The infinite time limit for the time-dependent Born-Oppenheimer approximation

1 AUTHOR:

Armin Kargol
Loyola University New Orle…

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The Infinite Time Limit for the Time-Dependent Born–Oppenheimer Approximation

Armin Kargol[*,**]

Center for Transport Theory and Mathematical Physics, Virginia Polytechnic Institute and State University, Blacksburg, Va 24061, USA. E-mail:kargol@math.vt.edu

Abstract: We analyze the Schrödinger equation $i\varepsilon^2 \frac{\partial}{\partial t}\Psi = H(\varepsilon)\Psi$, where $H(\varepsilon)$ is the hamiltonian of the molecular system consisting of nuclei with masses proportional to ε^{-4} and electrons with masses of order 1. Using the Born–Oppenheimer method we construct the leading order asymptotic expansion to the exact solutions of the equation. We show that if the particles interact through smooth potentials decaying suitably as the distance between particles tends to ∞, then the expansion holds uniformly for all times $t \in [0, \infty)$. By similar analysis one can show validity of the expansion for $t \in (-\infty, 0]$, thus our results hold for scattering theory.

1. Introduction

This work is devoted to the analysis of the dynamics of molecular systems. By molecular systems we mean quantum mechanical systems consisting of two types of particles: heavy (further referred to as nuclei) and light (electrons). It is known that for such systems the task of solving the Schrödinger equation becomes quite difficult, one of the reasons being the large number of particles involved. Therefore one usually resorts to an approximation.

In 1927 M. Born and R. Oppenheimer proposed an approximate method of solving the time-independent Schrödinger equation. It proved to be very useful and became known as the Born–Oppenheimer approximation. The main idea was to exploit the disparity between masses of nuclei and electrons. Born and Oppenheimer postulated to use the fourth root of the ratio of electronic mass to nuclear mass as a small parameter ε and seek approximate energy levels and eigenfunctions of the molecular hamiltonian in forms of power series in ε. However, their calculations were only formal and, quite surprisingly, there was very little rigorous work done on this subject until late 1970's. Then Combes, Duclos, Seiler [1–3] and later Hagedorn [8, 9] proved that the Born–Oppenheimer series is asymptotic to the exact solution of the Schrödinger equation to arbitrary order in ε. Recently Klein et al. [11] showed similar result for polyatomic molecules.

The time-dependent Born–Oppenheimer approximation, which describes the dynamics of molecular systems, rather than energy levels, has been first rigorously formulated by Hagedorn [6] in 1980. The principal idea is similar to the time-independent case. Because of the disparity in masses, the electrons move much more rapidly than nuclei. For short times we can approximately find their motion by treating nuclei as fixed. On a longer time scale the electrons quickly adjust their motion to slowly varying position of the nuclei. Therefore we can use the adiabatic approximation to describe the dynamics of electrons. On the other hand the electrons generate an effective potential in which the nuclei, because of their large mass move semiclassically. These two approximations, adiabatic for electrons and semiclassical for nuclei, are however coupled to each other. In order to separate them we use so-called multiple scales technique, which will be described later.

Using this method and a certain semiclassical technique [5], Hagedorn [7] analyzed the dynamics of molecular systems with smooth potentials, on finite time interval $[0, T]$. He proved that solutions to the time-dependent Schrödinger equation have asymptotic expansions of arbitrary order in ε, but his estimates depend on T and therefore cannot be used to analyze scattering problems.

In this work we extend the ideas of Hagedorn [7] to show that the leading order asymptotic expansion obtained in such way is in fact uniform in time for $t \in [0, \infty)$. We restrict our attention to diatomic molecules and require potentials and their derivatives to decay sufficiently fast as the distance between particles increases to ∞. By mimicking our proofs one can show uniformity of the expansion for $t \in (-\infty, 0]$. Therefore our results justify use of this expansion in treating scattering problems.

The case of Coulomb potentials has been investigated by Hagedorn [10]. He proved a result similar to the smooth case, but again, for finite times only. We plan to analyze this problem in the context of scattering theory in the near future.

Finally, we mention the work by Klein, Martinez and Wang [12], who analyzed the Born–Oppenheimer approximation for wave operators. They also consider a diatomic molecule with smooth, short-range potentials. Their technique is, however, very different from ours since they consider the time-independent scattering theory.

This paper is organized as follows: in Sect. 2 we specify our choice of coordinate system and introduce necessary notation. We also define so-called semiclassical wave packets which we later use to describe the motion of nuclei. In Sect. 3 we investigate the asymptotic behavior of the eigenvalues of the electronic hamiltonian for small ε and large intercluster distance. Our main theorem is stated in Sect. 4. This section also describes the multiple scales technique which allows us to decouple the semiclassical and adiabatic aspects of our problem. Finally, the last section contains the rigorous proof of the theorem.

2. Notation

We consider a diatomic molecule with N electrons. The masses of nuclei are ε^{-4} and the masses of 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 $C_1 = \underbrace{\{1, \ldots, K^{(1)} + 1\}}_{K^{(1)} \text{ electrons, 1 nucleus}}$,

$C_2 = \underbrace{\{K^{(1)} + 2, \ldots, N + 2\}}_{K^{(2)}=N-K^{(1)} \text{ electrons, 1 nucleus}}$, we introduce the clustered Jacobi coordinates [13].

Indices $1, K^{(1)} + 2$ refer to the nuclei. Indices $2, \ldots, K^{(1)} + 1, K^{(1)} + 3, \ldots, N + 2$ refer to the electrons. Then $\xi_1^{(1)}, \ldots, \xi_{K^{(1)}}^{(1)}, \xi_1^{(2)}, \ldots, \xi_{K^{(2)}}^{(2)}$ 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). This choice simplifies the dependence of the potentials on ε (see the comment following formula (2c) below).
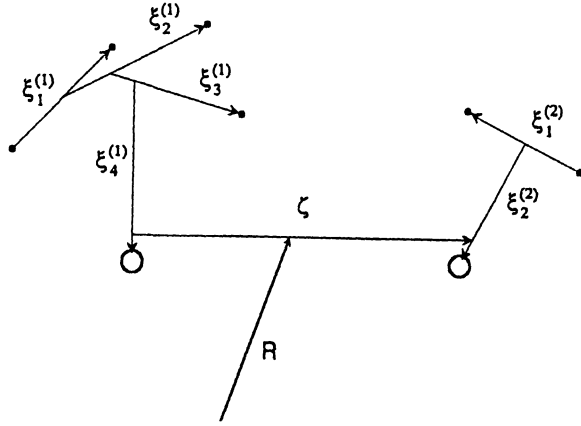

Fig. 1. An example of the clustered Jacobi coordinates ($N = 6$, $K^{(1)} = 4$, $K^{(2)} = 2$). ● electron; ○ nucleus

In these coordinates the hamiltonian becomes:

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

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

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

$$H = -\frac{\varepsilon^4}{2}\Delta_\zeta - \sum_{i=1}^{K^{(1)}}\frac{v_i^{(1)}(\varepsilon)}{2}\Delta_{\xi_i^{(1)}} - \sum_{i=1}^{K^{(2)}}\frac{v_i^{(2)}(\varepsilon)}{2}\Delta_{\xi_i^{(2)}} + V, \tag{1}$$

where:

