# Born-Oppenheimer Corrections Near a Renner-Teller Crossing

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ABSTRACT

We perform a rigorous mathematical analysis of the bending modes of a linear triatomic molecule that exhibits the Renner-Teller effect. Assuming the potentials are smooth, we prove that the wave functions and energy levels have asymptotic expansions in powers of $\epsilon$, where $\epsilon^4$ is the ratio of an electron mass to the mass of a nucleus. To prove the validity of the expansion, we must prove various properties of the leading order equations and their solutions. The leading order eigenvalue problem is analyzed in terms of a parameter $\tilde{b}$, which is equivalent to the parameter originally used by Renner. For $0 < \tilde{b} < 1$, we prove self-adjointness of the leading order Hamiltonian, that it has purely discrete spectrum, and that its eigenfunctions and their derivatives decay exponentially. Perturbation theory and finite difference calculations suggest that the ground bending vibrational state is involved in a level crossing near $\tilde{b} = 0.925$. We also discuss the degeneracy of the eigenvalues. Because of the crossing, the ground state is degenerate for $0 < \tilde{b} < 0.925$ and non-degenerate for $0.925 < \tilde{b} < 1$.

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# Dedication

To Rachael

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# Chapter 1

# Introduction and Formulation

## 1.1 Introduction

Consider a molecular system of $N$ electrons with positions $x_i$, mass $m$, and charge $-1$, together with $J$ nuclei with positions $R_j$, masses $M_j$, and charges $Z_j > 0$. Let $H_{TOT}$ be the Hamiltonian of the system

$$
\begin{aligned}
H_{TOT} &= H_{nuc} + H_{el}\ , \quad \text{where} \\
H_{nuc} &= -\sum_{j=1}^{J} \frac{1}{2M_j}\,\Delta_{R_j} + \sum_{j=1}^{J}\sum_{k>j}^{J} \frac{Z_j\ Z_k}{|\,R_j - R_k\,|}, \\
H_{el} &= -\frac{1}{2m}\sum_{i=1}^{N}\Delta_{x_i} - \sum_{i=1}^{N}\sum_{j=1}^{J}\frac{Z_j}{|\,x_i - R_j\,|} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{|\,x_i - x_j\,|}.
\end{aligned}
$$

The wave function satisfying the time independent Schrödinger equation

$H_{TOT}\Psi_{TOT} = E_{TOT}\Psi_{TOT}$, depends on the $R_j$ and $x_i$ (ignoring spin interactions),

$$\Psi_{TOT} =: \Psi_{TOT}(\, R_1\,,\, R_2\,,\, \ldots\,,\, R_J\,,\, x_1\,,\, x_2\,,\, \ldots\,,\, x_N\,) \in L^2(\mathbb{R}^{3(J+N)}).$$

A major breakthrough in the analysis of molecular systems came in the classic paper by Born and Oppenheimer [1]. They argued that since the electron mass is much smaller than the mass of atomic nuclei, the electrons will move much more rapidly. The electrons will respond to small changes in the positions of the nuclei and quickly adjust their positions. One therefore assumes that the electron motion has only parametric dependence on the nuclear positions, and the nuclei are thought to remain fixed in space as the behavior of the electrons is analyzed. After solving for the energy states of the electrons at various nuclear positions, this will give rise to potential energy surfaces that govern the motion of the nuclei. In particular, the decomposition

$$\Psi_{TOT} \;=\; \Psi_{nuc}(\, R_1,\, \ldots,\, R_J)\; \Psi_{el}(\, R_1\,,\, R_2\,,\, \ldots\,,\, R_J\,,\, x_1\,,\, x_2\,,\, \ldots\,,\, x_N\,)$$

is used, and assuming $H_{el},\ \Psi_{el}$, and $E_{el}$ have only parametric dependence on the $R_j$, we seek solutions to the electronic problem

$$H_{el}\ \Psi_{el} \;=\; E_{el}\ \Psi_{el} \tag{1.1.1}$$

at various positions $R_j$. Once we obtain a solution to (1.1.1) for all $R_j$, a particular electron state $\Psi_{el}$ is chosen, and we use this to obtain $\Psi_{TOT}$ and $E_{TOT}$.

In their original paper, [1], Born and Oppenheimer let $\epsilon^4$ be the ratio of the electron mass

to the nuclear mass and expanded the wave functions and eigenvalues of the time independent Schrödinger equation in powers of $\epsilon$. We shall refer to such an expansion as *a Born-Oppenheimer expansion.* Since $\epsilon$ is small, the first few orders of the expansions are thought to provide reasonably accurate results for the bound states of the molecular system. Often only the lowest (or leading) order terms of the expansions are even considered.

The focus of this paper is the Renner-Teller effect (also called the Renner effect), which later will be described in more detail. In short, a symmetry induced degeneracy exists in the electron states at a particular nuclear configuration, but when the nuclei move away from this configuration the degeneracy splits. As a result one cannot depart from a single particular solution of (1.1.1) when attempting to solve for $\Psi_{TOT}$ and $E_{TOT}$ using the Born-Oppenheimer approximation. This effect was first predicted in 1933 by Herzberg and Teller [2] and was analyzed one year later by Renner [3] in a simplified model. We consider the current paper as an extension of the mathematically rigorous works related to the Born-Oppenheimer approximation, such as [4, 5, 6, 7, 8, 9, 10], to the model originally considered by Renner [3]. We will rigorously show that a Born-Oppenheimer expansion exists to all orders of $\epsilon$, with minimal mathematical assumptions. We will prove that under our hypotheses, the molecular energy and wave function can be approximated by an asymptotic series in $\epsilon$ that is truncated at arbitrary order. The leading order equations we obtain are unitarily equivalent to those found by Renner in [3]. This is the first rigorous derivation of the leading order equations of which we are aware. We feel it is especially important to make contact with a rigorous Born-Oppenheimer expansion here, since the Renner-Teller effect is not a straightforward

application of the Born-Oppenheimer approximation. In their outstanding review of the subject [11], Perić and Peyerimhoff give several interpretations of the origin of the Renner-Teller effect, and in particular they state "from the quantum chemical standpoint, the RT effect is a consequence of violation of validity of the Born-Oppenheimer approximation." We will see that in the Renner-Teller case there is a valid Born-Oppenheimer expansion, but it differs significantly from the usual Born-Oppenheimer approximation since the degeneracy cannot be ignored. It must be analyzed in terms of degenerate perturbation theory.

In recent years there have been several mathematically rigorous results justifying the validity of Born-Oppenheimer expansions under various hypotheses. The first rigorous proof related to the Born-Oppenheimer approximation in a physically realistic model was given by Combes, Duclos, and Seiler [4, 5]. They proved the validity of the fourth order approximation for the eigenvalue and the leading order approximation for the eigenfunction. A few years later, Hagedorn proved [6] the existence of a Born-Oppenheimer expansion to all orders using the method of multiple scales, assuming that the potentials are smooth functions. In particular, he proved that for arbitrary $K$, there exist quasimode energies of the form $E_K(\epsilon) = \sum_{k=0}^{K} \epsilon^k E^{(k)}$ and quasimodes of the form $\Psi_K(\epsilon) = \sum_{k=0}^{K} \epsilon^k \Psi_\epsilon^{(k)}$, that asymptotically approximate an exact eigenvalue and eigenfunction below the essential spectrum of a Hamiltonian $H(\epsilon)$, in the sense that

$$||H(\epsilon)\,\Psi_K(\epsilon) - E_K(\epsilon)\,\Psi_K(\epsilon)|| \leq C_K\,\epsilon^{K+1}. \tag{1.1.2}$$

The first five orders of $E(\epsilon)$ were determined explicitly, and it is discussed how one could

proceed to any arbitrary order $K$. These results were then extended to the case of Coulomb potentials for diatomic molecules in [7] and to general polyatomic molecules by Klein *et al.* [8]. Here, we will assume that the potentials are smooth, but we believe our results can be extended in a similar manner to the case of Coulomb potentials. In both works [6, 7], Hagedorn discusses that the intuition behind the Born-Oppenheimer approximation may be better interpreted as a disparity in spatial scales rather than time scales as it is usually thought of [7]:

"...[from the] discussion in most physical text books on the subject, one would be led to believe that the disparity between time scales is the basis for the validity of the Born-Oppenheimer approximation. This is *not* the proper intuition, even in the time dependent approximation [12]. The crucial ingredient is a disparity in spatial scales. In the time that it takes the electrons to move a unit distance, the nuclei move a distance of order $\epsilon$. As a result, the appropriate technique for analyzing the motion is the "method of multiple scales" applied to the appropriate spatial variables. Born and Oppenheimer [1] were clearly aware of the role of spatial scaling, but did not have a clean formalism for dealing with more than one scale in the same variable."

While the method of multiple scales nicely separates the adiabatic and non-adiabatic effects, it is possible to use a Born-Oppenheimer expansion without multiple scales (see for instance [9]), which is what is done here.

### 1.1.1 What is the Renner-Teller Effect?

Consider a triatomic molecule and fix the reference frame so that when the molecule is in the linear configuration, the middle nucleus is at the origin and the $z$-axis passes through all three nuclei. Let $(0, 0, R_1)$ and $(0, 0, R_2)$ be the coordinates of the upper and lower nuclei (so $R_1 > 0$ and $R_2 < 0$). We consider the bending modes by clamping the upper and lower nuclei to their fixed positions on the $z$-axis and allowing the middle nucleus to move in the perpendicular plane. Let $(x, y, 0)$ be the cartesian coordinates of this middle nucleus, and let $(\tilde{\rho}, \phi)$ be the usual polar coordinates associated with $(x, y)$. If $(x_1, x_2, \cdots, x_N)$ are the N three-dimensional electron coordinates, the electronic Hamiltonian is

$$h(x, y) \;=\; -\frac{1}{2}\sum_{j=1}^{N} \Delta_{x_j} \;+\; V(x, y; x_1, x_2, \cdots, x_N),$$

where we have taken the electron mass to be 1, and the potential $V$ includes the repulsion forces between the nuclei, the attraction forces between the nuclei and electrons, and the repulsion forces between the electrons. We think of $h(x, y)$ as having parametric dependence on $(x, y)$ (*i.e.* it is a mapping from $\mathbb{R}^2$ to the linear operators on the electronic Hilbert space), and we assume it is a real symmetric operator. We assume that $V$ is a smooth function in all variables. Let $\epsilon^4$ be the ratio of the mass of an electron to the mass of the middle nucleus. Then, the full hamiltonian of this model is given by

$$H(\epsilon) \;=\; -\frac{\epsilon^4}{2}\,\Delta_{x,y} \;+\; h(x, y). \tag{1.1.3}$$

Let $\mathcal{H}_{nuc} \;=\; L^2(\mathbb{R}^2,\, dx\, dy)$ and $\mathcal{H}_{el} \;=\; L^2(\mathbb{R}^{3N})$, so that $H(\epsilon)$ acts on the Hilbert space $\mathcal{H}_{nuc} \otimes \mathcal{H}_{el}$. We denote the inner product and norm on $\mathcal{H}_{el}$ by $\langle\, \cdot,\, \cdot \,\rangle_{el}$ and $||\cdot||_{el}$ and similarly

on $\mathcal{H}_{nuc}$ by $\langle \cdot, \cdot \rangle_{nuc}$ and $||\cdot||_{nuc}$.

Let $L_z^{el}$ and $L_z^{nuc} = -i\,\frac{\partial}{\partial\phi}$ be the operators associated with the projections of the electronic and nuclear angular momenta on the $z$-axis, respectively. The operator of total angular momentum about the $z$-axis is denoted by $L_z^{TOT} = (I \otimes L_z^{el}) + (L_z^{nuc} \otimes I)$. We note that $H(\epsilon)$ commutes with $L_z^{TOT}$. We consider the electronic states when $(x, y) = (0, 0)$. In this case the electronic hamiltonian $h(0, 0)$ commutes with $L_z^{el}$ since the nuclei are in a linear arrangement. So, for $|l_z^{el}| \neq 0$ there are two-fold degenerate electronic vectors $\psi_1,\ \psi_2 \in \mathcal{H}_{el}$ satisfying $h(0,0)\,\psi_1 = E_0^{|l_z^{el}|}\,\psi_1$ and $h(0,0)\,\psi_2 = E_0^{|l_z^{el}|}\,\psi_2$, where $L_z^{el}\,\psi_1 = l_z^{el}\,\psi_1$ and $L_z^{el}\,\psi_2 = -l_z^{el}\,\psi_2$. Then, if the molecule is bent so that $(x, y) \neq (0, 0)$, this degeneracy splits since the nuclei are no longer in a linear arrangement, and $h(x, y)$ no longer commutes with $L_z^{el}$ (see [13] for a discussion directly relating the breaking of symmetry with the breaking of the degeneracy). This is the Renner-Teller effect [3]. As previously mentioned, the application of the Born-Oppenheimer approximation is not straightforward in this case.

Note that since changes in $\phi$ correspond to an overall molecular rotation, the eigenvalues of $h(x, y)$ are independent of $\phi$. Corresponding to the situation above where the electronic states at $\tilde{\rho} = 0$ are linear combinations of eigenstates of $L_z^{el}$ with eigenvalues $l_z^{el}$, $-l_z^{el} \neq 0$, suppose we have a pair of electronic eigenvalues $E_1(\tilde{\rho})$ and $E_2(\tilde{\rho})$ of $h(x, y)$ that are degenerate at $\tilde{\rho} = 0$ (we choose $E_1(0) = E_2(0) = 0$ for convenience), but the degeneracy breaks when $\tilde{\rho} \neq 0$. We refer to two such electronic states as an R-T pair with value $|l_z^{el}|$. The eigenvalues of $h(x, y)$ provide the usual potential energy surfaces for the nuclei, and there are several qualitatively different possibilities where the Renner Teller effect is important. For example,

both $E_1(\tilde{\rho})$ and $E_2(\tilde{\rho})$ can have local minima at $\tilde{\rho} = 0$ (sketch (a) of Figure 1.1), the lower curve can instead have a local maximum at $\tilde{\rho} = 0$ and a local minimum close by (sketch (b) of Figure 1.1), or both can have local maxima at $\tilde{\rho} = 0$ and local minima close by (sketch (c) on Figure 1.1).

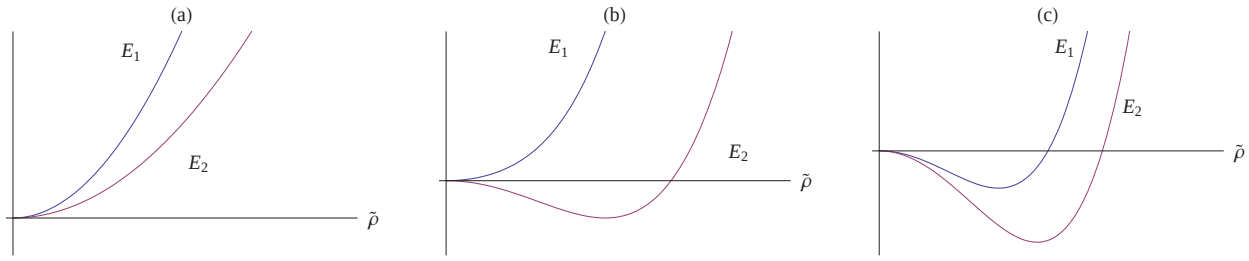


Figure 1.1: Potential energy surfaces of three qualitatively different cases corresponding to an R-T pair of electronic states.

