function

$$f^{S/A}(x_1,x_2,p_1,p_2) = \frac{1}{2(1 \pm |\langle\phi_1|\,\phi_2\rangle|^2)}\Big\{f^1(x_1,p_1)\,f^2(x_2,p_2)+$$

$$f^1(x_2,p_2)\,f^2(x_1,p_1) \pm W_{12}(x_2,p_2)\,W_{21}(x_1,p_1) \pm W_{12}(x_1,p_1)\,W_{21}(x_2,p_2)\Big\},$$

  Exchange integral

$$W_{kj}(x,p) = \frac{1}{2\pi\hbar}\int dx'\,e^{ipx'/\hbar}\,\phi_k^*\left(x+\frac{x'}{2}\right)\,\phi_j\left(x-\frac{x'}{2}\right).$$

- Dynamical evolution equations, if solved exactly, conserve initial symmetry of the Wigner function.

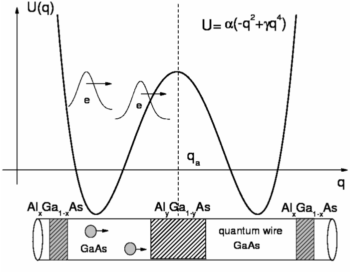
Example: Tunneling of interacting identical particles

Model: two electrons in a quantum wire.

$$H = \sum_{i=1}^{2}\left[\frac{p_i^2}{2m} + \alpha\left(-x_i^2 + \gamma x_i^4\right)\right] + U\left(|x_1 - x_2|\right),$$

$$U(x) = \lambda\frac{\sqrt{\pi}}{a} e^{x^2/a^2}\left[1 - \mathrm{erf}\left(\frac{x}{a}\right)\right], \; \lambda = \frac{e^2 m^{3/4}}{\hbar^{3/2}\alpha^{1/4}}$$

Long-time evolution: wave packets oscillate in double well potential.



- Tunneling probability (transmission)

$$T(x_a, t) = \frac{1}{N}\int_{x_a}^{\infty} \rho(x, t)\, dx,$$

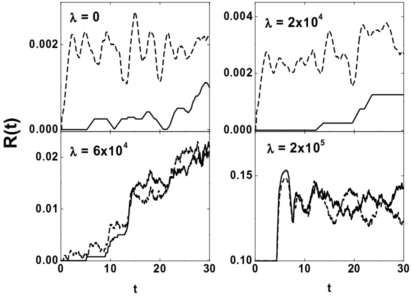
Probability density $\rho(x, t)$ and current $J(x, t)$

$$\rho(x, t) = \int dp\, f(x, p, t), \quad J(x, t) = \frac{\int dp\, p\, f(x, p, t)}{\int_0^\infty dt \int dp\, p\, f(x, p, t)}.$$

Tunneling probability

Question: influence of interaction and exchange on tunneling.

Time-dependence of the tunneling probability $T(t)$, with (without) exchange - solid (dashed) lines
Interaction strength: $\lambda = 0, \ldots, 2 \times 10^5$.



- Increase of λ increases fraction of high energy trajectories.
- Exchange effects reduce the tunneling probability.
- Period of oscilations decreases with increase of λ.

Equilibrium Results for U^{eff}

- Assume ideal system: $f_N = \prod_i f_i$

- Equilibrium distributions: $f_i^{EQ} = A \exp[-\beta p_i^2/2m]$

- evaluate $p-$derivatives, 1-dimensional case

$$U^{\text{eff}}(R;p,T) = \mathcal{U}(R) - \frac{\pi\Lambda_D^2}{12}\left(\frac{\beta}{m}p^2 - 3\right)\mathcal{U}''(R) \tag{28}$$

with thermal DeBroglie wave length $\Lambda_D^2 = \frac{\hbar^2}{2\pi m k_B T}$

- perform momentum average with f^{EQ}

$$\boxed{\langle U^{\text{eff}}(R,T)\rangle = \mathcal{U}(R) \underset{\uparrow}{-} \frac{\pi\Lambda_D^2}{12}(2\pi - 3)\,\mathcal{U}''(R)} \tag{29}$$

- Softening of potential due to spatial extension of quantum particle
- Effect depends on spatial scale l_U of potential $\mathcal{U}$, i.e. on $\left(\frac{\Lambda_D}{l_U}\right)^2$.
- No quantum effect on force for harmonic potential

