

Semiclassical approximations of quantum mechanical equilibrium distributions

Stefan Teufel
Universität Tübingen

March 2014, Warwick.

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

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

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

Classical Hamiltonian

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

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

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

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

where

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

1. Introduction

For more general Hamiltonians and distributions

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

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

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

where

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

with

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

1. Introduction

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

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

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

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

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

$$H(q, p) = \frac{1}{2}|p|^2 + H_{\text{el}}(q) \in \mathcal{L}_{\text{sa}}(L^2(\mathbb{R}^m))$$

1. Introduction

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

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

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 $H_{\text{el}}(x)$,

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

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

1. Introduction

One still has the identity

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

but it is not obvious how to get a useful expression from this.

However, it is not difficult to see that

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

with

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

Here

$$\mathrm{Ran} P_0 = \{ \Psi \in L^2(\mathbb{R}_x^n \times \mathbb{R}_y^m) \mid \Psi(x, \cdot) \in \mathrm{Ran} P_0(x) \}.$$

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

$$\mathcal{H} = L^2(\mathbb{R}_x^n) \otimes \mathcal{H}_f \cong L^2(\mathbb{R}_x^n, \mathcal{H}_f)$$

and Hamiltonian

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

for an operator valued symbol

$$H : \mathbb{R}^{2n} \rightarrow \mathcal{L}_{\text{sa}}(\mathcal{H}_f).$$

Here

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

is defined as in the case of scalar symbols.

2. Adiabatic slow-fast systems

Let

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

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

$$H : \mathbb{R}^{2n} \rightarrow \mathcal{L}_{\text{sa}}(\mathcal{H}_f),$$

i.e. a continuous function such that

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

and

$$[e(q, p) - \delta, e(q, p) + \delta] \cap \sigma(H_f(q, p)) = e(q, p)$$

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-Sordani 04, . . .)

Under suitable technical conditions there exists a projection operator \hat{P}^ε 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}^ε is $\mathcal{O}(\varepsilon^\infty)$ -almost block-diagonal with respect to \hat{P}^ε , while for \hat{P}_0 one only has

$$[\hat{P}_0, \hat{H}^\varepsilon] = \mathcal{O}(\varepsilon).$$

3. Results: First order corrections

Theorem (Stiepan, T.; CMP 320, 2013)

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

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

where

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

and

$$d\lambda^\varepsilon = (1 + i\varepsilon \mathrm{tr}_{\mathcal{H}_f} (P_0 \{P_0, P_0\})) dq dp$$

is the Liouville measure of the symplectic form

$$\sigma_{ij}^\varepsilon := \sigma_{ij}^0 - i\varepsilon \mathrm{tr}_{\mathcal{H}_f} (P_0 [\partial_{z_i} P_0, \partial_{z_j} P_0]) .$$

For the molecular Hamiltonian both correction terms vanish!

3. Application

The Hofstadter model

$$H_{\text{Hof}}^B = \sum_{|j|=1} T_j^B \quad \text{on} \quad \ell^2(\mathbb{Z}^2) \quad \text{with} \quad (T_j^B \psi)_i = e^{ij \cdot \mathbf{B}i} \psi_{i-j}$$

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

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

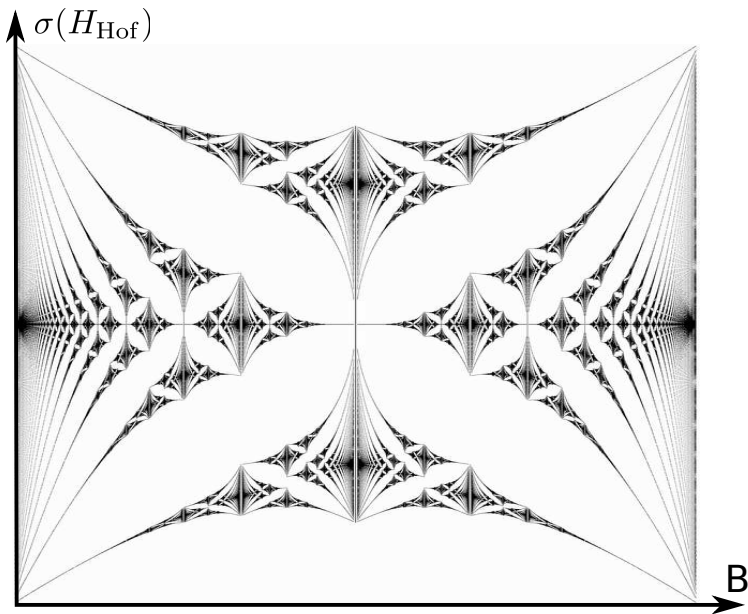
that

$$U^{B_0} H_{\text{Hof}}^B U^{B_0*} = H^{B_0}(k_1 + \frac{1}{2}ib\partial_{k_2}, k_2 - \frac{1}{2}ib\partial_{k_1})$$