See [13, 14] for further examples and discussion of Renner-Teller surfaces. We focus strictly on an R-T pair corresponding to sketch (a) of Figure 1.1, where both surfaces have local minima at $\tilde{\rho} = 0$. In this case the optimal nuclear configuration, corresponding to both electronic states of the R-T pair, is linear. This was the situation considered by Renner [3] in 1934. The first experimental observation of the Renner-Teller effect did not come until the mid 1950s in a study of $NH_2$ by Dressler and Ramsay [15, 16]. However, it involved the case corresponding to sketch (c) of Figure 1.1 which was not considered by Renner. Their results were further explained in relation to the Renner-Teller effect by Pople and Longuet-Higgins [17], who had access to the results of Dressler and Ramsay before publication (at the time,

it was thought to correspond to sketch (b) of Figure 1.1, but later the work of Dixon [18] suggested that it was likely the case in sketch (c)). Since then there have been numerous papers related to the Renner-Teller effect, few of which are relevant to our analysis here. We highlight one such paper by Brown and Jørgensen [19] for its completeness, and because it does discuss effects beyond the leading order. We encourage the reader interested to learn the historical development and recent findings of the theory to consult the extensive review by Perić and Peyerimhoff [11].

Throughout this paper, we assume the following hypotheses: There is an R-T pair of states corresponding to sketch (a) of Figure 1.1, where both $E_1$ and $E_2$ have minima at $\tilde{\rho} = 0$. We assume that for some neighborhood of $\tilde{\rho} = 0$, $E_1$ and $E_2$ are isolated from the rest of the spectrum and are $C^\infty$ in $(x, y)$. This implies that $E_1(\tilde{\rho})$ and $E_2(\tilde{\rho})$ have asymptotic expansions in powers of $\tilde{\rho}^2$. We assume that splitting occurs at 2nd order, that is, that $E_1$ and $E_2$ are asymptotic to $\frac{a+b}{2}\,\tilde{\rho}^2$ and $\frac{a-b}{2}\,\tilde{\rho}^2$ for small $\tilde{\rho}$, respectively, for some $0 < b < a$. Renner [3] argued that an R-T pair with value $|l_z^{el}| = 1$ will exhibit splitting at 2nd order, an R-T pair with value $|l_z^{el}| = 2$ will exhibit splitting at 4th order, and in general an R-T pair with value $|l_z^{el}| = n$ will exhibit splitting at order $2n$. We instead assume 2nd order splitting occurs and later prove that the R-T pair has value $|l_z^{el}| = 1$, agreeing with Renner's argument.

## 1.2 Statement of the Main Theorem

We are now ready to state our main theorem.

**Theorem 1.2.1.** *Assume the hypotheses described in the preceding sections, in particular that the potentials are smooth and there is an R-T pair $E_1(\tilde{\rho})$, $E_2(\tilde{\rho})$ that are asymptotic to $\frac{a+b}{2}\tilde{\rho}^2$ and $\frac{a-b}{2}\tilde{\rho}^2$ respectively, where $0 < b < a$. Then for arbitrary $K$, there exist quasimode energies*

$$E_{\epsilon,K} \;=\; \sum_{k=0}^{K} \epsilon^k \, E^{(k)}$$

*and quasimodes*

$$\Phi_{\epsilon,K} \;=\; \sum_{k=0}^{K} \epsilon^k \, \Phi_{\epsilon}^{(k)}$$

*that satisfy*

$$|| \, ( \, H(\epsilon) \; - \; E_{\epsilon,K} \, ) \; \Phi_{\epsilon,K} \, ||_{\mathcal{H}_{nuc} \otimes \mathcal{H}_{el}} \;\leq\; C_K \, \epsilon^{K+1} \; || \, \Phi_{\epsilon,K} \, ||_{\mathcal{H}_{nuc} \otimes \mathcal{H}_{el}} \, .$$

*The quasimodes are associated with the local wells of $E_1$ and $E_2$ in a neighborhood of $\tilde{\rho} = 0$.*

Remarks:

1. Quasimode estimates correspond to discrete eigenvalues of $H(\epsilon)$ when $E_{\epsilon,K}$ lies below the essential spectrum as characterized by the HVZ theorem [21].

2. Since $[L_z^{TOT}, H(\epsilon)] = 0$, quasimodes can be constructed to be eigenfunctions of $L_z^{TOT}$, with eigenvalues $l_z^{TOT} \in \mathbb{Z}$. The eigenstates of $H(\epsilon)$ corresponding to $l_z^{TOT} = 0$ are non-degenerate, while the eigenstates corresponding to $|l_z^{TOT}| \neq 0$ are two-fold degenerate.

In particular, there is an $l_z^{TOT}$ state and a $-l_z^{TOT}$ state, with eigenfunctions that are complex conjugates of one another, that together form a degenerate pair of states associated with $H(\epsilon)$.

3. The first two orders $E^{(0)}$ and $E^{(1)}$ are zero and the second order $E^{(2)}$ is determined by the leading order eigenvalue equation $\mathbb{H}_2\Psi = E^{(2)}\Psi$, on the Hilbert space $L^2(I\!R^2,\, dX\, dY;\, \mathbb{C}^2)$, where

$$\mathbb{H}_2 \;=\; \begin{pmatrix} -\frac{1}{2}\,\Delta_{X,\,Y} \;+\; \frac{a+b}{2}\,X^2 \;+\; \frac{a-b}{2}\,Y^2 & b\,X\,Y \\ b\,X\,Y & -\frac{1}{2}\,\Delta_{X,\,Y} \;+\; \frac{a-b}{2}\,X^2 \;+\; \frac{a+b}{2}\,Y^2 \end{pmatrix}.$$

The higher order $E^{(k)}$ are determined through the perturbation formulas presented in chapter 2. All odd order $E^{(k)}$ are zero (see chapter 6).

4. The presence of the two levels $E_1(\tilde{\rho})$ and $E_2(\tilde{\rho})$ gives rise to twice the number of vibrational levels as usual in the following sense:

   If $b = 0$, the upper and lower component equations of the leading order equation which determines $E^{(2)}$, are both two-dimensional harmonic oscillator equations. So, there will be two eigenfunctions, one associated with the each of the upper and lower components, for each of the usual eigenstates of the usual harmonic oscillator. Then for small $b$, this will give rise to two vibrational states via a perturbative approach, for each of the usual harmonic oscillator states. This is shown in detail in chapter 4.

5. For small $b$ and $\epsilon$, the ground state of $H(\epsilon)$ (meaning the lowest vibrational level corresponding to the R-T pair we are considering) is degenerate, corresponding to a

pair of states which are eigenfunctions of $L_z^{TOT}$ with eigenvalues $l_z^{TOT} = \pm 1$. In chapter 4, we give plots which suggest that for approximately $0.925a < b < a$ it is likely that the ground state is non-degenerate, corresponding to a state with $l_z^{TOT} = 0$.

Before we begin the formal expansion in chapter 2, we first look at some properties of the electronic eigenvectors and eigenvalues, and construct electronic basis vectors that are smooth in terms of the nuclear coordinates.

## 1.3 Properties of the Electronic Eigenvectors and Eigenvalues

For the N electrons, as well as the nuclei, we use the same fixed reference frame previously described. Let $(r_j,\, \theta_j,\, z_j)$ be the cylindrical coordinates of the $jth$ electron in this frame. Suppose that for $\tilde{\rho} > 0$, $\psi(x, y;\, \theta_1, \theta_2, \cdots, \theta_N) : I\!R^2 \rightarrow \mathcal{H}_{el}$ is an electronic eigenvector of $h(x, y)$. We have suppressed the dependence on $r_j$ and $z_j$ because it is irrelevant to the discussion here. The electronic eigenfunctions are invariant with respect to a rotation of the entire molecule. So, the eigenfunctions have the property

$$\psi(x,\, y;\, \theta_1, \theta_2, \cdots, \theta_N) \,=\, \psi(\tilde{\rho},\, 0;\, \theta_1 - \phi, \theta_2 - \phi, \cdots, \theta_N - \phi)$$

for $\tilde{\rho} > 0$. It follows that if $\psi(x, y)$ is continuous at $\tilde{\rho} = 0$, then $\psi(0, 0)$ has no $\theta_j$ dependence. Therefore, we do not have well-defined continuous electronic eigenfunctions of $h(x, y)$ in a neighborhood of $\tilde{\rho} = 0$, that correspond to an R-T pair with value $|l_z^{el}| > 0$, since an eigen-

vector corresponding to an R-T pair with positive $|l_z^{el}|$ value will have some $\theta_j$ dependence at $\tilde{\rho} = 0$. We need basis vectors for the two-dimensional eigenspace of $E_1(\tilde{\rho})$ and $E_2(\tilde{\rho})$ that are smooth in $x$ and $y$. These can only be constructed by taking appropriate linear combinations of the electronic eigenvectors, but are not eigenvectors themselves. One may think that it is possible to smooth the electronic eigenvector by multiplying by a phase factor that depends on the nuclear angle $\phi$, but the example below illustrates that linear combinations of the eigenvectors are needed before the smoothing phase factor is applied. For simplicity, the example is done for the one electron case but we believe the argument can be generalized to any number of electrons.

### 1.3.1 An Illustrative Example: The One Electron Case

For simplicity, suppose that there is only one electron in the problem, and let $\theta$ be the polar angle in the $xy$-plane for this electron. Assume that $E_1(\tilde{\rho})$ and $E_2(\tilde{\rho})$ correspond to an R-T pair with $|l_z^{el}| = 1$. Let $\tilde{\Psi}_1(x,\, y;\, \theta)$ and $\tilde{\Psi}_2(x,\, y;\, \theta)$ be the corresponding electronic eigenvectors for $\tilde{\rho} \neq 0$, with eigenvalues $E_1(\tilde{\rho})$ and $E_2(\tilde{\rho})$ respectively. We assume that these eigenvectors are chosen orthonormal in $\mathcal{H}_{el}$ for each $(x, y)$ away from the origin. Since the eigenvalues are non-degenerate away from $\tilde{\rho} = 0$ and $h(x, y)$ commutes with complex conjugation, we know that we can arrange for $\tilde{\Psi}_1$ and $tl\Psi_2$ to be real, which we assume has been done. From above we have

$$\tilde{\Psi}_1(x,\, y;\, \theta) \,=\, \tilde{\Psi}_1(\tilde{\rho},\, 0;\, \theta - \phi), \qquad \tilde{\Psi}_2(x,\, y;\, \theta) \,=\, \tilde{\Psi}_2(\tilde{\rho},\, 0;\, \theta - \phi).$$

Suppose that $\tilde{\Psi}_1(\tilde{\rho}, 0; \theta)$ and $\tilde{\Psi}_2(\tilde{\rho}, 0; \theta)$ approach eigenvectors of $h(0,0)$ as $\tilde{\rho}$ approaches 0. The $\theta$ dependence of the eigenvectors at $\tilde{\rho} = 0$ is known, since the eigenvectors are linear combinations of $|l_z^{el}| = 1$ states. Since these vectors were chosen real, we must have (up to a minus sign)

$$\lim_{\tilde{\rho}\to 0} \tilde{\Psi}_1(\tilde{\rho}, 0; \theta) \,=\, (\alpha\, \cos(\theta) \,+\, \beta\, \sin(\theta))\, f, \quad \lim_{\tilde{\rho}\to 0} \tilde{\Psi}_2(\tilde{\rho}, 0; \theta) \,=\, (-\beta\, \cos(\theta) \,+\, \alpha\, \sin(\theta))\, f,$$

for some $\alpha,\ \beta \in I\!R$ and real valued function $f \in \mathcal{H}_{el}$ with no $\theta$ dependence. Then, we know that along the sector $\phi = \phi_0$, these vectors approach

$$\lim_{\tilde{\rho}\to 0} \tilde{\Psi}_1(\tilde{\rho}, \phi_0; \theta) \,=\, \lim_{\tilde{\rho}\to 0} \tilde{\Psi}_1(\tilde{\rho}, 0; \theta - \phi_0) \,=\, (\alpha\, \cos(\theta - \phi_0) \,+\, \beta\, \sin(\theta - \phi_0))\, f,$$

$$\lim_{\tilde{\rho}\to 0} \tilde{\Psi}_2(\tilde{\rho}, \phi_0; \theta) \,=\, \lim_{\tilde{\rho}\to 0} \tilde{\Psi}_2(\tilde{\rho}, 0; \theta - \phi_0) \,=\, (-\beta\, \cos(\theta - \phi_0) \,+\, \alpha\, \sin(\theta - \phi_0))\, f.$$

We see that the only linear combinations of these functions that are orthonormal in $\mathcal{H}_{el}$ and smooth in $(x, y)$, are linear combinations of functions of the form

$$\Psi_1 \,=\, \frac{1}{\sqrt{2}}\, e^{i\phi}\, (\tilde{\Psi}_1 \,+\, i\, \tilde{\Psi}_2),$$

$$\Psi_2 \,=\, \frac{1}{\sqrt{2}}\, e^{-i\phi}\, (\tilde{\Psi}_1 \,-\, i\, \tilde{\Psi}_2),$$

which follows from

$$\begin{aligned}
\lim_{\tilde{\rho}\to 0} \Psi_1(\tilde{\rho}, \phi; \theta) \;&=\; \lim_{\tilde{\rho}\to 0} \frac{1}{\sqrt{2}}\, e^{i\phi}\, (\tilde{\Psi}_1 \,+\, i\, \tilde{\Psi}_2) \\
&=\; \frac{1}{\sqrt{2}}\, e^{i\phi}\, (\alpha \,-\, i\, \beta)\, (\cos(\theta - \phi) \,+\, i\, \sin(\theta - \phi)) f \\
&=\; \frac{1}{\sqrt{2}}\, e^{i\theta}\, (\alpha \,-\, i\, \beta)\, f
\end{aligned}$$

and

$$\begin{aligned}\lim_{\tilde{\rho}\to 0}\,\Psi_2(\tilde{\rho},\phi;\theta) &= \lim_{\tilde{\rho}\to 0}\,\frac{1}{\sqrt{2}}\,e^{-i\phi}\,(\tilde{\Psi}_1\,-\,i\,\tilde{\Psi}_2)\\ &= \frac{1}{\sqrt{2}}\,e^{-i\phi}\,(\alpha\,+\,i\,\beta)\,(\cos(\theta-\phi)\,-\,i\,\sin(\theta-\phi))f\\ &= \frac{1}{\sqrt{2}}\,e^{-i\theta}\,(\alpha\,+\,i\,\beta)\,f.\end{aligned}$$

In any case, we see that any orthonormal basis vectors for the two-dimensional eigenspace of $E_1(\tilde{\rho})$ and $E_2(\tilde{\rho})$ that are smooth in $x$ and $y$, are not eigenvectors of $h(x,y)$ themselves.

