Adiabatic decoupling
and the partial classical limit

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IMA Tutorial:
Fundamentals of chemical dynamics simulations
11. January 2009
0. Basic principle: adiabatic decoupling

Under appropriate conditions, one can describe the dynamics of the slow degrees of freedom approximately through effective equations of motion. They contain the fast degrees of freedom only in a "reduced" form, but not as dynamical degrees of freedom.

⇒ Reduction of complexity in large systems.

Adiabatic decoupling and the partial classical limit January 2009
Goal: Effective equations of motion only for the slow variables

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**0. Basic principle: adiabatic decoupling**

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**Example: Spinning top**

Slow degree of freedom = rotation axis

Fast degree of freedom = rotation angle
0. Examples in quantum dynamics

- **Molecules:**
  
  slow nuclei $\Leftrightarrow$ fast electrons
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• **Molecules:**
  
  slow nuclei ⇔ fast electrons

• **Charged particles in the radiation field:**
  
  slow particles ⇔ fast photons
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  slow macroscopic dynamics ⇔ fast dynamics on the scale of the lattice
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- **Strong constraining forces:**
  slow motion tangent to the constraint manifold ⇔ fast motion normal to the constraint manifold
0. Contents of my lectures

1. **Time-dependent quantum mechanics:**
   A crash course and some remarks on composite systems
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2. **Adiabatic decoupling and the partial semiclassical limit:**
   The time-dependent Born-Oppenheimer approximation
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2. **Adiabatic decoupling and the partial semiclassical limit:**
   The time-dependent Born-Oppenheimer approximation

3. **Adiabatic perturbation theory:**
   General slow-fast systems
1. \textit{Time-dependent quantum mechanics}

1. \textbf{State space:}

The state space of a quantum system is a complex Hilbert space $\mathcal{H}$, i.e., a complex vector space with an inner product $\langle \cdot, \cdot \rangle$. The inner product induces a norm

$$\| \psi \| = \sqrt{\langle \psi, \psi \rangle}.$$
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**Examples:**

For a single spinless particle moving in $\mathbb{R}^3$ the state space is

$$\mathcal{H} = L^2(\mathbb{R}^3) := \left\{ \psi : \mathbb{R}^3 \to \mathbb{C} \mid \| \psi \|^2 = \int_{\mathbb{R}^3} |\psi(x)|^2 \, dx < \infty \right\},$$

with inner product

$$\langle \psi, \phi \rangle = \int_{\mathbb{R}^3} \psi(x)^* \phi(x) \, dx.$$
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Examples:
For $N$ distinguishable spinless particles moving in $\mathbb{R}^3$ the state space is

$$\mathcal{H} = L^2(\mathbb{R}^{3N}) := \left\{ \psi : \mathbb{R}^{3N} \to \mathbb{C} \mid \|\psi\|^2 = \int_{\mathbb{R}^{3N}} |\psi(x)|^2 \, dx < \infty \right\}$$

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Examples:
For a single spin-$\frac{1}{2}$ degree of freedom the state space is

$$\mathcal{H} = \mathbb{C}^2 = \{ \psi = (\psi_1, \psi_2) \mid \psi_1, \psi_2 \in \mathbb{C} \}$$

with the inner product

$$\langle \psi, \phi \rangle = \sum_{j=1}^{2} \psi_j^* \phi_j.$$

Adiabatic decoupling and the partial classical limit
1. Time-dependent quantum mechanics

For composite systems the Hilbert space of the full system is obtained as the tensor product denoted by “⊗” of the subsystem Hilbert spaces.

Examples:

Two single particles ⇒ System of two particles

\[ \psi(x) \text{ “+” } \phi(y) \quad \text{(ψ ⊗ φ)(x, y) = ψ(x)φ(y)} \]
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\[ \psi(x) \text{ “+” } \phi(y) \quad \Rightarrow \quad (\psi \otimes \phi)(x, y) = \psi(x)\phi(y) \]

\[ L^2(\mathbb{R}^3) \text{ “+” } L^2(\mathbb{R}^3) \quad \Rightarrow \quad L^2(\mathbb{R}^3) \otimes L^2(\mathbb{R}^3) \cong L^2(\mathbb{R}^6) \cong L^2(\mathbb{R}^3, L^2(\mathbb{R}^3)) \]

A generic function in \( L^2(\mathbb{R}^6) \) is just a square integrable function \( \Psi(x, y) \) of two variables in \( \mathbb{R}^3 \).
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A generic function in \(L^2(\mathbb{R}^6)\) is just a square integrable function \(\Psi(x, y)\) of two variables in \(\mathbb{R}^3\).

