NUMERICAL ANALYSIS OF HIGH-DIMENSIONAL QUANTUM DYNAMICS

CAROLINE LASSER

For preparing the lectures I have used:

- the review *Computing quantum dynamics in the semiclassical regime* by Christian Lubich and myself, that will appear at Acta Numerica some time this year. A preprint version is available at `https://arxiv.org/abs/2002.00624`.
- the blue book *From quantum to classical molecular dynamics: reduced models and numerical analysis* by Christian Lubich, EMS, 2008.

Date: Lectures at ENPC, Paris, version of March 13, 2020. The last two lectures scheduled for March 13th, 2020, have been cancelled because of the coronavirus pandemic.

1. Variational approximation (March 4th, 14:00-16:00)

(1) The equation:

$$\mathrm{i}\varepsilon\partial_t\psi = -\tfrac{\varepsilon^2}{2}\Delta_x\psi + V\psi, \qquad \psi(0)=\psi_0,$$

where $\varepsilon > 0$ is small, $V : \mathbb{R}^d \to \mathbb{R}$ is smooth and subquadratic, $\psi_0 \in L^2(\mathbb{R}^d)$.

(2) The ε-d combination:
  (a) $\psi : \mathbb{R}^\times\mathbb{R}^d \to \mathbb{C}$ is highly oscillatory,

$$\forall\alpha \in \mathbb{N}_0^{d+1}\ \exists C_\alpha > 0 : \|(\varepsilon\partial_{t,x})^\alpha\psi(t)\|_{L^2(\mathbb{R}^d)} < C_\alpha.$$

  (b) ψ is highly localized in space and frequency.
  (c) $d \gg 1$.

(3) Meshfree instead of grid-based discretization.

(4) If V is smooth and subquadratic, then $H = -\frac{\varepsilon^2}{2}\Delta + V$ is self-adjoint on $D(H)$, and we mean by the solution of the Schrödinger equation the function

$$\psi(t) = \mathrm{e}^{-\mathrm{i}Ht/\varepsilon}\psi(0), \quad t \in \mathbb{R}.$$

(5) Time-dependent Dirac–Frenkel variational principle: Let $\mathcal{M}$ be a sub-manifold of $L^2(\mathbb{R}^d)$ such that for all $u \in \mathcal{M}$ the tangent space $\mathcal{T}_u\mathcal{M}$ is a complex linear vector space with $u \in \mathcal{T}_u\mathcal{M}$. Assume $\psi_0 \in \mathcal{M}$. Let $P_u : L^2(\mathbb{R}^d) \to \mathcal{T}_u\mathcal{M}$ denote the orthogonal projection on $\mathcal{T}_u\mathcal{M}$. We hope that the solution $u(t) \in \mathcal{M}$ of

$$\mathrm{i}\varepsilon\partial_t u = P_u H u, \quad u(0) = \psi_0,$$

is a good approximation to $\psi(t)$.

(6) Notation: We denote for $f, g \in L^2(\mathbb{R}^d)$

$$\langle f \mid g\rangle = \int_{\mathbb{R}^d} \overline{f(x)}g(x)\mathrm{d}x \quad \text{and} \quad \|f\| = \sqrt{\langle f \mid f\rangle}.$$

(7) Orthogonal projections: We consider a finite-dimensional subspace V with an orthonormal basis $v_1, \dots, v_n$. Then, the orthogonal projection

$$Pw = \sum_{k=1}^n \langle v_k \mid w\rangle v_k, \qquad w \in L^2(\mathbb{R}^d),$$

is indeed a projection ($P^2 = P$) and orthogonal in the sense that $P^* = P$, since we have for all $w, w' \in L^2(\mathbb{R}^d)$,

$$P^2 w = \sum_{k=1}^{n} \langle v_k \mid Pw \rangle v_k = \sum_{k,\ell=1}^{n} \langle v_\ell \mid w \rangle \underbrace{\langle v_k \mid v_\ell \rangle}_{=\delta_{k\ell}} v_k = Pw,$$

$$\langle w \mid Pw' \rangle = \sum_{k=1}^{n} \langle w \mid v_k \rangle \langle v_k \mid w' \rangle = \langle Pw \mid w' \rangle.$$

(8) Norm and energy conservation: We have

$$\|\psi(t)\| = \|u(t)\| = \|\psi_0\| \quad \text{and}$$
$$\langle \psi(t) \mid H\psi(t) \rangle = \langle u(t) \mid Hu(t) \rangle = \langle \psi_0 \mid H\psi_0 \rangle$$

for all t.

(9) *Proof.* We work with $A = \mathbb{I}$ and $A = H$. We differentiate

$$\tfrac{\mathrm{d}}{\mathrm{d}t} \langle \psi(t) \mid A\psi(t) \rangle = \tfrac{1}{\mathrm{i}\varepsilon} \langle \psi(t) \mid [A, H]\psi(t) \rangle = 0,$$
$$\tfrac{\mathrm{d}}{\mathrm{d}t} \langle u(t) \mid Au(t) \rangle = \tfrac{1}{\mathrm{i}\varepsilon} \langle u(t) \mid [A, P_u H]u(t) \rangle = 0.$$

For the variational energy conservation, we rewrite the variational evolution $\mathrm{i}\varepsilon\partial_t u = P_u H u$ as

$$\partial_t u \in \mathcal{T}_u\mathcal{M} \quad \text{and} \quad \forall v \in \mathcal{T}_u\mathcal{M} : \langle v \mid \mathrm{i}\varepsilon\partial_t u - Hu \rangle = 0.$$

Then, since H is self-adjoint and $\partial_t u \in \mathcal{T}_u\mathcal{M}$,

$$\begin{aligned} \tfrac{\mathrm{d}}{\mathrm{d}t} \langle u(t) \mid Hu(t) \rangle &= 2\,\mathrm{Re}\,\langle \partial_t u(t) \mid Hu(t) \rangle \\ &= 2\,\mathrm{Re}\,\langle \partial_t u(t) \mid i\varepsilon\partial_t u(t) \rangle = 0. \end{aligned}$$

□

(10) A posteriori error (cf. Lubich' 05):

$$\|\psi(t) - u(t)\| \le \int_0^t \|\tfrac{1}{\mathrm{i}\varepsilon} P_{u(s)}^{\perp} Hu(s)\| \,\mathrm{d}s,$$

where $P_u^{\perp} = \mathbb{I} - P_u$ denotes the projection on the orthogonal complement of $\mathcal{T}_u\mathcal{M}$. Note that

$$\|\tfrac{1}{\mathrm{i}\varepsilon} P_{u(s)}^{\perp} Hu(s)\| = \mathrm{dist}\big(\tfrac{1}{\mathrm{i}\varepsilon} Hu(s), \mathcal{T}_{u(s)}\mathcal{M}\big)\,.$$

Proof. We check the Duhamel principle,

$$\psi(t) - u(t) = \frac{1}{\mathrm{i}\varepsilon} \int_0^t \mathrm{e}^{-\mathrm{i}H(t-s)/\varepsilon} (H - P_{u(s)}H) u(s) \mathrm{d}s,$$

by differentiating the left and the right hand side. Indeed,

$$e(t) = \frac{1}{\mathrm{i}\varepsilon}\int_0^t \mathrm{e}^{-\mathrm{i}H(t-s)/\varepsilon}(H - P_{u(s)}H)u(s)\mathrm{d}s$$

satisfies

$$\mathrm{i}\varepsilon\partial_t e(t) = (H - P_{u(t)}H)u(t) + He(t),$$

whereas

$$\mathrm{i}\varepsilon\partial_t(\psi(t) - u(t)) = (H - P_{u(t)}H)u(t) + H(\psi(t) - u(t)).$$

Since $\mathrm{e}^{-\mathrm{i}Ht/\varepsilon}$ is unitary and thus norm-conserving, we obtain the claimed estimate. □

(11) The stability point of view: We have just encountered that $e(t) = \psi(t) - u(t)$ satisfies the Schrödinger equation

$$\partial_t e = \frac{1}{\mathrm{i}\varepsilon}He + d, \quad e(0) = 0$$

up to a defect $d(t) = \frac{1}{\mathrm{i}\varepsilon}P^{\perp}_{u(t)}Hu(t)$. The a posteriori estimate can be rephrased as

$$\|e(t)\| \le \int_0^t \|d(s)\|\mathrm{d}s.$$

(12) Our first example: Gaussians. Let $z = (q, p) \in \mathbb{R}^{2d}$ and

$$g_z(x) = (\pi\varepsilon)^{-d/4}\exp(-\tfrac{1}{2\varepsilon}|x - q|^2 + \tfrac{\mathrm{i}}{\varepsilon}p^T(x - q)).$$

Then,

$$\begin{aligned}\|g_z\|^2 &= (\pi\varepsilon)^{-d/2}\int_{\mathbb{R}^d}\exp(-\tfrac{1}{\varepsilon}|x - q|^2)\mathrm{d}x\\ &= \pi^{-d/2}\int_{\mathbb{R}^d}\exp(-|y|^2)\mathrm{d}y = 1\end{aligned}$$

and

$$\langle g_z \mid xg_z\rangle = \pi^{-d/2}\int_{\mathbb{R}^d}(y + q)\exp(-|y|^2)\mathrm{d}y = q.$$

(13) Fourier transform: Let

$$\widehat{\psi}(\xi) = (2\pi\varepsilon)^{-d/2}\int_{\mathbb{R}^d}\mathrm{e}^{-\mathrm{i}x\cdot\xi/\varepsilon}\psi(x)\mathrm{d}x$$

for $\psi \in L^2(\mathbb{R}^d)$. Then,

$$\begin{aligned}\widehat{g}_{(q,p)}(\xi) &= \text{const.}\, \mathrm{e}^{-\mathrm{i}p\cdot q/\varepsilon} \int_{\mathbb{R}^d} \mathrm{e}^{-\mathrm{i}x\cdot(\xi-p)/\varepsilon} \exp(-\tfrac{1}{2\varepsilon}|x-q|^2)\mathrm{d}x \\ &= \text{const.}\, \mathrm{e}^{-\mathrm{i}\xi\cdot q/\varepsilon} \int_{\mathbb{R}^d} \mathrm{e}^{-\mathrm{i}y\cdot(\xi-p)/\varepsilon} \exp(-\tfrac{1}{2\varepsilon}|y|^2)\mathrm{d}y \\ &= (\pi\varepsilon)^{-d/4} \mathrm{e}^{-\mathrm{i}\xi\cdot q/\varepsilon} \exp(-\tfrac{1}{2\varepsilon}|\xi-p|^2) \\ &= \mathrm{e}^{-\mathrm{i}q\cdot p/\varepsilon} g_{(p,-q)}(\xi).\end{aligned}$$

We observe that

$$\begin{pmatrix} p \\ -q \end{pmatrix} = \begin{pmatrix} 0 & \mathbb{I} \\ -\mathbb{I} & 0 \end{pmatrix} \begin{pmatrix} q \\ p \end{pmatrix}.$$

In particular,

$$\langle g_z \mid (-\mathrm{i}\varepsilon\nabla) g_z \rangle = \langle \hat{g}_z \mid \xi \hat{g}_z \rangle = p.$$

(14) General Gaussians: Consider the Siegel half-space

$$\mathfrak{S}_+(d) = \left\{ C \in \mathbb{C}^{d\times d} \mid C = C^T,\, \operatorname{Im} C > 0 \right\}.$$

Note, since $C \in \mathfrak{S}_+(d)$ is complex symmetric,

$$\operatorname{Im} C = \tfrac{1}{2\mathrm{i}}(C - C^*) = \tfrac{1}{2\mathrm{i}}(C - \overline{C}).$$

We consider

$$\begin{aligned} g[C,z](x) &= (\pi\varepsilon)^{-d/4} \det(\operatorname{Im} C)^{1/4} \\ &\quad \times \exp(\tfrac{\mathrm{i}}{2\varepsilon}(x-q)^T C(x-q) + \tfrac{\mathrm{i}}{\varepsilon} p^T(x-q)).\end{aligned}$$

Note that

$$g[\mathrm{i}\mathbb{I}, z] = g_z.$$

(15) The Gaussian manifold: Consider

$$\mathcal{M} = \left\{ u = \mathrm{e}^{\mathrm{i}S} g[C,z] \mid z \in \mathbb{R}^{2d}, C \in \mathfrak{S}_+(d), S \in \mathbb{R} \right\}.$$

For all $u \in \mathcal{M}$ any $v \in \mathcal{T}_u\mathcal{M}$ has the form

$$v = \tfrac{\mathrm{i}}{\varepsilon}\varphi u,$$

where

$$\varphi(x) = \\ \dot{S} + \tfrac{1}{2}(x-q)^T \dot{C}(x-q) - \dot{q}^T(C(x-q)+p) + \dot{p}^T(x-q)$$

with arbitrary $(\dot{q},\dot{p}) \in \mathbb{R}^{2d}$, $\dot{C} \in \mathbb{C}^{d\times d}$, $\dot{S} \in \mathbb{R}$. Therefore,

$$\mathcal{T}_u\mathcal{M} = \{\phi u \mid \phi \text{ complex polynomial of degree } \leq 2\}.$$

(16) Exactness for quadratic potentials: If V is a polynomial of degree ≤ 2, then all $u \in \mathcal{M}$ satisfy

$$-\tfrac{\varepsilon^2}{2}\Delta_x u, Vu \in \mathcal{T}_u\mathcal{M}$$

and therefore also

$$P_u^\perp H u = 0.$$

By the a posteriori estimate, we obtain

$$u(t) = \psi(t) \quad \text{for all } t.$$

2. Thawed Gaussians (March 5th, 13:30-15:30)

(1) Towards an a posteriori error estimate: We recall the Gaussian manifold

$$\mathcal{M} = \left\{ u = \mathrm{e}^{\mathrm{i}S} g[C,z] \mid z \in \mathbb{R}^{2d}, C \in \mathfrak{S}_+(d), S \in \mathbb{R} \right\}.$$

and the general variational a posteriori error estimate

$$\|\psi(t) - u(t)\| \le \int_0^t \|\tfrac{1}{\mathrm{i}\varepsilon} P^\perp_{u(s)} H u(s)\| \,\mathrm{d}s,$$

where $P_u^\perp = \mathbb{I} - P_u$ and P_u is the orth. projection onto $\mathcal{T}_u\mathcal{M}$.