We now show that by making a particular choice of real valued linear combinations of the smooth vectors $\Psi_1$ and $\Psi_2$ constructed above, we can construct electronic basis vectors that give rise to the same matrix elements of $h(x,y)$ that will be derived in the next section. Choose $\Xi_1$ and $\Xi_2$ to be the following real valued, smooth linear combinations of the above $\Psi_1$ and $\Psi_2$:

$$\begin{aligned}\Xi_1 &= \frac{1}{\sqrt{2}}\,(\Psi_1\,+\,\Psi_2)\,=\,\cos(\phi)\,\tilde{\Psi}_1\,-\,\sin(\phi)\,\tilde{\Psi}_2\\ \Xi_2 &= \frac{1}{\sqrt{2}\,i}\,(\Psi_1\,-\,\Psi_2)\,=\,\sin(\phi)\,\tilde{\Psi}_1\,+\,\cos(\phi)\,\tilde{\Psi}_2\,.\end{aligned}$$

If we now use $h(x,y)\,\tilde{\Psi}_1\,=\,E_1(\tilde{\rho})\,\tilde{\Psi}_1$ and $h(x,y)\,\tilde{\Psi}_2\,=\,E_2(\tilde{\rho})\,\tilde{\Psi}_2$, along with $E_1(\tilde{\rho}) = \frac{a+b}{2}\tilde{\rho}^2 + O(\tilde{\rho}^4)$ and $E_2(\tilde{\rho}) = \frac{a-b}{2}\tilde{\rho}^2 + O(\tilde{\rho}^4)$, we find that

$$\begin{aligned}\langle\,\Xi_1,\,h(x,y)\,\Xi_1\,\rangle_{el} &= \cos^2(\phi)\,E_1\,+\,\sin^2(\phi)\,E_2\\ &\sim \frac{a}{2}\,\tilde{\rho}^2\,+\,\frac{b}{2}\,\tilde{\rho}^2\,(\cos^2(\phi)\,-\,\sin^2(\phi))\\ &= \frac{a+b}{2}\,x^2\,+\,\frac{a-b}{2}\,y^2 \qquad (1.3.4)\end{aligned}$$

$$\begin{aligned} \langle\, \Xi_2,\, h(x,y)\, \Xi_1 \,\rangle_{el} \,=\, \langle\, \Xi_1,\, h(x,y)\, \Xi_2 \,\rangle_{el} \;&=\; \sin(\phi)\, \cos(\phi)\, (E_1 \,-\, E_2) \\ &\sim\; b\, \tilde{\rho}^2\, \sin(\phi)\, \cos(\phi) \\ &=\; b\, x\, y \end{aligned} \tag{1.3.5}$$

$$\begin{aligned} \langle\, \Xi_2,\, h(x,y)\, \Xi_2 \,\rangle_{el} \;&=\; \sin^2(\phi)\, E_1 \,+\, \cos^2(\phi)\, E_2 \\ &\sim\; \frac{a}{2}\, \tilde{\rho}^2 \,-\, \frac{b}{2}\, \tilde{\rho}^2\, (\cos^2(\phi) \,-\, \sin^2(\phi)) \\ &=\; \frac{a-b}{2}\, x^2 \,+\, \frac{a+b}{2}\, y^2 \end{aligned} \tag{1.3.6}$$

In this example we assumed there was only one electron, and that the R-T pair had value $|l_z^{el}| = 1$. Without these assumptions, it is shown in the next section that these are the only possible matrix elements, up to an $(x, y)$ independent unitary transformation, assuming only second order splitting.

## 1.4 Construction of the Basis Vectors For the Electronic Eigenspace

In order to employ a Born-Oppenheimer expansion, we must have basis vectors for the electronic eigenspace corresponding to the R-T pair that have asymptotic expansions in the coordinate $\tilde{\rho}$. Typically this has been done using basis vectors that exhibit the same discontinuity in $\phi$ at $\tilde{\rho} = 0$ as the eigenvectors (as discussed in the previous section). For

example, Renner [3] used basis vectors $\tilde{\Psi}_1$ and $\tilde{\Psi}_2$ with

$$\lim_{\tilde{\rho}\to 0} \tilde{\Psi}_1(\tilde{\rho},\phi;\theta) \,=\, \cos(\theta-\phi)\, f, \quad \lim_{\tilde{\rho}\to 0} \tilde{\Psi}_2(\tilde{\rho},\phi;\theta) \,=\, \sin(\theta-\phi)\, f,$$

similar to the vectors in the previous section. He then used the derivatives of these expressions with respect to $\phi$ (appearing from the nuclear Laplacian) to derive the leading order equation. Of course the coordinate $\phi$ is not well defined at $\tilde{\rho}=0$, so the validity of this is not obvious. Something similar is done in [11] and [19], by defining the electron coordinates in reference to the molecular plane. In the one electron approximation discussed in the previous section, this is akin to describing the model in terms of the new coordinates $\chi=\phi$ and $\eta=\theta-\phi$. The basis vectors are then expanded as

$$\tilde{\Psi}_1 \,=\, \sum_{n=0}^{\infty} \tilde{\Psi}_1^{(n)}\, \tilde{\rho}^n, \quad \tilde{\Psi}_2 \,=\, \sum_{n=0}^{\infty} \tilde{\Psi}_2^{(n)}\, \tilde{\rho}^n,$$

where $\tilde{\Psi}_1^{(n)}$ and $\tilde{\Psi}_2^{(n)}$ have $\eta$ dependence but do not depend on $\chi$ explicitly. The angular momentum operators are then defined in terms of this coordinate system using the chain rule:

$$L_z^{el} \,=\, -i\,\frac{\partial}{\partial\eta}, \quad L_z^{nuc} \,=\, -i\left(\frac{\partial}{\partial\chi} - \frac{\partial}{\partial\eta}\right), \quad L_z^{TOT} \,=\, -i\,\frac{\partial}{\partial\chi}.$$

The matrix elements of $L_z^{el}$ in the basis $\tilde{\Psi}_1^{(0)}$ and $\tilde{\Psi}_2^{(0)}$ are then used to derive the leading order equations. Again, the coordinate $\phi$, and thus also $\eta$, are not well defined in a neighborhood of $\tilde{\rho}=0$. So, the validity of the above expansions in $\tilde{\rho}$ is unclear, and as a result, the validity of using the matrix elements of the operator $L_z^{el}$ in this way comes into question. While it is likely that this can be formulated in a rigorous manner, it is not obvious, and we choose instead to avoid this issue completely by constructing basis vectors that are smooth in $(x,y)$,

which is done below. The matrix elements of $h(x, y)$ in our electronic basis determine the form of the leading order equations presented in chapter 2. We note that in deriving these matrix elements, we do not use the matrix elements of $L_z^{el}$. Only second order splitting in $E_1$ and $E_2$ is needed, as well as the fact that our smooth basis vectors are not eigenvectors of $h(x, y)$. This gives rise to off-diagonal terms in the basis representation of $h(x, y)$. In this sense, the unusual form of the leading order equations can be thought of as a result of the discontinuity of the electronic eigenvectors in the nuclear coordinates, *i.e.* there is no smooth electronic basis that diagonalizes the electronic hamiltonian. In a discussion of the Renner-Teller effect in relation to the geometric phase effect [20], Yarkony presents analogous matrix elements from a slightly different point of view. We note that the matrix elements we derive here, are related by an $(x, y)$-independent unitary transformation to those given by Yarkony. We believe Yarkony was well aware of the argument we use to derive the matrix elements of $h(x, y)$.

We now describe our approach. Choose any two normalized orthogonal electronic vectors $\psi_1$ and $\psi_2$ that span the eigenvalue 0 eigenspace of $h(0, 0)$. Let $P(x,\, y)$ denote the two dimensional projection onto the electronic eigenspace associated to the two eigenvalues of $h(x,\, y)$. For small $x$ and $y$, define

$$\Psi_1(x,\, y) \;=\; \frac{1}{\sqrt{\langle\, \psi_1,\, P(x,\, y)\, \psi_1 \rangle}}\; P(x,\, y)\, \psi_1. \tag{1.4.7}$$

Let $P_1(x,\, y)$ denote the orthogonal projection onto this vector, *i.e.*,

$$P_1(x,\, y) \;=\; |\, \Psi_1(x,\, y)\, \rangle\, \langle\, \Psi_1(x,\, y)\, |\,.$$

Next, define

$$\chi(x,\, y) \;=\; (\,1 \,-\, P_1(x,\, y)\,)\;\, P(x,\, y)\;\psi_2,$$

and

$$\Psi_2(x,\, y) \;=\; \frac{1}{\sqrt{\langle\, \chi(x,\, y),\, \chi(x,\, y)\,\rangle}}\;\chi(x,\, y). \tag{1.4.8}$$

Then $\{\, \Psi_1(x,\, y),\, \Psi_2(x,\, y)\,\}$ is an orthonormal basis for the range of $P(x,\, y)$. From the formula [21]

$$P(x,y) \;=\; \frac{1}{2\pi i}\int_C (\lambda - h(x,y))^{-1}\, d\lambda,$$

where $C$ is a closed path in the complex plane encircling $E_1(\tilde{\rho})$ and $E_2(\tilde{\rho})$ but no other spectrum of $h(x,y)$, we see that these vectors are smooth in $x$ and $y$, since we have assumed that the potentials are smooth and hence the resolvent of $h(x,y)$ is as well (recall we are only working in a neighborhood of the origin $(x,y) = (0,0)$). Note that we can arrange for these vectors to be real, which we assume has been done.

The span of $\{\, \Psi_1(x,\, y),\, \Psi_2(x,\, y)\,\}$ is an invariant subspace for $h(x,\, y)$. Using coordinates in this basis, the restriction of $h(x,\, y)$ to this subspace is unitarily equivalent to the real symmetric matrix

$$\begin{pmatrix} h_{11}(x,\, y) & h_{12}(x,\, y) \\ \\ h_{21}(x,\, y) & h_{22}(x,\, y) \end{pmatrix},$$

where

$$h_{jk}(x,y) \;=\; \langle\, \Psi_j(x,\, y),\, h(x,\, y)\, \Psi_k(x,\, y)\,\rangle.$$

Again, since we have smooth potentials, $h_{ij}(x,y)$ can be expanded in powers of $x$ and $y$. Since we assume the degeneracy splits at second order, the eigenvalues of this matrix are

$E_1(x,\,y) = \frac{a+b}{2}\,(x^2+y^2) + O(\tilde{\rho}^4)$ and $E_2(x,\,y) = \frac{a-b}{2}\,(x^2+y^2) + O(\tilde{\rho}^4)$. Using these expressions for the eigenvalues we show that up to an $(x, y)$-independent unitary transformation, this matrix is

$$\begin{pmatrix} \frac{a+b}{2}\,x^2 \;+\; \frac{a-b}{2}\,y^2 & \pm\, b\,x\,y \\ \pm\, b\,x\,y & \frac{a-b}{2}\,x^2 \;+\; \frac{a+b}{2}\,y^2 \end{pmatrix}, \tag{1.4.9}$$

up to second order in $\tilde{\rho}$ (compare with equations (1.3.4), (1.3.5), and (1.3.6) ). To show this, we consider a traceless, real symmetric matrix

$$\begin{pmatrix} \tilde{h}_{11}(x,\,y) & \tilde{h}_{12}(x,\,y) \\ \tilde{h}_{21}(x,\,y) & -\tilde{h}_{11}(x,\,y) \end{pmatrix}, \tag{1.4.10}$$

with eigenvalues $\tilde{E}_{\pm}(x,\,y) = \pm\,\tilde{\rho}^2 + O(\tilde{\rho}^4)$. The form in (1.4.9) will follow from the analysis below. Using (1.4.10), we have the characteristic equation

$$\tilde{E}_{\pm}^2 \;+\; O(\tilde{\rho}^6) = \;\tilde{h}_{11}^2 \;+\; \tilde{h}_{12}^2. \tag{1.4.11}$$

By expanding in powers of $x$ and $y$ and equating orders in the above equation, it can be easily shown that the constant and linear terms of $\tilde{h}_{11}$ and $\tilde{h}_{12}$ must vanish. We then write,

$$\begin{pmatrix} \tilde{h}_{11}(x,\,y) & \tilde{h}_{12}(x,\,y) \\ \tilde{h}_{21}(x,\,y) & -\tilde{h}_{11}(x,\,y) \end{pmatrix} \;=\; A\,x^2 \;+\; B\,y^2 \;+\; C\,xy \;+\; O(\tilde{\rho}^3), \tag{1.4.12}$$

where $A$, $B$, and $C$ are traceless 2 by 2 matrices with constant entries. We can apply a constant unitary transformation to (1.4.12) that diagonalizes $A$, which we assume has been done. An obvious consequence of (1.4.11) and $\tilde{E}_{\pm}(x,\,y) \;=\; \pm\,\tilde{\rho}^2 \;+\; O(\tilde{\rho}^4)$ is that if $A$ is

diagonal, it must be

$$A = \begin{pmatrix} 1 & 0 \\ \\ 0 & -1 \end{pmatrix}.$$

We let

$$B = \begin{pmatrix} b_{11} & b_{12} \\ \\ b_{12} & -b_{11} \end{pmatrix}, \quad \text{and} \quad C = \begin{pmatrix} c_{11} & c_{12} \\ \\ c_{12} & -c_{11} \end{pmatrix},$$

and use (1.4.11) with $\tilde{E}_{\pm}(x,\, y) = \pm\,\tilde{\rho}^2 + O(\tilde{\rho}^4)$ to solve for $b_{ij}$ and $c_{ij}$ by equating the powers of $x$ and $y$. This gives us four equations, the first equation comes from the $y^4$ coefficients, the second comes from the $x^2y^2$ coefficients, etc.

$$y^4: \qquad 1 \;=\; b_{11}^2 \,+\, b_{12}^2 \tag{1.4.13}$$

$$x^2y^2: \qquad 2 \;=\; 2\,b_{11} \,+\, c_{11}^2 \,+\, c_{12}^2 \tag{1.4.14}$$

$$xy^3: \qquad 0 \;=\; 2(b_{11}c_{11} \,+\, b_{12}c_{12}) \tag{1.4.15}$$

$$x^3y: \qquad 0 \;=\; 2c_{11} \tag{1.4.16}$$

These equations have 3 solutions. Two of the solutions are

$$(b_{11}, b_{12}, c_{11}, c_{12}) \;=\; (-1, 0, 0, \pm 2),$$

which give

$$\begin{pmatrix} \tilde{h}_{11}(x,\, y) & \tilde{h}_{12}(x,\, y) \\ \\ \tilde{h}_{21}(x,\, y) & -\tilde{h}_{11}(x,\, y) \end{pmatrix} = \begin{pmatrix} x^2 - y^2 & \pm\, 2xy \\ \\ \pm\, 2xy & -(x^2 - y^2) \end{pmatrix}.$$

These solutions give rise to (1.4.9). The only other solution of equations (1.4.13)-(1.4.16) is

$$(b_{11}, b_{12}, c_{11}, c_{12}) \;=\; (1, 0, 0, 0),$$

which gives rise to

$$\begin{pmatrix} h_{11}(x,\, y) & h_{12}(x,\, y) \\ h_{21}(x,\, y) & h_{22}(x,\, y) \end{pmatrix} = \begin{pmatrix} \dfrac{a+b}{2}\,\tilde{\rho}^2 & 0 \\ 0 & \dfrac{a-b}{2}\,\tilde{\rho}^2 \end{pmatrix}.$$

Aside from being an uninteresting case, this would imply that the basis vectors are the eigenfunctions of $h(x,\, y)$ which we know not to be the case. We will assume the off diagonal terms in (1.4.9) are $bxy$ since the $-bxy$ case is related by the trivial change of coordinates $y \mapsto -y$.