Hence not all functions in \(L^2(\mathbb{R}^6)\) are given by products \(\Psi(x, y) = \psi(x)\phi(y)\). But they can always be approximated by linear combinations of products.
1. *Time-dependent quantum mechanics*

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**Examples:**

Single spinless particle + spin $\Rightarrow$ Single spin-$\frac{1}{2}$ particle

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L^2(\mathbb{R}^3) \quad \text{“+”} \quad \mathbb{C}^2 \quad \quad L^2(\mathbb{R}^3) \otimes \mathbb{C}^2 \cong L^2(\mathbb{R}^3, \mathbb{C}^2)
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A generic function in $L^2(\mathbb{R}^3, \mathbb{C}^2)$ is of the form

\[
\psi(x) = \begin{pmatrix} \psi_1(x) \\ \psi_2(x) \end{pmatrix}.
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Sometimes it is convenient to write

\[
\Psi(j, x) = \psi_j(x),
\]

where \(j = 1, 2\).
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For composite systems the Hilbert space of the full system is obtained as the tensor product denoted by “⊗” of the subsystem Hilbert spaces.

Examples:

\[ N \text{ single spin-} \frac{1}{2} \text{ particles} \Rightarrow \text{System of } N \text{ spin-} \frac{1}{2} \text{ particles} \]

\[ L^2(\mathbb{R}^3, \mathbb{C}^2)^\otimes N \cong L^2(\mathbb{R}^3)^\otimes N \otimes (\mathbb{C}^2)^\otimes N \cong L^2(\mathbb{R}^{3N}) \otimes \mathbb{C}^{2N} \cong L^2(\mathbb{R}^{3N}, \mathbb{C}^{2N}) \]

A generic function in \( L^2(\mathbb{R}^{3N}, \mathbb{C}^{2N}) \) is of the form

\[ \Psi(x) = \begin{pmatrix} \psi_1(x_1, \ldots, x_N) \\ \vdots \\ \psi_2N(x_1, \ldots, x_N) \end{pmatrix}, \]

where again it is convenient to write

\[ \psi_j(x) = \psi(j_1, \ldots, j_N, x_1, \ldots x_N) \]

with \( j_k = 1, 2 \) and \( x_k \in \mathbb{R}^3 \).
1. Time-dependent quantum mechanics

2. Physical interpretation:

If the state of the $N$-particle system is $\Psi(j,x)$, then the probability that the particles have a configuration $X = (X_1, \ldots, X_N)$ in a region $\Lambda \subset \mathbb{R}^{3N}$ of configuration space $\mathbb{R}^{3N}$ is

$$P(X \in \Lambda) = \sum_{j=1}^{2^N} \int_{\Lambda} |\Psi(j,x)|^2 \, dx.$$ 

This is called **Born's statistical interpretation** or postulate.
1. **Time-dependent quantum mechanics**

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This is called **Born's statistical interpretation** or postulate.

Everything else (other observables etc.) follows from this postulate, the collapse postulate and an analysis of the dynamics.
1. *Time-dependent quantum mechanics*

3. **Dynamics of states:**

In general the state of a system changes with time. The dynamics for the time-dependent state $\Psi(t)$ is determined by the **time-dependent Schrödinger equation**

$$i\frac{d}{dt}\Psi(t) = H\Psi(t).$$

Here $H$ is a linear mapping

$$H : \mathcal{H} \supset D \rightarrow \mathcal{H}$$

the so called Hamilton operator or **Hamiltonian**.
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The solution of the Schrödinger equation with initial value $\Psi(0) = \Psi_0$ is

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The exponential $e^{-itH}$ of the Hamiltonian is called the propagator and
defines a unitary evolution group

$$\|e^{-itH}\psi\| = \|\psi\|. $
1. Time-dependent quantum mechanics

Examples:
- For a spin-$\frac{1}{2}$ in a magnetic field $B$ the Hamiltonian $H : \mathbb{C}^2 \to \mathbb{C}^2$ is the complex $2 \times 2$-matrix

\[ H = B \cdot \sigma = B_x \sigma_x + B_y \sigma_y + B_z \sigma_z, \]

where $\sigma = (\sigma_x, \sigma_y, \sigma_z)$ is the vector of Pauli matrices.

