THE BORN-OPPENHEIMER APPROXIMATION IN SCATTERING THEORY

by

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(ABSTRACT)

We analyze the Schrödinger equation $i\epsilon^2 \frac{\partial}{\partial t}\Psi = H(\epsilon)\Psi$, where $H(\epsilon) = -\frac{\epsilon^4}{2}\Delta_X + h(X)$ is the hamiltonian of a molecular system consisting of nuclei with masses of order ϵ^{-4} and electrons with masses of order 1. The Born-Oppenheimer approximation consists of the adiabatic approximation to the motion of electrons and the semiclassical approximation to the time evolution of nuclei. The quantum propagator associated with this Schrödinger equation is $\exp(-\frac{itH(\epsilon)}{\epsilon^2})$. We use the Born-Oppenheimer method to find the leading order asymptotic expansion in ϵ to $\exp(-\frac{itH(\epsilon)}{\epsilon^2})\Psi$, i.e. we find $\Psi(t)$ such that:

$$\|e^{-\frac{itH(\epsilon)}{\epsilon^2}}\Psi(0) - \Psi(t)\| \leq C\epsilon \tag{1}$$

We show that if $H(\epsilon)$ describes a diatomic molecule with smooth short range potentials, then the estimate (1) is uniform in time; hence the leading order approximation to the wave operators can be constructed. We also comment on the generalization of our method to polyatomic molecules and to Coulomb systems.

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I. INTRODUCTION

Since the origin of modern quantum mechanics in 1925-26 the study of molecular systems has become one of the most important applications of this theory. It quickly became obvious that the Schrödinger equation could easily be written down, but had analytic solutions for only very few simple cases.

The situation is even worse for molecular systems, because of the large number of particles involved. For a system of N particles the time-dependent Schrödinger equation is a partial differential equation in $3N+1$ variables, and it is not very practical to attempt to solve such an equation, even numerically. Thus, in order to understand the behavior of quantum systems, one usually must resort to an approximation.

I.1. History of the Born-Oppenheimer approximation

In 1927 M. Born and R. Oppenheimer published a remarkable paper [BO] in which they analyzed the energy levels of molecules. The molecular hamiltonian they studied had a naturally built-in small parameter ϵ related to the ratio of electronic to the nuclear mass. For real molecules and atoms this ratio began with 1/1836 for the hydrogen atom and became much smaller

for heavier nuclei. Born and Oppenheimer suggested that if one took ϵ to be the fourth root of the mass ratio, then the approximate eigenvalue of the hamiltonian could be found in the form of power series in ϵ. Guided by physical intuition they formally derived the correct fourth order expansion for the energy. This expansion had very clear physical interpretation. The 0-th order term was the electronic energy, the second order terms corresponded to the molecular vibrational energy, and the molecular rotational energy was of the fourth order. The first and third order terms vanished identically. This method proved to be very useful in physics and quantum chemistry and became commonly known as the Born-Oppenheimer approximation.

However, Born and Oppenheimer's calculations were only formal and, quite surprisingly, there was very little mathematical work done on the subject until late 1970's. In 1975-81 Combes, Duclos, and Seiler published a series of papers [C1], [C2], [CDS], in which they proved that the formal fourth order expansion was asymptotic to the exact energy levels of molecules. Their method consisted of computing the upper and lower bounds to the eigenvalues. They showed that as $\epsilon \to 0$ these bounds asymptotically agree up to fourth order. However, it was not clear whether the method could be generalized to higher order. Also, the bounds on the eigenvalues became worse for higher energies, so only the bottom of the spectrum could be determined this way. In 1987 Hagedorn, using a different technique, showed that the

Born-Oppenheimer method gives the asymptotic expansion of arbitrary order to eigenvalues and eigenfunctions of molecular hamiltonians with smooth [H1] and Coulombic [H2] potentials. The latter result was true for diatomic molecules only, but it has been recently generalized [KMSW] to polyatomic molecules for certain class of potentials including the Coulomb potential.

In this work we are concerned with the time-dependent Born-Oppenheimer approximation, which describes the time evolution of molecules, rather than the energy levels and bound states. Despite being called the Born-Oppenheimer approximation, the time-dependent problem was never studied by Born and Oppenheimer. Apparently the first person who tried to apply these ideas to the analysis of dynamics of molecules was F. London [L]. However, his contribution is rarely mentioned in literature. As with the time-independent case there was a long delay before any rigorous results were obtained. The problem was first precisely formulated by Hagedorn in 1980 [H3].

The time-dependent approximation uses ideas similar to those which guided Born and Oppenheimer, but it also requires an appropriate choice of time scale, so that the resulting dynamics is nontrivial. It is shown [H3], [H4] that one can construct an approximate solution to the time-dependent Schrödinger equation, which is asymptotic to the exact solution on a finite

time interval. These results are, however, restricted to systems with smooth potentials. The situation is much more difficult for the Coulomb potential, since the singularity of the potential causes cusps in the electronic wavefunction. The resulting lack of differentiability can be overcome [H5] by a nonlinear change of coordinates.

As mentioned, Hagedorn's results [H3], [H4], [H5] are true on a finite time interval. In this work we present our own results [K] concerning the approximation to the quantum propagation of certain states with errors uniform in time. One can then construct the approximation to the action of the wave operators on a certain class of states, and ultimately to the S-matrix. Similar results were obtained in [KMW] in the time-independent scattering formalism.

Finally, to complete our review of literature on the subject, we mention the work of Hagedorn [H6], [H7] on the energy level crossings. As we explain later, one of the basic assumptions which allows us to develop the time-dependent Born-Oppenheimer formalism is that the so-called electronic hamiltonian has an isolated eigenvalue, which remains isolated near the classical trajectory of the nuclei. However, in nature there are many examples of crossings of such energy surfaces, and the standard Born-Oppenheimer approximation breaks down. Hagedorn classified all possible minimal multi-

plicity energy level crossings and, for each type, used a matched asymptotic expansions technique to construct the Born-Oppenheimer approximation near the energy level crossings.

I.2. Physical interpretation

As we already mentioned, the physical intuition is very important for the development of the Born-Oppenheimer approximation. Hence we would like to describe briefly the ideas underlying the time-dependent approximation.

The hamiltonian for a molecular system is of the form:

$$H(\epsilon) = -\frac{\epsilon^4}{2}\Delta_X + h(X),$$

where X is the nuclear configuration, and $h(X)$ is the so-called electronic hamiltonian. In realistic models $h(X)$ contains the kinetic energy of the electrons and the interaction between all particles, and is parametrized by the position of nuclei. One of the basic assumptions is that $h(X)$ has an eigenvalue $E(X)$ which is isolated near the classical position of nuclei. Our main goal is to find approximate solutions to the Schrödinger equation:

$$i\epsilon^2 \frac{\partial \Psi}{\partial t} = H(\epsilon)\Psi$$

in the form of power series in ϵ. The leading order in this expansion has a very nice physical interpretation. Because of the disparity between the masses of

the nuclei and electrons, the latter move much more rapidly. Thus, we can find the electrons' wavefunction by solving the eigenvalue problem for $h(X)$, for each fixed nuclear configuration X. The electrons can quickly adjust their motion to the slowly varying position of the nuclei. Hence if they are initially in the eigenstate of $h(X)$ associated with $E(X)$, they approximately remain in this state as the nuclei move. This justifies use of the adiabatic approximation for the electrons.

On the other hand the nuclei move very slowly and their dynamics can be approximated using semiclassical methods. However, the electrons generate the effective potential $E(X)$ which influences the nuclear motion. Thus, the Born-Oppenheimer method consists of two different approximation schemes coupled to each other. Unfortunately, it is rather difficult to convert this intuitive picture into a rigorous mathematical problem. We need to develop techniques to treat both aspects of our problem and to find a way to separate them from each other. The precise mathematical formulation of the problem is given in the following chapters.

The rest of this work is organized as follows. Chapter 2 is a brief review of scattering theory. Chapter 3 describes the particular physical model we analyze and introduces all necessary notation and assumptions. In chapter 4 we present the semiclassical method which, as indicated above, is the crucial

part of the Born-Oppenheimer method. In chapter 5 we analyze properties of the electronic hamiltonian, and, in particular, the behavior of $E(X)$ for large $|X|$. Chapter 6 is devoted to the Born-Oppenheimer method. We state there our main results, present the formal derivation of the expansion and give estimates leading to the rigorous proofs of the theorems. Finally, in chapter 7 we discuss open problems and possible generalizations of our method including the higher order expansion, polyatomic molecules and the long range potentials.

II. SCATTERING THEORY

The time evolution of a quantum system is described by a solution to the Schrödinger equation:

$$i\hbar\frac{\partial\Psi}{\partial t} = H\Psi, \tag{2.1}$$

where H is a hamiltonian. For systems we consider here H is a selfadjoint operator acting on a Hilbert space $\mathcal{H}$. As such, it generates a unitary group, which we denote by $\exp(-\frac{itH}{\hbar})$. Then, given the initial condition $\Psi_0 \in \mathcal{H}$, the function $\Psi(t) = \exp(-\frac{itH}{\hbar})\Psi_0$ is a solution to (2.1). We refer to the unitary group $\exp(-\frac{itH}{\hbar})$ as the quantum propagator, and we call $\Psi(t)$ the scattering state.

Scattering theory is concerned with the study of asymptotics of $\Psi(t) = \exp(-\frac{itH}{\hbar})\Psi_0$ for large $|t|$. One usually hopes that for $t \to \pm\infty$, $\Psi(t) = \exp(-\frac{itH}{\hbar})\Psi_0$ becomes "asymptotically free", i.e. it "looks like" $\exp(-\frac{itH_0}{\hbar})\Psi_\pm$ for some states $\Psi_\pm$ (further referred to as free states). The $\exp(-\frac{itH_0}{\hbar})$ is called the free propagator and has to be specified for each particular problem. In many applications the full hamiltonian H is of the form:

$$H = H_0 + V,$$

where V is a potential function and the free hamiltonian H_0 is $H_0 = -\Delta$,

where Δ is the Laplacian.

A number of questions naturally arise in this formalism. First, there is the problem of existence and uniqueness of scattering states. Given a free incoming state Ψ_- one needs to ask whether there is a state Ψ_0 such that $\Psi(t) := \exp(-\frac{itH}{\hbar})\Psi_0$ approaches $\exp(-\frac{itH_0}{\hbar})\Psi_-$ as $t \to -\infty$, and whether this Ψ_0 is unique. Similarly in the future: given the outgoing free state Ψ_+ we need to verify the existence and uniqueness of the scattering state which asymptotically behaves like $\exp(-\frac{itH}{\hbar})\Psi_+$. Both questions are quite natural from an experimental point of view. In practice one prepares the experiment in such a way that initially the particles are very far apart and are considered non-interacting. They can be described by a free state. As the experiment proceeds, the particles approach each other, interact, and fly apart, so that as $t \to \infty$ they become free again. Their time evolution is described by the solution to the Schrödinger equation (2.1). Of course, we would like to believe that this scattering state is uniquely determined by the way we prepared the experiment, i.e. by the incoming free state. Mathematically this is equivalent to the question we have just stated.

The second question that needs to be answered involves asymptotic completeness. Denote by $\mathcal{H}_-$ the set of interacting states which were asymptoti-

cally free in the past, i.e.:

$$(2.2)\quad \mathcal{H}_- = \{\Psi_0 \in \mathcal{H} : \exists \Psi_- \text{ such that } \text{“}\lim_{t\to-\infty}\text{”}(e^{-\frac{itH_0}{\hbar}}\Psi_- - e^{-\frac{itH}{\hbar}}\Psi_0) = 0\}.$$

Similarly $\mathcal{H}_+$ is the set of states that become free in the future:

$$(2.3)\quad \mathcal{H}_+ = \{\Psi_0 \in \mathcal{H} : \exists \Psi_+ \text{ such that } \text{“}\lim_{t\to\infty}\text{”}(e^{-\frac{itH_0}{\hbar}}\Psi_+ - e^{-\frac{itH}{\hbar}}\Psi_0) = 0\}.$$

Weak asymptotic completeness then means that these two set are equal, i.e. an interacting state which was free in the distant past will become free in the distant future and vice versa.

One usually requires more than just the weak asymptotic completeness. We will specify this more restrictive condition shortly. But first, we formulate the above questions rigorously. We need to specify what we mean by saying that Ψ_0 "looked like" Ψ_- in the past, and in what sense the limit in (2.2) and (2.3) is taken. In quantum scattering this means that:

$$(2.4)\qquad \lim_{t\to-\infty} \|e^{-\frac{itH_0}{\hbar}}\Psi_- - e^{-\frac{itH}{\hbar}}\Psi_0\| = 0$$

and similarly for the future.

Since $\exp(-\frac{itH}{\hbar})$ is a unitary operator, the natural object to study is the strong limit:

$$\mathrm{s}-\lim_{t\to\pm\infty} e^{\frac{itH}{\hbar}}e^{-\frac{itH_0}{\hbar}}.$$

Therefore, we define the wave operators to be:

$$\Omega^{\mp} = \mathrm{s} - \lim_{t \to \pm\infty} e^{\frac{itH}{\hbar}} e^{-\frac{itH_0}{\hbar}} P_{ac}(H_0), \tag{2.5}$$

where $P_{ac}(H_0)$ is the spectral projection associated with the absolutely continuous spectrum of H_0. Then $\mathcal{H}_- = Ran\ \Omega^+$, $\mathcal{H}_+ = Ran\ \Omega^-$. The existence and uniqueness of scattering states is therefore equivalent to the existence of $\Omega^{\mp}$. The weak asymptotic completeness means $Ran\ \Omega^+ = Ran\ \Omega^-$. We also say that the wave operators are complete if :

$$Ran\ \Omega^+ = Ran\ \Omega^- = Ran\ P_{ac}(H). \tag{2.6}$$

These problems were studied by numerous authors and the existence and completeness of the wave operators for potentials we consider here were proved. A review of these results could be found e.g. in [RS1], [P] or [BW].

Having established existence and completeness of the wave operators, one can describe the most important object in scattering theory: the scattering operator (or S-matrix). We define it as:

$$S = (\Omega^-)^* \Omega^+. \tag{2.7}$$

If $\Omega^{\mp}$ are complete, then S is a unitary operator.

The S-matrix contains all physically important information about the scattering process. It maps the incoming free state onto the corresponding

outgoing free state. The expectation values of this operator are the scattering amplitudes which can be measured experimentally.