Equilibrium Results for V^{eff}

$$\begin{aligned}
\nabla_{R_{i\alpha}} V^{\mathrm{eff}}(R_i - R_j)\nabla_{p_{i\alpha}} f_N &= \nabla_{R_{i\alpha}} V(R_i - R_j)\nabla_{p_{i\alpha}} f_N \\
&- \frac{\hbar^2}{24}\nabla_{R_{i\alpha}}\nabla_{R_{i\beta}}\nabla_{R_{i\gamma}} V^{\mathrm{eff}}(R_i - R_j)\nabla_{p_{i\alpha}}\nabla_{p_{i\beta}}\nabla_{p_{i\gamma}} f_N
\end{aligned}$$

Solve 2-particle problem in equilibrium (neglect exchange):

$$\begin{aligned}
f_{12}(R_1, p_1, R_2, p_2) &= f(p_1)f(p_2)g(R_1 - R_2) \\
f(p_i) &= A\exp[-\beta p_i^2/2m] \\
g(R) &= e^{-\beta V^{\mathrm{eff}}(R)}
\end{aligned}$$

For Coulomb potential this expansion does not converge.

Quantum potential for Coulomb interaction

Calculation in coordinate representation (Bloch equations) necessary.

- Weak coupling solution for Coulomb case (Kelbg 1965): $x_{ij} = r_{ij}/\lambda_{ij}$

$$\Phi^K(R;T) = \frac{q_i q_j}{\lambda_{ij} x_{ij}} \left\{ 1 - e^{-x_{ij}^2} + \sqrt{\pi} x_{ij} \left[1 - \mathrm{erf}(x_{ij}) \right] \right\} \qquad (30)$$

- Extension to strong coupling (Filinov, Bonitz):

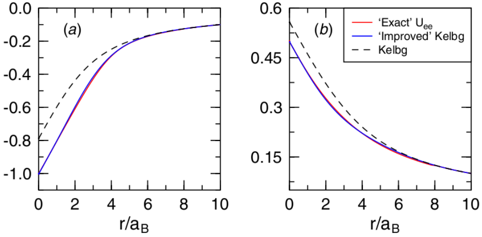
$$\Phi^K(R;T) = \frac{q_i q_j}{\lambda_{ij} x_{ij}} \left\{ 1 - e^{-x_{ij}^2} + \sqrt{\pi} \frac{x_{ij}}{\gamma_{ij}} \left[1 - \mathrm{erf}\left(\frac{x_{ij}}{\gamma_{ij}} \right) \right] \right\} \qquad (31)$$

Phys. Rev. E 70 (2004) 046411

Quantum potential for Coulomb interaction

- Weak coupling solution for Coulomb case (Kelbg): $x_{ij} = r_{ij}/\lambda_{ij}$

$$\Phi^K(R;T) = \frac{q_i q_j}{\lambda_{ij} x_{ij}} \left\{ 1 - e^{-x_{ij}^2} + \sqrt{\pi} x_{ij} \left[1 - \mathrm{erf}(x_{ij})\right] \right\}$$



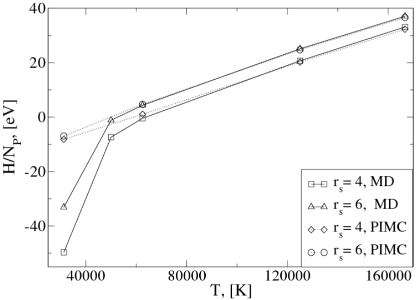
a (b) electron-proton (electron-electron) potential at $T = 106K$.
Dashed lines: Kelbg potential
Solid blue line: Improved Kelbg potential
Solid red line: Exact pair potential.

Distances are in units of a_B, energies in Ha = 2 Ryd.

Example: Semiclassical MD - Dense Hydrogen Plasma

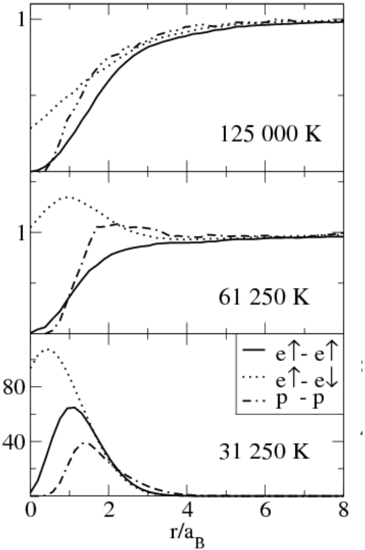
Additional exchange term to treat electrons with different spin:

$$\begin{aligned}\Phi^K_{ee}(R;T) &= \Phi^K(R;T)\\ &- \frac{1}{\beta}\ln\left\{1 \pm e^{-r^2/\lambda_{ee}}\right\}\end{aligned}$$



