Semiclassical approximations of quantum mechanical equilibrium distributions

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based on joint work with **Wolfgang Gaim** and **Hans Stiepan**.

1. Introduction

Eugene Wigner, Phys. Rev. 40, 1932:

On the Quantum Correction For Thermodynamic Equilibrium

Quantum Hamiltonian

$\hat{h}^{\varepsilon} : D(\hat{h}^{\varepsilon}) \to L^2(\mathbb{R}^n)$

$\hat{h}^{\varepsilon} = -\frac{\varepsilon^2}{2}\Delta_x + V(x) = h(x, -\mathrm{i}\varepsilon\nabla_x)$

Classical Hamiltonian

$h : \mathbb{R}^{2n} \to \mathbb{R}$

$h(q,p) = \frac{1}{2}|p|^2 + V(q)$

Equilibrium expectation values in the semiclassical regime $\varepsilon \ll 1$:

$$\mathrm{Tr}\left(\hat{a}^{\varepsilon}\,\mathrm{e}^{-\beta\hat{h}^{\varepsilon}}\right) \approx \frac{1}{(2\pi\varepsilon)^n}\int_{\mathbb{R}^{2n}} \mathrm{d}q\mathrm{d}p\; a(q,p)\,\mathrm{e}^{-\beta h(q,p)}\,\left(1 + \varepsilon^2 C(q,p)\right)$$

where

$$C(q,p) = \frac{\beta^3}{24}\left(|\nabla V(q)|^2 + \langle p, D^2V(q)p\rangle_{\mathbb{R}^n} - \frac{3}{\beta}\,\Delta V(q)\right)$$

1. Introduction

For more general Hamiltonians and distributions

$$h : \mathbb{R}^{2n} \to \mathbb{R}\,, \quad \hat{h}^{\varepsilon} = h(x, -\mathrm{i}\varepsilon\nabla_x)\,, \quad f : \mathbb{R} \to \mathbb{C}\,,$$

it holds (by definition of the Weyl quantization rule) that

$$\mathrm{Tr}\left(\hat{a}^{\varepsilon}\, f(\hat{h}^{\varepsilon})\right) = \frac{1}{(2\pi\varepsilon)^n} \int_{\mathbb{R}^{2n}} \mathrm{d}q\mathrm{d}p\; a(q,p)\, f^{\varepsilon}(q,p)\,,$$

where

$$f^{\varepsilon} := \mathrm{Symb}\left(f(\hat{h}^{\varepsilon})\right) = f \circ h + \varepsilon^2 f_2 + \mathcal{O}(\varepsilon^3)$$

with

$$f_2 = \tfrac{1}{12}\left(f'''(h) \sum_{|\alpha+\beta|=2} \frac{(-1)^{\beta}}{\alpha!\beta!} (\partial_q^{\alpha}\partial_p^{\beta} h)(\partial_q h)^{\beta}(\partial_p h)^{\alpha} + f''(h)\,\{h,h\}_2\right)$$

1. Introduction

Can one find similar expressions for systems described by Hamiltonians with matrix- or operator-valued symbols?

$$H : \mathbb{R}^{2n} \to \mathcal{L}_{\mathrm{sa}}(\mathcal{H}_{\mathrm{f}})\,, \quad \hat{H}^{\varepsilon} = H(x, -\mathrm{i}\varepsilon\nabla_x) \in \mathcal{L}_{\mathrm{sa}}(L^2(\mathbb{R}^n, \mathcal{H}_{\mathrm{f}}))$$

Example: The Hamiltonian describing a molecule with nucleonic configuration $x \in \mathbb{R}^n$ and electronic configuration $y \in \mathbb{R}^m$ has the form

$$\hat{H}^{\varepsilon} = -\frac{\varepsilon^2}{2}\Delta_x \underbrace{-\frac{1}{2}\Delta_y + V(x,y)}_{H_{\mathrm{el}}(x)}$$

with $\varepsilon^2 = \frac{1}{M}$ and

$$H(q,p) = \frac{1}{2}|p|^2\,\mathbf{1}_{\mathcal{H}_{\mathrm{f}}} + H_{\mathrm{el}}(q) \quad \in \mathcal{L}_{\mathrm{sa}}(L^2(\mathbb{R}^m_y))$$

1. Introduction

In the **Born-Oppenheimer approximation** one replaces

$$\hat{H}^{\varepsilon} = -\frac{\varepsilon^2}{2}\Delta_x + H_{\mathrm{el}}(x)$$

by the effective Hamiltonian

$$\hat{h}^{\varepsilon} = -\frac{\varepsilon^2}{2}\Delta_x + e_0(x)\,,$$

where $e_0(x)$ is the lowest eigenvalue of $H_{\mathrm{el}}(x)$,

$$H_{\mathrm{el}}(x)\,P_0(x) = e_0(x)\,P_0(x)\,,$$

and $P_0(x)$ the corresponding spectral projection.

