

First-Order Adiabatic Theory in Quantum Dynamics

Sebastian Gherghe

May 19 2021

Abstract

In my last talk, I discussed some properties of the spectrum of Hamiltonian operators in order to better understand the stationary states of quantum systems. I introduced the basic perturbation theory developed by Kato and Rellich and the main scenario of interest was the general problem of molecular dynamics, using the approximation first introduced by Born and Oppenheimer as inspiration.

In this talk I will approach the problem of quantum *dynamics* and introduce the basic tools of the so-called adiabatic perturbation theory. We will consider quantum systems that have a clear separation of scales. An example in classical physics is a spinning top: while it is spinning at a high frequency the rotation axis is usually precessing much slower. In the quantum realm the prototypical example is that of molecular dynamics. Our main interest will be the phenomenon that fast degrees of freedom become completely dependent on the slow degrees of freedom which in turn evolve autonomously. This is referred to as *adiabatic decoupling*.

The abstract mathematical problem we will consider is the limit $\epsilon \downarrow 0$ in Schrödinger's equation:

$$i\epsilon \frac{\partial}{\partial t} \psi^\epsilon(t, x) = H(x, -i\epsilon \nabla_x) \psi^\epsilon(t, x) \quad (1)$$

where H is a special kind of Hamiltonian. As will be explained, the parameter $0 < \epsilon \ll 1$ controls the separation of scales: the smaller ϵ the better is the slow time scale separated from the fixed fast time scale. Roughly speaking, the general goal of such approaches is to find asymptotic solutions to the initial value problem (1) as solutions of an effective Schrödinger equation for the slow degrees of freedom alone. This talk will focus on some basic first-order results.

The Born-Oppenheimer approximation will again serve as the main application.

1 First-Order Results

We shall begin our analysis of the problem starting from equation (1). In the future, we shall derive (1) from the normal Schrödinger equation. Let's make some introductory remarks before describing the first-order result. Our main reference for this set of notes is [1].

Definition 1. A unitary propagator is a jointly strongly continuous family $U(s, t)$ of unitary operators satisfying:

$$(i) \quad U(s, r)U(r, t) = U(s, t) \text{ for all } s, t, r \in \mathbb{R},$$

$$(ii) \quad U(s, s) = 1_{\mathcal{H}} \text{ for any } s \in \mathbb{R}.$$

Let $H(s)$, $s \in \mathbb{R}$ be a family of bounded, self-adjoint operators on some Hilbert space \mathcal{H} . If the map $s \mapsto H(s)$ is strongly continuous, then one can construct a unitary propagator $\tilde{U}^\epsilon(s, s_0)$ solving the initial value problem:

$$i \frac{d}{ds} \tilde{U}^\epsilon(s, s_0) = H(\epsilon s) \tilde{U}^\epsilon(s, s_0), \quad \tilde{U}^\epsilon(s_0, s_0) = 1 \quad (2)$$

using a construction known as a Dyson Expansion, see [2] Section X.12. Clearly, if $\tilde{U}^\epsilon(s, s_0)$ solves (2), then $\psi(s) := \tilde{U}^\epsilon(s, s_0)\psi_0$ solves the Schrödinger equation

$$i \frac{d}{ds} \psi(s) = H(\epsilon s) \psi(s), \text{ with } \psi(s_0) = \psi_0. \quad (3)$$

The parameter $0 < \epsilon \ll 1$ in the above equations (2) and (3) is called the *adiabatic parameter* and its role is to control the separation of time-scales. In this report we shall consider two time-scales: the *fast* or *microscopic* time-scale is denoted by the letter s . (This is the time-scale that we normally solve the Schrödinger equation on.) The *slow* or *macroscopic* time-scale is denoted by $t := \epsilon s$ and this is the time-scale in which we expect the slow degrees of freedom to evolve. In many applications, the appearance of different time-scales is closely related to the existence of different spatial scales, hence the terms micro- and macroscopic.

Switching (3) to the slow time scale, we recover the propagator equation for equation (1),

$$i \epsilon \frac{d}{dt} U^\epsilon(t, t_0) = H(t) U^\epsilon(t, t_0), \quad U^\epsilon(t, t_0) = 1 \quad (4)$$

where $U^\epsilon(t, t_0) := \tilde{U}^\epsilon(t/\epsilon, t_0/\epsilon)$. As H varies on the slow time-scale, we expect non-trivial effects to occur on the time-scale t and thus we will examine equation (4) in what follows.

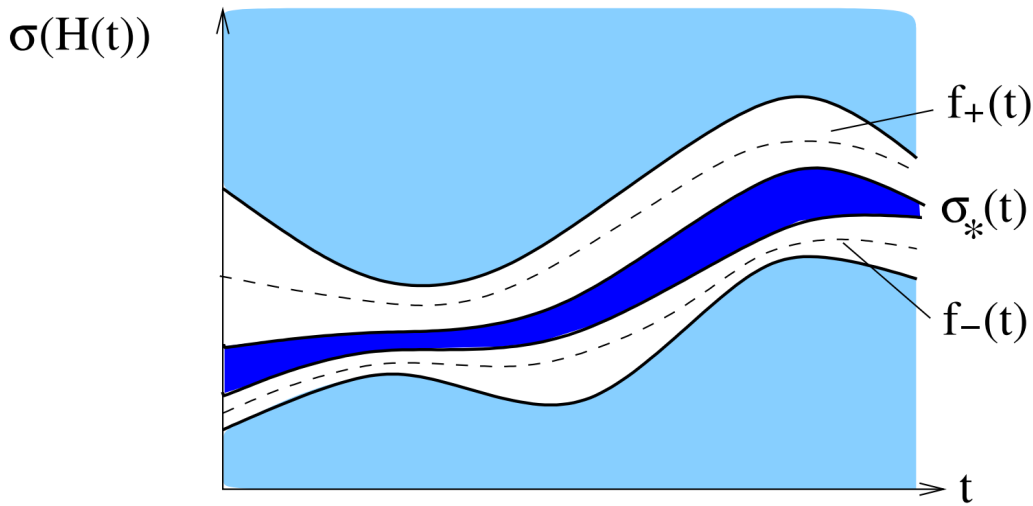
Our first result is the *time-adiabatic theorem*: it essentially states that $U^\epsilon(t, t_0)$ approximately transports the time-dependent spectral subspaces of $H(t)$ which vary sufficiently

smoothly as t changes. For the classical, first-order result, we shall consider spectral subspaces which are separated by a gap from the remainder.