Total energy: Semiclassical MD vs. quantum Monte Carlo

Pair distributions



Quantum Molecular Dynamics

- quantum Liouville equation for f_N (right hand side $= 0$)

$$\left\{ \frac{\partial}{\partial t} + \sum_{i=1}^{N} \frac{p_i}{m_i} \nabla_{R_i} \right\} f(R_1 p_1, \dots, R_N p_N, t)$$

$$- \quad \frac{1}{i\hbar} \sum_{1 \le i < j \le N} V_N^{(ij)} - \frac{1}{i\hbar} \sum_i U_N^{(i)} = 0 \qquad \text{with}$$

$$\begin{aligned}
V_N^{(ij)} \quad &= \quad \int \frac{dr_{ij} d\bar{p}_i}{(2\pi\hbar)^3} \exp\{-i\,(p_i - \bar{p}_i)\, r_{ij}/\hbar\} \\
&\times \quad \left\{ V\left(R_i - R_j + \frac{r_{ij}}{2}\right) - V\left(R_i - R_j - \frac{r_{ij}}{2}\right) \right\} \\
&\times \quad f_{1\dots N}(R_1, p_1, \dots, R_i, \bar{p}_i, \dots, R_j, p_i - \bar{p}_i + p_j, \dots, R_k, p_k, t) \\
U_N^{(i)} \quad &= \quad \int \frac{dr_i d\bar{p}_i}{(2\pi\hbar)^3} \exp\{-i\,(p_i - \bar{p}_i)\, r_i/\hbar\} \\
&\times \quad \left\{ \mathcal{U}\left(R_i + \frac{r_i}{2}\right) - \mathcal{U}\left(R_i - \frac{r_i}{2}\right) \right\} \\
&\times \quad f_{1\dots N}(R_1, p_1, \dots, R_{i-1}, p_{i-1} R_i, \bar{p}_i, R_{i+1}, p_{i+1}, \dots, R_N, p_N, t)
\end{aligned}$$

Quantum Molecular Dynamics

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$$\left\{\frac{\partial}{\partial t} + \sum_{i=1}^{N} \frac{p_i}{m_i}\nabla_{R_i}\right\} f(R_1 p_1, \dots, R_N p_N, t)$$

$$- \quad \frac{1}{i\hbar} \sum_{1\le i<j\le N} V_N^{(ij)} - \frac{1}{i\hbar}\sum_i U_N^{(i)} = 0 \qquad \text{with}$$

$$\begin{aligned} V_N^{(ij)} \quad &= \quad \int \frac{dr_{ij}\, d\bar{p}_i}{(2\pi\hbar)^3}\, \exp\{-i\,(p_i - \bar{p}_i)\, r_{ij}/\hbar\} \\ &\times \quad \left\{ V\left(R_i - R_j + \frac{r_{ij}}{2}\right) - V\left(R_i - R_j - \frac{r_{ij}}{2}\right)\right\} \end{aligned}$$

More compact notation

$p = (\mathbf{p}_1, \dots \mathbf{p}_N),\ q = (\mathbf{R}_1, \dots \mathbf{R}_N)$

replace $\sum_i$ by scalar products

replace $e^{ix}[V_+ - V_i] \to 2i \sin x \cdot V_+$

use total potential V - sum of external and interaction potentials

define classical force $\boldsymbol{F}(\boldsymbol{q}) = -\boldsymbol{\nabla}_q V(\boldsymbol{q})$

Quantum Molecular Dynamics

Isolate classical force contribution $\sim F$:

$$\frac{\partial f}{\partial t} + \frac{\boldsymbol{p}}{m} \cdot \boldsymbol{\nabla}_q f + \boldsymbol{F}(\boldsymbol{q}) \cdot \boldsymbol{\nabla}_p f = \int ds\, f\,(p - s, q, t)\, \omega\,(s, q, t)\,, \qquad (32)$$

s is $3N-$dimensional momentum shift of f

$\boxed{\omega \text{ is difference of quantum and classical force contribution}}$

$$\omega\,(s, q, t) = \frac{2}{(\pi\hbar^2)^{Nd}} \int dq'\; V\,(q - q', t)\, \sin\left(\frac{2sq'}{\hbar}\right) + \boldsymbol{F}\,(q) \cdot \boldsymbol{\nabla}_s \delta\,(s) \qquad (33)$$

Further strategy:

convert Eq. (32) into integral equation and develop iterative solution.