## 1.5 Summary of Results and Organization of the Thesis

In chapter 2, we derive perturbation formulas to construct the quasimodes that will enter in our main theorem. Formulas are given to arbitrary order.

In chapter 3, we prove various properties of the leading order Hamiltonian that are needed to prove the main theorem. The leading order Hamiltonian $\mathbb{H}_2$ is analyzed in terms of a parameter $\tilde{b}$, which is equivalent to the one used by Renner [3]. For $0 < \tilde{b} < 1$, we prove self-adjointness of $\mathbb{H}_2$, that it has purely discrete spectrum, and also exponential decay of the eigenfunctions, and of their derivatives.

In chapter 4, we analyze the leading order eigenvalue problem in terms of $\tilde{b}$. Only some of the eigenvalues and eigenfunctions of the leading order equation are solved for exactly. The other

eigenvalues and eigenfunctions are examined using a perturbative approach following Renner [3], and are compared with the results of an elementary finite difference scheme. We provide plots that suggest the existence of a crossing near $\tilde{b} = 0.925$ involving the ground state of $\mathbb{H}_2$. The crossing would imply that the ground state of $\mathbb{H}_2$ is degenerate for $0 < \tilde{b} < 0.925$, and non-degenerate for $0.925 < \tilde{b} < 1$.

In chapter 5, the degeneracy structure of the full Hamiltonian $H(\epsilon)$ is discussed and we show that a crossing involving the ground state of $\mathbb{H}_2$ would imply that the ground vibrational state of $H(\epsilon)$ corresponding to the R-T pair, would be degenerate for $0 < \tilde{b} < 0.925$, and non-degenerate for $0.925 < \tilde{b} < 1$.

In chapter 6, we use the perturbation formulas given in chapter 2 to show that all of the odd order coefficients of $E_{\epsilon,K} = \sum_{k=0}^{K} E^{(k)} \epsilon^k$, given in the statement of the main theorem, are zero.

In chapter 7, we use the results of the previous chapters to prove the main theorem.

# Chapter 2

# The Construction of the Quasimodes

To construct the quasimodes in theorem 1.2.1, we introduce the scaled variables $(X, Y) = (x/\epsilon, y/\epsilon)$. The intuition of the Born-Oppenheimer approximation suggests that the adiabatic effects will occur on the $(x, y) = (\epsilon X, \epsilon Y)$ scale, whereas the semi-classical motion of the nuclei is determined on the $(X, Y)$ scale. In terms of the $(X, Y)$ variables, the Hamiltonian in (1.1.3) is

$$H(\epsilon) \;=\; -\,\frac{\epsilon^2}{2}\,\Delta_{X,\,Y} \;+\; h(\epsilon\, X,\, \epsilon\, Y).$$

We define $\mathcal{H}$ to be the Hilbert space $L^2(I\!R^2,\, dX\, dY;\, \mathbb{C}^2)$ and we denote the inner product on this space by $\langle\, \cdot,\, \cdot\,\rangle_{\mathcal{H}}$.

We seek solutions to $H(\epsilon)\ \Psi(\epsilon,\, X,\, Y) = E(\epsilon)\ \Psi(\epsilon,\, X,\, Y)$. The wave function $\Psi(\epsilon,\, X,\, Y)$ can be written in terms of the orthonormal basis functions $\{\, \Psi_1(x,\, y),\, \Psi_2(x,\, y)\,\}$ from (1.4.7)

and (1.4.8) as

$$\Psi(\epsilon,\, X,\, Y) = f(\epsilon,\, X,\, Y)\ \Psi_1(\epsilon\, X,\, \epsilon\, Y) + g(\epsilon,\, X,\, Y)\ \Psi_2(\epsilon\, X,\, \epsilon\, Y) + \psi_\perp(\epsilon,\, X,\, Y), \qquad (2.0.1)$$

where $\langle\ \psi_\perp,\ \Psi_i\ \rangle_{el} = 0$.

Substituting (2.0.1) in $H(\epsilon)\ \Psi(\epsilon,\, X,\, Y) = E(\epsilon)\ \Psi(\epsilon,\, X,\, Y)$ gives three equations; one along $\Psi_1$, one along $\Psi_2$, and one in $span\{\Psi_1,\ \Psi_2\}^\perp$. We denote the projection on $span\{\Psi_1,\ \Psi_2\}^\perp$ by $P_\perp$. Along $\Psi_1$:

$$\begin{aligned}
&-\frac{\epsilon^2}{2}\,\Delta_{X,Y}\ f\ +\ h_{11}\ f\ +\ h_{12}\ g\ -\ \frac{\epsilon^2}{2}\,\langle\ \Psi_1,\ \Delta_{X,Y}\ \psi_\perp\ \rangle_{el}\ -\ \frac{\epsilon^4}{2}\ f\ \langle\ \Psi_1, \Delta_{x,y}\ \Psi_1\ \rangle_{el} \\
&-\frac{\epsilon^4}{2}\ g\ \langle\ \Psi_1, \Delta_{x,y}\ \Psi_2\ \rangle_{el}\ -\ \epsilon^3\ \left(\ \frac{\partial g}{\partial X}\ \langle\ \Psi_1, \frac{\partial \Psi_2}{\partial x}\ \rangle_{el}\ +\ \frac{\partial g}{\partial Y}\ \langle\ \Psi_1, \frac{\partial \Psi_2}{\partial y}\ \rangle_{el}\ \right) \\
&=\ E(\epsilon)\ f. \qquad (2.0.2)
\end{aligned}$$

Above we have used that $\langle\ \Psi_i, \frac{\partial \Psi_i}{\partial x}\ \rangle_{el}\ =\ 0$, which we know from normalization and the fact that the electronic basis vectors were chosen real. Along $\Psi_2$ we get a similar equation with $f \leftrightarrow g,\ \Psi_1 \leftrightarrow \Psi_2,\ h_{11} \leftrightarrow h_{22},\ h_{12} \leftrightarrow h_{21}$.

In $span\{\Psi_1,\ \Psi_2\}^\perp$:

$$\begin{aligned}
&-\frac{\epsilon^2}{2}\ P_\perp[\ \Delta_{X,Y}\ \psi_\perp\ ]\ +\ (h\ P_\perp)\ \psi_\perp\ -\ \frac{\epsilon^4}{2}\ f\ P_\perp[\ \Delta_{x,y}\ \Psi_1\ ]\ -\ \frac{\epsilon^4}{2}\ g\ P_\perp[\ \Delta_{x,y}\ \Psi_2\ ] \\
&-\epsilon^3\ \left(\ \frac{\partial f}{\partial X}\ P_\perp\left[\ \frac{\partial \Psi_1}{\partial x}\ \right]\ +\ \frac{\partial f}{\partial Y}\ P_\perp\left[\ \frac{\partial \Psi_1}{\partial y}\ \right] +\ \frac{\partial g}{\partial X}\ P_\perp\ \left[\ \frac{\partial \Psi_2}{\partial x}\ \right] +\ \frac{\partial g}{\partial Y}\ P_\perp\ \left[\ \frac{\partial \Psi_2}{\partial y}\ \right]\ \right) \\
&=\ E(\epsilon)\ \psi_\perp. \qquad (2.0.3)
\end{aligned}$$

We adopt the following notation for simplicity:

$$\begin{aligned} T_{ij}(x,\, y) &= \langle\, \Psi_i, \Delta_{x,\,y}\ \Psi_j\ \rangle_{el}, \\ A_{ij}(x,\, y) &= \left\langle\, \Psi_i, \frac{\partial \Psi_j}{\partial x} \right\rangle_{el}, \\ B_{ij}(x,\, y) &= \left\langle\, \Psi_i, \frac{\partial \Psi_j}{\partial y} \right\rangle_{el}. \end{aligned}$$

We have identities involving these quantities since $\{\, \Psi_1,\ \Psi_2\, \}$ are orthonormal and real valued. For instance we know the diagonal elements of $A$ and $B$ are zero and $A_{12} = -A_{21},\ B_{12} = -B_{21}$.

Now we expand all functions and operators with $\epsilon$ dependence. For example, $f(\epsilon,\, X,\, Y) = \sum_{k=0}^{\infty} \epsilon^k\ f^{(k)}(X,\, Y)$ . For functions and operators with exclusively $(x,\, y)$ dependence, we know the form of the expansions. For example, $\Psi_1(x,\, y) = \Psi_1(\epsilon\, X,\, \epsilon\, Y) = \sum_{k=0}^{\infty} \epsilon^k\ \Psi_1^{(k)}(X,\, Y)$, where $\Psi_1^{(k)}(X,\, Y) = \sum_{j=0}^{k} \frac{1}{j!(k-j)!}\ \frac{\partial^k \Psi_1}{\partial x^j \partial y^{k-j}}\,(0,0)\ X^k\ Y^{k-j}$. Equations (2.0.2) and (2.0.3) become:

$$\begin{aligned} &\sum_{k=2}^{\infty} \epsilon^k \left(-\frac{1}{2}\right) \Delta_{X,\,Y}\ f^{(k-2)} + \sum_{k=0}^{\infty} \epsilon^k \sum_{j=0}^{k} \left[\, h_{11}^{(j)}\ f^{(k-j)} + h_{12}^{(j)}\ g^{(k-j)}\, \right] \\ &+ \sum_{k=2}^{\infty} \epsilon^k \sum_{j=2}^{k} \left(-\frac{1}{2}\right) \langle\, \Psi_1^{(j-2)},\ \Delta_{X,\,Y}\ \psi_{\perp}^{(k-j)}\, \rangle_{el} \\ &+ \sum_{k=4}^{\infty} \epsilon^k \sum_{j=4}^{k} \left(-\frac{1}{2}\right) \left[\, T_{11}^{(j-4)}\ f^{(k-j)} + T_{12}^{(j-4)}\ g^{(k-j)}\, \right] \end{aligned}$$

$$+ \sum_{k=3}^{\infty} \epsilon^k \sum_{j=3}^{k} \left[ - A_{12}^{(j-3)} \frac{\partial}{\partial X} - B_{12}^{(j-3)} \frac{\partial}{\partial Y} \right] g^{(k-j)}$$

$$= \sum_{k=0}^{\infty} \epsilon^k \sum_{j=0}^{k} E^{(j)} f^{(k-j)} \tag{2.0.4}$$

and

$$\sum_{k=2}^{\infty} \epsilon^k \sum_{j=2}^{k} \left(-\frac{1}{2}\right) P_{\perp}^{(j-2)} \left[ \Delta_{X,Y} \psi_{\perp}^{(k-j)} \right] + \sum_{k=0}^{\infty} \epsilon^k \sum_{j=0}^{k} (h P_{\perp})^{(j)} \psi_{\perp}^{(k-j)}$$

$$+ \sum_{k=4}^{\infty} \epsilon^k \sum_{j=4}^{k} \sum_{l=4}^{j} \left(-\frac{1}{2}\right) \Big( P_{\perp}^{(j-l)} \left[ (\Delta_{x,y} \Psi_1)^{(l-4)} \right] f^{(k-j)}$$

$$+ P_{\perp}^{(j-l)} \left[ (\Delta_{x,y} \Psi_2)^{(l-4)} \right] g^{(k-j)} \Big)$$

$$+ \sum_{k=3}^{\infty} \epsilon^k \sum_{j=3}^{k} \sum_{l=3}^{j} \Bigg( - P_{\perp}^{(j-l)} \left[ \left( \frac{\partial \Psi_1}{\partial x} \right)^{(l-3)} \right] \frac{\partial}{\partial X}$$

$$- P_{\perp}^{(j-l)} \left[ \left( \frac{\partial \Psi_1}{\partial y} \right)^{(l-3)} \right] \frac{\partial}{\partial Y} \Bigg) f^{(k-j)}$$

$$+ \sum_{k=3}^{\infty} \epsilon^k \sum_{j=3}^{k} \sum_{l=3}^{j} \Bigg( - P_{\perp}^{(j-l)} \left[ \left( \frac{\partial \Psi_2}{\partial x} \right)^{(l-3)} \right] \frac{\partial}{\partial X}$$

$$- P_{\perp}^{(j-l)} \left[ \left( \frac{\partial \Psi_2}{\partial y} \right)^{(l-3)} \right] \frac{\partial}{\partial Y} \Bigg) g^{(k-j)}$$

$$= \sum_{k=0}^{\infty} \epsilon^k \sum_{j=0}^{k} E^{(j)} \psi_{\perp}^{(k-j)}. \tag{2.0.5}$$

We now collect terms at each order of $\epsilon$. Recall there is an equation along $\Psi_2$ analogous to (2.0.4). At each order, we will combine these two similar equations into one matrix equation.

**Order 0** The $\epsilon^0$ terms require

$$\begin{pmatrix} h_{11}^{(0)} & h_{12}^{(0)} \\ h_{21}^{(0)} & h_{22}^{(0)} \end{pmatrix} \begin{pmatrix} f^{(0)} \\ g^{(0)} \end{pmatrix} = E^{(0)} \begin{pmatrix} f^{(0)} \\ g^{(0)} \end{pmatrix}, \tag{2.0.6}$$

$$(h\,P_\perp)^{(0)}\ \psi_\perp^{(0)} = E^{(0)}\ \psi_\perp^{(0)}. \tag{2.0.7}$$

The $h_{ij}(x,\,y)$ vanish until second order, so this forces $E^{(0)} = 0$ in (2.0.6), and consequently $\psi_\perp^{(0)} = 0$ after applying the reduced resolvent $[(\,h(x,y)\,P_\perp(x,y))^{(0)}\,]_r^{-1}$ in (2.0.7).

**Order 1** As above, the $\epsilon^1$ terms reduce to

$$E^{(1)} \begin{pmatrix} f^{(0)} \\ g^{(0)} \end{pmatrix} = 0,$$

$$(h\,P_\perp)^{(0)}\ \psi_\perp^{(1)} = 0.$$

So we get $E^{(1)} = 0$ and $\psi_\perp^{(1)} = 0$.

