

Time-Dependent Perturbation and the Born-Oppenheimer Approximation

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(ABSTRACT)

We discuss the physical problem of a molecule interacting with an electromagnetic field pulse and model the problem using a time-dependent perturbation of the Born-Oppenheimer approximation to the Schrödinger equation. Using previous results that develop asymptotic series solutions in the Born-Oppenheimer parameter ϵ , we derive a formal Dyson series expansion in the perturbation parameter μ , which is proportional to the electromagnetic field strength. We then prove that this series is asymptotically accurate in both parameters, provided that the Hamiltonian for the electrons has purely discrete spectrum. Under more general hypotheses, we show that the series is accurate to first order in μ , and that it is accurate to one higher order if we place conditions on the abruptness of the EM pulse. We also show how this series development provides a justification for the Franck-Condon factors in the case of a diatomic molecule.

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Dedication

To my loving parents, whose support and encouragement have made my greatest educational goal a reality.

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Chapter 1

Introduction

Physicists have long been familiar with the process by which an atom, when illuminated by electromagnetic radiation, can undergo an electron energy-level transition. When the frequency of the incoming light is such that the energy of a photon is exactly equal to the energy gap between electron energy levels, the electron can be excited from one level to another. At typical light intensities, an impinging photon of an energy that does not match an atomic energy level gap has only a small chance of being absorbed and causing an electron transition.

Only when the intensity of the electromagnetic radiation is high enough so that it subjects the atom to an electric field comparable in strength to the internal electric field created by its constituent particles is there a significant possibility of multiple photon transitions. In a multiple photon transition, the large field intensity allows two or more photons of the “wrong” frequency to interact with the electron on an extremely short time scale, thereby allowing the photons to “combine forces” and cause an electron transition to an allowed energy state. In other words, the Heisenberg uncertainty principle allows the electron to remain in a forbidden energy state only for an amount of time $\Delta t \lesssim \hbar/\Delta E$, where ΔE is the difference between the forbidden energy and an allowed energy level. Hence the intensity of the electric field must cause multiple photons to interact with the electron during this

period. The needed field strength is on the order of 10^{11} V/m, and can be achieved in the laboratory through very intense laser pulses [13].

In this dissertation we study the quantum physics of a molecule subjected to a very short laser pulse of the type described above, but we restrict attention to a pulse of weak intensity. This particular physical system has been utilized in a very high profile experimental application. The 1999 Nobel Prize in Chemistry was awarded to Dr. Ahmed Zewail of Caltech for his foundational work in femtochemistry [14]. Zewail uses laser pulses on the order of 10^{-15} seconds in length to take “snapshots” of the dynamics of molecular formation. A powerful “pump pulse” is used to initiate a molecular reaction, then, a series of “probe pulses” actually allow the observer to study the changing configuration of the molecule as the reaction takes place. The emission spectrum caused by the excitation of a particular molecular configuration by a laser pulse can be calculated using theoretical techniques in quantum mechanics such as those described in this dissertation, so that the experimental data can be interpreted. This dissertation provides rigorous mathematical justification for some common techniques used in studying the physical model used in femtochemistry.

Since the actual equations cannot be solved in closed form, we choose to model the evolution of the molecular motion using the Born-Oppenheimer approximation, which will allow us to find an asymptotic series solution. In the Born-Oppenheimer approximation, we treat the nuclei as extremely massive in comparison with the electrons. The electrons “orbit” the nuclei very rapidly, and hence changes in the nuclear configuration are on a long time scale compared to the electronic motion. This approximation allows us to develop the electronic motion adiabatically—as if the electrons adjust their dynamical state immediately to the relatively slow motion of the nuclei. Thus, if the electrons start in a bound state configuration, they will always occupy that bound state configuration as if the nuclei were fixed.

The electron configuration determines an effective potential in which the nuclei move. Because of the relatively large nuclear mass, we may describe the nuclear motion semiclassically in this effective potential. To illustrate, when we study the Born-Oppenheimer approxima-

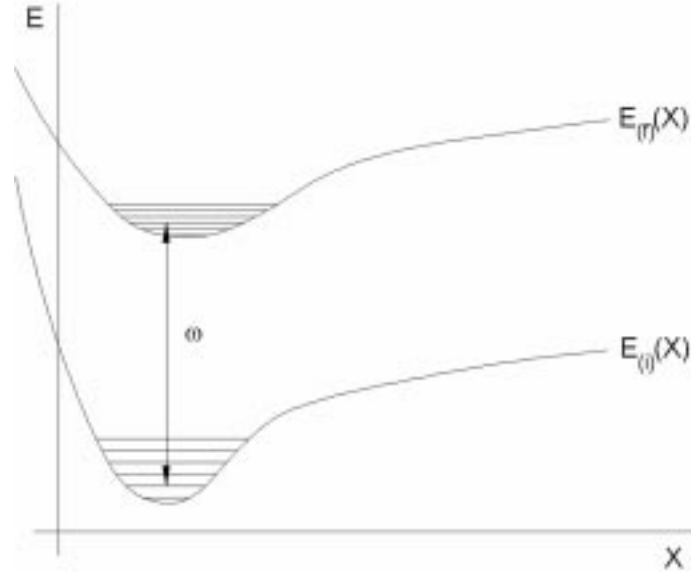


Figure 1.1: One-dimensional diagram of the electron energy levels and nuclear bound states.

tion, the Schrödinger equation looks like

$$i\epsilon^2 \frac{\partial \Psi}{\partial t} = -\frac{\epsilon^4}{2} \frac{\partial^2 \Psi}{\partial X^2} + h(X)\Psi \quad (1.1)$$

where ϵ^4 is a small parameter equal to the ratio of the electron and nuclear mass, $\Psi(X, x, t)$ is the wavefunction depending on nuclear configuration X , electronic configuration x , and time t . By $h(X)$, we denote a family of electron hamiltonians parameterized by the nuclear configuration X . If we have a solution $\Phi(x)$ to the time-independent Schrödinger equation

$$h(X)\Phi(X, x) = E(X)\Phi(X, x) \quad (1.2)$$

that holds for any X , then the approximation says that to leading order

$$\Psi(X, x, t) = \phi(X, t)\Phi(X, x) \quad (1.3)$$

and that $\phi(X, t)$ describes the semiclassical motion of the nuclei as the solution of

$$i\epsilon^2 \frac{\partial \phi}{\partial t} = -\frac{\epsilon^4}{2} \Delta_X \phi + E(X)\phi \quad (1.4)$$

The Born-Oppenheimer approximation has been well-studied by Hagedorn [4] and also by Combes, et al. [2]. Several results have been rigorously demonstrated. Hagedorn has derived

rigorous asymptotic estimates in ϵ for low-lying eigenvalues and bound states in the time-independent case [4, see also [2]]. In the time-dependent Born-Oppenheimer approximation (1.1), Hagedorn has also derived rigorous asymptotics for the propagation of wave packets in situations with and without electron energy level crossings [5]. These last results are discussed in detail in Chapter 3.

The interaction of a dynamical system with an electromagnetic field is commonly studied using one of three types of models. The first is a semiclassical model, whereby the radiation is treated as a classical perturbation to the potential in the Schrödinger equation of the particle. Another model fully quantizes the electromagnetic field, and uses principles from quantum field theory. Intermediate to these is the Floquet state approach described in [3].

We choose to treat the addition of an electromagnetic interaction by the addition of a perturbation consisting of an AC electric field $\mu x \cos(\omega t/\epsilon^2)$ multiplied by a function $f(t/\epsilon^2)$ of compact support to produce a pulse. The factor of ϵ^{-2} scales the electric field oscillation so that this perturbation affects mostly the electrons. In other words, the photon energy is approximately the same size as the energy gap between the different electron levels. Since the energy gaps between nuclear configurations within each electron level are of order ϵ^2 , the perturbation itself should have only a minor effect on the nuclear dynamics. Physically, one expects the most significant change in the nuclear dynamics to occur via the electron energy level transition, which alters the effective potential felt by the nuclei.

Yajima [16] has studied the behavior of a particle in a potential under a permanent AC electric field perturbation, but as of yet there are no rigorous results for such a perturbation applied to the Born-Oppenheimer approximation, and Yajima's results have not been extended to allow for a non-periodic time-dependent perturbation such as the one aforementioned.

The principal theorems of this dissertation are an extension of the asymptotics of Hagedorn

to equations similar in form to

$$i\epsilon^2 \frac{\partial \Psi}{\partial t} = -\frac{\epsilon^4}{2} \frac{\partial^2 \Psi}{\partial X^2} + \frac{1}{2} \frac{\partial^2 \Psi}{\partial x^2} + V(X, x)\Psi + \mu x f(t/\epsilon^2) \cos(\omega t/\epsilon^2)\Psi \quad (1.5)$$

The results are valid for a perturbation linearly dependent on the molecular variables, with a time-dependency that is a function of compact support. We establish results for smooth potentials $V(X, x)$ and compute asymptotics to any order in ϵ , and provided that the electron hamiltonian has purely discrete spectrum, to any order in μ .

As an application of the Dyson series we derive in Chapter 4, we attempt to justify in Chapter 5 the formulas for some Franck-Condon coefficients in the one-dimensional case, which describe the probabilities of ending up in a particular nuclear bound-state after an electron transition occurs. These coefficients are simply the inner product between two nuclear bound states in the different effective potentials generated by the respective electron configurations, but a rigorous justification of their accuracy from a time-dependent standpoint is in order.

Chapter 2

Mathematical Preliminaries

Suppose the molecule under consideration has n_1 nuclei of masses $M_1\epsilon^{-4}, \dots, M_{n_1}\epsilon^{-4}$ and charges q_1, \dots, q_{n_1} and n_2 electrons of mass m_e and charge q_e , making a total of $n = n_1 + n_2$ particles. Let $\mathfrak{X} = \{\xi_1, \dots, \xi_{n_1}, \eta_1, \dots, \eta_{n_2}\} \in \mathbb{R}^{3n}$ denote the configuration vector of the molecule, where ξ_i denotes a nuclear coordinate and η_i an electron coordinate. Assume that the particles interact pairwise under a smooth potential $V(\mathfrak{x}_i - \mathfrak{x}_j, q_i, q_j)$ where $i, j = 1, \dots, n$. and $\mathfrak{x}_i \in \mathbb{R}^3$ is the coordinate vector of the i th particle. Then the Schrödinger equation of interest is

$$i\epsilon^2 \frac{\partial \Psi}{\partial t} = \left(-\frac{\epsilon^4}{2} \sum_i^{n_1} \frac{\Delta_{\xi_i}}{M_i} - \frac{1}{2} \sum_j^{n_2} \frac{\Delta_{\eta_j}}{m_e} + \sum_{i,j} V(\mathfrak{x}_i - \mathfrak{x}_j, q_i, q_j) + \mu \left(\sum_k^n c_k \mathfrak{x}_k \right) F(t/\epsilon^2) \right) \Psi \quad (2.1)$$

The perturbation parameter is μ .

The function F is required to be bounded and of compact support, which rules out the uniform AC Stark perturbation. The motivating example, the electromagnetic pulse, is the specific case

$$\mu \left(E \cdot \sum_k^n q_k \mathfrak{x}_k \right) f(t/\epsilon^2) \cos(\omega t/\epsilon^2) \quad (2.2)$$

where $f(t/\epsilon^2)$ is bounded and of compact support. For a physically interesting application, one typically wants f to be supported over several periods of the cosine function, since f is intended to be the “shape” of a laser pulse. The integrability of f models the condition that our pulse turns “on” at some time in the past, and then turns “off” at some time in the future. If the masses of the nuclei are all equal, and the charges of the particles all have the same magnitude, one may easily extend our results to include $F(t/\epsilon^2) \in L^1(-\infty, \infty)$.

2.1 Clustered Jacobi Coordinates

It is convenient to transform (2.1) into clustered Jacobi coordinates as described in [15, vol. III]. We define cluster \mathcal{C}_1 to be the n_1 nuclear coordinates and cluster \mathcal{C}_2 to be the n_2 electron coordinates. Then we compute the respective centers of mass of \mathcal{C}_1 and \mathcal{C}_2

$$R_1 = \left(\sum_i^{n_1} M_i \right)^{-1} \sum_i^{n_1} M_i \xi_i \quad (2.3)$$

$$R_2 = \frac{1}{n_2} \sum_j^{n_2} \eta_j \quad (2.4)$$

We then let

$$\zeta_1 = R_2 - R_1 \quad (2.5)$$

$$\zeta_2 = \frac{(\sum M_i \epsilon^{-4}) R_1 + n_2 m_e R_2}{\sum M_i \epsilon^{-4} + n_2 m_e} \quad (2.6)$$

Note that ζ_1 is intuitively the intercluster distance, and ζ_2 is the total center of mass of the molecule.

Define new nuclear and electron coordinates by using the Jacobi coordinates inside each cluster

$$X_i = \xi_{i+1} - \left(\sum_{k \leq i} M_j \right)^{-1} \left(\sum_{k \leq i} M_k \xi_k \right) \quad i = 1, \dots, n_1 - 1 \quad (2.7)$$

$$x_j = \eta_{j+1} - \frac{1}{j} \sum_{k \leq j} \eta_k \quad j = 1, \dots, n_2 - 1 \quad (2.8)$$

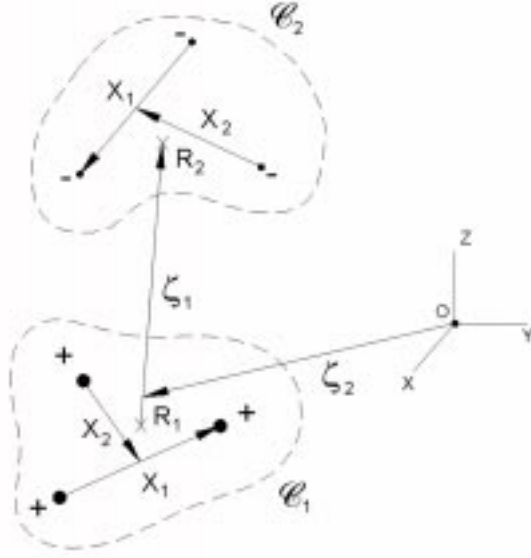


Figure 2.1: An example of clustered Jacobi coordinates for a molecular system.

The coordinates $\{X_1, \dots, X_{n_1-1}, \zeta_1, \zeta_2, x_1, \dots, x_{n_2-1}\}$ form clustered Jacobi coordinates for the problem in question. After transformation into these coordinates, the total center of mass coordinate ζ_2 does not appear in the potential V . Since we are not interested in the center of mass motion of the molecule under the perturbation (the solution to that problem is known), but rather in the energy level transitions of molecule, we drop coordinate ζ_2 from the equation entirely and define $\zeta_1 \equiv \zeta$. We also use the shorthand $X \equiv (X_1, \dots, X_{n_1-1})$, and $x \equiv (x_1, \dots, x_{n_2-1})$. Let us abuse notation slightly and call the new vector of coordinates $(X, \zeta, x) \equiv \mathfrak{X}$ also.

After this transformation, we now have

$$i\epsilon^2 \frac{\partial \Psi}{\partial t} = - \left(\sum_i^{n_1-1} \frac{\epsilon^4}{2} \Delta_{X_i} + c(\epsilon^4) \Delta_\zeta + \sum_j^{n_2-1} \frac{\Delta_{x_j}}{2} \right) \Psi + V(\mathfrak{X}, \mathbf{q}) \Psi + \mu \left(\sum_i C_i(\epsilon^4) X_i + C_\zeta(\epsilon^4) \zeta + \sum_j C_j(\epsilon^4) x_j \right) F(t/\epsilon^2) \quad (2.9)$$

The C_i and c are easily verified to be smooth functions of ϵ^4 at $\epsilon = 0$. They are merely coefficients resulting from the coordinate transformation, hence they depend on the masses

and the charges of the particles involved.

We will change coordinates once more to put (2.9) in a standard form. The final equation

$$i\epsilon^2 \frac{\partial \Psi}{\partial t} = -\frac{1}{2} \left(\sum_i^{n_1-1} \epsilon^4 \Delta_{X_i} + \Delta_\zeta + \sum_j^{n_2-1} \Delta_{x_j} \right) \Psi + V(\mathfrak{X}, \epsilon^4, \mathbf{q}) \Psi + \mu \mathfrak{X} \cdot \mathbf{C}(\epsilon) F(t/\epsilon^2) \quad (2.10)$$

is obtained by merely multiplying various coordinates by scale factors depending on ϵ^4 , the masses, and the charges. The various C_i have been condensed into a vector $\mathbf{C}(\epsilon)$.

Remark. The potential $V(\mathfrak{X}, \epsilon^4, \mathbf{q})$ and the C_i can be expanded in a Taylor series in ϵ^4 about 0, valid for $\epsilon > 0$. That is, we may substitute

$$V = \sum \epsilon^{4p} \frac{V^{(p)}}{p!}$$

$$C_i = \sum \epsilon^{4p} \frac{C_i^{(p)}}{p!}$$

and calculate additional corrections to the asymptotic series we will derive in Chapter 4 at orders of ϵ divisible by 4. In the sequel, then, it will be assumed that the V and the C_i are not dependent on ϵ for ease in exposition. The reader will observe that the proof given is applicable even if such corrections are added, and the calculational modifications follow from regular perturbation theory.

In (2.10), we identify

$$h(X) = -\frac{1}{2} \left(\Delta_\zeta + \sum_j^{n_2-1} \Delta_{x_j} \right) + V(\mathfrak{X}, \mathbf{q})$$

as the electron Hamiltonian depending parametrically on the nuclear variables. Then, we further abbreviate

$$H(\epsilon) \equiv -\frac{\epsilon^4}{2} \sum_i^{n_1-1} \Delta_{X_i} + h(X), \quad (2.11)$$

so that the unperturbed equation to be solved will be

$$i\epsilon^2 \frac{\partial}{\partial t} \Psi = H(\epsilon) \Psi \quad (2.12)$$

Furthermore,

$$H_1(t/\epsilon^2) \equiv \left(C_\zeta \zeta + \sum_j C_j x_j \right) F(t/\epsilon^2) \quad (2.13)$$

will abbreviate the expression for the perturbation. To simplify the exposition, we have left out the X_j terms in the time-dependent perturbation. As will be explained in Chapter 3, those terms will have little effect. Since the nuclear masses are large, the resonance frequency required for the electric field pulse to excite transitions between nuclear bound states within a particular electron energy level is much smaller than any of the significant frequency components of $F(t/\epsilon^2)$.

2.2 Existence of Unitary Propagator

Any time-dependent perturbation modifies the propagation operator that develops the solution from its initial conditions. Thus, a common technique in time-dependent perturbation theory is to develop an asymptotic series for the new propagator, thereby allowing us to approximate the perturbed solution at any future time.

Definition 2.1 *A two-parameter family of unitary operators $U(t, s)$, where $s, t \in \mathbb{R}$, which is called a **unitary propagator** if all the following are satisfied:*

- a) $U(t, s)U(s, r) = U(t, r)$
- b) $U(t, t) = I$
- c) $U(t, s)$ is jointly strongly continuous in s and t .

The following theorem from [15, vol.II] demonstrates the existence of a unitary propagator for *bounded* Hamiltonians by constructing a Dyson expansion that converges uniformly to the desired propagator.

Theorem 2.1 (see Theorem X.69, in [15]) *Let $t \rightarrow H(t)$ be a strongly continuous map of \mathbb{R} onto the bounded self-adjoint operators on a Hilbert space \mathcal{H} . Then there is a unitary propagator on \mathcal{H} so that, for all $\Psi \in \mathcal{H}$,*

$$\varphi_s(t) = U(t, s)\Psi \quad \text{satisfies} \quad \frac{d}{dt}\varphi_s(t) = -iH(t)\varphi_s(t), \quad \varphi_s(s) = \Psi$$

The Born-Oppenheimer Hamiltonian we are interested in is *not* bounded, hence, if we formally calculate a unitary propagator using a Dyson series, we will have to prove that it is asymptotic to the propagator.