A similar scattering formalism can be developed for classical mechanics. For example, for one particle in the external field given by a potential V, the state is defined as a pair $(a, \eta) \in \mathbb{R}^6$, where a is the position and η is the momentum of the particle. Given an initial condition $(a_0, \eta_0) \in \mathbb{R}^6$ the interacting dynamics is given by a solution $(a(t), \eta(t))$ to the Newton's equations:

$$\dot{a}(t) = \eta(t) \tag{2.8}$$
$$\dot{\eta}(t) = -V(a(t))$$

satisfying:

$$a(0) = a_0 \tag{2.9}$$
$$\eta(0) = \eta_0.$$

Quite naturally the free dynamics is given as a map:

$$(a_\pm, \eta_\pm) \to (a_\pm + \eta_\pm t, \eta_\pm). \tag{2.10}$$

It can be shown ([S], [H8]) that for the potentials we consider here (see (3.3)) there is a set $\Sigma \subset \mathbb{R}^6$ of measure zero, such that for $(a_-, \eta_-) \in \mathbb{R}^6 \backslash \Sigma$ there is

a solution $(a(t), \eta(t))$ to (2.8) satisfying

$$\lim_{t \to -\infty} |a(t) - a_- - \eta_- t| = 0 \tag{2.11}$$

$$\lim_{t \to -\infty} |\eta(t) - \eta_-| = 0.$$

and similarly, given $(a_+, \eta_+) \in \mathbb{R}^6 \backslash \Sigma$ there is a solution $(a(t), \eta(t))$ to (2.8) satisfying asymptotic conditions analogous to (2.11) at $+\infty$. The classical wave operators are then defined as:

$$\Omega_{cl}^{\mp}(a_\pm, \eta_\pm) = (a(0), \eta(0)). \tag{2.12}$$

Again, the questions of existence and completeness of the wave operators have been answered affirmatively [S], [He].

The scattering formalism for quantum mechanics, which we outlined here is mathematically rigorous and links solutions to the Schrödinger equation with results of scattering experiments. However, as we already mentioned in the introduction, it is usually not easy to write down the wave operators explicitly and compute scattering amplitudes. In practice, the best one can hope for is to approximate the wave operators. In this work we use the idea of the time-dependent Born-Oppenheimer expansion to construct an approximation to the quantum wave operators acting on certain coherent states for a class of hamiltonians which we specify in the following chapter. As we already indicated, our technique involves the semiclassical method,

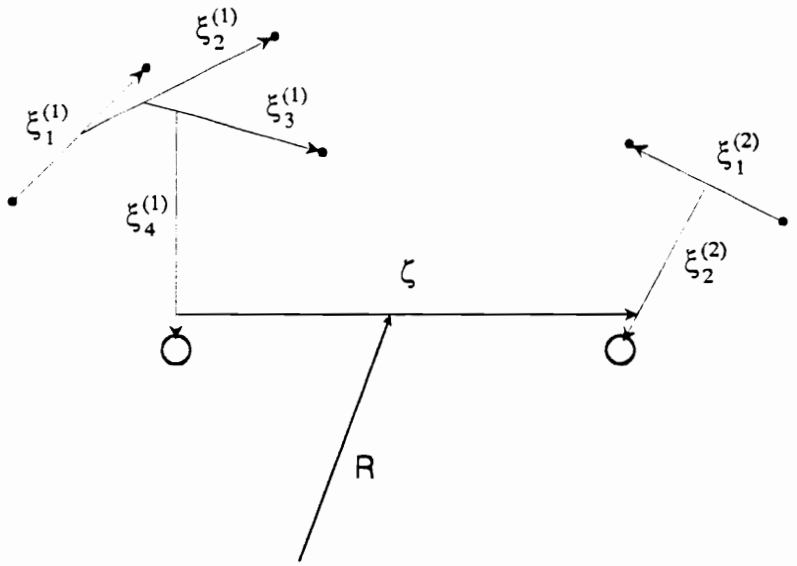
and, as we shall see, the approximation is determined by a solution to the corresponding classical problem.

III. NOTATION

In this chapter we specify the physical model under consideration and introduce the necessary notation.

III.1. The Hamiltonian for a diatomic molecule

We consider a diatomic molecule with N electrons. The masses of the nuclei are ϵ^{-4} and the masses of the electrons are 1 (we rescale the coordinates if necessary). We want to analyze the particular scattering channel where the molecule splits into two clusters, each consisting of a nucleus and a certain number of electrons. For this cluster decomposition $\{C_1, C_2\}$, where $C_1 = \underbrace{\{1, \ldots, K^{(1)}+1\}}_{K^{(1)}\ electrons,\ 1\ nucleus}$, $C_2 = \underbrace{\{K^{(1)}+2, \ldots, N+2\}}_{K^{(2)}=N-K^{(1)}\ electrons,\ 1\ nucleus}$, we introduce the clustered Jacobi coordinates [RS1]. Indices 1 and $K^{(1)}$+2 refer to the nuclei. Indices 2, ..., $K^{(1)}$+1, $K^{(1)}$+3, ..., N+2 refer to the electrons. Then $\xi_1^{(1)}$, ..., $\xi_{K^{(1)}}^{(1)}$, $\xi_1^{(2)}$, ..., $\xi_{K^{(2)}}^{(2)}$ are the internal coordinates for the clusters (the upper index refers to the cluster), ζ is the coordinate between the centers of mass of the clusters, and R is the total center of mass coordinate. In particular we choose ξ's so that $\xi_1^{(1)}, \ldots, \xi_{K^{(1)}-1}^{(1)}$, (resp. $\xi_1^{(2)}, \ldots, \xi_{K^{(2)}-1}^{(2)}$) involve only electrons and $\xi_{K^{(1)}}^{(1)}$, (resp. $\xi_{K^{(2)}}^{(2)}$) is the vector from the center of mass of all electrons in given cluster to the nucleus of the cluster (see Fig.1).



• electron

○ nucleus

Fig. 1. An example of the clustered Jacobi coordinates (N=6, $K^{(1)}$=4, $K^{(2)}$=2)

This choice simplifies the dependence of the potentials on ϵ (see the comment following formula (3.2c) below).

In these coordinates the hamiltonian becomes:

$$\tilde{H} = -\frac{1}{2\epsilon^{-4} + N}\Delta_R - \frac{\epsilon^4}{2}\mu(\epsilon)\Delta_\zeta - \sum_{i=1}^{K^{(1)}} \frac{\nu_i^{(1)}(\epsilon)}{2}\Delta_{\xi_i^{(1)}} - \sum_{i=1}^{K^{(2)}} \frac{\nu_i^{(2)}(\epsilon)}{2}\Delta_{\xi_i^{(2)}} + V,$$

where $\mu(\epsilon)$ and $\nu_i^{(j)}(\epsilon)$ are rational functions of ϵ^4 tending to nonzero constants as $\epsilon \to 0$.

We remove the center of mass motion and rescale ζ, so that:

$$H = -\frac{\epsilon^4}{2}\Delta_\zeta - \sum_{i=1}^{K^{(1)}} \frac{\nu_i^{(1)}(\epsilon)}{2}\Delta_{\xi_i^{(1)}} - \sum_{i=1}^{K^{(2)}} \frac{\nu_i^{(2)}(\epsilon)}{2}\Delta_{\xi_i^{(2)}} + V \tag{3.1}$$

is an operator acting on $L^2(\mathbb{R}^3, d\zeta) \otimes L^2(\mathbb{R}^{3N}, d\xi)$. Here:

$$V = V^{(C_1)} + V^{(C_2)} + V_{D,\epsilon},$$

where $V^{(C_j)}$ is the interaction within the j-th cluster, and $V_{D,\epsilon}$ is the inter-

cluster interaction. Explicitly:

$$(3.2a) \qquad V^{(C_1)} = \sum_{2\le i<j\le K^{(1)}+1} V_{ij}\left(\sum_{k=1}^{K^{(1)}-1}\mu_k^{(1)}\xi_k^{(1)}\right) + \\ + \sum_{i=2}^{K^{(1)}+1} V_{i,1}\left(\sum_{k=1}^{K^{(1)}}\tilde{\mu}_k^{(1)}\xi_k^{(1)}\right)$$

$$(3.2b) \qquad V^{(C_2)} = \sum_{K^{(1)}+3\le i<j\le N+2} V_{ij}\left(\sum_{k=1}^{K^{(2)}-1}\mu_k^{(2)}\xi_k^{(2)}\right) + \\ + \sum_{i=K^{(1)}+3}^{N+2} V_{i,K^{(1)}+2}\left(\sum_{k=1}^{K^{(2)}}\tilde{\mu}_k^{(2)}\xi_k^{(2)}\right)$$

$$(3.2c) \qquad V_{D,\epsilon} = \sum_{i\in C_1, j\in C_2} V_{ij}\left(\tau(\epsilon)\zeta + \sum_{l=1}^{2}\sum_{k=1}^{K^{(l)}}\tau_k^{(l)}(\epsilon)\xi_k^{(l)}\right).$$

The coefficients $\tau_k^{(l)}$, $\mu_k^{(l)}$, and $\tilde{\mu}_k^{(l)}$ obviously depend on i, j and our choice of Jacobi coordinates. One can also see that $\tau_k^{(l)}$ equal zero or constants for $k = 1, \ldots, K^{(l)} - 1$. The $\tau_{K^{(l)}}^{(l)}$ are rational functions of ϵ^4 that approach constants as $\epsilon \to 0$ or tend to 0 like ϵ^4. $\mu_k^{(l)}$ and $\tilde{\mu}_k^{(l)}$ are ϵ-independent.

V_{ij} are the two-body potentials depending only on the relative positions of the particles i and j. We also assume that they are at least C^3 and decay

at infinity according to:

$$(3.3a) \qquad |V(x)| \leq C_1(1+|x|)^{-1-\delta}$$

$$(3.3b) \qquad |\partial_{x^i} V(x)| \leq C_2(1+|x|)^{-2-\delta}$$

$$(3.3c) \qquad |\partial_{x^i}\partial_{x^j} V(x)| \leq C_3(1+|x|)^{-3-\delta}$$

$$(3.3d) \qquad |\partial_{x^i}\partial_{x^j}\partial_{x^k} V(x)| \leq C_4(1+|x|)^{-4-\delta}$$

for some constants $C_1, \ldots, C_4$ and $\delta > 0$.

We use the following notation:

$$(3.4) \qquad h_D^{(1)}(\epsilon) = -\frac{1}{2}\sum_{i=1}^{K^{(1)}} \nu_i^{(1)}(\epsilon)\Delta_{\xi_i^{(1)}} + V^{(C_1)}$$

$$(3.5) \qquad h_D^{(2)}(\epsilon) = -\frac{1}{2}\sum_{i=1}^{K^{(2)}} \nu_i^{(2)}(\epsilon)\Delta_{\xi_i^{(2)}} + V^{(C_2)}.$$

Then we can write the hamiltonian H as a sum of the nuclear kinetic part $-\frac{\epsilon^4}{2}\Delta_\zeta$ and the so-called electronic hamiltonian $h_\epsilon(\zeta)$, where:

$$(3.6) \qquad \begin{aligned} h_\epsilon(\zeta) =& h_D^{(1)}(0) + h_D^{(2)}(0) - \frac{1}{2}\sum_{l=1}^{2}\sum_{k=1}^{K^{(l)}} (\nu_k^{(l)}(\epsilon) - \nu_k^{(l)}(0))\Delta_{\xi_k^{(l)}} \\ &+ V_{D,\epsilon}(\zeta, \xi^{(1)}, \xi^{(2)}) \\ =& h_D + \epsilon^4 D(\epsilon) + V_{D,\epsilon}(\zeta, \xi^{(1)}, \xi^{(2)}). \end{aligned}$$

Here we use the abbreviations:

$$h_D = h_D^{(1)}(0) + h_D^{(2)}(0),$$

$$\epsilon^4 D(\epsilon) = -\frac{1}{2}\sum_{l=1}^{2}\sum_{k=1}^{K^{(l)}}(\nu_k^{(l)}(\epsilon) - \nu_k^{(l)}(0))\Delta_{\xi_k^{(l)}},$$

$$\xi = (\xi^{(1)}, \xi^{(2)}),$$

$$\xi^{(1)} = (\xi_1^{(1)}, \ldots, \xi_K^{(1)}),$$

$$\xi^{(2)} = (\xi_1^{(2)}, \ldots, \xi_K^{(2)}).$$

III.2. Semiclassical wave packets

We use certain Gaussian states, which we call semiclassical wave packets, introduced by Hagedorn [H8]. The precise definition is the following.

Definition 3.1.

Let A, B be 3×3 matrices such that:

(3.7a) *A and B are invertible,*

(3.7b) *BA^{-1} is symmetric,*

(3.7c) *$Re\ BA^{-1} = \frac{1}{2}[BA^{-1} + (BA^{-1})^*]$ is strictly positive definite,*

(3.7d) $(Re\ BA^{-1})^{-1} = AA^*$.

Let $a \in \mathbb{R}^3$, $\eta \in \mathbb{R}^3$, $\hbar > 0$. Then we define:

$$\phi(A, B, \hbar, a, \eta, x) := \pi^{-\frac{3}{4}} \hbar^{-\frac{3}{4}} (\det A)^{-\frac{1}{2}} \exp\left(-\frac{\langle (x-a), BA^{-1}(x-a) \rangle}{2\hbar} + i\frac{\langle \eta, (x-a) \rangle}{\hbar}\right). \tag{3.8}$$

Remark.

In the rest of this work, whenever we write $\phi(A, B, \hbar, a, \eta, x)$ it will be assumed that conditions (3.7) are satisfied.

The semiclassical wave packets behave very nicely under the Fourier transform.

Definition 3.2.

The scaled Fourier transform on $L^2(\mathbb{R}^3)$ is defined as:

$$(\mathcal{F}_\hbar \Psi)(\xi) = (2\pi\hbar)^{-\frac{3}{2}} \int_{\mathbb{R}^3} \Psi(x) \exp\left(-\frac{i}{\hbar}\langle \xi, x \rangle\right) dx$$

Lemma 3.3. *[H8]*

$$(\mathcal{F}_\hbar \phi(A, B, \hbar, a, \eta, \cdot))(\xi) = e^{-\frac{i}{\hbar}\langle \eta, a \rangle} \phi(B, A, \hbar, \eta, -a, \xi).$$

The semiclassical wave packets are essentially normalized, scaled and translated Gaussians concentrated around a with the width determined by the matrix A (see condition (3.7d)). Lemma 3.3 shows that under the Fourier transform the roles of the vectors a and η are reversed and the roles of the matrices A and B interchange. This is crucial to the interpretation we give these quantities in chapter 4.

IV. SEMICLASSICAL APPROXIMATION

As we mentioned in the introduction, the Born-Oppenheimer approximation has two basic ingredients: the adiabatic approximation to the motion of electrons and the semiclassical approximation to the nuclear dynamics. In this chapter we describe the latter. The theorem below was proved by Hagedorn [H8] using the Trotter product formula. We present here a new, shorter proof, which is also more in the spirit of the rest of this work.

We consider the Schrödinger equation:

$$i\hbar\frac{\partial\Psi}{\partial t} = H(\hbar)\Psi, \tag{4.1}$$

where:

$$H(\hbar) = -\frac{\hbar^2}{2}\Delta + V, \tag{4.2}$$

and V is a smooth potential decaying according to (3.3). We are interested in the $\hbar \to 0$ limit of quantum dynamics generated by the hamiltonian (4.2). The notation $\hbar$ for the small parameter is motivated by physics, where it is known as Planck's constant. Later, in the application to the Born-Oppenheimer approximation we replace $\hbar$ by ϵ^2.

We have the following:

Theorem 4.1.

