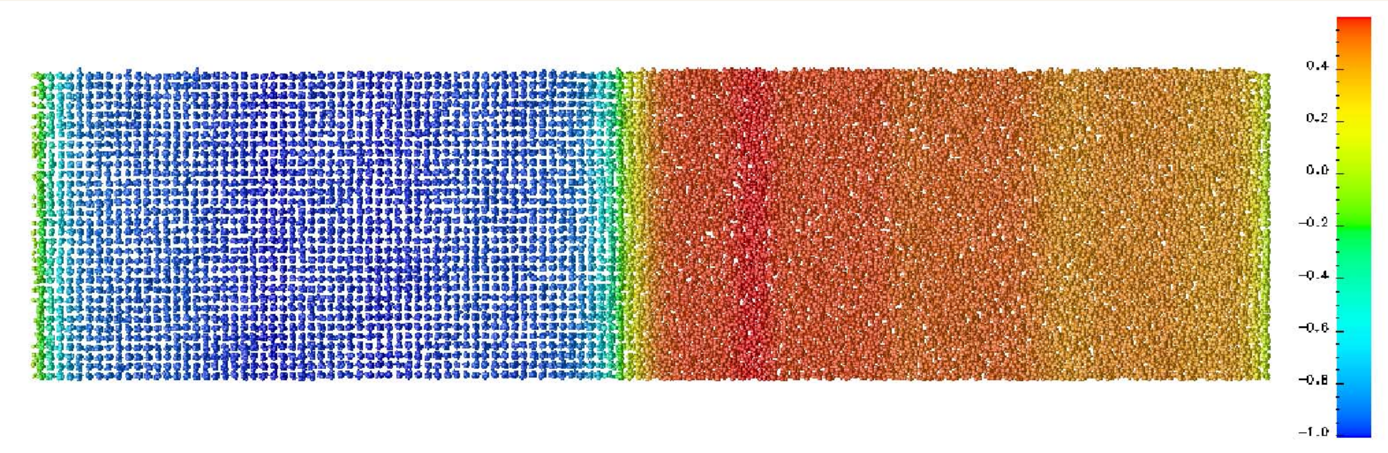
How accurate is molecular dynamics?

Christian Bayer
Håkon Hoel
Petr Plechac
Anders Szepessy
Raul Tempone



In what sense?

Compare with the time-independent Schrödinger

$$H\Phi = E\Phi$$

using observables

$$\int_{\mathbb{R}^{3(N+J)}} g(X)\Phi(x,X)^*\Phi(x,X)\,dxdX - \lim_{T\to\infty} T^{-1}\int_0^T g\big(X(t)\big)dt$$

Which Molecular Dynamics?

$$\ddot{X} = -\lambda'(X) + \,?$$

- What is λ?
- Which observable can be computed and how accurate?
- Which discretization?
- How model temperature T, dissipation and fluctuations?

The Usual MD Derivation

Usual start from *time-dependent* Schrödinger equation [1]:

- self consistent field equation: wave function separated
- Ehrenfest dynamics: classical nuclei paths for large nuclei mass
- Born-Oppenheimer approximation: electron wave function is the ground state.

---

[1] Bornemann F.A., Nettesheim P. and Schütte C., J. Chem. Phys, **105** (1996) 1074–1083;
Tully J.C., Faraday Discuss., **110** (1998) 407–419;
Marx D. and Hutter J., *Ab initio molecular dynamics: Theory and implementation, Modern Methods and Algorithms of Quantum Chemistry*, J.Grotendorst(Ed.), John von Neumann Institute for Computing, Jülich, NIC Series, Vol. 1, ISBN 3-00-005618-1, pp. 301-449, 2000

A Different Derivation

- time-independent Schrödinger as Hamiltonian system
- Hamilton-Jacobi stability theory for different Hamiltonians
- infinite time issue reduced to finite time hitting problem

Inspired by Maslov

Compare with observables from *time-independent* Schrödinger:

- Modify Maslov's WKB-Ansatz[2]:
  - introduce time by momentum in characteristics
  - introduce integrating factor from divergence of momentum
    - modify multicomponent Eikonal and transport eqs.
- Use Hamilton-Jacobi-theory to estimate difference of value functions by difference of Hamiltonians
    - difference of phase functions from difference of Hamiltonians of MD and Schrödinger
    - difference of densities from difference of (differentiated) phase.

[2] Maslov V. P. and Fedoriuk M. V., *Semi-Classical Approximation in Quantum Mechanics*, D. Reidel Publishing (1981)

Difference Between the Two?

+ experimental accuracy of time-independent Schrödinger
+ long time stability and improved convergence rates
+ nuclei paths behave classically without separation and small support
+ stochastic perturbation of ground state leads to Langevin

* only equilibrium situations (?)