We will denote the propagator for the unperturbed Hamiltonian $H(\epsilon)$ by $e^{-i(t-s)H(\epsilon)/\epsilon^2} \equiv U_\epsilon(t, s)$, and that of the perturbed Hamiltonian $H(\epsilon) + \mu H_1$ by $U_{\epsilon, \mu}(t, s)$.

Because of the singular nature of the time-dependent perturbation H_1 , it is not immediately apparent that the propagator $U_{\epsilon, \mu}(t, s)$ exists. However, in the spirit of Yajima [16], we may introduce a transformation of (2.10)

$$\mathfrak{x}_i \rightarrow \mathfrak{x}_i - \mu C_i \int dt \int dt F(t/\epsilon^2). \quad (2.14)$$

By $\int dt$, we mean integration from some T_l , a value below the compact support of F , up to t . Under this transformation, if Ψ solves (2.10), then $\Psi_D \equiv T(t)^{-1}\Psi$ solves

$$i\epsilon^2 \frac{\partial \Psi_D}{\partial t} = -\frac{1}{2} \left(\sum_i^{n_1-1} \epsilon^4 \Delta_{X_i} + \Delta_\zeta + \sum_j^{n_2-1} \Delta_{x_j} \right) \Psi + V(\mathfrak{x} + \mu \mathfrak{C} \int dt \int dt F(t/\epsilon^2)) \Psi \quad (2.15)$$

where the operator $T(t)$ is unitary and is expressed by

$$\begin{aligned} T(t)f = \exp \left\{ i\mu \mathfrak{C} \cdot \mathfrak{x} \left(\int F(t/\epsilon^2) dt \right) + i(\mu|\mathfrak{C}|)^2 \left(\int dt \int dt F(t/\epsilon^2) \right) \left(\int F(t/\epsilon^2) dt \right) \right. \\ \left. - i(\mu|\mathfrak{C}|)^2/2 \left(\int dt \left(\int F(t/\epsilon^2) dt \right)^2 \right) - i(\mu|\mathfrak{C}|)^2 \left(\int dt \left(F(t/\epsilon^2) \int dt \int dt F(t/\epsilon^2) \right) \right) \right\} \\ \times f(\mathfrak{x} - \mu \mathfrak{C} \int dt \int dt F(t/\epsilon^2)) \quad (2.16) \end{aligned}$$

Thus, by a unitary transformation, we can bring the time-dependency inside the argument of the potential V , and we notice that a unitary propagator exists for this new Hamiltonian.

Remark. We will always develop the solution from $t = T_l$, that is, from some finite time before the pulse turns “on”. Thus, we assume that we know, as an initial condition, the wavepacket solution of the time-dependent molecular Schrödinger equation at that time.

Definition 2.2 Suppose $\Psi_0(t)$ is a solution of the Schrödinger equation $i\frac{\partial\Psi}{\partial t} = H_0\Psi$, where H_0 is some unperturbed Hamiltonian, and $U(\cdot, \cdot)$ is the unitary propagator for H_0 . Then a **formal Dyson series solution** for the perturbed Schrödinger equation

$$i\frac{\partial\Psi}{\partial t} = (H_0 + \mu H_1)\Psi$$

is given by

$$\begin{aligned} \Psi(t) = \Psi_0(t) + \sum_{n=1}^N (-i\mu)^n \int_{T_l}^t U(t, s_N) H_1(s_N) \int_{T_l}^{s_N} U(s_N, s_{N-1}) H_1(s_{N-1}) \dots \\ \times H_2(s_2) \int_{T_l}^{s_2} U(s_2, s_1) H_1(s_1) U(s_1, T_l) \Psi_0(T_l) ds_N \dots ds_1 \quad (2.17) \end{aligned}$$

In the next chapter, we examine the known asymptotic series solution for the unperturbed time-dependent Born-Oppenheimer approximation. We will then use the solution described there as a base from which we will develop a formal Dyson series solution to the perturbed equation.

2.3 Semiclassical Wave Packets

In order to study the propagation of a wave-packet under the electromagnetic field perturbation, we shall utilize a special basis for the nuclear wavefunction space. This basis is constructed from the solutions of the generalized n-dimensional quantum harmonic oscillator, giving the basis useful properties for obtaining estimates of the errors made in semiclassical propagation. The theorems quoted here, as well as other properties, are given a complete discussion in [6]. The proofs stated here, with a single exception, are drawn from that source.

We will assume $a, \eta \in \mathbb{R}^{n_1}$, and matrices $A, B \in \mathbb{C}^{n_1 \times n_1}$ satisfying the normalization conditions

$$A^t B - B^t A = 0 \quad (2.18)$$

$$A^* B + B^* A = 2I \quad (2.19)$$

These conditions ensure most importantly that

- 1) A and B are invertible matrices.
- 2) BA^{-1} has the form [real symmetric + i real symmetric].
- 3) $(\text{Re } BA^{-1})^{-1} = AA^*$, which is strictly positive definite.

We next let $l = (l_1, \dots, l_{n_1})$ be a multi-index, i.e., any ordered n -tuple of nonnegative integers. We interpret $|l| = \sum_{j=1}^{n_1} l_j$, $l! = l_1! l_2! \dots l_{n_1}!$, $D^l = \frac{\partial^{|l|}}{(\partial X_1)^{l_1} (\partial X_2)^{l_2} \dots (\partial X_{n_1})^{l_{n_1}}}$, and finally, the monomial $x^l = x_1^{l_1} \dots x_{n_1}^{l_{n_1}}$.

For any multi-index l , then

$$\begin{aligned} \varphi_l(A, B, \hbar, a, \eta, X) &= 2^{-|l|/2} (l!)^{-1/2} \pi^{-n_1/4} \hbar^{-n_1/4} (\det A)^{-1/2} \times \\ &\mathcal{H}_l(A; \hbar^{-1/2} |A|^{-1} (X - a)) \exp\{-\langle (X - a), BA^{-1} (X - a) \rangle / 2\hbar + i \langle \eta, (X - a) \rangle / \hbar\} \end{aligned} \quad (2.20)$$

where \mathcal{H}_l is the generalized Hermite polynomial defined in [6].

These functions form a complete orthonormal basis for $L^2(\mathbb{R}^{n_1})$. Suppose $\alpha(t), \beta(t), \gamma(t)$ are continuous real $n_1 \times n_1$ matrix-valued functions, $\delta(t), \epsilon(t)$ are continuous \mathbb{R}^{n_1} vector-valued functions, and $\zeta(t)$ is continuous and real-valued. Identifying $p \equiv -i\hbar \nabla_X$, we then focus our consideration on the Hamiltonian

$$H(x, p, t) = \frac{1}{2} \begin{pmatrix} p \\ x \end{pmatrix} \cdot \begin{pmatrix} \alpha(t) & \beta(t) \\ \beta^t(t) & \gamma(t) \end{pmatrix} \begin{pmatrix} p \\ x \end{pmatrix} + \langle \delta(t), p \rangle + \langle \epsilon(t), x \rangle + \zeta(t) \quad (2.21)$$

which describes a generalized n_1 -dimensional quantum harmonic oscillator system.

Now given initial conditions $(A(T_l), B(T_l), a(T_l), \eta(T_l), S(T_l))$, the classical equations of motion

$$\begin{aligned}
\dot{a}(t) &= \beta(t)a(t) + \alpha(t)\eta(t) + \delta(t) \\
\dot{\eta}(t) &= -\gamma(t)a(t) - \beta^t(t)\eta(t) - \epsilon(t) \\
\dot{A}(t) &= \beta(t)A(t) + i\alpha(t)B(t) \\
\dot{B}(t) &= i\gamma(t)A(t) - \beta^t(t)B(t) \\
\dot{S}(t) &= \alpha(t)\frac{\eta(t)^2}{2} - \gamma(t)\frac{\alpha(t)^2}{2} - \epsilon(t)a(t) - \zeta(t)
\end{aligned} \tag{2.22}$$

have a unique solution $(A(t), B(t), a(t), \eta(t), S(t))$. In the classical motion, $a(t)$ represents the position vector, $\eta(t)$ the momentum vector, and $S(t)$ the classical action. It is helpful to identify these same quantities with the wave packets we will propagate semiclassically.

The following theorem is verified by an elementary induction in [6] using the raising and lowering operators for solutions of the form (2.20).

Theorem 2.2 *Let $\alpha(t), \beta(t), \gamma(t), \delta(t), \epsilon(t), \zeta(t)$ be as above and let $(A(t), B(t), a(t), \eta(t), S(t))$ be any solution to the system (2.22). Then, for any multi-index k ,*

$$\Psi(\hbar, t) = e^{iS(t)/\hbar} \varphi_k(A(k), B(t), \hbar, a(t), \eta(t), x)$$

exactly solves the Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = H(x, p, t) \Psi$$

where $H(x, p, t)$ is the Hamiltonian in (2.21).

Of central importance in the estimation of semiclassical propagation errors is the asymptotic semiclassical expansion theorem below.

Theorem 2.3 *Suppose $N \geq 1$, and $V \in C^{N+2}(\mathbb{R}^{n_1})$ satisfies $-C_1 \leq V(X) \leq C_2 e^{Mx^2}$ for some C_1, C_2 , and M . Let $(A(t), B(t), a(t), \eta(t), S(t))$ be a solution to the following system*

of equations

$$\begin{aligned}
\dot{a}(t) &= \eta(t) \\
\dot{\eta}(t) &= -V^{(1)}(a(t)) \\
\dot{A}(t) &= iB(t) \\
\dot{B}(t) &= iV^{(2)}(a(t))A(t) \\
\dot{S}(t) &= \frac{\eta(t)^2}{2} - V(a(t))
\end{aligned} \tag{2.23}$$

and let $H(\epsilon) = -\frac{\epsilon^4}{2}\Delta_X + V(X)$. Then given coefficients $c_j(T_l)$, there exists time-dependent coefficients $c_j(t, \epsilon)$ such that

$$\left\| e^{-itH(\epsilon)/\epsilon^2} \sum_{|j| \leq J} c_j(T_l) \varphi_j(A(T_l), B(T_l), \epsilon^2, a(T_l), \eta(T_l), X) - e^{iS(t)/\epsilon^2} \sum_{|j| \leq J+3N-3} c_j(t, \epsilon) \varphi_j(A(t), B(t), \epsilon^2, a(t), \eta(t), X) \right\| \leq C_3 \epsilon^N \tag{2.24}$$

We require the following elementary but crucial lemma for the proof and elsewhere in the sequel.

Lemma 2.1 *Suppose $H(\epsilon, t)$ is a family of possibly time-dependent self-adjoint operators for $\epsilon > 0$, and $U(\cdot, \cdot)$ is the unitary propagator for $H(\epsilon, t)$. Suppose $\psi(t, \epsilon)$ belongs to the domain of $H(\epsilon, t)$, is continuously differentiable in t , and approximately solves the Schrödinger equation in the sense that*

$$i\epsilon^2 \frac{\partial \psi}{\partial t}(t, \epsilon) = H(\epsilon, t)\psi(t, \epsilon) + \xi(t, \epsilon) \tag{2.25}$$

where $\xi(t, \epsilon)$ satisfies

$$\|\xi(t, \epsilon)\| \leq \mu(t, \epsilon).$$

Then,

$$\|U(t, T_l)\psi(T_l, \epsilon) - \psi(t, \epsilon)\| \leq \epsilon^{-2} \int_{T_l}^t \mu(s, \epsilon) ds. \tag{2.26}$$

Proof. We directly estimate

$$\begin{aligned} & \|U(t, T_l)\psi(T_l, \epsilon) - \psi(t, \epsilon)\| \\ &= \|\psi(T_l, \epsilon) - U(T_l, t)\psi(t, \epsilon)\| \end{aligned}$$

which can be rewritten using the fundamental theorem of calculus as

$$\begin{aligned} &= \left\| \int_{T_l}^t \frac{\partial}{\partial s} (\psi(T_l, \epsilon) - U(T_l, s)\psi(s, \epsilon)) ds \right\| \\ &= \left\| \int_{T_l}^t \left(-i\epsilon^{-2}U(T_l, s)H(\epsilon, s)\psi(s, \epsilon) - U(T_l, s)\frac{\partial\psi}{\partial s}(s, \epsilon) \right) ds \right\| \\ &= \left\| \int_{T_l}^t i\epsilon^{-2}U(T_l, s)\zeta(s, \epsilon) \right\| \\ &\leq \epsilon^{-2} \int_{T_l}^t \mu(s, \epsilon) ds \end{aligned}$$

by the unitarity of the propagator $U(0, s)$. \blacksquare

Proof of Theorem. The proof given here summarizes the one found in [8], which is more direct and intuitive than the one found in [6]. We first derive a semiclassical expansion and then use Lemma 2.1 to bound the error.

By hypothesis, we wish to solve the equation

$$i\epsilon^2 \frac{\partial\psi}{\partial t} = -\frac{\epsilon^4}{2}\Delta\psi + V(X)\psi \quad (2.27)$$

with initial conditions

$$\psi(X, T_l, \epsilon) = \sum_{|j| \leq J} c_j(T_l) \varphi_j(A(T_l), B(T_l), \epsilon^2, a(T_l), \eta(T_l), X) \quad (2.28)$$

Let us write the exact solution to the above problem in terms of the basis consisting of elements of the form (2.20). Then

$$\psi(X, t, \epsilon) = e^{iS(t)/\epsilon^2} \sum_j c_j(t, \epsilon) \varphi_j(A(t), B(t), \epsilon^2, a(t), \eta(t), X) \quad (2.29)$$

Furthermore, let us express the operator $H(\epsilon)$ in terms of this same basis, and denote that infinite self-adjoint matrix by $K(t, \epsilon)$. By denoting the time-dependent coefficients $c_j(t, \epsilon)$ as

the infinite vector \mathbf{c} , we may then rewrite our initial problem as

$$i\epsilon^2 \dot{\mathbf{c}}(t, \epsilon) = K(t, \epsilon) \mathbf{c}(t, \epsilon) \quad (2.30)$$

Now we formally expand $K(t, \epsilon)$, and $\mathbf{c}(t, \epsilon)$ in powers of ϵ , giving

$$\mathbf{c}(t, \epsilon) \sim \sum_k \epsilon^k \mathbf{c}^{(k)}(t) \quad (2.31)$$

$$K(t, \epsilon) \sim \sum_{k=3} \epsilon^k K^{(k)}(t) \quad (2.32)$$

Note that by Theorem 2.2, the expansion of $K(t, \epsilon)$ has leading order ϵ^3 , and that each term has the form

$$K^{(k)}(t) = \frac{V^{(k)}(a(t))}{k!} \mathcal{X}(t)^k \quad (2.33)$$

which is just a term in the formal Taylor series expansion of $V(X)$ around $X = a(t)$. Further, $\mathcal{X}(t)$ is the infinite matrix representation of $\epsilon^{-1}(X - a(t))$ in our special basis. [6] shows, however, that the entries of $\mathcal{X}(t)$ do not depend on ϵ .

We now simply substitute the above expansions into (2.30) and equate like powers of ϵ , keeping in mind the initial conditions.

Order 0. The process begins with

$$i\dot{\mathbf{c}}^{(0)} = 0. \quad (2.34)$$

We see immediately that we must have $c_j^{(0)}(t) = c_j(T_l)$.

Order 1. Next,

$$i\dot{\mathbf{c}}^{(1)} = K^{(3)}(t) \mathbf{c}^{(0)}(t). \quad (2.35)$$

This equation can be explicitly integrated, using the initial condition $\mathbf{c}^{(1)}(T_l) = 0$. Because $X(t)$ is tridiagonal, it is clear that $K^{(3)}$, which is proportional to $X(t)^3$, will be a banded matrix with seven diagonals. We conclude that the only nonzero entries of $\mathbf{c}^{(1)}$ have $|j| \leq J + 3$.

Order 2. To continue, we must solve

$$i\dot{\mathbf{c}}^{(2)} = K^{(4)}(t)\mathbf{c}^{(0)}(t) + K^{(3)}(t)\mathbf{c}^{(1)}(t), \quad (2.36)$$

which may again be solved by integration. The $K_3(t)\mathbf{c}^{(1)}(t)$ term may generate nonzero entries for $|j| \leq J + 6$, but otherwise, the entries of $\mathbf{c}^{(2)}$ will be zero.

Order n. Inductively, the general condition on $\mathbf{c}^{(n)}$ is

$$i\dot{\mathbf{c}}^{(n)} = \sum_{k=0}^{n-1} K^{(n+2-k)}(t)\mathbf{c}^{(k)}(t). \quad (2.37)$$

After integrating, we discover that $\mathbf{c}^{(n)}$ has nonzero entries only if $|j| \leq J + 3n$.

We now take our approximate solution, using the coefficients obtained above, up to order $N - 1$, insert [5] into (2.29), and determine the truncation error

$$\zeta_t(X, t, \epsilon) = i\epsilon^2 \frac{\partial \tilde{\psi}}{\partial t} - H(\epsilon)\tilde{\psi}. \quad (2.38)$$

Cancellations occur by virtue of (2.34), (2.35), (2.36), etc., leaving us with

$$\zeta_N(X, t, \epsilon) = e^{iS(t)/\epsilon^2} \sum_{k=0}^{N-1} \left(\epsilon^k R^{(N+1-k)}(X) \times \sum_{|j| \leq J+3N-3} c_j^{(k)}(t) \varphi_j(A(t), B(t), \epsilon^2, a(t), \eta(t), X) \right) \quad (2.39)$$

where $R^{(q)}(X)$ denotes the Taylor series error

$$\sum_{|m|=q+1} \frac{D^m V(\bar{\zeta}_q)}{m!} (X - a(t))^m \quad (2.40)$$

We have assumed that V is C^{N+2} , so that the Taylor series errors are bounded. By [6, see p.98],

$$\|(X - a(t))^m \varphi_j(A(t), B(t), \epsilon^2, a(t), \eta(t), X)\| \leq C\epsilon^{|m|}$$

thus, examination of (2.39) shows that $\|\zeta(t, \epsilon)\|$ is $O(\epsilon^{N+2})$. Using Lemma 2.1, we obtain the result that our approximate solution is accurate to $O(\epsilon^N)$. ■

The following lemma will be used later to justify small corrections to the semiclassical propagation resulting from the addition of a time-dependent perturbation in the nuclear variables.

Lemma 2.2 *Let $F(t/\epsilon^2)$ be a bounded function of compact support, with V meeting the conditions of Theorem 2.3. Suppose that we have a solution to the system (2.23). If $(A(t), B(t), a(t), \eta(t), S(t))$ is a solution to the modified system of equations*

$$\begin{aligned}
\dot{a}(t) &= \eta(t) \\
\dot{\eta}(t) &= -V^{(1)}(a(t)) - \mu F(t/\epsilon^2) \\
\dot{A}(t) &= iB(t) \\
\dot{B}(t) &= iV^{(2)}(a(t))A(t) \\
\dot{S}(t) &= \frac{\eta(t)^2}{2} - V(a(t)) - \mu \left(\sum_i C_i(a(t))_i \right) F(t/\epsilon^2)
\end{aligned} \tag{2.41}$$

with the same initial conditions as the solution to (2.23), then the limit as $\epsilon \rightarrow 0$ of each of the quantities $A(t), B(t), a(t), \eta(t), S(t)$ exists.

Proof. We need only consider the solutions of the coupled equations

$$\begin{aligned}
\dot{a}(t) &= \eta(t) \\
\dot{\eta}(t) &= -V^{(1)}(a(t)) - \mu F(t/\epsilon^2).
\end{aligned} \tag{2.42}$$

If $a(t)$ and $\eta(t)$ have defined limits, then clearly the other quantities also have defined limits from the form of their differential equations. We assume a solution to the two analogous equations from (2.23) and proceed to develop a formal approximate solution to our revised equations. We then rigorously verify that these approximate solutions give us the limits we desire.