Time Gap Condition: Assume that the spectrum $\sigma(t)$ of $H(t)$ contains a subset $\sigma_*(t) \subset \sigma(t)$ such that there exist 2 bounded continuous functions $f_{\pm} \in C_b(\mathbb{R}, \mathbb{R})$ defining an interval $I(t) = [f_-(t), f_+(t)]$ so that

$$\sigma_*(t) \subset I(t), \quad \inf_{t \in \mathbb{R}} \text{dist}(I(t), \sigma(t) \setminus \sigma_*(t)) =: g > 0 \quad (5)$$

We can summarize this condition with the following figure:



Denote by $P_*(t)$ the spectral projection of $H(t)$ onto $\sigma_*(t)$ (a good reference for spectral projections or Riesz projections is [3] Chapter 6 or [4] Section XII.2.) Assuming sufficient regularity of $H(t)$, the time-adiabatic theorem of quantum mechanics in its simplest form states that there exists a constant $C < \infty$ such that

$$\|(1 - P_*(t))U^\epsilon(t, t_0)P_*(t)\|_{\mathcal{L}(\mathcal{H})} \leq C\epsilon(1 + |t - t_0|) \quad (6)$$

Lets interpret this statement physically. It essentially says that, if a state is initially in the state $\psi_0 \in P_*(t)\mathcal{H}$ (in the subspace associated with spectrum $\sigma_*(t)$), then the state of the system at later times $\psi(t)$, given via the solution of (3), stays in the subspace $P_*(t)\mathcal{H}$ up to an error of order $O(\epsilon(1 + |t - t_0|)\|\psi_0\|)$. A similar statement holds true if ψ_0 belongs to the orthogonal complement of $P_*(t_0)\mathcal{H}$.

The phenomenon that spectral subspaces, which in some sense depend slowly on some parameter, are approximately invariant under the quantum mechanical time-evolution is referred to as *adiabatic decoupling*.

1.1 The Time-Adiabatic Theorem

Let us now formulate rigorously the time-adiabatic theorem. We consider time-dependent Hamiltonians $H(t)$ which are not necessarily bounded. In order to define the propagator in this case, we refer to very general result on contraction semigroups, see Theorem X.70 in [2]. The following proposition is an immediate consequence and will not be proven:

Proposition 1. *For some open interval $J \subset \mathbb{R}$, let $H(t)$, $t \in J$, be a family of self-adjoint operators on some Hilbert space \mathcal{H} with a common dense domain $\mathcal{D} \subset \mathcal{H}$, equipped with the graph norm of $H(t)$ for some $t \in J$, such that*

$$(i) \ H(\cdot) \in C_b^1(J, \mathcal{L}(\mathcal{D}, \mathcal{H}))$$

$$(ii) \ \text{There exists a constant } C > -\infty \text{ such that } H(t) \geq C \text{ for all } t \in J.$$

Then there exists a unitary propagator U^ϵ such that for $t, t_0 \in J$, $\psi_0 \in \mathcal{D}$, a solution to the time-dependent Schrödinger equation

$$i\epsilon \frac{d}{dt} \psi(t) = H(t) \psi(t), \quad \psi(t_0) = \psi_0 \quad (7)$$

is given through $\psi(t) = U^\epsilon(t, t_0) \psi_0$.

Before stating the time-adiabatic theorem, we quickly define the *adiabatic Hamiltonian*

$$H_a(t) = H(t) - i\epsilon P_*(t) \dot{P}_*(t) - i\epsilon P_*^\perp(t) \dot{P}_*^\perp(t), \quad (8)$$

which generates the *adiabatic propagator*, which satisfies

$$i\epsilon \frac{d}{dt} U_a^\epsilon(t, t_0) = H_a(t) U_a^\epsilon(t, t_0), \quad U_a^\epsilon(t_0, t_0) = 1. \quad (9)$$

We remark after the statement of the theorem on the particular choice of $H_a(t)$ and its consequence.

Theorem 1. *Let $H(t)$ satisfy the assumptions of Proposition 1, with $H(\cdot) \in C_b^2(J, \mathcal{L}(\mathcal{D}, \mathcal{H}))$. Let $\sigma_*(t) \subset \sigma(H(t))$ satisfy the Gap condition (5) on $J \subset \mathbb{R}$. Then, $P_*(\cdot) \in C_b^2(J, \mathcal{L}(\mathcal{H}))$ and there is a constant $C < \infty$ such that for $t, t_0 \in J$:*

$$\|U^\epsilon(t, t_0) - U_a^\epsilon(t, t_0)\| \leq C\epsilon(1 + |t - t_0|) \quad (10)$$

The right-hand side of (10) can be replaced by

$$\epsilon \left(\|F(t)\| + \|F(t_0)\| + \left| \int_{t_0}^t \left(\|\dot{P}(s)\| + \|F(s) [\dot{P}(s), P(s)]\| \right) ds \right| \right) \quad (11)$$

where $F(t)$ is a function defined in (22).

Remark. *It can be shown that the adiabatic propagator is constructed so that it intertwines the spectral subspaces $P_*(t)$ at different times exactly, i.e.*

$$P_*(t)U_a^\epsilon(t, t_0) = U_a^\epsilon(t, t_0)P_*(t_0), \quad \forall t, t_0 \in \mathbb{R} \quad (12)$$

Using (12), it is straightforward to recover (6) from (10). Notice that the latter statement is stronger than the former, since it yields not only approximate invariance of the spectral subspace, but it also gives information about the effective-time evolution inside the decoupled subspace.

Proof of (12). We begin by computing (and using equation (9)):

$$\begin{aligned} \frac{\partial}{\partial t}(U_a^\epsilon(t, t_0)^{-1}P_*(t)U_a^\epsilon(t, t_0)) &= -\frac{1}{i\epsilon}H_a(t)U_a^\epsilon(t_0, t)P_*(t)U_a^\epsilon(t, t_0) \\ &\quad + U_a^\epsilon(t, t_0)P_*(t)\frac{1}{i\epsilon}H_a(t)U_a^\epsilon(t, t_0) \\ &\quad + U_a^\epsilon(t, t_0)\dot{P}_*(t)U_a^\epsilon(t, t_0) \\ &= U_a^\epsilon(t, t_0) \left(\dot{P}_*(t) - \left[\frac{1}{i\epsilon}[H_a(t), P_*(t)] \right] \right) U_a^\epsilon(t, t_0) \end{aligned}$$

Let us now examine the term $\dot{P}_*(t) - \frac{1}{i\epsilon}[H_a(t), P_*(t)]$. Using the definition of the adiabatic Hamiltonian,

$$\dot{P}_*(t) - \frac{1}{i\epsilon}[H_a(t), P_*(t)] = \dot{P}_*(t) + P_*(t)[\dot{P}_*(t), P_*(t)] - [\dot{P}_*(t), P_*(t)]P_*(t) =: B(t)$$

where the term $\frac{1}{i\epsilon}[H(t), P_*(t)]$ vanishes since $P_*(t)$ is a spectral projection and hence commutes with $H(t)$. Now observe the identity

$$\dot{P}_*(t) = \frac{d}{dt}P_*^2(t) = P_*(t)\dot{P}_*(t) + \dot{P}_*(t)P_*(t) \quad (13)$$

which implies that $P_*(t)\dot{P}_*(t)P_*(t) = 0$. Expanding the commutators and using identity (13),

$$B(t) = P_*(t)\dot{P}_*(t)P_*(t) - P_*(t)\dot{P}_*(t) - \dot{P}_*(t)P_*(t) + P_*(t)\dot{P}_*(t)P_*(t) + \dot{P}_*(t) = 0$$

Hence the entire derivative vanishes. Integrating in s from t_0 to t and using the initial condition $U_a^\epsilon(t_0, t_0) = 1$, we obtain (12). \square

Before giving a proof of Theorem 1, let's take a look at a more explicit bound in the case an isolated eigenvalue.