Time-independent Schrödinger

Schrödinger: $H(x,X)\Phi(x,X) = E\Phi(x,X)$

$$H(x,X) = V(x,X) - \frac{1}{2M}\sum_{n=1}^{N}\Delta_{X^n}, \quad M \gg 1$$

$$V(x,X) := -\frac{1}{2}\sum_{j=1}^{J}\Delta_{x^j} + \sum_{1\le k<j\le J}\frac{1}{|x^k - x^j|}$$

$$-\sum_{n=1}^{N}\sum_{j=1}^{J}\frac{Z_n}{|x^j - X^n|} + \sum_{1\le n<m\le N}\frac{Z_n Z_m}{|X^n - X^m|}$$

$\Phi \in$ anti-symmetric/symmetric solution space

Error in Observables

Schrödinger observable approximated by molecular dynamics

$$\int_{\mathbb{R}^{3N}} g(X) \underbrace{\Phi \cdot \Phi}_{\int_{\mathbb{R}^{3J}} \Phi^*(x,X)\Phi(x,X)\,dx =: \rho_S} dX - \underbrace{\lim_{T\to\infty} T^{-1} \int_0^T g(X_t)dt}_{=\int g(X)\rho_{MD}(X)dX} =?$$

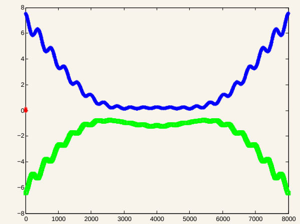
Molecular dynamics example

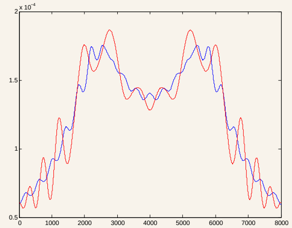
$$\ddot{X}_t = -\lambda'(X_t)$$

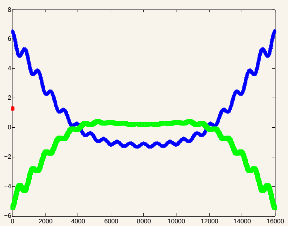
for electron eigenvalue

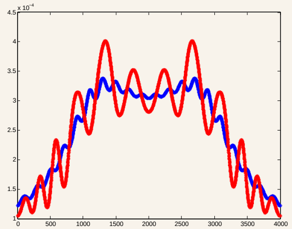
$$V(\cdot, X)\Psi_0(X) = \lambda(X)\Psi_0(X)$$

Electron eigenvalues and density of X: $M = 10, 1000$

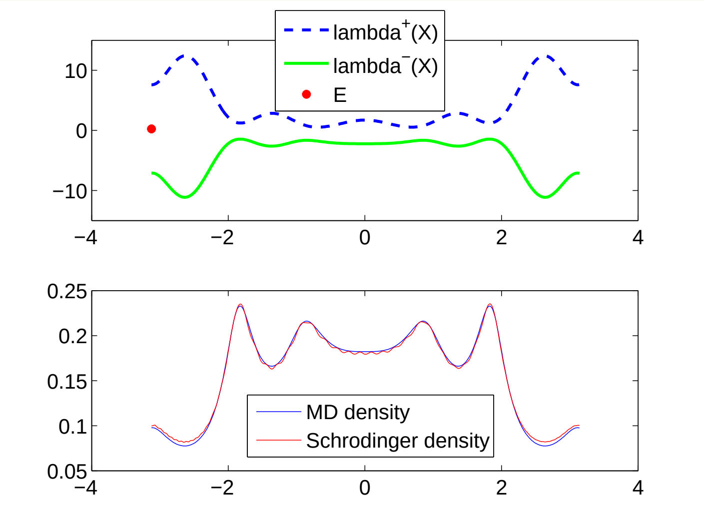


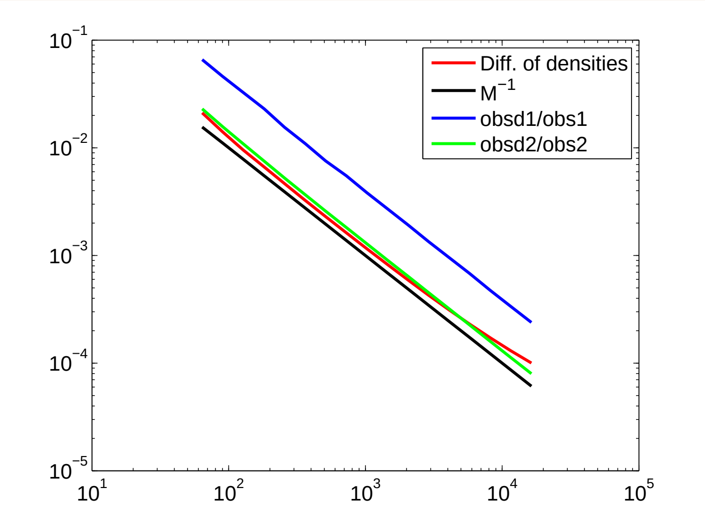




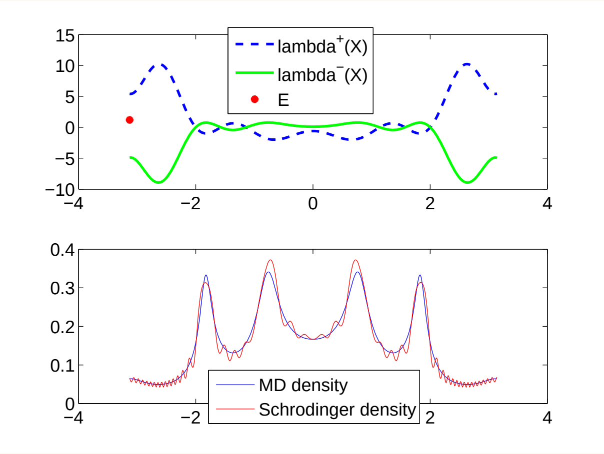


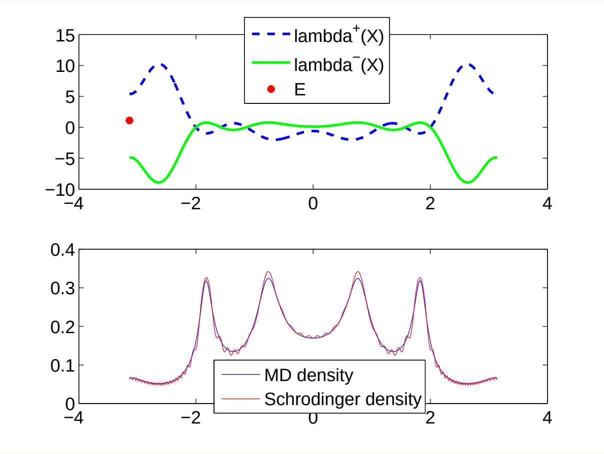
Electron eigenvalues with spectral gap and density