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

$V^{(C_j)}$ is the interaction within j-th cluster, $V_{D,\varepsilon}$ is the intercluster interaction. Explicitly:

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

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

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

Here $\tau_k^{(l)}$, $\mu_k^{(l)}$, 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 $k = 1, \dots, K^{(l)} - 1$. $\tau_{K^{(l)}}^{(l)}$ are rational functions of ε^4 that approach constants as $\varepsilon \to 0$ 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 interacting particles. We also assume that they are at least C^3 and decay at infinity according to:

$$|V(x)| \le C_1(1 + |x|)^{-1-\delta}, \tag{3a}$$

$$|\partial_{x^i} V(x)| \le C_2(1 + |x|)^{-2-\delta}, \tag{3b}$$

$$|\partial_{x^i} \partial_{x^j} V(x)| \le C_3(1 + |x|)^{-3-\delta}, \tag{3c}$$

$$|\partial_{x^i} \partial_{x^j} \partial_{x^k} V(x)| \le C_4(1 + |x|)^{-4-\delta}, \tag{3d}$$

for some constants $C_1, \dots, C_4$ and $\delta > 0$. We will use the following notation:

$$h_D^{(1)}(\varepsilon) = -\frac{1}{2} \sum_{i=1}^{K^{(1)}} v_i^{(1)}(\varepsilon) \Delta_{\xi_i^{(1)}} + V^{(C_1)}, \tag{4}$$

$$h_D^{(2)}(\varepsilon) = -\frac{1}{2} \sum_{i=1}^{K^{(2)}} v_i^{(2)}(\varepsilon) \Delta_{\xi_i^{(2)}} + V^{(C_2)}. \tag{5}$$

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

$$h_\varepsilon(\zeta) = h_D^{(1)}(0) + h_D^{(2)}(0) - \frac{1}{2} \sum_{l=1}^{2} \sum_{k=1}^{K^{(l)}} (v_k^{(l)}(\varepsilon) - v_k^{(l)}(0)) \Delta_{\xi_k^{(l)}}$$

$$+ V_{D,\varepsilon}(\zeta, \xi^{(1)}, \xi^{(2)})$$

$$= h_D + \varepsilon^4 D(\varepsilon) + V_{D,\varepsilon}(\zeta, \xi^{(1)}, \xi^{(2)}). \tag{6}$$

Here we used the obvious abbreviation:

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

$$\varepsilon^4 D(\varepsilon) = -\frac{1}{2} \sum_{l=1}^{2} \sum_{k=1}^{K^{(l)}} (v_k^{(l)}(\varepsilon) - v_k^{(l)}(0)) \varDelta_{\xi_k^{(l)}},$$

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

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

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

To complete the notation we define so-called semiclassical wave packets [5], which will be used later to describe the motion of nuclei in the potential given by $E(x)$.

Definition. *Let A, B be complex 3×3 matrices such that*:

$$A \text{ and } B \text{ are invertible}, \tag{7a}$$

$$BA^{-1} \text{ is symmetric}, \tag{7b}$$

$$\mathrm{Re}BA^{-1} = \frac{1}{2}[BA^{-1} + (BA^{-1})^*] \text{ is strictly positive definite}, \tag{7c}$$

$$(\mathrm{Re}BA^{-1})^{-1} = AA^*. \tag{7d}$$

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

$$\varphi(A, B, \varepsilon^2, a, \eta, x) :=$$

$$\pi^{-\frac{3}{4}} \varepsilon^{-\frac{3}{2}} (\det A)^{-\frac{1}{2}} \exp\left(-\frac{\langle (x-a), BA^{-1}(x-a) \rangle}{2\varepsilon^2} + i\frac{\langle \eta, (x-a) \rangle}{\varepsilon^2}\right). \tag{8}$$

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

$$\frac{d\eta(t)}{dt} = -E'(a(t)), \tag{9a}$$

$$\frac{da(t)}{dt} = \eta(t), \tag{9b}$$

$$\frac{dA(t)}{dt} = iB(t), \tag{9c}$$

$$\frac{dB(t)}{dt} = iE''(a(t))A(t), \tag{9d}$$

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

One can show [5] that if $E(x)$ satisfies conditions (3) then there is a unique solution $a(t), \eta(t), A(t), B(t)$ to (9) satisfying the following conditions:

$$\lim_{t \to \infty} \|A(t) - A_+ - iB_+ t\| = 0, \tag{10a}$$

$$\lim_{t \to \infty} \|B(t) - B_+\| = 0, \tag{10b}$$

$$\lim_{t \to \infty} |a(t) - a_+ - \eta_+ t| = 0 \,, \tag{10c}$$

$$\lim_{t \to \infty} |\eta(t) - \eta_+| = 0 \,. \tag{10d}$$

Finally we define:

$$S(t) = \int_0^t \left(\frac{\eta(s)^2}{2} - E(a(s)) \right) ds \,. \tag{11}$$

Here the first two equations (9a, b) are just the Newton's equations with $a(t)$ being the classical path and $\eta(t)$ – the classical momentum. Matrices $A(t)$ and $B(t)$ describe "spreading" of the wave packet in position and momentum space. Conditions (10) mean that in the limit $t \to \infty$ the dynamics of the interacting clusters approaches that of the noninteracting ones.

3. Properties of the Electronic Hamiltonian

Usually the electronic hamiltonian is defined by formal substitution $\varepsilon = 0$ in (1). Then it becomes an operator acting on functions of "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 $h_\varepsilon(\zeta)$ defined by (6). This is the result of our choice of coordinates. By using the Jacobi coordinates we avoided so-called Hughes–Eckart terms 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 $v_k^{(i)}$ on ε can be easily taken care of. One can see that $D(\varepsilon)$ is relatively bounded with respect to h_D and therefore it is a regular perturbation. It causes the eigenvalues and eigenvectors of $h_D + \varepsilon^4 D(\varepsilon) + V_{D,\varepsilon}(\zeta, \xi)$ 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 behavior of the eigenvalues $E_\varepsilon(\zeta)$ 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 $E_\varepsilon(\zeta)$ of $h_\varepsilon(\zeta)$ which tends to E_D as $|\zeta| \to \infty$ and $\varepsilon \to 0$. We denote the corresponding eigenvector by $\varphi_\varepsilon(\xi, \zeta)$.