The propagator is given by the convergent power series

\[ e^{-i t H} = \sum_{n=0}^{\infty} \frac{(-i t H)^n}{n!}. \]
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$$e^{-itH} = \sum_{n=0}^{\infty} \frac{(-itH)^n}{n!}.$$

- For a single non-relativistic charged particle of mass $m$ moving in a potential $V : \mathbb{R}^3 \to \mathbb{R}$ the Hamiltonian $H : L^2(\mathbb{R}^3) \supset D \to L^2(\mathbb{R}^3)$ is the differential operator

$$H = -\frac{1}{2m} \Delta + V(x, y, z)$$

with the Laplace operator $\Delta := \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$. 

Adiabatic decoupling and the partial classical limit
1. Time-dependent quantum mechanics

Example: Molecules

$N_n$ nuclei, each with mass $M$ \hspace{1cm} ($N_n = 3$ for CO$_2$)

$N_e$ electrons, mass $m$ \hspace{1cm} ($N_e = 22$ for CO$_2$)

The Hamiltonian is

$$H_{\text{mol}} = \sum_{j=1}^{N_n} \left( -\frac{1}{2M} \Delta x_j \right) + \sum_{k=1}^{N_e} \left( -\frac{1}{2m} \Delta y_k \right) +$$

$$+ \sum_{i<j=1}^{N_n} \frac{Z_j Z_i}{|x_i - x_j|} + \sum_{k<l=1}^{N_e} \frac{1}{|y_k - y_l|} - \sum_{j=1}^{N_n} \sum_{k=1}^{N_e} \frac{Z_j}{|y_k - x_j|}$$

acting on

$$\mathcal{H} = L^2(\mathbb{R}^{3(N_n+N_e)}) \cong L^2(\mathbb{R}_x^{3N_n}) \otimes L^2(\mathbb{R}_y^{3N_e}) \cong L^2(\mathbb{R}_x^{3N_n}, \mathcal{H}_e).$$

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acting on

\[
\mathcal{H} = \frac{L^2(\mathbb{R}^{3(N_n+N_e)})}{L^2(\mathbb{R}^{75}) \text{ for CO}_2} \cong L^2(\mathbb{R}^{3N_n}_x) \otimes L^2(\mathbb{R}^{3N_e}_y) \cong L^2(\mathbb{R}^{3N_n}_x, \mathcal{H}_e).
\]
1. *Time-dependent quantum mechanics*

**Observation of Born and Oppenheimer (1928):**

The small mass ratio

\[
\frac{m}{M} \approx 10^{-4} \ldots 10^{-5}
\]

can be used as the parameter for an asymptotic expansion of the eigenvalues

⇒ “asymptotic expansion” in

\[ \varepsilon = \sqrt{\frac{m}{M}} \]
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In atomic units \((m = 1)\) we have

\[
H_{\text{mol}} = -\frac{\varepsilon^2}{2} \Delta_x + H_e(x) \quad \text{on} \quad \mathcal{H} = L^2(\mathbb{R}^{N_n}_x, \mathcal{H}_e)
\]

with

\[
H_e(x) = -\frac{1}{2} \Delta_y + V(x,y) \quad \text{on} \quad \mathcal{H}_e = L^2(\mathbb{R}^{3N_e}_y).
\]
2. The time-dependent Born-Oppenheimer approximation

If $H_e(x)$ was real-valued instead of operator valued, then the limit $\varepsilon \to 0$ for

$$i\varepsilon \frac{\partial}{\partial t} \psi(t, x) = \left(-\frac{\varepsilon^2}{2} \Delta_x + H_e(x)\right) \psi(t, x)$$

would just be the standard semiclassical limit.
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However, on eigenstates \( H_e(x) \) acts as a real-valued multiplication operator

\[
    H_e(x) \chi(x) = E(x) \chi(x).
\]
2. The time-dependent Born-Oppenheimer approximation

For a diatomic molecule a schematic picture of the spectral surfaces is

We consider an isolated eigenvalue surface $E(x)$ with

$$H_e(x) \chi(x, y) = E(x) \chi(x, y)$$

and normalized eigenfunctions

$$\|\chi(x, \cdot)\| = 1.$$
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Let $P_E \mathcal{H} \subset \mathcal{H}$ be the subspace of functions of the form

$$\psi(x, y) = \phi(x) \chi(x, y), \quad \text{where} \quad \phi \in L^2(\mathbb{R}^{3N_n}).$$