Let us set $s = t/\epsilon^2$ and assume series solutions of the form

$$a(s, t) = a_0(s, t) + \epsilon^2 a_2(s, t) + \epsilon^4 a_4(s, t) + \dots \tag{2.43}$$

$$\eta(s, t) = \eta_0(s, t) + \epsilon^2 \eta_2(s, t) + \epsilon^4 \eta_4(s, t) + \dots \tag{2.44}$$

We proceed to find a solution now to our equations by the method of multiple scales. Rewriting (2.42) to reflect our two independent time scales s and t ,

$$\begin{aligned}\dot{a} + \epsilon^{-2}a' &= \eta \\ \dot{\eta} + \epsilon^{-2}\eta' &= -V^{(1)}(a) - \mu F(s).\end{aligned}\tag{2.45}$$

where $\dot{}$ denotes differentiation with respect to t , and $'$ denotes differentiation with respect to s .

By substituting our series (2.43) into (2.45) and expanding $V^{(1)}(a)$ in powers of ϵ^2 , we may begin solving for the terms in the series by matching up powers of ϵ .

Order ϵ^{-2} . We have

$$a'_0 = 0\tag{2.46}$$

$$\eta'_0 = 0\tag{2.47}$$

so that a_0 and η_0 depend only on t .

Order 1. The next set of equations is

$$\dot{a}_0 + a'_2 = \eta_0\tag{2.48}$$

$$\dot{\eta}_0 + \eta'_2 = -V^{(1)}(a_0) - F(s)\tag{2.49}$$

Because $a'_2 = \eta_0 - \dot{a}_0$, and we wish to eliminate secular behavior in the s variable, we require $a'_2 = 0$ and $\dot{a}_0 = \eta_0$. Note that this latter equation is satisfied by the $a(t)$ solution to (2.23). Further, we have $\eta'_2 = -V^{(1)}(a_0) - \dot{\eta}_0 - F(s)$. Because F is of compact support, we avoid secular behavior by requiring that

$$\eta_2(s, t) = - \int_{T_1/\epsilon^2}^s F(s') ds' + f_2(t)\tag{2.50}$$

$$\dot{\eta}_0 = -V^{(1)}(a_0).\tag{2.51}$$

The latter equation once again is satisfied by the $\eta(t)$ solution to (2.23). We now have found (a_0, η_0) , which are completely determined by the initial conditions to (2.23). We have

also completely determined the s -dependence of (a_2, η_2) . At this point let us reiterate that the initial conditions to our problem are independent of ϵ , so that $a_j(T_l/\epsilon^2, T_l) = 0$ and $\eta_j(T_l/\epsilon^2, T_l) = 0$ for $j \geq 2$.

Order ϵ^2 . The last set of equations we will need to solve will be

$$\dot{a}_2 + a'_4 = \eta_2 \quad (2.52)$$

$$\dot{\eta}_2 + \eta'_4 = -V^{(2)}(a_0)a_2 \quad (2.53)$$

Using what we have learned before

$$a'_4 = - \int_{T_l/\epsilon^2}^s F(s') ds' + f_2(t) - \dot{a}_2 \quad (2.54)$$

in which we can avoid secular behavior by choosing

$$\dot{a}_2 = f_2(t) - \int_{T_l/\epsilon^2}^{\infty} F(s') ds' \quad (2.55)$$

$$a_4(s, t) = - \int_{T_l/\epsilon^2}^s ds' \int_{T_l/\epsilon^2}^{s'} F(s'') ds'' - s \int_{T_l/\epsilon^2}^{\infty} F(s') ds' + g_4(t) \quad (2.56)$$

Further, we have

$$\eta'_4 = -\dot{f}_2 - V^{(2)}(a_0)a_2 \quad (2.57)$$

and so we must choose

$$f_2(t) = - \int_0^t V^{(2)}(a_0)a_2 dt'. \quad (2.58)$$

But putting (2.55) and (2.58) together

$$\ddot{a}_2 = -V^{(2)}(a_0)a_2 \quad (2.59)$$

which can only have the trivial solution because of our initial conditions. Thus we have formally determined an approximate solution

$$a(s, t) = a_0(t) + O(\epsilon^4) \quad (2.60)$$

$$\eta(s, t) = \eta_0(t) - \epsilon^2 \int_{T_l/\epsilon^2}^s F(s') ds' + O(\epsilon^4) + \dots \quad (2.61)$$

For convenience, let us write the system (2.42) as

$$\begin{pmatrix} \dot{a} \\ \dot{\eta} \end{pmatrix} = \begin{pmatrix} \eta \\ -V^{(1)}(a) \end{pmatrix} - \begin{pmatrix} 0 \\ \mu F(t/\epsilon^2) \end{pmatrix} \quad (2.62)$$

The right-hand side of this equation is a function of a and η whose derivative with respect to (a, η) is

$$\begin{pmatrix} 0 & 1 \\ -V^{(2)}(a) & 0 \end{pmatrix}. \quad (2.63)$$

We claim that this derivative is bounded, and therefore that the right-hand side of (2.62) is Lipschitz. To see this, we note that (2.60) is an approximate solution to the first two equations of (2.23) and that when we substitute the former into the latter we obtain a truncation error that is $O(\mu)$. We appeal to Gronwall's Lemma in [12, p.380], and note that the right-hand side of (2.23) is already known to be Lipschitz (because the exact solution (a, η) of (2.23) is contained within a compact set by conservation of energy). We learn from Gronwall's Lemma that the solutions (2.60) are also contained within a compact set, hence the derivative (2.63) is bounded.

We now note that the truncation error resulting from substituting (2.60) into (2.62) is

$$\begin{pmatrix} \epsilon^2 \int_{T_1/\epsilon^2}^{t/\epsilon^2} F(s') ds' \\ 0 \end{pmatrix} \quad (2.64)$$

which is $O(\epsilon^2)$. By the preceding argument we appeal to Gronwall's Lemma again to show that the difference between the exact solutions to (2.42) and (2.60) is in fact of $O(\epsilon^2)$. This is enough to show that the limits as $\epsilon \rightarrow 0$ of the exact solutions to (2.42) are in fact the solutions to (2.23), which is enough to prove the lemma. ■

Chapter 3

The Unperturbed Case

The asymptotics for the unperturbed time-dependent Born-Oppenheimer equation were first developed by Hagedorn in 1986 [5]. Because our perturbation in (2.10) can be rendered into a part depending only on nuclear variables X and a part depending only on electronic variables ζ, x , we will choose to treat these parts differently. The part containing the nuclear variables will be subsumed by the semiclassical mechanics of the nuclear variables, since these equations of motion (2.23) can still be solved in terms of the special basis of semiclassical wave packets described in Chapter 2. Only the perturbation terms involving the electronic variables will figure in the Dyson series solution.

We summarize here portions of the theorem of Hagedorn [7] respecting the unperturbed asymptotics. The proof has been modified to reflect the additional time-dependent term $\mu \sum_i C_i X_i F(t/\epsilon^2)$. We will show that this part of the time-dependent perturbation can safely be treated by means of small corrections to the equations (2.23), but after we have done so, we will proceed to drop this term from the exposition entirely in the interest of clarity, and assume that our perturbation includes only the electron variables, as in the definition of H_1 . This simplification by no means reduces the mathematical strength of the results—in fact, in the physical problem motivating this study, a molecule containing nuclei of equal masses is perturbed by a term containing only the electron variables.

Theorem 3.1 *Suppose $h(\cdot)$ is a smooth time-independent electron Hamiltonian and suppose that there is an open set $U \in \mathbb{R}^{n_1}$ such that $h(X)$ has discrete, multiplicity 1 eigenvalues $E_{(i)}(X)$ for $X \in U$ that depend smoothly on X , and furthermore, do not cross, i.e. $E_{(i)}(X) \neq E_{(j)}(X)$ for any $X \in U$. Suppose that $a(t)$ and $\eta(t)$ satisfy (2.23), and assume that $a(t) \in U$ for all t . Then we can choose $\delta > 0$, such that $\{X : |X - a(t)| \leq 2\delta\} \subset U$ for all t , and define $U_1(t) = \{|X : |X - a(t)| \leq \delta\}$ and $U_2(t) = \{|X : |X - a(t)| \leq 2\delta\}$. We choose a C^∞ function $G : \mathbb{R}^{n_1} \rightarrow [0, 1]$, such that $G(X) = 0$ for $|X| \geq 2\delta$ and $G(X) = 1$ for $|X| \leq \delta$. Then for small $\epsilon > 0$ there exist functions $\Psi_j(\epsilon, X, \zeta, x, t)$ with the properties*

- (1) *For any smooth choice of initial normalized electron eigenfunction $\Phi_{(i)}(X, T_l)$ corresponding to the eigenvalue $E_{(i)}(X)$ for $X \in U_2(T_l)$, there exists a smooth function $\Phi_{(i)}(X, t)$ on the set $\{(X, t) : X \in U_2(t), t \in [T_l, T]\}$ that is a normalized eigenfunction corresponding to $E_{(i)}(X)$. Furthermore, we may choose the phase such that*

$$\left\langle \Phi_{(i)}(X, t), \left(i \frac{\partial}{\partial t} + i\eta(t) \cdot \nabla_X \right) \Phi_{(i)}(X, t) \right\rangle = 0$$

for all $X \in U_2(t)$ and $t \in [T_l, T]$.

- (2) *The function $\sum_{j=0}^J \Psi_j(\epsilon, X, t)\epsilon^j$ is a J th order asymptotic approximation to a solution of the Schrödinger equation in the sense that*

$$\left\| e^{-itH(\epsilon)/\epsilon^2} \sum_{j=0}^J \Psi_j(\epsilon, X, \zeta, x, T_l)\epsilon^j - \sum_{j=0}^J \Psi_j(\epsilon, X, \zeta, x, t)\epsilon^j \right\| \leq C_J \epsilon^{J+1}$$

- (3) *For each j , $\|\Psi_j(\epsilon, X, \zeta, x, t)\|$ is bounded as $\epsilon \searrow 0$.*

- (4) *The Ψ_j 's have support only on the support of G .*

Remarks.

1. The function G merely serves to focus our attention on the propagation of the portion of the wavepacket with nuclear coordinates contained in the set U where the electron eigenvalues $E_{(i)}$ satisfy the hypotheses of the theorem.

2. The functions $\Psi_j(\epsilon, X, \zeta, x, t)$ can be calculated explicitly by extending the formal process outlined in the proof below.
3. The proof of the theorem requires three steps. The technique of multiple scales transforms the problem into a higher-dimensional one, which is then formally solved. We then apply Lemma 2.1 to the results of the calculations to obtain the estimates in the first conclusion of the theorem.

Proof. We refer the reader to [7] for a proof of the first conclusion of the theorem, since that conclusion does not utilize any machinery vital for the proof of the perturbed case. We will, however, assume that the phases for the functions $\Phi_{(i)}(X, t)$ have been chosen in accordance with the first conclusion in the sequel.

Instead of calculating the solution $\Psi_j(X, \zeta, x, t)$, however, we will search for a solution $\hat{\Psi}_j(z, y, \zeta, x, t)$ and obtain our desired solution by setting

$$\Psi_j(z, y, \zeta, x, t) = \hat{\Psi}_j\left(X, \frac{X - a(t)}{\epsilon}, \zeta, x, t\right). \quad (3.1)$$

We artificially solve a higher-dimensional problem in order to effectively separate the adiabatic motion of the electrons from the semiclassical motion of the nuclei. The quantities $z = X$ and $y = (X - a(t))/\epsilon$, although not independent, will behave approximately independently as $\epsilon \searrow 0$. In this transformation, we are exploiting the method of multiple scales. Intuitively, the electronic motion depends on the position of the nuclei on a length scale of order 1, but quantum mechanical fluctuations of the nuclear variables about $a(t)$ occur on a length scale of order ϵ . Thus, the electronic motion is not affected significantly by the coordinate y .

In our transformation of (2.10), we have some liberty as to when we replace X by z , and

when we instead replace it by $a(t) + \epsilon y$. We make choices resulting in the following:

$$i\epsilon^2 \frac{\partial \hat{\Psi}}{\partial t} = \left[-\frac{\epsilon^4}{2} \Delta_z - \epsilon^3 \nabla_z \cdot \nabla_y - \frac{\epsilon^2}{2} \Delta_y + i\epsilon \eta(t) \cdot \nabla_y + E_{(i)}(a(t) + \epsilon y) - E_{(i)}(z) + h(z) + \mu \left(\sum_i C_i(a(t) + \epsilon y)_i \right) F(t/\epsilon^2) \right] \hat{\Psi} \quad (3.2)$$

We wish to construct approximate solutions to (3.2), and so we make the ansatz

$$\hat{\Psi}(z, y, t) = e^{S_{(i)}(t)/\epsilon^2} e^{i\eta_{(i)}(t) \cdot y/\epsilon} G(z - a(t)) \chi(z, y, t) \quad (3.3)$$

with

$$\chi(z, y, t) = \psi_0(z, y, t) + \epsilon \psi_1(z, y, t) + \epsilon^2 \psi_2(z, y, t) + \dots \quad (3.4)$$

and $S_{(i)}(t), \eta_{(i)}(t)$ satisfying the classical equations of motion

$$S(t) = \int_{-\infty}^t \left[\frac{\eta(s)^2}{2} - E_{(i)}(a(s)) - \mu \left(\sum_i C_i(a(s))_i \right) F(s/\epsilon^2) \right] ds \quad (3.5)$$

$$\eta(t) = -E_{(i)}^{(1)}(a(t)) - \mu \sum_i C_i F(t/\epsilon^2) \quad (3.6)$$

The solutions $a(t)$ and $\eta(t)$ to these classical equations of motion and the quantity $S(t)$ are all dependent on ϵ , but they have a defined limit as $\epsilon \rightarrow 0$ by Lemma 2.2.

Upon substitution of the ansatz into (3.2), we notice many terms containing derivatives of G . All the functions ψ_j turn out to be exponentially small on the support of the derivatives of the G , i.e., a fixed distance δ away from $a(t)$. Thus these terms make no contribution to the expansion, and are dropped from further consideration. As warned earlier, since we have justified correcting the equations of motion for the semiclassical wave packets for the time-dependent perturbation in the nuclear variables, we now completely drop that part of the perturbation from consideration. For now, $a(t)$ and $\eta(t)$ will have no ϵ dependence. Instead, we find an equation that $\chi(z, y, t)$ must satisfy

$$i\epsilon^2 \frac{\partial \chi}{\partial t} = \left[\frac{\epsilon^4}{2} \Delta_z - \epsilon^3 \nabla_z \cdot \nabla_y - \frac{\epsilon^2}{2} \Delta_y - i\epsilon^2 \eta(t) \cdot \nabla_z + [E_{(i)}(a(t) + \epsilon y) - E_{(i)}(a(t)) - \epsilon y \cdot E_{(i)}^{(1)}(a(t))] + [h(z) - E_{(i)}(z)] \right] \chi \quad (3.7)$$

Putting (3.4) into (3.7), and expanding $E_{(i)}(a(t) + \epsilon y)$ in its Taylor series in ϵ , we then compare the like powers of ϵ on both sides of this result, and begin solving for the ψ_j .

Order 0. We begin by solving

$$[h(z) - E_{(i)}(z)]\psi_0 = 0. \quad (3.8)$$

The solution must be

$$\psi_0(z, y, t) = g_0(z, y, t)\Phi_{(i)}(z) \quad (3.9)$$

where g_0 is an as yet undetermined complex-valued function.

Order 1. Likewise,

$$[h(z) - E_{(i)}(z)]\psi_1 = 0. \quad (3.10)$$

The solution must be

$$\psi_1(z, y, t) = g_1(z, y, t)\Phi_{(i)}(z) \quad (3.11)$$

where g_1 is an as yet undetermined complex-valued function.

Order 2. The next step is more interesting, since we must solve

$$i\dot{\psi}_0 = -\frac{1}{2}\Delta_y\psi_0 + E_{(i)}^{(2)}(a(t))\frac{y^2}{2}\psi_0 - i\eta(t) \cdot \nabla_z\psi_0 + [h(z) - E_{(i)}(z)]\psi_2 \quad (3.12)$$

Here, we use $E_{(i)}^{(2)}(a(t))\frac{y^2}{2}$ as shorthand for $\frac{1}{2}\sum_{i,j}\frac{\partial^2 E}{\partial y_i\partial y_j}(a(t))y_i y_j$. We choose to separate (3.12) into an equation containing the terms that are scalar multiples of $\Phi_{(i)}(z)$ and an equation whose terms are orthogonal to $\Phi_{(i)}(z)$. This procedure yields

$$i\dot{g}_0 = -\frac{1}{2}\Delta_y g_0 + E_{(i)}^{(2)}(a(t))\frac{y^2}{2}g_0 - i\eta(t) \cdot \nabla_z g_0 \quad (3.13)$$

$$[h(z) - E_{(i)}(z)]\psi_2 = ig_0(\eta(t) \cdot \nabla_z \Phi(z)) \quad (3.14)$$

If we make the change of variables $f_0(w, y, t) = g_0(w + a(t), y, t)$ in (3.13),

$$if_0 = -\frac{1}{2}\Delta_y f_0 + E_{(i)}^{(2)}(a(t))\frac{y^2}{2}f_0 \quad (3.15)$$

which we may solve by Theorem 2.2,

$$f_0(w, y, t) = \sum_{|k| \leq \alpha} d_k \epsilon^{-n_1/2} \varphi_k(A(t), B(t), 1, 0, 0, y)$$

or

$$g_0(z, y, t) = \sum_{|k| \leq \alpha} d_k \epsilon^{-n_1/2} \varphi_k(A(t), B(t), 1, 0, 0, y). \quad (3.16)$$

To solve (3.14), we split ψ_2 into components parallel and perpendicular to $\Phi_{(i)}(z)$, and we obtain solutions

$$\psi_2^\perp(z, y, t) = i g_0(z, y, t) [h(z) - E_{(i)}(z)]^{-1} (\eta(t) \cdot \nabla_z \Phi(z)) \quad (3.17)$$

$$\psi_2^\parallel(z, y, t) = g_2(z, y, t) \Phi(z) \quad (3.18)$$

where again g_2 is yet undetermined.

Order 3. The relevant equation for the third order terms is

$$\begin{aligned} i\dot{\psi}_1 = & -\frac{1}{2} \Delta_y \psi_1 + E_{(i)}^{(2)}(a(t)) \frac{y^2}{2} \psi_1 + E_{(i)}^{(3)}(a(t)) \frac{y^3}{6} \psi_0 \\ & - i\eta(t) \cdot \nabla_z \psi_1 - \nabla_z \cdot \nabla_y \psi_0 + [h(z) - E_{(i)}(z)] \psi_3 \end{aligned} \quad (3.19)$$

We once again split the above equation into a relationship between terms that are multiples of $\Phi_{(i)}(z)$, and one between terms that are orthogonal to $\Phi_{(i)}(z)$. Letting P_\parallel and P_\perp denote the respective projections,

$$\begin{aligned} iP_\parallel \dot{\psi}_1 = & -\frac{1}{2} \Delta_y \psi_1 + E_{(i)}^{(2)}(a(t)) \frac{y^2}{2} \psi_1 + E_{(i)}^{(3)}(a(t)) \frac{y^3}{6} \psi_0 \\ & - iP_\parallel \eta(t) \cdot \nabla_z \psi_1 - P_\parallel \nabla_z \cdot \nabla_y \psi_0 \end{aligned} \quad (3.20)$$

$$[h(z) - E_{(i)}(z)] \psi_3 = iP_\perp \dot{\psi}_1 + iP_\perp \eta(t) \cdot \nabla_z \psi_1 - P_\perp \nabla_z \cdot \nabla_y \psi_0 \quad (3.21)$$

Now, (3.20) can be used to determine g_1 , so again we substitute $f_1(w - a(t), y, t) = g_1(w, y, t)$ and obtain

$$\begin{aligned} i\dot{f}_1 = & -\frac{1}{2}\Delta_y f_1 + E_{(i)}^{(2)}(a(t))\frac{y^2}{2}f_1 + E_{(i)}^{(3)}(a(t))\frac{y^3}{6}f_0 \\ & - \nabla_w \cdot \nabla_y f_0 - (\nabla_y f_0) \cdot \langle \Phi(w + a(t), t), \nabla \Phi(w + a(t), t) \rangle_{\mathcal{H}_{ei}} \end{aligned} \quad (3.22)$$

Since f_0 does not depend on w , the $\nabla_w \cdot \nabla_y$ term can be dropped, making this a nonhomogeneous equation in y and t for f_1 , however we may fix w . We may solve this equation by Theorem 2.3 and put z back in to find

$$g_1(z, y, t) = \sum_{|k| \leq \alpha+3} d_{k,1}(z + a(t), t) \epsilon^{-n_1/2} \varphi_k(A(t), B(t), 1, 0, 0, y), \quad (3.23)$$

where the coefficients $d_{k,1}$ may be solved for using the procedure outlined in the proof of Theorem 2.3.