(2) Theorem: We assume the following:
   (a) The potential V is smooth and subquadratic.
   (b) The initial data are normalised and satisfy $\psi_0 \in \mathcal{M}$.
   (c) The eigenvalues of the imaginary part $\operatorname{Im} C(t)$ of the width matrix of the time-evolved Gaussian $u(t)$ are bounded from below by a constant $\rho > 0$ for all $t \in [0, \bar{t}]$.

   Then, there exists a constant $c > 0$ that is independent of ε, ρ, and t, but dependent on V, such that

$$\|\psi(t) - u(t)\| \le c\, t \sqrt{\varepsilon} \rho^{-3/2}, \qquad t \in [0, \bar{t}].$$

(3) *Proof.* Let $q \in \mathbb{R}^d$ be the position center of $u \in \mathcal{M}$. We decompose

$$V = U_q + W_q$$

into its second order Taylor polynomial U_q around q and the corresponding remainder W_q. Then,

$$-\tfrac{\varepsilon^2}{2}\Delta u + V_q u \in \mathcal{T}_u\mathcal{M}$$

and

$$P_u^\perp H u = W_q u.$$

Since V is smooth and subquadratic, we can write

$$W_q(x) = \sum_{|k|=3} (x-q)^k b_q(x),$$

where b_q is smooth and bounded. It remains to observe that

$$\|W_{q(s)} u(s)\| \le \|b_{q(s)}\|_\infty \|(x - q(s))^3 u(s)\| \le c\,(\varepsilon/\rho)^{3/2},$$

where the last Gaussian moment estimate will be verified in the next Lemma. □

(4) Moments: For all $m \geq 0$, there exists $c_m > 0$ such that for all bounded, measurable functions b,

$$\|(x-q)^m bu\| \leq c_m \|b\|_\infty (\varepsilon/\rho)^{m/2}.$$

The constant c_m is independent of ε and ρ.

(5) *Proof.* Let $\lambda_1, \ldots, \lambda_d \geq \rho$ be the eigenvalues of $\operatorname{Im} C$. Then,

$$\begin{aligned}
&\|(x-q)^m bu\|^2 \\
&\leq \|b\|_\infty (\pi\varepsilon)^{-d/2} \det(\operatorname{Im} C)^{1/2} \\
&\quad \times \int_{\mathbb{R}^d} |y|^{2m} \exp(-\tfrac{1}{\varepsilon}(\lambda_1 y_1^2 + \cdots + \lambda_d y_d^2))\, \mathrm{d}y \\
&\leq \|b\|_\infty (\pi\varepsilon)^{-d/2} \det(\operatorname{Im} C)^{1/2} \int_{\mathbb{R}^d} |y|^{2m} \exp(-\tfrac{\rho}{\varepsilon}|y|^2)\, \mathrm{d}y \\
&= \|b\|_\infty (\varepsilon/\rho)^m \ \pi^{-d/2} \int_{\mathbb{R}^d} |x|^{2m}. \exp(-|x|^2)\, \mathrm{d}x
\end{aligned}$$

□

(6) We recall for $u \in \mathcal{M}$ the tangent space description

$$\mathcal{T}_u\mathcal{M} = \{\phi u \mid \phi \text{ complex polynomial of degree } \leq 2\}.$$

For detemining the variational equations of motion, we calculate the orthogonal projection P_u.

(7) An orthonormal basis: We note that

$$\begin{aligned}
|u(x)|^2 &= \text{const.} \times \exp(-\tfrac{1}{\varepsilon}(x-q)^T \operatorname{Im} C(x-q)) \\
&= \text{const.} \times \exp(-|y(x)|^2)
\end{aligned}$$

with

$$y(x) = \tfrac{1}{\sqrt{\varepsilon}} Q^{-1}(x-q) \quad \text{if} \quad \operatorname{Im} C = (QQ^T)^{-1}.$$

Let $h_0(t) = 1$, $h_1(t) = \sqrt{2}t$ and $h_2(t) = (-1+2t^2)/\sqrt{2}$ denote normalized Hermite polynomials. Then,

$$\varphi_k(x) = \prod_{j=1}^d h_{k_j}(y_j) u(y), \qquad |k| = 2,$$

defines an orthonormal basis of $\mathcal{T}_u\mathcal{M}$, and

$$P_u\psi = \sum_{|k|=2} \langle \varphi_k \mid \psi \rangle \varphi_k, \quad \psi \in L^2(\mathbb{R}^d).$$

(8) Averages: We will soon encounter more averages and denote them by

$$\langle f\rangle_u = \int_{\mathbb{R}^d} f(x)|u(x)|^2 \mathrm{d}x.$$

(9) For a smooth function $W : \mathbb{R}^d \to \mathbb{R}$ of polynomial growth with $\langle \nabla W\rangle_u = 0$ and $\langle \nabla^2 W\rangle_u = 0$, we have

$$P_u W u = \langle W\rangle_u u.$$

(10) *Proof.* We examine the basis functions order by order. For the zeroth one, we have

$$\langle \varphi_0 \mid Wu\rangle\varphi_0 = \langle u \mid Wu\rangle u = \langle W\rangle_u u.$$

For the first order terms, we observe

$$\begin{aligned}\langle \varphi_1 \mid Wu\rangle &= \text{const.} \times \int_{\mathbb{R}^d} y(x)W(x)|u(x)|^2 \mathrm{d}x \\ &= \text{const.} \times \langle \nabla W\rangle_u = 0,\end{aligned}$$

where we have used integration by parts. For the second order terms, we write

$$\sum_{|k|=2} \langle \varphi_k \mid Wu\rangle\varphi_k = \mathrm{tr}(\langle \Phi_2 \mid Wu\rangle\Phi_2)$$

with

$$\Phi_2(x) = \tfrac{1}{\sqrt{2}}(-\mathbb{I}_d + 2yy^T)u(x) \in \mathbb{C}^{d\times d}.$$

Two integrations by parts provide

$$\begin{aligned}\langle \Phi_2 \mid Wu\rangle &= \text{const.} \times \int_{\mathbb{R}^d} (-\mathbb{I}_d + 2yy^T)W(x)|u(x)|^2 \mathrm{d}x \\ &= \text{const.} \times \langle \nabla^2 W\rangle_u = 0.\end{aligned}$$

□

(11) For a smooth function V of polynomial growth,

$$P_u V u = (\alpha + a^T(x-q) + \tfrac{1}{2}(x-q)^T A(x-q))u,$$

where

$$\begin{aligned}\alpha &= \langle V\rangle_u - \tfrac{\varepsilon}{4}\mathrm{tr}((\operatorname{Im} C)^{-1}\langle \nabla^2 V\rangle_u), \\ a &= \langle \nabla V\rangle_u, \\ A &= \langle \nabla^2 V\rangle_u.\end{aligned}$$

(12) *Proof.* We set $\alpha_0 = \langle V \rangle_u$ and write

$$V = \alpha_0 + a^T(x-q) + \tfrac{1}{2}(x-q)^T A(x-q) + W.$$

Then,

$$P_u V u =$$
$$(\alpha_0 + a^T(x-q) + \tfrac{1}{2}(x-q)^T A(x-q))u + P_u W u.$$

Now we observe that

$$\begin{aligned}\langle W \rangle_u &= -\tfrac{1}{2}\langle (x-q)^T A(x-q)\rangle_u \\ &= -\tfrac{\varepsilon}{4}\mathrm{tr}((\mathrm{Im}\, C)^{-1}\langle \nabla^2 V\rangle_u).\end{aligned}$$

We calculate

$$\begin{aligned}\nabla V &= a + A(x-q) + \nabla W, \\ \nabla^2 V &= A + \nabla^2 W,\end{aligned}$$

which implies $\langle \nabla W \rangle_u = 0$, $\langle \nabla^2 W \rangle_u = 0$, and by the previous Lemma $P_u W u = \langle W \rangle_u u$. □

(13) Variational equations of motion:

$$\begin{aligned}\dot{q} &= p, \\ \dot{p} &= -\langle \nabla V \rangle_u, \\ \dot{C} &= -C^2 - \langle \nabla^2 V \rangle_u, \\ \dot{S} &= \tfrac{1}{2}|p|^2 - \langle V \rangle_u + \tfrac{\varepsilon}{4}\mathrm{tr}((\mathrm{Im}\, C)^{-1}\langle \nabla^2 V \rangle_u).\end{aligned}$$

Proof. We observe that both $i\varepsilon\partial_t u$ and $P_u H u$ are products of a second order polynomial with u. Matching the polynomial terms order by order, we obtain the equations of motion. □

(14) Once more averages: For smooth subquadratic functions f, we have

$$|f(q) - \langle f \rangle_u| \le c\,\varepsilon/\rho,$$

where the constant $c > 0$ is independent of ε and ρ.

(15) *Proof.* We Taylor expand

$$f(x) = f(q) + \nabla f(q)^T(x-q) + \tfrac{1}{2}(x-q)^T B_q(x)(x-q)$$

with B_q bounded and obtain

$$|f(q) - \langle f \rangle_u| \le \text{const.}\ \|B_q\|_\infty \int_{\mathbb{R}^d} |x-q|^2 |u(x)|^2 \mathrm{d}x.$$

□

3. Born–Oppenheimer appr. (March 5th, 15:45-17:45)

(1) The molecular Hamiltonian: We describe a molecule in terms of nuclei and electrons with configurations

$$x = (x_1, \dots, x_N) \quad \text{with } x_n \in \mathbb{R}^3,$$
$$y = (y_1, \dots, y_L) \quad \text{with } y_\ell \in \mathbb{R}^3.$$

We write the molecular Hamiltonian as

$$H = T + V,$$

where the kinetic energy operator is given by

$$T = T_N + T_e \quad \text{with}$$
$$T_N = -\sum_{n=1}^{N} \frac{\hbar^2}{2M_n}\Delta_{x_n}, \quad T_e = -\sum_{\ell=1}^{L} \frac{\hbar^2}{2m_e}\Delta_{y_\ell}.$$

The potential

$$V(x, y) = V_{NN}(x) + V_{Ne}(x, y) + V_{ee}(y)$$

is built of Coulomb interactions between the nuclei, the nuclei and electrons, and the electrons, respectively.

(2) The electronic Hamiltonian: Fixing a nuclear configuration x, we define the electronic Hamiltonian

$$H_e(x) = T_e + V_{Ne}(x, y) + V_{ee}(y)$$

and write the molecular Hamiltonian as

$$H = T_N + V_{NN}(x) + H_e(x).$$

(3) Electronic ground state energy: The electronic Hamiltonian $H_e(x)$ has a real eigenvalue $E(x)$ as its lowest point of the spectrum,

$$E(x) = \min \sigma(H_e(x)).$$

Together with an eigenfunction $\Phi(x, \cdot)$ (the ground state) it satisfies the electronic Schrödinger equation

$$H_e(x)\Phi(x, \cdot) = E(x)\Phi(x, \cdot).$$

(4) Potential energy surfaces: One can characterize the ground state energy by a minmax principle,

$$E(x) = \inf_{\dim(U)=1} \sup_{\phi \in U, \|\phi\|=1} \langle \phi, H_e(x)\phi \rangle_y,$$

and more generally eigenvalues by

$$E_m(x) = \inf_{\dim(U)=m} \sup_{\phi\in U, \|\phi\|=1} \langle \phi, H_e(x)\phi\rangle_y, \qquad m \geq 1.$$

The functions $x \mapsto E_m(x)$ are called potential energy surfaces.

(5) Lipschitz regularity: Hunziker and Günther ('80) proved the existence of $\beta > 0$ such that for all m and $x, \widetilde{x}$

$$|E_m(x) - E_m(\widetilde{x})| \leq \beta |x - \widetilde{x}|.$$

(6) Analyticity: Hunziker ('86) proved that a nondegenerate eigenvalue $E_m(x)$ is analytic in a neighbourhood of x with $x_n \neq x_{n'}$ if $n \neq n'$.

(7) Rellich's example: Nondegeneracy is essential for having analyticity, as the following example shows. The matrix

$$\begin{pmatrix} x_1 & x_2 \\ x_2 & -x_1 \end{pmatrix}, \qquad x = (x_1, x_2) \in \mathbb{R}^2,$$

has the eigenvalues $\pm|x|$.