Corollary 1. Let $H(\cdot) \in C_b^2(J, \mathcal{L}(\mathcal{H}))$ and $\sigma_*(t) = \{E(t)\}$ be an isolated eigenvalue. Denote by $\Delta(t)$ the size of the gap, i.e.

$$\Delta(t) := \text{dist}(E(t), \sigma(H(t)) \setminus E(t)) \quad (14)$$

Then, (10) holds with the right-hand side replaced by

$$2\epsilon \left(\frac{\|\dot{P}_*(t)\|}{\Delta(t)} + \frac{\|\dot{P}_*(t_0)\|}{\Delta(t_0)} + \left| \int_{t_0}^t \left(\frac{2\|\dot{P}_*(s)\|^2}{\Delta(s)} + \frac{\|\ddot{P}_*(s)\|}{\Delta(s)} + \frac{\|\dot{P}_*(s)\|\|\dot{H}(s)\|}{\Delta(s)^2} \right) ds \right| \right) \quad (15)$$

While not optimal, the form of the bound in Corollary 1 displays the two mechanisms responsible for adiabatic decoupling: the size of the error depends on the size of the gap and on the variation of the eigenspace. If either the gap is too small, or the variation of the eigenspace is too large, then the adiabatic decoupling will break down. It is also clear that if the eigenspaces are constant and only the eigenvalue vanishes, the subspaces decouple exactly!

Proof of Theorem 1. We shall break the proof of the theorem into two steps. In the first step, we show the regularity of $P_*(t)$ (from the regularity of $H(t)$ and the gap condition). In the second step, we attack the bound (10).

Step 1: Let us first show the regularity of the resolvent operator $R(z, t) := (H(t) - z)^{-1}$. Consider that $H(\cdot) \in C_b^n(I, \mathcal{L}(\mathcal{D}, \mathcal{H}))$ for some open interval $I \subset J$. Then it follows that $R(z, \cdot) \in C_b^n(I, \mathcal{L}(\mathcal{H}, \mathcal{D}))$ for all $z \in \mathbb{C} \setminus \cup_{t \in I} \sigma(H(t))$.

First, we show that $R(z, \cdot) \in C_b(I, \mathcal{L}(\mathcal{H}, \mathcal{D}))$. Note that by definition, $R(z, \cdot) \in \mathcal{L}(\mathcal{H}, \mathcal{D})$ for all $t \in I$. Hence, by the what is called the 2nd resolvent identity,

$$R(z, t) - R(z, s) = R(z, t)(H(s) - H(t))R(z, s)$$

So $H(\cdot) \in C_b(I, \mathcal{L}(\mathcal{D}, \mathcal{H}))$ implies $R(z, \cdot) \in C_b(I, \mathcal{L}(\mathcal{H}, \mathcal{D}))$. Differentiability also follows from the above,

$$\dot{R}(z, t) = -R(z, t)\dot{H}(t)R(z, t)$$

and so on for higher derivatives. So $H(\cdot) \in C_b^n(I, \mathcal{L}(\mathcal{D}, \mathcal{H}))$, $R(z, \cdot) \in C_b(I, \mathcal{L}(\mathcal{H}, \mathcal{D}))$ implies that $R(z, \cdot) \in C_b^n(I, \mathcal{L}(\mathcal{H}, \mathcal{D}))$.

Now, consider the spectral projection $P_*(t)$. Using Riesz' formula, the spectral projection can be written as

$$P_*(t) = -\frac{1}{2\pi i} \oint_{\Gamma(t)} R(z, t) dz \quad (16)$$

where $\Gamma(t) \subset \mathbb{C}$ is a positively oriented closed curve encircling $\sigma_*(t)$ once, such that

$$\inf_{t \in J} \text{dist}(\Gamma(t), \sigma(H(t))) = \frac{1}{2}g$$

where recall g is the size of the gap. For a reference, please see [3] or [4]. Of course, such a family of contours $\Gamma(t)$ exists because of the gap condition (5). Using the continuity of the functions f_{\pm} , for any $\tau \in J$, there exists a neighbourhood $I(\tau)$ of τ so that

$$\inf_{t \in I(\tau)} \text{dist}(\Gamma(\tau), \sigma(H(t))) \geq \frac{1}{4}g$$

So for any $t \in I(\tau)$,

$$P_*(t) = -\frac{1}{2\pi i} \oint_{\Gamma(\tau)} R(z, t) dz \quad (17)$$

and hence we can differentiate (17) with respect to t ,

$$\frac{d^n}{dt^n} P_*(t) = -\frac{1}{2\pi i} \oint_{\Gamma(\tau)} \frac{d^n}{dt^n} R(z, t) dz$$

Hence the claimed regularity that $P_*(\cdot) \in C_b^2(J, \mathcal{L}(\mathcal{H}))$ follows using $n = 2$. Furthermore, this implies that $H_a^\epsilon(t)$ satisfies the assumptions of Proposition 1 and hence U_a^ϵ defines a propagator on \mathcal{D} .

Step 2: Now we consider the bound in (10). Like in the proof of the intertwining property (12), we can express the difference of the unitary propagators in terms of the differences of the generators:

$$\begin{aligned} U^\epsilon(t, t_0) - U_a^\epsilon(t, t_0) &= -U^\epsilon(t, t_0) \int_{t_0}^t \frac{d}{dt'} (U^\epsilon(t_0, t) U_a^\epsilon(t', t_0)) dt' \\ &= \frac{1}{i\epsilon} U^\epsilon(t, t_0) \int_{t_0}^t U^\epsilon(t_0, t') (H(t') - H_a(t')) U_a^\epsilon(t', t_0) dt' \\ &= -U^\epsilon(t, t_0) \int_{t_0}^t u^\epsilon(t_0, t') [\dot{P}_*(t'), P_*(t')] U_a^\epsilon(t', t_0) dt' \end{aligned} \quad (18)$$

Taking a very coarse bound here would yield a bound of $O(1)$. The key observation for the adiabatic theory is that the integrand in (18) oscillates and can be written as the time-derivative of a function which is of order ϵ (as an example, consider the integrand being $e^{it'/\epsilon}$, which is $O(1)$, but integrated is $O(\epsilon)$).