Let A_+, B_+ be 3×3 matrices satisfying conditions (3.7) and $a_+, \eta_+ \in \mathbb{R}^3$, $\eta_+ \neq 0$. Consider the system of equations:

$$\frac{d\eta(t)}{dt} = -V'(a(t)) \tag{4.3a}$$

$$\frac{da(t)}{dt} = \eta(t) \tag{4.3b}$$

$$\frac{dA(t)}{dt} = iB(t) \tag{4.3c}$$

$$\frac{dB(t)}{dt} = iV''(a(t))A(t). \tag{4.3d}$$

where V' denotes the gradient of V and V'' is the matrix of second derivatives of V.

If $V(x)$ satisfies conditions (3.3) then there is a unique solution $a(t)$, $\eta(t)$, $A(t)$, $B(t)$ to (4.3) satisfying the following conditions:

$$\lim_{t\to\infty} |a(t) - a_+ - \eta_+ t| = 0 \tag{4.4a}$$

$$\lim_{t\to\infty} |\eta(t) - \eta_+| = 0. \tag{4.4b}$$

$$\lim_{t\to\infty} \|A(t) - A_+ - iB_+ t\| = 0 \tag{4.4c}$$

$$\lim_{t\to\infty} \|B(t) - B_+\| = 0 \tag{4.4d}$$

Moreover we define the action integral:

$$S(t) = \int_0^t \left(\frac{\eta(s)^2}{2} - V(a(s))\right) ds. \tag{4.5}$$

Then:

$$(4.6) \qquad \|e^{-\frac{itH(\hbar)}{\hbar}}\phi(A(0),B(0),\hbar,a(0),\eta(0),\cdot) - e^{\frac{iS(t)}{\hbar}}\phi(A(t),B(t),\hbar,a(t),\eta(t),\cdot)\| < C\hbar^{\lambda}$$

for all $\lambda < 1/2$, *uniformly for* $t \in [0,\infty)$.

Remarks.

1. Equations (4.3a,b) are just the Newton's equations with $a(t)$ being the classical trajectory and $\eta(t)$ the classical momentum. Conditions (4.4a,b) mean that the classical dynamics of the interacting particles approaches that of the noninteracting ones.

2. The theorem simply says that in the leading order, the time evolution of the semiclassical wave packet is determined by the corresponding classical time evolution, i.e. a quantum state that is initially a Gaussian, approximately remains a Gaussian concentrated at the classical trajectory of particles in position and momentum space, as $t \to \infty$. The matrices $A(t)$ and $B(t)$ determine the "spreading" of the wave packet in position and momentum space, respectively.

3. The estimate (4.6) is uniform in time for $t \in [0,\infty)$. One can mimic the proof to get the estimate for $t \in (-\infty,0]$. 4. It can be shown ([H8], Lemma 3.1) that matrices $A(t)$, $B(t)$ satisfy conditions (3.7).

Before we proceed with the proof of theorem 4.1, we state two preliminary lemmas.

Lemma 4.2.

Let $\Psi(t)$ be a differentiable vector-valued function, whose values belong to the domain of $H(\hbar)$ for all $t \in [0, \infty)$. If Ψ satisfies:

$$i\hbar\dot{\Psi} = H\Psi + R(t), \tag{4.7}$$

where:

$$\|R(t)\| \leq F(t)\hbar^{\lambda+1} \tag{4.8}$$

for some $F \in L^1(\mathbb{R}, dt)$, then:

$$\|e^{-\frac{itH(\hbar)}{\hbar}}\Psi(0) - \Psi(t)\| \leq C\hbar^{\lambda}, \tag{4.9}$$

where $C = \int_0^\infty F(t)dt$.

Proof. It is enough to prove:

$$\|\Psi(0) - e^{\frac{itH(\hbar)}{\hbar}}\Psi(t)\| \leq C\hbar^{\lambda}. \tag{4.10}$$

To show this we use the fundamental theorem of calculus:

$$\Psi(0) - e^{\frac{itH(\hbar)}{\hbar}}\Psi(t) = \int_0^t e^{\frac{isH(\hbar)}{\hbar}}[-\dot{\Psi}(s) - \frac{i}{\hbar}H(\hbar)\Psi(s)]ds.$$

We insert the norm under the integral and use (4.8):

$$\begin{aligned}\|\Psi(0) - e^{\frac{itH(\hbar)}{\hbar}}\Psi(t)\| &\leq \int_0^t \|e^{\frac{isH(\hbar)}{\hbar}}[\dot{\Psi}(s) + \frac{i}{\hbar}H(\hbar)\Psi(s)]\|ds \\ &= \frac{1}{\hbar}\int_0^t \|R(s)\|ds \\ &\leq \frac{1}{\hbar}\int_0^\infty F(s)\hbar^{\lambda+1}ds \\ &= C\hbar^\lambda\end{aligned}$$

□

Lemma 4.3.

Define $W_y(x)$ *to be:*

$$W_y(x) = V(y) + \langle V'(y), (x-y)\rangle + \frac{1}{2}\langle (x-y), V''(y)(x-y)\rangle$$

where: V' *is the gradient of* V, *and* V'' *denotes the matrix of second derivatives of* V. *Then under the assumptions of theorem 4.1 we have:*

$$(4.11) \qquad \||V - W_{a(t)}|\phi(A(t), B(t), h, a(t), \eta(t), \cdot)\| \leq F(t)h^{\lambda+1}$$

for some positive $F \in L^1(\mathbb{R}, dt)$.

Proof of lemma 4.3 is similar to the proof of lemma 3.2 in [H8].

Equipped with these two results we can prove theorem 4.1.

Proof of theorem 4.1. We substitute the function

$$\Psi(t) = e^{\frac{iS(t)}{\hbar}} \phi(A(t), B(t), \hbar, a(t), \eta(t), x)$$

into equation (4.1) and compute the error $R(t)$ explicitly.

Since $a(t)$, $\eta(t)$, $A(t)$ and $B(t)$ satisfy equations (4.3), we obtain:

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2} \Delta \Psi + W_{a(t)} \Psi.$$

Thus $R(t) = (W_{a(t)} - V)\Psi$, and, by lemma 4.3, condition (4.8) is satisfied. Hence, the application of lemma 4.2 concludes the proof.

□

Theorem 4.1 gives the semiclassical approximation to the quantum propagation of the semiclassical wave packet $\phi(A(0), B(0), \hbar, a(0), \eta(0), x)$. We use the term semiclassical dynamics, when referring to $e^{\frac{iS(t)}{\hbar}} \phi(A(t), B(t), \hbar, a(t), \eta(t), x)$.

For potentials we consider here one can very easily find the semiclassical approximation to the corresponding free quantum dynamics (i.e. dynamics generated by a free hamiltonian $H_0(\hbar) = -\frac{\hbar^2}{2}\Delta$) and, in fact, it is exact.

Lemma 4.4. *[H8]*

Denote $H_0(\hbar) = -\frac{\hbar^2}{2}\Delta$. *Then:*

$$e^{-\frac{itH_0(\hbar)}{\hbar}}\phi(A_+, B_+, \hbar, a_+, \eta_+, x) = e^{\frac{it(\eta_+,\eta_+)}{2\hbar}}\phi(A_+ + itB_+, B_+, \hbar, a_+ + t\eta_+, \eta_+, x).$$

Proof. By explicit computations. □

In analogy to the interacting case we will refer to $e^{\frac{it(\eta_+,\eta_+)}{2\hbar}}$ $\phi(A_+ + itB_+, B_+, \hbar, a_+ + t\eta_+, \eta_+, x)$ as the semiclassical free dynamics.

Using theorem 4.1 and lemma 4.4 one can find the leading order approximation to the quantum wave operator. In our notation the map Ω_{cl}^- : $(a_+, \eta_+) \to (a(0), \eta(0))$ is the classical wave operator. Then as one can expect, the map:

$$\phi(A_+, B_+, \hbar, a_+, \eta_+, \cdot) \to \phi(A(0), B(0), \hbar, a(0), \eta(0), \cdot)$$

approximates the action of the quantum wave operator on the free state of the form $\phi(A_+, B_+, \hbar, a_+, \eta_+, x)$. In fact we have:

Theorem 4.5.

Assume the hypotheses of theorem 4.1. Then:

$$\|\Omega^{-}\phi(A_+, B_+, \hbar, a_+, \eta_+, \cdot) - \phi(A(0), B(0), \hbar, a(0), \eta(0), \cdot)\| \leq C\hbar^{\lambda}.$$

Proof. Consider:

$$\begin{aligned}
&\|e^{-\frac{itH_0(\hbar)}{\hbar}}\phi(A_+, B_+, \hbar, a_+, \eta_+, \cdot) \\
&\qquad - e^{-\frac{itH(\hbar)}{\hbar}}\phi(A(0), B(0), \hbar, a(0), \eta(0), \cdot)\| \\
\leq\ &\|e^{-\frac{itH_0(\hbar)}{\hbar}}\phi(A_+, B_+, \hbar, a_+, \eta_+, \cdot) \\
&\qquad - e^{\frac{it\langle\eta_+,\eta_+\rangle}{2\hbar}}\phi(A_+ + itB_+, B_+, \hbar, a_+ + t\eta_+, \eta_+, \cdot)\| \\
+&\|e^{\frac{it\langle\eta_+,\eta_+\rangle}{2\hbar}}\phi(A_+ + itB_+, B_+, \hbar, a_+ + t\eta_+, \eta_+, \cdot) \\
&\qquad - e^{\frac{iS(t)}{\hbar}}\phi(A(t), B(t), \hbar, a(t), \eta(t), \cdot)\| \\
+&\|e^{\frac{iS(t)}{\hbar}}\phi(A(t), B(t), \hbar, a(t), \eta(t), \cdot) \\
&\qquad - e^{-\frac{itH(\hbar)}{\hbar}}\phi(A(0), B(0), \hbar, a(0), \eta(0), \cdot)\| \\
&\qquad = I_1 + I_2 + I_3
\end{aligned}$$

The first term (I_1) is identically zero by lemma 4.4. The last term (I_3) is bounded by $C\hbar^{\lambda}$ uniformly in time by theorem 4.1. By the dominated convergence theorem and conditions (4.4), given $\delta > 0$ there is $T > 0$ such

that for $t > T$ the middle term (I_2) is bounded by δ. Thus:

$$\forall \delta > 0 \ \exists T, \text{such that } \forall t > T$$

$$\|e^{-\frac{itH_0(\hbar)}{\hbar}}\phi(A_+, B_+, \hbar, a_+, \eta_+, \cdot) - e^{-\frac{itH(\hbar)}{\hbar}}\phi(A(0), B(0), \hbar, a(0), \eta(0), \cdot)\| \leq$$

$$\leq C\hbar^{\lambda} + \delta$$

□

Several other authors have obtained related results. We mention here the work of Hagedorn [H9], [H10], [H11], where he generalized results of [H8] to higher order. He used certain modifications of the semiclassical wave packets (Def. 3.1). He then showed that the quantum evolution can be approximated up to arbitrary order in $\hbar$ by a superposition of these generalized wave packets. Robinson [R] extended results of [H8] to more general initial states. Finally, similar results can be found in [Y1]; however the author's Fourier integral operator approach is restricted to the momentum representation, while our technique is applicable in the position representation also.

V. PROPERTIES OF THE ELECTRONIC HAMILTONIAN

Usually the electronic hamiltonian is defined by formal substitution $\epsilon = 0$ in (3.1). Then it becomes an operator acting on functions of the "electronic" coordinates ξ, depending parametrically on the intercluster distance ζ. Our choice is slightly different. We allow certain ϵ-dependence in the electronic hamiltonian, which we denote by a subscript, as in $h_\epsilon(\zeta)$ defined by (3.6). This is the result of our choice of coordinates. By using Jacobi coordinates we avoid so-called Hughes-Eckart terms (mixed derivatives) in the kinetic part, but we have to deal with ϵ-dependence of both the kinetic part of the electronic hamiltonian and the intercluster interaction. The dependence of the reduced masses $\nu_k^{(i)}$ on ϵ can easily be taken care of. One can see that $D(\epsilon)$ is relatively bounded with respect to h_D and is therefore a regular perturbation. It causes the eigenvalues and eigenvectors of $h_D + \epsilon^4 D(\epsilon) + V_{D,\epsilon}(\zeta, \xi)$ to be smooth functions of ϵ^4.

Unfortunately ϵ also appears in the argument of the intercluster interaction. The rest of this section is devoted to the analysis of the behavior of the eigenvalues $E_\epsilon(\zeta)$ for large ζ and small ϵ.

We assume that h_D has a simple isolated eigenvalue E_D with eigenvector

$\varphi_D(\xi)$ and that this eigenvalue is stable, i.e. there is a unique simple isolated eigenvalue $E_\epsilon(\zeta)$ of $h_\epsilon(\zeta)$ which tends to E_D as $|\zeta| \to \infty$ and $\epsilon \to 0$. We denote the corresponding eigenvector by $\varphi_\epsilon(\xi, \zeta)$.

In the following we assume that $|\zeta|$ is large enough and ϵ small enough, so we can find $\beta > 0$ such that E_D and $E_\epsilon(\zeta)$ lie inside the circle $|z - E_D| = \frac{\beta}{2}$ and there is no other eigenvalue in $|z - E_D| \leq \beta$.

We first prove a technical lemma which we use to show the main result of this chapter - lemma 5.5.

Lemma 5.1. *[RS2]*

Let V be a potential satisfying (3.3), $H_0 = -\Delta$. Then for $z \notin \sigma(H_0 + V)$ the resolvent $(H_0 + V - z)^{-1}$ is a bounded operator from L^2_μ to L^2_μ for arbitrary μ, where L^2_μ is the weighted L^2-space (i.e. $f \in L^2_\mu$ iff $\|f\|_\mu := \|(1 + |\cdot|^2)^{\frac{\mu}{2}} f(\cdot)\|_{L^2} \leq \infty$).

Proof. The proof for $0 < \mu \leq 1$ and $V = 0$ can be found in [RS2]. Here we outline the general inductive argument. This will also make it clear how one can generalize this result to obtain Lemma 5.2 below.

We want to show:

if

(5.1) $(H_0 + V - z)^{-1}$ is bounded $L^2_n \to L^2_n$

and $\partial_i(H_0 + V - z)^{-1}$ is bounded $L^2_n \to L^2_n$

then

(5.2) $(H_0 + V - z)^{-1}$ and $\partial_i(H_0 + V - z)^{-1}$

are bounded $L^2_{n+\delta} \to L^2_{n+\delta}$ *for* $0 < \delta \leq 1$.

First we show the induction hypotheses for n=0. To simplify the notation we write R for $(H_0 + V - z)^{-1}$ and denote $\rho = (1 + |x|^2)^{\frac{1}{2}}$.

a) $(H_0 + V - z)^{-1}$.

We start with formal calculations:

$$[R, \rho^\delta] = -R[H_0, \rho^\delta]R = \sum_i (R\partial_i)(\partial_i \rho^\delta)R + R(\partial_i \rho^\delta)(\partial_i R).$$

Applied to Schwarz functions the computations are legitimate. Moreover R, $\partial_i R$, and multiplication by $\partial_i \rho^\delta$ are bounded on L^2. Thus:

$$\|[R, \rho^\delta]\Psi\| \leq const \ \|\Psi\|$$

for any Schwarz function, and therefore for any $\Psi \in L^2$. Then we conclude:

$$\|R\Psi\|_\delta := \|\rho^\delta R\Psi\|$$

$$\leq \|R\rho^\delta\Psi\| + \|[R,\rho^\delta]\Psi\| \leq const\ \|\Psi\|_\delta$$

i.e. $(H_0 + V - z)^{-1}$ is bounded $L^2_\delta \to L^2_\delta$ for $0 < \delta \leq 1$.

b) $\partial_i(H_0 + V - z)^{-1}$.