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

Lemma 1. *Assume that the potentials satisfy (3). Let $P_\varepsilon(\zeta)$ be the projection onto the eigenvector $\varphi_\varepsilon(\xi, \zeta)$ associated with the eigenvalue $E_\varepsilon(\zeta)$ of $h_\varepsilon(\zeta)$. Then:*

$$\||\partial_{\zeta^i} P_\varepsilon(\zeta) \varphi_D(\xi)\|_{L^2(\mathbb{R}^{3N}, d\xi)} \leqq C_1 (1 + |\zeta|)^{-2-\delta} \,, \tag{12a}$$

$$\||\partial_{\zeta^i} \partial_{\zeta^j} P_\varepsilon(\zeta) \varphi_D(\xi)\|_{L^2(\mathbb{R}^{3N}, d\xi)} \leqq C_2 (1 + |\zeta|)^{-3-\delta} \,, \tag{12b}$$

$$\||\partial_{\zeta^i} \partial_{\zeta^j} \partial_{\zeta^k} P_\varepsilon(\zeta) \varphi_D(\xi)\|_{L^2(\mathbb{R}^{3N}, d\xi)} \leqq C_3 (1 + |\zeta|)^{-4-\delta} \,, \tag{12c}$$

uniformly for small ε, where δ is the same constant as in (3).

Proof. a) From:

$$\partial_{\zeta^i} P_\varepsilon(\zeta)\varphi_D = \frac{1}{2\pi i} \int\limits_{|z-E_D|=\gamma} (h_\varepsilon(\zeta) - z)^{-1}(\partial_{\zeta^i} V_{D,\varepsilon})(h_\varepsilon(\zeta) - z)^{-1}\varphi_D dz\,,$$

we get:

$$\|\partial_{\zeta^i} P_\varepsilon(\zeta)\varphi_D\|_{L^2(\mathbb{R}^{3N},d\xi)} \leqq C_4 \int\limits_{|z-E_D|=\gamma} \|(h_\varepsilon(\zeta) - z)^{-1}\|_{\mathrm{op}}\|(\partial_{\zeta^i} V_{D,\varepsilon})g\|_{L^2(\mathbb{R}^{3N},d\xi)}dz$$

$$\leqq C_5 \sup_{|z-E_D|=\gamma} (\|(h_\varepsilon(\zeta) - z)^{-1}\|_{\mathrm{op}}\|(\partial_{\zeta^i} V_{D,\varepsilon})g\|_{L^2(\mathbb{R}^{3N},d\xi)})\,,$$

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

Therefore, conclusion (12a) will be proved if we can show:

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

The eigenvector φ_D decays exponentially so it is in the weighted L^2 space (L^2_μ) for arbitrary μ (i.e. $\|\varphi_D\|_\mu := \|(1 + |\xi|^2)^{\frac{\mu}{2}}\varphi_D(\xi)\|_{L^2(d\xi)} < \infty$). It is proved [14] (see Appendix, Lemma A) 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:

$$\|(1 + |\xi^{(1)}_1|^2)^{\frac{\mu}{2}} \ldots (1 + |\xi^{(2)}_{K^{(2)}}|^2)^{\frac{\mu}{2}} g(\xi^{(1)}_1, \ldots, \xi^{(2)}_{K^{(2)}})\|_{L^2(\mathbb{R}^3,d\xi)} \leqq C_7$$

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

In order to estimate $\|(\partial_{\zeta^i} V_{D,\varepsilon})g\|_{L^2(\mathbb{R}^{3N},d\xi)}$ we split $\partial_{\zeta^i} V_{D,\varepsilon}$ according to (2c). We show calculations for the term where all $\tau'_j s$ are nonzero. In other terms if one or more of $\tau'_j s$ are zero then the corresponding variables $\xi^{(k)}_j$ 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

$$g^1(\xi^{(1)}_2, \ldots, \xi^{(2)}_{K^{(2)}}) := [\int |g(\xi^{(1)}_1, \xi^{(1)}_2, \ldots, \xi^{(2)}_{K^{(2)}})|^2 d^3\xi^{(1)}_1]^{\frac{1}{2}}$$

is in $L^2_\mu(\mathbb{R}^{3N-3}, d\xi^{(1)}_2 \ldots \xi^{(2)}_{K^{(2)}})$. This way we eliminate all the coordinates $\xi^{(k)}_j$ for which $\tau^{(k)}_j = 0$ and we are back to the general situation.

Hence we need to estimate:

$$\left\|\partial_{\zeta_i} V_{mn}\left(\tau(\varepsilon)\zeta + \sum_{k=1}^{K^{(1)}} \tau^{(1)}_k(\varepsilon)\xi^{(1)}_k + \sum_{k=1}^{K^{(2)}} \tau^{(2)}_k(\varepsilon)\xi^{(2)}_k\right) \cdot g(\xi^{(1)}, \xi^{(2)})\right\|_{L^2(\mathbb{R}^{3N},d\xi)}\,. \quad (13)$$

We separate $\xi^{(1)}_1$ in the argument of $\partial_{\zeta_i} V_{mn}$ and call the rest u_1, i.e.:

$$u_1 = \tau(\varepsilon)\zeta + \sum_{k=2}^{K^{(1)}} \tau^{(1)}_k(\varepsilon)\xi^{(1)}_k + \sum_{k=1}^{K^{(2)}} \tau^{(2)}_k(\varepsilon)\xi^{(2)}_k$$

and do the $\xi^{(1)}_1$ integral in (13). Let:

$$B^1_1 = \{y : |u_1 + y| \leqq \kappa|u_1|\}\,,$$

$$B^1_2 = \{y : |u_1 + y| > \kappa|u_1|\}$$

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

$$\|(\partial_{\zeta^i} V_{mn}(u_1 + \tau_1^{(1)}(\varepsilon)\xi_1^{(1)})) \cdot g(\xi)\|_{L^2(\mathbb{R}^3, d\xi_1^{(1)})}$$

$$= \tau_1^{(1)}(\varepsilon)^{-\frac{3}{2}} \|\chi_1^1(y_1)(\partial_{\zeta^i} V_{mn}(u_1 + y_1)) \cdot g(\tau_1^{(1)}(\varepsilon)^{-1} y_1, \xi_2^{(1)}, \ldots, \xi_{K(2)}^{(2)})\|_{L^2(\mathbb{R}^3, dy_1)}$$

$$+ \tau_1^{(1)}(\varepsilon)^{-\frac{3}{2}} \|\chi_2^1(y_1) \cdot (\partial_{\zeta^i} V_{mn}(u_1 + y_1)) \cdot g(\tau_1^{(1)}(\varepsilon)^{-1} y_1, \xi_2^{(1)}, \ldots, \xi_{K(2)}^{(2)})\|_{L^2(\mathbb{R}^3, dy_1)}$$

$$= I_1(u_1) + I_2(u_1).$$

For $I_2(u_1)$ we note:

$$I_2(u_1) \leq \tau_1^{(1)}(\varepsilon)^{-\frac{3}{2}} \|\chi_2^1(y_1) \partial_{\zeta^i} V_{mn}(u_1 + y_1)\|_\infty$$

$$\times \|g(\tau_1^{(1)}(\varepsilon)^{-1} y_1, \xi_2^{(1)}, \ldots, \xi_{K(2)}^{(2)})\|_{L^2(\mathbb{R}^3, dy_1)}$$

$$\leq \tau_1^{(1)}(\varepsilon)^{-\frac{3}{2}} \|\chi_2^1(y_1) \partial_{\zeta^i} V_{mn}(u_1 + y_1)\|_\infty$$