In order to motivate the following definition, consider for a moment the special case of $\sigma_*(t) = \{E(t)\}$, a single eigenvalue $E(t)$. We seek to construct a function $F(t)$ such that

$$[H(t), F(t)] = [\dot{P}_*(t), P_*(t)] \quad (19)$$

One such candidate is:

$$F(t) := -\left(R(E(t), t) \dot{P}_*(t) P_*(t) + P_*(t) \dot{P}_*(t) R(E(t), t)\right) \quad (20)$$

Using (13), we can write

$$\dot{P}_*(t) = P_*^\perp(t)\dot{P}_*(t)P_*(t) + P_*(t)\dot{P}_*(t)P_*^\perp(t) \quad (21)$$

and thus we can see that the resolvent term $R(E(t), t)$ in the definition of $F(t)$ (20) acts only on $P_*^\perp(t)\mathcal{H}$, where as a consequence of the gap condition it is uniformly bounded. Hence, by equation (19), the integrand in (18) can be written as a commutator of $F(t)$ with $H(t)$, and thus at least approximately as the time derivative of $-i\epsilon U^\epsilon(t_0, t)F(t)U^\epsilon(t, t_0)$.

Hence, generalizing (20) to arbitrary $\sigma_*(t)$, we define

$$F(t) = \frac{1}{2\pi i} \oint_{\Gamma(t)} dz P_*^\perp(t) R(z, t) \dot{R}(z, t) + \text{adj.} \quad (22)$$

where adj. means the adjoint of all the operators to the left. Using the identities $H(t)R(z, t) = 1 + zR(z, t)$ and $\dot{R}(z, t)(H(t) - z) = -R(z, t)\dot{H}(t)$, we can compute:

$$\begin{aligned} [H(t), F(t)] &= \frac{1}{2\pi i} \oint_{\Gamma(t)} dz [H(t), P_*^\perp(t) R(z, t) \dot{R}(z, t)] - \text{adj.} \\ &= \frac{1}{2\pi i} \oint_{\Gamma(t)} dz P_*^\perp(t) \left[(1 + zR(z, t)) \dot{R}(z, t) - R(z, t) \dot{R}(z, t) H(t) \right] - \text{adj.} \\ &= P_*^\perp(t) \dot{P}_*(t) - \frac{1}{2\pi i} \oint_{\Gamma(t)} dz P_*^\perp(t) R(z, t) \dot{R}(z, t) (H(t) - z) - \text{adj.} \\ &= P_*^\perp(t) \dot{P}_*(t) + \frac{1}{2\pi i} \oint_{\Gamma(t)} dz P_*^\perp(t) R(z, t)^2 \dot{H}(t) - \text{adj.} \end{aligned}$$

Now, note that $z \mapsto P_*^\perp(t) R(z, t)^2 \dot{H}(t)$ is a holomorphic function inside of $\Gamma(t)$, so the integral vanishes. A similar situation occurs in the adjoint case, leaving out a $\dot{P}_*(t)P_*^\perp(t)$ term in front. Hence,

$$[H(t), F(t)] = P_*^\perp(t) \dot{P}_*(t) - \dot{P}_*(t) P_*^\perp(t)$$

Using (21), we observe that $[P_*^\perp(t), \dot{P}_*(t)] = [\dot{P}_*(t), P_*(t)]$, and thus

$$[H(t), F(t)] = [\dot{P}_*(t), P_*(t)] \quad (23)$$

Now, we define

$$A(t) := -i\epsilon U^\epsilon(t_0, t) F(t) U^\epsilon(t, t_0) \quad (24)$$

Since $P_*(\cdot) \in C_b^2(\mathbb{R}, \mathcal{L}(\mathcal{H}))$, it follows that $F(\cdot) \in C_b^1(\mathbb{R}, \mathcal{L}(\mathcal{H}))$, and thus:

$$\begin{aligned} \frac{d}{dt} A(t) &= U^\epsilon(t_0, t) [H(t), F(t)] U^\epsilon(t, t_0) - i\epsilon U^\epsilon \dot{F}(t) U^\epsilon(t, t_0) \\ &= U^\epsilon(t_0, t) [\dot{P}_*(t), P_*(t)] U^\epsilon(t, t_0) + O(\epsilon) \end{aligned} \quad (25)$$

Hence, the derivative of $A(t)$ is approximately the integrand in (18). Thus inserting (25) into (18) we obtain:

$$\begin{aligned} U^\epsilon(t, t_0) - U_a^\epsilon(t, t_0) &= -U^\epsilon(t, t_0) \int_{t_0}^t dt' U^\epsilon(t_0, t') [\dot{P}_*(t'), P_*(t')] U^\epsilon(t', t_0) U_a^\epsilon(t', t_0) \\ &= -U^\epsilon(t, t_0) \int_{t_0}^t dt' \left[\frac{d}{dt'} A(t') + i\epsilon U^\epsilon(t_0, t') \dot{F}(t') U^\epsilon(t', t_0) \right] U^\epsilon(t_0, t') U_a^\epsilon(t', t_0) \\ &= -U^\epsilon(t, t_0) \int_{t_0}^t dt' \left(\frac{d}{dt'} A(t') \right) U^\epsilon(t_0, t') U_a^\epsilon(t', t_0) \end{aligned} \quad (26)$$

$$- i\epsilon U^\epsilon(t, t_0) \int_{t_0}^t dt' U^\epsilon(t_0, t') \dot{F}(t') U_a^\epsilon(t', t_0) \quad (27)$$

Denote the integrals on lines (26) and (27) by B and C , respectively. Then, note that

$$\|C\| \leq \epsilon |t - t_0| \sup_{s \in [t_0, t]} \|\dot{F}(s)\| = O(\epsilon |t - t_0|). \quad (28)$$

Integrating B by parts, we obtain

$$B = A(t') U^\epsilon(t_0, t') U_a^\epsilon(t', t_0) \Big|_{t_0}^t - \int_{t_0}^t dt' A(t') \frac{d}{dt'} (U^\epsilon(t_0, t') U_a^\epsilon(t', t_0))$$

Observe that $\|A(t)\| = O(\epsilon)$ uniformly for $t \in \mathbb{R}$, and also that

$$\left\| \frac{d}{dt'} (U^\epsilon(t_0, t') U_a^\epsilon(t', t_0)) \right\| = \|U^\epsilon(t_0, t') [\dot{P}_*(t'), P_*(t')] U_a^\epsilon(t', t_0)\| = O(1)$$

Hence,

$$\begin{aligned} \|B\| &\leq \|A(t)\| + \|A(t_0)\| + \left\| \int_{t_0}^t dt' A(t') \frac{d}{dt'} (U^\epsilon(t_0, t') U_a^\epsilon(t', t_0)) \right\| \\ &\leq 2O(\epsilon) + O(\epsilon |t - t_0|) \end{aligned} \quad (29)$$

Hence, combining (28), (28) we obtain the bound (10), as desired. \square

1.2 The Space-Adiabatic Theorem: Fibered Hamiltonians

In this section, we will present a small generalization of the time-adiabatic theorem, Theorem 1, that lends itself better to applications. We seek to now split the Hilbert space \mathcal{H} into two pieces. In physical applications, this splitting of the Hilbert space corresponds to the splitting of the system into slow and fast degrees of freedom. The Hilbert space for the fast degrees of freedom will be denoted by \mathcal{H}_f , and its explicit form is irrelevant for the following analysis.