Similarly:

$$\|\rho^\delta \partial_i R\Psi\| \leq \|\partial_i R\rho^\delta\Psi\| + \|[\rho^\delta, \partial_i R]\psi\|.$$

The first term on the r.h.s. is bounded by $const\ \|\rho^\delta\Psi\|$ since $\partial_i R$ is bounded on L^2. We expand the commutator in the second term as:

$$[\rho^\delta, \partial_i R] = \rho^\delta \partial_i R - \partial_i R\rho^\delta$$

$$= R[H_0, \rho^\delta]\partial_i R - R(\partial_i R)R[H_0, \rho^\delta]R - R(\partial_i \rho^\delta).$$

All terms are bounded on L^2, therefore:

$$\|[\rho^\delta, \partial_i R]\Psi\| \leq const\|\Psi\| \leq const\|\Psi\|_\delta$$

Thus the second hypothesis in (5.1) holds for $n = 0$.

c) We also estimate $(H_0 + V - z)^{-1}\partial_i$.

Note that $\partial_i R$ and $R\partial_i$ differ only by $-R(\partial_i V)R$, i.e.

$$\|R\partial_i\Psi\|_\delta \leq \|\partial_i R\Psi\|_\delta + \|R(\partial_i V)R\Psi\|_\delta.$$

The first term of the r.h.s. is bounded by $const\|\Psi\|_\delta$. For the second one we get:

$$\|\rho^\delta R(\partial_i V)R\Psi\| \leq \|R(\partial_i V)R\rho^\delta\Psi\| + \|R(\partial_i V)[R,\rho^\delta]\Psi\| + \|[R,\rho^\delta](\partial_i V)R\Psi\|.$$

Thus this statement follows from a) and b).

Now we show the implication (5.1) $\Rightarrow$ (5.2).

Assume (5.1). Then:

$$\|R\Psi\|_{n+\delta} = \|\rho^\delta R\Psi\|_n \leq \|R\rho^\delta\Psi\|_n + \|[\rho^\delta, R]\Psi\|_n.$$

The first term is bounded by $\|\rho^\delta\Psi\|_n = \|\Psi\|_{n+\delta}$ by hypothesis. In the second term we expand the commutator as in part a). By assumption R, $\partial_i R$ are bounded on L^2_n. By mimicking the proof of c) one can show that $R\partial_i$ is also bounded. Moreover the multiplication by $\partial_i\rho^\delta$ is bounded $L^2_n \to L^2_n$. Thus:

$$\|[\rho^\delta, R]\Psi\|_n \leq const\|\Psi\|_n \leq const\|\Psi\|_{n+\delta}$$

i.e. the first conclusion in (5.2) holds.

The proof of boundedness of $\partial_i R$ goes along the same lines. We write:

$$\|\partial_i R\Psi\|_{n+\delta} = \|\rho^\delta\partial_i R\Psi\|_n \leq \|\partial_i R\rho^\delta\Psi\|_n + \|[\rho^\delta, \partial_i R]\psi\|_n$$

and expand the commutator on the r.h.s. as in b). Then the second conclusion in (5.2) follows from the induction assumptions.

□

For our purposes we also need:

Lemma 5.2.

Let h_ϵ be defined by (3.6). Then the operator:

$$(1+|\tau(\epsilon)x+\sum_{k=1}^{K^{(1)}}\tau_k^{(1)}(\epsilon)\xi_k^{(1)}+\sum_{k=1}^{K^{(2)}}\tau_k^{(2)}(\epsilon)\xi_k^{(2)})|)^{2+\delta}(h_\epsilon(x)+z)^{-1} \qquad (5.3)$$
$$(1+|\tau(\epsilon)x+\sum_{k=1}^{K^{(1)}}\tau_k^{(1)}(\epsilon)\xi_k^{(1)}+\sum_{k=1}^{K^{(2)}}\tau_k^{(2)}(\epsilon)\xi_k^{(2)})|)^{-2-\delta},$$

is bounded L^2_μ to L^2_μ for arbitrary μ.

Here we use the same notation as throughout this entire work. Proof of this lemma can be obtained by mimicking the proof of lemma 5.1.

Lemma 5.3.

Assume that the potentials satisfy (3.3). Let $P_\epsilon(\zeta)$ be the projection onto the eigenvector $\varphi_\epsilon(\xi,\zeta)$ associated with the eigenvalue $E_\epsilon(\zeta)$ of $h_\epsilon(\zeta)$. Then:

$$(5.4a) \qquad \|\partial_{\zeta^i}P_\epsilon(\zeta)\varphi_D(\xi)\|_{L^2(\mathbb{R}^{3N},d\xi)} \le C_1(1+|\zeta|)^{-2-\delta}$$

$$(5.4b) \qquad \|\partial_{\zeta^i}\partial_{\zeta^j}P_\epsilon(\zeta)\varphi_D(\xi)\|_{L^2(\mathbb{R}^{3N},d\xi)} \le C_2(1+|\zeta|)^{-3-\delta}$$

$$(5.4c) \qquad \|\partial_{\zeta^i}\partial_{\zeta^j}\partial_{\zeta^k}P_\epsilon(\zeta)\varphi_D(\xi)\|_{L^2(\mathbb{R}^{3N},d\xi)} \le C_3(1+|\zeta|)^{-4-\delta},$$

uniformly for small ϵ, where δ is the same constant as in (3.3).

Proof.

a) From:

$$\partial_{\zeta^i} P_\epsilon(\zeta)\varphi_D = \frac{1}{2\pi i}\int_{|z-E_D|=\beta} (h_\epsilon(\zeta)-z)^{-1}(\partial_{\zeta^i} V_{D,\epsilon})(h_\epsilon(\zeta)-z)^{-1}\varphi_D \, dz$$

we get:

$$\begin{aligned}
&\|\partial_{\zeta^i} P_\epsilon(\zeta)\varphi_D\|_{L^2(\mathbb{R}^{3N},d\xi)} \\
&\quad \le C_4 \int_{|z-E_D|=\beta} \|(h_\epsilon(\zeta)-z)^{-1}\|_{op}\|(\partial_{\zeta^i} V_{D,\epsilon})g\|_{L^2(\mathbb{R}^{3N},d\xi)} \, dz \\
&\quad \le C_5 \sup_{|z-E_D|=\beta} (\|(h_\epsilon(\zeta)-z)^{-1}\|_{op}\|(\partial_{\zeta^i} V_{D,\epsilon})g\|_{L^2(\mathbb{R}^{3N},d\xi)}),
\end{aligned}$$

where $g(\xi) := (h_\epsilon(\zeta)-z)^{-1}\varphi_D(\xi)$ and $\|\cdot\|_{op}$ denotes the operator norm. Note that $\sup_{|z-E_D|=\gamma}(\|(h_\epsilon(\zeta)-z)^{-1}\|_{op})$ is bounded uniformly in ζ for large $|\zeta|$ by our assumption on $E_\epsilon(\zeta)$.

Therefore, conclusion (5.4a) will be proved if we can show:

$$\|(\partial_{\zeta^i} V_{D,\epsilon})g\|_{L^2(\mathbb{R}^{3N},d\xi)} \le C_6(1+|\zeta|)^{-2-\delta}.$$

The eigenvector φ_D decays exponentially so it is in the weighted L^2 space (L^2_μ) for arbitrary μ (i.e. $\|\varphi_D\|_\mu := \|(1+|\xi|^2)^{\frac{\mu}{2}}\varphi_D(\xi)\|_{L^2(d\xi)} < \infty$). Lemma 5.2 tells us that, for suitable potentials, $(-\Delta+V-z)^{-1}$ is a bounded operator from L^2_μ to L^2_μ. It follows that $g(\xi)$ is in L^2_μ for any μ. In particular:

$$\|(1+|\xi_1^{(1)}|^2)^{\frac{\mu}{2}}\ldots(1+|\xi_{K(2)}^{(2)}|^2)^{\frac{\mu}{2}} g(\xi_1^{(1)},\ldots,\xi_{K(2)}^{(2)})\|_{L^2(\mathbb{R}^{3N},d\xi)} \le C_7$$

for any $\mu > 0$. Moreover, the constant C_7 is ζ-independent.

In order to estimate $\|(\partial_{\zeta^i} V_{D,\epsilon})g\|_{L^2(\mathbb{R}^{3N},d\xi)}$ we split $\partial_{\zeta^i} V_{D,\epsilon}$ according to (3.2c). We show the calculations for the term where all $\tau_j'^s$ are nonzero. In the other terms if one or more of $\tau_j'^s$ are zero then the corresponding variables $\xi_j^{(k)}$ appear only in g. For example, if $\tau_1^{(1)} = 0$, then we can do the integral with respect to $\xi_1^{(1)}$. Note that

$$g^1(\xi_2^{(1)},\ldots,\xi_{K^{(2)}}^{(2)}) := \left[\int |g(\xi_1^{(1)},\xi_2^{(1)},\ldots,\xi_{K^{(2)}}^{(2)})|^2 \; d^3\xi_1^{(1)}\right]^{\frac{1}{2}}$$

is in $L^2_\mu(\mathbb{R}^{3N-3}, d\xi_2^{(1)}\ldots\xi_{K^{(2)}}^{(2)})$. This way we eliminate all the coordinates $\xi_j^{(k)}$ for which $\tau_j^{(k)} = 0$, and we are back to the general situation.

Hence we need to estimate:

(5.5)

$$\|\partial_{\zeta_i} V_{mn}\left(\tau(\epsilon)\zeta + \sum_{k=1}^{K^{(1)}} \tau_k^{(1)}(\epsilon)\xi_k^{(1)} + \sum_{k=1}^{K^{(2)}} \tau_k^{(2)}(\epsilon)\xi_k^{(2)}\right) \cdot g(\xi^{(1)},\xi^{(2)})\|_{L^2(\mathbb{R}^{3N},d\xi)}.$$

We separate $\xi_1^{(1)}$ in the argument of $\partial_{\zeta_i} V_{mn}$ and call the rest u_1, i.e.:

$$u_1 = \tau(\epsilon)\zeta + \sum_{k=2}^{K^{(1)}} \tau_k^{(1)}(\epsilon)\xi_k^{(1)} + \sum_{k=1}^{K^{(2)}} \tau_k^{(2)}(\epsilon)\xi_k^{(2)}$$

and do the $\xi_1^{(1)}$ integral in (5.5). Let:

$$B_1^1 = \{y : |u_1 + y| \leq \kappa|u_1|\}$$

$$B_2^1 = \{y : |u_1 + y| > \kappa|u_1|\}$$

for some $0 < \kappa < 1$, and let χ_1^1, χ_2^1 be the corresponding characteristic functions. Then:

$$\begin{aligned}
&\|(\partial_{\zeta^i} V_{mn}(u_1 + \tau_1^{(1)}(\epsilon)\xi_1^{(1)})) \cdot g(\xi)\|_{L^2(\mathbb{R}^3, d\xi_1^{(1)})} = \\
&\quad = \tau_1^{(1)}(\epsilon)^{-\frac{3}{2}} \|\chi_1^1(y_1)(\partial_{\zeta^i} V_{mn}(u_1 + y_1))\cdot \\
&\qquad \cdot g(\tau_1^{(1)}(\epsilon)^{-1} y_1, \xi_2^{(1)}, \ldots, \xi_{K^{(2)}}^{(2)})\|_{L^2(\mathbb{R}^3, dy_1)} + \\
&\quad + \tau_1^{(1)}(\epsilon)^{-\frac{3}{2}} \|\chi_2^1(y_1) \cdot (\partial_{\zeta^i} V_{mn}(u_1 + y_1))\cdot \\
&\qquad \cdot g(\tau_1^{(1)}(\epsilon)^{-1} y_1, \xi_2^{(1)}, \ldots, \xi_{K^{(2)}}^{(2)})\|_{L^2(\mathbb{R}^3, dy_1)} \\
&= I_1(u_1) + I_2(u_1).
\end{aligned}$$

For $I_2(u_1)$ we note:

$$\begin{aligned}
I_2(u_1) \leq & \tau_1^{(1)}(\epsilon)^{-\frac{3}{2}} \|\chi_2^1(y_1)\partial_{\zeta^i} V_{mn}(u_1 + y_1)\|_\infty \\
& \|g\left(\tau_1^{(1)}(\epsilon)^{-1} y_1, \xi_2^{(1)}, \ldots, \xi_{K^{(2)}}^{(2)}\right)\|_{L^2(\mathbb{R}^3, dy_1)} \\
\leq & \tau_1^{(1)}(\epsilon)^{-\frac{3}{2}} \|\chi_2^1(y_1)\partial_{\zeta^i} V_{mn}(u_1 + y_1)\|_\infty \\
& \|(1 + |\tau_1^{(1)}(\epsilon)^{-1} y_1|^2)^{\frac{\mu}{2}} g\left(\tau_1^{(1)}(\epsilon)^{-1} y_1, \ldots, \xi_{K^{(2)}}^{(2)}\right)\|_{L^2(\mathbb{R}^3, dy_1)} \\
& \|(1 + |\tau_1^{(1)}(\epsilon)^{-1} y_1|^2)^{-\frac{\mu}{2}}\|_\infty,
\end{aligned}$$

where $\|\cdot\|_\infty$ denotes the L^∞ norm in variable $\xi_1^{(1)}$. Here:

$$\|(1 + |\tau_1^{(1)}(\epsilon)^{-1} y_1|^2)^{-\frac{\mu}{2}}\|_\infty = 1.$$

Also:

$$g^1(\xi_2^{(1)},\ldots,\xi_{K^{(2)}}^{(2)}) :=$$

$$:= \tau_1^{(1)}(\epsilon)^{-\frac{3}{2}} \| (1+|\tau_1^{(1)}(\epsilon)^{-1} y_1|^2)^{\frac{\mu}{2}} g\left(\tau_1^{(1)}(\epsilon)^{-1} y_1,\ldots,\xi_{K^{(2)}}^{(2)}\right) \|_{L^2(\mathbb{R}^3, dy_1)}$$

$$= \| (1+|\xi_1^{(1)}|^2)^{\frac{\mu}{2}} g(\xi_1^{(1)},\ldots,\xi_{K^{(2)}}^{(2)}) \|_{L^2(\mathbb{R}^3, d\xi_1^{(1)})}$$

is in $L^2_\mu(\mathbb{R}^{3N-3}, d\xi_2^{(1)},\ldots,\xi_{K^{(2)}}^{(2)})$ and

$$\| \chi_2^1(y_1) \left(\partial_{\zeta^i} V_{mn}(u_1+y_1)\right) \|_\infty = \sup_{y_1 \in B_2^1} | \left(\partial_{\zeta^i} V_{mn}(u_1+y_1)\right) |$$
$$\leq C_8 (1+\kappa|u_1|)^{-2-\delta}.$$

Then:

$$I_2(u_1) \leq \frac{C_8}{\kappa^{2+\delta}} (1+|u_1|)^{-2-\delta} g^1(\xi_2^{(1)},\ldots,\xi_{K^{(2)}}^{(2)}).$$