$$\times \|(1 + |\tau_1^{(1)}(\varepsilon)^{-1} y_1|^2)^{\frac{\mu}{2}} g(\tau_1^{(1)}(\varepsilon)^{-1} y_1, \ldots, \xi_{K(2)}^{(2)})\|_{L^2(\mathbb{R}^3, dy_1)}$$

$$\times \|(1 + |\tau_1^{(1)}(\varepsilon)^{-1} y_1|^2)^{-\frac{\mu}{2}}\|_\infty,$$

where $\|\cdot\|_\infty$ denotes the L^∞ norm in variable $\xi_1^{(1)}$. Here $\|(1 + |\tau_1^{(1)}(\varepsilon)^{-1} y_1|^2)^{-\frac{\mu}{2}}\|_\infty = 1$.
Also:

$$g^1(\xi_2^{(1)}, \ldots, \xi_{K(2)}^{(2)}) := \tau_1^{(1)}(\varepsilon)^{-\frac{3}{2}} \|(1 + |\tau_1^{(1)}(\varepsilon)^{-1} y_1|^2)^{\frac{\mu}{2}} g$$

$$\times (\tau_1^{(1)}(\varepsilon)^{-1} y_1, \ldots, \xi_{K(2)}^{(2)})\|_{L^2(\mathbb{R}^3, dy_1)}$$

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

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

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

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:

$$I_1(u_1) = \tau_1^{(1)}(\varepsilon)^{-\frac{3}{2}} \|\chi_1^1(y_1)(\partial_{\zeta^i} V_{mn}(u_1 + y_1)) g(\tau_1^{(1)}(\varepsilon)^{-1} y_1, \xi_2^{(1)}, \ldots, \xi_{K^{(2)}}^{(2)})\|_{L^2(\mathbb{R}^3, dy_1)}$$

$$\leqq \tau_1^{(1)}(\varepsilon)^{-\frac{3}{2}} \|\chi_1^1(y_1)(\partial_{\zeta^i} V_{mn}(u_1 + y_1))\|_\infty$$

$$\times \|\chi_1^1(y_1) g(\tau_1^{(1)}(\varepsilon)^{-1} y_1, \xi_2^{(1)}, \ldots, \xi_{K^{(2)}}^{(2)})\|_{L^2(\mathbb{R}^3, dy_1)}$$

$$\leqq C_9 \tau_1^{(1)}(\varepsilon)^{-\frac{3}{2}} \|\chi_1^1(y_1)(1 + |\tau_1^{(1)}(\varepsilon) y_1|^2)^{-\frac{\mu}{2}} (1 + |\tau_1^{(1)}(\varepsilon)^{-1} y_1|^2)^{\frac{\mu}{2}}$$

$$\times g(\tau_1^{(1)}(\varepsilon)^{-1} y_1, \xi_2^{(1)}, \ldots, \xi_{K^{(2)}}^{(2)})\|_{L^2(\mathbb{R}^3, dy_1)}$$

$$\leqq C_9 \tau_1^{(1)}(\varepsilon)^{-\frac{3}{2}} \|\chi_1^1(y_1)(1 + |\tau_1^{(1)}(\varepsilon)^{-1} y_1|^2)^{-\frac{\mu}{2}}\|_\infty$$

$$\times \|(1 + |\tau_1^{(1)}(\varepsilon) y_1|^2)^{\frac{\mu}{2}} g(\tau_1^{(1)}(\varepsilon)^{-1} y_1, \xi_2^{(1)}, \ldots, \xi_{K^{(2)}}^{(2)})\|_{L^2(\mathbb{R}^3, dy_1)}$$

$$\leqq C_{10}(1 + \tau_1^{(1)}(\varepsilon)^{-2} |u_1|^2 (1 - \kappa^2))^{-\frac{\mu}{2}} g^1(\xi_2^{(1)}, \ldots, \xi_{K^{(2)}}^{(2)}) \,.$$

One can show that $(1 + \tau_1^{(1)}(\varepsilon)^{-2}(1 - \kappa^2)|u_1|^2)^{-\frac{\mu}{2}}$ 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:

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

Then:

$$\|(\partial_{\zeta^i} V_{mn}(u_1 + \tau_1^{(1)}(\varepsilon)\xi_1^{(1)})) g(\xi_1^{(1)}, \ldots, \xi_{K^{(2)}}^{(2)})\|_{L^2(\mathbb{R}^3, d\xi_1^{(1)})}$$

$$\leqq C_{12}(1 + |u_1|)^{-2-\delta} g^1(\xi_2^{(1)}, \ldots, \xi_{K^{(2)}}^{(2)}) \,.$$

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

$$B_1^2 = \{y : |u_2 + y| \leqq \kappa |u_2|\} \,,$$

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

where

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

After N steps we obtain:

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

$$\leqq C_{13}(1 + |\zeta|)^{-2-\delta} \,.$$

To prove parts b) and c) we compute derivatives explicitly. In part b), for example, we get:

$$\partial_{\zeta^i}\partial_{\zeta^j}P_\varepsilon(\zeta)\varphi_D(\xi)$$

$$= -\frac{1}{2\pi i}\Bigg[\int\limits_{|z-E_D|=\gamma}(h_\varepsilon(\zeta)-z)^{-1}(\partial_{\zeta^j}V_{D,\varepsilon})(h_\varepsilon(\zeta)-z)^{-1}$$

$$\times(\partial_{\zeta^i}V_{D,\varepsilon})(h_\varepsilon(\zeta)-z)^{-1}\varphi_D(\xi)dz$$

$$-\int\limits_{|z-E_D|=\gamma}(h_\varepsilon(\zeta)-z)^{-1}(\partial_{\zeta^i}\partial_{\zeta^j}V_{D,\varepsilon})(h_\varepsilon(\zeta)-z)^{-1}\varphi_D(\xi)dz$$

$$+\int\limits_{|z-E_D|=\gamma}(h_\varepsilon(\zeta)-z)^{-1}(\partial_{\zeta^i}V_{D,\varepsilon})(h_\varepsilon(\zeta)-z)^{-1}$$

$$\times(\partial_{\zeta^j}V_{D,\varepsilon})(h_\varepsilon(\zeta)-z)^{-1}\varphi_D(\xi)dz\Bigg].$$

The middle term can be handled as in part a). To estimate the remaining two terms we write $V_{D,\varepsilon}$ as in (2c). Below we outline the procedure for a generic term V_{mn}. We rewrite the integrand as:

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

$$\times\left(1+\left|\tau(\varepsilon)\zeta+\sum_{k=1}^{K^{(1)}}\tau_k^{(1)}(\varepsilon)\xi_k^{(1)}+\sum_{k=1}^{K^{(2)}}\tau_k^{(2)}(\varepsilon)\xi_k^{(2)}\right|\right)^{2+\delta}$$

$$\times(h_\varepsilon(\zeta)-z)^{-1}(\partial_{\zeta^i}V_{mn})(h_\varepsilon(\zeta)-z)^{-1}\varphi_D(\xi).$$