The Hilbert space for the slow degrees of freedom will be $L^2(\mathbb{R}^d)$ (or in more generality, L^2 over some other configuration space). While in some cases, the identification of the slow and fast degrees of freedom is obvious (i.e. in molecular dynamics, the nuclei move much slower than the electrons), in other cases some work is required to cast a Hamiltonian into the following form.

The key insight is that one can think of $i\epsilon\partial_t$ as a perturbation of the family $H(t)$ of self-adjoint operators: while the spectral subspaces of $H(t)$ are not invariant under time-evolution (because the commutator $[i\epsilon\partial_t, H(t)]$ does not vanish), for ϵ small the commutator is small, thus like in the proof of the time-adiabatic theorem, one can show that the spectral subspaces corresponding to spectrum separated by a gap are approximately invariant.

The proof of Theorem 1 can be generalized in a straightforward way in the case where $H_0(x)$ is a family of self-adjoint operators on some Hilbert space \mathcal{H}_f , depending on the parameter $x \in \mathbb{R}^d$, and the Hamiltonian in question looks like:

$$H^\epsilon = f(-i\epsilon\nabla_x) \otimes 1 + \int_{\mathbb{R}^d}^{\oplus} dx H_0(x) \quad (30)$$

The Hamiltonian H^ϵ now acts on $\mathcal{H} = L^2(\mathbb{R}^d) \otimes \mathcal{H}_f := L^2(\mathbb{R}^d, \mathcal{H}_f)$, and $f(-i\epsilon\nabla_x)$ with $f : \mathbb{R}^d \rightarrow \mathbb{R}$ is the perturbation which in some sense has generalized $-i\epsilon\partial_t$. We think of (30) as a “small” perturbation of a *fibred* Hamiltonian H_0 .

Remark. A self-adjoint operator H acting on the Hilbert space

$$L^2(\mathbb{R}^d) \otimes \mathcal{H}_f = \int_{\mathbb{R}^d}^{\oplus} dx \mathcal{H}_f$$

is called *fibred* if there is a family $H(x), x \in \mathbb{R}^d$, of self-adjoint operators on \mathcal{H}_f such that the map $x \mapsto \langle \psi, (H(x) - i)^{-1} \phi \rangle$ is measurable for all $\psi, \phi \in \mathcal{H}_f$ and such that

$$(H - i)^{-1} = \int_{\mathbb{R}^d}^{\oplus} dx (H(x) - i)^{-1}$$

In this case, one writes

$$H = \int_{\mathbb{R}^d}^{\oplus} dx H(x)$$

We will call the set

$$\Sigma = \{(x, s) \in \mathbb{R}^d \times \mathbb{R} \mid s \in \sigma(H_0(x))\} \quad (31)$$

the *fibred spectrum* of H_0 . As before, we shall impose conditions on the regularity of $H(\cdot)$, which ensure that Σ is defined without ambiguities about null sets.

As before, consider a subset of the fibered spectrum, $\sigma_* \subset \Sigma$ be such that $x \mapsto P_*(x)$ is measurable, where $P_*(x)$ denotes the spectral projection of $H_0(x)$ associated with $\sigma_*(x)$. Then,

$$P_* = \int_{\mathbb{R}^d}^{\oplus} dx P_*(x)$$

is an orthogonal projection which commutes with H_0 , but which is in general not a spectral projection of H_0 . In particular, the subspace $P_*\mathcal{H}$ is an invariant subspace for the dynamics generated by H_0 , i.e.

$$[e^{iH_0 s}, P_*] = 0$$

We expect that the perturbation $f(-i\epsilon\nabla_x) \otimes 1$ in (30) is small in the sense that

$$[H^\epsilon, P_*] = [f(-i\epsilon\nabla_x) \otimes 1, P_*] = O(\epsilon)$$

and thus the subspaces $P_*\mathcal{H}$ are at least approximately invariant for small ϵ , i.e.

$$[e^{-iH^\epsilon s}, P_*] = O(\epsilon|s|)$$

For finite macroscopic times $t = \epsilon s$, the above becomes

$$[e^{-iH^\epsilon t/\epsilon}, P_*] = O(|t|)$$

which does not become small with ϵ . This is the same situation as in (18). Using the same kind of argument as in the proof of Theorem 1, we can improve to

$$[e^{-iH^\epsilon t/\epsilon}, P_*] = O(\epsilon(1 + |t|))$$

if we assume some sort of gap between $\sigma_*(x)$ and the remainder of the spectrum of $H_0(x)$ uniformly for $x \in \mathbb{R}^d$.

Space Gap Condition: Assume that the spectrum $\sigma(x)$ of $H_0(x)$ contains a subset $\sigma_*(x) \subset \sigma(x)$ such that there exist real-valued functions $f_\pm \in C_b(\mathbb{R}^d)$ defining an interval $I(x) = [f_-(x), f_+(x)]$ such that

$$\sigma_*(x) \subset I(x) \quad \text{and} \quad \inf_{x \in \mathbb{R}^d} \text{dist}(I(x), \sigma(x) \setminus \sigma_*(x)) =: g > 0 \quad (32)$$

In this space-adiabatic setting, the adiabatic evolution is generated by the diagonal Hamiltonian:

$$H_{diag}^\epsilon = P_* H^\epsilon P_* + P_*^\perp H^\epsilon P_*^\perp \quad (33)$$

which by construction satisfies

$$[e^{-iH_{diag}^\epsilon t/\epsilon}, P_*] = 0.$$

We shall now state the general scheme of space-adiabatic theory under rather simplifying and restrictive assumptions. We refer the reader to [1] for the details of the proof, which in main ideas follows the proof of Theorem 1.