Now let's concentrate on I_1:

$$
\begin{aligned}
&I_1(u_1) = \\
&= \tau_1^{(1)}(\epsilon)^{-\frac{3}{2}} \| \chi_1^1(y_1) \left(\partial_{\zeta^i} V_{mn}(u_1 + y_1) \right) \cdot \\
&\quad \cdot g \left(\tau_1^{(1)}(\epsilon)^{-1} y_1, \xi_2^{(1)}, \ldots, \xi_{K^{(2)}}^{(2)} \right) \|_{L^2(\mathbb{R}^3, dy_1)} \\
&\leq \tau_1^{(1)}(\epsilon)^{-\frac{3}{2}} \| \chi_1^1(y_1) \left(\partial_{\zeta^i} V_{mn}(u_1 + y_1) \right) \|_\infty \cdot \\
&\quad \cdot \| \chi_1^1(y_1) \; g \left(\tau_1^{(1)}(\epsilon)^{-1} y_1, \xi_2^{(1)}, \ldots, \xi_{K^{(2)}}^{(2)} \right) \|_{L^2(\mathbb{R}^3, dy_1)} \\
&\leq C_9 \tau_1^{(1)}(\epsilon)^{-\frac{3}{2}} \| \chi_1^1(y_1) (1 + |\tau_1^{(1)}(\epsilon) y_1|^2)^{-\frac{\mu}{2}} (1 + |\tau_1^{(1)}(\epsilon)^{-1} y_1|^2)^{\frac{\mu}{2}} \cdot \\
&\quad \cdot g \left(\tau_1^{(1)}(\epsilon)^{-1} y_1, \xi_2^{(1)}, \ldots, \xi_{K^{(2)}}^{(2)} \right) \|_{L^2(\mathbb{R}^3, dy_1)} \\
&\leq C_9 \tau_1^{(1)}(\epsilon)^{-\frac{3}{2}} \| \chi_1^1(y_1) (1 + |\tau_1^{(1)}(\epsilon)^{-1} y_1|^2)^{-\frac{\mu}{2}} \|_\infty \cdot \\
&\quad \cdot \| (1 + |\tau_1^{(1)}(\epsilon) y_1|^2)^{\frac{\mu}{2}} \; g \left(\tau_1^{(1)}(\epsilon)^{-1} y_1, \xi_2^{(1)}, \ldots, \xi_{K^{(2)}}^{(2)} \right) \|_{L^2(\mathbb{R}^3, dy_1)} \\
&\leq C_{10} \left(1 + \tau_1^{(1)}(\epsilon)^{-2} |u_1|^2 (1 - \kappa^2) \right)^{-\frac{\mu}{2}} g^1(\xi_2^{(1)}, \ldots, \xi_{K^{(2)}}^{(2)}).
\end{aligned}
$$

One can show that $\left(1 + \tau_1^{(1)}(\epsilon)^{-2} (1 - \kappa^2) |u_1|^2 \right)^{-\frac{\mu}{2}}$ is bounded by $const \cdot (1 + |u_1|^2)^{-\frac{\mu}{2}}$ for ϵ small enough, where the constant is ϵ-independent. Because μ is arbitrary this term decays like an arbitrary power of $|u_1|^{-1}$ when $|u_1| \to \infty$, in particular faster than I_2.

Now we take μ big enough, so that:

$$
I_1(u_1) \leq C_{11} (1 + |u_1|)^{-2-\delta} \; g^1(\xi_2^{(1)}, \ldots, \xi_{K^{(2)}}^{(2)}).
$$

Then:

$$\| \left(\partial_{\zeta^i} V_{mn}(u_1 + \tau_1^{(1)}(\epsilon)\xi_1^{(1)}) \right) \, g(\xi_1^{(1)}, \ldots, \xi_{K^{(2)}}^{(2)}) \|_{L^2(\mathbb{R}^3, d\xi_1^{(1)})}$$
$$\leq C_{12}(1 + |u_1|)^{-2-\delta} g^1(\xi_2^{(1)}, \ldots, \xi_{K^{(2)}}^{(2)}).$$

As a next step we separate $\xi_2^{(1)}$ and follow a similar procedure, choosing:

$$B_1^2 = \{y : |u_2 + y| \leq \kappa |u_2|\}$$
$$B_2^2 = \{y : |u_2 + y| > \kappa |u_2|\},$$

where:

$$u_2 = \tau(\epsilon)\zeta + \sum_{k=3}^{K^{(1)}} \tau_k^{(1)}(\epsilon)\xi_k^{(1)} + \sum_{k=1}^{K^{(2)}} \tau_k^{(2)}(\epsilon)\xi_k^{(2)}.$$

After N steps we obtain:

$$\|\partial_{\zeta_i} V_{mn} \left(\tau(\epsilon)\zeta + \sum_{k=1}^{K^{(1)}} \tau_k^{(1)}(\epsilon)\xi_k^{(1)} + \sum_{k=1}^{K^{(2)}} \tau_k^{(2)}(\epsilon)\xi_k^{(2)} \right) \, g(\xi^{(1)}, \xi^{(2)}) \|_{L^2(\mathbb{R}^{3N}, d\xi)}$$
$$\leq C_{13}(1 + |\zeta|)^{-2-\delta}.$$

To prove parts b) and c) we compute derivatives explicitly. In part b),

for example, we get:

$$\partial_{\zeta^i}\partial_{\zeta^j} P_\epsilon(\zeta)\varphi_D(\xi) =$$
$$-\frac{1}{2\pi i}[\int_{|z-E_D|=\beta} (h_\epsilon(\zeta)-z)^{-1}(\partial_{\zeta^j} V_{D,\epsilon})(h_\epsilon(\zeta)-z)^{-1}\cdot$$
$$\cdot(\partial_{\zeta^i} V_{D,\epsilon})(h_\epsilon(\zeta)-z)^{-1}\varphi_D(\xi)\, dz$$
$$-\int_{|z-E_D|=\beta} (h_\epsilon(\zeta)-z)^{-1}(\partial_{\zeta^i}\partial_{\zeta^j} V_{D,\epsilon})(h_\epsilon(\zeta)-z)^{-1}\varphi_D(\xi)\, dz$$
$$+\int_{|z-E_D|=\beta} (h_\epsilon(\zeta)-z)^{-1}(\partial_{\zeta^i} V_{D,\epsilon})(h_\epsilon(\zeta)-z)^{-1}\cdot$$
$$\cdot(\partial_{\zeta^j} V_{D,\epsilon})(h_\epsilon(\zeta)-z)^{-1}\varphi_D(\xi)\, dz].$$

The middle term can be handled as in part a). To estimate the remaining two terms we write $V_{D,\epsilon}$ as in (3.2c). Below we outline the procedure for a generic term V_{mn}. We rewrite the integrand as:

$$(h_\epsilon(\zeta)-z)^{-1}(\partial_{\zeta^j} V_{mn})\cdot$$
$$\cdot\left(1+|\tau(\epsilon)\zeta+\sum_{k=1}^{K^{(1)}}\tau_k^{(1)}(\epsilon)\xi_k^{(1)}+\sum_{k=1}^{K^{(2)}}\tau_k^{(2)}(\epsilon)\xi_k^{(2)}|\right)^{-2-\delta}\cdot$$
$$\cdot\left(1+|\tau(\epsilon)\zeta+\sum_{k=1}^{K^{(1)}}\tau_k^{(1)}(\epsilon)\xi_k^{(1)}+\sum_{k=1}^{K^{(2)}}\tau_k^{(2)}(\epsilon)\xi_k^{(2)}|\right)^{2+\delta}\cdot$$
$$\cdot(h_\epsilon(\zeta)-z)^{-1}(\partial_{\zeta^i} V_{mn})(h_\epsilon(\zeta)-z)^{-1}\varphi_D(\xi).$$

Here $(h_\epsilon(\zeta)-z)^{-1}\varphi_D(\xi)\in L^2_\mu$ by lemma 5.1. If we denote:

$$g(\xi)=\left(1+|\tau(\epsilon)\zeta+\sum_{k=1}^{K^{(1)}}\tau_k^{(1)}(\epsilon)\xi_k^{(1)}+\sum_{k=1}^{K^{(2)}}\tau_k^{(2)}(\epsilon)\xi_k^{(2)}|\right)^{2+\delta}\cdot$$
$$\cdot(h_\epsilon(\zeta)-z)^{-1}(\partial_{\zeta^i} V_{mn})(h_\epsilon(\zeta)-z)^{-1}\varphi_D(\xi),$$

then lemma 5.2 shows that $g(\xi)$ is also in L^2_μ. Thus the proof of b) is reduced to showing that:

$$\|\partial_{\zeta^j} V_{mn}\left(\tau(\epsilon)\zeta + \sum_{k=1}^{K^{(1)}} \tau_k^{(1)}(\epsilon)\xi_k^{(1)} + \sum_{k=1}^{K^{(2)}} \tau_k^{(2)}(\epsilon)\xi_k^{(2)}\right) \cdot$$
$$\cdot \left(1 + |\tau(\epsilon)\zeta + \sum_{k=1}^{K^{(1)}} \tau_k^{(1)}(\epsilon)\xi_k^{(1)} + \sum_{k=1}^{K^{(1)}} \tau_k^{(2)}(\epsilon)\xi_k^{(2)}|\right)^{-2-\delta} g(\xi)\|_{L^2(\mathbb{R}^{3N}, d\xi)}$$
$$\leq C_{13}(1 + |\zeta|)^{-3-\delta}.$$

We use the decay properties of $g(\xi)$ and $\partial_{\zeta^i} V_{mn}$ to show conclusion b) exactly the same way as we did for a).

Proof for part c) is similar to b). By explicit calculations $\partial_{\zeta^i}\partial_{\zeta^j}\partial_{\zeta^k} P_\epsilon(\zeta)\varphi_D$ is a sum of terms of three types:

1) $(h_\epsilon(\zeta) - z)^{-1}(\partial_{\zeta^i}\partial_{\zeta^j}\partial_{\zeta^k} V_{D,\epsilon})(h_\epsilon(\zeta) - z)^{-1}\varphi_D$,

2) $(h_\epsilon(\zeta) - z)^{-1}(\partial_{\zeta^i}\partial_{\zeta^j} V_{D,\epsilon})(h_\epsilon(\zeta) - z)^{-1}(\partial_{\zeta^k} V_{D,\epsilon})(h_\epsilon(\zeta) - z)^{-1}\varphi_D$,

3) $(h_\epsilon(\zeta) - z)^{-1}(\partial_{\zeta^i} V_{D,\epsilon})(h_\epsilon(\zeta) - z)^{-1}(\partial_{\zeta^j} V_{D,\epsilon})(h_\epsilon(\zeta) - z)^{-1}(\partial_{\zeta^k} V_{D,\epsilon})$
$(h_\epsilon(\zeta) - z)^{-1}\varphi_D$.

The first type can be handled as in part a), while estimates for terms of type 2) and 3) are similar to those outlined in part b).

□

Remark.

Martinez et al. [KMW] give a shorter proof for a similar result (Theorem 2.2).

However, we refer to our proof several times, hence we present the estimates in detail.

Corollary 5.4.

$$|\langle \varphi_D, P_\epsilon(\zeta)\varphi_D\rangle - 1| \leq C_1\epsilon^4 + \theta(\zeta), \tag{5.6}$$

where:

$$\theta(\zeta) \leq C_2(1+|\zeta|)^{-1-\delta}$$

and δ is as in (3.3).

Proof. Write $P_\epsilon(\zeta)\varphi_D$ as:

$$\begin{aligned} P_\epsilon(\zeta)\varphi_D =& P_D\varphi_D + \frac{1}{2\pi i}\int_{|z-E_D|=\beta}(h_\epsilon(\zeta)-z)^{-1}[\epsilon^4 D(\epsilon)](h_D(\zeta)-z)^{-1}\varphi_D\, dz \\ &+ \frac{1}{2\pi i}\int_{|z-E_D|=\beta}(h_\epsilon(\zeta)-z)^{-1}V_{D,\epsilon}\cdot(h_D(\zeta)-z)^{-1}\varphi_D\, dz. \end{aligned}$$

The last term can be estimated as above in part a) of the proof of lemma 5.3, yielding:

$$\begin{aligned} \|\frac{1}{2\pi i}\int_{|z-E_D|=\beta}(h_\epsilon(\zeta)-z)^{-1}V_{D,\epsilon}\,(h_D(\zeta)-z)^{-1}\varphi_D\, dz\|_{L^2(\mathbb{R}^{3N},d\xi)} \leq \\ \leq C_3(1+|\zeta|)^{-1-\delta}. \end{aligned}$$

Note that $D(\epsilon)$ is relatively bounded with respect to h_D, so:

$$\begin{aligned}
&\|\frac{\epsilon^4}{2\pi i}\int_{|z-E_D|=\beta}(h_\epsilon - z)^{-1}D(\epsilon)(h_D - z)^{-1}\varphi_D dz\| \leq \\
&\quad \leq \frac{\epsilon^4}{2\pi}\int_{|z-E_D|=\beta}\|(h_\epsilon - z)^{-1}\|_{op}\|D(\epsilon)(h_D - z)^{-1}\varphi_D\|dz \\
&\quad \leq C_4\epsilon^4\int_{|z-E_D|=\beta}(a\|h_D(h_D - z)^{-1}\varphi_D\| + b\|(h_D - z)^{-1}\varphi_D\|)dz \\
&\quad \leq C_5\epsilon^4.
\end{aligned}$$

□

Now we denote:

$$\tilde{E}_\epsilon(\zeta) = E_\epsilon(\zeta) - E_D = \frac{\langle P_\epsilon(\zeta)\varphi_D(\xi), (\epsilon^4 D(\epsilon) + V_{D,\epsilon})\varphi_D(\xi)\rangle}{\langle \varphi_D(\xi), P_\epsilon(\zeta)\varphi_D(\xi)\rangle}. \tag{5.7}$$

Using lemma 5.3 and corollary 5.4 we can bound the corrections to the energy level.

Lemma 5.5.

$$|\tilde{E}_\epsilon^{(\alpha)}(\zeta)| \leq C(1 + |\zeta|)^{-1-\alpha-\delta} \tag{5.8}$$

for $\alpha = 1, 2, 3$, where the superscript (α) means the partial derivatives of $\tilde{E}_\epsilon$ of order α with respect to the components of ζ.

Proof. We use estimates:

$$\|V_{D,\epsilon}^{(\alpha)}\varphi_D\|_{L^2(d\xi)} \leq C_\alpha(1+|\zeta|)^{-1-\alpha-\delta} \tag{5.9}$$

for $\alpha = 1,2,3$, and ϵ small enough, which follow from our assumptions on V_{mn}. The proof of this is similar to the estimates in the proof of lemma 5.3, part a). Also, as mentioned above, $D(\epsilon)$ is relatively bounded with respect to h_D.