**Order 2** Using the known second order terms for the $h_{ij}(x,y)$, the $\epsilon^2$ terms require

$$\mathbb{H}_2 \begin{pmatrix} f^{(0)} \\ g^{(0)} \end{pmatrix} = E^{(2)} \begin{pmatrix} f^{(0)} \\ g^{(0)} \end{pmatrix},$$

$$(h\,P_\perp)^{(0)}\ \psi_\perp^{(2)} = 0,$$

where

$$\mathbb{H}_2 = \begin{pmatrix} -\frac{1}{2}\,\Delta_{X,\,Y} + \frac{a+b}{2}\,X^2 + \frac{a-b}{2}\,Y^2 & b\,X\,Y \\ b\,X\,Y & -\frac{1}{2}\,\Delta_{X,\,Y} + \frac{a-b}{2}\,X^2 + \frac{a+b}{2}\,Y^2 \end{pmatrix}.$$

We have assumed the $bxy$ case for the off diagonal entries since the $-bxy$ case is equivalent through the change of coordinates $y \mapsto -y$. By again applying the reduced resolvent in the last equation we have $\psi_{\perp}^{(2)} = 0$. In chapter 3 we will show that $\mathbb{H}_2$ is self-adjoint (on the correct domain) and has purely discrete spectrum with infinitely many eigenstates for $a > b > 0$. We are only able to solve for some of them exactly. In chapter 4 we show that there is at most a two-fold degeneracy in the eigenstates of $\mathbb{H}_2$, but that no splitting occurs in the quasimode eigenvalues, i.e., the degeneracy remains to all orders of $\epsilon$. So, we may proceed as if the eigenstates of $\mathbb{H}_2$ were non-degenerate, since we can take any linear combination of degenerate states for $f^{(0)}$ and $g^{(0)}$, and we know it will lead to a valid quasimode and energy $E(\epsilon)$. Fix $E^{(2)}$, $f^{(0)}$ and $g^{(0)}$ corresponding to one of the states of $\mathbb{H}_2$.

**Order 3** The $\epsilon^3$ terms require

$$\mathbb{H}_3 \begin{pmatrix} f^{(0)} \\ \\ g^{(0)} \end{pmatrix} + \left(\mathbb{H}_2 - E^{(2)}\right) \begin{pmatrix} f^{(1)} \\ \\ g^{(1)} \end{pmatrix} = E^{(3)} \begin{pmatrix} f^{(0)} \\ \\ g^{(0)} \end{pmatrix}, \tag{2.0.8}$$

$$\begin{aligned} \left(h\, P_{\perp}\right)^{(0)}\ \psi_{\perp}^{(3)} \quad = \quad & \left( P_{\perp}^{(0)} \left[ \left( \frac{\partial \Psi_1}{\partial x} \right)^{(0)} \right] \frac{\partial}{\partial X} + P_{\perp}^{(0)} \left[ \left( \frac{\partial \Psi_1}{\partial y} \right)^{(0)} \right] \frac{\partial}{\partial Y} \right) f^{(0)} \\ & + \left( P_{\perp}^{(0)} \left[ \left( \frac{\partial \Psi_2}{\partial x} \right)^{(0)} \right] \frac{\partial}{\partial X} + P_{\perp}^{(0)} \left[ \left( \frac{\partial \Psi_2}{\partial y} \right)^{(0)} \right] \frac{\partial}{\partial Y} \right) g^{(0)}, \end{aligned} \tag{2.0.9}$$

where

$$\mathbb{H}_3 = \begin{pmatrix} h_{11}^{(3)} & h_{12}^{(3)} \\ \\ h_{21}^{(3)} & h_{22}^{(3)} \end{pmatrix} + \begin{pmatrix} 0 & -A_{12}^{(0)} \frac{\partial}{\partial X} - B_{12}^{(0)} \frac{\partial}{\partial Y} \\ \\ -A_{21}^{(0)} \frac{\partial}{\partial X} - B_{21}^{(0)} \frac{\partial}{\partial Y} & 0 \end{pmatrix}.$$

Since $\mathbb{H}_2$ is self-adjoint, we can take inner products of both sides in (2.0.8) with $\begin{pmatrix} f^{(0)} \\ g^{(0)} \end{pmatrix}$ to obtain

$$E^{(3)} \;=\; \left\langle \begin{pmatrix} f^{(0)} \\ g^{(0)} \end{pmatrix}, \mathbb{H}_3 \begin{pmatrix} f^{(0)} \\ g^{(0)} \end{pmatrix} \right\rangle_{\mathcal{H}} .$$

We will show in chapter 6 that all of the odd order $E^{(k)}$ are zero. Let $Q_\perp$ be the projection in $\mathcal{H}$ onto the subspace perpendicular to the eigenspace of the eigenvalue $E^{(2)}$ of $\mathbb{H}_2$. Adopting "intermediate normalization" we may choose the non-zero order wave functions perpendicular to the eigenspace of $E^{(2)}$ (note that this will produce a non-normalized quasimode), so that

$$\begin{pmatrix} f^{(k)} \\ g^{(k)} \end{pmatrix} \;=\; Q_\perp \begin{pmatrix} f^{(k)} \\ g^{(k)} \end{pmatrix},$$

for $k \geq 1$. Then from (2.0.8) we get

$$\begin{pmatrix} f^{(1)} \\ g^{(1)} \end{pmatrix} \;=\; -\left[\mathbb{H}_2 - E^{(2)}\right]_r^{-1} \; Q_\perp \, \mathbb{H}_3 \begin{pmatrix} f^{(0)} \\ g^{(0)} \end{pmatrix}. \tag{2.0.10}$$

From (2.0.9) we have

$$\begin{aligned} \psi_\perp^{(3)} \;=\; & \left[ (h\, P_\perp)^{(0)} \right]_r^{-1} \left[ \left( P_\perp^{(0)} \left[ \left( \frac{\partial \Psi_1}{\partial x} \right)^{(0)} \right] \frac{\partial}{\partial X} \;+\; P_\perp^{(0)} \left[ \left( \frac{\partial \Psi_1}{\partial y} \right)^{(0)} \right] \frac{\partial}{\partial Y} \right) f^{(0)} \right. \\ & \left. +\; \left( P_\perp^{(0)} \left[ \left( \frac{\partial \Psi_2}{\partial x} \right)^{(0)} \right] \frac{\partial}{\partial X} \;+\; P_\perp^{(0)} \left[ \left( \frac{\partial \Psi_2}{\partial y} \right)^{(0)} \right] \frac{\partial}{\partial Y} \right) g^{(0)} \right]. \end{aligned} \tag{2.0.11}$$

**Order 4** The $\epsilon^4$ terms require

$$\left(\mathbb{H}_2 - E^{(2)}\right) \begin{pmatrix} f^{(2)} \\ \\ g^{(2)} \end{pmatrix} + \left(\mathbb{H}_3 - E^{(3)}\right) \begin{pmatrix} f^{(1)} \\ \\ g^{(1)} \end{pmatrix} + \left(\mathbb{H}_4 - E^{(4)}\right) \begin{pmatrix} f^{(0)} \\ \\ g^{(0)} \end{pmatrix} = 0, \quad (2.0.12)$$

$$(h\ P_\perp)^{(0)}\ \psi_\perp^{(4)} = -\ (h\, P_\perp)^{(1)}\ \psi_\perp^{(3)} \quad (2.0.13)$$

$$+ \frac{1}{2}\Big(\ P_\perp^{(0)}\left[\ (\Delta_{x,y}\ \Psi_1)^{(0)}\ \right]\ f^{(0)} + P_\perp^{(0)}\left[\ (\Delta_{x,y}\ \Psi_2)^{(0)}\ \right]\ g^{(0)}\ \Big)$$

$$+ \sum_{j=3}^{4}\sum_{l=3}^{j}\left(P_\perp^{(j-l)}\left[\left(\frac{\partial\Psi_1}{\partial x}\right)^{(l-3)}\right]\frac{\partial}{\partial X} + P_\perp^{(j-l)}\left[\left(\frac{\partial\Psi_1}{\partial y}\right)^{(l-3)}\right]\frac{\partial}{\partial Y}\right) f^{(4-j)}$$

$$+ \sum_{j=3}^{4}\sum_{l=3}^{j}\left(P_\perp^{(j-l)}\left[\left(\frac{\partial\Psi_2}{\partial x}\right)^{(l-3)}\right]\frac{\partial}{\partial X} + P_\perp^{(j-l)}\left[\left(\frac{\partial\Psi_2}{\partial y}\right)^{(l-3)}\right]\frac{\partial}{\partial Y}\right) g^{(4-j)},$$

where

$$\mathbb{H}_4 = \left(-\frac{1}{2}\right)\begin{pmatrix} T_{11}^{(0)} & T_{12}^{(0)} \\ \\ T_{21}^{(0)} & T_{22}^{(0)} \end{pmatrix} + \begin{pmatrix} h_{11}^{(4)} & h_{12}^{(4)} \\ \\ h_{21}^{(4)} & h_{22}^{(4)} \end{pmatrix} + \begin{pmatrix} 0 & -A_{12}^{(1)}\frac{\partial}{\partial X} - B_{12}^{(1)}\frac{\partial}{\partial Y} \\ \\ -A_{21}^{(1)}\frac{\partial}{\partial X} - B_{21}^{(1)}\frac{\partial}{\partial Y} & 0 \end{pmatrix}.$$

Using what we know through order 3, we can solve (2.0.12) and (2.0.13). From (2.0.12) we obtain:

$$E^{(4)} = \left\langle \begin{pmatrix} f^{(0)} \\ \\ g^{(0)} \end{pmatrix}, \left(\mathbb{H}_3 - E^{(3)}\right) \begin{pmatrix} f^{(1)} \\ \\ g^{(1)} \end{pmatrix} \right\rangle_{\mathcal{H}} + \left\langle \begin{pmatrix} f^{(0)} \\ \\ g^{(0)} \end{pmatrix}, \mathbb{H}_4 \begin{pmatrix} f^{(0)} \\ \\ g^{(0)} \end{pmatrix} \right\rangle_{\mathcal{H}}$$

and

$$\begin{pmatrix} f^{(2)} \\ \\ g^{(2)} \end{pmatrix} \;=\; -\left[\mathbb{H}_2 - E^{(2)}\right]_r^{-1} Q_\perp \left[ \left(\mathbb{H}_3 - E^{(3)}\right) \begin{pmatrix} f^{(1)} \\ \\ g^{(1)} \end{pmatrix} + \mathbb{H}_4 \begin{pmatrix} f^{(0)} \\ \\ g^{(0)} \end{pmatrix} \right].$$

From (2.0.13) we get

$$\begin{aligned}
\psi_\perp^{(4)} \;=\; & \left[ (\, h\; P_\perp)^{(0)} \right]_r^{-1} \left[ -\; (\, h\, P_\perp)^{(1)}\; \psi_\perp^{(3)} \right. \\
& + \frac{1}{2} \Big( \; P_\perp^{(0)} \left[ (\Delta_{x,\,y}\; \Psi_1)^{(0)} \right] \; f^{(0)} \; + \; P_\perp^{(0)} \left[ (\Delta_{x,\,y}\; \Psi_2)^{(0)} \right] \; g^{(0)} \; \Big) \\
& + \sum_{j=3}^{4} \sum_{l=3}^{j} \left( P_\perp^{(j-l)} \left[ \left( \frac{\partial \Psi_1}{\partial x} \right)^{(l-3)} \right] \frac{\partial}{\partial X} \; + \; P_\perp^{(j-l)} \left[ \left( \frac{\partial \Psi_1}{\partial y} \right)^{(l-3)} \right] \frac{\partial}{\partial Y} \right) \; f^{(4-j)} \\
& \left. + \sum_{j=3}^{4} \sum_{l=3}^{j} \left( P_\perp^{(j-l)} \left[ \left( \frac{\partial \Psi_2}{\partial x} \right)^{(l-3)} \right] \frac{\partial}{\partial X} \; + \; P_\perp^{(j-l)} \left[ \left( \frac{\partial \Psi_2}{\partial y} \right)^{(l-3)} \right] \frac{\partial}{\partial Y} \right) \; g^{(4-j)} \right].
\end{aligned}$$

**Order $k \geq 5$** We now show that we can proceed in this manner to any order of $\epsilon$ desired. In chapter 3 we will show that all of the quantities involved exist in the relevant Hilbert space. If $k \geq 5$, the $\epsilon^k$ terms require

$$\begin{aligned}
& \left(\mathbb{H}_2 - E^{(2)}\right) \begin{pmatrix} f^{(k-2)} \\ \\ g^{(k-2)} \end{pmatrix} + \left(\mathbb{H}_3 - E^{(3)}\right) \begin{pmatrix} f^{(k-3)} \\ \\ g^{(k-3)} \end{pmatrix} + \sum_{j=4}^{k-1} \left(\mathbb{H}_j - E^{(j)}\right) \begin{pmatrix} f^{(k-j)} \\ \\ g^{(k-j)} \end{pmatrix} \\
& + \left(\mathbb{H}_k - E^{(k)}\right) \begin{pmatrix} f^{(0)} \\ \\ g^{(0)} \end{pmatrix} + \sum_{j=2}^{k-3} \left(-\frac{1}{2}\right) \begin{pmatrix} \langle\; \Psi_1^{(j-2)},\; \Delta_{X,\,Y}\; \psi_\perp^{(k-j)} \;\rangle_{el} \\ \\ \langle\; \Psi_2^{(j-2)},\; \Delta_{X,\,Y}\; \psi_\perp^{(k-j)} \;\rangle_{el} \end{pmatrix} = 0, \qquad (2.0.14)
\end{aligned}$$

$$
\begin{aligned}
(h\ P_\perp)^{(0)}\ \psi_\perp^{(k)} \ &= \ \sum_{j=2}^{k-3}\ \frac{1}{2}\ P_\perp^{(j-2)}\left[\ \Delta_{X,Y}\ \psi_\perp^{(k-j)}\ \right]\ -\ \sum_{j=1}^{k-3}\ (h\,P_\perp)^{(j)}\ \psi_\perp^{(k-j)} \\
&+\ \sum_{j=4}^{k}\ \sum_{l=4}^{j}\ \frac{1}{2}\Big(\ P_\perp^{(j-l)}\left[\ (\Delta_{x,y}\ \Psi_1)^{(l-4)}\ \right]\ f^{(k-j)}\ +\ P_\perp^{(j-l)}\left[\ (\Delta_{x,y}\ \Psi_2)^{(l-4)}\ \right]\ g^{(k-j)}\ \Big) \\
&+\ \sum_{j=3}^{k}\ \sum_{l=3}^{j}\ \left(\ P_\perp^{(j-l)}\left[\ \left(\frac{\partial\Psi_1}{\partial x}\right)^{(l-3)}\ \right]\ \frac{\partial}{\partial X}\ +\ P_\perp^{(j-l)}\left[\ \left(\frac{\partial\Psi_1}{\partial y}\right)^{(l-3)}\ \right]\ \frac{\partial}{\partial Y}\ \right)\ f^{(k-j)} \\
&+\ \sum_{j=3}^{k}\ \sum_{l=3}^{j}\ \left(\ P_\perp^{(j-l)}\left[\ \left(\frac{\partial\Psi_2}{\partial x}\right)^{(l-3)}\ \right]\ \frac{\partial}{\partial X}\ +\ P_\perp^{(j-l)}\left[\ \left(\frac{\partial\Psi_2}{\partial y}\right)^{(l-3)}\ \right]\ \frac{\partial}{\partial Y}\ \right)\ g^{(k-j)} \\
&+\ \sum_{j=2}^{k-3}\ E^{(j)}\ \psi_\perp^{(k-j)}, \qquad (2.0.15)
\end{aligned}
$$

where

$$
\begin{aligned}
\mathbb{H}_j \ &= \ \left(-\frac{1}{2}\right)\ \begin{pmatrix} T_{11}^{(j-4)} & T_{12}^{(j-4)} \\ \\ T_{21}^{(j-4)} & T_{22}^{(j-4)} \end{pmatrix}\ +\ \begin{pmatrix} h_{11}^{(j)} & h_{12}^{(j)} \\ \\ h_{21}^{(j)} & h_{22}^{(j)} \end{pmatrix}\ + \\
&\qquad \begin{pmatrix} 0 & -\ A_{12}^{(j-3)}\ \dfrac{\partial}{\partial X}\ -\ B_{12}^{(j-3)}\ \dfrac{\partial}{\partial Y} \\ \\ -\ A_{21}^{(j-3)}\ \dfrac{\partial}{\partial X}\ -\ B_{21}^{(j-3)}\ \dfrac{\partial}{\partial Y} & 0 \end{pmatrix},
\end{aligned}
$$

for $j \geq 4$.