1. Introduction

One still has the identity

$$\mathrm{Tr}\left(\hat{a}^{\varepsilon}\, f(\hat{H}^{\varepsilon})\right) = \frac{1}{(2\pi\varepsilon)^n}\int_{\mathbb{R}^{2n}} \mathrm{d}q\mathrm{d}p\; a(q,p)\, \mathrm{tr}_{\mathcal{H}_\mathrm{f}}\Big(\mathrm{Symb}\left(f(\hat{H}^{\varepsilon})\right)\Big)\;,$$

but it is not obvious how to get a useful expression from this. However, it is not difficult to see that

$$\mathrm{Tr}\left(\hat{a}^{\varepsilon}\, f(\hat{H}^{\varepsilon})\, P_0\right) = \frac{1}{(2\pi\varepsilon)^n}\left(\int_{\mathbb{R}^{2n}} \mathrm{d}q\mathrm{d}p\; a(q,p)\, f(h_0(q,p)) + \mathcal{O}(\varepsilon)\right)$$

with

$$h_0(q,p) = \frac{1}{2}|p|^2 + e_0(q)\,.$$

Here

$$\mathrm{Ran}P_0 = \{\Psi \in L^2(\mathbb{R}^n_x \times \mathbb{R}^m_y)\,|\,\Psi(x,\cdot) \in \mathrm{Ran}P_0(x)\}\,.$$

Question: Is this the right quantity to compute and what are the higher order corrections?

2. Adiabatic slow-fast systems

Consider a composite system with Hilbert space

$$\mathcal{H} = L^2(\mathbb{R}^n_x) \otimes \mathcal{H}_\mathrm{f} \cong L^2(\mathbb{R}^n_x, \mathcal{H}_\mathrm{f})$$

and Hamiltonian

$$\hat{H}^\varepsilon = H(x, -\mathrm{i}\varepsilon\nabla_x) \in \mathcal{L}_\mathrm{sa}(L^2(\mathbb{R}^n, \mathcal{H}_\mathrm{f}))$$

for an operator valued symbol

$$H : \mathbb{R}^{2n} \to \mathcal{L}_\mathrm{sa}(\mathcal{H}_\mathrm{f})\,.$$

Here

$$(\hat{H}^\varepsilon \psi)(x) = \frac{1}{(2\pi\varepsilon)^n} \int_{\mathbb{R}^n} \mathrm{d}p\, \mathrm{d}y\, \mathrm{e}^{\mathrm{i}p\cdot(x-y)/\varepsilon}\, H\left(\tfrac{1}{2}(x+y), p\right)\, \psi(y)$$

is defined as in the case of scalar symbols.

2. Adiabatic slow-fast systems

Let

$$e : \mathbb{R}^{2n} \to \mathbb{R}$$

be a **non-degenerate and isolated eigenvalue band** for

$$H : \mathbb{R}^{2n} \to \mathcal{L}_{\mathrm{sa}}(\mathcal{H}_{\mathrm{f}}),$$

i.e. a continuous function such that

$$H(q,p)\, P_0(q,p) = e(q,p)\, P_0(q,p)$$

and

$$[e(q,p) - \delta, e(q,p) + \delta] \cap \sigma(H_{\mathrm{f}}(q,p)) = e(q,p)$$

for all $(q,p) \in \mathbb{R}^{2n}$ and some $\delta > 0$.

2. Adiabatic slow-fast systems

Adiabatic projections:

(Helffer-Sjöstrand 90, Emmrich-Weinstein 96, Nenciu-Sordoni 04,...)