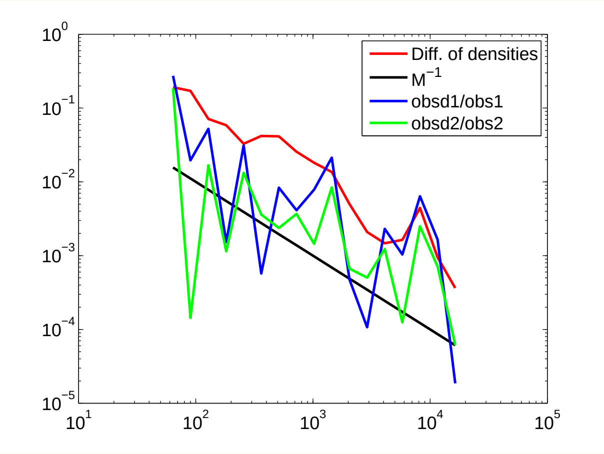




Crossing electron eigenvalues and density







Plan

- WKB-Ansatz
- Eikonal & transport eq. & Born-Oppenheimer
- A theorem on accuracy of BO-approximation
- Stability from Hamilton-Jacobi
- Symplectic Euler
- Caustics

The WKB-Ansatz

$$\Phi(x,X) = \psi(x,X)e^{iM^{1/2}\theta(X)}$$ (Fourier integral for caustics)

implies

$$\begin{aligned}
&(H-E)\psi e^{iM^{1/2}\theta(X)} \\
&= \Big((\frac{|\theta'|^2}{2} + V - E)\psi \\
&\quad - \frac{i}{M^{1/2}}(\psi' \bullet \theta' + \frac{1}{2}\psi\theta'') - \frac{1}{2M}\psi'' \Big) e^{iM^{1/2}\theta},
\end{aligned} \tag{1}$$

HJ:

$$0 = \frac{|\theta'(X)|^2}{2} + \underbrace{\frac{\psi \cdot V(X)\psi}{\psi \cdot \psi}}_{=:V_0(X)} - E + \text{h.o.t.}$$

$$v \cdot w := \int_{\mathbb{R}^{3J}} v^*(x,X)w(x,X)\,dx$$

Eikonal and transport equations

Eikonal:

$$0 = \frac{|\theta'(X)|^2}{2} + V_0(X) - E = 0$$

where

$$V_0(X) := \frac{\psi(X,\cdot)\cdot V(X,\cdot)\psi(X,\cdot)}{\psi(X,\cdot)\cdot\psi(X,\cdot)}$$

with Hamiltonian $|p|^2/2 + V_0(X) - E$ has characteristics

$$\dot{X}_t = p_t$$
$$\dot{p}_t = -V_0'(X_t)$$

Determine ψ:

$$
\begin{aligned}
0 &= (H - E)\psi e^{iM^{1/2}\theta(X)} \\
&= \Big((\frac{|\theta'|^2}{2} + V_0 - E)\psi \\
&\qquad - \frac{i}{M^{1/2}}(\psi' \bullet \theta' + \frac{1}{2}\psi\theta'') + (V - V_0)\psi - \frac{1}{2M}\psi'' \Big) e^{iM^{1/2}\theta}
\end{aligned}
$$

Characteristics

$$\dot{\psi} = \psi'_X \bullet \dot{X} = \psi'_X \bullet \theta'_X$$

and weight function definition

$$\frac{d}{dt}\log G_t = \frac{1}{2}\theta''$$

gives transport equation

$$\frac{i}{M^{1/2}}\frac{d}{dt}(\psi G) = (V - V_0)\psi G - \frac{G}{2M}\psi''$$

with $\varphi := \psi G$

$$\frac{i}{M^{1/2}}\dot{\varphi} = (V - V_0)\varphi - \frac{G}{2M}(\frac{\varphi}{G})''$$

Born-Oppenheimer approximation:

Electron eigenvalue gap implies $\varphi = \Psi_{BO} + \mathcal{O}(M^{-1/2})$ for electron eigenvalue problem

$$V(X, \cdot)\Psi_{BO} = \lambda(X)\Psi_{BO}$$

In the case $\varphi = \Psi_{BO}$:

Hamilton-Jacobi equation

$H_{BO} = \frac{|p|^2}{2} + \lambda(X) - E = 0,$ eigenvalueproblem $V\Psi_{BO} = \lambda\Psi_{BO}$

with $p = \theta'(X)$ has Hamiltonian system

$$\begin{aligned} \dot{X}_t &= p_t \\ \dot{p}_t &= -\lambda'(X_t) \end{aligned}$$

called Born-Oppenheimer dynamics.