We now turn our attention to (3.21), which we handle again by splitting $\psi_3 = \psi_3^\parallel + \psi_3^\perp$. Thus,

$$\psi_3^\perp = [h(z) - E_{(i)}(z)]^{-1} \left(i g_1 \eta(t) \cdot \nabla_z \Phi_{(i)}(z) + P_\perp(\nabla_y g_0) \cdot \nabla_z \Phi_{(i)}(z) \right) \quad (3.24)$$

$$\psi_3^\parallel = g_3(z, y, t) \Phi_{(i)}(z) \quad (3.25)$$

with undetermined g_3 .

Order 4. The step involving the fourth order terms is essentially the same as the induction step. We break the equation

$$\begin{aligned} i\dot{\psi}_2 = & -\frac{1}{2}\Delta_y \psi_2 + E_{(i)}^{(2)}(a(t))\frac{y^2}{2}\psi_2 + E_{(i)}^{(3)}(a(t))\frac{y^3}{6}\psi_1 \\ & + E_{(i)}^{(4)}(a(t))\frac{y^4}{24}\psi_0 - i\eta(t) \cdot \nabla_z \psi_2 - \nabla_z \cdot \nabla_y \psi_1 \\ & - \frac{1}{2}\Delta_z \psi_0 + [h(z) - E_{(i)}(z)]\psi_4 \end{aligned} \quad (3.26)$$

into an equation of terms that are scalar multiples of $\Phi_{(i)}(z)$ and an equation involving terms orthogonal to $\Phi_{(i)}(z)$. We solve the former for g_2 by using the technique in Theorem 2.3.

The latter is solved by breaking ψ_4 into ψ_4^{\parallel} and ψ_4^{\perp} . ψ_4^{\parallel} gives rise to an undetermined g_4 which we will solve for in step 6.

Proceeding in this manner, we see that the j th order terms from (3.7) determine g_{j-2} and ψ_j^{\perp} . We may now insert the calculated quantities into the asymptotic expansion. After changing back to the original coordinates via $\Psi(X, \zeta, x, t) = \hat{\Psi}(X, \frac{X-a(t)}{\epsilon}, \zeta, x, t)$, the second conclusion of the theorem is apparent. To prove the first conclusion, let us calculate the truncation error of

$$\Psi(\mathfrak{X}, t) = \sum_{j=0}^J \Psi_j(\mathfrak{X}, t)\epsilon^j + \Psi_{J+1}^{\perp}(\mathfrak{X}, t)\epsilon^{J+1} + \Psi_{J+2}^{\perp}(\mathfrak{X}, t)\epsilon^{J+2},$$

which is

$$\zeta(\mathfrak{X}, t) = i\epsilon^2 \frac{\partial \Psi}{\partial t}(\mathfrak{X}, t) - H(\epsilon)\Psi(\mathfrak{X}, t)$$

Upon explicit calculation, many terms cancel because of the formal calculations done to determine the terms of the asymptotic series. Terms containing derivatives of G have exponential falloff [7], some terms contain functions with bounded norms times ϵ^l with $l \geq J+3$, and some terms are handled by means of the Taylor series remainder technique used in the proof of Theorem 2.3. The truncation error has order ϵ^{J+3} , then, and the first conclusion of the Theorem then follows from Lemma 2.1. ■

Chapter 4

The Time-Dependent Perturbation

In this chapter, we seek to develop a formal Dyson series expansion for the effect of the time-dependent perturbation on the asymptotic series developed in Chapter 3. We then prove that this series is accurate to the required orders in μ and in ϵ .

The first result develops the Dyson series for any smooth potential V , but only up to an accuracy of $O(\mu)$. The series will be accurate to any order in ϵ . We consider the case where there are no electron energy level crossings. In principle, this technique could be used in conjunction with solution to the unperturbed case with crossings developed in [5], but the calculations involved would be daunting. After discussing the problem in that generality, we then restrict attention to smooth potentials such that our unperturbed electron hamiltonian has purely discrete spectrum. Under this restriction, we can develop the series to any order in μ . The failure of this technique to provide any greater accuracy in the general case will be discussed in detail in section 5.

4.1 Notation

We will use $\hat{\Psi}(\epsilon, \mu, t)$ to denote the formal Dyson series expansion, and $\Psi(\epsilon, t)$ to denote the solution to the unperturbed case discussed in Chapter 3. As before, the i th electron eigenfunction of

$$h(X) = \frac{1}{2} \left(\Delta_\zeta + \sum_j^{n_2-1} \Delta_{x_j} \right) + V(X, \zeta, x, \mathbf{q})$$

is represented by $\Phi_{(i)}(X)$, with corresponding eigenvalue $E_{(i)}(X)$.

In the development of the solution to the perturbed case, we will discover that the event of an electron transition at time s_1 will change the dynamics of the nuclei at that time. Before s_1 , the nuclei will propagate under the influence of the effective potential created by the initial electron energy level, say $E_{(i)}(X)$, and then afterward will propagate under the influence of the excited electron energy level $E_{(j)}$. To denote the effect of multiple electron transitions, we will use a convenient shorthand notation.

Whenever we wish to designate the semiclassical state $\varphi_j(A^{(i)}(t), B^{(i)}(t), \epsilon^2, a^{(i)}(t), \eta^{(i)}(t), X)$ propagating using the effective potential from the i th electron energy level, we will use the shorthand $\varphi_j^{(i)}(t)$. Furthermore, by the expression $\varphi_j^{(i, k_1, \dots, k_n)}(s_1, \dots, s_n, t)$ we will mean the semiclassical state that propagates using the effective potential from the i th electron energy level in the time interval $(T_l, s_1]$, using the effective potential from the k_1 th electron energy level in the time interval $(s_1, s_2]$, and so on, using the dynamics in the k_n th level during the interval $(s_n, t]$. Thus,

$$\varphi_j^{(i, k_1, \dots, k_n)}(s_1, \dots, s_n, t) = \begin{cases} \varphi_j^{(i)}(\tau) & -\infty < \tau < s_1, \\ \varphi_j^{(k_1)}(\tau) & s_1 \leq \tau < s_2, \\ \vdots & \\ \varphi_j^{(k_n)}(\tau) & s_n \leq \tau < t. \end{cases} \quad (4.1)$$

It is understood that the solutions to (2.23) in each interval will be chosen to make the function continuous on the interval boundaries. Let $\Psi_{(i),n}(\epsilon, t)$ be the asymptotic series from

Theorem 3.1, calculated from the starting electron eigenfunction $\Phi_{(i)}(X)$, truncated at the ϵ^n term, plus the perpendicular terms for the next two orders. That is,

$$\Psi_{(i),n}(\epsilon, t) \equiv \sum_{k=0}^n \Psi_k(X, t)\epsilon^k + \Psi_{n+1}^\perp(X, t)\epsilon^{n+1} + \Psi_{n+2}^\perp(X, t)\epsilon^{n+2} \quad (4.2)$$

as calculated in Chapter 3. When we talk about $\Psi_{(i,k_1,\dots,k_n),n}(\epsilon, s_1, \dots, s_n, t)$ we will mean that all the φ_j 's in the formula are in fact of the form $\varphi_j^{(i,k_1,\dots,k_n)}(s_1, \dots, s_n, t)$. Finally, note that by our definition, an expression like $\Psi_{(i,k_1),n}(\epsilon, s_1, s_1)$ would mean that the φ_j 's in the formula are $\varphi_j^{(i)}$'s up to but not including time s_1 , and that at the time s_1 , they are $\varphi_j^{(k_1)}$'s.

We will use similar notation with the analogue of the classical action $S^{(i)}(t)$.

4.2 Orthogonality Lemma

In our calculation of the formal Dyson expansions, we will require the fact that series determined in Chapter 3 from different electron eigenfunctions $\Phi_{(i)}(X)$ are approximately orthogonal in the space of the ζ and x variables.

Lemma 4.1 *For any time t ,*

$$\langle \Psi_{(i),n}(\epsilon, t), \Psi_{(j),n}(\epsilon, t) \rangle_{\zeta, x} = O(\epsilon^{n+1}) \quad (4.3)$$

Proof. Consider a revised Born-Oppenheimer equation

$$i\epsilon^2 \frac{\partial \Psi}{\partial t} = -\frac{\epsilon^4}{2} f(t) \Delta_X \Psi + h(X) \Psi + \mu \sum_i C_i X_i F(t/\epsilon^2) \quad (4.4)$$

or

$$i\epsilon^2 \frac{\partial \Psi}{\partial t} = H'(\epsilon, \mu, t) \Psi \quad (4.5)$$

Here, $f(t) \in C^\infty$ is chosen to be identically one on the interval $(T_l, 0)$, and identically zero on the interval $(1, \infty)$. Thus, the asymptotic series solutions to (4.4) are exactly those calculated

in Chapter 3 when $t < 0$. We will show that the approximate solutions that result from an application of Theorem 3.1 are exactly orthogonal when $t > 1$, and then apply the propagator for this new equation to show that the approximate solutions were almost orthogonal even when $t < 0$. Since the propagator is unitary, this procedure will prove the lemma. To find asymptotic series solutions to (4.4), one may carry out computations in exactly the same manner as in Chapter 3. The presence of $f(t)$ requires only minor modifications in certain formulas there. We will show that all ψ_j^\perp terms will vanish for $t > 1$. Since all the ψ_j^\parallel terms are multiples of the electron eigenfunctions, the truncated approximations $\Psi_{(i),n}(\epsilon, t)$ will all be exactly orthogonal for different i when $t > 1$.

Now, ψ_0 and ψ_1 are both completely parallel to the electron eigenfunctions, so we begin our consideration with the equation determining ψ_2^\perp .

$$\psi_2^\perp(z, y, t) = ig_0(z, y, t)[h(z) - E_{(i)}(z)]^{-1}(f(t)\eta(t) \cdot \nabla_z \Phi(z)) \quad (4.6)$$

It is clear that when $t > 1$, then $f(t) = 0$, and hence ψ_2^\perp vanishes.

For ψ_3^\perp , we have the equation

$$\psi_3^\perp = [h(z) - E_{(i)}(z)]^{-1} \left(ig_1 f(t) \eta(t) \cdot \nabla_z \Phi_{(i)}(z) + P_\perp f(t) (\nabla_y g_0) \cdot \nabla_z \Phi_{(i)}(z) \right) \quad (4.7)$$

Each term contains an $f(t)$, and hence vanishes when $t > 1$.

For the induction step ($j \geq 4$), we have that

$$\begin{aligned} \psi_j^\perp = [h(z) - E_{(i)}(z)]^{-1} & \left[iP_\perp \dot{\psi}_{j-2} - \left(\frac{1}{2} f(t) \Delta_y \psi_{j-2}^\perp - \sum_{k=2}^j E_{(i)}^{(k)} \frac{y^k}{k!} \psi_{j-k}^\perp \right) \right. \\ & \left. + iP_\perp f(t) \eta(t) \cdot \nabla_z \psi_{j-2} + P_\perp f(t) \nabla_z \cdot \nabla_y \psi_{j-3} + \frac{1}{2} P_\perp f(t) \Delta_z \psi_{j-4} \right] \quad (4.8) \end{aligned}$$

Most terms contain $f(t)$. Terms containing ψ_{j-k}^\perp for $k \geq 2$ are already zero by the previous parts of the induction. One term contains a derivative of ψ_{j-2}^\perp , hence will contain $f(t)$ and its derivatives, which are also identically zero for $t > 1$. Thus we see that all ψ_j^\perp terms vanish for $t > 1$, hence we have exact orthogonality on that interval.

Now consider

$$\begin{aligned} & \frac{\partial}{\partial t} \langle \Psi_{(i),n}(\epsilon, t), \Psi_{(j),n}(\epsilon, t) \rangle_{\zeta, x} \\ &= \left\langle \frac{\partial}{\partial t} \Psi_{(i),n}(\epsilon, t), \Psi_{(j),n}(\epsilon, t) \right\rangle + \left\langle \Psi_{(i),n}(\epsilon, t), \frac{\partial}{\partial t} \Psi_{(j),n}(\epsilon, t) \right\rangle \end{aligned} \quad (4.9)$$

By equation (4.5) and Theorem 3.1, we can substitute

$$\begin{aligned} &= \left\langle \frac{H'(\epsilon)}{i\epsilon^2} \Psi_{(i),n}(\epsilon, t) + O(\epsilon^{n+1}), \Psi_{(j),n}(\epsilon, t) \right\rangle + \left\langle \Psi_{(i),n}(\epsilon, t), \frac{H'(\epsilon)}{i\epsilon^2} \Psi_{(j),n}(\epsilon, t) + O(\epsilon^{n+1}) \right\rangle \\ &= O(\epsilon^{n+1}) + \left\langle \frac{H'(\epsilon)}{i\epsilon^2} \Psi_{(i),n}(\epsilon, t), \Psi_{(j),n}(\epsilon, t) \right\rangle + \left\langle \Psi_{(i),n}(\epsilon, t), \frac{H'(\epsilon)}{i\epsilon^2} \Psi_{(j),n}(\epsilon, t) \right\rangle \end{aligned} \quad (4.10)$$

Because the operator $H'(\epsilon)$ is self-adjoint, the last two terms in the last step above cancel. The conclusion must be that the lemma holds for the revised equation (4.4). Since for $t < 0$ the states of the revised equation are identical to those of our original equation, the above argument repeated with $H(\epsilon)$ in place of $H'(\epsilon)$ shows that the lemma holds for (2.12). ■

4.3 General Case

Theorem 4.1 *Let $h(X)$ satisfy the conditions of Theorem 3.1, and suppose that for any particular X , $\tilde{P}(X)$ is the projection, defined on the electron Hilbert space, determined by the set of eigenvalues $E_{(i)}(X)$ of $h(X)$. Further define*

$$\tilde{\mathcal{P}} = \int_{\mathbb{R}^{3n_1}}^{\oplus} (\tilde{P}(X)) dX \quad (4.11)$$

Then an approximate formal Dyson series solution to $O(\mu)$ for wavefunctions $\tilde{\mathcal{P}}\hat{\Psi}(\epsilon, \mu, t)$ where $\hat{\Psi}$ satisfies

$$i\epsilon^2 \frac{\partial}{\partial t} \hat{\Psi}(\epsilon, \mu, t) = (H(\epsilon) + \mu H_1) \hat{\Psi}(\epsilon, \mu, t) \quad (4.12)$$

is given by

$$\begin{aligned} \tilde{\mathcal{P}}\hat{\Psi}(\epsilon, \mu, t) &= \Psi_{(i),n}(\epsilon, t) e^{iS^{(i)}(t)/\epsilon^2} \\ &\quad - \frac{i\mu}{\epsilon^2} \int_{T_1}^t ds_1 \sum_{k_1} \langle \Psi_{(i,k_1),n}(\epsilon, s_1, s_1) | H_1(s_1/\epsilon^2) \Psi_{(i),n}(\epsilon, s_1) \rangle_{\zeta, x} \Psi_{(i,k_1),n}(\epsilon, s_1, t) e^{iS^{(i,k_1)}(s_1, t)/\epsilon^2}. \end{aligned} \quad (4.13)$$

This approximation is asymptotic in the sense that it satisfies

$$\left\| U_{\epsilon,\mu}(t, T_l) \hat{\Psi}(\epsilon, \mu, T_l) - \hat{\Psi}(\epsilon, \mu, t) \right\| \leq C_n \epsilon^{n+1} + K \mu^2 \quad (4.14)$$

Remark. We will compute this approximation only for wavefunctions $\tilde{\mathcal{P}}\hat{\Psi}(\epsilon, \mu, t)$. Thus, we are ignoring the piece of the wavefunction where any electrons are removed to the continuum, or ionized. One can physically measure the result of this projection, and hence, in a practical sense, one can afford to ignore the continuum in this expansion. For all $s \leq t$, the electronic configuration state in what we are computing is given by some linear combination of the electronic eigenfunctions $\Phi_{(i)}$.

Proof. We will first verify formula (4.13) from the definition of the formal Dyson series expansion. The first term is given by

$$U_\epsilon(t, T_l) \Psi_{(i),n}(\epsilon, T_l) = e^{iS^{(i)}(t)/\epsilon^2} \Psi_{(i),n}(\epsilon, t) \quad (4.15)$$

and introduces an error of only $O(\epsilon^{n+1})$ by Theorem 3.1.

The second term is given by

$$\frac{-i\mu}{\epsilon^2} \int_{T_l}^t ds_1 U_\epsilon(t, s_1) H_1(s_1/\epsilon^2) U_\epsilon(s_1, T_l) \Psi_{(i),n}(\epsilon, T_l) \quad (4.16)$$

Of course, in (4.16)

$$U_\epsilon(s_1, T_l) \Psi_{(i),n}(\epsilon, T_l) = e^{iS^{(i)}(s_1)/\epsilon^2} \Psi_{(i),n}(\epsilon, s_1),$$

once again making an acceptable error of $O(\epsilon^{n+1})$. Lemma 4.1 allows us to easily calculate components in the $\Psi_{(k_1),n}$ direction. So we now express $H_1(s_1/\epsilon^2)$ applied to the right hand side of (4.3) as

$$\sum_{k_1} \langle \Psi_{(i,k_1),n}(\epsilon, s_1, s_1) | H_1(s_1/\epsilon^2) \Psi_{(i),n}(\epsilon, s_1) \rangle_{\zeta,x} \Psi_{(i,k_1),n}(\epsilon, s_1, s_1) e^{iS^{(i)}(s_1)/\epsilon^2} \quad (4.17)$$

with an error of $O(\epsilon^{n+1})$. Note that the inner product here is taken in the space of the electron variables so that the expansion is in terms of a complete basis for the range of $\tilde{\mathcal{P}}$.

Now we apply $U_\epsilon(t, s_1)$ to (4.17), and the propagator acts differently on the individual terms of the sum, moving the nuclei semiclassically inside the effective potential of the k_1 th level. So, in fact, the first order term of the Dyson series can be written

$$-\frac{i\mu}{\epsilon^2} \int_{T_1}^t ds_1 \sum_{k_1} \langle \Psi_{(i,k_1),n}(\epsilon, s_1, s_1) | H_1(s_1/\epsilon^2) \Psi_{(i),n}(\epsilon, s_1) \rangle_{\zeta,x} \Psi_{(i,k_1),n}(\epsilon, s_1, t) e^{iS^{(i,k_1)}(s_1,t)/\epsilon^2}. \quad (4.18)$$

At no stage in this calculation have we introduced an error of more than $O(\epsilon^{n+1})$ by propagating or taking inner products with the truncated approximations $\Psi_{(i),n}(\epsilon, t)$. It remains to be shown, however, that this calculation has produced an accurate approximation to the solution of the problem perturbed in μ . The appropriate quantity to investigate comes from Lemma 2.1.

$$\left(i\epsilon^2 \frac{\partial}{\partial t} - (H(\epsilon) + \mu H_1) \right) \left[\Psi_{(i),n}(\epsilon, t) e^{iS^{(i)}(t)/\epsilon^2} - \frac{i\mu}{\epsilon^2} \int_{T_1}^t ds_1 \sum_{k_1} \langle \Psi_{(i,k_1),n}(\epsilon, s_1, s_1) | H_1(s_1/\epsilon^2) \Psi_{(i),n}(\epsilon, s_1) \rangle_{\zeta,x} \Psi_{(i,k_1),n}(\epsilon, s_1, t) e^{iS^{(i,k_1)}(s_1,t)/\epsilon^2} \right] \quad (4.19)$$

We will break this computation into several steps.