Theorem 2. Let $H_0(x), x \in \mathbb{R}^d$, be a family of bounded self-adjoint operators such that $H_0(\cdot) \in C_b^2(\mathbb{R}^d, \mathcal{L}(\mathcal{H}_f))$ and let $\sigma_*(x) \subset \sigma(x)$ satisfy the space gap condition (32). Let $f \in \mathcal{S}(\mathbb{R}^d)$ be real-valued and H^ϵ be the bounded self-adjoint operator on $\mathcal{H} = L^2(\mathbb{R}^d, \mathcal{H})f$ given through (30). Then, there is a constant $C < \infty$ such that for all $t \in \mathbb{R}$,

$$\|e^{-iH^\epsilon t/\epsilon} - e^{-iH_{diag}^\epsilon t/\epsilon}\|_{\mathcal{L}(\mathcal{H})} \leq C\epsilon(1 + |t|) \quad (34)$$

Sketch of Proof of Theorem 2. Like in the proof of Theorem 1, we conclude that $P_*(\cdot) \in C_b^2(\mathbb{R}^d, \mathcal{L}(\mathcal{H}))$. Also like in (18), we find

$$e^{-iH^\epsilon t/\epsilon} - e^{-iH_{diag}^\epsilon t/\epsilon} = -\frac{i}{\epsilon} e^{-iH_{diag}^\epsilon t/\epsilon} \int_0^t dt' e^{iH^\epsilon t'/\epsilon} H_{od}^\epsilon e^{-iH_{diag}^\epsilon t'/\epsilon} \quad (35)$$

where the off-diagonal part of the Hamiltonian H_{od}^ϵ is defined as

$$H_{od}^\epsilon = H^\epsilon - H_{diag}^\epsilon = P_*^\perp [(f(-i\epsilon\nabla_x) \otimes 1_{\mathcal{H}_f}), P_*] P_* + adj. \quad (36)$$

This is analogous to the time-adiabatic case, where we obtained the simple expression $[-i\epsilon\partial_t, P_*] = -i\epsilon\dot{P}_*$. However, the remainder is now $O(\epsilon^2)$. Analogous to the proof of Theorem 1, one defines

$$F(x) = \frac{1}{2\pi i} \oint_{\Gamma(x)} dz P_*^\perp(x) R(z, x) (\nabla R)(z, x) + adj. \quad (37)$$

and proceeds slightly differently. □

2 The Born-Oppenheimer Approximation

In this second half of the presentation we will first describe the space-adiabatic structure of molecular dynamics, and then consider an application of Theorem 2.

2.1 Physical Motivation

Molecules, broadly speaking, consist of light electrons (mass m_e) and heavy nuclei (mass m_n , which depends on the type of nucleus). Born and Oppenheimer [5] wanted to explore the general features of molecular spectra, and realized that as the mass ratio m_e/m_n is very small, it could be used as an expansion parameter for the energy levels of the molecular Hamiltonian. This time-independent Born-Oppenheimer theory was put on firm mathematical grounds by [6, 7].

For l nuclei with positions $x = \{x_1, \dots, x_l\}$ and k electrons with positions $y = y_1, \dots, y_k$, the molecular Hamiltonian is of the form

$$H_{mol} = -\frac{\hbar^2}{2m_n}\Delta_x - \frac{\hbar^2}{2m_e}\Delta_y + V_e(y) + V_{en}(x, y) + V_n(x) \quad (38)$$

with dense domain $H^2(\mathbb{R}^{2(l+k)}) \subset L^2(\mathbb{R}^{2(l+k)})$, where for notational simplicity, we have ignored spin degrees of freedom and have assumed that all nuclei have the same mass m_n . V_e, V_n are the electronic, respectively nucleonic repulsions, while V_{en} is the attraction between the electrons and the nuclei. V_e, V_n may also contain an external electrostatic potential.

Consider a simple molecule such as CO_2 . It contains 3 nuclei and 22 electrons. A direct numerical treatment of the time-dependent Schrödinger equation

$$i\hbar \frac{d}{ds}\psi(s) = H_{mol}\psi(s), \quad \psi(s_0) = \psi_0 \in L^2(\mathbb{R}^{2(l+k)}) \quad (39)$$

is far beyond current computational capabilities. This is due to the high dimensionality of the configuration space (i.e. $3(l+k) = 75$ in the case of CO_2) as well as the fact that long microscopic times s must be considered in order to observe finite motion of the nuclei. So, good approximation schemes for solving (39) are of great interest to many fields in chemistry, biophysics, etc.

If the kinetic energies of the nuclei and the electrons are of comparable magnitude, then one finds that for the speeds,

$$|v_n| \approx (m_e/m_n)^{1/2}|v_e| = \epsilon|v_e|$$

which means that the nuclei move much slower than the electrons. Hence, because of their large mass, the movement of the nuclei (which can be approximated by a classical trajectory) disrupts the electrostatic equilibrium of the electrons, and as the electrons respond quickly, they settle into the most optimal configuration. If the electronic state is initially an eigenstate, then by the time-adiabatic theorem (provided the gap condition holds) it will remain approximately an eigenstate at later times. The state of electrons follows adiabatically the motion of the nuclei.

Hence, one argues that, by conservation of energy, the influence of the electrons on the motion of the nuclei is well-approximated through the effective energy potential of the eigenstate. In the first step the configuration of nuclei is fixed and one solves for the eigenstate of the electron configuration. The dynamics of nuclei are then modelled by using the ground state energy of the electron configuration as the potential (interaction) energy of the nuclear motion.

Since the nuclei are expected to move with a speed of order ϵ , their dynamics must be followed over microscopic times of order ϵ^{-1} to observe motion over finite distances. Hence,

(39) becomes

$$i\epsilon \frac{d}{dt} \psi(t) = H_{mol}^\epsilon \psi(t), \quad \psi(t_0) = \psi_0 \in L^2(\mathbb{R}^{3(l+k)}) \quad (40)$$

We have recovered equation (1), which was claimed to be the starting point of our adiabatic analysis.

2.2 Application to Molecular Dynamics

We now apply the first-order space-adiabatic scheme (Theorem 2) to the full molecular Hamiltonian for l nuclei, k electrons, with an added external magnetic field $B = \nabla \times A$ where $A : \mathbb{R}^3 \rightarrow \mathbb{R}^3$ is its vector potential.

$$H_{mol} = \frac{1}{2m_n} \sum_{n=1}^l (-i\hbar \nabla_{x_n} + A(x_n))^2 + \frac{1}{2m_e} \sum_{n=1}^k (-i\hbar \nabla_{y_n} - A(y_n))^2 + V_e(y) + V_{en}(x, y) + V_n(x) \quad (41)$$

The electrons are modelled as point charges and the electronic repulsion is thus given through the Coulomb potential energy:

$$V_e(y) = \sum_{n=1}^k \sum_{m=n+1}^k \frac{1}{|y_n - y_m|} \quad (42)$$

Modification: For technical and physical reasons, the nuclei are modelled as smear rigid charge distributions $\rho \in C_0^\infty(\mathbb{R}^3)$, $\rho \geq 0$ and $\|\rho\|_{L^1} = 1$. These are referred to in the literature as *form factors*. The potential for nuclear repulsion is thus:

$$V_n(x) = \sum_{n=1}^{l-1} \sum_{m=n+1}^l \int_{\mathbb{R}^6} dz dz' \frac{\rho(z - x_n) \rho(z' - x_m)}{|z - z'|} \quad (43)$$

and the attractive potential between electrons and nuclei is:

$$V_{en}(x, y) = - \sum_{n=1}^l \sum_{m=1}^k \int_{\mathbb{R}^3} dz \frac{\rho(z - x_n)}{|z - y_m|} \quad (44)$$