(8) Variational approximation: For solving the molecular Schrödinger equation

$$\mathrm{i}\hbar\partial_t \Psi = H\Psi, \qquad \Psi(0) = \Psi_0,$$

we consider the ground state approximation space

$$\mathcal{M} = \{u(x,y) = \psi(x)\Phi(x,y) \mid \psi \in L^2_x\}.$$

(9) Towards the variational Hamiltonian: We denote by P the orthogonal projection onto $\mathcal{M}$ and compute for $u \in \mathcal{M}$

$$\begin{aligned} PHu(x,y) &= P(T_N + V_{NN}(x))u(x,y) + PH_e(x)u(x,y) \\ &= PT_N\psi(x)\Phi(x,y) + (V_{NN}(x) + E(x))\psi(x)\Phi(x,y). \end{aligned}$$

We have

$$\Delta_x(\psi\Phi) = (\Delta_x\psi)\Phi + 2\nabla_x\psi \cdot \nabla_x\Phi + \psi\Delta_x\Phi$$

and therefore

$$\begin{aligned} &P\Delta_x(\psi\Phi) = \\ &(\Delta_x\psi + 2\langle\Phi \mid \nabla_x\Phi\rangle_y \cdot \nabla_x\psi + \langle\Phi \mid \Delta_x\Phi\rangle_y\psi)\Phi. \end{aligned}$$

(10) Gauging: For the normalized eigenfunction $\Phi(x,\cdot)$ we have

$$\nabla_x\|\Phi(x)\|^2_y = 2\,\mathrm{Re}\,\langle\Phi(x) \mid \nabla_x\Phi(x)\rangle_y = 0.$$

If $\Phi(x, y)$ is real and smoothly depending on x, then

$$\langle \Phi \mid \nabla_x \Phi \rangle_y = 0.$$

(11) The variational Hamiltonian: In the real smooth case, we have

$$PHu(x, y) = (H_N \psi(x))\Phi(x, y)$$

with

$$H_N = T_N + V_{NN} + E - \sum_{n=1}^{N} \frac{\hbar^2}{2M_n} \langle \Phi \mid \nabla^2_{x_n} \Phi \rangle_y$$

(12) Accuracy: Recall that

$$\Psi(t) - u(t) = \frac{1}{\mathrm{i}\varepsilon} \int_0^t \mathrm{e}^{-\mathrm{i}H(t-s)/\hbar} P^\perp Hu(s) \mathrm{d}s.$$

We therefore calculate

$$\begin{aligned} &P^\perp Hu(x, y) \\ &= P^\perp (T_N + V_{NN}(x))u(x, y) + P^\perp H_e(x) u(x, y) \\ &= P^\perp T_N \psi(x) \Phi(x, y). \end{aligned}$$

If $\mathrm{ran}(P^\perp) = \mathrm{span}(\Phi^\perp)$, then

$$\begin{aligned} &P^\perp \Delta_x (\psi\Phi) = \\ &(2\langle \Phi^\perp \mid \nabla_x \Phi \rangle_y \cdot \nabla_x \psi + \langle \Phi^\perp \mid \Delta_x \Phi \rangle_y \psi)\Phi^\perp. \end{aligned}$$

(13) Hellmann–Feynman: We differentiate the equation $H_e \Phi = E\Phi$ with respect to x,

$$\nabla_x H_e \Phi + H_e \nabla_x \Phi = \nabla_x E \Phi + E \nabla_x \Phi$$

and multiply with Φ,

$$\langle \Phi \mid \nabla_x H_e \Phi \rangle_y + E \underbrace{\langle \Phi \mid \nabla_x \Phi \rangle_y}_{=0} = \nabla E + E \underbrace{\langle \Phi \mid \nabla_x \Phi \rangle_y}_{=0},$$

we obtain

$$\nabla_x E = \langle \Phi \mid \nabla_x H_e \Phi \rangle_y.$$

(14) First order coupling: We multiply with $\Phi^\perp$,

$$\langle \Phi^\perp \mid \nabla_x H_e \Phi \rangle_y + E^\perp \langle \Phi^\perp \mid \nabla_x \Phi \rangle_y = E \langle \Phi^\perp \mid \nabla_x \Phi \rangle_y,$$

and obtain

$$\langle \Phi^\perp \mid \nabla_x \Phi \rangle_y = \frac{\langle \Phi^\perp \mid \nabla_x H_e \Phi \rangle_y}{E - E^\perp}.$$

(15) Second order coupling: We calculate the divergence

$$\nabla_x \cdot \langle \Phi^\perp \mid \nabla_x \Phi \rangle_y = \underbrace{\langle \nabla_x \Phi^\perp \mid \nabla_x \Phi \rangle_y}_{=:r(x)} + \langle \Phi^\perp \mid \Delta_x \Phi \rangle_y$$

and obtain

$$\langle \Phi^\perp \mid \Delta_x \Phi \rangle_y = \nabla_x \cdot \langle \Phi^\perp \mid \nabla_x \Phi \rangle_y + r(x)$$

Since $\langle \Phi \mid \nabla_x \Phi \rangle_y = 0$ and $\langle \Phi^\perp \mid \nabla_x \Phi^\perp \rangle_y = 0$ one might want to neglect $r(x)$, in particular if E and $E^\perp$ are well separated from the rest of the electronic spectrum.

(16) Mass scaling: Let $M = \min\{M_1, \dots, M_N\}$ be the minimal nucleonic mass. We rescale

$$x_n \mapsto \sqrt{\frac{M_n}{M}} x_n$$

and obtain

$$H = -\frac{\hbar^2}{2M}\Delta_x - \frac{\hbar^2}{2m}\Delta_y + \widetilde{V}_{NN}(x) + \widetilde{V}_{Ne}(x,y) + V_{ee}(y).$$

(17) Non-dimensionalisation: Consider $x \mapsto \ell_c x$ and $y \mapsto \ell_c y$ and $t \mapsto s_c t$ with

$$\ell_c = \sqrt{\frac{\hbar}{m_e s_c^{-1}}}$$

the characteristic length. (Recall that $\hbar$ is an action, that is, energy times time, that is measured in $J \cdot s = N \cdot m \cdot s = kg \cdot m^2 \cdot s^{-1}$.) Then,

$$H = \left(-\frac{m_e}{2M}\Delta_x - \frac{1}{2}\Delta_y + V^\flat(x,y) \right) \cdot \frac{\hbar}{s_c}$$

(18) Rescaling of time: Denote

$$\varepsilon = \sqrt{\frac{m_e}{M}}$$

and rescale time $t \mapsto t/\varepsilon$. Then, the molecular Schrödinger equation takes the form

$$\mathrm{i}\varepsilon \partial_t \Psi = \left(-\frac{\varepsilon^2}{2}\Delta_x - \frac{1}{2}\Delta_y + V^\natural(x,y) \right) \Psi.$$

(19) The nucleonic Hamiltonian

$$H_N = T_N + V_{NN} + E - \sum_{n=1}^{N} \frac{\hbar^2}{2M_n} \langle \Phi \mid \nabla_{x_n}^2 \Phi \rangle_y,$$

takes the form

$$H_N^\natural = -\frac{\varepsilon^2}{2}\Delta_x + V_{NN}^\natural + E^\natural - \frac{\varepsilon^2}{2} \langle \Phi^\natural \mid \nabla_x^2 \Phi^\natural \rangle_y$$

4. Hagedorn's wave packets (March 6th, 10:00-12:00)

(1) Symplectic decomposition: For any $C \in \mathfrak{S}_+(d)$ there exist invertible matrices $Q, P \in \mathbb{C}^{d\times d}$ such that $C = PQ^{-1}$ and

$$Q^T P - P^T Q = 0 \text{ and } Q^* P - P^* Q = 2i\mathbb{I}.$$

(2) *Proof.* Let $Q = (\operatorname{Im} C)^{-1/2}$ and $P = CQ$. Then,

$$\begin{aligned} &Q^T P - P^T Q \\ &= (\operatorname{Im} C)^{-1/2} C (\operatorname{Im} C)^{-1/2} - (\operatorname{Im} C)^{-1/2} C (\operatorname{Im} C)^{-1/2} = 0, \\ &Q^* P - P^* Q \\ &= (\operatorname{Im} C)^{-1/2} C (\operatorname{Im} C)^{-1/2} - (\operatorname{Im} C)^{-1/2} \bar{C} (\operatorname{Im} C)^{-1/2} = 2i\mathbb{I}. \end{aligned}$$

□

(3) Unicity: The decomposition is not unique, since multiplying Q and P from the right with a unitary matrix keeps the three properties.

(4) Symplecticity: The matrix

$$Y = \begin{pmatrix} \operatorname{Re} Q & \operatorname{Im} Q \\ \operatorname{Re} P & \operatorname{Im} P \end{pmatrix},$$

that is built from the real and imaginary part of the entries of Q and P, is symplectic, that is,

$$Y^T J Y = J \quad \text{with} \quad J = \begin{pmatrix} 0 & -\mathbb{I} \\ \mathbb{I} & 0 \end{pmatrix}.$$

(5) *Proof.* We have

$$\begin{aligned} &0 = \operatorname{Re}(Q^T P - P^T Q) = \\ &(\operatorname{Re} Q)^T \operatorname{Re} P - (\operatorname{Re} P)^T \operatorname{Re} Q - (\operatorname{Im} Q)^T \operatorname{Im} P + (\operatorname{Im} P)^T \operatorname{Im} Q \\ &0 = \operatorname{Re}(Q^* P - P^* Q) = \\ &(\operatorname{Re} Q)^T \operatorname{Re} P - (\operatorname{Re} P)^T \operatorname{Re} Q + (\operatorname{Im} Q)^T \operatorname{Im} P - (\operatorname{Im} P)^T \operatorname{Im} Q, \end{aligned}$$

which implies that the upper left block of $Y^T J Y$ vanishes. Analogous arguments apply for the other three blocks. □

(6) The imaginary part: We always have $\operatorname{Im} C = (QQ^*)^{-1}$.

Proof.

$$\begin{aligned}\operatorname{Im} C &= \frac{1}{2\mathrm{i}}(PQ^{-1} - Q^{-*}P^*) \\ &= \frac{1}{2\mathrm{i}}Q^{-*}(Q^*P - P^*Q)Q^{-1} = (QQ^*)^{-1}.\end{aligned}$$

□

(7) Riccati equation: The solution of

$$\dot{C} = -C^2 - \langle \nabla^2 V \rangle_u, \quad C(0) = PQ^{-1}$$

satisfies $C(t) = P(t)Q(t)^{-1}$, where

$$\dot{Q} = P, \quad \dot{P} = -\langle \nabla^2 V \rangle_u Q.$$

(8) *Proof.*

$$\frac{\mathrm{d}}{\mathrm{d}t}(PQ^{-1}) = \dot{P}Q^{-1} - PQ^{-1}\dot{Q}Q^{-1} = -\langle \nabla^2 V \rangle_u - C^2.$$

□

(9) The time evolution respects the two QP-conditions:

$$\begin{aligned}&\frac{\mathrm{d}}{\mathrm{d}t}(Q^TP - P^TQ) = \dot{Q}^TP - Q^T\dot{P} - \dot{P}^TQ - P^T\dot{Q} \\ &= P^TP - Q^T\langle \nabla^2 V \rangle_u Q + Q^T\langle \nabla^2 V \rangle_u Q - P^TP = 0,\end{aligned}$$

and similarly for $Q^*P - P^*Q = 2\mathrm{i}\mathbb{I}$.

(10) Commutation relations: The position and momentum operators $\hat{q}\psi(x) = x\psi(x)$ and $\hat{p}\psi(x) = -\mathrm{i}\varepsilon\nabla_x\psi(x)$ satisfy

$$\frac{1}{\mathrm{i}\varepsilon}[\hat{q}_j, \hat{p}_k] = \delta_{jk}, \qquad j,k = 1,\dots,d.$$

Proof.

$$x_j\partial_k\psi(x) - \partial_k(x_j\psi(x)) = -\delta_{jk}\psi(x).$$

□

(11) Ladders: The operators

$$\mathcal{A} = \frac{\mathrm{i}}{\sqrt{2\varepsilon}}(Q^T\hat{p} - P^T\hat{q}) \quad \text{and} \quad \mathcal{A}^\dagger = -\frac{\mathrm{i}}{\sqrt{2\varepsilon}}(Q^*\hat{p} - P^*\hat{q})$$

satisfy the commutation relation

$$[\mathcal{A}_j, \mathcal{A}_k^\dagger] = \delta_{jk}, \qquad j,k = 1,\dots,d.$$

(12) *Proof.*

$$\begin{aligned}[\mathcal{A}_j, \mathcal{A}_k^\dagger] &= \frac{1}{2\varepsilon}\sum_{m,n=1}^d [Q_{jm}^T\hat{p}_m - P_{jm}^T\hat{q}_m, Q_{kn}^*\hat{p}_n - P_{kn}^*\hat{q}_n] \\ &= \frac{1}{2\varepsilon}\sum_{m,n=1}^d \left(-Q_{jm}^T P_{kn}^*[\hat{p}_m,\hat{q}_n] - P_{jm}^T Q_{kn}^*[\hat{q}_m,\hat{p}_n]\right) \\ &= \frac{\mathrm{i}}{2}\sum_{m=1}^d \left(Q_{jm}^T P_{km}^* - P_{jm}^T Q_{km}^*\right) \\ &= -\frac{\mathrm{i}}{2}(Q^*P - P^*Q)_{kj} = \delta_{jk}.\end{aligned}$$

□

(13) Null-space: The null-space of $\mathcal{A}$ is spanned by $g[0, C]$.