Method of characteristics

The solution of the classical Liouville equation ($\omega \equiv 0$) is known and can be expressed by the Green function

$$G(p, q, t; p_0, q_0, t_0) = \delta[p - \overline{p}(t; t_0, p_0, q_0)]\, \delta[q - \overline{q}(t; t_0, p_0, q_0)],$$

where $\overline{p}$ and $\overline{q}$ are the phase space trajectories, which are the solutions of Hamilton's equations together with the initial conditions at $t = t_0 = 0$,

$$\begin{aligned} d\bar{q}/d\tau &= \bar{p}(\tau)/m; \quad \bar{q}(0) = q_0 \\ d\bar{p}/d\tau &= \boldsymbol{F}(\bar{q}(\tau)); \quad \bar{p}(0) = p_0 \end{aligned} \tag{34}$$

G propagates system from phase space point $(p_0, q_0, t = 0)$ to (p, q, t).

Using G, the classical Liouville equation is solved by

$$f(p, q, t) = \int dp_0 dq_0\, G(p, q, t; p_0, q_0, 0)\, f_0(p_0, q_0). \tag{35}$$

Solution of the quantum Liouville equation (QLE)

The QLE is an *inhomogeneous partial differential equation* with the homogeneous part being the classical LE and the inhomogeneity ω.
Formal solution:

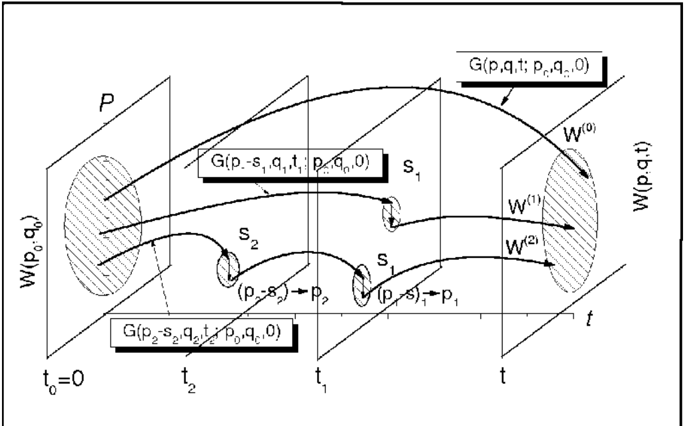
$$\begin{aligned} f(p,q,t) &= \int dp_0 dq_0\, G(p,q,t;p_0,q_0,0)\, f_0(p_0,q_0) \\ &+ \int_0^t dt_1 \int dp_1 dq_1\, G(p,q,t;p_1,q_1,t_1) \int ds_1\, \omega(s_1,q_1,t_1)\, f(p_1-s_1,q_1,t_1). \end{aligned}$$

- Exact *integral* equation, fully equivalent to the QLE (32).
- But: not an explicit solution for f, it also appears under the integral.

Idea (V. Filinov):
attempt iterative solution, considering ω small (small deviations from classical case).
0th order: $f = f^{(0)}$ is 1st line of (36),
1st order: $f = f^{(1)}$ follows from replacing under integral $f \rightarrow f^{(0)}$ etc.

Iteration series

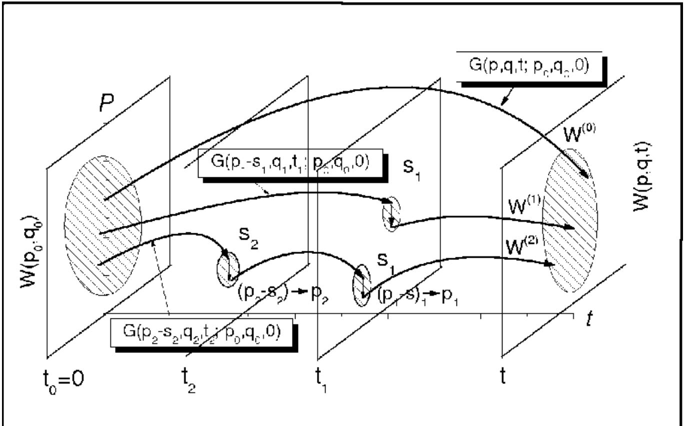
$$f(p,q,t) \quad = \quad f^{(0)}(p,q,t) + f^{(1)}(p,q,t) + f^{(2)}(p,q,t) + \dots$$