Step A. Because of Theorem 3.1, we already know that

$$\begin{aligned} \left(i\epsilon^2 \frac{\partial}{\partial t} - (H(\epsilon) + \mu H_1) \right) \Psi_{(i),n}(\epsilon, t) e^{iS^{(i)}(t)/\epsilon^2} \\ = O(\epsilon^{n+3}) - \mu H_1(t/\epsilon^2) \Psi_{(i),n}(\epsilon, t) e^{iS^{(i)}(t)/\epsilon^2}. \end{aligned} \quad (4.20)$$

Step B. Take the derivative

$$\begin{aligned}
& i\epsilon^2 \frac{\partial}{\partial t} \left(-\frac{i\mu}{\epsilon^2} \int_{T_l}^t ds_1 \sum_{k_1} \langle \Psi_{(i,k_1),n}(\epsilon, s_1, s_1) | H_1(s_1/\epsilon^2) \Psi_{(i),n}(\epsilon, s_1) \rangle_{\zeta,x} \Psi_{(i,k_1),n}(\epsilon, s, t) e^{iS^{(i,k_1)}(s_1,t)/\epsilon^2} \right) \\
&= \mu \sum_{k_1} \langle \Psi_{(i,k_1),n}(\epsilon, t, t) | H_1(t/\epsilon^2) \Psi_{(i),n}(\epsilon, t) \rangle_{\zeta,x} \Psi_{(i,k_1),n}(\epsilon, t, t) e^{iS^{(i)}(t)/\epsilon^2} \\
&\quad - \frac{i\mu}{\epsilon^2} \int_{T_l}^t ds_1 \sum_{k_1} \langle \Psi_{(i,k_1),n}(\epsilon, s_1, s_1) | H_1(s_1/\epsilon^2) \Psi_{(i),n}(\epsilon, s_1) \rangle_{\zeta,x} \times \\
&\qquad\qquad\qquad \left(i\epsilon^2 \frac{\partial}{\partial t} \right) [\Psi_{(i,k_1),n}(\epsilon, s_1, t) e^{iS^{(i,k_1)}(s_1,t)/\epsilon^2}]
\end{aligned} \tag{4.21}$$

Step C. We apply $-(H(\epsilon) + H_1(t/\epsilon^2))$ to the quantity of which we took the derivative in Step B. The result is

$$\begin{aligned}
& \frac{i\mu}{\epsilon^2} \int_{T_l}^t ds_1 \sum_{k_1} \langle \Psi_{(i,k_1),n}(\epsilon, s_1, s_1) | H_1(s_1/\epsilon^2) \Psi_{(i),n}(\epsilon, s_1) \rangle_{\zeta,x} H(\epsilon) \Psi_{(i,k_1),n}(\epsilon, s_1, t) e^{iS^{(i,k_1)}(s_1,t)/\epsilon^2} \\
&\quad + \frac{i\mu^2}{\epsilon^2} H_1(t/\epsilon^2) \int_{T_l}^t ds_1 \sum_{k_1} \langle \Psi_{(i,k_1),n}(\epsilon, s_1, s_1) | H_1(s_1/\epsilon^2) \Psi_{(i),n}(\epsilon, s_1) \rangle_{\zeta,x} \\
&\qquad\qquad\qquad \times \Psi_{(i,k_1),n}(\epsilon, s_1, t) e^{iS^{(i,k_1)}(s_1,t)/\epsilon^2}
\end{aligned} \tag{4.22}$$

If we apply Lemma 2.1 to the sum of the results of the above three steps, we will obtain an estimate on the size of the error in our approximation (4.13).

The first term of (4.20) gives us an $O(\epsilon^{n+1})$ error to the wavefunction. Now consider the sum of the first term on the RHS of (4.21) with the μ term of (4.20). Because of Lemma 4.1, we must conclude that the sum has the form

$$\mu \epsilon^{n+1} \xi(t/\epsilon^2) \tag{4.23}$$

This term contributes an error bounded by

$$\epsilon^{-2} \int_{T_l}^t ds \mu \epsilon^{n+1} \xi(s/\epsilon^2) \tag{4.24}$$

and once we carry out the integral via the substitution $u = s/\epsilon^2$, we see that it is bounded by $O(\mu \epsilon^{n+1})$.

Next, the second term of (4.21) and the first term of (4.22) combine by virtue of Theorem 3.1 to give

$$-\frac{i\mu}{\epsilon^2} \int_{T_i}^t ds_1 \sum_{k_1} \langle \Psi_{(i,k_1),n}(\epsilon, s_1, s_1) | H_1(s_1/\epsilon^2) \Psi_{(i),n}(\epsilon, s_1) \rangle_{\zeta,x} \times O(\epsilon^{n+1}) \quad (4.25)$$

and again, using the substitution $u = s_1/\epsilon^2$ to do the integral, this term is $O(\epsilon^{n+1})$.

Our calculation leaves us with only the term

$$\frac{i\mu^2}{\epsilon^2} H_1(t/\epsilon^2) \int_{T_i}^t ds_1 \sum_{k_1} \langle \Psi_{(i,k_1),n}(\epsilon, s_1, s_1) | H_1(s_1/\epsilon^2) \Psi_{(i),n}(\epsilon, s_1) \rangle_{\zeta,x} \Psi_{(i,k_1),n}(\epsilon, s_1, t) e^{iS^{(i,k_1)}(s_1,t)/\epsilon^2},$$

and we choose to use substitution in the integral again to get

$$i\mu^2 H_1(t/\epsilon^2) \int_{T_i/\epsilon^2}^{t/\epsilon^2} du \sum_{k_1} \langle \Psi_{(i,k_1),n}(\epsilon, \epsilon^2 u, \epsilon^2 u) | H_1(u) \Psi_{(i),n}(\epsilon, \epsilon^2 u) \rangle_{\zeta,x} \\ \times \Psi_{(i,k_1),n}(\epsilon, \epsilon^2 u, \epsilon^2 t) e^{iS^{(i,k_1)}(u,t)/\epsilon^2}$$

which contributes an error bounded by

$$\epsilon^{-2} \int_{T_i}^t ds i\mu^2 H_1(s/\epsilon^2) \\ \times \int_{T_i/\epsilon^2}^{s/\epsilon^2} du \sum_{k_1} \langle \Psi_{(i,k_1),n}(\epsilon, \epsilon^2 u, \epsilon^2 u) | H_1(u) \Psi_{(i),n}(\epsilon, \epsilon^2 u) \rangle_{\zeta,x} \Psi_{(k_1),n}(\epsilon, \epsilon^2 u, \epsilon^2 s) e^{iS^{(i,k_1)}(u,s)/\epsilon^2}. \quad (4.26)$$

We use the substitution $v = s/\epsilon^2$ to see that this term is $O(\mu^2)$. Hence the conclusion of Theorem 4.1. \blacksquare

4.4 Molecule Without Continuum

Theorem 4.2 *Let $h(X)$ satisfy the conditions of Theorem 3.1, with the additional condition that the spectrum of $h(X)$ contains only the set of eigenvalues $E_{(i)}(X)$. That is, $h(X)$ has*

purely discrete spectrum. Then an approximate formal Dyson series solution to $O(\mu^m)$ for the equation

$$i\epsilon^2 \frac{\partial}{\partial t} \hat{\Psi}(\epsilon, \mu, t) = (H(\epsilon) + \mu H_1) \hat{\Psi}(\epsilon, \mu, t) \quad (4.27)$$

is given by

$$\begin{aligned} \hat{\Psi}(\epsilon, \mu, t) &= \Psi_{(i),n}(\epsilon, t) e^{iS^{(i)}(t)/\epsilon^2} \\ &- \frac{i\mu}{\epsilon^2} \int_{T_l}^t ds_1 \sum_{k_1} \langle \Psi_{(i,k_1),n}(\epsilon, s_1, s_1) | H_1(s_1/\epsilon^2) \Psi_{(i),n}(\epsilon, s_1) \rangle_{\zeta,x} \Psi_{(i,k_1),n}(\epsilon, s_1, t) e^{iS^{(i,k_1)}(s_1,t)/\epsilon^2} + \dots \\ &\dots + (-1)^m \left(\frac{i\mu}{\epsilon^2} \right)^m \int_{T_l}^t ds_m \int_{T_l}^{s_m} ds_{m-1} \dots \int_{T_l}^{s_2} ds_1 \\ &\times \sum_{k_m} \left\langle \Psi_{(i,k_1,\dots,k_m),n}(\epsilon, s_1, s_2, \dots, s_m, s_m) \middle| H_1(s_m/\epsilon^2) \right. \\ &\times \sum_{k_{m-1}} \left\langle \Psi_{(i,k_1,\dots,k_{m-1}),n}(\epsilon, s_1, s_2, \dots, s_{m-1}, s_{m-1}) \middle| H_1(s_{m-1}/\epsilon^2) \dots \right. \\ &\times \sum_{k_1} \left\langle \Psi_{(i,k_1),n}(\epsilon, s_1, s_1) | H_1(s_1/\epsilon^2) \Psi_{(i),n}(\epsilon, s_1) \right\rangle \Psi_{(i,k_1),n}(\epsilon, s_1, s_2) \dots \left. \right\rangle \\ &\times \Psi_{(i,k_1,\dots,k_{m-1}),n}(\epsilon, s_1, \dots, s_m) \left. \right\rangle \Psi_{(i,k_1,\dots,k_m),n}(\epsilon, s_1, \dots, s_m, t) e^{iS^{(i,k_1,\dots,k_m)}(s_1,\dots,s_m,t)/\epsilon^2} \end{aligned} \quad (4.28)$$

This approximation is asymptotic in the sense that it satisfies

$$\left\| U_{\epsilon,\mu}(t, T_l) \hat{\Psi}(\epsilon, \mu, T_l) - \hat{\Psi}(\epsilon, \mu, t) \right\| \leq C_n \epsilon^{n+1} + K_m \mu^{m+1} \quad (4.29)$$

Remarks.

1. The zeroth and first order terms (in μ) are identical to those found in (4.13). The additional assumption that the electrons have no continuum to which to escape allows us to extend the series.
2. We may summarize the intuitive meaning of each term of the Dyson series. The leading order term is propagation with no electron transitions. The $O(\mu)$ term covers all the

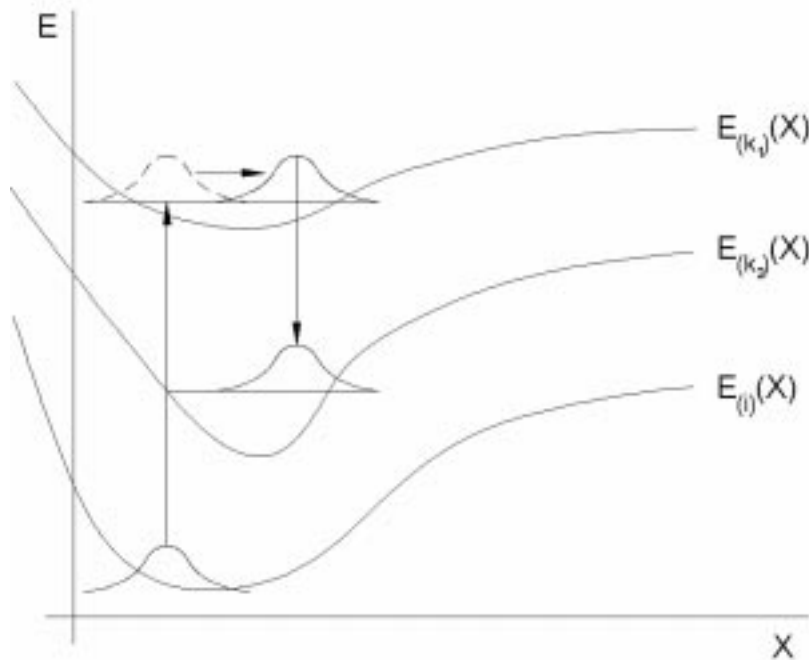


Figure 4.1: One possible transition sequence occurring in the $O(\mu^2)$ term.

possible situations where the molecule begins with initial electron energy state $E_{(i)}$ and then at some time s_1 makes an electron transition to some other state $E_{(k_1)}$. If we sum over all the excited states k_1 and integrate over all the possible times s_1 when this transition can occur, we get the first order term of the Dyson expansion (4.28). In general, the $O(\mu^m)$ term covers all the possibilities for m electron transitions.

As one can see from looking at Definition 2.17, the process of calculating additional terms is recursive. We show the calculation of the second order term (in μ). The other terms are computed in a completely analogous manner. Let us denote the second term of (4.28) evaluated at $t = T_l$ by $\hat{\Psi}_1(\epsilon, \mu, T_l)$.

The third term of the Dyson expansion would be

$$\frac{-i\mu}{\epsilon^2} \int_{T_l}^t ds_1 U_\epsilon(t, s_2) H_1(s_2/\epsilon^2) U_\epsilon(s_2, T_l) \hat{\Psi}_1(\epsilon, \mu, T_l). \quad (4.30)$$

Applying $U_\epsilon(s_2, T_l)$, we have

$$-\frac{i\mu}{\epsilon^2} \int_{T_l}^{s_2} ds_1 \sum_{k_1} \langle \Psi_{(i,k_1),n}(\epsilon, s_1, s_1) | H_1(s_1/\epsilon^2) \Psi_{(i),n}(\epsilon, s_1) \rangle_{\zeta,x} \Psi_{(i,k_1),n}(\epsilon, s_1, s_2) e^{iS^{(i,k_1)}(s_1,s_2)/\epsilon^2} \quad (4.31)$$

while making an error of $O(\epsilon^{n+1})$.

We also expand the operator $H_1(s_2)$ in the approximate basis of Lemma 4.1 to obtain

$$\begin{aligned} & -\frac{i\mu}{\epsilon^2} \sum_{k_2} \left\langle \Psi_{(i,k_1,k_2),n}(\epsilon, s_1, s_2, s_2) \middle| H_1(s_2/\epsilon^2) \right. \\ & \quad \times \int_{T_l}^{s_2} ds_1 \sum_{k_1} \langle \Psi_{(i,k_1),n}(\epsilon, s_1, s_1) | H_1(s_1/\epsilon^2) \Psi_{(i),n}(\epsilon, s_1) \rangle \\ & \quad \left. \times \Psi_{(i,k_1),n}(\epsilon, s_1, s_2) e^{iS^{(i,k_1)}(s_1,s_2)/\epsilon^2} \right\rangle \Psi_{(i,k_1,k_2),n}(\epsilon, s_1, s_2, s_2) \quad (4.32) \end{aligned}$$

After interchanging the order of integration over s_1 with the inner product integration and the sum over the electron states (k_2), we then apply $U_\epsilon(t, s_2)$ to

$$\begin{aligned} & -\frac{i\mu}{\epsilon^2} \int_{T_l}^{s_2} ds_1 \sum_{k_2} \left\langle \Psi_{(i,k_1,k_2),n}(\epsilon, s_1, s_2, s_2) \middle| H_1(s_2/\epsilon^2) \right. \\ & \quad \times \sum_{k_1} \langle \Psi_{(i,k_1),n}(\epsilon, s_1, s_1) | H_1(s_1/\epsilon^2) \Psi_{(i),n}(\epsilon, s_1) \rangle \\ & \quad \left. \times \Psi_{(i,k_1),n}(\epsilon, s_1, s_2) \right\rangle \Psi_{(i,k_1,k_2),n}(\epsilon, s_1, s_2, s_2) e^{iS^{(i,k_1)}(s_1,s_2)/\epsilon^2}. \quad (4.33) \end{aligned}$$

We apply this operator inside the integral sign and, per the Dyson expansion procedure, integrate over s_2 to find the final form of the term

$$\begin{aligned} & -\left(\frac{i\mu}{\epsilon^2}\right)^2 \int_{T_l}^t ds_2 \int_{T_l}^{s_2} ds_1 \sum_{k_2} \left\langle \Psi_{(i,k_1,k_2),n}(\epsilon, s_1, s_2, s_2) \middle| H_1(s_2/\epsilon^2) \right. \\ & \quad \times \sum_{k_1} \left\langle \Psi_{(i,k_1),n}(\epsilon, s_1, s_1) | H_1(s_1/\epsilon^2) \Psi_{(i),n}(\epsilon, s_1) \right\rangle \Psi_{(i,k_1),n}(\epsilon, s_1, s_2) \Big\rangle \\ & \quad \times \Psi_{(i,k_1,k_2),n}(\epsilon, s_1, s_2, t) e^{iS^{(i,k_1,k_2)}(s_1,s_2,t)/\epsilon^2}. \quad (4.34) \end{aligned}$$

At no stage in this calculation have we introduced an error of more than $O(\epsilon^{n+1})$ by propagating or taking inner products with the truncated approximations $\Psi_{(i,k_1),n}(\epsilon, s_1, t)$. It remains

to be shown, once again, that this calculation has produced an accurate approximation to the solution of the problem perturbed in μ . The proof of Theorem 4.1 provides us with the anchor to an induction proof in m . We will assume that we have carried out the calculation of the truncation error from Lemma 2.1 on the series up to the $(m-1)$ st term and were left with terms that will produce a solution error of $O(\epsilon^{n+1})$ and a term of the form

$$\begin{aligned}
& (-1)^m \left(\frac{(i\mu)^m}{\epsilon^{2(m-1)}} \right) H_1(t/\epsilon^2) \\
& \int_{T_l}^t ds_{m-1} \int_{T_l}^{s_{m-1}} ds_{m-2} \dots \int_{T_l}^{s_2} ds_1 \sum_{k_{m-1}} \left\langle \Psi_{(i,k_1, \dots, k_{m-1}),n}(\epsilon, s_1, s_2, \dots, s_{m-1}, s_{m-1}) \middle| H_1(s_{m-1}/\epsilon^2) \right. \\
& \times \sum_{k_{m-2}} \left\langle \Psi_{(i,k_1, \dots, k_{m-2}),n}(\epsilon, s_1, s_2, \dots, s_{m-2}, s_{m-2}) \middle| H_1(s_{m-2}/\epsilon^2) \dots \right. \\
& \times \sum_{k_1} \left\langle \Psi_{(i,k_1),n}(\epsilon, s_1, s_1) \middle| H_1(s_1/\epsilon^2) \Psi_{(i),n}(\epsilon, s_1) \Psi_{(i,k_1),n}(\epsilon, s_1, s_2) \dots \right\rangle \\
& \times \left. \Psi_{(i,k_1, \dots, k_{m-2}),n}(\epsilon, s_1, \dots, s_{m-1}) \right\rangle \Psi_{(i,k_1, \dots, k_{m-1}),n}(\epsilon, s_1, \dots, s_{m-1}, t) e^{iS^{(i,k_1, \dots, k_{m-1})}(s_1, \dots, s_{m-1}, t)/\epsilon^2}
\end{aligned} \tag{4.35}$$

We need to calculate the truncation error from just the $O(\mu^m)$ term of (4.28).

$$\begin{aligned}
& \left(i\epsilon^2 \frac{\partial}{\partial t} - (H(\epsilon) + \mu H_1) \right) \\
& \left[(-1)^m \left(\frac{i\mu}{\epsilon^2} \right)^m \int_{T_l}^t ds_m \int_{T_l}^{s_m} ds_{m-1} \dots \int_{T_l}^{s_2} ds_1 \sum_{k_m} \left\langle \Psi_{(i,k_1, \dots, k_m),n}(\epsilon, s_1, s_2, \dots, s_m, s_m) \middle| H_1(s_m/\epsilon^2) \right. \right. \\
& \times \sum_{k_{m-1}} \left\langle \Psi_{(i,k_1, \dots, k_{m-1}),n}(\epsilon, s_1, s_2, \dots, s_{m-1}, s_{m-1}) \middle| H_1(s_{m-1}/\epsilon^2) \dots \right. \\
& \times \sum_{k_1} \left\langle \Psi_{(i,k_1),n}(\epsilon, s_1, s_1) \middle| H_1(s_1/\epsilon^2) \Psi_{(i),n}(\epsilon, s_1) \right\rangle \Psi_{(i,k_1),n}(\epsilon, s_1, s_2) \dots \left. \right\rangle \\
& \times \left. \Psi_{(i,k_1, \dots, k_{m-1}),n}(\epsilon, s_1, \dots, s_m) \right\rangle \Psi_{(i,k_1, \dots, k_m),n}(\epsilon, s_1, \dots, s_m, t) e^{iS^{(i,k_1, \dots, k_m)}(s_1, \dots, s_m, t)/\epsilon^2} \left. \right]
\end{aligned} \tag{4.36}$$

The computation involves two steps.