Densities: $\rho_{MD} = ?$ $\quad \rho_S = ?$

Two ways:

I. Conservation $\text{div}(\rho_{MD}\,\theta') = 0$

implies $\dot{\rho}_{MD} = -\rho_{MD}\,\theta''$.

II. $\Phi \simeq \Psi_{BO} G^{-1} e^{iM^{1/2}\theta}$ implies

$\rho_{MD} = G^{-2}$ and G-definition gives

$$\frac{d}{dt} \log G^{-2} = -\theta''$$

Equation for $\rho_S = \Phi \cdot \Phi = \psi \cdot \psi$

Multiply (1) by ψ^* integrate in dx; take complex conjugate of (1) multiply by ψ integrate in dx; subtract these:

$$\begin{aligned} -M^{-1/2}\Im(\psi \cdot \Delta_X \psi) &= (\psi'_X \cdot \psi + \psi \cdot \psi'_X) \bullet \theta'_X + \psi \cdot \psi \Delta_X \theta \\ &= \mathrm{div}(\rho_S \theta'_X) \\ &= \rho'_S \bullet \theta'_X + \rho_S \Delta_X \theta \end{aligned}$$

we have $\dot{\rho}_S = \rho'_S \bullet \theta'_X$

so for $\theta = \theta_S$

$$\dot{\rho}_S = -\rho_S \Delta_X \theta_S - M^{-1/2}\Im(\psi \cdot \Delta_X \psi).$$

Compare for $\theta = \theta_{MD}$

$$\dot{\rho}_{MD} = -\rho_{MD} \Delta_X \theta_{MD}$$

The Born-Oppenheimer Approximation

Take electron eigenstate: $\varphi = \Psi_n \ , \quad V(X)\Psi_n = \lambda_n(X)\Psi_n$
implies BO-approximation

$$\dot{X}_t = p_t$$
$$\dot{p}_t = -\lambda_n'(X_t)$$

$$(H-E)\Phi_{MD} = \mathcal{O}(M^{-1/2})$$

Theorem. *Assume*[3] *electron eigenvalue gap*[4]*, bounded hitting time and smooth* θ*, then for any* $\delta > 0$

$$\int g(X)\big(\rho_{MD}-\rho_S\big)dX = \int g(X)\Big(\Phi_{MD}\cdot\Phi_{MD}-\Phi\cdot\Phi\Big)dX = \mathcal{O}(M^{-1+\delta})$$

[3] caustics: $\Phi(x,X) = \int_{\mathbb{R}^d} \psi(x,\hat{X},\check{X}) e^{iM^{1/2}(\check{X}\cdot\check{p}-\tilde{\theta}(\hat{X},\check{p}))} d\check{p}$

[4] non degenerate eigenvalue crossings: $\mathcal{O}(M^{-1/2})$

Difference of Hamiltonians Determines the Error:

1. Use density eqs for ρ_S and ρ_{MD}, Eikonal eqs for θ_S and θ_{MD}
2. Use stability of corresponding Hamilton-Jacobi hitting time eq. for θ: phase perturbation bounded by Hamiltonian perturbation
3. Use stability of Hamilton-Jacobi equation for ρ

2. Stability of Hamiltonian Systems from Hamilton-Jacobi Eq.

Stability of Hamilton-Jacobi equations

$$H(Y, \partial_Y \theta) = 0$$
$$\tilde{H}(\tilde{Y}, \partial_{\tilde{Y}} \tilde{\theta}) = 0$$

gives

$$\|\theta - \tilde{\theta}\|_{L^\infty} \leq C\|H - \tilde{H}\|_{L^\infty}$$

Hamilton-Jacobi density eq.

$$\theta' \bullet (\log \rho)' = -\mathrm{div}\,\theta' - M^{-1/2}\Im(\psi \cdot \Delta_X \psi)$$

Hamiltonians

$$
\begin{aligned}
H_S &= \frac{|p|^2}{2} + \underbrace{\frac{\psi \cdot V\psi}{\psi \cdot \psi}}_{=V_0(X)} - E \\
H_{BO} &= \frac{|p|^2}{2} + \lambda_0(X) - E
\end{aligned}
$$

Hitting problem

$$
\theta(Y_0) = \theta(Y_\tau) - \int_0^\tau h(q_s, Y_s) ds
$$

$$
\begin{aligned}
h_S &= E + \frac{|p|^2}{2} - V_0(X) \\
h_{BO} &= E + \frac{|p|^2}{2} - \lambda_0(X)
\end{aligned}
$$

satisfies the Legendre transform

$$
H(q, X) = \sup_p \big(q \bullet \partial_p H(p, X) - h(p, X) \big).
$$

Stability for Hamilton-Jacobi eq.

$$\underbrace{\tilde\theta(\tilde Y_{\tilde\tau}) - \int_0^{\tilde\tau} \tilde h(\tilde q_t, \tilde Y_t)\,\mathrm{d}t}_{\tilde\theta(\tilde Y_0)} - \underbrace{\Big(\theta(Y_\tau) - \int_0^{\tau} h(q_t, Y_t)\,\mathrm{d}t\Big)}_{\theta(Y_0)}$$

$$= -\int_0^{\tilde\tau} \tilde h(\tilde q_t, \tilde Y_t)\,\mathrm{d}t + \theta(\tilde Y_{\tilde\tau}) - \underbrace{\theta(Y_0)}_{\theta(\tilde Y_0)} + \tilde\theta(\tilde Y_{\tilde\tau}) - \theta(\tilde Y_{\tilde\tau})$$