Iteration series

$$f(p,q,t) = f^{(0)}(p,q,t) + f^{(1)}(p,q,t) + f^{(2)}(p,q,t) + \ldots$$

$$f^{(0)}(p,q,t) = \int dp_0 dq_0 \, G(p,q,t;p_0,q_0,0) f_0(p_0,q_0),$$



Iteration series

$$\begin{aligned} f\,(p,q,t) &= f^{(0)}(p,q,t) + f^{(1)}\,(p,q,t) + f^{(2)}\,(p,q,t) + \dots \\ f^{(0)}(p,q,t) &= \int dp_0 dq_0\, G(p,q,t;p_0,q_0,0) f_0(p_0,q_0), \\ f^{(1)}\,(p,q,t) &= \int_0^t dt_1 \int dp_1 dq_1\, G(p,q,t;p_1,q_1,t_1) \int ds_1\, \omega(s_1,q_1,t_1) \\ &\times \int dp_0 dq_0\, G(p_1 - s_1, q_1, t_1; p_0, q_0, 0) f_0(p_0,q_0). \end{aligned}$$

f^0: classical propagation G: $(p,q,t) \longleftarrow (\underline{p_0},\underline{q_0},0)$
$\underline{\text{integration}}$ over all possible $\underline{p_0},\underline{q_0}$ with distribution f_0

f^1: two pieces of classical trajectories G:
$(p,q,t) \longleftarrow (\underline{p_1},\underline{q_1},\underline{t_1}) \Longleftarrow (\underline{p_1} - \underline{s_1},\underline{q_1},\underline{t_1}) \longleftarrow (\underline{p_0},\underline{q_0},0)$
in addition: jump of momentum $p_1 \Longleftarrow p_1 - s_1$ with weight $\omega(s)$

Iteration series

Second order term

$$
\begin{aligned}
& f^{(2)}(p, q, t) = \\
& \int_0^t dt_1 \int dp_1 dq_1\, G(p, q, t; p_1, q_1, t_1) \int ds_1\, \omega(s_1, q_1, t_1) \times \\
& \int_0^{t_1} dt_2 \int dp_2 dq_2\, G(p_1 - s_1, q_1, t_1; p_2, q_2, t_2) \int ds_2\, \omega(s_2, q_2, t_2) \times \\
& \int dp_0 dq_0\, G(p_2 - s_2, q_2, t_2; p_0, q_0, 0)\, f_0(p_0, q_0).
\end{aligned}
$$

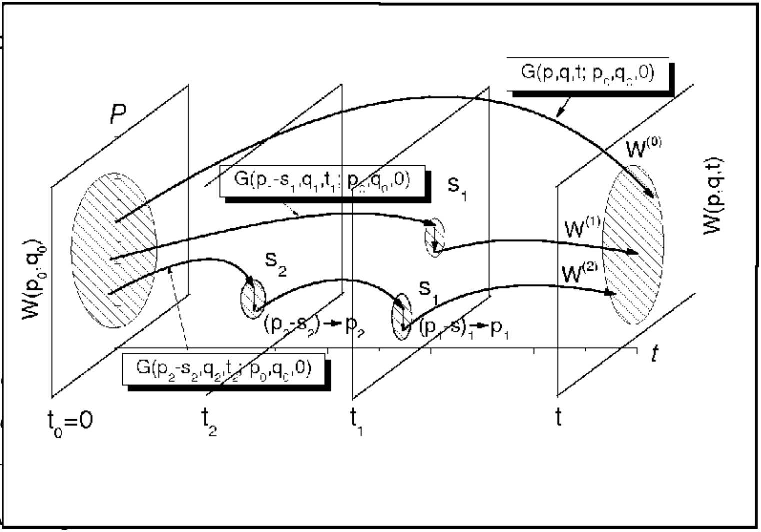
Three classical trajectories G separated by two momentum jumps:

$$
\begin{aligned}
& (p, q, t) \longleftarrow (\underline{p_1}, \underline{q_1}, \underline{t_1}) \Longleftarrow (\underline{p_1} - \underline{s_1}, \underline{q_1}, \underline{t_1}) \longleftarrow \\
& \longleftarrow (\underline{p_2}, \underline{q_2}, \underline{t_2}) \Longleftarrow (\underline{p_2} - \underline{s_2}, \underline{q_2}, \underline{t_2}) \longleftarrow (\underline{p_0}, \underline{q_0}, 0)
\end{aligned}
$$

Obvious generalization to $n-$th order iteration term.
Momentum jumps are consequence of Heisenberg uncertainty.