Step A. Take the derivative

$$\begin{aligned}
& i\epsilon^2 \frac{\partial}{\partial t} \left[(-1)^m \left(\frac{i\mu}{\epsilon^2} \right)^m \int_{T_i}^t ds_m \int_{T_i}^{s_m} ds_{m-1} \dots \int_{T_i}^{s_2} ds_1 \right. \\
& \quad \times \sum_{k_m} \left\langle \Psi_{(i,k_1,\dots,k_m),n}(\epsilon, s_1, s_2, \dots, s_m, s_m) \middle| H_1(s_m/\epsilon^2) \right. \\
& \quad \times \sum_{k_{m-1}} \left\langle \Psi_{(i,k_1,\dots,k_{m-1}),n}(\epsilon, s_1, s_2, \dots, s_{m-1}, s_{m-1}) \middle| H_1(s_{m-1}/\epsilon^2) \dots \right. \\
& \quad \times \sum_{k_1} \left\langle \Psi_{(i,k_1),n}(\epsilon, s_1, s_1) \middle| H_1(s_1/\epsilon^2) \Psi_{(i),n}(\epsilon, s_1) \right\rangle \Psi_{(i,k_1),n}(\epsilon, s_1, s_2) \dots \left. \right\rangle \\
& \quad \times \left. \Psi_{(i,k_1,\dots,k_{m-1}),n}(\epsilon, s_1, \dots, s_m) \right\rangle \Psi_{(i,k_1,\dots,k_m),n}(\epsilon, s_1, \dots, s_m, t) e^{iS^{(i,k_1,\dots,k_m)}(s_1,\dots,s_m,t)/\epsilon^2} \left. \right] \\
& \hspace{15em} (4.37)
\end{aligned}$$

with the result

$$\begin{aligned}
& = (-1)^m \left(\frac{(i\mu)^m}{\epsilon^{2(m-1)}} \right) \sum_{k_m} \left\langle \Psi_{(i,k_1,\dots,k_m),n}(\epsilon, s_1, s_2, \dots, t, t) \middle| H_1(t/\epsilon^2) \right. \\
& \quad \int_{T_i}^t ds_{m-1} \dots \int_{T_i}^{s_2} ds_1 \sum_{k_{m-1}} \left\langle \Psi_{(i,k_1,\dots,k_{m-1}),n}(\epsilon, s_1, s_2, \dots, s_{m-1}, s_{m-1}) \middle| H_1(s_{m-1}/\epsilon^2) \dots \right. \\
& \quad \times \sum_{k_1} \left\langle \Psi_{(i,k_1),n}(\epsilon, s_1, s_1) \middle| H_1(s_1/\epsilon^2) \Psi_{(i),n}(\epsilon, s_1) \right\rangle \Psi_{(i,k_1),n}(\epsilon, s_1, s_2) \dots \left. \right\rangle \\
& \quad \times \left. \Psi_{(i,k_1,\dots,k_{m-1}),n}(\epsilon, s_1, \dots, s_{m-1}, t) \right\rangle \Psi_{(i,k_1,\dots,k_m),n}(\epsilon, s_1, \dots, t, t) e^{iS^{(i,k_1,\dots,k_{m-1})}(s_1,\dots,s_{m-1},t)/\epsilon^2} + \dots \\
& \hspace{15em} (4.4a)
\end{aligned}$$

$$\begin{aligned}
& \dots + (-1)^m \left(\frac{i\mu}{\epsilon^2} \right)^m \int_{T_i}^t ds_m \int_{T_i}^{s_m} ds_{m-1} \dots \int_{T_i}^{s_2} ds_1 \\
& \quad \times \sum_{k_m} \left\langle \Psi_{(i,k_1, \dots, k_m), n}(\epsilon, s_1, s_2, \dots, s_m, s_m) \middle| H_1(s_m/\epsilon^2) \right. \\
& \quad \times \sum_{k_{m-1}} \left\langle \Psi_{(i,k_1, \dots, k_{m-1}), n}(\epsilon, s_1, s_2, \dots, s_{m-1}, s_{m-1}) \middle| H_1(s_{m-1}/\epsilon^2) \dots \right. \\
& \quad \times \sum_{k_1} \left\langle \Psi_{(i,k_1), n}(\epsilon, s_1, s_1) \middle| H_1(s_1/\epsilon^2) \Psi_{(i), n}(\epsilon, s_1) \right\rangle \Psi_{(i,k_1), n}(\epsilon, s_1, s_2) \dots \left. \right\rangle \\
& \quad \times \Psi_{(i,k_1, \dots, k_{m-1}), n}(\epsilon, s_1, \dots, s_m) \left. \right\rangle \left(i\epsilon^2 \frac{\partial}{\partial t} \right) \Psi_{(i,k_1, \dots, k_m), n}(\epsilon, s_1, \dots, s_m, t) e^{iS^{(i,k_1, \dots, k_m)}(s_1, \dots, s_m, t)/\epsilon^2}
\end{aligned} \tag{4.4b}$$

Step B. We apply $-(H(\epsilon) + H_1(t/\epsilon^2))$ to the quantity of which we took the derivative in Step A. The result is

$$\begin{aligned}
& -(-1)^m \left(\frac{i\mu}{\epsilon^2} \right)^m \int_{T_i}^t ds_m \int_{T_i}^{s_m} ds_{m-1} \dots \int_{T_i}^{s_2} ds_1 \sum_{k_m} \left\langle \Psi_{(i,k_1, \dots, k_m), n}(\epsilon, s_1, s_2, \dots, s_m, s_m) \middle| H_1(s_m/\epsilon^2) \right. \\
& \quad \times \sum_{k_{m-1}} \left\langle \Psi_{(i,k_1, \dots, k_{m-1}), n}(\epsilon, s_1, s_2, \dots, s_{m-1}, s_{m-1}) \middle| H_1(s_{m-1}/\epsilon^2) \dots \right. \\
& \quad \times \sum_{k_1} \left\langle \Psi_{(i,k_1), n}(\epsilon, s_1, s_1) \middle| H_1(s_1/\epsilon^2) \Psi_{(i), n}(\epsilon, s_1) \right\rangle \Psi_{(i,k_1), n}(\epsilon, s_1, s_2) \dots \left. \right\rangle \\
& \quad \times \Psi_{(i,k_1, \dots, k_{m-1}), n}(\epsilon, s_1, \dots, s_m) \left. \right\rangle H(\epsilon) \Psi_{(i,k_1, \dots, k_m), n}(\epsilon, s_1, \dots, s_m, t) e^{iS^{(i,k_1, \dots, k_m)}(s_1, \dots, s_m, t)/\epsilon^2} - \dots
\end{aligned} \tag{4.4a}$$

$$\begin{aligned}
& \dots - (-1)^m \left(\frac{(i\mu)^{m+1}}{\epsilon^{2m}} \right) H_1(t/\epsilon^2) \\
& \int_{T_l}^t ds_m \int_{T_l}^{s_m} ds_{m-1} \dots \int_{T_l}^{s_2} ds_1 \sum_{k_m} \left\langle \Psi_{(i,k_1,\dots,k_m),n}(\epsilon, s_1, s_2, \dots, s_m, s_m) \middle| H_1(s_m/\epsilon^2) \right. \\
& \times \sum_{k_{m-1}} \left\langle \Psi_{(i,k_1,\dots,k_{m-1}),n}(\epsilon, s_1, s_2, \dots, s_{m-1}, s_{m-1}) \middle| H_1(s_{m-1}/\epsilon^2) \dots \right. \\
& \times \sum_{k_1} \left\langle \Psi_{(i,k_1),n}(\epsilon, s_1, s_1) \middle| H_1(s_1/\epsilon^2) \Psi_{(i),n}(\epsilon, s_1) \right\rangle \Psi_{(i,k_1),n}(\epsilon, s_1, s_2) \dots \left. \right\rangle \\
& \times \Psi_{(i,k_1,\dots,k_{m-1}),n}(\epsilon, s_1, \dots, s_m) \left. \right\rangle \left(i\epsilon^2 \frac{\partial}{\partial t} \right) \Psi_{(i,k_1,\dots,k_m),n}(\epsilon, s_1, \dots, s_m, t) e^{iS^{(i,k_1,\dots,k_m)}(s_1,\dots,s_m,t)/\epsilon^2}
\end{aligned} \tag{4.4b}$$

If we apply Lemma 2.1 to the sum of the results of the above three steps, we will obtain an estimate on the size of the error in our approximation (4.28).

We notice that (4.4a) is just the expansion of (4.35) in the approximate basis of Lemma 4.1, with the opposite sign. The sum of these two terms gives us an $O(\epsilon^{n+1})$ error to the wavefunction by applying the reasoning of (4.24). Now consider the sum of (4.4b) and (4.4a). By virtue of Theorem 3.1,

$$\begin{aligned}
& -(-1)^m \left(\frac{i\mu}{\epsilon^2} \right)^m \int_{T_l}^t ds_m \int_{T_l}^{s_m} ds_{m-1} \dots \int_{T_l}^{s_2} ds_1 \sum_{k_m} \left\langle \Psi_{(i,k_1,\dots,k_m),n}(\epsilon, s_1, s_2, \dots, s_m, s_m) \middle| H_1(s_m/\epsilon^2) \right. \\
& \times \sum_{k_{m-1}} \left\langle \Psi_{(i,k_1,\dots,k_{m-1}),n}(\epsilon, s_1, s_2, \dots, s_{m-1}, s_{m-1}) \middle| H_1(s_{m-1}/\epsilon^2) \dots \right. \\
& \times \sum_{k_1} \left\langle \Psi_{(i,k_1),n}(\epsilon, s_1, s_1) \middle| H_1(s_1/\epsilon^2) \Psi_{(i),n}(\epsilon, s_1) \right\rangle \Psi_{(i,k_1),n}(\epsilon, s_1, s_2) \dots \left. \right\rangle \\
& \times \Psi_{(i,k_1,\dots,k_{m-1}),n}(\epsilon, s_1, \dots, s_m) \left. \right\rangle \times O(\epsilon^{n+1})
\end{aligned} \tag{4.40}$$

and again, using the substitution $u = s_1/\epsilon^2$ to do the integral, this term is $O(\epsilon^{n+1})$.

Our calculation leaves us with only the term (4.4b). By using the analogous reasoning in the proof of Theorem 4.1 on this term, we obtain the result that this term is $O(\mu^{m+1})$. Hence the conclusion of Theorem 4.2. \blacksquare

4.5 A Discussion of the Continuum Problem

The expansion in Theorem 4.2 is not valid past $O(\mu)$ in the case where the electron Hamiltonian $h(X)$ has continuous spectrum. The $O(\mu)$ term includes the portions of the future dynamics where an electron can make a single transition from one state to another. In Theorem 4.1 we specifically excluded calculations of the state where the electron can escape to the continuum due to excitation, because the Born-Oppenheimer approximation is no longer valid, and we cannot describe the motion of the nuclei as semiclassical under the effective potential produced by the electron configuration. We cannot use this model to make claims about the development of the molecular system and escaped electron while the molecule is ionized.

The $O(\mu^2)$ term, then, represents the dynamics of the molecule where the electronic configuration may make two electron energy level transitions. If we were to calculate this term of the Dyson expansion using the $O(\mu)$ term of Theorem 4.1, we would be neglecting the case where an electron may escape to the continuum for a time, yet is recaptured by the molecule. If the portion of the $O(\mu)$ term that denotes an escaping electron were small, i.e., were $O(\mu^2)$ or less, then we could effectively neglect this case without affecting the accuracy of our asymptotic expansion. We will utilize these ideas to derive a condition on the pulse under which we can obtain additional accuracy.

Theorem 4.3 *Let the hypotheses of Theorem 4.1 be satisfied, and let H_1 have the special form $H_1(t/\epsilon^2) \equiv (C_\zeta \zeta + \sum_j C_j x_j) f(t/\epsilon^2) \cos(\omega s/\epsilon^2)$. We stipulate that for a particular i ,*

$$E_{(i)}(X) + \omega \leq \lambda \tag{4.41}$$

for all λ in the continuous spectrum of $h(X)$. Suppose that the Fourier transform of f , that is, $\hat{f}(\omega)$, satisfies $|\hat{f}(\omega)| \leq M_1 \mu^2$ for any values of ω that do not satisfy (4.41), with M_1 a constant possibly depending on ω . Let $G_\pm^{(k)}(t, s) = \pm \omega s + S^{(i,k)}(t, s)$, and assume that for

any $k, t, s, \frac{\partial}{\partial s} G_{\pm}^{(k)}(t, s) \neq 0$. Then if for all k ,

$$\left| \frac{f'(s/\epsilon^2)}{\frac{\partial}{\partial s} G_{\pm}^{(k)}(t, s)} \right| \leq M_2 \mu \quad (4.42)$$

for some constant M_2 , then the conclusions of Theorem 4.2 hold for $m \leq 2$.

Remark. It is understood that the plus and minus senses of G_{\pm} are to be considered separately.

Proof. We have hypothesized that, to the order of accuracy in which we are interested, the pulse does not have frequency components that correspond to energies greater than the ionization energy of the molecule from its initial state. This requirement covers the physically interesting case. We need to determine the probability of ionization by frequency components of the pulse corresponding to energies less than the ionization energy. We expect large transition probabilities only when ω corresponds to an energy gap between electron energy levels, and very small transition probabilities otherwise. If the contributions when ω was not tuned to an energy gap were $O(\mu^2)$, then we could effectively neglect transitions to the continuum at this order.

Therefore, we are interested in showing the term

$$\begin{aligned} -\frac{i\mu}{\epsilon^2} \int_{T_1}^t ds \langle \Psi_{(i,k),n}(\epsilon, s, s) | (C_{\zeta}\zeta + \sum_j C_j x_j) f(s/\epsilon^2) \cos(\omega s/\epsilon^2) \Psi_{(i),n}(\epsilon, s) \rangle_{\zeta, x} \\ \times \Psi_{(i,k),n}(\epsilon, s, t) e^{iS^{(i,k)}(s,t)/\epsilon^2} \end{aligned} \quad (4.43)$$

to be $O(\mu^2)$ when the frequency is not tuned to the energy gap between the i th and k th energy level. To that end, we would like to compute

$$|\epsilon^{-2} \int_{T_1}^t ds f(s/\epsilon^2) \cos(\omega s/\epsilon^2) e^{iS^{(i,k)}(s,t)/\epsilon^2}| \quad (4.44)$$

because the other quantities are all norm-bounded. For example, the electron eigenfunctions are known to decay exponentially. We would like this quantity to be $O(\mu)$. We rewrite it as

$$\|(\epsilon^{-2}/2) \int_{T_1}^t ds f(s/\epsilon^2) (e^{i\omega s/\epsilon^2} + e^{-i\omega s/\epsilon^2}) e^{iS^{(i,k)}(t,s)/\epsilon^2}\| \quad (4.45)$$

Remember that $G_{\pm}(t, s)^{(k)} = \pm\omega s + S^{(i,k)}(t, s)$ and that we are assuming $\frac{\partial}{\partial s}G_{\pm}(t, s)^{(k)} \neq 0$. This condition simply means that the energy of our laser pulse is not coincident with the energy difference between initial and final states of the molecule at any time between $-\infty$ and t when the pulse is on. Now we can write the integral inside the above norm

$$\int_{T_i}^t ds \epsilon^2 \frac{f(s/\epsilon^2)}{\frac{\partial}{\partial s}G_{\pm}^{(k)}} \frac{\frac{\partial}{\partial s}G_{\pm}^{(k)}}{\epsilon^2} e^{iG_{\pm}^{(k)}/\epsilon^2} \quad (4.46)$$

Integration by parts yields

$$\frac{f(s/\epsilon^2)\epsilon^2}{\frac{\partial}{\partial s}G_{\pm}^{(k)}} e^{iG_{\pm}^{(k)}/\epsilon^2} \Big|_{T_i}^t - \int_{T_i}^t ds \epsilon^2 \frac{\partial}{\partial s} \left(\frac{f(s/\epsilon^2)}{G_{\pm}^{(k)}} \right) e^{iG_{\pm}^{(k)}/\epsilon^2} \quad (4.47)$$

Now the boundary term has an extra ϵ^2 so we can neglect it. Now the other term is

$$- \int_{T_i}^t ds \frac{\epsilon^2 f(s/\epsilon^2) \frac{\partial^2}{\partial s^2} G_{\pm}^{(k)} - f'(s/\epsilon^2) \frac{\partial}{\partial s} G_{\pm}^{(k)}}{(\frac{\partial}{\partial s} G_{\pm}^{(k)})^2} e^{iG_{\pm}^{(k)}/\epsilon^2} \quad (4.48)$$

The term with the extra ϵ^2 can be neglected. The other term requires f' small compared with $\frac{\partial}{\partial s}G_{\pm}^{(k)}$. Under the hypotheses of the theorem, the remaining term is $O(\mu)$, which gives the necessary estimate on the error made by neglecting the possibility of a transition to the continuum. ■

Chapter 5

Franck-Condon Factors

The statement that, to leading order in ϵ , a transition from one electronic state to another occurs too quickly for any simultaneous adjustment in the nuclear vibrational configuration is known to physical chemists as an expression of the Franck-Condon principle. This principle leads in an intuitive way to a means for calculating transition probabilities between two vibrational bound states when given initial and final electron energy levels. The inner products which lead to those particular probabilities are termed Franck-Condon factors. In the one-dimensional case, the analysis of the time-dependent problem in the previous chapters will furnish a mathematical proof of the validity of certain Franck-Condon factors, as they will appear in the $O(\mu)$ term of the expansion, the very term which governs the situation of a single electronic transition.

The method will allow us to justify only the Franck-Condon factors for a molecule beginning in the lowest nuclear bound states of an arbitrary electron energy level. This limitation arises because at present, the means of expressing excited nuclear bound states in terms of the basis of the time-dependent semiclassical wave packets of Section 2.3 is unknown. Previous results by Hagedorn [9] allow one to identify only the lowest N bound states in a well with the first N semiclassical wave packets and make only a small error. Hagedorn and Robinson [10] demonstrate that, in one-dimension, one may use a Born-Sommerfeld type

technique to approximately construct the bound states by integrating semiclassical wave packets over a classical orbit.

An elementary physical chemistry text begins the development of the Franck-Condon factors as follows: “When considering the intensity of a joint electronic transition, we may use the fact that the wavefunctions are the products of the respective electronic and vibrational wavefunctions.” [1] This “fact” is by no means mathematically apparent when the electron levels are coupled by a perturbation such as our electromagnetic pulse. We will devote the first section of this chapter to a proof of a somewhat weaker principle in one dimension. Since diatomic molecules will involve one nuclear coordinate (in the Jacobi coordinates), this result gives us an effective means to study the Franck-Condon factors for them.

After justifying the statement to leading order in ϵ , an elementary treatment proceeds by designating $Q_{(i)}^n(x)$ as the n th eigenstate solving the nuclear Schrödinger equation

$$-\frac{\epsilon^4}{2} \frac{\partial^2 \psi}{\partial X^2} + E_{(i)}(X)\psi = E_{(i)}^n \psi \quad (5.1)$$

where $E_{(i)}(X)$ as before is the i th eigenvalue satisfying the electron Schrödinger equation

$$-\frac{1}{2} \frac{\partial^2 \Phi}{\partial x^2} + V(x, X)\Phi = E_{(i)}(X)\Phi. \quad (5.2)$$

We then express the initial state as $\Psi_i = \Phi_{(i)}(x, X)Q_{(i)}^n(X)$.