$$= -\int_0^{\tilde\tau} \tilde h(\tilde q_t, \tilde Y_t)\,\mathrm{d}t + \int_0^{\tilde\tau} \mathrm{d}\theta(\tilde Y_t) + \tilde\theta(\tilde Y_{\tilde\tau}) - \theta(\tilde Y_{\tilde\tau})$$

$$= \int_0^{\tilde\tau} \underbrace{-\tilde h(\tilde q_t, \tilde Y_t) + \theta'(\tilde Y_t) \bullet \partial_q \tilde H(\tilde q_t, \tilde Y_t)}_{\le \tilde H\left(\theta'(\tilde Y_t), \tilde Y_t\right)}\,\mathrm{d}t + \tilde\theta(\tilde Y_{\tilde\tau}) - \theta(\tilde Y_{\tilde\tau})$$

$$\le \int_0^{\tilde\tau} (\tilde H - H)\big(\theta'(\tilde Y_t), \tilde Y_t\big)\,\mathrm{d}t + \tilde\theta(\tilde Y_{\tilde\tau}) - \theta(\tilde Y_{\tilde\tau})$$

Symplectic Euler simulations:

For Born-Oppenheimer Hamiltonian $H_{BO} := \frac{1}{2}|p|^2 + \lambda_0(X) - E$

$$\bar{X}_{n+1} = \bar{X}_n + \Delta t \partial_p H_{BO}(\bar{X}_n, \bar{p}_{n+1})$$
$$\bar{p}_{n+1} = \bar{p}_n - \Delta t \partial_X H_{BO}(\bar{X}_n, \bar{p}_{n+1})$$

define

$$\bar{\theta}(\bar{X}_t) = \int_t^{(n+1)\Delta t} \Big(\lambda_0(\bar{X}_m) - \frac{1}{2}|\bar{p}_{m+1}|^2 - E\Big) ds + \bar{\theta}(\bar{X}_{n+1})$$

then

$$\Big| H_{BO}\big(\partial_X \bar{\theta}(X), X\big)\Big| = \mathcal{O}(\Delta t)$$

yields explicit construction of perturbed Hamiltonian system as in M. Sandberg & A. Sz. M2AN 2006 using[5]:

[5] not based on formal modified equation expansion

steps in 2006 proof

- symplectic $\iff \partial_X \bar{\theta}(X_n, t_n) = \bar{p}_n$
- continuous piecewise linear extension $(\bar{X}_t, \bar{p}_t)$
- $d\bar{\theta}(\bar{X}_t, t)/dt = \ldots$ along optimal path

HJ stability with this perturbed Hamiltonian yields accuracy

$$\int g(X)\big(\rho_{MDN} - \rho_S)dX = \mathcal{O}(M^{-1} + \Delta t)$$

Caustics

WKB Ansatz

$$\Phi(X,x) = \int_{\mathbb{R}^d} \tilde{\psi}(X,x) e^{iM^{1/2}(\check{X}\bullet\check{p} - \tilde{\theta}(\hat{X},\check{p}))} d\check{p}$$

Schrödinger solution

$$0 = (H - E)\Phi$$

$$= \int_{\mathbb{R}^d} \Big(\frac{|\partial_{\hat{X}}\tilde{\theta}(\hat{X},\check{p})|^2}{2} + \frac{|\check{p}|^2}{2} + V_0(X) - E \Big) \tilde{\psi}(X,x) e^{iM^{1/2}\left(\check{X}\bullet\check{p} - \tilde{\theta}(\hat{X},\check{p})\right)} d\check{p}$$

$$- \int_{\mathbb{R}^d} \Big(iM^{-1/2}(\partial_{\hat{X}}\tilde{\psi} \bullet \partial_{\hat{X}}\tilde{\theta} + \partial_{\check{X}}\tilde{\psi} \bullet \check{p} + \frac{1}{2}\tilde{\psi}\partial_{\hat{X}\hat{X}}\tilde{\theta})$$

$$- (V - V_0)\tilde{\psi} - \frac{1}{2M}\partial_{XX}\tilde{\psi} \Big) e^{iM^{1/2}\left(\check{X}\bullet\check{p} - \tilde{\theta}(\hat{X},\check{p})\right)} d\check{p}.$$

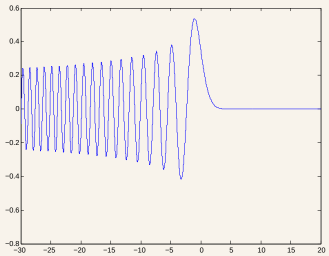
Simplest caustic

Scaled Airy-function

$$u(x) = C \int_{\mathbb{R}} e^{iM^{1/2}(xq - q^3/3)} dq.$$

solves Schrödinger

$$-M^{-1}u''(x) - xu(x) = 0.$$



Eikonal equation

Eikonal eq.

$$\frac{|\partial_{\hat{X}}\tilde{\theta}(\hat{X},\check{p})|^2}{2} + \frac{|\check{p}|^2}{2} + V_0\big(\hat{X}, \partial_{\check{p}}\tilde{\theta}(\hat{X},\check{p})\big) - E = 0$$

gives

$$\int_{\mathbb{R}^d} \Big(\frac{|\partial_{\hat{X}}\tilde{\theta}|^2}{2} + \frac{|\check{p}|^2}{2} + V_0(X) - E\Big) e^{iM^{1/2}\left(\check{X}\bullet\check{p} - \tilde{\theta}(\hat{X},\check{p})\right)} d\check{p}$$
$$= M^{-1/2} \underbrace{s(\hat{X},\check{X})}_{s_0 + iM^{-1/2}s_1} \int_{\mathbb{R}^d} e^{iM^{1/2}\left(\check{X}\bullet\check{p} - \tilde{\theta}(\hat{X},\check{p})\right)} d\check{p}$$