In order to simplify our notation, we change to atomic units ($m_e = 1 = \hbar$) and extend $A : \mathbb{R}^3 \rightarrow \mathbb{R}^3$ to $A : \mathbb{R}^{3l} \rightarrow \mathbb{R}^{3l}$ by repeating it l -times. Introduce the small parameter

$$\epsilon = \sqrt{\frac{m_e}{m_n}} \quad (45)$$

which will serve as our adiabatic constant. Hence, we can rewrite (41) as

$$H_{mol}^\epsilon = \frac{\epsilon^2}{2}(-i\nabla_x + A(x))^2 + \int_{\mathbb{R}^{3l}}^\oplus dx H_e(x) \quad (46)$$

where

$$H_e(x) = \frac{1}{2}(-i\nabla_y - A(y))^2 + V_e(y) + V_{en}(x, y) + V_n(x) \quad (47)$$

is self-adjoint with x -independent domain $\mathcal{D}(H_e) = H^2(\mathbb{R}^{2k}) \subset L^2(\mathbb{R}^{3k})$ under appropriate conditions on A . It is thus emphasized that we will treat the nuclear kinetic energy as a small perturbation.

Remark. *The specific form (47) of the electronic Hamiltonian is of no importance for the results that follow. As before, consider an arbitrary separable Hilbert space \mathcal{H}_e for the electronic degrees of freedom. For the electronic Hamiltonian, we only need to assume that*

$$H_e = \int_{\mathbb{R}^d}^\oplus dx H_e(x), \quad H_e(x) = H_{e0} + H_{e1}(x) \quad (48)$$

where H_{e0} is self-adjoint on some dense domain $\mathcal{D} \subset \mathcal{H}_e$ and bounded from below, and $H_{e1}(x) \in \mathcal{L}(\mathcal{H}_e)$ is a continuous family of self-adjoint operators, bounded uniformly for $x \in \mathbb{R}^d$.

Under these conditions H_e is self-adjoint on $\mathcal{D}(H_e) = L^2(\mathbb{R}^d) \otimes \mathcal{D} \subset \mathcal{H} := L^2(\mathbb{R}^d) \otimes \mathcal{H}_e$, and bounded from below. To properly define $L^2(\mathbb{R}^d) \otimes \mathcal{D}$, we equip \mathcal{D} with the graph norm $\|\Psi\|_{H_{e0}} := \|H_{e0}\psi\| + \|\psi\|$ for $\psi \in \mathcal{D}$.

These general assumptions on $H_e(x)$ allow for the inclusion of the spin of the electrons and relativistic corrections, in addition to (48).

We assume that $A \in C_b^1(\mathbb{R}^d, \mathbb{R}^d)$. Then $\frac{\epsilon^2}{2}(-i\nabla_x + A(x))^2$ is self-adjoint on $H^2(\mathbb{R}^d)$, since $-i\nabla_x$ is infinitesimally operator-bounded with respect to $-\Delta_x$. Hence,

$$H^\epsilon := \frac{\epsilon^2}{2}(-i\nabla_x + A(x))^2 \otimes 1 + H_e \quad (49)$$

is self-adjoint on $\mathcal{D}(H^\epsilon) = H^2(\mathbb{R}^d) \otimes \mathcal{H}_e \cap \mathcal{D}(H_e)$.

Previously we had assumed that the relevant part of the spectrum of the fibered Hamiltonian $\sigma_*(x)$ was separated by a gap for x in all of \mathbb{R}^d . Of course in applications, like in the present case, this may be too much to ask for. For example, $H_e(x)$ has isolated energy bands in general only locally in the configuration space of the nuclei.

In the following, denote by $\Lambda \subset \mathbb{R}^d$ the region of configuration space of the nuclei that we are interested in. There are two scenarios: the “local” setting, where Λ is a strict subset

of \mathbb{R}^d , and the global case $\Lambda = \mathbb{R}^d$. In this report we shall only consider the global case $\Lambda = \mathbb{R}^d$. We refer the reader to [1] for the discussion of the local case.

For $x \in \Lambda$, $\Lambda \subset \mathbb{R}^d$ open, we require some regularity for $H_e(x)$ as a function of x .

Condition H_k : $H_{e1}(\cdot) \in C_b^k(\Lambda, \mathcal{L}(\mathcal{H}_e))$

The exact value of k will depend on whether we are in the local or global case. For the molecular Hamiltonian with smeared nucleonic charges (41), Condition H_k is easily checked and only puts constraints on the smoothness of the external potentials and on the smoothness and decay of the charge distribution of the nuclei. For point nuclei, this condition fails and a generalization of the Hunziker distribution method would be necessary, see [7].

Gap Condition for Λ : For $x \in \Lambda$, let $\sigma_*(x) \subset \sigma(H_e(x))$ be such that there are functions $f_{\pm} \in C_b(\Lambda, \mathbb{R})$, defining an interval $I(x) = [f_-(x), f_+(x)]$ such that

$$\sigma_*(x) \subset I(x), \text{ and } \inf_{x \in \Lambda} \text{dist}(I(x), \sigma(H_e(x)) \setminus \sigma_*(x)) =: g > 0 \quad (50)$$

As before, set $P_* = \int_{\Lambda}^{\oplus} dx P_*(x)$ where $P_*(x)$ is the spectral projection of $H_e(x)$ with respect to $\sigma_*(x)$. Define as before

$$H_{diag}^{\epsilon} := P_* H^{\epsilon} P_* + P_*^{\perp} H^{\epsilon} P_*^{\perp} \quad (51)$$

We also introduce the Sobolev spaces with respect to the ϵ -scaled gradient, i.e.

$$H^{1,\epsilon}(\mathbb{R}^d) := \{\phi \in L^2(\mathbb{R}^d) \mid \|\phi\|_{H^{1,\epsilon}}^2 := \|\epsilon |\nabla \phi|\|^2 + \|\phi\|^2 < \infty\}$$

and

$$H^{2,\epsilon}(\mathbb{R}^d) := \{\phi \in L^2(\mathbb{R}^d) \mid \|\phi\|_{H^{2,\epsilon}}^2 := \|\epsilon^2 \Delta \phi\|^2 + \|\phi\|^2 < \infty\}$$

Furthermore, we can define the projection on finite total energies, $\mathcal{E}(H^{\epsilon}) := 1_{(-\infty, \mathcal{E}]}(H^{\epsilon})$ as the projection on total energies smaller than \mathcal{E} .