Iteration series

Sec



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Momentum jumps are consequence of Heisenberg uncertainty.

Computational evaluation of iteration series

$$\begin{aligned} f(p,q,t) &= f^{(0)}(p,q,t) + f^{(1)}(p,q,t) + f^{(2)}(p,q,t) + \ldots \\ f^{(0)}(p,q,t) &= \int dp_0 dq_0 \, G(p,q,t;p_0,q_0,0) f_0(p_0,q_0), \end{aligned}$$

- Initial state: randomly generate phase space points (p_0, q_0) with probability f_0,
- $f^{(0)}$: from each point (p_0, q_0) propagate classical trajectory
- better: to compute $f^{(0)}(p,q,t)$ propagate classical trajectory backward to $(p_0, q_0, 0)$ (use reversibility)
- add up all trajectories by integrating $\int dp_0 dq_0$,
  $6N-$dim integral done by Monte Carlo.

Computation of first iteration term

$$
\begin{aligned}
f^{(1)}(p,q,t) &= \int_0^t dt_1 \int dp_1 dq_1\, G(p,q,t;p_1,q_1,t_1) \int ds_1\, \omega(s_1,q_1,t_1) \\
&\times \int dp_0 dq_0\, G(p_1 - s_1, q_1, t_1; p_0, q_0, 0) f_0(p_0,q_0).
\end{aligned}
$$

- To compute $f^{(1)}(p,q,t)$ propagate classical trajectory backward to (p_1, q_1, t_1)
- Randomly choose time $0 \leq t_1 \leq t$ and momentum s_1, perform momentum shift.
- add up all trajectories, by integrating $\int dp_0 dq_0 dp_1 dq_1 ds_1$, $(6+6+3)N-$dim integral and one time integral done by Monte Carlo.
- additional iteration terms done analogously

Summing up the iteration series

$$\begin{aligned} f(p,q,t) &= f^{(0)}(p,q,t) + f^{(1)}(p,q,t) + f^{(2)}(p,q,t) + \ldots \\ \langle A \rangle &= \langle A \rangle^{(0)} + \langle A \rangle^{(1)} + \langle A \rangle^{(2)} + \ldots \\ \langle A \rangle^{(i)} &= \int dpdq\, A(p,q) f^{(i)}(p,q,t) \end{aligned}$$

- All relevant terms in $f(p,q,t)$ are computed *at once* using importance sampling
- Crucial: for $f^{(0)}$ choose high quality initial distribution, e.g. from equilibrium quantum Monte Carlo calculation.
  This allows to “build in” quantum and spin effects exactly.
- Repeat procedure for any point of (discretized) phase space
- More efficient alternative: skip last step, by computing ensemble average $\langle A \rangle$ instead of $f(p,q,t)$ using Wigner representation (Weyl symbol) of operator A.

Summary

- We considered two methods of quantum molecular dynamics:
- First: semiclassical MD, i.e. classical MD with effective quantum external or pair potentials.
    1. So far this works well in equilibrium, for static properties
    2. Examples, dense hydrogen plasma with electron spin, atoms and molecules [see A. Filinov et al., J. Phys. A: Math. Gen. **36**, 5957 and PRE **70**, 046411 (2004)]
    3. To be included: exchange effects of three and more electrons (clusters) and nonequilibrium effects
- Second: Wigner function QMD – potentially exact quantum method in phase space. “Only” problem: extremely computationally expensive, subject of ongoing research.
- For details see our book “Introduction to Computational Methods for many-body Physics”, M. Bonitz and D. Semkat (eds.), Rinton Press, Princeton 2006 and V. Filinov, M. Bonitz, A. Filinov, and V. Golubnychiy, *Wigner Function Quantum Molecular Dynamics*, ArXiv: cond-mat/0611560, Chapter in: Springer Lecture Notes in Physics **739**, 41, (2008)