Then

$$H_e(x) P_E = E(x) P_E.$$
2. The time-dependent Born-Oppenheimer approximation

The full Hamiltonian

\[ H_{\text{mol}} = -\frac{\varepsilon^2}{2} \Delta x + H_e(x) \]

acts on functions in \( P_E \mathcal{H} \) as

\[ H_{\text{mol}} \phi(x) \chi(x, y) = \left[ \left( -\frac{\varepsilon^2}{2} \Delta x + E(x) \right) \phi(x) \right] \chi(x, y) + R^\varepsilon \]

with

\[ R^\varepsilon = -\varepsilon (\varepsilon \nabla_x \phi(x)) \cdot \nabla_x \chi(x, y) + \frac{\varepsilon^2}{2} \phi(x) \Delta x \chi(x, y) = \mathcal{O}(\varepsilon). \]
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Let

\[ H_{\text{BO}} \phi(x) \chi(x, y) = \left[ \left( -\frac{\varepsilon^2}{2} \Delta x + E(x) \right) \phi(x) \right] \chi(x, y) \]

be the effective “Born-Oppenheimer” Hamiltonian for the nuclei corresponding to the energy surface \( E(x) \) on the adiabatic subspace \( P_E \mathcal{H} \).
2. The time-dependent Born-Oppenheimer approximation

The time-dependent Born-Oppenheimer approximation

For an initial wave function $\Psi_0(x, y) = \phi_0(x) \chi(x, y) \in P_E$ solve the effective Schrödinger equation for the nucleonic wave function

$$i\varepsilon \frac{\partial}{\partial t} \phi(t, x) = \left(-\frac{\varepsilon^2}{2} \Delta_x + E(x)\right) \phi(t, x)$$

with initial value $\phi(0, x) = \phi_0(x)$. 
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Now one expects that

$$\Psi_{BO}(t, x, y) = \phi(t, x)\chi(x, y)$$

is an approximate solution of the full Schrödinger equation

$$i\varepsilon \frac{\partial}{\partial t}\psi(t, x, y) = \left(-\frac{\varepsilon^2}{2} \Delta_x + H_\text{e}(x)\right)\psi(t, x, y).$$
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Is this really correct?
2. The time-dependent Born-Oppenheimer approximation

Is this really correct? We checked that

\[(H - H_{BO})P_E = \mathcal{O}(\varepsilon),\]

but we don’t know whether the true solution remains in the range of \(P_E\).
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\[\|\Psi(t) - \Psi_{BO}(t)\| = \left\|\left(e^{-i\frac{H}{\varepsilon}t} - e^{-i\frac{H_{BO}}{\varepsilon}t}\right)\phi\chi\right\|\]
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\[
\|\Psi(t) - \Psi_{BO}(t)\| = \left\| \left( e^{-iH t \varepsilon / \varepsilon} - e^{-iH_{BO} t \varepsilon / \varepsilon} \right) \phi \chi \right\|
\]

\[
= \left\| e^{-iH t \varepsilon / \varepsilon} \left( 1 - e^{iH t \varepsilon / \varepsilon} e^{-iH_{BO} t \varepsilon / \varepsilon} \right) \phi \chi \right\|
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\[
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\]
2. The time-dependent Born-Oppenheimer approximation

Is this really correct? We checked that

\[(H - H_{BO})P_E = \mathcal{O}(\varepsilon),\]

but we don’t know whether the true solution remains in the range of \(P_E\).

\[
\|\psi(t) - \psi_{BO}(t)\| = \left\| \left( e^{-iH^{t}/\varepsilon} - e^{-iH_{BO}^{t}/\varepsilon} \right) \phi\chi \right\| \\
= \left\| e^{-iH^{t}/\varepsilon} \left( 1 - e^{iH_{BO}^{t}/\varepsilon} \right) \phi\chi \right\| \\
= \left\| \int_{0}^{t} \frac{d}{ds} \left( 1 - e^{iH_{BO}^{s}/\varepsilon} \phi\chi \right) ds \right\| \\
= \left\| \frac{i}{\varepsilon} \int_{0}^{t} e^{iH_{BO}^{s}/\varepsilon} (H - H_{BO}) e^{-iH_{BO}^{s}/\varepsilon} \phi\chi ds \right\| \\
= \mathcal{O}(\varepsilon).
\]