To prove the lemma we compute derivatives of $\tilde{E}_\epsilon(\zeta)$ explicitly. For $\alpha = 1$, for instance, we get:

$$\begin{aligned}
&\partial_{\zeta^i}\tilde{E}_\epsilon(\zeta) = \\
&= \frac{\langle \partial_{\zeta^i}P_\epsilon(\zeta)\varphi_D(\xi), (\epsilon^4 D(\epsilon)+V_{D,\epsilon})\varphi_D(\xi)\rangle + \langle P_\epsilon(\zeta)\varphi_D(\xi), (\partial_{\zeta^i}V_{D,\epsilon})\varphi_D(\xi)\rangle}{\langle \varphi_D(\xi), P_\epsilon(\zeta)\varphi_D(\xi)\rangle} \\
&- \frac{\langle P_\epsilon(\zeta)\varphi_D(\xi), (\epsilon^4 D(\epsilon)+V_{D,\epsilon})\varphi_D(\xi)\rangle\langle \varphi_D(\xi), \partial_{\zeta^i}P_\epsilon(\zeta)\varphi_D(\xi)\rangle}{(\langle \varphi_D(\xi), P_\epsilon(\zeta)\varphi_D(\xi)\rangle)^2}.
\end{aligned}$$

Then we use the Schwarz lemma, lemma 5.3, corollary 5.4 and the above estimates (5.9) on $\|V_{D,\epsilon}^{(\alpha)}\varphi_D\|_{L^2(d\xi)}$.

□

Remark.

By a similar argument one can show:

$$|E_\epsilon(\zeta) - E_D| \leq C\epsilon^4 + C'(1+|\zeta|)^{-1-\delta}.$$

VI. THE BORN-OPPENHEIMER APPROXIMATION

This chapter contains our results for the Born-Oppenheimer approximation to the quantum propagator for molecular systems. In the preceding two chapters we have developed all necessary tools. Our analysis here is somewhat parallel to the method used in chapter 4. In order to find the approximate solution to the molecular Schrödinger equation we first formally construct a suitable candidate. As one can expect from our heuristic argument in chapter 1, this candidate ought to be a certain combination of the semiclassical wave packets defined in chapter 3 and the eigenfunction of the electronic hamiltonian. We do this formal construction using the so-called multiple scales technique, which we describe below.

Having constructed the approximate solution formally we proceed as in chapter 4. We substitute this formal solution to the Schrödinger equation and compute the error term $R(t)$ (cf. (4.7)). If we can bound the error term as in (4.8), then lemma 4.2 gives us a rigorous proof.

In this chapter we first show the formal construction of the approximation to the quantum time evolution. Then we state our theorem and give the rigorous proof of the theorem. A similar analysis leads to the Born-

Oppenheimer approximation to the free dynamics. Then we can use both results to find the approximate wave operators.

VI.1. Formal construction

The Schrödinger equation we consider has the form:

$$i\epsilon^2 \frac{\partial \Psi}{\partial t} = -\frac{\epsilon^4}{2}\Delta_\zeta + h_\epsilon(\zeta), \tag{6.1}$$

where $h_\epsilon(\zeta)$ is defined by eq (3.6). In particular we are interested in the asymptotics of solutions for small ϵ.

We first assume that $a_\epsilon(t)$, $\eta_\epsilon(t)$, $A_\epsilon(t)$, $B_\epsilon(t)$ is a solution to the system of ordinary differential equations (4.3) with $V(x)$ replaced by $E_\epsilon(x)$, satisfying conditions (4.4) for some a_+, $\eta_+ \neq 0$, and matrices A_+, B_+ satisfying conditions (3.7). Existence of such a solution follows from lemma 5.5 and lemma 3.1 of [H8].

Instead of analyzing equation (6.1) directly we look at the higher dimensional problem defined by a formal change of variables to:

$$x = \zeta$$

$$y = \frac{\zeta - a_\epsilon(t)}{\epsilon}$$

in (6.1). This is the multiple scales technique. The adiabatic effects occur in the variable x, while y is the "semiclassical" variable. In the limit $\epsilon \to 0$ these variables become "independent" and we can separate the two aspects of our problem. As a result of this change of variables we obtain:

$$(6.2) \qquad i\epsilon^2 \frac{\partial \Psi}{\partial t} = [-\frac{\epsilon^4}{2}\Delta_x - \epsilon^3 \nabla_x \cdot \nabla_y - \frac{\epsilon^2}{2}\Delta_y + i\epsilon\eta_\epsilon(t) \cdot \nabla_y + E_\epsilon(a_\epsilon(t) + \epsilon y) + h_\epsilon(x) - E_\epsilon(x)]\Psi.$$

We assume eq. (6.2) has a solution of the form:

$$(6.3) \qquad \Psi(x, y, \xi, t) = e^{\frac{iS(t)}{\epsilon^2}} e^{\frac{i\langle \eta_\epsilon(t), y \rangle}{\epsilon}} [\psi_{0,\epsilon}(x, y, \xi, t) + \epsilon\psi_{1,\epsilon}(x, y, \xi, t) + \ldots].$$

In order to determine the functions $\psi_{k,\epsilon}$ we simply substitute (6.3) into (6.2) and collect terms of the same order in ϵ. Using equations (4.3) we obtain for the zero-th order terms :

$$(6.4) \qquad [h_\epsilon(x) - E_\epsilon(x)]\psi_{0,\epsilon} = 0.$$

Hence $\psi_{0,\epsilon}$ must be some function of x, y and t multiplied by $\varphi_\epsilon(x, \xi)$.

$$(6.5) \qquad \psi_{0,\epsilon} = f_{0,\epsilon}(x, y, t)\varphi_\epsilon(x, \xi).$$

The equation for the first order terms is similar to (6.4):

$$[h_\epsilon(x) - E_\epsilon(x)]\psi_{1,\epsilon} = 0.$$

Thus $\psi_{1,\epsilon}$ is also a function of x, y and t multiplied by $\varphi_\epsilon(x, \xi)$. The second order terms satisfy:

$$(6.6) \qquad i\dot{\psi}_{0,\epsilon} = -\frac{1}{2}\Delta_y \psi_{0,\epsilon} + E_\epsilon^{(2)}(a_\epsilon(t))\frac{y^2}{2}\psi_{0,\epsilon} - i\eta_\epsilon(t) \cdot \nabla_x \psi_{0,\epsilon} + [h_\epsilon(x) - E_\epsilon(x)]\psi_{2,\epsilon},$$

where $E_\epsilon^{(2)}(a_\epsilon(t))\frac{y^2}{2}$ is a shorthand notation for $\frac{1}{2}\sum_{i,j} y_i y_j (\partial_{y_i}\partial_{y_j} E_\epsilon)(a_\epsilon(t))$. Equation (6.6) in fact imposes two conditions. We split it into two parts: one containing only terms which are multiples of $\varphi_\epsilon(x,\xi)$ and the second containing terms orthogonal to $\varphi_\epsilon(x,\xi)$ in $L^2(d\xi)$. Thus we get:

$$i\dot{\psi}_{0,\epsilon} = -\frac{1}{2}\Delta_y \psi_{0,\epsilon} + E_\epsilon^{(2)}(a_\epsilon(t))\frac{y^2}{2}\psi_{0,\epsilon}, \tag{6.7}$$

$$[h_\epsilon(x) - E_\epsilon(x)]\psi_{2,\epsilon} = -i\eta_\epsilon(t)\cdot\nabla_x\psi_{0,\epsilon}. \tag{6.8}$$

One can show by explicit computations that if:

$$f_{0,\epsilon} = \epsilon^{-\frac{3}{2}}\phi(A_\epsilon(t), B_\epsilon(t), 1, 0, 0, y) \tag{6.9}$$

then the function (6.5) satisfies eq. (6.7). Thus $\psi_{0,\epsilon}$ is determined completely by the initial conditions. In order to analyze (6.8) we denote by $r(x)$ the reduced resolvent of $h_\epsilon(x)$ at $E_\epsilon(x)$, i.e.:

$$r(x) = (h_\epsilon(x) - E_\epsilon(x))^{-1}(1 - P_\epsilon(x)), \tag{6.10}$$

where $P_\epsilon(x)$ is the spectral projection onto the eigenvalue $\varphi_\epsilon(x,\xi)$ associated with $E_\epsilon(x)$. We also write $\psi_{2,\epsilon}$ as a sum of two components:

$$\psi_{2,\epsilon} = \psi_{2,\epsilon}^{\parallel} + \psi_{2,\epsilon}^{\perp},$$

where $\psi_{2,\epsilon}^{\parallel}$ is a multiple of $\varphi_\epsilon(x,\xi)$ and $\psi_{2,\epsilon}^{\perp}$ is orthogonal to $\varphi_\epsilon(x,\xi)$ in $L^2(d\xi)$. Eq. (6.8) determines $\psi_{2,\epsilon}^{\perp}$:

$$\begin{aligned}\psi_{2,\epsilon}^{\perp} =& ir(x)\eta_\epsilon(t)\cdot\nabla_x\psi_{0,\epsilon} \\ =& i\epsilon^{-\frac{3}{2}}\phi(A_\epsilon(t), B_\epsilon(t), 1, 0, 0, y)\; r(x)\; \eta_\epsilon(t)\cdot\nabla_x\varphi_\epsilon(x,\xi).\end{aligned} \tag{6.11}$$

It turns out that the only terms contributing to the 0-th order approximation are (6.9) and (6.11).

This construction can be continued to arbitrary order. In general, the n-th order equation determines $\psi^{\|}_{n-2,\epsilon}$ and $\psi^{\perp}_{n,\epsilon}$. We refer the interested reader to [H4] and since we already constructed terms of interest for us, we stop here.

VI.2. The approximation to the quantum propagation

Having constructed our approximate solution formally we can proceed with rigorous estimates. We state here the result and give the proof in the following section.

Fix 3×3 matrices A_+, B_+ satisfying (3.7), and vectors a_+, $\eta_+ \in \mathbb{R}^3$, $\eta_+ \neq 0$. By lemma 5.5 and [H4] there exists a solution $a_\epsilon(t)$, $\eta_\epsilon(t)$, $A_\epsilon(t)$, $B_\epsilon(t)$ to the system (4.3) satisfying the asymptotic conditions (4.4). Then we have:

Theorem 6.1.

Let H be defined by equations (3.1), (3.2). Assume the potentials satisfy

(3.3). Also assume the conditions on E_D and $E_\epsilon(\zeta)$ stated in chapter 5 are satisfied. Let $a_\epsilon(t)$, $\eta_\epsilon(t)$, $A_\epsilon(t)$, $B_\epsilon(t)$ be as above and $S(t)$ be defined by (4.5). Then the function:

$$\psi_\epsilon(\xi,\zeta,t) = e^{\frac{iS(t)}{\epsilon^2}}\phi(A_\epsilon(t),B_\epsilon(t),\epsilon^2,a_\epsilon(t),\eta_\epsilon(t),\zeta) \left[\varphi_\epsilon(\xi,\zeta) + i\epsilon^2 r(\zeta)\eta_\epsilon(t)\cdot\nabla_\xi\varphi_\epsilon(\xi,\zeta)\right], \tag{6.12}$$

where $r(\zeta)$ is defined by (6.10), is the 0-th order asymptotic expansion of the solution to equation:

$$i\epsilon^2\frac{\partial\Psi(\xi,\zeta,t)}{\partial t} = \left[-\frac{\epsilon^4}{2}\Delta_\zeta + h_\epsilon(\zeta)\right]\Psi(\xi,\zeta,t), \tag{6.13}$$

i.e. the following holds:

$$\|e^{-\frac{itH}{\epsilon^2}}\psi_\epsilon(\xi,\zeta,0) - \psi_\epsilon(\xi,\zeta,t)\| \le C\epsilon \tag{6.14}$$

uniformly for $t \in [0,\infty)$.

Remarks.

1. It is trivial to check that the function:

$$\Psi(x,y,\xi,t) = e^{\frac{iS(t)}{\epsilon^2}}e^{\frac{i(\eta_\epsilon(t),y)}{\epsilon}}[\psi_{0,\epsilon}(x,y,\xi,t) + \epsilon^2\psi^{\perp}_{2,\epsilon}(x,y,\xi,t)] \tag{6.15}$$

constructed in previous section becomes (6.12) if we return to our original variables ζ, ξ.

2. This theorem gives the leading order approximation to the full quantum evolution of the system uniformly in time. If one constructs the corresponding free evolution (using lemma 4.4) then the approximation to the wave operator can be found (see Theorem 6.6).

VI.3. Proof of theorem 6.1

As already mentioned, our proof is simply an application of lemma 4.2. We remain in the multiple scales framework and calculate the error terms in eq. (6.2) using the function (6.16). The result is:

$$
\begin{aligned}
(6.16)\quad R(t) = & \\
&= e^{\frac{iS(t)}{\epsilon^2}} e^{\frac{i\eta_\epsilon(t)\cdot y}{\epsilon}} \{\epsilon^3 \nabla_y f_{0,\epsilon}(y) \cdot \nabla_x \varphi_\epsilon(\xi, x) \\
&+ \epsilon^4 [f_{0,\epsilon}(y)\ r(x)\ E'_\epsilon(a_\epsilon(t)) \cdot \nabla_x \varphi_\epsilon(\xi, x) + \frac{1}{2} f_{0,\epsilon}(y)\ \Delta_x \varphi_\epsilon(\xi, x) \\
&\quad - f_{0,\epsilon}(y)\ \eta_\epsilon(t) \cdot \nabla_x \varphi_{1,\epsilon}(\xi, x)] \\
&+ \epsilon^5 i\ \nabla_y f_{0,\epsilon}(y) \cdot \nabla_x \varphi_{1,\epsilon}(\xi, x) \\
&+ \epsilon^6 \frac{i}{2}\ f_{0,\epsilon}(y)\ \Delta_x \varphi_{1,\epsilon}(\xi, x) \\
&- [E_\epsilon(a_\epsilon(t) + \epsilon y) - E_\epsilon(a_\epsilon(t)) - \epsilon y E'_\epsilon(a_\epsilon(t)) - \frac{\epsilon^2 y^2}{2} E''_\epsilon(a_\epsilon(t))] \cdot \\
&\quad \cdot [f_{0,\epsilon}(y)\ \varphi_\epsilon(\xi, x) + i\epsilon^2 f_{0,\epsilon}(y)\ \varphi_{1,\epsilon}(\xi, x)]\},
\end{aligned}
$$

where:

$$
f_{0,\epsilon}(y) = \epsilon^{-\frac{3}{2}} \phi(A_\epsilon(t), B_\epsilon(t), 1, 0, 0, y)
$$

$$\varphi_{1,\epsilon}(\xi, x) = r(x)\, \eta_\epsilon(t) \cdot \nabla_x \varphi_\epsilon(\xi, x).$$

We begin the analysis with the first four terms. They are basically of the form $f_{0,\epsilon}(y)$ (or $\nabla_y f_{0,\epsilon}(y)$) multiplied by $\nabla_x \varphi_\epsilon$ (or $\nabla_x \varphi_{1,\epsilon}$). Note that the first factor is concentrated near $\zeta = a_\epsilon(t)$ while the second near $\zeta = 0$. Using their decay properties we can prove the desired estimates.

Lemma 6.2.