Under suitable technical conditions there exists a projection operator $\hat{P}^{\varepsilon}$ with symbol

$$P(\varepsilon, q, p) = P_0(q, p) + \mathcal{O}(\varepsilon)$$

such that

$$[\hat{P}^{\varepsilon}, \hat{H}^{\varepsilon}] = \mathcal{O}(\varepsilon^{\infty}) .$$

Hence, $\hat{H}^{\varepsilon}$ is $\mathcal{O}(\varepsilon^{\infty})$-almost block-diagonal with respect to $\hat{P}^{\varepsilon}$,

$$\hat{H}^{\varepsilon} = \hat{P}^{\varepsilon}\,\hat{H}^{\varepsilon}\,\hat{P}^{\varepsilon} + (1-\hat{P}^{\varepsilon})\,\hat{H}^{\varepsilon}\,(1-\hat{P}^{\varepsilon}) + \mathcal{O}(\varepsilon^{\infty}) ,$$

while for $\hat{P}_0^{\varepsilon}$ one only has

$$\hat{H}^{\varepsilon} = \hat{P_0}^{\varepsilon}\,\hat{H}^{\varepsilon}\,\hat{P_0}^{\varepsilon} + (1-\hat{P_0}^{\varepsilon})\,\hat{H}^{\varepsilon}\,(1-\hat{P_0}^{\varepsilon}) + \mathcal{O}(\varepsilon) .$$

3. Results: First order corrections

Theorem (Stiepan, Teufel; CMP 320, 2013)

Under suitable conditions on H and f it holds that for all $a \in \mathcal{A} \subset C^\infty(\mathbb{R}^{2n}) \cap L^1(\mathbb{R}^{2n})$

$$\mathrm{Tr}\left(\hat{a}^\varepsilon\, f(\hat{H}^\varepsilon)\, \hat{P}^\varepsilon\right) = \frac{1}{(2\pi\varepsilon)^n}\left(\int_{\mathbb{R}^{2n}} \mathrm{d}\lambda^\varepsilon\; a(q,p)\, f(h^\varepsilon(q,p)) \;+\; \mathcal{O}(\varepsilon^2 \|a\|_{L^1})\right)$$

where

$$h^\varepsilon(q,p) = e(q,p) + \varepsilon \tfrac{\mathrm{i}}{2}\,\mathrm{tr}_{\mathcal{H}_\mathrm{f}}\{P_0|H|P_0\} =: e(q,p) + \varepsilon m(q,p)$$

and

$$\mathrm{d}\lambda^\varepsilon = \left(1 + \mathrm{i}\varepsilon \mathrm{tr}_{\mathcal{H}_\mathrm{f}}(P_0\{P_0, P_0\})\right)\mathrm{d}q\,\mathrm{d}p$$

is the Liouville measure of the symplectic form

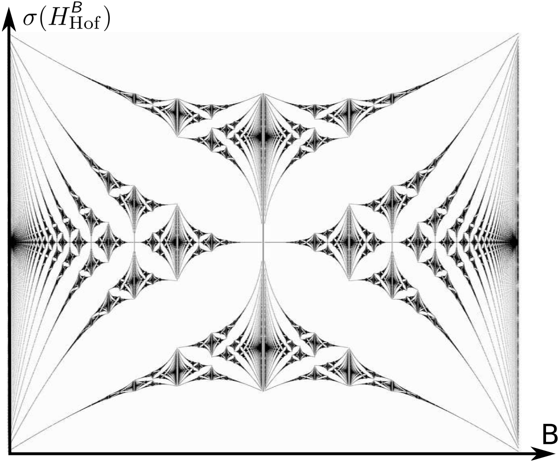
$$\sigma^\varepsilon_{ij} := \sigma^0_{ij} - \mathrm{i}\,\varepsilon\,\mathrm{tr}_{\mathcal{H}_\mathrm{f}}\left(P_0[\partial_{z_i}P_0, \partial_{z_j}P_0]\right)\,.$$

For the molecular Hamiltonian both correction terms vanish!

3. Application

The Hofstadter model

$$H^B_{\mathrm{Hof}} = \sum_{|j|=1} T^B_j \quad \text{on} \quad \ell^2(\mathbb{Z}^2) \quad \text{with} \quad (T^B_j \psi)_i = \mathrm{e}^{\mathrm{i} j \cdot \mathbf{B} i} \psi_{i-j}$$