So a direct computation suggest that while \(H - H_{BO}\) is of order \(\varepsilon\) on \(P_E\) might add up to difference of order one over times of order \(1/\varepsilon\).
2. The time-dependent Born-Oppenheimer approximation

\[ \| \Psi(t) - \Psi_{BO}(t) \| = \frac{1}{\varepsilon} \left\| \int_0^t e^{iH_s^\varepsilon(H - H_{BO})} e^{-iH_{BO}^s} \phi \chi \, ds \right\| \]

\[ = \frac{1}{\varepsilon} \left\| \int_0^t e^{iH_s^\varepsilon(P_E + P_E^\perp)}(H - H_{BO}) e^{-iH_{BO}^s} \phi \chi \, ds \right\| \]

\[ \leq \frac{1}{\varepsilon} \left\| \int_0^t e^{iH_s^\varepsilon(P_EHP_E - H_{BO})} e^{-iH_{BO}^s} \phi \chi \, ds \right\| \]

\[ + \frac{1}{\varepsilon} \left\| \int_0^t e^{iH_s^\varepsilon P_E^\perp HPE} e^{-iH_{BO}^s} \phi \chi \, ds \right\| \]

So we have to define \( H_{BO} \) such that

\[ P_EHP_E - H_{BO} = O(\varepsilon^2) \]

and to show that

\[ \int_0^t e^{iH_s^\varepsilon P_E^\perp HPE} e^{-iH_{BO}^s} \phi \chi \, ds = O(\varepsilon) . \]
2. The time-dependent Born-Oppenheimer approximation

If one includes $P_E R^\varepsilon P_E$ in the effective Hamiltonian and defines

$$H_{BO} = \frac{\varepsilon^2}{2} \left(-i\nabla_x + A_B(x)\right)^2 + E(x)$$

with the Berry connection coefficient

$$A_B(x) = i\langle \chi(x), \nabla_x \chi(x) \rangle_{\mathcal{H}_e},$$

the following statement is true:
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the following statement is true:

**Theorem:**
There is a constant $C < \infty$ such that for all $t \in \mathbb{R}$ and for all $\phi(0) \in L^2(\mathbb{R}^{3Nn})$ with $\Psi(0) = \phi(0)\chi \in \text{Ran } P_E 1(H \leq \epsilon)$ it holds that

$$\|\psi^\epsilon(t) - \psi_{BO}^\epsilon(t)\| \leq C \epsilon (1 + \epsilon)(1 + |t|)\|\phi(0)\|.$$

2. *The time-dependent Born-Oppenheimer approximation*

In particular this implies:

- Initial data in the subspace $P_E \mathcal{H}$ will approximately remain in this subspace under the time evolution.
  ⇒ One says that the subspace is adiabatically decoupled from the rest.
2. The time-dependent Born-Oppenheimer approximation

In particular this implies:

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- Within the decoupled subspace $P_E \mathcal{H}$ the dynamics is much simpler: an approximate solution to the full Schrödinger equation for $\Psi(0) = \phi(0) \chi$ is obtained by solving the effective equation for the nuclei
  \[
  i\varepsilon \frac{d}{dt}\phi(t) = \left(\frac{\varepsilon^2}{2} \left(-i \nabla_x + A_B(x)\right)^2 + E(x)\right) \phi(t).
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  \]

- The effective equation is of the standard semiclassical form for $\varepsilon \to 0$. Thus one can use standard semiclassical methods to find approximate solutions of this effective equation.
2. The time-dependent Born-Oppenheimer approximation

Can one improve the result by choosing a better $H_{BO}$? E.g. by adding the $O(\varepsilon^2)$ term from the expansion of $P_E H P_E$?
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No, since the piece of the solution leaving $P_E \mathcal{H}$ is of order $O(\varepsilon)$, i.e.,

$$\| (1 - P_E) \Psi(t) \| \geq C\varepsilon$$

in general.
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Can one improve the adiabatic approximation at all?