Following what we have seen through order 4, assume from previous orders that

$$
\begin{pmatrix} f^{(j)} \\ \\ g^{(j)} \end{pmatrix}\ \text{for } j = 0, 1, \ldots, k-3, \qquad E^{(j)}\ \text{and}\ \psi_\perp^{(j)}\ \text{for } j = 0, 1, \ldots, k-1,
$$

are already determined. Then, we can solve (2.0.14) and (2.0.15) for $f^{(k-2)}$, $g^{(k-2)}$, $\psi_\perp^{(k)}$, and

$E^{(k)}$. From (2.0.14) we obtain:

$$E^{(k)} = \sum_{j=3}^{k-1} \left\langle \begin{pmatrix} f^{(0)} \\ g^{(0)} \end{pmatrix}, \left(\mathbb{H}_j - E^{(j)}\right) \begin{pmatrix} f^{(k-j)} \\ g^{(k-j)} \end{pmatrix} \right\rangle_{\mathcal{H}} + \left\langle \begin{pmatrix} f^{(0)} \\ g^{(0)} \end{pmatrix}, \mathbb{H}_k \begin{pmatrix} f^{(0)} \\ g^{(0)} \end{pmatrix} \right\rangle_{\mathcal{H}}$$
$$- \frac{1}{2} \sum_{j=2}^{k-3} \left\langle \begin{pmatrix} f^{(0)} \\ g^{(0)} \end{pmatrix}, \begin{pmatrix} \langle\ \Psi_1^{(j-2)},\ \Delta_{X,Y}\ \psi_\perp^{(k-j)}\ \rangle_{el} \\ \langle\ \Psi_2^{(j-2)},\ \Delta_{X,Y}\ \psi_\perp^{(k-j)}\ \rangle_{el} \end{pmatrix} \right\rangle_{\mathcal{H}} \tag{2.0.16}$$

and

$$\begin{pmatrix} f^{(k-2)} \\ g^{(k-2)} \end{pmatrix} = -\left[\mathbb{H}_2 - E^{(2)}\right]_r^{-1} Q_\perp \left[ \sum_{j=3}^{k-1} \left(\mathbb{H}_j - E^{(j)}\right) \begin{pmatrix} f^{(k-j)} \\ g^{(k-j)} \end{pmatrix} \right.$$
$$\left. + \mathbb{H}_k \begin{pmatrix} f^{(0)} \\ g^{(0)} \end{pmatrix} - \frac{1}{2} \sum_{j=2}^{k-3} \begin{pmatrix} \langle\ \Psi_1^{(j-2)},\ \Delta_{X,Y}\ \psi_\perp^{(k-j)}\ \rangle_{el} \\ \langle\ \Psi_2^{(j-2)},\ \Delta_{X,Y}\ \psi_\perp^{(k-j)}\ \rangle_{el} \end{pmatrix} \right]. \tag{2.0.17}$$

From (2.0.15) we get

$$\psi_\perp^{(k)} = \left[\left(h\ P_\perp\right)^{(0)}\right]_r^{-1} \left[ \sum_{j=2}^{k-3} \frac{1}{2}\ P_\perp^{(j-2)} \left[\ \Delta_{X,Y}\ \psi_\perp^{(k-j)}\ \right] - \sum_{j=1}^{k-3} \left(h\, P_\perp\right)^{(j)}\ \psi_\perp^{(k-j)} \right.$$
$$+ \sum_{j=4}^{k} \sum_{l=4}^{j} \frac{1}{2} \left( P_\perp^{(j-l)} \left[ \left(\Delta_{x,y}\ \Psi_1\right)^{(l-4)} \right] f^{(k-j)} + P_\perp^{(j-l)} \left[ \left(\Delta_{x,y}\ \Psi_2\right)^{(l-4)} \right] g^{(k-j)} \right)$$
$$+ \sum_{j=3}^{k} \sum_{l=3}^{j} \left( P_\perp^{(j-l)} \left[ \left(\frac{\partial \Psi_1}{\partial x}\right)^{(l-3)} \right] \frac{\partial}{\partial X} + P_\perp^{(j-l)} \left[ \left(\frac{\partial \Psi_1}{\partial y}\right)^{(l-3)} \right] \frac{\partial}{\partial Y} \right) f^{(k-j)}$$
$$+ \sum_{j=3}^{k} \sum_{l=3}^{j} \left( P_\perp^{(j-l)} \left[ \left(\frac{\partial \Psi_2}{\partial x}\right)^{(l-3)} \right] \frac{\partial}{\partial X} + P_\perp^{(j-l)} \left[ \left(\frac{\partial \Psi_2}{\partial y}\right)^{(l-3)} \right] \frac{\partial}{\partial Y} \right) g^{(k-j)}$$
$$\left. + \sum_{j=2}^{k-3} E^{(j)}\ \psi_\perp^{(k-j)} \right]. \tag{2.0.18}$$

So we can proceed in this manner to obtain $\Psi(\epsilon)$ and $E(\epsilon)$ up to any order in $\epsilon$.

# Chapter 3

# Properties of the Leading Order Hamiltonian

We adopt the following notation throughout:

1. We let $I_2 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$. If $A$ is an operator on the Hilbert space $L^2(\mathbb{R}^2,\, dX\, dY)$, then $A \otimes I_2$, is the operator on $\mathcal{H}$ given by $\begin{pmatrix} A & 0 \\ 0 & A \end{pmatrix}$.

2. If $D(A)$ is the domain of the operator $A$ on the Hilbert space $L^2(\mathbb{R}^2,\, dX\, dY)$, then $D(A \otimes I_2) = D(A) \oplus D(A) \subset \mathcal{H}$.

In what follows, we prove various needed properties for the expansion to all orders.

Let

$$\mathbb{H}_2 \;= -\,\frac{1}{2}\,\Delta_{X,Y}\otimes I_2 \;+\; \begin{pmatrix} \dfrac{a+b}{2}\,X^2 \;+\; \dfrac{a-b}{2}\,Y^2 & b\,X\,Y \\ b\,X\,Y & \dfrac{a-b}{2}\,X^2 \;+\; \dfrac{a+b}{2}\,Y^2 \end{pmatrix}.$$

Note that if we let $(\tilde{X},\,\tilde{Y}) = (a^{1/4}\,X,\,a^{1/4}\,Y)$ and $\tilde{b} = \dfrac{b}{a}$, then

$$\begin{aligned} \mathbb{H}_2 \quad = \quad \sqrt{a}\,\Bigg[ \Bigg( -\,\frac{1}{2}\,\Delta_{\tilde{X},\tilde{Y}} \;+\; \frac{1}{2}\,(\tilde{X}^2+\tilde{Y}^2)\Bigg)\otimes I_2 \\ + \,\tilde{b}\begin{pmatrix} \dfrac{1}{2}\,\left(\tilde{X}^2-\tilde{Y}^2\right) & \tilde{X}\,\tilde{Y} \\ \tilde{X}\,\tilde{Y} & -\,\dfrac{1}{2}\,\left(\tilde{X}^2-\tilde{Y}^2\right) \end{pmatrix}\Bigg]. \end{aligned} \tag{3.0.1}$$

We now use the Kato-Rellich Theorem [22] to prove self-adjointness of $\mathbb{H}_2$.

**Theorem 3.0.1.** *If $a > b > 0$, then $\mathbb{H}_2$ is self-adjoint on $D_{HO}\oplus D_{HO}$, where $D_{HO}$ is the usual Harmonic oscillator domain in $L^2(\mathbb{R}^2, dX\,dY)$, and essentially self-adjoint on $\tilde{D}_{HO}\oplus\tilde{D}_{HO}$, where $\tilde{D}_{HO}$ is any core for the usual Harmonic oscillator.*

**Proof:**

Define

$$H_{HO} \;=\; \Bigg( -\,\frac{1}{2}\,\Delta_{X,Y} \;+\; \frac{1}{2}\,(X^2+Y^2)\Bigg)\otimes I_2$$

and

$$V(\tilde{b}) \;=\; \tilde{b}\begin{pmatrix} \dfrac{1}{2}\,\left(X^2-Y^2\right) & X\,Y \\ X\,Y & -\,\dfrac{1}{2}\,\left(X^2-Y^2\right) \end{pmatrix}.$$

We prove that for $0 < \tilde{b} < 1$, $V(\tilde{b})$ is relatively bounded with respect to $H_{H0}$, with relative bound $\tilde{b}$. The conclusion then follows from the Kato-Rellich theorem [22] and (3.0.1).

For each fixed $X$ and $Y$, the eigenvalues of $V(b)$ are $\pm \frac{\tilde{b}}{2}(X^2 + Y^2)$. It follows that

$$\left\| V(\tilde{b})\, v \right\|_e \;\leq\; \tilde{b} \;\left\| \left( \frac{1}{2}(X^2 + Y^2) \otimes I_2 \right) v \right\|_e ,$$

where $v \in \mathbb{C}^2$ is any two component vector, and we use the usual Euclidean norm. This inequality implies the $L^2(\mathbb{R}^2,\, dX\, dY;\, \mathbb{C}^2) = \mathcal{H}$ norm estimate

$$\left\| V(\tilde{b})\, \psi \right\|_{\mathcal{H}} \;\leq\; \tilde{b} \;\left\| \left( \frac{1}{2}(X^2 + Y^2) \otimes I_2 \right) \psi \right\|_{\mathcal{H}} ,$$

where $\psi(X,\, Y) \in \mathcal{H}$ is a two-component vector-valued function.

We now show that

$$\| V(\tilde{b})\, \psi \|_{\mathcal{H}} \;\leq\; \tilde{b} \;\left\| \left( \frac{1}{2}(X^2 + Y^2) \otimes I_2 \right) \psi \right\|_{\mathcal{H}} \;\leq\; \tilde{b}\, \| H_{HO}\, \psi \|_{\mathcal{H}} \;+\; \tilde{b}\, \| \psi \|_{\mathcal{H}}. \tag{3.0.2}$$

for all $\psi \in D_{HO} \oplus D_{HO}$ .

We have already shown the first inequality. The hard part is the second estimate, which follows from

$$\left\| \left( \left( X^2 + Y^2 \right) \otimes I_2 \right) \psi \right\| \quad \leq \quad \left\| \left( \left( -\Delta_{X,Y} + X^2 + Y^2 \right) \otimes I_2 \right) \psi \right\| \;+\; 2\, \| \psi \|.$$

This easily follows from

$$\left\| \left( \left( X^2 + Y^2 \right) \otimes I_2 \right) \psi \right\|^2 \quad \leq \quad \left\| \left( \left( -\Delta_{X,Y} + X^2 + Y^2 \right) \otimes I_2 \right) \psi \right\|^2 \;+\; 4\, \| \psi \|^2.$$

(3.0.3)

Rather than proving this directly, let us first prove a simpler relative bound estimate for the operators on $L^2(I\!R, dx)$. We show that for $\phi \in D\left(-\frac{\partial^2}{\partial x^2} + x^2\right)$,

$$\| x^2 \phi \|^2 \quad \leq \quad \left\| \left( -\frac{\partial^2}{\partial x^2} + x^2 \right) \phi \right\|^2 + 2 \| \phi \|^2. \tag{3.0.4}$$

To prove this, let $p = -i\frac{\partial}{\partial x}$, and calculate the commutators

$$[x, p] = i \qquad \text{and} \qquad [x, p^2] = 2ip.$$

We have

$$\begin{aligned} \| x^2 \phi \|^2 &= \langle \phi, x^4 \phi \rangle \\ &= \langle \phi, \left( (p^2 + x^2)^2 - x^2p^2 - p^2x^2 - p^4 \right) \phi \rangle \\ &\leq \| \left( p^2 + x^2 \right) \phi \|^2 - \langle \phi, \left( x^2p^2 + p^2x^2 \right) \phi \rangle. \end{aligned} \tag{3.0.5}$$

In this last expression, we use the commutators above to write

$$\begin{aligned} \langle \phi, \left( x^2p^2 + p^2x^2 \right) \phi \rangle &= \langle \phi, \left( xp^2x + x[x, p^2] + xp^2x + [p^2, x]x \right) \phi \rangle \\ &= 2 \langle \phi, xp^2x \phi \rangle + 2i \langle \phi, (xp - px) \phi \rangle \\ &= 2 \langle \phi, xp^2x \phi \rangle - 2 \langle \phi, \phi \rangle. \end{aligned}$$

In this last expression, the first inner product is the expectation of a positive operator (since $xp^2x$ has the form $A^*A$ with $A = px$). Using this and (3.0.5), we see that

$$\| x^2 \phi \|^2 \leq \| \left( p^2 + x^2 \right) \phi \|^2 + 2 \| \phi \|^2,$$

and (3.0.4) is proved.