Theorem 3. Assume Condition H_3 and Condition Gap for $\Lambda = \mathbb{R}^d$. Then H_{diag}^{ϵ} is self-adjoint on the domain of H^{ϵ} . There are constants $C, \tilde{C} < \infty$ such that for all $t \in \mathbb{R}$,

$$\|e^{-iH^{\epsilon}t/\epsilon} - e^{-iH_{diag}^{\epsilon}t/\epsilon}\|_{\mathcal{L}(H^{2,\epsilon} \otimes \mathcal{H}_e, \mathcal{H})} \leq \epsilon C(1 + |t|)^3 \quad (52)$$

and for all $\mathcal{E} \in \mathbb{R}$,

$$\|(e^{-iH^{\epsilon}t/\epsilon} - e^{-iH_{diag}^{\epsilon}t/\epsilon})\mathcal{E}(H^{\epsilon})\|_{\mathcal{L}(\mathcal{H})} \leq \epsilon \tilde{C}(1 + |\mathcal{E}|)(1 + |t|) \quad (53)$$

The space $\mathcal{L}(H^{2,\epsilon} \otimes \mathcal{H}_e, \mathcal{H})$ denotes the space of bounded linear operators from $H^{2,\epsilon} \otimes \mathcal{H}_e$ to \mathcal{H} equipped with the operator norm.

Let us quickly remark on the features of the bound (52). Physically, one expects the adiabatic decoupling, which relies on the separation of time-scales, to hold when the nuclei move slowly compared to the electrons. This is of course only true if the kinetic energies of the nuclei and electrons are of the same order of magnitude and thus breaks down if the nuclei become arbitrarily fast. The bound (52) holds only uniformly for bounded kinetic energies of the nuclei, as controlled by the $\mathcal{L}(H^{2,\epsilon} \otimes \mathcal{H}_e, \mathcal{H})$ norm. Bounding $\|\psi_0\|_{H^{2,\epsilon}}$ for the initial wavefunction by a constant independent of ϵ corresponds to bounding the initial velocities of the nuclei on the macroscopic time-scale by a constant also independent of ϵ . Denote by p the average kinetic energy. Then if $\epsilon^2 p^2 \approx \text{constant}$, $p \approx \text{constant}$, so

$$v_{micro} = \frac{p}{m_n} \approx \epsilon$$

and hence

$$v_{macro} = \frac{v_{micro}}{\epsilon} \approx \text{constant}.$$

In the bound (53), a bound on the total energy of the system implies a uniform bound also on the kinetic energy of the nuclei and thus adiabatic decoupling holds uniformly on the finite-energy subspaces.

We conclude with a brief sketch of the proof of Theorem 3. The reader is referred to [1], Theorem 2.10, for more details.

Sketch of Proof of Theorem 3. As in the proof of Theorem 1, we conclude that $P_*(\cdot) \in C_b^3(\mathbb{R}^d, \mathcal{L}(\mathcal{H}_e))$, since $H_e(\cdot) \in C_b^3(\mathbb{R}^3, \mathcal{L}(\mathcal{D}, \mathcal{H}_e))$.

To conclude that H_{diag}^ϵ is self-adjoint on the domain of H^ϵ , one shows that the operator $H^\epsilon - H_{diag}^\epsilon$ is infinitesimally operator bounded with respect to H^ϵ , by writing the off-diagonal terms as a commutator

$$H^\epsilon - H_{diag}^\epsilon = P_*^\perp H^\epsilon P_* + adj. = P_*^\perp \left[\frac{\epsilon^2}{2} (-i\nabla_x + A(x))^2, P_* \right] P_* + adj. \quad (54)$$

which can be easily computed.

The next steps again follow the argument in Theorem 1, but this time are much more complicated. One notes that

$$e^{-iH_{diag}^\epsilon t/\epsilon} - e^{-iH^\epsilon t/\epsilon} = \frac{i}{\epsilon} e^{-iH_{diag}^\epsilon t/\epsilon} \int_0^t dt' e^{iH_{diag}^\epsilon t'/\epsilon} (H^\epsilon - H_{diag}^\epsilon) e^{-iH^\epsilon t'/\epsilon} \quad (55)$$

and proceeds by using (54). The proof proceeds as before by defining $F(x)$ analogously to before and computing $[H_e(x), F(x)]$ the same way, but the situation is slightly more complicated as the integrand above is not $O(\epsilon)$ as a bounded operator, but only in the norm $\mathcal{L}(H^{1,\epsilon} \otimes \mathcal{H}_e, \mathcal{H})$. \square

3 Brief Summary of Talk

1. The phenomenon of separation of scales in quantum mechanical systems offers a valuable insight into understanding their dynamics. The prototypical example is that of molecular dynamics, where the slow, heavy nuclei move much slower than the fast, light electrons. Deriving effective dynamics for the nuclei from the full Schrödinger equation is a problem with many useful applications.
2. The phenomenon that spectral subspaces, which in some sense depend slowly on the adiabatic parameter, are approximately invariant under the quantum mechanical time-evolution is referred to as *adiabatic decoupling*. The gap condition on the spectrum, that there exists a piece of the spectrum of interest σ_* (say a few eigenvalues) separated from the rest, plays a crucial part in our results.
3. For time-dependent Hamiltonians, the time-adiabatic theorem provides a first-order bound. It states that if a state is initially in the subspace with spectra in σ_* , then the state up to later times t will remain in that subspace up to first order error in the adiabatic parameter ϵ and time.
4. A straightforward generalization of the time-adiabatic theorem, referred to as the space-adiabatic theorem, allows one to generalize the above result to the case of fibered Hamiltonians, in which the general Hilbert space splits into two orthogonal pieces, corresponding to the fast and slow degrees of freedom respectively. This framework is more applicable to the scenario of molecular dynamics.
5. The last main result is the space-adiabatic theorem applied to the Born-Oppenheimer approximation. We obtain a uniform error bound for the dynamics of the nuclei of order ϵ , but only for uniformly bounded kinetic energies of the nuclei. This is to be expected as otherwise, argued on basic physical principles, if the distribution of energy is not even amongst the particles, the separation of time scales breaks down.

References

- [1] Tufel, S., *Adiabatic Perturbation Theory in Quantum Dynamics*. Springer-Verlag Berlin Heidelberg 2003
- [2] Reed. M., Simon. B. : *Fourier Analysis. Self- Adjointness*. Methods of Modern Mathematical Physics. Vol 2 Academic Press (1978)
- [3] Hislop, P.D., and Sigal, I.M.: *Introduction to spectral theory*. Applied Mathematical Sciences 133, NY: Springer, 1996
- [4] Reed. M., Simon. B. : *Analysis of Operators*. Methods of Modern Mathematical Physics. Vol 4 Academic Press (1978)
- [5] M. Born and R. Oppenheimer. Zur Quantentheorie der Molekeln, Ann. Phys. (Leipzig) 84, 457–484 (1927).
- [6] Combes, J.-M., Duclos P., and Seiler, R.: *The Born-Oppenheimer approximation, in: Rigorous Atomic and Molecular Physics* (eds. G. Velo, A. Wightman), New York, Plenum, 185–212 (1981).
- [7] Klein M., Martinez A., Seiler R., and Wang X.P., *On the Born-Oppenheimer expansion for polyatomic molecules*, Commun. Math. Phys. 143, 607–639 (1992)
- [8] Gustafson, S.J., and Sigal, I.M.: *Mathematical Concepts of Quantum Mechanics* 3rd ed., Springer Universitext, 2020