Yes, by approximating the solution not on the adiabatic subspace $P_E \mathcal{H}$, but on suitable super-adiabatic subspaces!
3. General structure of adiabatic problems

1. Hilbert space

\[ \mathcal{H} = \mathcal{H}_s \otimes \mathcal{H}_f = L^2(M) \otimes \mathcal{H}_f \cong L^2(M, \mathcal{H}_f) \]
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2. Hamiltonian

\[ H^\varepsilon = H(x, -i \varepsilon \nabla_x) := \text{Op}^W H \]

\(^H^\varepsilon\) is the Weyl-quantization of an operator-valued symbol

\[ H : T^*M \to \mathcal{L}_{sa}(\mathcal{H}_f). \]

The symbol \( H(q, p) \) is the Hamiltonian for the fast system, when the slow system has configuration \( q \) and momentum \( p \).
3. General structure of adiabatic problems

For molecular dynamics we had

Hamiltonian:

\[ H^\varepsilon_{\text{mol}} = -\frac{\varepsilon^2}{2} \Delta x + H_e(x) \text{ on } L^2(\mathbb{R}^{3N_n}, L^2(\mathbb{R}^{3N_e})) \]

Symbol:

\[ H_{\text{mol}}(q, p) = \frac{1}{2} p^2 + H_e(q) \]
3. General structure of adiabatic problems

1. Hilbert space

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3. Spectral gap

The spectrum \( \sigma(H(q, p)) \) contains a subset \( \sigma_*(q, p) \), which is separated by a gap from the remainder \( \sigma(H(q, p)) \setminus \sigma_*(q, p) \) for all \( (q, p) \in T^*M \).
3. **General structure of adiabatic problems**

### 3. Spectral gap

The spectrum $\sigma(H(q,p))$ contains a subset $\sigma_*(q,p)$, which is separated by a **gap** from the remainder $\sigma(H(q,p)) \setminus \sigma_*(q,p)$ for all $(q,p) \in T^*M$.
1. Approximately invariant subspaces

Let $P_\star(q, p)$ be the spectral projection of $H(q, p)$ corresponding to $\sigma_\star(q, p)$. Then one can construct an orthogonal projection $P^\varepsilon_N$ such that

$$\| [ H^\varepsilon, P^\varepsilon_N ] \| = \mathcal{O}(\varepsilon^{N+1})$$

and

$$\| P^\varepsilon_N - \mathcal{O}^\varepsilon P_\star \| = \mathcal{O}(\varepsilon).$$

Thus the subspace $\text{Ran } P^\varepsilon_N \subset \mathcal{H}$ is invariant under the time-evolution up to $\mathcal{O}(\varepsilon^N)$.

[based on Emmrich, Weinstein ’96 and Martinez, Nenciu, Sordoni ’01]
3. Adiabatic perturbation theory: results

2. Transformation to a simple representation space

The subspace $P^\varepsilon_N \mathcal{H}$ of the big space $\mathcal{H}$ depends on $\varepsilon$ and its elements can not be easily characterized.

⇒ We construct a unitary operator $U^\varepsilon_N$, which maps the almost invariant subspace to a space appropriate for representing the slow degrees of freedom:

$$U^\varepsilon_N : P^\varepsilon_N \mathcal{H} \rightarrow \mathcal{K} = L^2(M, \mathcal{K}_f).$$

If $\dim(\text{Ran} P_*(q, p)) = n < \infty$, then $\mathcal{K}_f = \mathbb{C}^n$. 
3. Adiabatic perturbation theory: results

3. The effective Hamiltonian

\[ H_{\text{eff}}^\epsilon := H^\epsilon \]
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\[ H_{\text{eff}}^\varepsilon := P_N^\varepsilon H^\varepsilon P_N^\varepsilon \]
3. *Adiabatic perturbation theory: results*

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\[ H_{\text{eff}}^\varepsilon := U_N^\varepsilon P_N^\varepsilon H^\varepsilon P_N^\varepsilon U_N^\varepsilon* \quad \text{on} \quad \mathcal{K}. \]
3. Adiabatic perturbation theory: results

3. The effective Hamiltonian

\[ H_{\text{eff}}^{\varepsilon} := U_N^{\varepsilon} P_N^{\varepsilon} H^{\varepsilon} P_N^{\varepsilon} U_N^{\varepsilon*} \quad \text{on} \quad \mathcal{K}. \]