Proof. Since

$$\nabla_x g[0, C](x) = \frac{\mathrm{i}}{\varepsilon} Cxg[0, C](x),$$

we have

$$\begin{aligned}\mathcal{A}g[0, C] &= \frac{\mathrm{i}}{\sqrt{2\varepsilon}}(Q^T\hat{p} - P^T\hat{q})g[0, C] \\ &= \frac{\mathrm{i}}{\sqrt{2\varepsilon}}(Q^TC - P^T)\hat{q}g[0, C] \\ &= \frac{\mathrm{i}}{\sqrt{2\varepsilon}}(Q^TP - P^TQ)Q^{-1}\hat{q}g[0, C] = 0.\end{aligned}$$

Moreover, any solution φ of the first order linear system $\mathcal{A}\varphi = 0$ is a multiple of $g[0, C]$. □

(14) Hagedorn's wave packets: We set $\varphi_0 = g[0, C]$ and define

$$\varphi_{k+\langle j\rangle} = \frac{1}{\sqrt{k_j + 1}}\mathcal{A}_j^\dagger\varphi_k, \quad k \in \mathbb{N}_0^d, \quad j = 1, \ldots, d.$$

(15) Lowering: The observation that

$$\mathcal{A}_j\varphi_{\langle j\rangle} = \mathcal{A}_j\mathcal{A}_j^\dagger\varphi_0 = (\mathcal{A}_j^\dagger\mathcal{A}_j + \mathbb{I})\varphi_0 = \varphi_0$$

together with an inductive argument proves that

$$\varphi_{k-\langle j\rangle} = \frac{1}{\sqrt{k_j}}\mathcal{A}_j\varphi_k.$$

(16) The wave packets are mutually orthogonal,

$$\langle \varphi_k \mid \varphi_\ell \rangle = 0, \quad k \neq \ell.$$

This is proved by combining the observation that

$$\langle \varphi_0 \mid \varphi_{\langle j \rangle} \rangle = \langle \varphi_0 \mid \mathcal{A}_j^\dagger \varphi_0 \rangle = \langle \mathcal{A}_j \varphi_0 \mid \varphi_0 \rangle = 0$$

with an inductive argument.

(17) Normalisation:

$$\|\varphi_k\| = 1, \quad k \in \mathbb{N}_0^d,$$

since

$$\|\varphi_{\langle j \rangle}\|^2 = \langle \varphi_0 \mid \underbrace{\mathcal{A}_j \mathcal{A}_j^\dagger}_{=\mathcal{A}_j^\dagger \mathcal{A}_j + \mathbb{I}} \varphi_0 \rangle = \langle \varphi_0 \mid \varphi_0 \rangle = 1.$$

(18) One can prove that the φ_k, $k \in \mathbb{N}$, form an orthonormal basis of $L^2(\mathbb{R}^d)$.

(19) 3-term recurrence:

$$\left(\sqrt{k_j + 1} \varphi_{k + \langle j \rangle} \right)_{j=1}^d = \sqrt{\frac{2}{\varepsilon}} Q^{-1} x \varphi_k - Q^{-1} \bar{Q} \left(\sqrt{k_j} \varphi_{k - \langle j \rangle} \right)_{j=1}^d$$

Proof. We deduce from $C = C^T$ that $PQ^{-1} = Q^{-T} P^T$ and from $\operatorname{Im} C = (QQ^*)^{-1}$ that $QQ^* = \bar{Q} Q^T$. We use these relations to write

$$\begin{aligned}
\mathcal{A}^\dagger &= -\tfrac{\mathrm{i}}{\sqrt{2\varepsilon}} (Q^* \hat{p} - P^* \hat{q}) \\
&= -\tfrac{\mathrm{i}}{\sqrt{2\varepsilon}} (Q^* Q^{-T} (\tfrac{\sqrt{2\varepsilon}}{\mathrm{i}} \mathcal{A} + P^T \hat{q}) - P^* \hat{q}) \\
&= -Q^* Q^{-T} \mathcal{A} - \tfrac{\mathrm{i}}{\sqrt{2\varepsilon}} (Q^* Q^{-T} P^T - P^*) \hat{q} \\
&= -Q^{-1} \bar{Q} \mathcal{A} - \tfrac{\mathrm{i}}{\sqrt{2\varepsilon}} (Q^* P - P^* Q) Q^{-1} \hat{q} \\
&= -Q^{-1} \bar{Q} \mathcal{A} - \sqrt{\tfrac{2}{\varepsilon}} Q^{-1} \hat{q}
\end{aligned}$$

□

(20) If the unitary matrix $Q^{-1}\bar{Q}$ is diagonal, then φ_k is the product of a tensor product of scaled Hermite polynomials times the complex-valued Gaussian.

(21) Ladders with centers: The previous construction keeps its properties, when translating the ladders by $(q,p) \in \mathbb{R}^{2d}$, that is,

$$\mathcal{A} = \frac{\mathrm{i}}{\sqrt{2\varepsilon}}(Q^T(\hat{p}-p) - P^T(\hat{q}-q)),$$

$$\mathcal{A}^\dagger = -\frac{\mathrm{i}}{\sqrt{2\varepsilon}}(Q^*(\hat{p}-p) - P^*(\hat{q}-q)).$$

5. Potpourri (March 6th, 14:00-16:00)

(1) Quadratic ladder evolution. If V is a polynomial of degree ≤ 2, then

$$\dot{\mathcal{A}}_j = \frac{1}{\mathrm{i}\varepsilon}[\mathcal{A}_j, H] \quad \text{and} \quad \dot{\mathcal{A}}_j^\dagger = -\frac{1}{\mathrm{i}\varepsilon}[\mathcal{A}_j^\dagger, H]$$

Proof. We calculate

$$\dot{\mathcal{A}} = \frac{\mathrm{i}}{\sqrt{2\varepsilon}}(P^T(\hat{p}-p) + Q^T\nabla V(q) + Q^T\nabla^2 V(q)(\hat{q}-q) + P^T p) = \frac{\mathrm{i}}{\sqrt{2\varepsilon}}(P^T\hat{p} + Q^T\nabla V(\hat{q}))$$

and

$$\begin{aligned}[\mathcal{A}, H] &= \tfrac{\mathrm{i}}{\sqrt{2\varepsilon}}\Big([P^T\hat{q}, -\tfrac{\varepsilon^2}{2}\Delta_x] - [Q^T\hat{p}, V]\Big) \\ &= \tfrac{\mathrm{i}}{\sqrt{2\varepsilon}}(-\tfrac{\mathrm{i}}{\varepsilon}P^T\hat{p} - \tfrac{\mathrm{i}}{\varepsilon}Q^T\nabla V(\hat{q})).\end{aligned}$$

□

(2) If V is a polynomial of degree ≤ 2, then

$$\mathrm{e}^{-\mathrm{i}Ht/\varepsilon}\varphi_k[z(0), Z(0)] = \mathrm{e}^{\mathrm{i}S(t)/\varepsilon}\varphi_k[z(t), Z(t))].$$

Proof. We argue by induction, by proving that if $\psi(t)$ is the solution of the Schrödinger equation with initial datum $\psi(0)$, then $\mathcal{A}_j^\dagger\psi(t)$ is the solution of the equation with initial datum $\mathcal{A}_j^\dagger\psi(0)$. Indeed,

$$\mathrm{i}\varepsilon\partial_t(\mathcal{A}_j^\dagger\psi) = -[\mathcal{A}_j^\dagger, H]\psi + \mathcal{A}_j^\dagger H\psi = H\mathcal{A}_j^\dagger\psi.$$

□

(3) Semi-variational approximation: Let $z(t), Z(t), S(t)$ be the solutions to

$$\begin{aligned}&\dot{q} = p,\ \dot{p} = -\nabla V(q),\\ &\dot{Q} = P,\ \dot{P} = -\nabla^2 V(q)Q,\ \dot{S} = \tfrac{1}{2}|p|^2 - V(q).\end{aligned}$$

and denote $\varphi_k(t) = \mathrm{e}^{\mathrm{i}S(t)/\varepsilon}\varphi_k[z(t), Z(t)]$. Let $\mathcal{K} \subset \mathbb{N}_0^d$. We consider

$$\mathcal{M}(t) = \big\{u = \sum_{k\in\mathcal{K}} c_k\varphi_k(t) \mid c_k \in \mathbb{C},\ k \in \mathcal{K}\big\}.$$

and approximate the Schrödinger equation $\psi(t)$ by the variational solution $u(t)$ determined by

$$\forall \ell \in \mathcal{K} : \langle \varphi_\ell(t) \mid \mathrm{i}\varepsilon\partial_t u(t) - Hu(t)\rangle = 0.$$

(4) The semi-variational approximation is norm- but not energy-conserving

(5) Galerkin matrix: We compute

$$\begin{aligned}
&\mathrm{i}\varepsilon\partial_t(c_k\varphi_k) - H(c_k\varphi_k)\\
&= \mathrm{i}\varepsilon(\partial_t c_k)\varphi_k + c_k\left(\mathrm{i}\varepsilon\partial_t\varphi_k + \tfrac{\varepsilon^2}{2}\varphi_k - U_q\varphi_k\right) - c_k W_q\varphi_k\\
&= \mathrm{i}\varepsilon(\partial_t c_k)\varphi_k - c_k W_q\varphi_k,
\end{aligned}$$

and obtain the Galerkin system for the coefficients

$$\mathrm{i}\varepsilon\partial_t c = Gc, \qquad G_{k,\ell} = (\langle\varphi_k \mid W_q\varphi_\ell\rangle)_{k,\ell\in\mathcal{K}}\,.$$

One can prove that

$$\sup_{t\in[0,\bar t]} |G_{k,\ell}(t)| \le c\,\varepsilon^{\mu/2} \quad \text{with} \quad \mu = \max(|k-\ell|, 3),$$

where the constant $c > 0$ is independent of ε but depends on ρ and k, ℓ.

(6) Higher-order bound: Let $N \ge 2$ and $k_0 \in \mathbb{N}_0^d$ be such that

$$\{k \in \mathbb{N}_0^d \mid |k - k_0| < 3N\} \subseteq \mathcal{K}.$$

If the initial data $\psi_0 \in \mathcal{M}(0)$ satisfy $c_k(0) = \delta_{k,k_0}$, then

$$\|\psi(t) - u(t)\| \le c\,\varepsilon^{N/2} \quad \text{for all } t \in [0, \bar t],$$

where the constant $c > 0$ is independent of ε and N, but depends on ρ, k_0 and $\mathcal{K}$.

(7) Born–Oppenheimer approximation (cf. Spohn/Teufel '01): We assume the following:
   (a) There exists $\delta > 0$ such that for all x

   $$\operatorname{dist}(\{E(x)\}, \sigma(H_e(x) \setminus \{E(x)\})) \ge \delta.$$

   (b) All Coulomb interactions with respect to the nuclei are mollified, and there exists a constant $C > 0$ such that

   $$\|\nabla_x V^\natural(x,y)\| \le C \quad \text{for all } x \text{ and } y.$$

   (c) The initial data $\Psi_0(x,y) = \psi_0(x)\Phi(x,y)$ are normalized and satisfy $\sup_{\varepsilon>0} \|H_{BO}\psi_0\| < \infty$, where

   $$H_{BO} = -\frac{\varepsilon^2}{2}\Delta_x + V_{NN}^\natural + E^\natural.$$

Then, there exists a constant $c > 0$, that is independent of ε and t, such that

$$\|\Psi(t) - \psi(t)\Phi\| \leq c(1+t)\varepsilon, \qquad t \in [0, \bar{t}],$$

where

$$\psi(t) = \mathrm{e}^{-\mathrm{i}H_{BO}t/\varepsilon}\psi_0.$$

(8) *Proof.* We write

$$\Psi(t) - u(t) = \frac{1}{\mathrm{i}\varepsilon}\int_0^t \mathrm{e}^{-\mathrm{i}(t-s)H/\varepsilon} P^{\perp} H P u(s) \mathrm{d}s.$$

We construct $\vec{F}$ and R such that

$$P^{\perp} H P = \varepsilon[H, \vec{F} \cdot \varepsilon \nabla_x] + \varepsilon^2 R,$$

where

$$\begin{aligned} \|(\vec{F} \cdot \varepsilon \nabla x) u\| &\leq c_1 \left(\|\psi\|^2 + \|\varepsilon \nabla \psi\|\right)^{1/2} =: c_1 \|\psi\|_1, \\ \|Ru\| &\leq c_2 \left(\|\psi\|^2 + \|\varepsilon^2 \Delta_x \psi\|\right)^{1/2} =: c_2 \|\psi\|_2. \end{aligned}$$

Then,

$$\begin{aligned} &\Psi(t) - u(t) \\ &= \mathrm{e}^{-\mathrm{i}tH/\varepsilon} \ \tfrac{1}{\mathrm{i}} \int_0^t \mathrm{e}^{\mathrm{i}sH/\varepsilon}[H, \vec{F} \cdot \varepsilon \nabla_x] u(s) \mathrm{d}s + O(\varepsilon), \end{aligned}$$

where the error depends on $\sup_{s\in[0,t]} \|\psi(s,\cdot)\|_2$. We calculate derivatives:

$$\begin{aligned} &\mathrm{e}^{\mathrm{i}sH/\varepsilon}[H, \vec{F} \cdot \varepsilon \nabla_x] \mathrm{e}^{-\mathrm{i}sH/\varepsilon} \\ &= -\mathrm{i}\varepsilon \frac{\mathrm{d}}{\mathrm{d}s}\left(\mathrm{e}^{\mathrm{i}sH/\varepsilon}(\vec{F} \cdot \varepsilon \nabla_x) \mathrm{e}^{-\mathrm{i}sH/\varepsilon}\right) \end{aligned}$$

and

$$\frac{\mathrm{d}}{\mathrm{d}s}\left(\mathrm{e}^{\mathrm{i}sH/\varepsilon} u(s)\right) = \frac{\mathrm{i}}{\varepsilon} \mathrm{e}^{\mathrm{i}sH/\varepsilon}(H - PH) u(s).$$