The Franck-Condon principle indicates that at the instant the transition occurs, the nuclear vibrational wavefunction should be unchanged, so that $\Psi_f = \Phi_{(f)}(x, X)Q_{(i)}^n(X)$. The time-dependent development of an initial state in the Dyson series of Theorem 4.2 essentially contains the Franck-Condon principle, and in this form, we have rigorously justified it. To retrieve the Franck-Condon factors, we note that a measurement performed on the post-transition molecule, must realize one of the vibrational bound states associated with electronic wavefunction $\Phi_{(f)}(x, X)$. Now $Q_{(i)}^n(x) = \sum_m \langle Q_{(f)}^m(x) | Q_{(i)}^n(x) \rangle Q_{(f)}^m(x)$, and thus the probability of a transition to the measured state $\Psi_f = \Phi_{(f)}(x, X)Q_{(f)}^m(X)$ is given by the square of the absolute value of the inner product $\langle Q_{(f)}^m(x) | Q_{(i)}^n(x) \rangle$. These inner products

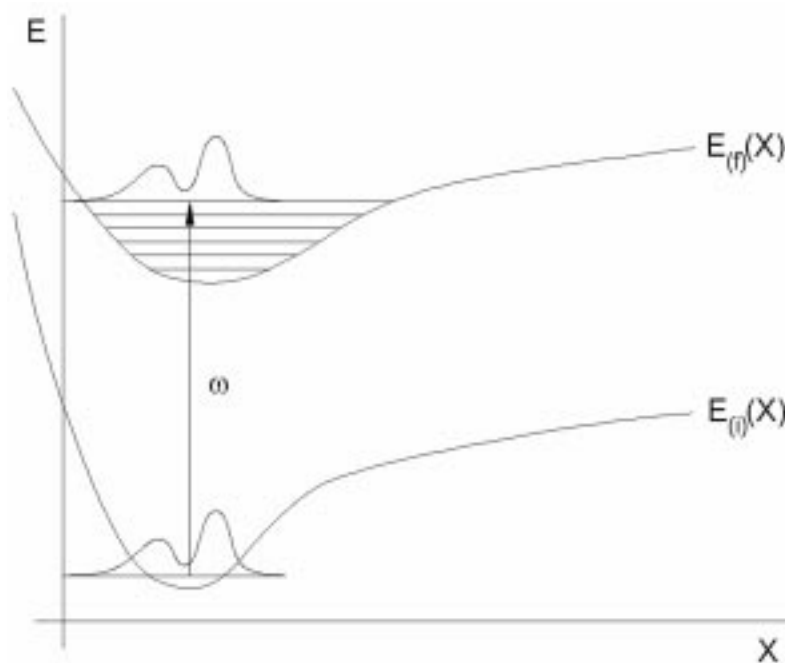


Figure 5.1: An illustration of the Franck-Condon principle applied to a "vertical transition."

are the Franck-Condon factors, which must appear as factors in the probability of a joint electronic and vibrational transition.

5.1 Approximate Form of Bound States

Let $X \in \mathbb{R}$ and suppose $H(X)$ is the electron hamiltonian of a diatomic molecule in 1-d with purely discrete spectrum $\{E_{(i)}(X)\}_{i=1}^{\infty}$. We work in one dimension to simplify the argument—we focus our attention on the vibrational levels with spacing $O(\epsilon^2)$ without needing to consider the rotational modes of a three-dimensional molecule, which have spacing $O(\epsilon^4)$. Rotational modes do not particularly affect our results, since the electric field will only couple rotational modes that differ by one quanta of angular momentum. This limited coupling is not enough to adversely impact the accuracy of our conclusions.

Suppose further that there are no electron energy level crossings. Then

$$H(X)\Phi_{(i)}(X) = E_{(i)}(X)\Phi_{(i)}(X) \quad (5.3)$$

and, assuming that $H(X)$ commutes with the conjugation operator, which is not highly restrictive in physical applications, we choose the phases of the eigenfunctions $\Phi_{(i)}(X)$ such that $\Phi_{(i)}(X)$ is real and the inner product over the electron variables $\langle \Phi_{(i)}, \Phi'_{(i)} \rangle_x = 0$. Let $P_{(i)}(X)$ be the projection onto the span of $\Phi_{(i)}(X)$. The resulting Schrödinger equation of the molecule is

$$-\frac{\epsilon^4}{2} \frac{\partial^2 \Psi}{\partial X^2} + \left(\sum_{i=1}^{\infty} E_{(i)}(X) P_{(i)}(X) \right) \Psi = E \Psi \quad (5.4)$$

The solution to this equation can be written in the form $\Psi = \sum_{i=1}^{\infty} f_i(X) \Phi_{(i)}(X)$. With this substitution, (5.4) becomes

$$-\frac{\epsilon^4}{2} \left(\sum f_i'' \Phi_{(i)} + 2 \sum f_i' \Phi'_{(i)} + \sum f_i \Phi''_{(i)} \right) + \sum E_i f_i \Phi_{(i)} = E \sum f_i \Phi_{(i)} \quad (5.5)$$

Define $F_{ij}(X) = \langle \Phi'_{(i)}, \Phi_{(j)} \rangle_x = -F_{ji}(X)$. The last equality is easily verified by integration by parts. Then we may identify

$$\Phi'_{(i)} = \sum_{j \neq i} \langle \Phi'_{(i)}, \Phi_{(j)} \rangle_x \Phi_{(j)} = \sum_{j \neq i} F_{ij} \Phi_{(j)} \quad (5.6)$$

$$\Phi''_{(i)} = \sum_{j \neq i} (F'_{ij} \Phi_{(j)} + F_{ij} \Phi'_{(j)}) = \sum_{j \neq i} (F'_{ij} \Phi_{(j)} - F_{ij}^2 \Phi_{(i)}) \quad (5.7)$$

We may then write the Schrödinger equation formally as an equation for the $f_i(X)$'s

$$-\frac{\epsilon^4}{2} \frac{\partial^2}{\partial x^2} \mathbf{f} + \mathbf{E} \mathbf{f} - \epsilon^4 \mathbf{V}_1 \mathbf{f} + \epsilon^4 \mathbf{V}_2 \mathbf{f} = E \mathbf{f} \quad (5.8)$$

using the infinite matrices

$$\mathbf{f} = \left(f_1 \quad f_2 \quad f_3 \quad \dots \quad f_i \quad \dots \right)^T \quad (5.9)$$

$$\mathbf{E} = \begin{pmatrix} E_{(1)}(X) & 0 & 0 & \dots & 0 & \dots \\ 0 & E_{(2)}(X) & 0 & \dots & 0 & \dots \\ 0 & 0 & E_{(3)}(X) & \dots & 0 & \dots \\ \vdots & & & \ddots & & \\ 0 & 0 & 0 & \dots & E_{(i)}(X) & \dots \\ \vdots & & & & & \end{pmatrix} \quad (5.10)$$

$$\mathbf{V}_1 = \begin{pmatrix} 0 & F_{12} \frac{\partial}{\partial X} & F_{13} \frac{\partial}{\partial X} & \dots & F_{1i} \frac{\partial}{\partial X} & \dots \\ F_{21} \frac{\partial}{\partial X} & 0 & F_{23} \frac{\partial}{\partial X} & \dots & F_{2i} \frac{\partial}{\partial X} & \dots \\ F_{31} \frac{\partial}{\partial X} & F_{32} \frac{\partial}{\partial X} & 0 & \dots & F_{3i} \frac{\partial}{\partial X} & \dots \\ \vdots & & & \ddots & \vdots & \\ F_{i1} \frac{\partial}{\partial X} & F_{i2} \frac{\partial}{\partial X} & F_{i3} \frac{\partial}{\partial X} & \dots & F_{i,i-1} \frac{\partial}{\partial X} & 0 & F_{i,i+1} \frac{\partial}{\partial X} & \dots \\ \vdots & & & & \vdots & & & \end{pmatrix} \quad (5.11)$$

$$\mathbf{V}_2 = \begin{pmatrix} \sum_{j \neq 1} F_{1j}^2 & F'_{12} & F'_{13} & \dots & F'_{1i} & \dots \\ F'_{21} & \sum_{j \neq 2} F_{2j}^2 & F'_{23} & \dots & F'_{2i} & \dots \\ F'_{31} & F'_{32} & \sum_{j \neq 3} F_{3j}^2 & \dots & F'_{3i} & \dots \\ \vdots & & & \ddots & \vdots & \\ F'_{i1} & F'_{i2} & F'_{i3} & \dots & F'_{i,i-1} & \sum_{j \neq i} F_{ij}^2 & F'_{i,i+1} & \dots \\ \vdots & & & & \vdots & & & \end{pmatrix}. \quad (5.12)$$

We may now consider the problem of determining the nuclear wavefunctions $f_i(X)$ as a perturbation problem. We recognize that for the unperturbed equation

$$-\frac{\epsilon^4}{2} \frac{\partial^2}{\partial X^2} \mathbf{f} + \mathbf{E} \mathbf{f} = \mathbf{E} \mathbf{f} \quad (5.13)$$

the f_i 's are just the nuclear vibrational bound states $Q_{(i)}^n$ satisfying (5.1). Hence the unperturbed problem gives us approximate molecular bound states, with spacing $O(\epsilon^2)$ for each i , that have the form $Q_{(i)}^n(X) \Phi_{(i)}(X)$. Since this solution is the one desired for calculating the

Franck-Condon factors, we need to show that corrections in the wavefunction introduced by the other two terms are small when ϵ is small. We may assume that the term with \mathbf{V}_2 is a regular perturbation. In physically interesting cases, we are considering a molecule whose particles remain in a spatially bounded area, hence all the entries of \mathbf{V}_2 are nice bounded functions. Thus, that term introduces corrections only at $O(\epsilon^4)$ and can be ignored. The term with \mathbf{V}_1 , however, produces functions that oscillate on the ϵ^2 distance scale when it is applied to the unperturbed eigenfunctions. Thus it appears that this term could introduce an $O(\epsilon^2)$ correction to the bound state energies, which is of the same size as the energy level spacing. Such a situation would be disastrous for our purposes, hence we give further consideration to the offending term in the following Lemma.

One further consideration is whether or not there are any other eigenfunctions not found in the formal solution of this perturbation problem that do not have the desired product form. This question is a difficult one, and we do not answer it here. Instead, we show that there is always an eigenfunction of the perturbed problem close enough to the desired product form so that the product form can be used as a close approximation. We cannot at this time rule out other eigenfunctions which cannot be written as a series in ϵ . We term states not found using the formal perturbation theory **anomalous eigenstates**, and explicitly assume them away in the following lemma. It is important to note, however, that no physical states have ever been observed that do not fall under the hypotheses of the following lemma. Our rigorous Franck-Condon results, then, will hold for any states which can currently be observed.

Lemma 5.1 *Let $Q_{(i)}^n(X)\Phi_{(i)}(X)$ be an eigenfunction of (5.13) and $E_{(i)}^n$ its corresponding eigenvalue. Further, let \mathcal{F} be a finite subset of the eigenfunctions of (5.13) with the properties that*

1. $Q_{(i)}^n(X)\Phi_{(i)}(X) \in \mathcal{F}$
2. *The electron level indices (k) of the elements of \mathcal{F} all differ.*

Further suppose that there are no anomalous eigenstates with eigenvalue within $O(\epsilon^2)$ of $E_{(i)}^n$.

Then for each $E_{(i)}^n$ there exists at least one eigenvalue \mathcal{E} and a corresponding eigenfunction $\Psi(x, X)$ of (5.4) such that

$$\|\Psi(x, X) - \sum_{\mathcal{F}} c_k Q_{(k)}^m(X) \Phi_{(k)}(X)\| \leq C_1 \epsilon^2 \quad \text{and} \quad |E_{(i)}^n - \mathcal{E}| \leq C_2 \epsilon^4 \quad (5.14)$$

for some constants C_1, C_2 possibly depending on i and n .

Proof. From the preceding discussion, we wish to discuss the formal perturbation problem

$$\left(-\frac{\epsilon^4}{2} \frac{\partial^2}{\partial X^2} + \mathbf{E} - \epsilon^4 \mathbf{V}_1\right) \mathbf{f} = E \mathbf{f}. \quad (5.15)$$

Note that the term containing \mathbf{V}_2 that we are omitting would prevent us from making any stronger estimates than those stated in the lemma.

We distinguish the nondegenerate, degenerate, and ‘‘almost degenerate’’ cases. Which case we find ourselves in may depend on ϵ , but we deal with this in the following way. From standard results using Weyl asymptotics (see [15, vol.IV]), near the fixed energy $E_{(i)}^n$, the spacing of the eigenvalues for the k th electron energy level alone is $a_k \epsilon^2$. If we pick $K = \min\{a_k\}/2$, then there are only a finite number of electron energy levels that have eigenvalues within $K \epsilon^2$ of $E_{(i)}^n$, and furthermore, there is only one eigenvalue from each of these select few levels. Thus, with this fixed K , any particular value of ϵ puts us in one of three cases we must analyze.

Case 1. $|E_{(i)}^n - E_{(j)}^m| \geq K \epsilon^2$, where K is the aforementioned constant, whenever $i \neq j$.

Let us designate the unperturbed operator by H_0 and the perturbed operator by H , and let us follow the standard method by supposing a series solution to

$$(H_0 + \epsilon^4 \mathbf{V}_1) \Psi(\epsilon) = \mathcal{E}(\epsilon) \Psi(\epsilon) \quad (5.16)$$

with

$$\mathcal{E}(\epsilon) = E_{(i)}^n + \epsilon^2 \mathcal{E}_1 + \dots \quad (5.17)$$

$$\Psi(\epsilon) = Q_{(i)}^n \Phi_{(i)} + \epsilon^2 \Psi_1 + \dots \quad (5.18)$$

At $O(\epsilon^2)$, noting that the $\epsilon^4 V_1$ term could really be of this order, we must have

$$(H_0 - E_{(i)}^n) \Psi_1 = \mathcal{E}_1 Q_{(i)}^n \Phi_{(i)} - \epsilon^2 \mathbf{V}_1 Q_{(i)}^n \Phi_{(i)}. \quad (5.19)$$

Because the right-hand side cannot have a component that is a scalar multiple of $Q_{(i)}^n \Phi_{(i)}$, we must have $\mathcal{E}_1 = \langle Q_{(i)}^n \Phi_{(i)}, \mathbf{V}_1 Q_{(i)}^n \Phi_{(i)} \rangle = 0$, since \mathbf{V}_1 is offdiagonal. When the condition for Case 1 holds, $(H_0 - E_{(i)}^n)^{-1}$ is well-defined and

$$\Psi_1 = -(H_0 - E_{(i)}^n)^{-1} \epsilon^2 \mathbf{V}_1 Q_{(i)}^n \Phi_{(i)}. \quad (5.20)$$

Now $\mathbf{V}_1 Q_{(i)}^n \Phi_{(i)} \in \text{Ran}(1 - P_{(i)})$, so

$$\Psi_1 = \epsilon^2 \sum_{k \neq i} \sum_l (E_{(k)}^l - E_{(i)}^n)^{-1} Q_{(k)}^l \Phi_{(k)} \langle Q_{(k)}^l, F_{ik} \frac{\partial}{\partial X} (Q_{(i)}^n) \rangle_X. \quad (5.21)$$

The factor $(E_{(k)}^l - E_{(i)}^n)^{-1}$ could be large, if by chance the two energy levels were to lie very near each other. The hypothesis of this case requires this factor to be as big as $O(\epsilon^{-2})$. The derivative in the inner product may produce an additional factor of ϵ^{-2} , making our correction too large. Nevertheless, we examine the factor $\langle Q_{(k)}^l, F_{ik} \frac{\partial}{\partial X} (Q_{(i)}^n) \rangle_X$.

We may choose to express the bound states $Q_{(k)}^l$ using the Born-Sommerfeld rules of [10]. In doing so, we make an error that is only of $O(\epsilon^3)$.

$$Q_{(k)}^l = \int_0^{\tau(E_{(k)}^l)} C_1 \epsilon^{-1/2} e^{it(E_{(k)}^l + \frac{\pi \epsilon^2}{\tau(E_{(k)}^l)}) + iS_{(k)}(t)/\epsilon^2} \varphi_0^{(k)} dt_1 \quad (5.22)$$

$$Q_{(i)}^n = \int_0^{\tau(E_{(i)}^n)} C_2 \epsilon^{-1/2} e^{it(E_{(i)}^n + \frac{\pi \epsilon^2}{\tau(E_{(i)}^n)}) + iS_{(i)}(t)/\epsilon^2} \varphi_0^{(i)} dt_2 \quad (5.23)$$

Using a couple of identities from [6], $F_{ik} \frac{\partial}{\partial X} (Q_{(i)}^n)$ has the form

$$\int_0^{\tau(E_{(i)}^n)} C_2 \epsilon^{-1/2} e^{it(E_{(i)}^n + \frac{\pi \epsilon^2}{\tau(E_{(i)}^n)}) + iS_{(i)}(t)/\epsilon^2} \left(\frac{-B}{\sqrt{2}\epsilon} \varphi_1^{(i)} + \frac{i\eta}{\epsilon^2} \varphi_0^{(i)} \right) dt_2 \quad (5.24)$$

We now take the inner product of (5.22) with (5.24) and find

$$\int_{-\infty}^{\infty} \left(\int \int dt_1 dt_2 C_1 \epsilon^{-1/2} e^{it(E_{(k)}^l + \frac{\pi \epsilon^2}{\tau(E_{(k)}^l)}) + iS_{(k)}(t)/\epsilon^2} \varphi_0^{(k)} C_2 \epsilon^{-1/2} e^{it(E_{(i)}^n + \frac{\pi \epsilon^2}{\tau(E_{(i)}^n)}) + iS_{(i)}(t)/\epsilon^2} \right. \\ \left. \times \left(\frac{-B}{\sqrt{2}\epsilon} \varphi_1^{(i)} + \frac{i\eta}{\epsilon^2} \varphi_0^{(i)} \right) \right) dX \quad (5.25)$$

and switching the X integration with the time integrals

$$\int \int dt_1 dt_2 C_1 \epsilon^{-1/2} e^{it(E_{(k)}^l + \frac{\pi\epsilon^2}{\tau(E_{(k)}^l)} + iS_{(k)}(t)/\epsilon^2} C_2 \epsilon^{-1/2} e^{it(E_{(i)}^n + \frac{\pi\epsilon^2}{\tau(E_{(i)}^n)} + iS_{(i)}(t)/\epsilon^2} \\ \times \left(\int_{-\infty}^{\infty} \varphi_0^{(k)} \left(\frac{-B}{\sqrt{2}\epsilon} \varphi_1^{(i)} + \frac{i\eta}{\epsilon^2} \varphi_0^{(i)} \right) dX \right) \quad (5.26)$$

The innermost integral in (5.26) is an inner product of φ 's. Now we appeal to Propositions 4 and 7 of [10] to conclude that $\|\langle Q_{(k)}^l, F_{ik} \frac{\partial}{\partial X} (Q_{(i)}^n) \rangle_X\| \leq C'' e^{-\gamma\epsilon^{-2}}$ for some $\gamma > 0$. Thus our error is dominated by the error produced by approximating using the Born-Sommerfeld technique. We have the conclusion $\|\Psi_1\| \leq C'\epsilon^3$. Not only is the first order term not made large by virtue of the derivative in V_1 , but surprisingly, it is much smaller than one might usually expect.

We now substitute our truncated formal solution, normalizing if necessary, into (5.15) and determine the truncation error. By virtue of the formal calculations above, we discover many cancellations and the relationship

$$\|(H - E_{(i)}^n)Q_{(i)}^n \Phi_{(i)}\| = \|\epsilon^2(H_0 - E_{(i)}^n)\Psi_1\| \quad (5.27)$$

which is at worst $O(\epsilon^5)$. By a standard spectral theorem argument, the conclusion $|E_{(i)}^n - \mathcal{E}| \leq C_2\epsilon^4$ is justified.