In summary we thus have

\[ \left\| \left( e^{-iH^{\varepsilon} t/\varepsilon} - U_N^{\varepsilon*} e^{-iH_{\text{eff}}^{\varepsilon} t/\varepsilon} U_N^{\varepsilon} \right) P_N^{\varepsilon} \right\| = \mathcal{O} \left( \varepsilon^N |t| \right). \]
4. Asymptotic expansion of $H_{\text{eff}}^\varepsilon$

\[ H_{\text{eff}}^\varepsilon = \text{Op}^W H_{\text{eff}}(\varepsilon) \]

with

\[ H_{\text{eff}}(\varepsilon, q, p) \asymp \sum_{n=0}^{\infty} \varepsilon^n h_n(q, p). \]

The effective Hamiltonian $H_{\text{eff}}^\varepsilon$ must be computed up to order $\varepsilon^{N+1}$ to obtain an approximation to $e^{-iH_{\text{eff}}^\varepsilon t/\varepsilon}$ up to order $\varepsilon^N$. 
5. Important special case: isolated eigenvalue

Let $\sigma_*(q,p) = \{E(q,p)\}$ be $\ell$-times degenerate.

Then the natural representation space is $\mathcal{K} = L^2(M;\mathbb{C}^\ell)$. One finds that

$$h_0(q,p) = E(q,p)1_{\mathbb{C}^\ell},$$

which is known in physics as “Peierls substitution”. 
3. Adiabatic perturbation theory: results

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which is known in physics as “Peierls substitution”.

The first correction to “Peierls’ substitution” is

$$h_1(q,p)_{\alpha\beta} = -\frac{i}{2} \langle \psi_\alpha(q,p), (H(q,p) - E(q,p)\mathbf{1}_{\mathcal{H}_f}), \psi_\beta(q,p) \rangle_{\mathcal{H}_f},$$

where $\{\psi_\alpha(q,p)\}_{\alpha=1}^\ell$ is an orthonormal basis of $P_*(q,p)\mathcal{H}_f$. 

Adiabatic decoupling and the partial classical limit January 2009
For the **Born-Oppenheimer approximation** one finds

\[
H_{\text{BO}}(q,p) = \frac{1}{2} (p + \varepsilon A_B(q))^2 + E(q)
\]

\[
+ \frac{\varepsilon^2}{2} \text{Tr}_{H_e} \left( \nabla P_*(q) \cdot \nabla P_*(q) (1 - P_*(q)) \right)
\]

\[
- \varepsilon^2 \text{Tr}_{H_e} \left( (p \cdot \nabla P_*(q))^2 (H_e(q) - E(q))^{-1} (1 - P_*(q)) \right)
\]

\[
+ O(\varepsilon^3).
\]
3. Other applications

- **Solid State Physics:**
  Peierls substitution and the semiclassical model of solids including new corrections, Piezo effect
  (with G. Panati, H. Spohn, C. Sparber)
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  Effective dynamics for slow charged particles ← no spectral gap
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3. **Other applications**

- **Solid State Physics:**
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  Effective dynamics for slow charged particles $\leftarrow$ no spectral gap
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- **Constraints in Quantum Dynamics:**
  Effective dynamics on constraint manifolds
  (with J. Wachsmuth)
3. Beyond the adiabatic approximation

- In the presence of (nontrivial) eigenvalue crossings, e.g. conical crossings, the adiabatic approximation breaks down.
  ⇒ Quantitative description of transitions between adiabatic subspaces near crossings
  (with C. Lasser)
3. **Beyond the adiabatic approximation**

- In the presence of (nontrivial) eigenvalue crossings, e.g. conical crossings, the adiabatic approximation breaks down.
  ⇒ Quantitative description of transitions between adiabatic subspaces near crossings
  (with C. Lasser)

- Even in the presence of a spectral gap, the adiabatic subspaces are approximately but **not** exactly invariant.
  However, the transitions are exponentially small with respect to $\varepsilon$, i.e. of order $e^{-c/\varepsilon}$ for some $c > 0$.
  ⇒ beyond perturbation theory
  (with V. Betz)
3. The end

Thank you for listening and thanks to my collaborators

Volker Betz (Warwick)  Caroline Lasser (FU Berlin)  Gianluca Panati (Rom I)  Herbert Spohn (TU Munich)

Hans Stiepan (Tübingen)  Lucattilio Tenuta (Tübingen)  Jakob Wachsmuth (Tübingen)