Here $(h_\varepsilon(\zeta)-z)^{-1}\varphi_D(\xi)\in L_\mu^2$ by Lemma A in the Appendix. If we denote:

$$g(\xi)=\left(1+\left|\tau(\varepsilon)\zeta+\sum_{k=1}^{K^{(1)}}\tau_k^{(1)}(\varepsilon)\xi_k^{(1)}+\sum_{k=1}^{K^{(2)}}\tau_k^{(2)}(\varepsilon)\xi_k^{(2)}\right|\right)^{2+\delta}(h_\varepsilon(\zeta)-z)^{-1}.$$

$$\times(\partial_{\zeta^i}V_{mn})(h_\varepsilon(\zeta)-z)^{-1}\varphi_D(\xi),$$

then Lemma B shows that $g(\xi)$ is also in L_μ^2. Thus the proof of b) is reduced to showing that:

$$\left\|\partial_{\zeta^j}V_{mn}\left(\tau(\varepsilon)\zeta+\sum_{k=1}^{K^{(1)}}\tau_k^{(1)}(\varepsilon)\xi_k^{(1)}+\sum_{k=1}^{K^{(2)}}\tau_k^{(2)}(\varepsilon)\xi_k^{(2)}\right)\right.$$

$$\left.\times\left(1+\left|\tau(\varepsilon)\zeta+\sum_{k=1}^{K^{(1)}}\tau_k^{(1)}(\varepsilon)\xi_k^{(1)}+\sum_{k=1}^{K^{(1)}}\tau_k^{(2)}(\varepsilon)\xi_k^{(2)}\right|\right)^{-2-\delta}g(\xi)\right\|_{L^2(\mathbb{R}^{3N},d\xi)}$$

$$\leqq C_{13}(1+|\zeta|)^{-3-\delta}.$$

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). $\square$

Remark. Martinez et al. [12] give a much shorter proof for a similar result (Theorem 2.2). However, we will later refer to our proof several times, hence we present the estimates in detail.

Corollary 2.
$$|\langle \varphi_D, P_\varepsilon(\zeta)\varphi_D \rangle - 1| \leq C_1\varepsilon^4 + \theta(\zeta),$$

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

and δ is as in (3).

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

$$P_\varepsilon(\zeta)\varphi_D = P_D\varphi_D + \frac{1}{2\pi i} \int_{|z-E_D|=\gamma} (h_\varepsilon(\zeta) - z)^{-1}[\varepsilon^4 D(\varepsilon)](h_D(\zeta) - z)^{-1}\varphi_D dz$$

$$+ \frac{1}{2\pi i} \int_{|z-E_D|=\gamma} (h_\varepsilon(\zeta) - z)^{-1} V_{D,\varepsilon} \cdot (h_D(\zeta) - z)^{-1}\varphi_D dz.$$

The last term can be estimated as above in part a) of the proof of Lemma 1, yielding:

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

In the middle term we note that $D(\varepsilon)$ is relatively bounded with respect to h_D, so:

$$\left\| \frac{\varepsilon^4}{2\pi i} \int_{|z-E_D|=\gamma} (h_\varepsilon - z)^{-1} D(\varepsilon)(h_D - z)^{-1}\varphi_D dz \right\|$$

$$\leq \frac{\varepsilon^4}{2\pi} \int_{|z-E_D|=\gamma} \|(h_\varepsilon - z)^{-1}\|_{op}\|D(\varepsilon)(h_D - z)^{-1}\varphi_D\| dz$$

$$\leq C_4\varepsilon^4 \int_{|z-E_D|=\gamma} (a\|h_D(h_D - z)^{-1}\varphi_D\| + b\|(h_D - z)^{-1}\varphi_D\|) dz$$

$$\leq C_5\varepsilon^4.$$

$\square$

Now we denote:

$$\tilde{E}_\varepsilon(\zeta) = E_\varepsilon(\zeta) - E_D = \frac{\langle P_\varepsilon(\zeta)\varphi_D(\xi), (\varepsilon^4 D(\varepsilon) + V_{D,\varepsilon})\varphi_D(\xi) \rangle}{\langle \varphi_D(\xi), P_\varepsilon(\zeta)\varphi_D(\xi) \rangle}. \tag{14}$$

Using Lemma 1 and the above corollary we can bound the corrections to the energy level.

Lemma 3.
$$|\tilde{E}_\varepsilon^{(\alpha)}(\zeta)| \leq C(1 + |\zeta|)^{-1-\alpha-\delta}$$

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

Proof. We use estimates:

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

for $\alpha = 1, 2, 3$, 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 1, part a).

Also, as mentioned above, $D(\varepsilon)$ is relatively bounded with respect to h_D.

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

$$\partial_{\zeta^i}\tilde{E}_\varepsilon(\zeta) = \frac{\langle \partial_{\zeta^i}P_\varepsilon(\zeta)\varphi_D(\xi), (\varepsilon^4 D(\varepsilon) + V_{D,\varepsilon})\varphi_D(\xi)\rangle + \langle P_\varepsilon(\zeta)\varphi_D(\xi), (\partial_{\zeta^i}V_{D,\varepsilon})\varphi_D(\xi)\rangle}{\langle \varphi_D(\xi), P_\varepsilon(\zeta)\varphi_D(\xi)\rangle}$$

$$- \frac{\langle P_\varepsilon(\zeta)\varphi_D(\xi), (\varepsilon^4 D(\varepsilon) + V_{D,\varepsilon})\varphi_D(\xi)\rangle \langle \varphi_D(\xi), \partial_{\zeta^i}P_\varepsilon(\zeta)\varphi_D(\xi)\rangle}{(\langle \varphi_D(\xi), P_\varepsilon(\zeta)\varphi_D(\xi)\rangle)^2}.$$

Then we use the Schwarz lemma, Lemma 1, Corollary 2 and the above estimates on $\|V_{D,\varepsilon}^{(\alpha)}\varphi_D\|_{L^2(d\xi)}$. $\square$

Remark. By a similar argument one can show:

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

4. The Born–Oppenheimer Approximation

Our goal, as mentioned in the introduction, is to construct the approximate solution to the time-dependent Schrödinger equation, which is asymptotic to the exact one in the leading order. We begin by stating our main result.