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For $B_0 = 2\pi \frac{p}{q}$ and $B = B_0 + b$ one obtains through a magnetic Bloch-Floquet transformation

$$U^{B_0} : \ell^2(\mathbb{Z}^2) \to L^2(M_q; \mathbb{C}^q)$$

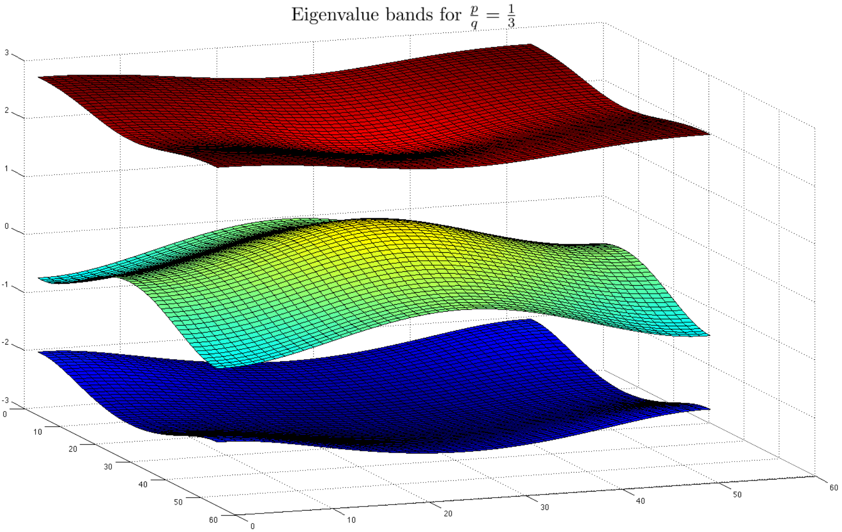
that

$$U^{B_0}\, H^B_{\mathrm{Hof}} U^{B_0 *} = H^{B_0}(k_1 + \tfrac{1}{2}\mathrm{i} b \partial_{k_2}, k_2 - \tfrac{1}{2}\mathrm{i} b \partial_{k_1})$$

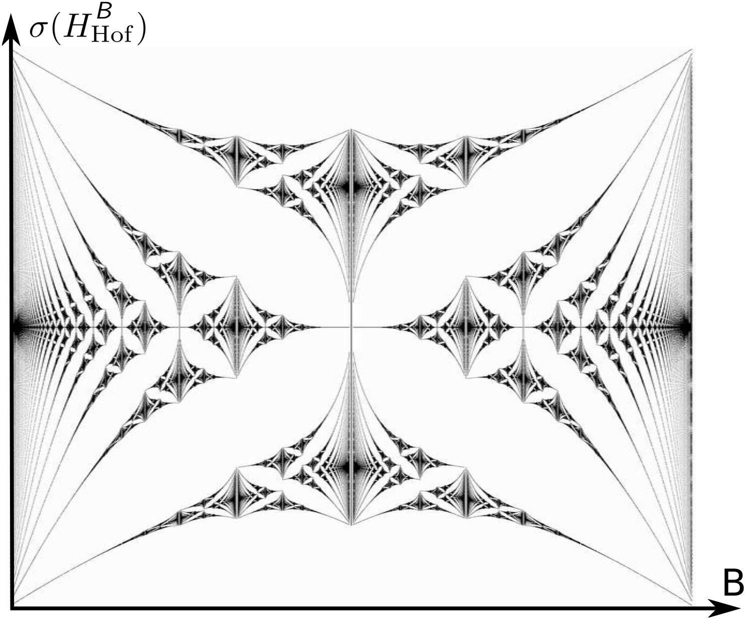
with

$$H^{B_0}(k) = \begin{pmatrix} 2\cos(k_2) & \mathrm{e}^{-\mathrm{i}k_1} & 0 & \cdots & \mathrm{e}^{\mathrm{i}k_1} \\ \mathrm{e}^{\mathrm{i}k_1} & 2\cos(k_2 + B_0) & \mathrm{e}^{-\mathrm{i}k_1} & \cdots & 0 \\ 0 & \mathrm{e}^{\mathrm{i}k_1} & 2\cos(k_2 + 2B_0) & \cdots & 0 \\ \vdots & \ddots & \ddots & \ddots & 0 \\ 0 & & & & \mathrm{e}^{-\mathrm{i}k_1} \\ \mathrm{e}^{-\mathrm{i}k_1} & 0 & \cdots & \mathrm{e}^{\mathrm{i}k_1} & 2\cos(k_2 + (q-1)B_0) \end{pmatrix}$$

3. Application



3. Application



3. Application

The free energy per unit area in the Hofstadter model with magnetic field $B = B_0 + b$, inverse temperature β and chemical potential μ is

$$p(b, \beta, \mu) = \tfrac{1}{\beta} \lim_{n\to\infty} \frac{1}{\|\chi_n\|_{L^1}} \mathrm{tr}_{\ell^2(\mathbb{Z}^2)} \left(\chi_n(\ x) \ln \left(1 + \mathrm{e}^{-\beta(H^B_{\mathrm{Hof}} - \mu)} \right) \right) .$$