Transport equation

$$iM^{-1/2}(\dot{\tilde{\psi}} + \tilde{\psi}\frac{\dot{G}}{G}) = (V - V_0)\tilde{\psi} - (2M)^{-1}(\partial_{XX}\tilde{\psi} + s_1\tilde{\psi})$$

for G defined by

$$\frac{d}{dt}\log G = \frac{1}{2}\big(s_0(X) + \partial_{\hat{X}\hat{X}}\hat{\theta}(X)\big),$$

gives actual Schrödinger solution (not only asymptotic solution).

Schrödinger density

$$\int \underbrace{g(X)\tilde{\psi} \cdot \tilde{\psi}}_{=:\tilde{g}(X)} e^{iM^{1/2}(\check{X} \bullet \check{p} - \tilde{\theta}(\hat{X},\check{p}))} e^{-iM^{1/2}(\check{X} \bullet \check{q} - \tilde{\theta}(\hat{X},\check{q}))} d\check{p} d\check{q} dX$$

$$= \int \hat{\tilde{g}}(\hat{X}, M^{1/2}(\check{p} - \check{q})) e^{iM^{1/2}(\tilde{\theta}(\hat{X},\check{q}) - \tilde{\theta}(\hat{X},\check{p}))} d\check{p} d\check{q} d\hat{X}$$

$$= \int \hat{\tilde{g}}(\hat{X}, M^{1/2}(\check{p} - \check{q})) e^{iM^{1/2}(2^{-1}(\check{p}-\check{q})\bullet\partial_{\check{p}})^3 \tilde{\theta}(\hat{X},(\check{p}+\check{q})/2+\gamma(\check{p}-\check{q})/2)/3} \times$$

$$\times\, e^{iM^{1/2} 2^{-1}(\check{p}-\check{q})\bullet\partial_{\check{p}}\tilde{\theta}(\hat{X},(\check{p}+\check{q})/2)} d(\check{p} - \check{q}) d(\check{p} + \check{q}) d\hat{X}/4$$

$$= \int \tilde{g} * A_M\big(\hat{X}, \underbrace{\partial_{\check{p}}\tilde{\theta}(\hat{X}, (\check{p} + \check{q})/2)}_{=\check{X}}\big) d(\check{p} + \check{q}) d\hat{X}/2$$

$$= \int \tilde{g} * A_M(\hat{X}, \partial_{\check{p}}\tilde{\theta}(\hat{X}, \check{X})) |\mathsf{det} \frac{\partial(\check{p})}{\partial(\check{X})}| dX$$

In the convolution $\tilde{g} * A_M$, the function A_M is the Fourier transform of

$$e^{i(\omega\bullet\partial_{\check{p}})^3 \tilde{\theta}(\hat{X},\check{p})/M}\Big|_{\check{p}=((\check{p}+\check{q})/2+\gamma\omega}$$

$$
\begin{aligned}
\int_{\mathbb{R}^d} A_M(\check{X}) d\check{X} &= 1, \\
\int_{\mathbb{R}^d} \check{X}_i A_M(\check{X}) d\check{X} &= 0, \\
\int_{\mathbb{R}^d} \check{X}_i \check{X}_j A_M(\check{X}) d\check{X} &= 0, \\
M \int_{\mathbb{R}^d} \check{X}_i \check{X}_j \check{X}_k A_M(\check{X}) d\check{X} &= \mathcal{O}(1).
\end{aligned}
$$

Comparing Schrödinger and MD densities

$$\rho_S = e^{\int s_0 + \partial_{XX}\tilde{\theta} dt} \mathsf{det} \frac{\partial(\check{p})}{\partial(\check{X})}$$

$$\rho_{MD} = e^{\int \partial_{XX}\theta dt}$$

$$s_0 = \sum_j \partial_{\check{p}_j} V_j'(\hat{X}, \tilde{\theta}'(\check{p})) = \sum_j \frac{d}{dt} \log V_j' = -\sum_j \frac{d}{dt} \log(\check{p}_j \frac{\partial \check{p}_j}{\partial \check{X}_j})$$

$$\partial_{X_j X_j}\theta = \partial_{X_j} p_j = \frac{d}{dt} \log p_j$$

Idea: Transport equation is HS for Eikonal

HJ generates characteristics so that WKB Ansatz becomes a Schrödinger solution

- $\theta = \theta(X, \varphi^r), \quad \varphi = \varphi^r + i\varphi^i, \quad \psi(X, x) = \varphi(X, x)/G(X)$
- $\Phi(x, X_t) = \psi(x, X_t) e^{iM^{1/2} \int_0^t \partial_X \theta(X_s, \varphi^r_s) dX_s}$
- what are h.o.t?