Now we simply mimic the proof of (3.0.4) to prove (3.0.3). We write

$$\| \left( X^2 + Y^2 \right) \phi \|^2$$

$$= \left\langle \phi, \left( \left( -\Delta_{X,Y} + X^2 + Y^2 \right)^2 - \Delta_{X,Y}^2 + \Delta_{X,Y} \left( X^2 + Y^2 \right) + \left( X^2 + Y^2 \right) \Delta_{X,Y} \right) \phi \right\rangle$$

The operator $\Delta_{X,Y}^2$ is positive. The operator $-\Delta_X Y^2 = -Y^2 \Delta_X$ is also positive since it equals $A^* A$ with $A = p_X Y$. Similarly, $-\Delta_Y X^2 = -X^2 \Delta_Y$ is positive. By the commutator tricks we used above, $-\Delta_X X^2 - X^2 \Delta_X$ and $-\Delta_Y Y^2 - Y^2 \Delta_Y$ each are positive operators minus twice the identity. Thus for all $\phi \in D_{HO}$,

$$\left\langle \phi, \left( \left( -\Delta_{X,Y} + X^2 + Y^2 \right)^2 - \Delta_{X,Y}^2 + \Delta_{X,Y} \left( X^2 + Y^2 \right) + \left( X^2 + Y^2 \right) \Delta_{X,Y} \right) \phi \right\rangle$$

$$\leq \left\langle \phi, \left( -\Delta_{X,Y} + X^2 + Y^2 \right)^2 \phi \right\rangle + 4 \langle \phi, \phi \rangle$$

and hence,

$$\left\| \left( X^2 + Y^2 \right) \phi \right\|^2 \quad \leq \quad \left\| \left( -\Delta_{X,Y} + X^2 + Y^2 \right) \phi \right\|^2 + 4 \| \phi \|^2 .$$

It follows that (3.0.3) holds for all $\psi \in D_{HO} \oplus D_{HO}$ . This proves (3.0.2) and the theorem follows. □

Unless otherwise stated, it is assumed that by $\mathbb{H}_2$ we are referring to this operator with domain $D(\mathbb{H}_2) = D_{H0} \oplus D_{HO}$. We now show that $\mathbb{H}_2$ has purely discrete spectrum.

**Theorem 3.0.2.** *If* $a > b > 0$, $\mathbb{H}_2$ *has purely discrete spectrum, with countably many eigenvalues* $\{\mu_j(\mathbb{H}_2)\}_{j=1}^{\infty}$ *satisfying*

$$N\sqrt{a-b} \leq \mu_{N(N-1)+1}(\mathbb{H}_2) \leq \mu_{N(N-1)+2}(\mathbb{H}_2) \leq \ldots \leq \mu_{N(N+1)}(\mathbb{H}_2) \leq N\sqrt{a+b},$$

*for* $N = 1, 2, 3, \ldots$

**Proof:**

Let $(\rho, \phi)$ be the usual polar coordinates associated with $(X, Y)$. Define the unitary operators $U,\ W : \mathcal{H} \rightarrow \mathcal{H}$ by (defined as multiplication operators on $\mathcal{H}$):

$$U = \begin{pmatrix} \cos(\phi) & -\sin(\phi) \\ \\ \sin(\phi) & \cos(\phi) \end{pmatrix} \qquad \text{and} \qquad W = \frac{1}{\sqrt{2}} \begin{pmatrix} e^{i\phi} & e^{-i\phi} \\ \\ ie^{i\phi} & -ie^{-i\phi} \end{pmatrix}.$$

Define

$$\mathbb{H}_0 \ = \ U^{-1}\, \mathbb{H}_2\, U \ = \ \begin{pmatrix} -\frac{1}{2}\, \Delta_{\rho,\phi} \ + \ \frac{1}{2\rho^2} \ + \ \frac{a+b}{2}\, \rho^2 & \frac{1}{\rho^2}\, \frac{\partial}{\partial \phi} \\ \\ -\frac{1}{\rho^2}\, \frac{\partial}{\partial \phi} & -\frac{1}{2}\, \Delta_{\rho,\phi} \ + \ \frac{1}{2\rho^2} \ + \ \frac{a-b}{2}\, \rho^2 \end{pmatrix},$$

and

$$\mathbb{H}_0^{\pm} \ = \ \begin{pmatrix} -\frac{1}{2}\, \Delta_{\rho,\phi} \ + \ \frac{1}{2\rho^2} \ + \ \frac{a \pm b}{2}\, \rho^2 & \frac{1}{\rho^2}\, \frac{\partial}{\partial \phi} \\ \\ -\frac{1}{\rho^2}\, \frac{\partial}{\partial \phi} & -\frac{1}{2}\, \Delta_{\rho,\phi} \ + \ \frac{1}{2\rho^2} \ + \ \frac{a \pm b}{2}\, \rho^2 \end{pmatrix},$$

and note that $\mathbb{H}_0^- \ \leq \ \mathbb{H}_0 \ \leq \ \mathbb{H}_0^+$. Now we define

$$\mathbb{H}_1^{\pm} \ = \ W^{-1}\, \mathbb{H}_0^{\pm}\, W \ = \ \begin{pmatrix} -\frac{1}{2}\, \Delta_{\rho,\phi} \ + \ \frac{a \pm b}{2}\, \rho^2 & 0 \\ \\ 0 & -\frac{1}{2}\, \Delta_{\rho,\phi} \ + \ \frac{a \pm b}{2}\, \rho^2 \end{pmatrix}.$$

In the context of the min/max principle [21], for all $n \in \mathbb{N}$,

$$\mu_n(\mathbb{H}_1^-) \;=\; \mu_n(\mathbb{H}_0^-) \;\leq\; \mu_n(\mathbb{H}_0) \;=\; \mu_n(\mathbb{H}_2) \;=\; \mu_n(\mathbb{H}_0) \;\leq\; \mu_n(\mathbb{H}_0^+) \;=\; \mu_n(\mathbb{H}_1^+).$$

The operators $\mathbb{H}_1^{\pm}$ have purely discrete spectrum, with $2N$-fold degenerate eigenvalues of $N\sqrt{a \pm b}$ for $N = 1, 2, \ldots$ So, $\mathbb{H}_2$ must have purely discrete spectrum with eigenvalues $\mu_1(\mathbb{H}_2) \leq \mu_2(\mathbb{H}_2) \leq \ldots$ satisfying

$$N\sqrt{a-b} \leq \mu_{N(N-1)+1}(\mathbb{H}_2) \leq \mu_{N(N-1)+2}(\mathbb{H}_2) \leq \ldots \leq \mu_{N(N+1)}(\mathbb{H}_2) \leq N\sqrt{a+b},$$

for $N = 1, 2, 3, \ldots$ $\square$

To prove the quasimode can be expanded to any order in $\epsilon$, we must show the terms arising at arbitrary order in the equations of chapter 2 will be in $\mathcal{H}$. This will follow from the propositions and lemmas we now prove. A similar analysis was needed in [10]. For our purposes it must be shown that the details can be extended to this situation on $\mathcal{H}$. The proofs presented here are analogous to those presented in [10]. We show full details for convenience of the reader.

**Lemma 3.0.3.** *Let $T(\alpha)$ be defined on a dense domain of a separable Hilbert space $H$, and suppose that $T(\alpha)$ is an analytic family in the sense of Kato for all $\alpha \in \mathbb{C}$, and self-adjoint for all $\alpha \in I\!R$. If, for all $\alpha \in I\!R$, $T(\alpha)$ has purely discrete spectrum with eigenvalues accumulating at $\infty$, then $T(\alpha)$ has purely discrete spectrum for all $\alpha \in \mathbb{C}$.*

**Proof:**

First we note that if a self-adjoint operator has purely discrete spectrum with eigenvalues accumulating at $\infty$, then it has compact resolvent by Theorem XIII.64 of [21]. We also note that for any closed operator $A$, $(A-\mu)^{-1}$ is compact for some $\mu \in \rho(A)$ if and only if $(A-\mu)^{-1}$ is compact for all $\mu \in \rho(A)$. This follows from the first resolvent formula.

We first show that if $T(\alpha)$ has compact resolvent for all $\alpha \in I\!R$, then $T(\alpha)$ has compact resolvent for all $\alpha \in \mathbb{C}$. We then show that if a closed operator defined on a separable Hilbert space has compact resolvent, then it must have purely discrete spectrum.

Since $T(\alpha)$ is an entire analytic family, the resolvent $R_\alpha(\lambda) = (T(\alpha) - \lambda)^{-1}$ is analytic in both $\alpha$ and $\lambda$ inside the set $R = \{ (\alpha, \lambda) : \alpha \in \mathbb{C}, \lambda \in \rho(T(\alpha)) \}$. From Theorem XII.7 of [21], R is open in both $\alpha$ and $\lambda$. Let $\mathfrak{B}(H)$ and $\mathfrak{C}(H)$ denote the bounded operators and compact operators on the Hilbert space $H$ respectively. It follows from the Hahn-Banach Theorem [23], that for any $B \in \mathfrak{B}(H) \setminus \mathfrak{C}(H)$, there exists $l_B \in \mathfrak{B}(H)^*$ such that $l_B(B) \neq 0$, and $l_B = 0$ on $\mathfrak{C}(H)$.

Note that since $T(\alpha)$ is an analytic family, we know the resolvent set is non-empty for all $\alpha \in \mathbb{C}$. Define the set

$$\Upsilon = \{ \alpha \in \mathbb{C} : R_\alpha(\lambda) \text{ is compact for all } \lambda \in \rho(T(\alpha)) \}.$$

We show that $\Upsilon = \mathbb{C}$.

Let $B_s(z)$ denote an open disk in the complex plane of radius $s > 0$, centered at $z \in \mathbb{C}$. Let $\lambda_0 \in \rho(T(0))$. Since the set $R$ is open, we know that there exists a disk $B_\delta(0)$, such that

$\lambda_0 \in \rho(T(\alpha))$ for all $\alpha \in B_\delta(0)$. Let $l \in \mathfrak{B}(H)^*$, such that $l$ is vanishing on $\mathfrak{C}(H)$. Then the function $f(\alpha) = l(R_\alpha(\lambda_0))$ defines an analytic map from $B_\delta(0)$ into $\mathbb{C}$. Since the resolvent is compact for $\alpha \in I\!R$, we know $f(\alpha) = 0$ for all $-\delta < \alpha < \delta$, which implies $f(\alpha) = 0$ for all $\alpha \in B_\delta(0)$. It follows that $R_\alpha(\lambda_0)$ is compact for all $\alpha \in B_\delta(0)$, and hence $B_\delta(0) \subset \Upsilon$.

We now assume that $\Upsilon \neq \mathbb{C}$ and show this leads to a contradiction. Let $r = \sup\{\delta > 0 : B_\delta(0) \subset \Upsilon\}$. Note that $0 < r < \infty$ since we have assumed $\Upsilon \neq \mathbb{C}$. Then, there exists $\alpha_0$ with $|\alpha_0| = r$, such that every neighborhood of $\alpha_0$ contains a point not in $\Upsilon$. Let $\lambda_0 \in \rho(T(\alpha_0))$ and choose $\delta' > 0$ small enough so that $\lambda_0 \in \rho(T(\alpha))$ for all $\alpha \in B_{\delta'}(\alpha_0)$. Then $g(\alpha) = l(R_\alpha(\lambda_0))$ is analytic on $B_{\delta'}(\alpha_0)$ and $g(\alpha) = 0$ on $B_r(0) \cap B_{\delta'}(\alpha_0)$. So, $g(\alpha) = 0$ on all of $B_{\delta'}(\alpha_0)$ and there exists an entire neighborhood of $\alpha_0$ in $\Upsilon$. This is a contradiction, so $\Upsilon = \mathbb{C}$.

We now show that a closed operator with compact resolvent has purely discrete spectrum. Let $A$ be a closed operator. Fix $\lambda \in \rho(A)$ and let $R(\lambda) = (A - \lambda)^{-1}$ be compact. Then the spectrum of $R(\lambda)$ is made up of at most countably many eigenvalues of finite multiplicity that can only accumulate at 0 **[23]**. For $E \neq \lambda$, we have

$$A - E = A - \lambda - (E - \lambda) = (E - \lambda)(A - \lambda)\left(\frac{1}{E - \lambda} - R(\lambda)\right).$$

From this we see that if $\frac{1}{E-\lambda} \in \rho(R(\lambda))$, then $E \in \rho(A)$. So, if $E \in \sigma(A)$, then $\frac{1}{E-\lambda} \in \sigma(R(\lambda))$ and thus $\frac{1}{E-\lambda}$ is an isolated eigenvalue of $R(\lambda)$ with finite multiplicity. Since,

$$R(\lambda)\Psi = \frac{1}{E - \lambda}\Psi \Leftrightarrow (E - \lambda)\Psi = (A - \lambda)\Psi \Leftrightarrow A\Psi = E\Psi,$$

it follows that $E$ is an isolated eigenvalue of $A$ with finite multiplicity. Therefore, $\sigma(A)$ is made up of at most countably many eigenvalues of finite multiplicity that can only accumulate at infinity. The conclusion of the Lemma follows. $\square$

Before we prove Proposition 3.0.4, we consider a different decomposition of $\mathbb{H}_2$. We define $H_0$ and $V$ to be

$$H_0 \;=\; -\,\frac{1}{2}\,\Delta_{X,Y}\otimes I_2 \;\text{ and }\; V \;=\; \begin{pmatrix} \dfrac{a+b}{2}\,X^2 \;+\; \dfrac{a-b}{2}\,Y^2 & bXY \\ bXY & \dfrac{a-b}{2}\,X^2 \;+\; \dfrac{a+b}{2}\,Y^2 \end{pmatrix},$$

so that $\mathbb{H}_2 \;=\; H_0 + V$. Note that for any $X,\; Y$, the eigenvalues of $V$ are $\frac{a+b}{2}\,(X^2+Y^2)$ and $\frac{a-b}{2}\,(X^2+Y^2)$. So for $f,\; g \in L^2(I\!R^2)$,

$$\begin{pmatrix} \bar{f} & \bar{g} \end{pmatrix} V \begin{pmatrix} f \\ g \end{pmatrix} \;\geq\; \frac{a-b}{2}\,(X^2+Y^2)\;\left(|f|^2+|g|^2\right)$$

at any $X,\; Y$. Then

$$\begin{aligned} \left\langle \begin{pmatrix} f \\ g \end{pmatrix}, V \begin{pmatrix} f \\ g \end{pmatrix} \right\rangle \;&=\; \int \begin{pmatrix} \bar{f} & \bar{g} \end{pmatrix} V \begin{pmatrix} f \\ g \end{pmatrix}\, dX\; dY \\ &\geq\; \frac{a-b}{2}\int (X^2+Y^2)\;\left(|f|^2+|g|^2\right)\, dX\; dY \\ &\geq\; 0. \end{aligned}$$

So $V$ is a positive operator.

**Proposition 3.0.4.** *Let* $\Psi = \begin{pmatrix} f \\ g \end{pmatrix} \in \mathcal{H}$ *be a solution of* $\mathbb{H}_2\Psi = E\Psi$, *with* $E > 0$. *Then,* $f,\ g \in C^\infty(I\!R^2)$, $\nabla f,\ \nabla g \in L^2(\mathbb{R}^2)$, *and for any* $\gamma > 0$,

$$f,\ g \in D(e^{\gamma\langle x\rangle}), \qquad \nabla f,\ \nabla g \in D(e^{\gamma\langle x\rangle}), \qquad \Delta f,\ \Delta g \in D(e^{\gamma\langle x\rangle}),$$

*where* $\langle x\rangle \ = \ \sqrt{1 + X^2 + Y^2}$.