Let $\omega(x)$ be a function $\mathbb{R}^3 \to \mathbb{R}$ satisfying $|\omega(x)| \leq (1 + |x|)^{-1-\delta}$, and let $f_{0,\epsilon}(y)$ be as defined above. Then:

$$\|f_{0,\epsilon}(\frac{\zeta - a_\epsilon(t)}{\epsilon})\, \omega(\zeta)\|_{L^2(\mathbb{R}^3, d\zeta)} \leq F(t) \tag{6.17}$$

for some $F \in L^1(\mathbb{R}, dt)$.

Proof. For $0 < \mu < 1$ we define the sets:

$$B_1 = \{\zeta : |\zeta - a_\epsilon(t)| \leq \mu |a_\epsilon(t)|\}$$

$$B_2 = \{\zeta : |\zeta - a_\epsilon(t)| > \mu |a_\epsilon(t)|\}$$

and let χ_1, χ_2 be the corresponding characteristic functions. Then:

$$\|f_{0,\epsilon}\omega\|_2 = \|\chi_1 f_{0,\epsilon}\omega\|_2 + \|\chi_2 f_{0,\epsilon}\omega\|_2 = I_1(t) + I_2(t).$$

By the Hölder inequality:

$$I_1(t) = \|\chi_1(\zeta)\ \omega(\zeta)\ f_{0,\epsilon}(\frac{\zeta - a_\epsilon(t)}{\epsilon})\|_2 \leq \|\chi_1(\zeta)\ \omega(\zeta)\|_\infty \|f_{0,\epsilon}(\frac{\zeta - a_\epsilon(t)}{\epsilon})\|_2.$$

The second factor equals 1 and from the definition of the set B_1 we see that the first factor is bounded by $C_1(1 + (1-\mu)|a_\epsilon(t)|)^{-1-\delta}$.

For I_2 we have:

$$\begin{aligned} I_2(t) &= \|\chi_2(\zeta) e^{-\frac{1}{4\epsilon^2}|A_\epsilon(t)^{-1}(\zeta - a_\epsilon(t))|^2}\|_\infty \cdot \\ &\qquad \cdot \|\omega(\zeta)\pi^{-\frac{3}{4}}\epsilon^{-\frac{3}{2}}|\det A_\epsilon(t)|^{-\frac{1}{2}} e^{-\frac{1}{4\epsilon^2}|A_\epsilon(t)^{-1}(\zeta - a_\epsilon(t))|^2}\|_2 \\ &\leq \|\chi_2(\zeta) e^{-\frac{1}{4\epsilon^2}|A_\epsilon(t)^{-1}(\zeta - a_\epsilon(t))|^2}\|_\infty \cdot \\ &\qquad \cdot \|\omega\|_q \|\pi^{-\frac{3}{4}}\epsilon^{-\frac{3}{2}}|\det A_\epsilon(t)|^{-\frac{1}{2}} e^{-\frac{1}{4\epsilon^2}|A_\epsilon(t)^{-1}(\zeta - a_\epsilon(t))|^2}\|_p, \end{aligned}$$

where $\frac{1}{p} + \frac{1}{q} = \frac{1}{2}$.

If we take $\frac{3}{1+\delta} < q < \frac{3}{1+\frac{\delta}{2}}$ then $\|\omega\|_q = C_2 < \infty$ and $-\frac{3}{q} < -(1 + \frac{\delta}{2})$. The last factor equals:

$$\begin{aligned} \|\pi^{-\frac{3}{4}}\epsilon^{-\frac{3}{2}}|\det A_\epsilon(t)|^{-\frac{1}{2}} e^{-\frac{1}{4\epsilon^2}|A_\epsilon(t)^{-1}(\zeta - a_\epsilon(t))|^2}\|_p = \\ = C_3\epsilon^{-3(\frac{1}{2}-\frac{1}{p})}|\det A_\epsilon(t)|^{-(\frac{1}{2}-\frac{1}{p})} \\ = C_3\epsilon^{-\frac{3}{q}}|\det A_\epsilon(t)|^{-\frac{1}{q}}. \end{aligned}$$

The first factor is bounded:

$$\|\chi_2(\zeta) e^{-\frac{1}{4\epsilon^2}|A_\epsilon(t)^{-1}(\zeta - a_\epsilon(t))|^2}\|_\infty \leq e^{-\frac{1}{4\epsilon^2}\|A_\epsilon(t)\|^{-2}\mu^2|a_\epsilon(t)|^2}$$

which, because of the asymptotics of $A_\epsilon(t)$ and $a_\epsilon(t)$, is bounded by $e^{-C_4\epsilon^{-2}}$ for all t. Thus we have the following bound on $I_2(t)$:

$$I_2(t) \leq C_5 e^{-C_4\epsilon^{-2}} \epsilon^{-\frac{3}{q}} |\det A_\epsilon(t)|^{-\frac{1}{q}}.$$

This bound decays to 0 as $\epsilon \to 0$, so we can find C_6 such that $I_2(t) \leq C_6 |\det A_\epsilon(t)|^{-\frac{1}{q}}$. Now, the asymptotic behavior of $A_\epsilon(t)$ and our choice of q guarantee the existence of an L^1-function $F_2(t)$ such that:

$$I_2(t) \leq C_6 F_2(t).$$

Combining the two bounds (for I_1 and I_2) we get the lemma.

□

Corollary 6.3.

The analogous conclusion holds if we multiply $f_{0,\epsilon}$ by any polynomial in y.

Proof. We need this bound for $f_{0,\epsilon}$ as well as for $\nabla_y f_{0,\epsilon}$. Thus we sketch the proof for the latter case below. We keep the notation of the proof of lemma 6.2.

We calculate $\nabla_y f_{0,\epsilon}$ explicitly:

$$\nabla_y f_{0,\epsilon}(y) = -C_7 \epsilon^{-\frac{3}{2}} (\det A_\epsilon(t))^{-\frac{1}{2}} B_\epsilon(t) A_\epsilon(t)^{-1} y e^{-\frac{1}{2}\langle y, B_\epsilon(t) A_\epsilon(t)^{-1} y\rangle}$$

and proceed as in the proof of lemma 6.2. Then:

(6.18)

$$\|\nabla_y f_{0,\epsilon}(\frac{\zeta - a_\epsilon(t)}{\epsilon})\|_2 = C_7 \epsilon^{-\frac{3}{2}} (\det A_\epsilon(t))^{-\frac{1}{2}} \cdot$$
$$\cdot \left(\int |B_\epsilon(t) A_\epsilon(t)^{-1} \frac{\zeta - a_\epsilon(t)}{\epsilon}|^2 e^{-\frac{1}{\epsilon^2}\langle \zeta - a_\epsilon(t), A_\epsilon(t)^{*-1} A_\epsilon(t)^{-1}(\zeta - a_\epsilon(t))\rangle} d^3\zeta \right)^{\frac{1}{2}}.$$

After the change of variable to $u = A_\epsilon(t)^{-1} \frac{\zeta - a_\epsilon(t)}{\epsilon}$, we see that (6.18) is bounded by $C_8 \|B_\epsilon(t)\|_{op}$. Since the operator norm of matrix $B_\epsilon(t)$ tends to a constant as $t \to \infty$, we get for I_1 a bound similar to that in the proof of lemma 6.2. The estimate for I_2 is essentially the same as in lemma 6.2.

□

Lemma 6.4.

Assume $h_\epsilon(x)$, $E_\epsilon(x)$ are as described in chapter 5. Let $\beta > 0$ be such that h_D has no eigenvalues in the closed ball $\overline{B(E_D, \beta)}$ other than E_D. Let $|x|$ be big enough so $E_\epsilon(x) \in B(E_D, \frac{\beta}{2})$ and $h_\epsilon(x)$ has no other eigenvalues in $B(E_D, \beta)$. Then the reduced resolvent $(h_\epsilon(x) - E_\epsilon(x))^{-1}(1 - P_\epsilon(x))$ and its first and second derivatives are bounded uniformly in x.

Proof. We consider $(h_\epsilon(x) - z)^{-1}(1 - P_\epsilon(x))$. This is the analytic part of the Laurent series of $(h_\epsilon(x) - z)^{-1}$ around $E_\epsilon(x)$. Thus it has a removable singularity at $E_\epsilon(x)$. By the assumption on the eigenvalues it can be continued analytically to the entire ball $B(E_D, \beta)$.

If we restrict $(h_\epsilon(x) - z)^{-1}(1 - P_\epsilon(x))$ to $B(E_D, \frac{\beta}{2})$, then by maximum modulus theorem it assumes its maximal value on the boundary $\partial B(E_D, \frac{\beta}{2})$ i.e.:

$$\begin{aligned}\|(h_\epsilon(x) - E_\epsilon(x))^{-1}(1 - P_\epsilon(x))\|_{op} &\leq \sup_{|z-E_D|=\frac{\beta}{2}} \|(h_\epsilon(x) - z)^{-1}(1 - P_\epsilon(x))\|_{op} \\ &\leq \sup_{|z-E_D|=\frac{\beta}{2}} \|(h_\epsilon(x) - z)^{-1}\|_{op} \leq \frac{2}{\beta}\end{aligned}$$

uniformly in x. This proves the first conclusion of the lemma.

To show boundedness of the derivative we write the reduced resolvent as:

$$(h_\epsilon(x) - z)^{-1}(1 - P_\epsilon(x)) = (1 - P_\epsilon(x))(h_\epsilon(x) - z)^{-1}(1 - P_\epsilon(x))$$

and compute the derivative:

(6.19)

$$\begin{aligned}&\partial_{x^i}\left((h_\epsilon(x) - z)^{-1}(1 - P_\epsilon(x))\right) = \\ &\quad = -(\partial_{x^i} P_\epsilon(x))(h_\epsilon(x) - z)^{-1}(1 - P_\epsilon(x)) \\ &\quad - (1 - P_\epsilon(x))(h_\epsilon(x) - z)^{-1}(\partial_{x^i} V_{D,\epsilon}(x))(h_\epsilon(x) - z)^{-1}(1 - P_\epsilon(x)) \\ &\quad - (h_\epsilon(x) - z)^{-1}(1 - P_\epsilon(x))(\partial_{x^i} P_\epsilon(x)).\end{aligned}$$

Our assumptions on $V_{D,\epsilon}$ guarantee that the operator norm of $\partial_{x^i} V_{D,\epsilon}$ is a constant.

To analyze $\partial_{x^i} P_\epsilon(x)$ we write:

$$\begin{aligned}\|\partial_{x^i} P_\epsilon(x)\| &\leq \frac{1}{2\pi} \int_{|z-E_D|=\beta} \|(h_\epsilon(x)-z)^{-1}\|^2 \ \|\partial_{x^i} V_{D,\epsilon}(x)\| \ dz \\ &\leq C \sup_{|z-E_D|=\beta} \|(h_\epsilon(x)-z)^{-1}\|^2 \|\partial_{x^i} V_{D,\epsilon}(x)\| \\ &\leq C'\end{aligned}$$

uniformly in x.

Since the reduced resolvent has just been shown to be uniformly bounded, the conclusion holds for the first derivative of the reduced resolvent.

For the second derivative we prove the estimate in a similar way. We write (6.19) as:

$$\begin{aligned}&\partial_{x^i} \left((h_\epsilon(x)-z)^{-1}(1-P_\epsilon(x))\right) = \\ &= -(\partial_{x^i} P_\epsilon(x))(1-P_\epsilon(x))(h_\epsilon(x)-z)^{-1}(1-P_\epsilon(x)) - \\ &-(1-P_\epsilon(x))(h_\epsilon(x)-z)^{-1}(1-P_\epsilon(x))(\partial_{x^i} V_{D,\epsilon}(x)) \cdot \\ &\quad \cdot (1-P_\epsilon(x))(h_\epsilon(x)-z)^{-1}(1-P_\epsilon(x)) - \\ &-(1-P_\epsilon(x))(h_\epsilon(x)-z)^{-1}(1-P_\epsilon(x))(\partial_{x^i} P_\epsilon(x))\end{aligned}$$

and compute the second derivative of $P_\epsilon(x)$ explicitly. It consists of terms containing products of the reduced resolvent, derivatives of $V_{D,\epsilon}$ and derivatives of $P_\epsilon(x)$ up to the second order. All of these factors, except $\partial_{x^i}\partial_{x^j} P_\epsilon(x)$,

have been shown to be bounded uniformly in x. To conclude the same for $\partial_{x^i}\partial_{x^j}P_\epsilon(x)$ we proceed exactly the same way as we did to show boundedness of the first derivative of $P_\epsilon(x)$. Finally we collect all these bounds to prove the last conclusion of the lemma.

□

Now we have tools to estimate all but the last term in (6.16). We first look at the x-dependent factors. Recall that the normalized eigenfunction $\varphi_\epsilon(\xi,x)$ of $h_\epsilon(x)$ is of the form:

$$\varphi_\epsilon(\xi,x)=\frac{P_\epsilon(x)\varphi_D(\xi)}{\langle\varphi_D(\xi),P_\epsilon(x)\varphi_D(\xi)\rangle}.$$

By explicit calculations and using lemma 5.3 and corollary 5.4 we conclude that:

(6.20a) $$\|\partial_{x^i}\varphi_\epsilon(\xi,x)\|\le C(1+|x|)^{-2-\delta}.$$

We can also use lemma 5.3 to show analogous bounds on the second and third derivatives of $\varphi_\epsilon(\xi,x)$:

(6.20b) $$\|\partial_{x^i}\partial_{x^j}\varphi_\epsilon(\xi,x)\|\le C(1+|x|)^{-3-\delta}$$

(6.20c). $$\|\partial_{x^i}\partial_{x^j}\partial_{x^k}\varphi_\epsilon(\xi,x)\|\le C(1+|x|)^{-4-\delta}$$

Combining (6.20 a,b and c) with lemma 6.4 we see that the x-dependent terms in (6.16) are the products of $|\eta_\epsilon(t)|$ and functions satisfying the hypothesis

of lemma 6.2. Here we return to our original variables by putting $x = \zeta$, $y = \frac{\zeta - a(t)}{\epsilon}$. By lemma 6.2 and asymptotics of $\eta_\epsilon(t)$ we see that all considered terms are bounded in norm by $C \cdot F(t)$ with $F \in L^1(\mathbb{R}, dt)$.

Note: in the above considerations we temporarily disregarded the factor $E'_\epsilon(a(t))$ appearing in one of the terms. We need to show that this factor remains bounded as $t \to \infty$. Lemma 5.5 says that it behaves even more nicely – it decays to 0.

To estimate the last term in (6.16) we use (5.7). Then, with an obvious abuse of notation, this term becomes:

$$(6.21) \quad [\tilde{E}_\epsilon(a(t) + \epsilon y) - \tilde{E}_\epsilon(a(t)) - \epsilon y \cdot \tilde{E}_\epsilon{}'(a(t)) - \frac{\epsilon^2 y^2}{2} \tilde{E}_\epsilon{}''(a(t))]$$
$$[f_{0,\epsilon}(y)\varphi_\epsilon(\xi, x) + i\epsilon^2 f_{0,\epsilon}(y)\varphi_{1,\epsilon}(\xi, x)].$$

We note that $\|\varphi_\epsilon(\xi, x) + i\epsilon^2 \varphi_{1,\epsilon}(\xi, x)\|_{L^2(d\xi)}$ is a bounded function of x. Also by lemma 5.5 we know that $\tilde{E}_\epsilon$ satisfies the hypotheses of lemma 4.3. This shows that the $L^2(d\zeta)$-norm of (6.16) is bounded by $F(t)\epsilon^3$ for some $F \in L^1(\mathbb{R}, dt)$. Application of lemma 4.2 concludes the proof.