The new WKB-Ansatz

$$
\begin{aligned}
&(H-E)\psi e^{iM^{1/2}\int \theta'_X(X_s,\varphi^r_s)dX_s} \\
&= \Big((\frac{|\theta'_X|^2}{2} + V_0 - E)\psi \\
&\underbrace{- \frac{i}{M^{1/2}}(\psi'_X \bullet \theta'_X + \frac{1}{2}\psi\theta'') + (V-V_0)\psi - \frac{1}{2M}\psi''}_{(*)} \Big) e^{iM^{1/2}\int \theta'_X(X,\varphi^r)dX} \\
&= 0,
\end{aligned}
$$

Introduce time by characteristics:

$$\psi' \bullet \theta' = \psi' \bullet p = \psi' \bullet \dot{X} = \dot{\psi}(X_t, x)$$

The idea:

[1] HJ: $|\theta'_X(X,\varphi^r)|^2/2 + V_0(X,\varphi) - E = 0$

[2] its characteristics implies $(*) = 0$.

Ehrenfest: neglect $\psi''/(2M)$

$$[1] \qquad H_E = \frac{|p|^2}{2} + V_0(X,\varphi) - E = 0 \qquad V_0 = ?$$

$$[2] \qquad -iM^{-1/2}G^{-1}\frac{d}{dt}(\psi G) + (V - V_0)\psi = 0, \qquad \dot{G}/G = \frac{1}{2}\mathsf{div}_X \theta'_X$$

$\varphi := \psi G$ implies time-dependent Schrödinger

$$i\dot{\varphi} = M^{1/2}(V - V_0)\varphi$$

Find V_0

$V_0 := 2^{-1} M^{1/2} \phi \cdot V \phi$ gives characteristics

$$\dot{X} = p \qquad (= \partial_p H_E)$$
$$\dot{p} = \frac{M^{1/2}}{2} \phi \cdot V' \phi \qquad (= -\partial_X H_E)$$
$$i M^{-1/2} \dot{\phi} = V \phi$$

The phase shift and normalization

$$\varphi = \phi e^{i \int V_0 ds} \qquad \frac{M^{1/2}}{2} = \frac{1}{\phi \cdot \phi}$$

imply

$$i M^{-1/2} \dot{\varphi} = (V - V_0) \varphi$$

so V_0 gives [1] & [2] and Schrödinger solution to M^{-1} accuracy

Modify Hamiltonian to also include $\frac{1}{2M}\psi''$

$$[1] \qquad H_S = \frac{|p|^2}{2} + V_S(X,\varphi) - E = 0$$

$$[2] \qquad i\dot{\varphi} = M^{1/2}\Big((V - V_0)\varphi - \frac{G}{M}\Delta_X(\frac{\varphi}{G})\Big)$$

$$H_S := \frac{|\theta'_X(X,\phi_r)|^2}{2} + V_S - E = 0$$

$$V_S := \frac{M^{1/2}}{2}\Big(\phi \cdot V\phi + \frac{G}{2M}\Delta\frac{\phi\cdot\phi}{G}\Big)$$

$$\frac{M^{1/2}}{2} = \frac{\int dX_0}{\int \phi_t \cdot \phi_t \, dX_0}$$

with X and (t, X_0) Eulerian-Lagrangian coordinate change.

The WKB Ansatz yields

$$(H - E)\psi e^{iM^{1/2}\int \theta'_X(X,\phi^r)dX}$$

$$= \Big((\frac{|\theta'_X|^2}{2} + V_S - E)\psi$$

$$- \frac{i}{M^{1/2}}(\psi'_X \bullet \theta'_X + \frac{1}{2}\psi\theta'') + (V - V_S)\psi - \frac{1}{2M}\psi''\Big) e^{iM^{1/2}\int \theta'_X(X,\phi^r)dX}$$

$$= 0,$$

and the Hamiltonian system is

$$\dot{X} = p \qquad (= \partial_p H_S)$$

$$\dot{p} = \frac{M^{1/2}}{2}\big(\phi \cdot V'\phi + \partial_X \frac{G}{2M} \Delta \frac{\phi \cdot \phi}{G}\big) \qquad (= -\partial_X H_S)$$

$$i\dot{\phi} = M^{1/2}\check{V}\phi$$

where

$$\check{V}\phi := V\phi - \frac{G}{2M}\Delta_X(\frac{\phi}{G})$$

$$\varphi = \phi\, e^{i\int V_S ds}$$

$$i\dot{\varphi} = M^{1/2}(\check{V} - V_S)\varphi$$

now includes the $\frac{1}{2M}\psi''$ term.

The Ehrenfest Approximation

$$\dot{X}_t = p_t$$
$$\dot{p}_t = -\phi_t \cdot V'(X_t)\phi_t$$
$$\frac{i}{M^{1/2}}\dot{\phi}_t = V(X_t)\phi_t$$

is Hamiltonian system for HJ

$$H_E := |p|^2/2 + \phi \cdot V(X)\phi - E = 0$$

with characteristics $(X, \varphi_r; p, \varphi_i)$ and $\varphi := 2^{1/2}M^{-1/4}\phi$;

and $\hat{\varphi}_t := \phi_t e^{iM^{1/2}\int_0^t \phi_s \cdot V(X_s)\phi_s ds}$ implies

$$\frac{i}{M^{1/2}}\dot{\hat{\varphi}}_t = (V - V_0)\hat{\varphi}_t$$

Ehrenfest Observables Accuracy

$$\hat{\Phi} := \hat{G}^{-1}\hat{\varphi}e^{iM^{1/2}\int \hat{\theta}'_X dX}$$

implies

$$(H-E)\hat{\Phi} = \mathcal{O}(M^{-1})$$

Theorem. *Assume*[6] *electron eigenvalue gap*[7], *bounded hitting time and smooth* θ, *then for any* $\delta > 0$

$$\int g(X)\big(\hat{\rho} - \rho\big)dX := \int g(X)\big(\hat{\Phi}\cdot\hat{\Phi} - \Phi\cdot\Phi\big)dX = \mathcal{O}(M^{-1+\delta}).$$