We obtain by integration by parts

$$\begin{aligned}
&\Psi(t) - u(t)\\
&= \mathrm{e}^{-\mathrm{i}tH/\varepsilon}\ \varepsilon \int_0^t \frac{\mathrm{d}}{\mathrm{d}s}\left(\mathrm{e}^{\mathrm{i}sH/\varepsilon}(\vec{F}\cdot\varepsilon\nabla_x)\mathrm{e}^{-\mathrm{i}sH/\varepsilon}\right)\mathrm{e}^{\mathrm{i}sH/\varepsilon}u(s)\mathrm{d}s\\
&\quad + O(\varepsilon)\\
&= \varepsilon\left((\vec{F}\cdot\varepsilon\nabla_x)u(t) - \mathrm{e}^{-\mathrm{i}tH/\varepsilon}(\vec{F}\cdot\varepsilon\nabla_x)u(0)\right)\\
&\quad - \int_0^t \mathrm{e}^{-\mathrm{i}(t-s)H/\varepsilon}(\vec{F}\cdot\varepsilon\nabla_x)P^\perp HPu(s)\mathrm{d}s + O(\varepsilon)\\
&= O(\varepsilon).
\end{aligned}$$

□

(9) Lemma:

$$P^\perp HP = -\varepsilon P^\perp(\nabla_x P)P\cdot\varepsilon\nabla_x - \tfrac{\varepsilon^2}{2}P^\perp(\Delta_x P)P$$

Proof. We calculate

$$\begin{aligned}
P^\perp HP &= P^\perp(-\tfrac{\varepsilon^2}{2}\Delta_x)P\\
&= -\varepsilon P^\perp(\nabla_x P)\cdot\varepsilon\nabla_x - \tfrac{\varepsilon^2}{2}P^\perp(\Delta_x P)P\\
&= -\varepsilon P^\perp(\nabla_x P)P\cdot\varepsilon\nabla_x - \tfrac{\varepsilon^2}{2}P^\perp(\Delta_x P)P
\end{aligned}$$

where the last equation relies on the fact that $P^2 = P$ implies $\nabla_x PP + P\nabla_x P = \nabla_x P$. □

(10) Lemma: Denote $H_e^\perp = P^\perp H_e P^\perp$ and

$$\vec{F} = -(H_e^\perp - E)^{-1}P^\perp\nabla_x PP.$$

Then,

$$P^\perp HP = \varepsilon[H, \vec{F}\cdot\varepsilon\nabla_x] + \varepsilon^2 R_2 + \varepsilon^3 R_3$$

with

$$R_2 = -\tfrac{1}{2}P^\perp(\Delta_x P)P - \nabla_x H_e\,\vec{F} + \nabla_x\vec{F}\cdot\varepsilon^2\Delta_x$$

and

$$R_3 = \tfrac{1}{2}\Delta_x\vec{F}\cdot\varepsilon\nabla_x.$$

Proof. We use the previous lemma and observe that

$$\begin{aligned}
[H_e, P^\perp\nabla_x P] &= [EP + H_e^\perp, P^\perp\nabla_x P]\\
&= -EP^\perp\nabla_x P + H_e^\perp P^\perp\nabla_x P,
\end{aligned}$$

that is,

$$-P^{\perp}\nabla_x P = [H_e, \vec{F}],$$

and

$$\begin{aligned} -P^{\perp}\nabla_x P &= [H, \vec{F}] - [T_N, \vec{F}] \\ &= [H, \vec{F}] + \varepsilon\nabla_x \vec{F} \cdot \varepsilon\nabla_x + \tfrac{\varepsilon^2}{2}\Delta_x \vec{F}. \end{aligned}$$

In summary,

$$\begin{aligned} P^{\perp}HP &= \varepsilon[H, \vec{F}] \cdot \varepsilon\nabla_x \\ &\quad - \tfrac{\varepsilon^2}{2}P^{\perp}(\Delta_x P)P + \varepsilon^2\nabla_x \vec{F} \cdot \varepsilon^2\Delta_x + \tfrac{\varepsilon^3}{2}\Delta_x \vec{F} \cdot \varepsilon\nabla_x. \end{aligned}$$

To conclude the proof, we write

$$\begin{aligned} \varepsilon[H, \vec{F}] \cdot \varepsilon\nabla_x &= \varepsilon[H, \vec{F} \cdot \varepsilon\nabla_x] + \varepsilon\vec{F}[H, \varepsilon\nabla_x] \\ &= \varepsilon[H, \vec{F} \cdot \varepsilon\nabla_x] - \varepsilon^2\nabla_x H_e\, \vec{F}. \end{aligned}$$

□

(11) Control in scaled Sobolev norms: With our assumptions, there exists a constant $c > 0$ such that the variational solution $u(t) \in \mathcal{M}$ satisfies

$$\|u(t)\|_2 \leq C(\|H_{BO}\psi_0\| + 1), \qquad t \in [0, \bar{t}].$$

(12) *Proof.* By the smoothness assumptions of the eigenvector Φ, we have for $\psi\Phi \in \mathcal{M}$,

$$\|\psi\Phi\|_2 \leq c\|\psi\|_2 \leq C(\|H_{BO}\psi\| + \|\psi\|).$$

This implies

$$\begin{aligned} \|u(t)\|_2 &\leq C(\|H_{BO}\psi(t)\| + \|u(t)\|) \\ &= C(\|H_{BO}\psi_0\| + 1). \end{aligned}$$

□

6. Cont. Gaussian superpositions (March 12th, 13:30-15:30)

(1) Wave packet transform: For any function $g : \mathbb{R}^d \to \mathbb{C}$ of Schwartz class and any $z = (q, p) \in \mathbb{R}^{2d}$, we define

$$g_z(x) = \varepsilon^{-d/4} g(\tfrac{x-q}{\sqrt{\varepsilon}})\, \mathrm{e}^{\mathrm{i}(x-q)\cdot p/\varepsilon}, \qquad x \in \mathbb{R}^d.$$

(2) Inversion formula: Let g be of Schwartz class and unit L^2-norm. Then, for any $\psi \in L^2(\mathbb{R}^d)$,

$$\psi = (2\pi\varepsilon)^{-d} \int_{\mathbb{R}^{2d}} \langle g_z \mid \psi \rangle g_z \,\mathrm{d}z$$

and

$$\|\psi\|^2 = (2\pi\varepsilon)^{-d} \int_{\mathbb{R}^{2d}} |\langle g_z \mid \psi \rangle|^2 \,\mathrm{d}z.$$

(3) *Proof.* We use the Fourier inversion formula to calculate

$$\begin{aligned}
&(2\pi\varepsilon)^{-d} \int_{\mathbb{R}^{2d}} \langle g_z \mid \psi \rangle g_z \,\mathrm{d}z \\
&= (2\pi\varepsilon)^{-d} \varepsilon^{-d/2} \int_{\mathbb{R}^{3d}} \overline{g(\tfrac{y-q}{\sqrt{\varepsilon}})}\, \psi(y)\, g(\tfrac{x-q}{\sqrt{\varepsilon}})\, \mathrm{e}^{\mathrm{i}(x-y)\cdot p/\varepsilon} \,\mathrm{d}(y,z) \\
&= \varepsilon^{-d/2} \int_{\mathbb{R}^d} |g(\tfrac{x-q}{\sqrt{\varepsilon}})|^2\, \psi(x) \,\mathrm{d}q \\
&= \psi(x).
\end{aligned}$$

Then, we also obtain that

$$\begin{aligned}
\|\psi\|^2 &= \langle \psi \mid \psi \rangle \\
&= (2\pi\varepsilon)^{-d} \int_{\mathbb{R}^{2d}} \langle g_z \mid \psi \rangle \langle \psi \mid g_z \rangle \,\mathrm{d}z \\
&= (2\pi\varepsilon)^{-d} \int_{\mathbb{R}^{2d}} |\langle g_z \mid \psi \rangle|^2 \,\mathrm{d}z.
\end{aligned}$$

□

(4) Gaussian beams:

$$\begin{aligned}
\mathrm{e}^{-\mathrm{i}Ht/\varepsilon}\psi_0 &= (2\pi\varepsilon)^{-d} \int_{\mathbb{R}^{2d}} \langle g_z \mid \psi \rangle \mathrm{e}^{-\mathrm{i}Ht/\varepsilon} g_z \,\mathrm{d}z \\
&\approx (2\pi\varepsilon)^{-d} \int_{\mathbb{R}^{2d}} \langle g_z \mid \psi \rangle\, \mathrm{e}^{\mathrm{i}S(t,z)/\varepsilon} g[z(t,z), Z(t,z)] \,\mathrm{d}z,
\end{aligned}$$

where the vector $z(t,z) = (q(t,z), p(t,z)) \in \mathbb{R}^{2d}$ and the matrix $Z(t,z) = (Q(t,z), P(t,z)) \in \mathbb{C}^{2d\times d}$ solve the classical equations of motion,

$$\dot q = p, \quad \dot p = -\nabla V(q), \quad \dot Q = P, \quad \dot P = -\nabla^2 V(q) Q,$$

with initial data $z(0) = z$ and $Z(0) = (\mathbb{I}, \mathrm{i}\mathbb{I})$, while the scalar $S(t) \in \mathbb{R}$ is the associated action integral,

$$\dot S = \tfrac{1}{2}|p|^2 - V(q), \quad S(0) = 0.$$

(5) Frozen Gaussian approximation

$$\mathrm{e}^{-\mathrm{i}Ht/\varepsilon}\psi_0 \approx (2\pi\varepsilon)^{-d} \int_{\mathbb{R}^{2d}} \langle g_z \mid \psi\rangle\, a_\natural(t,z)\, \mathrm{e}^{\mathrm{i}S(t,z)/\varepsilon} g_{z(t,z)}\, \mathrm{d}z,$$

where

$$a_\natural(t,z) = \sqrt{2^{-d} \det(Q_\natural(t,z) + \mathrm{i}P_\natural(t,z))}$$

is the Herman–Kluk prefactor that is built from

$$\dot Q_\natural = P_\natural, \quad \dot P_\natural = -\nabla^2 V(q) Q_\natural.$$

with initial condition

$$Z_\natural(0) = (\mathbb{I}, -\mathrm{i}\mathbb{I}).$$

(6) Analysing the Herman–Kluk propagator: We work with oscillatory integral operators of the form

$$\mathcal{I}(t)\psi(x) = (2\pi\varepsilon)^{-d} \times \int_{\mathbb{R}^{2d}} \langle g_z \mid \psi\rangle\, b(q(t,z),x)\,(x - q(t,z))^m\, a(t,z)\, g_{z(t,z)}\, \mathrm{d}z,$$

where $m = (m_1, \dots, m_d) \in \mathbb{N}_0^d$ is a multi-index, while the functions $b : \mathbb{R}^{2d} \to \mathbb{C}$ and $a : \mathbb{R}\times\mathbb{R}^{2d} \to \mathbb{C}$ are smooth and bounded together with all their derivatives.

(7) Basic norm bounds: Let g be an arbitrary Schwartz function of unit norm. We will prove later that

$$\|\mathcal{I}(t)\psi\| \;\le\; c_m\, \varepsilon^{|m|/2} \sup_{(t,z)} |a(t,z)| \sup_{(q,z)} |b(q,x)|\; \|\psi\|,$$

where the constant $c_m > 0$ only depends on the moments of the profile function g.

(8) Gaussian norm bounds: Let g be a standardized Gaussian. We account for the collective oscillations and write

$$\mathcal{I}(t)\psi(x) = (2\pi\varepsilon)^{-d}(\pi\varepsilon)^{-d/2} \times \int_{\mathbb{R}^{3d}} \mathrm{e}^{\mathrm{i}\Psi(t,x,y,z)/\varepsilon}\, b(q(t,z),x)\,(x-q(t,z))^m\, a(t,z)\,\mathrm{d}(y,z)$$

with phase function

$$\Psi(t,x,y,z) = \tfrac{\mathrm{i}}{2}|y-q|^2 + \tfrac{\mathrm{i}}{2}|x-q(t,z)|^2 - p\cdot(y-q) + p(t,z)\cdot(x-q(t,z)) + S(t,z).$$

A subtile integration by parts allows us to improve the polynomial power in the previous estimate from $|m|/2$ to $\lceil |m|/2 \rceil$.

(9) Defect calculation: We calculate and estimate the defect $d(t)$, that is defined by the time evolution of the error $e(t) = \psi(t) - \mathcal{I}(t)\psi_0$, that is,

$$d(t) = (\tfrac{1}{\mathrm{i}\varepsilon}H - \partial_t)\mathcal{I}(t)\psi_0.$$

By the previous lemma, one obtains $e(t) = O(\varepsilon)$.

(10) No conservation properties: Both Gaussian superpositions, the (frozen) Herman–Kluk propagator and the (thawed) Gaussian beams, are order ε accurate, but do neither conserve norm nor energy.

(11) Numerical algorithms (frozen and thawed Gaussians)

(a) Choose a set of numerical quadrature points z_i and weights w_i and evaluate the initial transform $\langle g_z \mid \psi_0\rangle$ at the z_i.