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For $B_0 = 2\pi\frac{p}{q}$ and q odd one obtains using the magnetic Bloch-Floquet transformation

$$\begin{aligned}
&\mathrm{tr}_{\ell^2(\mathbb{Z}^2)} \left(\chi_n(bx) \ln\left(1 + \mathrm{e}^{-\beta(H^B_{\mathrm{Hof}}-\mu)}\right)\right) = \\
&= \mathrm{tr}_{L^2(M_q,\mathbb{C}^q)} \left(\chi_n(\mathrm{i}b\nabla_k) \ln\left(1 + \mathrm{e}^{-\beta(H^{B_0}(k-\mathrm{i}\mathbf{b}\nabla_k)-\mu)}\right)\right) \\
&= \sum_{j=1}^{q} \mathrm{tr}_{L^2(M_q,\mathbb{C}^q)} \left(\chi_n(\mathrm{i}b\nabla_k) \ln\left(1 + \mathrm{e}^{-\beta(H^{B_0}(k-\mathrm{i}\mathbf{b}\nabla_k)-\mu)}\right) \hat{P}^b_j\right)
\end{aligned}$$

3. Results

Corollary (Stiepan, Teufel; CMP 320, 2013)

The free energy per unit area in the Hofstadter model with magnetic field $B = B_0 + b$, with $B_0 = 2\pi \frac{p}{q}$ and q odd, is

$$p(b,\beta,\mu) = \frac{q}{(2\pi)^2} \sum_{j=1}^{q} \int_{\mathbb{T}^*} \mathrm{d}k \, \big(1 + b\,\omega_j(k)\big) \, \ln\Big(1 + \mathrm{e}^{-\beta\left(e_j(k) + b m_j(k) - \mu\right)}\Big) + \mathcal{O}(b^2) \, .$$

From this one can compute, for example, the orbital magnetization

$$M(B_0,\beta,\mu) := \frac{\partial}{\partial b} p(b,\beta,\mu)\big|_{b=0} = \frac{q}{(2\pi)^2} \sum_{j=1}^{q} \int_{\mathbb{T}^*} \mathrm{d}k \, \Big[\frac{1}{\beta}\,\omega_j(k) \, \ln\Big(1 + \mathrm{e}^{-\beta\left(e_j(k) - \mu\right)}\Big) - m_j(k) \, \frac{1}{1 + \mathrm{e}^{\beta(e_j(k) - \mu)}} \Big]$$

Gat, Avron '03; Xiao, Shi, Niu 05'; Ceresoli, Thonhauser, Vanderbilt, Resta '06

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However, in order to compute the susceptibility

$$\chi(B_0, \beta, \mu) := \frac{\partial^2}{\partial b^2} p(b, \beta, \mu)\Big|_{b=0}$$

one needs to know the $\mathcal{O}(b^2)$ term explicitly.

Existing results:

Briet, Cornean, Savoie '11; Savoie '13; Schulz-Baldes, Teufel '13

3. Results

Related result on the time-evolution:

Theorem (Stiepan, Teufel; CMP 320, 2013)

Under suitable conditions on H and f it holds that for all $a \in \mathcal{A} \subset C^\infty(\mathbb{R}^{2n}) \cap L^1(\mathbb{R}^{2n})$

$$\left\| \hat{P}^\varepsilon \left(\mathrm{e}^{\mathrm{i}\hat{H}^\varepsilon \frac{t}{\varepsilon}} \, \hat{a}^\varepsilon \, \mathrm{e}^{-\mathrm{i}\hat{H}^\varepsilon \frac{t}{\varepsilon}} - \mathrm{Weyl}^\varepsilon(a \circ \Phi_t^\varepsilon) \right) \hat{P}^\varepsilon \right\| = \mathcal{O}(\varepsilon^2)$$

uniformly on bounded time intervals, where

$$\Phi_t^\varepsilon : \mathbb{R}^{2n} \to \mathbb{R}^{2n}$$

is the classical flow of h^ε with respect to the symplectic form σ^ε.