First fix 3×3 matrices A_+, B_+ and vectors $a_+, \eta_+ \in \mathbb{R}^3, \eta_+ \neq 0$. By Lemma 3 and [5] there exists a solution $a_\varepsilon(t), \eta_\varepsilon(t), A_\varepsilon(t), B_\varepsilon(t)$ to the system (9) satisfying the asymptotic conditions (10). Then we have:

Theorem. *Let H be defined by Eq. (1),(2). Assume the potentials satisfy (3). Also assume the conditions on E_D and $E_\varepsilon(\zeta)$ mentioned in the previous section are satisfied. Let $a_\varepsilon(t), \eta_\varepsilon(t), A_\varepsilon(t), B_\varepsilon(t)$ be as above. Then the function:*

$$\psi_\varepsilon(\xi, \zeta, t) = e^{\frac{iS(t)}{\varepsilon^2}} \varphi(A_\varepsilon(t), B_\varepsilon(t), \varepsilon^2, a_\varepsilon(t), \eta_\varepsilon(t), \zeta)$$

$$\times [\varphi_\varepsilon(\xi, \zeta) + i\varepsilon^2 r(\zeta)\eta_\varepsilon(t) \cdot \nabla_\zeta \varphi_\varepsilon(\xi, \zeta)], \qquad (15)$$

where $r(\zeta)$ is the reduced resolvent of $h_\varepsilon(\zeta)$ at $E_\varepsilon(\zeta)$, is the 0-th order asymptotic expansion of the solution to equation:

$$i\varepsilon^2 \frac{\partial \Psi(\xi, \zeta, t)}{\partial t} = \left[-\frac{\varepsilon^4}{2}\Delta_\zeta + h_\varepsilon(\zeta) \right] \Psi(\xi, \zeta, t), \qquad (16)$$

i.e. the following holds:

$$\left\| e^{-\frac{itH}{\varepsilon^2}} \psi_\varepsilon(\xi, \zeta, 0) - \psi_\varepsilon(\xi, \zeta, t) \right\| \leqq C\varepsilon \qquad (17)$$

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

Our main tool will be the following simple lemma [7]:

Lemma 4. *Let $\Psi(t)$ be a differentiable vector-valued function, whose values belong to the domain of H for all $t \in [0, \infty)$. If Ψ satisfies:*

$$i\varepsilon^2 \dot{\Psi} = H\Psi + \lambda(t),$$ (18)

where

$$\|\lambda(t)\| \leqq F(t)\varepsilon^3$$ (19)

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

$$\|e^{\frac{itH}{\varepsilon^2}} \Psi(0) - \Psi(t)\| \leqq C\varepsilon,$$ (20)

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

To prove our theorem we first formally construct the candidate for the approximate solution. Then we substitute it to Eq. (18) and calculate the error term $\lambda(t)$. Finally we show that the error term satisfies (19) and the application of Lemma 4 finishes the proof.

The details of these formal calculations have been shown in Sect. 3 of [7]. Here we only briefly describe the method used and state the results.

We use the so-called multiple scales technique to separate the adiabatic and semiclassical aspects of the problem. It consists in seeking the solution $\Phi(\xi, x, y, t)$ of the higher dimensional problem defined by a formal change of variables from (ξ, ζ, t) to (ξ, x, y, t), where $x = \zeta, y = \dfrac{\zeta - a_\varepsilon(t)}{\varepsilon}$, in the equation:

$$i\varepsilon^2 \frac{\partial \Psi(\xi, \zeta, t)}{\partial t} = \left[-\frac{\varepsilon^4}{2}\Delta_\zeta + h_\varepsilon(\zeta) \right] \Psi(\xi, \zeta, t).$$ (21)

The result is:

$$i\varepsilon^2 \frac{\partial \Phi}{\partial t} = \left[-\frac{\varepsilon^4}{2}\Delta_x - \varepsilon^3 \nabla_x \cdot \nabla_y - \frac{\varepsilon^2}{2}\Delta_y \right.$$

$$\left. + i\varepsilon\eta_\varepsilon(t) \cdot \nabla_y + E_\varepsilon(a_\varepsilon(t) + \varepsilon y) + h_\varepsilon(x) - E_\varepsilon(x) \right] \Phi.$$ (22)

We formally solve (22) assuming the solution in the form of power series in ε and collecting terms of the same order in ε. This generates a formal solution and finally, substituting back $x = \zeta, y = \dfrac{\zeta - a_\varepsilon(t)}{\varepsilon}$ we recover $\Psi(\xi, \zeta, t)$ – the formal solution to (21). The explicit formulae can be found in [7].

For our purposes it is important to note that the only terms contributing to the 0-th order approximation are:

$$\Psi_{0,\varepsilon} = \varepsilon^{-\frac{3}{2}} \varphi(A_\varepsilon(t), B_\varepsilon(t), 1, 0, 0, y)\varphi_\varepsilon(\xi, x),$$ (23a)

$$\Psi_{2,\varepsilon}^\perp = ir(x)\eta_\varepsilon(t) \cdot \nabla_x \Psi_{0,\varepsilon},$$ (23b)

where $r(x)$ is the reduced resolvent of $h_\varepsilon(x)$ at $E_\varepsilon(x)$:

$$r(x) = [h_\varepsilon(x) - E_\varepsilon(x)]^{-1}(1 - P_\varepsilon(x))$$

and $P_\varepsilon(x)$ is the spectral projector associated with the eigenvalue $E_\varepsilon(x)$. The function:

$$\Phi_\varepsilon(\xi, x, y, t) = e^{i\frac{S(t)}{\varepsilon^2}} e^{i\frac{\eta_\varepsilon(t) \cdot y}{\varepsilon}} (\Psi_{0,\varepsilon} + \varepsilon^2 \Psi_{2,\varepsilon}^\perp)$$ (24)

will serve as a candidate for our approximate solution. Note that upon returning to our original variables ξ, ζ, t the function (24) becomes (15).

5. Proof of the Theorem

We remain in the multiple scales framework and calculate the error terms in Eq. (18) using the function (24). The result is:

$$
\begin{aligned}
\lambda(t) = e^{\frac{iS(t)}{\varepsilon^2}} e^{\frac{i\eta_\varepsilon(t)\,\cdot\,y}{\varepsilon}} \Big\{ & \varepsilon^3 \nabla_y f_{0,\varepsilon}(y) \cdot \nabla_x \varphi_\varepsilon(\xi, x) \\
& + \varepsilon^4 \Big[f_{0,\varepsilon}(y) r(x) E'_\varepsilon(a_\varepsilon(t)) \cdot \nabla_x \varphi_\varepsilon(\xi, x) + \frac{1}{2} f_{0,\varepsilon}(y) \Delta_x \varphi_\varepsilon(\xi, x) \\
& \quad - f_{0,\varepsilon}(y) \eta_\varepsilon(t) \cdot \nabla_x \varphi_{1,\varepsilon}(\xi, x) \Big] \\
& + \varepsilon^5 i \nabla_y f_{0,\varepsilon}(y) \cdot \nabla_x \varphi_{1,\varepsilon}(\xi, x) \\
& + \varepsilon^6 \frac{i}{2} f_{0,\varepsilon}(y) \Delta_x \varphi_{1,\varepsilon}(\xi, x) \\
& - \Big[E_\varepsilon(a_\varepsilon(t) + \varepsilon y) - E_\varepsilon(a_\varepsilon(t)) - \varepsilon y E'_\varepsilon(a_\varepsilon(t)) - \frac{\varepsilon^2 y^2}{2} E''_\varepsilon(a_\varepsilon(t)) \Big] \\
& \times [f_{0,\varepsilon}(y) \varphi_\varepsilon(\xi, x) + i\varepsilon^2 f_{0,\varepsilon}(y) \varphi_{1,\varepsilon}(\xi, x)] \Big\},
\end{aligned}
\tag{25}
$$

where:

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

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

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

Lemma 5. *Let $\omega(x)$ be a function $\mathbb{R}^3 \to \mathbb{R}$ satisfying $|\omega(x)| \leqq (1 + |x|)^{-1-\delta}$, and let $f_{0,\varepsilon}(y)$ be as defined above. Then:*

$$
\left\| f_{0,\varepsilon}\left(\frac{\zeta - a_\varepsilon(t)}{\varepsilon} \right) \omega(\zeta) \right\|_{L^2(\mathbb{R}^3, d\zeta)} \leqq F(t)
\tag{26}
$$

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

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

$$
B_1 = \{ \zeta : |\zeta - a_\varepsilon(t)| \leqq \mu |a_\varepsilon(t)| \},
$$

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

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

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

By the Hölder inequality:

$$
I_1(t) = \left\| \chi_1(\zeta) \omega(\zeta) f_{0,\varepsilon}\left(\frac{\zeta - a_\varepsilon(t)}{\varepsilon} \right) \right\|_2 \leqq \| \chi_1(\zeta) \omega(\zeta) \|_\infty \left\| f_{0,\varepsilon}\left(\frac{\zeta - a_\varepsilon(t)}{\varepsilon} \right) \right\|_2.
$$

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

For I_2 we have:

$$I_2(t) = ||\chi_2(\zeta)e^{-\frac{1}{4\varepsilon^2}|A_\varepsilon(t)^{-1}(\zeta - a_\varepsilon(t))|^2}||_\infty ||\omega(\zeta)\pi^{-\frac{3}{4}}\varepsilon^{-\frac{3}{2}}$$

$$\times |\det A_\varepsilon(t)|^{-\frac{1}{2}}e^{-\frac{1}{4\varepsilon^2}|A_\varepsilon(t)^{-1}(\zeta - a_\varepsilon(t))|^2}||_2$$

$$\leqq ||\chi_2(\zeta)e^{-\frac{1}{4\varepsilon^2}|A_\varepsilon(t)^{-1}(\zeta - a_\varepsilon(t))|^2}||_\infty ||\omega||_q ||\pi^{-\frac{3}{4}}\varepsilon^{-\frac{3}{2}}$$

$$\times |\det A_\varepsilon(t)|^{-\frac{1}{2}}e^{-\frac{1}{4\varepsilon^2}|A_\varepsilon(t)^{-1}(\zeta - a_\varepsilon(t))|^2}||_p ,$$

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:

$$||\pi^{-\frac{3}{4}}\varepsilon^{-\frac{3}{2}}|\det A_\varepsilon(t)|^{-\frac{1}{2}}e^{-\frac{1}{4\varepsilon^2}|A_\varepsilon(t)^{-1}(\zeta - a_\varepsilon(t))|^2}||_p$$

$$= C_3\varepsilon^{-3(\frac{1}{2}-\frac{1}{p})}|\det A_\varepsilon(t)|^{-(\frac{1}{2}-\frac{1}{p})}$$

$$= C_3\varepsilon^{-\frac{3}{q}}|\det A_\varepsilon(t)|^{-\frac{1}{q}} .$$

The first factor is bounded by:

$$e^{-\frac{1}{4\varepsilon^2}||A_\varepsilon(t)||^{-2}\mu^2|a_\varepsilon(t)|^2}$$

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

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

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

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

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

Remark. A similar conclusion holds if we multiply $f_{0,\varepsilon}$ by any polynomial in y.

We will further need this bound for $f_{0,\varepsilon}$ as well as for $\nabla_y f_{0,\varepsilon}$, thus we sketch the proof for the latter case below. We keep notation of the proof of Lemma 5.

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

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

Then:

$$\left|\left|\nabla_y f_{0,\varepsilon}\left(\frac{\zeta - a_\varepsilon(t)}{\varepsilon}\right)\right|\right|_2 = C_7\varepsilon^{-\frac{3}{2}}(\det A_\varepsilon(t))^{-\frac{1}{2}}$$

$$\left(\int \left|B_\varepsilon(t)A_\varepsilon(t)^{-1}\frac{\zeta - a_\varepsilon(t)}{\varepsilon}\right|^2 e^{-\frac{1}{\varepsilon^2}\langle \zeta - a_\varepsilon(t), A_\varepsilon(t)^{*-1}A_\varepsilon(t)^{-1}(\zeta - a_\varepsilon(t))\rangle}d^3\zeta\right)^{\frac{1}{2}} . \tag{27}$$

After change of variables to $u = A_\varepsilon(t)^{-1} \dfrac{\zeta - a_\varepsilon(t)}{\varepsilon}$, we see that (27) is bounded by $C_8 \|B_\varepsilon(t)\|_{\mathrm{op}}$. Since the operator norm of matrix $B_\varepsilon(t)$ tends to a constant as $t \to \infty$ we get for I_1 a bound similar to that in the proof of Lemma 5. The estimate for I_2 is essentially the same as in Lemma 5.

Lemma 6. *Assume $h_\varepsilon(x), E_\varepsilon(x)$ are as described in the introduction. 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 $E_\varepsilon(x) \in B(E_D, \frac{\beta}{2})$ and $h_\varepsilon(x)$ has no other eigenvalues in $B(E_D, \beta)$. Then the reduced resolvent $(h_\varepsilon(x) - E_\varepsilon(x))^{-1}(1 - P_\varepsilon(x))$ and its first and second derivatives are bounded uniformly in x.*

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

If we restrict it 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.:

$$\|(h_\varepsilon(x) - E_\varepsilon(x))^{-1}(1 - P_\varepsilon(x))\|_{\mathrm{op}} \leqq \sup_{|z - E_D| = \frac{\beta}{2}} \|(h_\varepsilon(x) - z)^{-1}(1 - P_\varepsilon(x))\|_{\mathrm{op}}$$

$$\leqq \sup_{|z - E_D| = \frac{\beta}{2}} \|(h_\varepsilon(x) - z)^{-1}\|_{\mathrm{op}} \leqq \frac{2}{\beta}$$

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

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

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

and compute the derivative:

$$\partial_{x^i}((h_\varepsilon(x) - z)^{-1}(1 - P_\varepsilon(x))) = -(\partial_{x^i} P_\varepsilon(x))(h_\varepsilon(x) - z)^{-1}(1 - P_\varepsilon(x))$$

$$- (1 - P_\varepsilon(x))(h_\varepsilon(x) - z)^{-1}(\partial_{x^i} V_{D,\varepsilon}(x))(h_\varepsilon(x) - z)^{-1}(1 - P_\varepsilon(x))$$

$$- (h_\varepsilon(x) - z)^{-1}(1 - P_\varepsilon(x))(\partial_{x^i} P_\varepsilon(x)). \tag{28}$$

Our assumptions on $V_{D,\varepsilon}$ guarantee that the operator norm of $\partial_{x^i} V_{D,\varepsilon}$ is a constant. To analyze $\partial_{x^i} P_\varepsilon(x)$ we write:

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

$$\leqq C \sup_{|z - E_D| = \frac{\beta}{2}} \|(h_\varepsilon(x) - z)^{-1}\|^2 \|\partial_{x^i} V_{D,\varepsilon}(x)\|$$

$$\leqq C'$$

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 (28) as:

$$\partial_{x^i}((h_\varepsilon(x) - z)^{-1}(1 - P_\varepsilon(x))) = -(\partial_{x^i}P_\varepsilon(x))(1 - P_\varepsilon(x))(h_\varepsilon(x) - z)^{-1}(1 - P_\varepsilon(x))$$

$$- (1 - P_\varepsilon(x))(h_\varepsilon(x) - z)^{-1}(1 - P_\varepsilon(x))(\partial_{x^i}V_{D,\varepsilon}(x))$$

$$\times (1 - P_\varepsilon(x))(h_\varepsilon(x) - z)^{-1}(1 - P_\varepsilon(x))$$

$$- (1 - P_\varepsilon(x))(h_\varepsilon(x) - z)^{-1}(1 - P_\varepsilon(x))(\partial_{x^i}P_\varepsilon(x))$$

and compute the second derivative of $P_\varepsilon(x)$ explicitly. It consists of terms containing products of the reduced resolvent, derivatives of $V_{D,\varepsilon}$ and derivatives of $P_\varepsilon(x)$ up to the second order. All of these factors, except $\partial_{x^i}\partial_{x^j}P_\varepsilon(x)$, have been shown to be bounded uniformly in x. To conclude the same for $\partial_{x^i}\partial_{x^j}P_\varepsilon(x)$ we proceed exactly the same way as we did to show boundedness of the first derivative of $P_\varepsilon(x)$. Finally we collect all these bounds to prove the last conclusion of the lemma. $\square$

Now we have tools to estimate all but the last term in (25). We first look at the x-dependent factors. Recall that the normalized eigenfunction $\varphi_\varepsilon(\xi,x)$ of $h_\varepsilon(x)$ is of the form:

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

By explicit calculations and using Lemma 1 and Corollary 2 we conclude that:

$$\|\partial_{x^i}\varphi_\varepsilon(\xi,x)\| \leq C(1 + |x|)^{-2-\delta} . \tag{29}$$

We can also use Lemma 1 to show similar bounds on the second and third derivatives of $\varphi_\varepsilon(\xi,x)$.

Combining (29) (and corresponding bounds for higher derivatives of $\varphi_\varepsilon(\xi,x)$) with Lemma 6 we see that the x-dependent terms in (25) are the products of $|\eta_\varepsilon(t)|$ and functions satisfying the hypothesis of Lemma 5. Here we return to our original variables by putting $x = \zeta, y = \dfrac{\zeta - a(t)}{\varepsilon}$. By Lemma 5 and asymptotics of $\eta_\varepsilon(t)$ 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 $E_\varepsilon'(a(t))$ appearing in one of the terms. We need to show that this factor remains bounded as $t \to \infty$. Lemma 3 says that it behaves even more nicely – it decays to 0.

To estimate the last term in (25) we use (14). Then, with an obvious abuse of notation, this term becomes:

$$\left[\tilde{E}_\varepsilon(a(t) + \varepsilon y) - \tilde{E}_\varepsilon(a(t)) - \varepsilon y \cdot \tilde{E}_\varepsilon'(a(t)) - \frac{\varepsilon^2 y^2}{2}\tilde{E}_\varepsilon''(a(t))\right]$$

$$\times [f_{0,\varepsilon}(y)\varphi_\varepsilon(\xi,x) + i\varepsilon^2 f_{0,\varepsilon}(y)\varphi_{1,\varepsilon}(\xi,x)] . \tag{30}$$

We note that $\|\varphi_\varepsilon(\xi,x) + i\varepsilon^2\varphi_{1,\varepsilon}(\xi,x)\|_{L^2(d\xi)}$ is a bounded function of x. Also by Lemma 3 we know that $\tilde{E}_\varepsilon$ satisfies the hypothesis of Lemma 3.2 of [5]. This shows that the $L^2(d\zeta)$-norm of (30) is bounded by $F(t)\varepsilon^3$ for some $F \in L^1(\mathbb{R}, dt)$. Application of Lemma 4 concludes the proof. $\square$

Appendix

Lemma A. *Let V be a potential satisfying (3a, b), $H_0 = -\Delta$. Then for $z \notin \sigma(H_0 + V)$ the resolvent $(H_0 + V - z)^{-1}$ is a bounded operator from L_μ^2 to L_μ^2 for arbitrary μ.*

Proof. The proof for $0 < \mu \le 1$ and $V = 0$ can be found in [14], p. 170. Here we outline the general inductive argument. This will also make it clear how one can generalize this result to obtain Lemma B below.

We want to show:

if

$$(H_0 + V - z)^{-1} \text{ is bounded } L_n^2 \to L_n^2$$

$$\text{and } \partial_i (H_0 + V - z)^{-1} \text{is bounded } L_n^2 \to L_n^2 , \tag{A1}$$

then

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

$$\text{are bounded } L_{n+\delta}^2 \to L_{n+\delta}^2 \text{ for } 0 < \delta \le 1 . \tag{A2}$$

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

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:

$$||[R, \rho^\delta]\Psi|| \le \text{const}||\Psi||$$

for any $\Psi \in L^2$. Then we conclude:

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

$$\le ||R\rho^\delta \Psi|| + ||[R, \rho^\delta]\Psi|| \le \text{const}||\Psi||_\delta ,$$

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

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

Similarly:

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

The first term on the r.h.s. is bounded by $\text{const}||\rho^\delta \Psi||$ 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:

$$||[\rho^\delta, \partial_i R]\Psi|| \le \text{const}||\Psi|| \le \text{const}||\Psi||_\delta .$$

Thus the second hypothesis in (A1) 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.

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

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

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

Thus this statement follows from a) and b).

Now we show the implication $(A1) \Rightarrow (A2)$.

Let's assume (A1). Then:

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

The first term is bounded on L_n^2 by hypothesis. In the second term we expand the commutator as in part a). By assumption $R, \partial_i R$ are bounded on L_n^2. 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 $L_n^2 \to L_n^2$. Thus:

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

i.e. the first conclusion in (A2) holds.

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

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

and expand the commutator on the r.h.s. as in b). Then the second conclusion in (A2) follows from the induction assumptions.

$\square$

For our purposes we also need:

Lemma B. *Under similar assumptions the operator*:

$$\left(1 + \left|\tau(\varepsilon)x + \sum_{k=1}^{K} \tau_k^{(1)}(\varepsilon)\xi_k^{(1)} + \sum_{k=1}^{L} \tau_k^{(2)}(\varepsilon)\xi_k^{(2)}\right)\right|\right)^{2+\delta}(h_\varepsilon(x) + z)^{-1}$$

$$\left(1 + \left|\tau(\varepsilon)x + \sum_{k=1}^{K} \tau_k^{(1)}(\varepsilon)\xi_k^{(1)} + \sum_{k=1}^{L} \tau_k^{(2)}(\varepsilon)\xi_k^{(2)}\right)\right|\right)^{-2-\delta},$$

where $h_\varepsilon(x)$ is given by (6), is bounded from L_μ^2 to L_μ^2 for arbitrary μ.

Here we used the same notation as throughout the entire paper. Proof of this lemma can be obtained by mimicking the proof of Lemma A.

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