(b) Transport the points z_i by the classical flow. Compute the associated linearised flows and action integrals. The linearised motion is initialised as

$$Z(0,z_i) = (\mathbb{I}, \mathrm{i}\mathbb{I}) \quad \text{(thawed)},$$
$$Z_\natural(0,z_i) = (\mathbb{I}, -\mathrm{i}\mathbb{I}) \quad \text{(frozen)}.$$

(c) Compute either the width matrix or the Herman–Kluk prefactor, that is,

$$C(t,z_i) = P(t,z_i)Q(t,z_i)^{-1} \quad \text{(thawed)},$$
$$a_\natural(t,z_i) = \sqrt{2^{-d}\det(Q_\natural(t,z_i) + \mathrm{i}P_\natural(t,z_i))} \quad \text{(frozen)}.$$

Be careful when taking the complex square roots for normalising the thawed Gaussian by $\det(Q(t,z_i))^{-1/2}$ or computing $a_\natural(t,z_i)$. Continuity determines the choice of the branch.

(d) Form one of the sums for approximating $\mathcal{I}(t)\psi_0$,

$$(2\pi\varepsilon)^{-d}\sum_i \langle g_{z_i} \mid \psi_0\rangle\, \mathrm{e}^{\mathrm{i}S(t,z_i)/\varepsilon} g[z(t,z_i),Z(t,z_i)]w_i,$$

$$(2\pi\varepsilon)^{-d}\sum_i \langle g_{z_i} \mid \psi_0\rangle\, a_\natural(t,z_i)\, \mathrm{e}^{\mathrm{i}S(t,z_i)/\varepsilon} g_{z(t,z_i)} w_i.$$

(12) Basic norm bound: Let $g \in \mathcal{S}(\mathbb{R}^d)$ be of unit norm. Let $a : \mathbb{R}^{2d} \to \mathbb{C}$ be measurable and bounded. Let $\Phi : \mathbb{R}^{2d} \to \mathbb{R}^{2d}$ be a volume-preserving diffeomorphism. For $m \in \mathbb{N}_0^{2d}$ define

$$\mathcal{I}\psi(x) = (2\pi\varepsilon)^{-d} \times \int_{\mathbb{R}^{2d}} \langle g_z \mid \psi\rangle\, (x-\Phi_q(z))^m\, a(z)\, g_{\Phi(z)}\, \mathrm{d}z.$$

Then, $\mathcal{I}\psi$ is square integrable and satisfies

$$\|\mathcal{I}\psi\| \le c_m\, \varepsilon^{|m/2|}\, \|a\|_\infty \|\psi\|,$$

where the constant $c_m > 0$ depends only on the mth moment of g. In particular, $c_0 = 1$.

(13) *Proof.* For all $\varphi \in L^2(\mathbb{R}^d)$,

$$\langle \varphi \mid \mathcal{I}\psi\rangle = \langle (2\pi\varepsilon)^{-d/2}\langle (x-q)^m g_z \mid \varphi\rangle_x \circ \Phi \mid a(z)(2\pi\varepsilon)^{-d/2}\langle g_z \mid \psi\rangle_x\rangle_z.$$

By the Cauchy–Schwarz inequality,

$$\begin{aligned}|\langle \varphi \mid \mathcal{I}\psi\rangle| &\le \|a\|_\infty \cdot \|(2\pi\varepsilon)^{-d/2}\left\langle (x-q)^m g_z \mid \varphi\right\rangle_x \circ \Phi\|_z \cdot \|(2\pi\varepsilon)^{-d/2}\langle g_z \mid \psi\rangle_x\|_z \\ &= \|a\|_\infty \cdot \|(2\pi\varepsilon)^{-d/2}\langle (x-q)^m g_z \mid \varphi\rangle_x\|_z \cdot \|\psi\|_x \\ &= \|a\|_\infty \cdot \varepsilon^{|m|/2} \cdot \underbrace{\|x^m g\|_x}_{=:c_m} \cdot \|\varphi\|_z \cdot \|\psi\|_x.\end{aligned}$$

□

(14) Phase function: We have

$$(\mathrm{i}\partial_q + \partial_p)\Psi(t,x,y,z) = M(t,z)^T(x-q(t,z)),$$

where

$$M(t,z) = (\partial_q - \mathrm{i}\partial_p)q(t,z) + \mathrm{i}(\partial_q - \mathrm{i}\partial_p)p(t,z)$$

is an invertible $d \times d$ matrix with

$$|\det M|^2 = \det(\mathbb{I} + D\Phi^T D\Phi) \geq 1.$$

Note that

$$\dot{M} = (\partial_q - \mathrm{i}\partial_p)p - \mathrm{i}\nabla^2 V(q)(\partial_q - \mathrm{i}\partial_p)p,$$

which implies

$$M = Q_\natural + \mathrm{i}P_\natural.$$

In particular, if V is a polynomial of degree ≤ 2, then $M(t)$ does not depend on z.

(15) The defect is of the form

$$d(t,x) = (2\pi\varepsilon)^{-d} \times \int_{\mathbb{R}^{2d}} \langle g_z \mid \psi_0 \rangle\, \delta(t,x,z)\, \mathrm{e}^{\mathrm{i}S(t,z)/\varepsilon}\, g_{z(t,z)}\, \mathrm{d}z,$$

where

$$\delta(t,x,z) = \tfrac{1}{2} \sum_{k,\ell} (x - q(t,z))_k \times (\mathrm{i}\partial_q + \partial_p)_\ell \left(a_\natural(t,z)(-\mathbb{I} + \nabla^2 V(q(t,z)))M(t,z)^{-T})_{k\ell} \right) + \tfrac{1}{\mathrm{i}\varepsilon} a_\natural(t,z) W_{q(t,z)}(x).$$

(16) Quadratic exactness: Both continuous Gaussian approximations are exact, if V is polynomial of degree ≤ 2.

7. Wigner functions (March 12th, 15:45-17:45)

(1) Weyl quantization of polynomials: Let $j, k \geq 0$ and $a : \mathbb{R}^d \to \mathbb{C}$ with $a(q,p) = q^j p^k$. We define

$$\hat{a} = \mathrm{op}(a) = \frac{1}{(j+k)!} \sum_{\sigma \in S_{j+k}} \sigma(\underbrace{\hat{q}, \ldots, \hat{q}}_{j \text{ times}}, \underbrace{\hat{p}, \ldots, \hat{p}}_{k \text{ times}}).$$

(2) Weyl quantization of Schwartz functions: For $a : \mathbb{R}^{2d} \to \mathbb{R}$ of Schwartz class we define the Hermitian operator

$$\mathrm{op}(a)\psi(x) = \int_{\mathbb{R}^d} \kappa_a(x,y)\psi(y)\mathrm{d}y, \quad \psi \in L^2(\mathbb{R}^d)$$

with kernel

$$\kappa_a(x,y) = (2\pi\varepsilon)^{-d} \int_{\mathbb{R}^d} a(\tfrac{1}{2}(x+y), \xi)\, \mathrm{e}^{\mathrm{i}(x-y)\cdot\xi/\varepsilon}\, \mathrm{d}\xi.$$

(3) Schrödinger operators: Extending the above definition to the smooth and polynomially bounded functions $h(x,\xi) = \frac{1}{2}|\xi|^2 + V(x)$, one obtains

$$\hat{h} = \mathrm{op}(h) = -\tfrac{\varepsilon^2}{2}\Delta_x + V.$$

(4) A first commutator: For Schwartz functions $a : \mathbb{R}^{2d} \to \mathbb{R}$, we have

$$\tfrac{\mathrm{i}}{\varepsilon}[\mathrm{op}(a), -\tfrac{\varepsilon^2}{2}\Delta_x] = \mathrm{op}(-\nabla_x a \cdot \xi).$$

(5) *Proof.* Integration by parts provides that

$$\mathrm{op}(a)\Delta_x\varphi(x) =$$
$$(2\pi\varepsilon)^{-d} \int_{\mathbb{R}^{2d}} a(\tfrac{1}{2}(x+y), \xi)\mathrm{e}^{\mathrm{i}(x-y)\cdot\xi/\varepsilon}\Delta_y\varphi(y)\mathrm{d}(\xi, y) =$$
$$(2\pi\varepsilon)^{-d} \int_{\mathbb{R}^{2d}} \Delta_y \left(a(\tfrac{1}{2}(x+y), \xi)\mathrm{e}^{\mathrm{i}(x-y)\cdot\xi/\varepsilon}\right) \varphi(y)\mathrm{d}(\xi, y).$$

We observe that

$$\Delta_y \left(a(\tfrac{1}{2}(x+y), \xi)\mathrm{e}^{\mathrm{i}(x-y)\cdot\xi/\varepsilon}\right) = \Delta_x \left(a(\tfrac{1}{2}(x+y), \xi)\mathrm{e}^{\mathrm{i}(x-y)\cdot\xi/\varepsilon}\right)$$
$$- \tfrac{2\mathrm{i}}{\varepsilon}\nabla_x a(\tfrac{1}{2}(x+y), \xi) \cdot \xi\, \mathrm{e}^{\mathrm{i}(x-y)\cdot\xi/\varepsilon}.$$

This means, that

$$\mathrm{op}(a)\Delta_x = \Delta_x \mathrm{op}(a) - \tfrac{2\mathrm{i}}{\varepsilon}\mathrm{op}(\partial_x a \cdot \xi).$$

□

(6) The Poisson bracket: For smooth functions $f, g : \mathbb{R}^{2d} \to \mathbb{R}$ we denote

$$\{f, g\} = \partial_\xi f \cdot \partial_x g - \partial_x f \cdot \partial_\xi g = \nabla f \cdot \begin{pmatrix} 0 & -\mathbb{I} \\ \mathbb{I} & 0 \end{pmatrix} \nabla g.$$

(7) The basic commutator estimate: Let $a, b : \mathbb{R}^{2d} \to \mathbb{R}$ be smooth and subquadratic functions. Then, there exists a smooth function $[a, b]_\sharp : \mathbb{R}^{2d} \to \mathbb{R}$, that is bounded together with all its derivatives, such that $[\mathrm{op}(a), \mathrm{op}(b)] = \mathrm{op}([a, b]_\sharp)$. Moreover, there exists a constant $c_{ab} \geq 0$ such that for all $\varphi \in \mathcal{S}(\mathbb{R}^d)$,

$$\left\| \tfrac{\mathrm{i}}{\varepsilon}[\mathrm{op}(a), \mathrm{op}(b)]\varphi - \mathrm{op}(\{a, b\})\varphi \right\| \leq c\,\varepsilon^2 \|\psi\|.$$

The constant $c_{ab} \geq 0$ only depends on derivative bounds of a and b of order ≥ 3. In particular, if a or b is a polynomial of degree ≤ 2, then $c_{ab} = 0$.

(8) Note that $\{a, \frac{1}{2}|\xi|^2\} = -\partial_x a \cdot \xi$.

(9) Classical flow map: Let $\Phi^t : \mathbb{R}^{2d} \to \mathbb{R}^{2d}$ be defined by

$$\partial_t \Phi^t = \begin{pmatrix} 0 & \mathbb{I} \\ -\mathbb{I} & 0 \end{pmatrix} (\nabla h \circ \Phi^t), \quad \Phi^0 = \mathbb{I}.$$

(10) Lemma: For all smooth functions $a : \mathbb{R}^{2d} \to \mathbb{R}$,

$$\partial_t(a \circ \Phi^t) = \{h, a \circ \Phi^t\}.$$

(11) *Proof.*

$$\begin{aligned} \partial_t(a \circ \Phi^t) &= (\nabla a) \circ \Phi^t \cdot \partial_t \Phi^t \\ &= (\nabla a) \circ \Phi^t \cdot \begin{pmatrix} 0 & \mathbb{I} \\ -\mathbb{I} & 0 \end{pmatrix} (\nabla h \circ \Phi^t) \\ &= \{h, a\} \circ \Phi^t \\ &= \{h \circ \Phi^t, a \circ \Phi^t\} \\ &= \{h, a \circ \Phi^t\}, \end{aligned}$$

where we have used symplecticity of the flow map and energy conservation of Hamiltonian flows. □

(12) Egorov's theorem: We assume:
  (a) The potential function $V : \mathbb{R}^d \to \mathbb{R}$ is smooth and subquadratic.
  (b) The function $a : \mathbb{R}^{2d} \to \mathbb{R}$ that defines the observable is smooth and bounded together with all its derivatives.

Then, for all $\bar t > 0$ there exists $c > 0$ such that

$$\left|\langle \mathrm{op}(a)\rangle_{\psi(t)} - \langle \mathrm{op}(a\circ\Phi^t)\rangle_{\psi_0}\right| \le c\,t\,\varepsilon^2, \quad t\in[0,\bar t]$$

for all initial data ψ_0 that are Schwartz class and of unit norm.