3. Results

Theorem (Gaim, Teufel; work in progress)

Under suitable conditions on H and f it holds that for all $a \in \mathcal{A} \subset C^\infty(\mathbb{R}^{2n}) \cap L^1(\mathbb{R}^{2n})$

$$\mathrm{Tr}\left(\hat{a}^\varepsilon\, f(\hat{H}^\varepsilon)\, \hat{P}^\varepsilon\right) = \frac{1}{(2\pi\varepsilon)^n}\left(\int_{\mathbb{R}^{2n}} \mathrm{d}\lambda^\varepsilon\; a(q,p)\, f^\varepsilon(q,p) \;+\; \mathcal{O}(\varepsilon^3 \|a\|_{L^1})\right)\,,$$

where

$$f^\varepsilon = f \circ h^\varepsilon + \varepsilon^2 \left(f_2^{\mathrm{Wigner}}(e) + f_2^{\mathrm{adi}}(e, P_0)\right)$$

with

$$h^\varepsilon(q,p) = e(q,p) + \varepsilon m_1(q,p) + \varepsilon^2 m_2(q,p)$$

and

$$\mathrm{d}\lambda^\varepsilon = \left(1 + \varepsilon\,\lambda_1(q,p) + \varepsilon^2 \lambda_2(q,p)\right)\mathrm{d}q\,\mathrm{d}p\,.$$

3. Results

For the corrections to Born-Oppenheimer one finds:

$$h^{\varepsilon}(q,p) = \frac{1}{2}|p|^2 + e(q) + \varepsilon^2 \left(\langle p, C(q)p \rangle_{\mathbb{C}^n} + \tfrac{1}{2}\mathrm{tr}_{\mathbb{C}^n}\big(D(q)\big) \right) ,$$

$$\mathrm{d}\lambda^{\varepsilon} = \Big(1 + 2\,\varepsilon^2\,\mathrm{tr}_{\mathbb{C}^n}\big(C(q)\big)\Big)\mathrm{d}q\,\mathrm{d}p\,,$$

and

$$f_2^{\mathrm{adi}}(q,p) = f'\big(h_0(q,p)\big)\,\mathrm{tr}_{\mathbb{C}^n}\big(D(q)\big) + f''\big(h_0(q,p)\big)\,\langle p, D(q)p\rangle_{\mathbb{C}^n}\,.$$

with

$$C_{ij}(q) = \mathrm{tr}_{\mathcal{H}_\mathrm{f}}\Big(\partial_i P_0(q)\,\big(H_{\mathrm{el}}(q) - e(q)\big)^{-1}\,\partial_j P_0(q)\Big)$$

and

$$D_{ij}(q) = \mathrm{tr}_{\mathcal{H}_\mathrm{f}}\Big(P_0(q)\,\partial_i P_0(q)\,\partial_j P_0(q)\Big)$$

Thanks for your attention!

4. Strategy of proof (First order result)

With the identity

$$\mathrm{Tr}\left(\hat{a}^\varepsilon\, f(\hat{H}^\varepsilon)\,\hat{P}^\varepsilon\right) = \frac{1}{(2\pi\varepsilon)^n}\int_{\mathbb{R}^{2n}} \mathrm{d}q\mathrm{d}p\; a(q,p)\,\mathrm{tr}\Big(\mathrm{Symb}\left(f(\hat{H}^\varepsilon)\,\hat{P}^\varepsilon\right)\Big)\,,$$

we need to expand the symbol of $f(\hat{H}^\varepsilon)\,\hat{P}^\varepsilon$ in powers of ε.

To this end note that $[\hat{P}^\varepsilon,\, \hat{H}^\varepsilon] = \mathcal{O}(\varepsilon^\infty)$ implies

$$f(\hat{H}^\varepsilon)\,\hat{P}^\varepsilon = f(\hat{P}^\varepsilon\,\hat{H}^\varepsilon\,\hat{P}^\varepsilon) + \mathcal{O}(\varepsilon^\infty)\,.$$

Lemma: There is a scalar semiclassical symbol $h(\varepsilon, q, p)$ such that

$$\hat{P}^\varepsilon\,\hat{H}^\varepsilon\,\hat{P}^\varepsilon = \hat{P}^\varepsilon\,\hat{h}^\varepsilon\,\hat{P}^\varepsilon + \mathcal{O}(\varepsilon^2)$$

and thus

$$f(\hat{P}^\varepsilon\,\hat{H}^\varepsilon\,\hat{P}^\varepsilon) = f(\hat{P}^\varepsilon\,\hat{h}^\varepsilon\,\hat{P}^\varepsilon) + \mathcal{O}(\varepsilon^2)\,.$$

Lemma:

$$f(\hat{P}^\varepsilon\,\hat{h}^\varepsilon\,\hat{P}^\varepsilon) = \hat{P}^\varepsilon\, f(\hat{h}^\varepsilon)\,\hat{P}^\varepsilon + \mathcal{O}(\varepsilon^2)\,.$$