From this first conclusion and due to the explicit assumption that there are no anomalous eigenstates, we deduce that since the eigenvalues of H_0 have spacing $O(\epsilon^2)$, the eigenvalues of H also have a spacing of $O(\epsilon^2)$ nearby $E_{(i)}^n$. Now we construct the projection

$$P_{\perp} = 1 - |\Psi(x, X)\rangle\langle\Psi(x, X)| \quad (5.28)$$

Now

$$P_{\perp} Q_{(i)}^n \Phi_{(i)} = (H - z)^{-1} (H - z) P_{\perp} Q_{(i)}^n \Phi_{(i)} \quad \text{for } z \notin \sigma(H) \\ = (H - z)_r^{-1} P_{\perp} (H - z) Q_{(i)}^n \Phi_{(i)} \quad \text{since } (H - z)_r^{-1} = (H - z)^{-1} \text{ on the range of } P_{\perp}$$

We may now take the limit $z \rightarrow \mathcal{E}$, by the analyticity of the resolvent on the range of P_\perp .

$$\begin{aligned} P_\perp Q_{(i)}^n \Phi_{(i)} &= (H - \mathcal{E})_r^{-1} P_\perp (H - \mathcal{E}) Q_{(i)}^n \Phi_{(i)} \\ &= (H - \mathcal{E})_r^{-1} P_\perp [(E_{(i)}^n - \mathcal{E}) Q_{(i)}^n \Phi_{(i)} + O(\epsilon^4)] \\ &= (H - \mathcal{E})_r^{-1} P_\perp (O(\epsilon^4)) \end{aligned} \quad (5.29)$$

Thus, $\|P_\perp Q_{(i)}^n \Phi_{(i)}\| \leq O(\epsilon^2)$ since $\|(H - \mathcal{E})_r^{-1}\| = O(\epsilon^{-2})$ due to the spacing of the eigenvalues of H near $E_{(i)}^n$. We conclude, then, that $\|\Psi(x, X) - Q_{(i)}^n(X) \Phi_{(i)}(X)\| \leq C_1 \epsilon^2$.

Case 2. The elements of the finite set of energies $\{E_{(k_1)}^{m_1}, E_{(k_2)}^{m_2}, \dots, E_{(k_N)}^{m_N}\}$, among which is included $E_{(i)}^n$, are equal. Any other energies not in this set fall into Case 1. Denote the set of indices $\{m_1, \dots, m_N\}$ by \mathcal{M} .

Once again, because the spacing between electron hamiltonian eigenvalues is $O(1)$ and the spacing of the corresponding nuclear hamiltonian eigenvalues are $O(\epsilon^2)$, each degeneracy of the molecular energy levels must be finite.

Suppose the degenerate eigenstates are given by $\psi_{(k_i)}^{m_i} = Q_{(k_i)}^{m_i} \Phi_{(k_i)}$. The leading order solution must be some linear combination of them.

$$\Psi_0 = \sum_i^N c_{k_i} \psi_{(k_i)}^{m_i} \quad (5.30)$$

Note that this set over which the linear combination is taken will contain the set \mathcal{F} of our lemma's conclusions.

The $O(\epsilon^2)$ equation to be solved is then

$$(H_0 - E_{(i)}^n) \Psi_1 = (\mathcal{E}_1 - \epsilon^2 \mathbf{V}_1) \sum_j^N c_{k_j} \psi_{(k_j)}^{m_j} \quad (5.31)$$

Now in order to solve for Ψ_1 , the right-hand side of (5.31) must be in the null space of the projection onto the span of the degenerate eigenstates. This condition gives the following

eigenvalue problem to be solved:

$$\begin{pmatrix} 0 & \langle \psi_{(k_1)}^{m_1}, \mathbf{V}_1 \psi_{(k_2)}^{m_2} \rangle & \langle \psi_{(k_1)}^{m_1}, \mathbf{V}_1 \psi_{(k_3)}^{m_3} \rangle & \cdots & \langle \psi_{(k_1)}^{m_1}, \mathbf{V}_1 \psi_{(k_N)}^{m_N} \rangle \\ \langle \psi_{(k_2)}^{m_2}, \mathbf{V}_1 \psi_{(k_1)}^{m_1} \rangle & 0 & \langle \psi_{(k_2)}^{m_2}, \mathbf{V}_1 \psi_{(k_3)}^{m_3} \rangle & \cdots & \langle \psi_{(k_2)}^{m_2}, \mathbf{V}_1 \psi_{(k_N)}^{m_N} \rangle \\ \langle \psi_{(k_3)}^{m_3}, \mathbf{V}_1 \psi_{(k_1)}^{m_1} \rangle & \langle \psi_{(k_3)}^{m_3}, \mathbf{V}_1 \psi_{(k_3)}^{m_3} \rangle & 0 & \cdots & \langle \psi_{(k_3)}^{m_3}, \mathbf{V}_1 \psi_{(k_N)}^{m_N} \rangle \\ \vdots & & & \ddots & \vdots \\ \langle \psi_{(k_N)}^{m_N}, \mathbf{V}_1 \psi_{(k_1)}^{m_1} \rangle & \langle \psi_{(k_N)}^{m_N}, \mathbf{V}_1 \psi_{(k_2)}^{m_2} \rangle & \langle \psi_{(k_N)}^{m_N}, \mathbf{V}_1 \psi_{(k_3)}^{m_3} \rangle & \cdots & 0 \end{pmatrix} \begin{pmatrix} c_{k_1} \\ c_{k_2} \\ c_{k_3} \\ \vdots \\ c_{k_N} \end{pmatrix} = \mathcal{E}_1 \begin{pmatrix} c_{k_1} \\ c_{k_2} \\ c_{k_3} \\ \vdots \\ c_{k_N} \end{pmatrix}$$

Or, simplifying the easy inner products in the electron variable

$$\epsilon^2 \begin{pmatrix} 0 & \langle Q_{(k_1)}^{m_1}, F_{k_2 k_1} (Q_{(k_2)}^{m_2})' \rangle_X & \cdots & \langle Q_{(k_1)}^{m_1}, F_{k_N k_1} (Q_{(k_N)}^{m_N})' \rangle_X \\ \langle Q_{(k_2)}^{m_2}, F_{k_1 k_2} (Q_{(k_1)}^{m_1})' \rangle_X & 0 & \cdots & \langle Q_{(k_2)}^{m_2}, F_{k_N k_2} (Q_{(k_N)}^{m_N})' \rangle_X \\ \vdots & & \ddots & \vdots \\ \langle Q_{(k_N)}^{m_N}, F_{k_1 k_N} (Q_{(k_1)}^{m_1})' \rangle_X & \langle Q_{(k_N)}^{m_N}, F_{k_2 k_N} (Q_{(k_2)}^{m_2})' \rangle_X & \cdots & 0 \end{pmatrix} \begin{pmatrix} c_{k_1} \\ c_{k_2} \\ \vdots \\ c_{k_N} \end{pmatrix} = \mathcal{E}_1 \begin{pmatrix} c_{k_1} \\ c_{k_2} \\ \vdots \\ c_{k_N} \end{pmatrix} \quad (5.32)$$

We may assume that there are exactly N distinct eigenvectors $\vec{c}^{(1)}, \dots, \vec{c}^{(N)}$ and N distinct eigenvalues $\mathcal{E}_1^{(1)}, \dots, \mathcal{E}_1^{(N)}$ solving (5.32). If this is not the case, the energy levels do not completely split at this order of the calculation, and we may choose any solution to (5.32) for use in (5.33). Regardless, we have solutions $\mathcal{E}_1^{(j)}$ that are at biggest $O(\epsilon^2)$, any of which will serve in $\mathcal{E} = E_{(i)}^n + \epsilon^4 \mathcal{E}_1^{(j)} + \dots$ of our lemma's conclusions.

We may then calculate for any chosen eigenvalue/eigenvector pair

$$\Psi_{1,j} = -(H_0 - E_{(i)}^n)^{-1} (\mathcal{E}_1^{(j)} - \epsilon^2 \mathbf{V}_1) \sum_{k_p} c_{k_p}^{(j)} Q_{(k_p)}^{m_p} \Phi_{(k_p)}. \quad (5.33)$$

Because the vectors $\vec{c}^{(j)}$ and values $\mathcal{E}_1^{(j)}$ satisfy the eigenvalue equation (5.32), there are some cancellations, resulting in

$$\Psi_{1,j} = -\epsilon^2 \sum_p \sum_{q \neq k_p} \sum_{l \notin (\mathcal{M} - m_p)} (E_{(q)}^l - E_{(i)}^n)^{-1} c_{k_p}^{(j)} Q_{(q)}^l \Phi_{(q)} \langle Q_{(q)}^l, F_{q,k_p} \frac{\partial}{\partial X} (Q_{(k_p)}^{m_p}) \rangle_X. \quad (5.34)$$

We then immediately follow the logic of Case 1 to confirm that the conclusions of the lemma hold. The size of $\Psi_{1,j}$ is determined by the Born-Sommerfeld method to be small, and the truncation error calculated using the formal solution tells us that our energy eigenvalue is close enough to $E_{(i)}^n$. For the projection P_{\perp} we subtract from 1 the projections onto each of the states in the set \mathcal{F} . The perturbed resolvent acting on P_{\perp} will then be $O(\epsilon^{-2})$. In this case we may use any linear combination of product states resulting from an eigenvector solution to (5.32) along with its eigenvalue in the lemma's conclusions.

Case 3. For the finite set of energies $\mathfrak{E} = \{E_{(k_1)}^{m_1}, E_{(k_2)}^{m_2}, \dots, E_{(k_N)}^{m_N}\}$, among which is included $E_{(i)}^n$, we have $|E_{(k_i)}^{m_i} - E_{(i)}^n| \leq K\epsilon^2$. The set \mathcal{K} will denote the electron level indices $\{k_1, \dots, k_N\}$. For all other energies, Case 1 applies.

We write the perturbed operator differently for this case. Suppose first that we write the perturbed operator in the basis given by the eigenfunctions of the unperturbed operator. We remove from \mathbf{V}_1 the block of matrix elements indexed by all the ordered pairs in $\mathcal{K} \times \mathcal{K}$ and add them to H_0 , denoting the new infinite matrices $\tilde{\mathbf{V}}_1$ and \tilde{H}_0 . Since \mathbf{V}_1 was off-diagonal, we know that (if we permit ourselves to reorder the basis to bring the block together) \tilde{H}_0 now contains a non-diagonalized block of the form

$$\begin{pmatrix} E_{(k_1)}^{m_1} & \epsilon^4 \langle Q_{(k_1)}^{m_1}, F_{k_2 k_1} (Q_{(k_2)}^{m_2})' \rangle_X & \dots & \epsilon^4 \langle Q_{(k_1)}^{m_1}, F_{k_N k_1} (Q_{(k_N)}^{m_N})' \rangle_X \\ \epsilon^4 \langle Q_{(k_2)}^{m_2}, F_{k_1 k_2} (Q_{(k_1)}^{m_1})' \rangle_X & E_{(k_2)}^{m_2} & \dots & \epsilon^4 \langle Q_{(k_2)}^{m_2}, F_{k_N k_2} (Q_{(k_N)}^{m_N})' \rangle_X \\ \vdots & & \ddots & \vdots \\ \epsilon^4 \langle Q_{(k_N)}^{m_N}, F_{k_1 k_N} (Q_{(k_1)}^{m_1})' \rangle_X & \epsilon^4 \langle Q_{(k_N)}^{m_N}, F_{k_2 k_N} (Q_{(k_2)}^{m_2})' \rangle_X & \dots & E_{(k_N)}^{m_N} \end{pmatrix}$$

The rest of \tilde{H}_0 is diagonal. Let us explicitly diagonalize this block using a similarity transformation $\mathbf{C}^{-1}\tilde{H}_0\mathbf{C}$. Our estimate of the inner products in the off-diagonal elements tells us that their size is considerably smaller than $O(\epsilon^4)$. One of the eigenvalues of this block is then a successful candidate for the \mathcal{E} of the lemma's conclusions by the Gershgorin Circle Theorem [11, p.99]. The eigenvector corresponding to this eigenvalue must be a finite linear combination of product states, since all we have done by diagonalizing is change bases from the unperturbed solution basis.

The similarity transformation that diagonalizes the block changes $\tilde{\mathbf{V}}_1$ into \mathbf{W} , but this new (still off-diagonal) matrix cannot couple any pair of states whose eigenvalues belong to \mathcal{E} . The perturbation problem

$$(\mathbf{C}^{-1}\tilde{H}_0\mathbf{C} + \epsilon^4\mathbf{W})\Psi(\epsilon) = \mathcal{E}(\epsilon)\Psi(\epsilon) \quad (5.35)$$

can therefore be analyzed using the ideas of Case 1, since all the states coupled by \mathbf{W} have energies that are farther than $K\epsilon^2$ away from those of \mathcal{E} . ■

5.2 The Franck-Condon Factors

We are now ready to justify the Franck-Condon factors. The following theorem describes the transition probability between two molecular bound states that fall into Case 1 of Lemma 5.1, with appropriate bounds on the error.

Theorem 5.1 *Let $H(X)$ have purely discrete spectrum and $H_1 \equiv x F(t/\epsilon^2)$, where $F(t/\epsilon^2)$ is an integrable function of compact support, say on the interval $[T_l, T_u]$. Then choose $N < \infty$. Then the transition probability for a single transition between $\Psi_1(x, X)$ near, in the sense of Lemma 5.1, $Q_{(i)}^n \Phi_{(i)}$ (the approximate initial molecular bound state with electron level i and nuclear bound state $n \leq N$) and $\Psi_2(x, X)$ near, in the sense of Lemma 5.1, $Q_{(f)}^m \Phi_{(f)}$, (the approximate final molecular bound state with electron level f and nuclear bound state m) is*

given by

$$|\langle Q_{(f)}^m | Q_{(i)}^n \rangle_X \langle \Phi_{(f)} | x | \Phi_{(i)} \rangle_x \mu G(t)|^2 + K(N)O(\mu^4 \epsilon^2) \quad (5.36)$$

Remarks.

1. The estimate on the error is not uniform in N . In a particular calculation, then, this theorem does not guarantee the accuracy of the Franck-Condon factors when the nuclei are initially in a very excited vibrational state. The physical size of ϵ , especially, will limit the range of initial nuclear states covered by this theorem.
2. $G(t)$ contains various phase factors and depends on $F(t/\epsilon^2)$, i , and f , but it does not depend on n and m . Thus, the first inner product factor in (5.36) gives relative amplitudes for different values of m, n with everything else fixed.
3. The theorem may still be correct for any starting nuclear bound state, but as of this time, we do not know how to characterize the initial state accurately for large N .
4. We may apply the analysis in the proof below to molecular bound states falling into Cases 2 and 3 of Lemma 5.1. Instead of conditional transition probabilities between distinct initial and final states, however, we obtain a formula giving joint transition probabilities to or from a collection of degenerate or nearly degenerate molecular bound states.

Because of Lemma 5.1, we may write the initial molecular state as

$$e^{-i(t-T_i)E_{(i)}^n/\epsilon^2} Q_{(i)}^n(X) \Phi_{(i)} \quad (5.37)$$

and make an error of only $O(\epsilon^4)$. Now by [9], we may write (5.37) as

$$\Psi_{(i),0} = \varphi_n^{(i)}(X, t) \Phi_{(i)} + O(\epsilon^2) \quad (5.38)$$

by identifying the nuclear bound state and the semiclassical wave packet of Section 2.3. We do make an error that depends on N , but is still only $O(\epsilon^2)$.

We may now easily apply the formula of Theorem 4.2 to calculate the wavefunction of the molecule after the laser pulse has expired at time T_u .

$$\begin{aligned} & \varphi_n^{(i)}(X, T_u) \Phi_{(i)} e^{iS^{(i)}(T_u)/\epsilon^2} - \\ & \frac{i\mu}{\epsilon^2} \int_{T_l}^{T_u} ds \sum_k \langle \varphi_n^{(i,k)}(X, s, s) \Phi_{(k)} | H_1(s/\epsilon^2) \varphi_n^{(i)}(X, s) \Phi_{(i)} \rangle_x \varphi_n^{(i,k)}(X, s, t) \Phi_{(k)} e^{iS^{(i,k)}(s, T_u)/\epsilon^2} \\ & + K(N)O(\mu^2\epsilon) \end{aligned} \quad (5.39)$$

Now suppose we reverse the identification of the semiclassical wave packets with the nuclear bound states and simplify the inner product over the electron variables. Then we get

$$\begin{aligned} & e^{-i(T_u - T_l)E_{(i)}^n/\epsilon^2} Q_{(i)}^n(X) \Phi_{(i)} - \\ & \frac{i\mu}{\epsilon^2} \int_{T_l}^{T_u} ds \sum_k \langle \Phi_{(k)} | x | \Phi_{(i)} \rangle_x F(s/\epsilon^2) e^{-i(s - T_l)E_{(i)}^n/\epsilon^2} e^{-i(T_u - s)E_{(k)}/\epsilon^2} Q_{(i)}^n(X) \Phi_{(k)} + K(N)O(\mu^2\epsilon) \end{aligned} \quad (5.40)$$

Here $E_{(k)}$ denotes the energy of the initial wave packet in the new electron energy level. $E_{(k)}$ is some linear combination of the $E_{(k)}^m$'s.

After time T_u , we perform a measurement to determine the final molecular bound state. To calculate the transition probability, we take the inner product of (5.40) with the final molecular bound state (with error $O(\epsilon^4)$ by Lemma 5.1)

$$e^{-i(t - T_u)E_{(f)}^m/\epsilon^2} Q_{(f)}^m(X) \Phi_{(f)}. \quad (5.41)$$

The result is (5.36). ■

Chapter 6

Conclusions

We began by investigating the perturbation problem resulting from a semiclassical model of a molecule excited by an electromagnetic field pulse. Working from the asymptotic expansion for the solution of the unperturbed time-dependent Born-Oppenheimer problem, we developed another asymptotic expansion for the perturbed problem using the Dyson series technique. Under very general conditions, we found that the technique allows us to calculate the wavefunction up to first order in the perturbation parameter μ , but that the possibility of electrons escaping to the continuum prevented a further extension of the series. By placing restrictions on the abruptness of the laser pulse, we extended the series to second order in μ .

Under the supposition that our electron Hamiltonian had no continuous spectrum, we developed the Dyson series fully to all orders in μ and the Born-Oppenheimer parameter ϵ . Each term of the Dyson series can be interpreted physically as representing all the possibilities of n separate electron transitions. The nuclei then propagate semiclassically in the effective potential induced by the current electron state.

Using the resulting asymptotic expansion for the perturbed problem, we proceeded to justify, for the diatomic molecule, the Franck-Condon coefficients describing the transition probab-

ities between two nuclear bound states given initial and final electron energy levels. Central to this proof was the demonstration that we may write any molecular bound state as the product of a nuclear bound state and an electron eigenstate while making an error of only $O(\epsilon^4)$.

The Born-Oppenheimer approximation to the Schrödinger equation has many nuggets of truth yet to yield to the formalism of mathematics. Extensions of the above results to more general situations await more research, but our hope is that this modest contribution will add to the effort.

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Vita

Steven W. Jilcott, Jr. was born in Quantico, Virginia on November 28, 1973. His parents, Steven, Sr., and Jewell Jilcott, shortly thereafter moved to Pensacola, Florida, where he spent almost all of his childhood. He attended Pine Forest High School, where he was named valedictorian. He was honored to be the inaugural recipient of the National Merit Scholarship Corporation's John M. Stalnaker Memorial Merit Scholarship, named after their founding president.

Following high school, Steven began a challenging program of math and physics studies at the California Institute of Technology. He was a proud member of Fleming House, and enjoyed participating in many of the zany Fleming traditions. While at Caltech, he first got a taste of mathematics research during three Summer Undergraduate Research Fellowships. The 1995 Caltech graduation was held outdoors, in accordance with tradition, but, unexpectedly for Southern California, it rained. Fortunately, though, his diploma survived undamaged!

After a short break, Steven resumed graduate studies at Virginia Tech, and completed his master's degree and doctorate while working with Dr. George Hagedorn in Mathematical Physics. In the year 2000, Steven anticipates beginning a new career at Alphatech, Inc., in Burlington, MA, applying mathematical tools to strategic decision-making and systems analysis.