(13) *Proof.* We compare the quantum and the classical evolution,

$$\begin{aligned}
&\mathrm{e}^{\mathrm{i}Ht/\varepsilon}\mathrm{op}(a)\mathrm{e}^{-\mathrm{i}Ht/\varepsilon} - \mathrm{op}(a\circ\Phi^t)\\
&= \int_0^t \frac{\mathrm{d}}{\mathrm{d}s}\left(\mathrm{e}^{\mathrm{i}Hs/\varepsilon}\mathrm{op}(a\circ\Phi^{t-s})\mathrm{e}^{-\mathrm{i}Hs/\varepsilon}\right)\mathrm{d}s\\
&= \int_0^t \mathrm{e}^{\mathrm{i}Hs/\varepsilon}\left(\tfrac{1}{\mathrm{i}\varepsilon}[\mathrm{op}(h),\mathrm{op}(a\circ\Phi^{t-s})] - \mathrm{op}(\partial_t(a\circ\Phi^{t-s})\right)\mathrm{e}^{-\mathrm{i}Hs/\varepsilon}\mathrm{d}s.
\end{aligned}$$

By the Lemma,

$$\mathrm{op}(\partial_t(a\circ\Phi^{t-s}) = \mathrm{op}(\{h, a\circ\Phi^{t-s}\}).$$

By the commutator estimate, we have for all Schwartz class functions $\varphi : \mathbb{R}^d \to \mathbb{R}$,

$$\tfrac{1}{\mathrm{i}\varepsilon}[\mathrm{op}(h),\mathrm{op}(a\circ\Phi^{t-s})]\varphi - \mathrm{op}(\partial_t(a\circ\Phi^{t-s}))\varphi = r(t,s)$$

with

$$\sup_{s,t\in[0,\bar t]} \|r(t,s)\| \le c\,\varepsilon^2\|\varphi\|.$$

Using the unitarity of the quantum evolution, we have shown that

$$\left\|\mathrm{e}^{\mathrm{i}Ht/\varepsilon}\mathrm{op}(a)\mathrm{e}^{-\mathrm{i}Ht/\varepsilon}\psi_0 - \mathrm{op}(a\circ\Phi^t)\psi_0\right\| \le c\,t\,\varepsilon^2,$$

which in particular implies the claimed estimate on the expectation values. □

(14) Norm- and energy conservation: The Egorov approximation inherits the conservation of norm ($a = 1$) and energy ($a = h$) from the classical evolution.

(15) Wigner functions: We observe that for all Schwartz class observables a and all square integrable functions ψ,

$$\begin{aligned}
\langle \mathrm{op}(a)\rangle_\psi &= \int_{\mathbb{R}^d} \overline{\psi}(x)\,\mathrm{op}(a)\psi(x)\,\mathrm{d}x\\
&= (2\pi\varepsilon)^{-d}\int_{\mathbb{R}^{3d}} \overline{\psi}(x)\,a(\tfrac{x+y}{2},\xi)\mathrm{e}^{\mathrm{i}(x-y)\cdot\xi/\varepsilon}\psi(y)\,\mathrm{d}(x,y\xi)\\
&= \int_{\mathbb{R}^{2d}} a(x,\xi)\ (2\pi\varepsilon)^{-d}\int_{\mathbb{R}^d}\overline{\psi}(x+\tfrac12 y)\,\mathrm{e}^{\mathrm{i}y\cdot\xi/\varepsilon}\psi(x-\tfrac12 y)\,\mathrm{d}y\,\mathrm{d}(x,\xi),
\end{aligned}$$

where we have used the volume-preserving change of variables $(x,y) \mapsto (x+\frac{1}{2}y, x-\frac{1}{2}y)$. We therefore define

$$\mathcal{W}_\psi(x,\xi) = (2\pi\varepsilon)^{-d} \int_{\mathbb{R}^d} \overline{\psi}(x+\tfrac{1}{2}y)\, \psi(x-\tfrac{1}{2}y)\, \mathrm{e}^{\mathrm{i}y\cdot\xi/\varepsilon}\, \mathrm{d}y$$

and obtain

$$\langle \mathrm{op}(a) \rangle_\psi = \int_{\mathbb{R}^{2d}} a(x,\xi)\, \mathcal{W}_\psi(x,\xi)\, \mathrm{d}(x,\xi).$$

(16) Egorov's theorem can be recast in terms of the Wigner function of the initial data as

$$\langle \mathrm{op}(a) \rangle_{\psi(t)} = \int_{\mathbb{R}^{2d}} (a \circ \Phi^t)(z)\, \mathcal{W}_{\psi(0)}(z)\, \mathrm{d}z + O(\varepsilon^2).$$

8. Time integration (March 13th, 10:00-12:00)

(1) Numerical method for the computation of expectation values:

  (a) Choose a set of quadrature points $z_i \in \mathbb{R}^{2d}$ and evaluate the initial Wigner function $\mathcal{W}_{\psi(0)}$ at the points z_i.
  (b) Transport the points z_i by the classical flow and evaluate the observable a at the points $\Phi^t(z_i)$.
  (c) Sum the quantities computed in 1. and 2. according to the quadrature rule.

(2) Hudson's theorem: The Wigner function $\mathcal{W}_\psi$ of a square integrable function ψ is (pointwise) non-negative if and only if there exist $\gamma \in \mathbb{C}$, $z \in \mathbb{R}^{2d}$ and $C \in \mathcal{S}_+(d)$ such that $\psi = \gamma\, g[z, C]$.

(3) Hagedorn' wave packets: The Wigner function $\mathcal{W}_{\varphi_k}$ of the kth Hagedorn wave packet $\varphi_k = \varphi_k[z, Z]$ is

$$\mathcal{W}_{\varphi_k}(\zeta) = \frac{(-1)^{|k|}}{(\pi\varepsilon)^d} \prod_{n=1}^{d} L_{k_n}(\tfrac{2}{\varepsilon}|\ell_n(\zeta)|^2) \exp(-\tfrac{1}{\varepsilon}|\ell_n(\zeta)|^2),$$

where L_{k_n} denotes the k_nth (univariate) Laguerre polynomial and $\ell : \mathbb{R}^{2d} \to \mathbb{C}^{2d}$ the affine map

$$\ell(\zeta) = \begin{pmatrix} Q^T & P^T \end{pmatrix} \begin{pmatrix} 0 & -\mathbb{I} \\ \mathbb{I} & 0 \end{pmatrix} (\zeta - z).$$

(4) For any square-integrable ψ with $\psi(x) = -\psi(x)$ for all $x \in \mathbb{R}^d$, we have

$$\begin{aligned} \mathcal{W}_\psi(0) &= (2\pi\varepsilon)^{-d} \int_{\mathbb{R}^d} \overline{\psi}(\tfrac{1}{2}y)\psi(-\tfrac{1}{2}y)\mathrm{d}y \\ &= -(\pi\varepsilon)^{-d}\|\psi\|^2 \leq 0. \end{aligned}$$

(5) Symplecticity: The flow map $\Phi^t : \mathbb{R}^{2d} \to \mathbb{R}^{2d}$ of the Hamiltonian equations

$$\dot{q} = p, \quad \dot{p} = -\nabla V(q)$$

is symplectic, that is, for all $(t, z) \in \mathbb{R} \times \mathbb{R}^{2d}$,

$$D\Phi^t(z)^T J D\Phi^t(z) = J, \quad J = \begin{pmatrix} 0 & -\mathbb{I} \\ \mathbb{I} & 0 \end{pmatrix}.$$

(6) Volume-preservation: Symplectic maps preserve volume. One can easily derive from the above symplecticity condition that

$$\begin{aligned} 1 &= \det(J) = \det(D\Phi^t(z) J D\Phi^t(z)) \\ &= \det(D\Phi^t(z))^2 \det(J) = \det(D\Phi^t(z))^2, \end{aligned}$$

while a more involved argument actually proves that

$$\det(D\Phi^t(z)) = 1.$$

(7) Störmer–Verlet method as a composition method: For a small time step $\tau > 0$, the Störmer–Verlet method approximates

$$\Phi^\tau \approx \Sigma^\tau := \Phi_V^{\tau/2} \circ \Phi_T^\tau \circ \Phi_V^{\tau/2},$$

where

$$\begin{aligned} \Phi_V^\tau(q,p) &= (q, p - t\nabla V(q)), \\ \Phi_T^\tau(q,p) &= (q + tp, p). \end{aligned}$$

(8) Störmer-Verlet algorithm: To advance a point (q^n, p^n) at time $t^n = n\tau$ to the new approximation $(q^{n+1}, p^{n+1}) = \Sigma^\tau(q^n, p^n)$ at time t^{n+1}, we compute

$$\begin{aligned} p^{n+1/2} &= p^n - \tfrac{\tau}{2}\nabla V(q^n), \\ q^{n+1} &= q^n + \tau p^{n+1/2}, \\ p^{n+1} &= p^{n+1/2} - \tfrac{\tau}{2}\nabla V(q^{n+1/2}). \end{aligned}$$

(9) Symplecticity: As a composition of symplectic maps, the Störmer–Verlet method is symplectic and thus volume-preserving.

(10) Second-order accuracy: For a smooth potential V, the Störmer–Verlet method is second order, that is, for all $\bar{t} > 0$ and all compact sets $K \subset \mathbb{R}^{2d}$ there exists a constant $c > 0$ such that uniformly for all n and τ with $n\tau \le \bar{t}$ and all $z \in K$

$$|\Sigma^{n\tau}(z) - \Phi^{n\tau}(z)| \le c\tau^2.$$

For subquadratic potentials the error bound is uniform for all $z \in \mathbb{R}^{2d}$.

(11) Implementation: In practice, only the first and the last half-step have to be carried out, since

$$\Sigma^{n\tau} = \Phi_V^{\tau/2} \circ \Phi_T^\tau \circ \Phi_V^\tau \circ \Phi_T^\tau \cdots \circ \Phi_T^\tau \circ \Phi_V^{\tau/2}.$$

(12) Störmer–Verlet method for the linearized equations of motion: We apply the Störmer–Verlet method to the linearized equations of motion,

$$\begin{aligned} P^{n+1/2} &= P^n - \tfrac{\tau}{2}\nabla^2 V(q^n) Q^n, \\ Q^{n+1} &= Q^n + \tau P^{n+1/2}, \\ P^{n+1} &= P^{n+1/2} - \tfrac{\tau}{2}\nabla^2 V(q^{n+1/2}) Q^n. \end{aligned}$$

(13) Symplecticity: Phase space differentiation of the numerical flow map Σ^τ is equivalent to applying the integrator to the differentiated equations of motion. Therefore, for all n, the matrix

$$Y^n = \begin{pmatrix} \operatorname{Re} Q^n & \operatorname{Im} Q^n \\ \operatorname{Re} P^n & \operatorname{Im} P^n \end{pmatrix}$$

is symplectic, which is vital for the construction of associated Gaussian wave packets.

(14) Second order accuracy: (Q^n, P^n) are second order accurate in the same sense as (q^n, p^n).

(15) Strang splitting: For a small time-step $\tau > 0$, we approximate the unitary evolution

$$U(\tau) = \mathrm{e}^{-\mathrm{i}H\tau/\varepsilon}, \quad H = T + V = -\tfrac{\varepsilon^2}{2}\Delta_x + V$$

by

$$U(\tau) \approx S(\tau) := U_V(\tfrac{\tau}{2})^*\, U_T(\tau)\, U_V(\tfrac{\tau}{2}).$$

(16) Second-order accuracy in norm: Assume that V is a smooth and subquadratic function. Then, there exists a constant $c > 0$ such that

$$\|S(\tau)^n \psi_0 - \psi(n\tau)\| \le c\, n\tau\, \frac{\tau^2}{\varepsilon} \max_{0 \le t \le n\tau} \|\psi(t)\|_{\Sigma^2_\varepsilon},$$

where

$$\|\psi\|^2_{\Sigma^2_\varepsilon} = \sum_{|m| \le 2} \left(\|(\varepsilon \partial_x)^\alpha \psi\|^2 + \|x^\alpha \psi\|^2 \right).$$

The constant c is independent of ε, n and τ, but depends on derivative bounds for V.

(17) Second-order accuracy for observables: Assume that the potential $V : \mathbb{R}^d \to \mathbb{R}$ is smooth and subquadratic. Let $a : \mathbb{R}^{2d} \to \mathbb{R}$

be a Schwartz function. Then, for all $\bar{t} > 0$ there exists a constant $c > 0$ such that

$$\left|\langle \mathrm{op}(a)\rangle_{S(n\tau)\psi_0} - \langle \mathrm{op}(a)\rangle_{\psi(n\tau)}\right| \le n\tau\, c\,\tau^2 \sup_{0\le t\le n\tau} \|A(t)\|,$$

where the constant c is independent of ε, n and τ, but depends on derivative bounds for V and a.