□

VI.4. The wave operators

Following the same procedure one can develop an approximation to the free time evolution. Physically the term free evolution refers to the dynamics of two noninteracting clusters. Mathematically it corresponds to $V_{D,\epsilon} = 0$ in (3.1) and (3.6). Then most of our results leading to the proof of theorem 6.1 are satisfied trivially (e.g. in lemma 5.3 all constants are zero). Therefore as a corollary we get:

Corollary 6.5.

Let H_0 be $H(\epsilon) - V_{D,\epsilon}$. Let $E_{0,\epsilon}$ be the eigenvalue of $h_D(\epsilon) = h_D + \epsilon^4 D(\epsilon)$ with eigenvector $\varphi_{0,\epsilon}(\xi)$. Let a_+, η_+, A_+, B_+ be as in theorem 6.1 and $S_0(t) = -\frac{\eta_+^2}{2}t - E_{0,\epsilon}t$. Then the function:

$$\Psi_0(\xi,\zeta,t) = e^{\frac{iS_0(t)}{\epsilon^2}}\phi(A_+ + itB_+, B_+, \epsilon^2, a_+ + t\eta_+, \eta_+, \zeta)\varphi_{0,\epsilon}(\xi)$$

is the leading order asymptotic expansion to the solution to equation:

$$i\epsilon^2\frac{\partial\Psi}{\partial t} = [-\frac{\epsilon^4}{2}\Delta_\zeta + h_D(\epsilon)]\Psi \tag{6.22}$$

In fact this expansion is exact, i.e.:

$$\|e^{-\frac{itH_0}{\epsilon^2}}\Psi_0(\xi,\zeta,0) - \Psi_0(\xi,\zeta,t)\| = 0 \tag{6.23}$$

for all $t \in [0,\infty)$.

Proof. By inspection (6.22) is satisfied hence, by lemma 4.2, (6.23) also holds.

□

Similarly to what we have done in chapter 4, one can use the approximation to the full quantum dynamics (theorem 6.1) and the free dynamics (corollary 6.5) to find an approximation to the wave operator.

Theorem 6.6.

Assume hypotheses of theorem 6.1 and corollary 6.5. Then

$$\begin{aligned}
&\|\Omega^- \phi(A_+, B_+, \epsilon^2, a_+, \eta_+, \zeta)\varphi_{0,\epsilon}(\xi) \\
&\quad - \phi(A_\epsilon(0), B_\epsilon(0), \epsilon^2, a_\epsilon(0), \eta_\epsilon(0), \zeta)\cdot \\
&\qquad [\varphi_\epsilon(\xi,\zeta) + i\epsilon^2 r(\zeta)\eta_\epsilon(0)\cdot\nabla_\zeta\varphi_\epsilon(\xi,\zeta)\| \\
&\quad \leq C\epsilon
\end{aligned}$$

Proof. Consider:

$$\begin{aligned}
&\|e^{-\frac{itH_0}{\epsilon^2}}\phi(A_+,B_+,\epsilon^2,a_+,\eta_+,\zeta)\ \varphi_{0,\epsilon}(\xi)\\
&\quad - e^{-\frac{itH(\epsilon)}{\epsilon^2}}\phi(A_\epsilon(0),B_\epsilon(0),\epsilon^2,a_\epsilon(0),\eta_\epsilon(0),\zeta)\ [\varphi_\epsilon(\xi,\zeta)+i\epsilon^2\varphi_{1,\epsilon}(\xi,\zeta)\|\\
\le&\|e^{-\frac{itH_0}{\epsilon^2}}\phi(A_+,B_+,\epsilon^2,a_+,\eta_+,\zeta)\ \varphi_{0,\epsilon}(\xi)\\
&\quad - e^{\frac{iS_0(t)}{\epsilon^2}}\phi(A_+ + itB_+,B_+,\epsilon^2,a_+ + t\eta_+,\eta_+,\zeta)\ \varphi_{0,\epsilon}(\xi)\|\\
&\quad + \|e^{\frac{iS_0(t)}{\epsilon^2}}\phi(A_+ + itB_+,B_+,\epsilon^2,a_+ + t\eta_+,\eta_+,\zeta)\ \varphi_{0,\epsilon}(\xi)\\
&\quad - e^{\frac{iS(t)}{\epsilon^2}}\phi(A_\epsilon(t),B_\epsilon(t),\epsilon^2,a_\epsilon(t),\eta_\epsilon(t),\zeta)\ [\varphi_\epsilon(\xi,\zeta)+i\epsilon^2\varphi_{1,\epsilon}(\xi,\zeta)]\|\\
&\quad + \|e^{\frac{iS(t)}{\epsilon^2}}\phi(A_\epsilon(t),B_\epsilon(t),\epsilon^2,a_\epsilon(t),\eta_\epsilon(t),\zeta)\ [\varphi_\epsilon(\xi,\zeta)+i\epsilon^2\varphi_{1,\epsilon}(\xi,\zeta)]\\
&\quad - e^{-\frac{itH(\epsilon)}{\epsilon^2}}\phi(A_\epsilon(0),B_\epsilon(0),\epsilon^2,a_\epsilon(0),\eta_\epsilon(0),\zeta)\ [\varphi_\epsilon(\xi,\zeta)+i\epsilon^2\varphi_{1,\epsilon}(\xi,\zeta)\|
\end{aligned}$$

By corollary 6.5 the first term equals 0. By theorem 6.1 the last term is bounded by $C\epsilon$ uniformly in t for $t \in [0,\infty)$. We rewrite the middle term as:

$$\begin{aligned}
&\|e^{\frac{iS_0(t)}{\epsilon^2}}\phi(A_+ + itB_+,B_+,\epsilon^2,a_+ + t\eta_+,\eta_+,\zeta)\ \varphi_{0,\epsilon}(\xi)\\
&\quad - e^{\frac{iS(t)}{\epsilon^2}}\phi(A_\epsilon(t),B_\epsilon(t),\epsilon^2,a_\epsilon(t),\eta_\epsilon(t),\zeta)\ [\varphi_\epsilon(\xi,\zeta)+i\epsilon^2\varphi_{1,\epsilon}(\xi,\zeta)\|\\
&\quad \le \|[e^{\frac{iS_0(t)}{\epsilon^2}}\phi(A_+ + itB_+,B_+,\epsilon^2,a_+ + t\eta_+,\eta_+,\zeta)\\
&\quad - e^{\frac{iS(t)}{\epsilon^2}}\phi(A_\epsilon(t),B_\epsilon(t),\epsilon^2,a_\epsilon(t),\eta_\epsilon(t),\zeta)]\ \varphi_{0,\epsilon}(\xi)\|\\
&\quad + \|e^{\frac{iS(t)}{\epsilon^2}}\phi(A_\epsilon(t),B_\epsilon(t),\epsilon^2,a_\epsilon(t),\eta_\epsilon(t),\zeta)\ [\varphi_{0,\epsilon}(\xi)-\varphi_\epsilon(\xi,\zeta)]\|\\
&\quad + \epsilon^2\|e^{\frac{iS(t)}{\epsilon^2}}\phi(A_\epsilon(t),B_\epsilon(t),\epsilon^2,a_\epsilon(t),\eta_\epsilon(t),\zeta)\ \varphi_{1,\epsilon}(\xi,\zeta)\|
\end{aligned}$$

In the last term, $\|\varphi_{1,\epsilon}(\xi,\zeta)\|_{L^2(d\xi)}$ is a bounded function of ζ. Since ϕ is normalized, this term is bounded by $C\epsilon^2$.

We note that:

$$\lim_{t\to\infty} |S(t) - S_0(t)| = 0$$

This follows from (4.10) and the remark following lemma 5.5. Using this, asymptotic conditions (4.10) and the dominated convergence theorem we conclude that the first term tends to 0 as $t \to \infty$.

By mimicking the proof of corollary 5.4 we can show that $\omega(\zeta) = \|\varphi_{0,\epsilon}(\xi) - \varphi_\epsilon(\xi,\zeta)\|_{L^2(d\xi)}$ satisfies the asumption of lemma 6.2. Thus the middle term also tends to 0 as $t \to \infty$.

Therefore:

$$\lim_{t\to\infty} \|e^{\frac{itH(\epsilon)}{\epsilon^2}} e^{-\frac{itH_0(\epsilon)}{\epsilon^2}} \phi(A_+, B_+, \epsilon^2, a_+, \eta_+, \zeta)\varphi_{0,\epsilon}(\xi,\zeta) -$$
$$-e^{\frac{iS(0)}{\epsilon^2}} \phi(A(0), B(0), \epsilon^2, a(0), \eta(0), \zeta)[\varphi_\epsilon(\xi,\zeta) + i\epsilon^2\varphi_{1,\epsilon}(\xi,\zeta)]\| \leq C\epsilon$$

□

VII. OPEN PROBLEMS

In this last chapter we would like to comment about possible generalizations of our work and some open problems.

Theorem 6.1 gives the leading order approximation to the quantum propagation of the semiclassical wave packets. Hence it seems natural to ask about a higher order expansion. Hagedorn [H4] constructed such expansion on a finite time interval. The work is based on the higher order semiclassical approximation [H11]. We believe that our method of proof can be extended to this expansion, however since the formulae for the higher order corrections become more and more complicated, it would require rather tedious calculations.

The second possible generalization would be to include polyatomic molecules. As we stated in chapter 3 our work is valid only for diatomic molecules. The main reason for this restriction becomes clear if we look at equations (3.4)-(3.6). It is crucial for our technique that the reduced masses in the kinetic part of the electronic hamiltonian (cf. 3.4, 3.5) have nonzero limits as $\epsilon \to 0$. Then $\epsilon^4 D(\epsilon)$ (cf. 3.6) is a regular perturbation of h_D. For polyatomic molecules this is no longer true. Some of the $\nu_j^{(i)}(\epsilon)$ would tend to 0 as $\epsilon \to 0$, and the corresponding correction to h_D would be by no

means small compared to h_D. Then the dependence of $E_\epsilon(\zeta)$ on ϵ becomes much more complicated. One would need to use the time-independent Born-Oppenheimer method to find an approximation to $E_\epsilon(\zeta)$. One then would get an asymptotic expansion to $E_\epsilon(\zeta)$ in ϵ, where each term depends on ζ. It would be necessary to determine this relation explicitly for each term. If the analog of lemma 5.5 can be proved, then the rest would follow.

The last, and probably the most interesting extension of our results would be to allow the Coulomb or general long-range potentials in the hamiltonian. It is crucial for our estimates that the potentials decay faster than $\frac{1}{|\zeta|}$ as $|\zeta| \to \infty$, and the generalization to long-range potentials requires a major modification of our technique. We are currently investigating this problem for diatomic molecules with Coulomb potentials.

There are some interesting results [A], [AS], [CS], [MS] regarding the behavior of the eigenvalues $E(\zeta)$ of the electronic hamiltonian for large $|\zeta|$. The authors constructed the asymptotic expansion to $E(\zeta)$ in powers of $|\zeta|^{-1}$. These results would replace lemma 5.5 in the Coulomb case.

Another difficulty in this case is with the semiclassical approximation. It is well known [RS1] that the standard wave operators, as defined in (2.5) do not exist. However, it was proved by Dollard [D] that if one replaces the free

propagator $\exp(-itH_0/\hbar)$ by suitably defined modified free propagator (see [D], [Y2]) then the modified wave operators exist and are complete.

The semiclassical approximation to the modified wave operators was constructed by Yaijma [Y2] for general long range potentials. One can use these ideas to find fairly explicit formulae for the time evolution of semiclassical wave packets, generated by a hamiltonian of the form (4.2), with V being the Coulomb potential.

It is known [RS1] that the classical trajectory of a particle in the Coulomb potential does not approach the trajectory of a free particle for large time. In our formalism it means that there is a solution to the system (4.3) satisfying conditions:

$$(7.1a) \qquad \lim_{t\to\infty} |a(t) - b_+ - \eta_+ t - d_+ \log(4\eta_+^2 t)| = 0$$

$$(7.1b) \qquad \lim_{t\to\infty} |\eta(t) - \eta_+| = 0$$

$$(7.1c) \qquad \lim_{t\to\infty} \|A(t) - D_+ - iB_+ t - F_+ \log(4\eta_+^2 t)\| = 0$$

$$(7.1d) \qquad \lim_{t\to\infty} \|B(t) - B_+\| = 0$$

for some D_+, F_+, b_+, d_+ (depending on A_+, B_+, a_+, η_+), rather than conditions (4.4). Thus one can define the interacting semiclassical evolution as

in chapter 4, but the semiclassical free evolution would need to be redefined:

(7.2)

$$U_0(t)\phi(A_+, B_+, \hbar, a_+, \eta_+, x) \sim$$

$$\phi(D_+ + itB_+ + F_+ \log(4\eta_+^2 t), B_+, \hbar, b_+ + \eta_+ t + d_+ \log(4\eta_+^2 t), \eta_+, x)$$

However, with this change, neither lemma 4.4, nor theorem 4.1 is true. For the interacting dynamics we get:

$$(7.3) \qquad \|e^{-\frac{itH(\hbar)}{\hbar}}\phi(A(0), B(0), \hbar, a(0), \eta(0), \cdot) -$$

$$- e^{\frac{iS(t)}{\hbar}}\phi(A(t), B(t), \hbar, a(t), \eta(t), \cdot)\| < C\hbar^{\lambda}\log t$$

Similarly for the modified free propagator:

$$(7.4) \qquad \|e^{-\frac{itH_0(\hbar)}{\hbar}}\phi(A_+, B_+, \hbar, a_+, \eta_+, \cdot) -$$

$$- e^{\frac{it\langle\eta_+,\eta_+\rangle}{2\hbar}}\phi(D_+ + itB_+ + F_+ \log(4\eta_+^2 t), B_+,$$

$$\hbar, b_+ + \eta_+ t + d_+ \log(4\eta_+^2 t), \eta_+, \cdot)\| < C\hbar^{\lambda}\log t$$

Nevertheless, we can use these estimates to show that given $\delta > 0$ there is $\hbar_0$ such that for $\hbar < \hbar_0$:

$$(7.5) \qquad \|\Omega^{-}\phi(A_+, B_+, \hbar, a_+, \eta_+, \cdot) -$$

$$- \phi(A(0), B(0), \hbar, a(0), \eta(0), \cdot)\| \leq \delta$$

The proof is similar to the proof of theorem 4.5, but we first take t large enough, so that the difference between the full and modified free semiclassical dynamics is "small", and then we take $\hbar$ small enough, so that $C\hbar^{\lambda} \log t < \frac{\delta}{3}$.

One more difference between the smooth short-range potential we considered here and the Coulomb potentials has been already mentioned in the introduction. The singularity of the potential causes lack of differentiability of the electronic hamiltonian eigenfunction beyond the second order. In our estimates we explicitly used the third derivative of $\varphi_\epsilon(\zeta, \xi)$ (cf. lemma 5.3); hence some of our lemmas do not apply to systems with Coulomb potential. This problem was overcome by Hagedorn [H5] and we hope to apply his ideas to our problem.

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