---

[6] caustics: $\Phi(x,X) = \int_{\mathbb{R}^d} \psi(x,\hat{X},\check{X})e^{iM^{1/2}(\check{X}\cdot\check{p}-\tilde{\theta}(\hat{X},\check{p}))}d\check{p}$

[7] non degenerate eigenvalue crossings: $\mathcal{O}(M^{-1/2})$

Dynamics from the time-dependent Schrödinger

$$i\partial_t \Phi(x, X, t) = H(x, X)\Phi(x, X, t)$$

$$H(x, X) = V(x, X) - \frac{1}{2M}\sum_{n=1}^{N} \Delta_{X^n}, \quad M \gg 1$$

$$\begin{aligned} V(x, X) &= -\frac{1}{2}\sum_{j=1}^{J} \Delta_{x^j} + \sum_{1\leq k<j\leq J} \frac{1}{|x^k - x^j|} \\ &\quad - \sum_{n=1}^{N}\sum_{j=1}^{J} \frac{Z_n}{|x^j - X^n|} + \sum_{1\leq n<m\leq N} \frac{Z_n Z_m}{|X^n - X^m|} \\ &=: -\frac{1}{2}\sum_{j=1}^{J} \Delta_{x^j} + H_I \end{aligned}$$

$$v \cdot w := \int_{\mathbb{R}^{3J}} v^*(x, X, t) w(x, X, t)\, dx$$

$$\langle v, w \rangle := \int_{\mathbb{R}^{3N}} \int_{\mathbb{R}^{3J}} v^*(x, X, t) w(x, X, t)\, dx\, dX$$

Usual derivation:

1. self consistent field equation: wave function is product of nuclei and electron function
2. Ehrenfest dynamics: nuclei wave function becomes point measure
3. Born-Oppenheimer approximation: electron wave function is the ground state.

1. Time-dependent self consistent field equations

Approximation Ansatz of separation

$$\Phi(x, X, t) = \Psi_N(X, t)\Psi_E(x, t)\ \exp\left(i\int_0^t \underbrace{\langle \Psi_N^s \Psi_E^s, H_I \Psi_E^s \Psi_N^s\rangle}_{\bar{H}_I}\, ds\right)$$

satisfies time dependent *self consistent field equation*[8]

$$i\partial_t \Psi_N = \Big(-(2M)^{-1}\sum_{n=1}^{N}\Delta_{X_n} + \Psi_E \cdot H_I(X)\Psi_E\Big)\Psi_N,$$

$$i\partial_t \Psi_E = \Big(\int_{\mathbb{R}^{3N}} \Psi_N^*(X)V(X)\Psi_N(X)\, dX\Big)\Psi_E.$$

[8] Dirac P.A.M., Proc. Cambridge Phil. Soc. **26** (1930) 376–385.

Φ solves perturbed full Schrödinger

$$i\partial_t \Phi = \Big(-(2M)^{-1} \sum_{n=1}^{N} \Delta_{X_n} - \frac{1}{2} \sum_{j=1}^{J} \Delta_{x_j} + \Psi_E \cdot H_I \Psi_E + \int_{\mathbb{R}^{3N}} \Psi_N^* H_I \Psi_N dX - \bar{H}_I \Big) \Phi,$$

and compactly supported Ψ_N in δ small domain leads[9] to $\mathcal{O}(\delta)$ approximation of full Schrödinger in $L^2(dxdX)$.

[9] Bornemann F.A., Nettesheim P. and Schütte C., J. Chem. Phys, **105** (1996) 1074–1083.

2. Ehrenfest dynamics from WKB

$$\Psi_N = \psi e^{iM^{1/2}\theta}$$

leads to Ehrenfest

$$\begin{aligned} \ddot{X} &= -\Psi_E \cdot \partial_X V(X) \Psi_E \\ iM^{-1/2}\dot{\Psi}_E &= V\Psi_E \end{aligned}$$

(X, Ψ_E) approximates[10] TDSCF with error $\mathcal{O}(\delta^2 + M^{-1/2})$

---

[10] Bornemann F.A., Nettesheim P. and Schütte C., J. Chem. Phys, **105** (1996) 1074–1083.
Tully J.C., Faraday Discuss., **110** (1998) 407–419.
Marx D. and Hutter J., *Ab initio molecular dynamics: Theory and implementation, Modern Methods and Algorithms of Quantum Chemistry*, J.Grotendorst(Ed.), John von Neumann Institute for Computing, Jülich, NIC Series, Vol. 1, ISBN 3-00-005618-1, pp. 301-449, 2000

3. Born-Oppenheimer approximation: $\Psi_E =$ ground state

An electron eigenstate: $\Psi_E = \Psi_n$

$$V(X)\Psi_n = \lambda_n(X)\Psi_n$$

implies

$$\ddot{X} = -\Psi_n \cdot \partial_X V(X)\Psi_n = -\partial_X \lambda_n(X)$$

Spectral gap can be used to prove[11] $\mathcal{O}(M^{-1/4})$ approximation of Schrödinger in L^2.

[11] Hagedorn G.A., Commun. Math. Phys., **77** (1980) 1–19.
Panati G., Spohn H. and Teufel S., Math. Mod. Numer. Anal.