(18) *Proof.* We examine the time-derivatives of

$$A(t) = U(t)^*\mathrm{op}(a)U(t).$$

We have

$$\begin{aligned}
\tfrac{\mathrm{d}}{\mathrm{d}t}A(t) &= \tfrac{1}{\mathrm{i}\varepsilon}[H, A(t)],\\
\tfrac{\mathrm{d}^2}{\mathrm{d}t^2}A(t) &= \tfrac{1}{\mathrm{i}\varepsilon}[H, \tfrac{1}{\mathrm{i}\varepsilon}[H, A(t)]],\\
\tfrac{\mathrm{d}^3}{\mathrm{d}t^3}A(t) &= \tfrac{1}{\mathrm{i}\varepsilon}[H, \tfrac{1}{\mathrm{i}\varepsilon}[H, \tfrac{1}{\mathrm{i}\varepsilon}[H, A(t)]]].
\end{aligned}$$

and therefore

$$A(\tau) = \mathrm{op}(a)$$
$$+ \tau\,\tfrac{1}{\mathrm{i}\varepsilon}[H, \mathrm{op}(a)] + \tfrac{\tau^2}{2}\,\tfrac{1}{\mathrm{i}\varepsilon}[H, \tfrac{1}{\mathrm{i}\varepsilon}[H, \mathrm{op}(a)]] + \tau^3 R_\tau(\mathrm{op}(a), H)$$

with

$$\|R_\tau(\mathrm{op}(a), H)\varphi\| \le c\|\varphi\| \quad \text{uniformly in } \varepsilon,\ \varphi, \text{ and } \tau \le 1.$$

Analogously,

$$U_V(\tfrac{\tau}{2})^*\mathrm{op}(a)U_V(\tfrac{\tau}{2}) = \mathrm{op}(a)$$
$$+ \tfrac{\tau}{2}\,\tfrac{1}{\mathrm{i}\varepsilon}[V, \mathrm{op}(a)] + \tfrac{\tau^2}{4}\,\tfrac{1}{\mathrm{i}\varepsilon}[V, \tfrac{1}{\mathrm{i}\varepsilon}[V, \mathrm{op}(a)]] + \tau^3 R_{\tau/2}(\mathrm{op}(a), V)$$

and

$$U_T(\tau)^*\mathrm{op}(b)U_T(\tau) = \mathrm{op}(a)$$
$$+ \tau\,\tfrac{1}{\mathrm{i}\varepsilon}[T, \mathrm{op}(b)] + \tfrac{\tau^2}{2}\,\tfrac{1}{\mathrm{i}\varepsilon}[T, \tfrac{1}{\mathrm{i}\varepsilon}[T, \mathrm{op}(b)]] + \tau^3 R_\tau(\mathrm{op}(b), T).$$

Combining these expansions, we obtain

$$\|S(\tau)^*\mathrm{op}(a)S(\tau) - A(\tau)\| \le c\tau^3$$

and

$$\begin{aligned}
\|S(n\tau)^*\mathrm{op}(a)S(n\tau) - A(n\tau)\| &\le nc\tau^3 \sup_{0\le t\le n\tau}\|A(t)\|\\
&= c\,n\tau\,\tau^2 \sup_{0\le t\le n\tau}\|A(t)\|.
\end{aligned}$$

□

(19) Variational splitting method for $H = T + V$: To approximate the solution $u(t) \in \mathcal{M}$ of

$$\mathrm{i}\varepsilon\partial_t u = P_u H u, \quad u(0) = u_0,$$

we perform a Strang splitting as follows:

(a) Determine $u_+^n \in \mathcal{M}$ as the solution at time $\tau/2$ of

$$i\varepsilon\partial_t u = P_u V u, \quad u(0) = u^n.$$

(b) Determine $u_-^{n+1} \in \mathcal{M}$ as the solution at time τ of

$$i\varepsilon\partial_t u = P_u T u, \quad u(0) = u_+^n.$$

(c) Determine $u^{n+1} \in \mathcal{M}$ as the solution at time $\tau/2$ of

$$i\varepsilon\partial_t u = P_u V u, \quad u(0) = u_-^{n+1}.$$

(20) Accuracy: The variational Strang splitting provides

$$u^n - u(n\tau) = O(\tau^2/\varepsilon),$$
$$\langle \mathrm{op}(a)\rangle_{u^n} - \langle \mathrm{op}(a)\rangle_{u(n\tau)} = O(\tau^2).$$

9. High-dimensional quadrature (March 13th, 14:00-16:00)

(1) Simple Monte-Carlo method: Let μ be a probability measure on $\mathbb{R}^d$ and $f : \mathbb{R}^d \to \mathbb{C}$ an integrable function. We approximate the value of the integral

$$I = \int_{\mathbb{R}^d} f(x)\mathrm{d}\mu(x)$$

by taking $x_1, \dots, x_N \in \mathbb{R}^N$ independent samples of μ and setting

$$I_N = \frac{1}{N}\sum_{n=1}^{N} f(x_n).$$

(2) Basic Monte-Carlo estimate: The expected value of the squared error is given by

$$\mathbb{E}(|I - I_N|^2) = \frac{\mathbb{V}(f)}{N}$$

with the variance

$$\mathbb{V}(f) = \int_{\mathbb{R}^d} |f(x) - I|^2 \mathrm{d}\mu(x)$$
$$= \int_{\mathbb{R}^d} |f(x)|^2 \,\mathrm{d}\mu(x) - |I|^2.$$

(3) *Proof.* We observe that

$$\mathbb{E}(I_N) = \frac{1}{N}\sum_{n=1} \mathbb{E}(f) = I.$$

Since the samples are independent and identically distributed, we also have

$$\mathbb{E}(|I_N - I|^2) = \mathbb{V}(I_N) = \frac{1}{N^2}\sum_{n=1}^{N} \mathbb{V}(f) = \frac{\mathbb{V}(f)}{N}.$$

□

(4) An illustrative example: Let $\mu(x) = (2\pi\varepsilon)^{-d/2}\mathrm{e}^{-|x|^2/(2\varepsilon)}$ and $f_\xi(x) = (2\pi\varepsilon)^{-d/2}\mathrm{e}^{\mathrm{i}\xi\cdot x/\varepsilon}$ for $\xi \in \mathbb{R}^d$. Then,

$$I(f_\xi) = (2\pi\varepsilon)^{-d} \int_{\mathbb{R}^d} \mathrm{e}^{\mathrm{i}\xi\cdot x/\varepsilon}\mathrm{e}^{-|x|^2/(2\varepsilon)} \,\mathrm{d}x$$
$$= (2\pi\varepsilon)^{-d/2}\mathrm{e}^{-|\xi|^2/(2\varepsilon)}.$$

Note that f_ξ is scaled such that

$$\int_{\mathbb{R}^d} I(f_\xi)\,\mathrm{d}\xi = 1.$$

The variance satisfies

$$\begin{aligned}\mathbb{V}(f_\xi) &= \int_{\mathbb{R}^d} |f_\xi(x)|^2 \mathrm{d}\mu(x) - |I(f_\xi)|^2 \\ &= (2\pi\varepsilon)^{-d}(1 - \mathrm{e}^{-|\xi|^2/(2\varepsilon)}).\end{aligned}$$

(5) Frozen Gaussian approximation: We reconsider

$$\mathcal{I}(t)\psi_0 = (2\pi\varepsilon)^{-d} \int_{\mathbb{R}^{2d}} \langle g_z \mid \psi_0\rangle\, a_\natural(t,z)\, \mathrm{e}^{\mathrm{i}S(t,z)/\varepsilon} g_{\Phi^t(z)} \mathrm{d}z$$

for Gaussian wave packet initial data $\psi_0 = g_{z_0}$, $z_0 \in \mathbb{R}^d$. Then,

$$\langle g_z \mid \psi_0\rangle = \exp(-\tfrac{1}{4\varepsilon}|z - z_0|^2 + \tfrac{\mathrm{i}}{2\varepsilon}(p + p_0)\cdot(q - q_0)).$$

We write

$$(2\pi\varepsilon)^{-d}\langle g_z \mid \psi_0\rangle = r_0(z)\mu_0(z)$$

with

$$\begin{aligned}\mu_0(z) &= (4\pi\varepsilon)^{-d} \exp(-\tfrac{1}{4\varepsilon}|z - z_0|^2), \\ r_0(z) &= 2^d\, \exp(\tfrac{\mathrm{i}}{2\varepsilon}(p + p_0)\cdot(q - q_0)).\end{aligned}$$

We write the frozen approximation as

$$\mathcal{I}(t)\psi_0 = \int_{\mathbb{R}^{2d}} r_0(z)\, a_\natural(t,z)\, \mathrm{e}^{\mathrm{i}S(t,z)/\varepsilon} g_{\Phi^t(z)} \mathrm{d}\mu_0(z).$$

The variance of the integrand

$$f(t,z) = r_0(z)\, a_\natural(t,z)\, \mathrm{e}^{\mathrm{i}S(t,z)/\varepsilon} g_{\Phi^t(z)}$$

satisfies

$$\begin{aligned}\mathbb{V}(f(t)) &= \int_{\mathbb{R}^{2d}} \|f(t,z)\|^2\, \mathrm{d}\mu_0(z) - \|\mathcal{I}(t)\psi_0\|^2 \\ &= \int_{\mathbb{R}^{2d}} 4^d |a_\natural(t,z)|^2\, \mathrm{d}\mu_0(z) - \|\mathcal{I}(t)\psi_0\|^2 \\ &\sim 4^d - 1.\end{aligned}$$

It is ε-independent despite the ε-oscillations, but grows (exponentially) with respect to dimension d.

(6) Discrepancy: For $x_1, \dots, x_N \in \mathbb{R}^d$ and $x \in \mathbb{R}^N$ consider the discrepancy function

$$D_N(x_1, \dots, x_N; x) = \frac{1}{N} \sum_{n=1}^{N} \mathbb{I}_{]-\infty,x]}(x_n) - \mu(] - \infty, x]),$$

where $] - \infty, x] = \{y \in \mathbb{R}^d \mid y_1 \le x_1, \dots, y_d \le x_d\}$.

(7) The unit cube: For the uniform distribution μ on the unit cube $[0,1]^d$, there are well-known points $x_1, \dots, x_N \in [0,1]^d$ of low discrepancy. The Halton or the Sobol points satisfy

$$\sup_{x \in \mathbb{R}^d} |D_N(x_1, \dots, x_N; x)| = O((\log N)^{d-1}/N).$$

(8) Product measures: If μ is the product of univariate probability measures with accessible cumulative distribution functions, then $[0,1]^d$-uniform-distribution low discrepancy points can be lifted to $\mathbb{R}^d$-μ low discrepancy points.

(9) Quasi-Monte Carlo accuracy: Let $f : \mathbb{R}^d \to \mathbb{C}$ be a Schwartz function and μ a probability distribution on $\mathbb{R}^d$. Then, for all $x_1, \dots, x_N \in \mathbb{R}^d$,

$$\frac{1}{N} \sum_{n=1}^{N} f(x_n) - \int_{\mathbb{R}^d} f(x) \mathrm{d}\mu(x) =$$
$$(-1)^d \int_{\mathbb{R}^d} \partial_1 \cdots \partial_d f(x)\, D_N(x_1, \dots, x_N; x)\, \mathrm{d}x.$$

(10) *Proof.* We observe that

$$\begin{aligned} f(x) &= -\int_{x_1}^{\infty} \partial_1 f(y_1, x_2, \dots, x_d) \mathrm{d}y_1 \\ &= (-1)^d \int_{x_1}^{\infty} \cdots \int_{x_d}^{\infty} \partial_1 \cdots \partial_d f(y_1, y_2, \dots, y_d) \mathrm{d}y \\ &= (-1)^d \int_{[x,\infty[} \partial_1 \cdots \partial_d f(y) \mathrm{d}y \end{aligned}$$

This implies

$$\begin{aligned}\frac{1}{N}\sum_{n=1}^{N} f(x_n) &= \frac{(-1)^d}{N}\sum_{n=1}^{N}\int_{[x_n,\infty[} \partial_1\cdots\partial_d f(y)\mathrm{d}y\\ &= \frac{(-1)^d}{N}\sum_{n=1}^{N}\int_{\mathbb{R}^d} \mathbb{I}_{[x_n,\infty[}(y)\,\partial_1\cdots\partial_d f(y)\,\mathrm{d}y\end{aligned}$$

and, by Fubini's theorem,

$$\begin{aligned}\int_{\mathbb{R}^d} f(x)\mathrm{d}\mu(x) &= (-1)^d\int_{\mathbb{R}^d}\int_{[x,\infty[} \partial_1\cdots\partial_d f(y)\,\mathrm{d}(y,x)\\ &= (-1)^d\int_{\mathbb{R}^d} \mu(]-\infty,y])\,\partial_1\cdots\partial_d f(y)\,\mathrm{d}y.\end{aligned}$$

□

(11) Full tensor quadrature: Let Q_ℓ, $\ell \geq 0$, be a univariate quadrature rule with 2^ℓ nodes,

$$Q_\ell f = \sum_{i=1}^{2^\ell} w_i^\ell f(x_i^\ell) \approx \int_{\mathbb{R}} f(x)\mathrm{d}x, \quad f:\mathbb{R}\to\mathbb{C}.$$

A full tensor quadrature reads

$$\begin{aligned}(Q_L\otimes\cdots\otimes Q_L)f &= \sum_{i_1=1}^{2^L}\cdots\sum_{i_d=1}^{2^L} w_{i_1}^L\cdots w_{i_d}^L\, f(x_{i_1}^L,\ldots,x_{i_d}^L)\\ &\approx \int_{\mathbb{R}^d} f(x)\mathrm{d}x, \quad f:\mathbb{R}^d\to\mathbb{C},\end{aligned}$$

and uses 2^{dL} quadrature nodes.

(12) Differences of univariate quadratures: Let $\Delta_0 f = Q_0 f$ and

$$\Delta_\ell f = Q_\ell f - Q_{\ell-1} f, \quad \ell \geq 1.$$

We may write

$$Q_L f = \sum_{\ell=1}^{L} \Delta_\ell f, \quad f:\mathbb{R}\to\mathbb{C}.$$

In terms of the difference operators the full tensor quadrature can be written as

$$Q_L\otimes\cdots\otimes Q_L = \sum_{\ell_1=1}^{L}\cdots\sum_{\ell_d=1}^{L} \Delta_{\ell_1}\otimes\cdots\otimes\Delta_{\ell_d}.$$

(13) Smolyak quadrature: One uses the sparse grid

$$\left\{(x_{i_1}^{\ell_1}, \dots, x_{i_d}^{\ell_d}) \mid \ell_1 + \cdots \ell_d \leq L\right\},$$

that in comparison to the full grid with $(2^L)^d$, points has less than $2^L \log(2^L)^{d-1}$ points. The associated quadrature rule

$$S_L^d f = \sum_{\ell_1+\cdots+\ell_d \leq L} \Delta_{\ell_1} \otimes \cdots \otimes \Delta_{\ell_d} f$$

typically comes with error estimates that contain bounds on the mixed derivatives of the integrand $f : \mathbb{R}^d \to \mathbb{C}$.