with

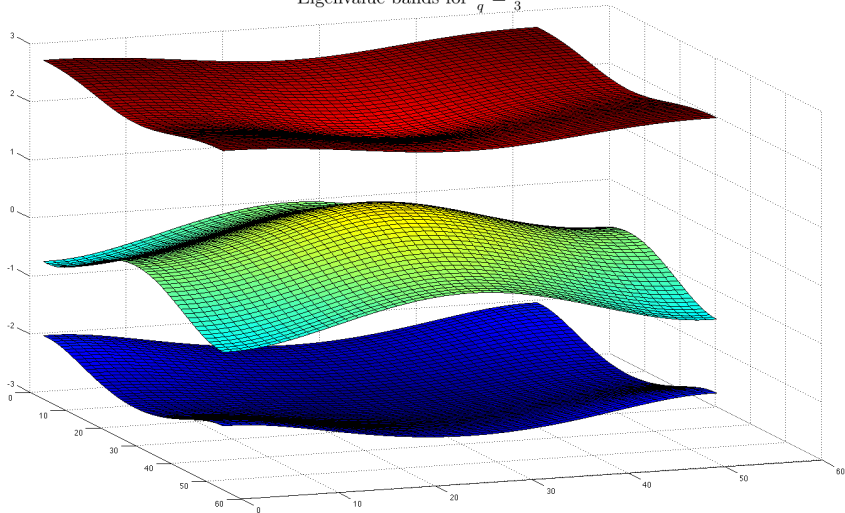
$$H^{B_0}(k) = \begin{pmatrix} 2 \cos(k_2) & e^{-ik_1} & 0 & \dots & e^{ik_1} \\ e^{ik_1} & 2 \cos(k_2 + B_0) & e^{-ik_1} & \dots & 0 \\ 0 & e^{ik_1} & 2 \cos(k_2 + 2B_0) & \dots & 0 \\ \vdots & \ddots & \ddots & \ddots & 0 \\ 0 & & & & e^{-ik_1} \\ e^{-ik_1} & 0 & \dots & e^{ik_1} & 2 \cos(k_2 + (q-1)B_0) \end{pmatrix}$$

3. Application



3. Application

Eigenvalue bands for $\frac{p}{q} = \frac{1}{3}$



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

$$\rho(b, \beta, \mu) = \frac{1}{\beta} \lim_{n \rightarrow \infty} \frac{1}{\|\chi_n\|_{L^1}} \operatorname{tr}_{\ell^2(\mathbb{Z}^2)} \left(\chi_n(x) \ln \left(1 + e^{-\beta(H_{\text{Hof}}^B - \mu)} \right) \right).$$

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

$$\rho(b, \beta, \mu) = \frac{1}{\beta} \lim_{n \rightarrow \infty} \frac{1}{\frac{1}{b^2} \|\chi_n\|_{L^1}} \operatorname{tr}_{\ell^2(\mathbb{Z}^2)} \left(\chi_n(bx) \ln \left(1 + e^{-\beta(H_{\text{Hof}}^B - \mu)} \right) \right).$$

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

$$\begin{aligned} & \operatorname{tr}_{\ell^2(\mathbb{Z}^2)} \left(\chi_n(bx) \ln \left(1 + e^{-\beta(H_{\text{Hof}}^B - \mu)} \right) \right) = \\ & = \operatorname{tr}_{L^2(M_q, \mathbb{C}^q)} \left(\chi_n(ib\nabla_k) \ln \left(1 + e^{-\beta(H(k - ib\nabla_k) - \mu)} \right) \right) \\ & = \sum_{j=1}^q \operatorname{tr}_{L^2(M_q, \mathbb{C}^q)} \left(\chi_n(ib\nabla_k) \ln \left(1 + e^{-\beta(H(k - ib\nabla_k) - \mu)} \right) \hat{P}_j^b \right) \end{aligned}$$

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

$$\rho(b, \beta, \mu) = \frac{q}{(2\pi)^2} \sum_{j=1}^q \int_{\mathbb{T}^*} dk (1 + b\omega_j(k)) \ln\left(1 + e^{-\beta(e_j(k) + bm_j(k) - \mu)}\right) + \mathcal{O}(b^2).$$

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

$$\begin{aligned} M(B_0, \beta, \mu) &:= \frac{\partial}{\partial b} \rho(b, \beta, \mu) \Big|_{b=0} \\ &= \frac{q}{(2\pi)^2} \sum_{j=1}^q \int_{\mathbb{T}^*} dk \left[\frac{1}{\beta} \omega_j(k) \ln\left(1 + e^{-\beta(e_j(k) - \mu)}\right) \right. \\ &\quad \left. - m_j(k) \frac{1}{1 + e^{\beta(e_j(k) - \mu)}} \right] \end{aligned}$$

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

$$\rho(b, \beta, \mu) = \frac{q}{(2\pi)^2} \sum_{j=1}^q \int_{\mathbb{T}^*} dk (1 + b\omega_j(k)) \ln\left(1 + e^{-\beta(e_j(k) + bm_j(k) - \mu)}\right) + \mathcal{O}(b^2).$$

However, in order to compute the susceptibility

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

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

Existing results:

Briet, Cornean, Savoie '11; Savoie '13; Schulz-Baldes, T. '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 $a \in \mathcal{A} \subset C^\infty(\mathbb{R}^{2n}) \cap L^1(\mathbb{R}^{2n})$

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

uniformly on bounded time intervals, where

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

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 $a \in \mathcal{A} \subset C^\infty(\mathbb{R}^{2n}) \cap L^1(\mathbb{R}^{2n})$

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

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

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

3. Results

For the corrections to Born-Oppenheimer one finds:

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

$$d\lambda^\varepsilon = \left(1 + 2\varepsilon^2 \text{tr}_{\mathbb{C}^n}(C(q)) \right) dq dp,$$

and

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

with

$$C_{ij}(q) = \text{tr}_{\mathcal{H}_f} \left(\partial_i P_0(q) (H_{\text{el}}(q) - e(q))^{-1} \partial_j P_0(q) \right)$$

and

$$D_{ij}(q) = \text{tr}_{\mathcal{H}_f} \left(P_0(q) \partial_i P_0(q) \partial_j P_0(q) \right)$$

4. Strategy of proof (First order result)

With the identity

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

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:

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

Thanks for your attention!