**Proof:**

Let $V_{11} \ = \ \frac{a+b}{2}\, X^2 \ + \ \frac{a-b}{2}\, Y^2, \quad V_{12} \ = \ V_{21} \ = \ bXY, \quad$ and $\quad V_{22} \ = \ \frac{a-b}{2}\, X^2 \ + \ \frac{a+b}{2}\, Y^2.$

Then, $f,\ g$ satisfy the following pair of equations:

$$(-\,\Delta \ + \ V_{11})\ f \ + \ V_{12}\, g \ \ = \ \ E\, f \tag{3.0.6}$$

$$(-\,\Delta \ + \ V_{22})\ g \ + \ V_{21}\, f \ \ = \ \ E\, g \tag{3.0.7}$$

To show that $f,\ g \in C^\infty(I\!R^2)$, we follow the proof of Theorem IX.26 of [22]. Let $\Omega$ be a bounded open set in $I\!R^2$. Since $f,\ g \in L^2(I\!R^2) \ = \ W_0$ and the $V_{ij} \in C^\infty$, we have $V_{11}f,\ V_{21}f,\ V_{12}g,\ V_{22}g \in W_0(\Omega)$. It follows from (3.0.6) and (3.0.7) that $\Delta f,\ \Delta g \in W_0(\Omega)$. Then by the Lemma on pg. 52 of [22], $f,\ g \in W_2(\Omega)$. Repeating the argument we get $f,\ g \in W_m(\Omega)\ \forall\ m \in \mathbb{Z}$. It follows from Sobolev's Lemma that $f,\ g \in C^\infty$ on $\Omega$. Since $\Omega$ was arbitrary $f,\ g \in C^\infty(I\!R^2)$.

We now show $\nabla f,\ \nabla g \in L^2$. We know $\Psi \in D(\mathbb{H}_2)$. Let $D(-\Delta)$ and $Q(-\Delta)$ be the domain of self-adjointness and quadratic form domain of $-\Delta$ respectively. Then

$$D(\mathbb{H}_2) \ \subset \ D(-\Delta) \oplus D(-\Delta) \ \subset \ Q(-\Delta) \oplus Q(-\Delta) \ = \ \left\{ \Psi \ = \ \begin{pmatrix} f \\ g \end{pmatrix} \ : \ \nabla f,\ \nabla g \in L^2(I\!R^2) \right\}.$$

We now do a Combes-Thomas argument (see theorem XIII.39 of [21]) to prove that $f,\ g \in D(e^{\gamma|X|})$. The argument can be repeated for $D(e^{\gamma|Y|})$, and since

$$e^{\gamma\langle x\rangle} \ \leq \ e^{\gamma}\ e^{\gamma(|X|+|Y|)} \ \leq \ e^{\gamma}\ e^{2\gamma\max\{|X|,|Y|\}} \ \leq \ e^{\gamma}\ \left(e^{2\gamma|X|}+e^{2\gamma|Y|}\right),$$

we then have $f,\ g \in D(e^{\gamma\langle x\rangle})$.

For $\alpha \in \mathbb{R}$, consider the unitary group $W(\alpha) = e^{i\alpha X} \otimes I_2$ and the operator $\mathbb{H}_2(\alpha) = W(\alpha)\mathbb{H}_2 W(\alpha)^{-1}$. We have

$$\mathbb{H}_2(\alpha) \ = \ \mathbb{H}_2 \ + \ \frac{\alpha^2}{2} \otimes I_2 \ + \ i\,\alpha\,\frac{\partial}{\partial X} \otimes I_2 \ .$$

The operator $i\,\frac{\partial}{\partial X}$ is form bounded with respect to $-\Delta$ with relative bound zero. Since $V$ is positive, it follows that $i\,\frac{\partial}{\partial X} \otimes I_2$ is form bounded with respect to $\mathbb{H}_2$ with relative bound zero. So, $\mathbb{H}_2(\alpha)$ is an entire analytic family in the sense of Kato on $D(\mathbb{H}_2)$. Furthermore, since $\mathbb{H}_2(\alpha)$ is unitarily equivalent to $\mathbb{H}_2$ for $\alpha \in I\!R$, we know that $\mathbb{H}_2(\alpha)$ is self-adjoint and $\sigma(\mathbb{H}_2) = \sigma(\mathbb{H}_2(\alpha))$ for $\alpha \in \mathbb{R}$. Since $\mathbb{H}_2$ has purely discrete spectrum, we know $\mathbb{H}_2(\alpha)$ has purely discrete spectrum for $\alpha \in \mathbb{R}$. It follows from lemma 3.0.3 that $\mathbb{H}_2(\alpha)$ has purely discrete spectrum $\forall\ \alpha \in \mathbb{C}$. Since $\mathbb{H}_2(\alpha)$ is an entire analytic family in the sense of Kato, the eigenvalues are analytic on $\mathbb{C}$ except possibly at isolated crossings [21]. $W(\alpha)$ unitary implies that the eigenvalues are constant in a neighborhood of the real axis and thus crossings will not be an issue. Therefore, the eigenvalues are entire functions and constant in $\alpha$.

Let $P(\alpha)$ be the projection onto the eigenspace corresponding to the eigenvalue E of $\mathbb{H}_2(\alpha)$. Then $P(\alpha)$ is entire in $\alpha$ and has the form

$$P(\alpha) \;=\; \frac{-1}{2\pi i} \int_{|\lambda - E| = \epsilon} (\,\mathbb{H}_2(\alpha) \;-\; \lambda\,)^{-1} \; d\lambda \;.$$

If $\alpha,\ \alpha_0 \in \mathbb{R}$,

$$\begin{aligned} P(\alpha + \alpha_0) \quad &= \quad \frac{-1}{2\pi i} \int_{|\lambda - E| = \epsilon} (\,\mathbb{H}_2(\alpha + \alpha_0) \;-\; \lambda\,)^{-1} \; d\lambda \\ &= \quad \frac{-1}{2\pi i} \int_{|\lambda - E| = \epsilon} \left( W(\alpha_0)\mathbb{H}_2(\alpha)W(\alpha_0)^{-1} \;-\; \lambda \right)^{-1} \; d\lambda \\ &= \quad \frac{-1}{2\pi i} \int_{|\lambda - E| = \epsilon} W(\alpha_0) \; (\,\mathbb{H}_2(\alpha) \;-\; \lambda\,)^{-1} \; W(\alpha_0)^{-1} d\lambda \\ &= \quad W(\alpha_0)P(\alpha)W(\alpha_0)^{-1} \;. \end{aligned}$$

For $\alpha_0 \in \mathbb{R}$, the operator valued function $f(\alpha) \;=\; W(\alpha_0)P(\alpha)W(\alpha_0)^{-1} - P(\alpha + \alpha_0)$ is entire in $\alpha$. Since it vanishes $\forall\ \alpha \in \mathbb{R}$, it is zero $\forall\ \alpha \in \mathbb{C}$. So $P(\alpha + \alpha_0) \;=\; W(\alpha_0)P(\alpha)W(\alpha_0)^{-1}$, for $\alpha_0 \in \mathbb{R}$ and $\alpha \in \mathbb{C}$. The hypotheses of O'Connors lemma are satisfied [21]. So, for the eigenvector $\Psi = \begin{pmatrix} f \\ \\ g \end{pmatrix}$, we know $\Psi(\alpha) = W(\alpha)\Psi$ has an analytic continuation to all of $\mathbb{C}$. Therefore $f,\ g \in D(e^{\gamma|X|})$ for any $\gamma > 0$.

From this it now follows that $\Delta f,\ \Delta g \in D(e^{\gamma\langle x \rangle})$, for any $\gamma > 0$. To see this, consider

$$\left|\left|\left|\begin{pmatrix} e^{\gamma\langle x\rangle}\ \Delta\ f \\ e^{\gamma\langle x\rangle}\ \Delta\ g \end{pmatrix}\right|\right|\right|^2 = 4\left|\left|\left|\begin{pmatrix} e^{\gamma\langle x\rangle}\ [\ (V_{11}\ -\ E\ )\ f\ +\ V_{12}\ g\ ] \\ e^{\gamma\langle x\rangle}\ [\ V_{21}\ f\ +\ (V_{22}\ -\ E\ )\ g\ ] \end{pmatrix}\right|\right|\right|^2$$

$$= 4\Big(\ ||\ e^{\gamma\langle x\rangle}\ (V_{11}\ -\ E\ )\ f\ +\ e^{\gamma\langle x\rangle}\ V_{12}\ g\ ||_2^2 + ||\ e^{\gamma\langle x\rangle}\ V_{21}\ f\ +\ e^{\gamma\langle x\rangle}\ (V_{22}\ -\ E\ )\ g\ ||_2^2\ \Big)$$

Let $\beta > 0$. Then,

$$\int e^{2\gamma\langle x\rangle}\ |\ V_{21}\ f\ |^2\ dX\,dY\ \le\ ||\ V_{21}^2\ e^{-2\beta\langle x\rangle}\ ||_\infty\ ||\ e^{2\langle x\rangle(\gamma+\beta)}\ f\ ||_2^2\ <\ \infty$$

So, $e^{\gamma\langle x\rangle}V_{21}f \in L^2(\mathbb{R}^2)$ and by similar arguments $e^{\gamma\langle x\rangle}(V_{11}-E)f,\ e^{\gamma\langle x\rangle}V_{12}g,\ e^{\gamma\langle x\rangle}(V_{22}-E)g \in L^2(\mathbb{R}^2)$. Hence,

$$\left|\left|\left|\begin{pmatrix} e^{\gamma\langle x\rangle}\ \Delta\ f \\ e^{\gamma\langle x\rangle}\ \Delta\ g \end{pmatrix}\right|\right|\right|^2 <\ \infty$$

and $\Delta f,\ \Delta g \in D(e^{\gamma\langle x\rangle})$.

For $\nabla f,\ \nabla g \in D(e^{\gamma\langle x\rangle})$, we apply Lemma 3.4 of [10]:

Let $p \in C^1(I\!R^N)$ and suppose for some $C < \infty$, $\left|\dfrac{\nabla p(x)}{p(x)}\right| \le 2C\ \ \forall\ x \in I\!R^N$. If $\int_{I\!R^N} (|\ f\ |^2\ +\ |\ \Delta f\ |^2)\,p\ dx < \infty$, then

$$\left(\int_{I\!R^N} |\ \nabla f\ |^2\,p\ dx\right)^{1/2}\ \le\ C\left(\int_{I\!R^N} |\ f\ |^2\,p\ dx\right)^{1/2} + \left[\left(\int_{I\!R^N} |\ f\ |^2\,p\ dx\right)^{1/2}\ \left(\int_{I\!R^N} |\ \Delta f\ |^2\,p\ dx\right)^{1/2}\ +\ C^2\int_{I\!R^N} |\ f\ |^2\,p\ dx\right]^{1/2}.$$

We let $p(X, Y) = e^{2\gamma\langle x\rangle}$. Then $\left|\frac{\nabla p(X, Y)}{p(X, Y)}\right| \leq 2\gamma \quad \forall\ (X, Y) \in I\!R^2$. We have already shown that for $f$ and $g$, the right hand side in the lemma is finite for any $\gamma > 0$. So, $\nabla f, \nabla g \in D(e^{\gamma\langle x\rangle})$ for any $\gamma > 0$. $\square$

**Corollary 3.0.5.** *Let $R(\lambda) = (\mathbb{H}_2 - \lambda)^{-1}$ for $\lambda \in \rho(\mathbb{H}_2)$. Let $P_E$ be the projection onto the eigenspace associated with $E$ and define $r(E) = [(\mathbb{H}_2 - E)|_{Ran(I-P_E)}]^{-1}$, the reduced resolvent at $E$. Then, $(e^{\gamma\langle x\rangle} \otimes I_2)\, R(\lambda)\, (e^{-\gamma\langle x\rangle} \otimes I_2)$ and $(e^{\gamma\langle x\rangle} \otimes I_2)\, r(E)\, (e^{-\gamma\langle x\rangle} \otimes I_2)$ are bounded on $\mathcal{H}$ for any $\gamma > 0$. In particular, if $\Psi \in D(e^{\gamma\langle x\rangle} \otimes I_2)$, then $R(\lambda)\,\Psi,\ r(E)\,\Psi \in D(e^{\gamma\langle x\rangle} \otimes I_2)$.*

**Proof:**

We know $\mathbb{H}_2(\alpha)$ is an analytic family with purely discrete spectrum for every $\alpha \in \mathbb{C}$. Furthermore, the eigenvalues are constant in $\alpha$. The resolvent $R_\alpha(\lambda) = (\mathbb{H}_2(\alpha) - \lambda)^{-1}$ is therefore compact and analytic in both $\alpha$ and $\lambda$ for all $\alpha \in \mathbb{C},\ \lambda \in \rho(\mathbb{H}_2)$. Then $R_{-i\gamma}(\lambda) = (e^{\gamma X} \otimes I_2)\, R(\lambda)\, (e^{-\gamma X} \otimes I_2)$ and $R_{i\gamma}(\lambda) = (e^{-\gamma X} \otimes I_2)\, R(\lambda)\, (e^{\gamma X} \otimes I_2)$ are both bounded on $\mathcal{H}$ for any $\gamma > 0$. It follows that $(e^{\gamma|X|} \otimes I_2)\, R(\lambda)\, (e^{-\gamma|X|} \otimes I_2)$ is bounded. Since the details are the same with $X$ replaced by $Y$, we know that $(e^{\gamma\langle x\rangle} \otimes I_2)\, R(\lambda)\, (e^{-\gamma\langle x\rangle} \otimes I_2)$ is bounded on $\mathcal{H}$ for any $\gamma > 0$.

Then, from the analyticity of $R_\alpha(\lambda)$, the map $(\lambda, \gamma) \mapsto \left|\left|(e^{\gamma\langle x\rangle} \otimes I_2)\, R(\lambda)(e^{-\gamma\langle x\rangle} \otimes I_2)\right|\right|$ is uniformly bounded on compact subsets of $\gamma \in I\!R$ and $\lambda \in \rho(\mathbb{H}_2)$. Since $E$ is isolated in the spectrum of $\mathbb{H}_2$, we have (see proof of part (d) of Theorem XII.5 in [21]),

$$r(E) = \frac{1}{2\pi i} \int_{|\lambda - E| = \Gamma > 0} R(\lambda)\, \frac{1}{\lambda - E}\, d\lambda, \tag{3.0.8}$$

where $\{\lambda \in \sigma(\mathbb{H}_2) \,:\, |\lambda - E| \leq \Gamma\} \,=\, E$. The boundedness of $(e^{\gamma\langle x\rangle} \otimes I_2)\, r(E)\, (e^{-\gamma\langle x\rangle} \otimes I_2)$ follows. $\square$

**Lemma 3.0.6.** *For fixed $t \in I\!R^n$, there exist $K > \tilde{K} > 0$ and $S(t) > 0$, such that if $p \in I\!R^n$ satisfies $\sum_{j=1}^n p_j^2 \geq S(t)^2$, then*

$$\tilde{K} \sum_{j=1}^{n} p_j^2 \leq \left| \sum_{j=1}^{n} (p_j + it_j)^2 \right| \leq K \sum_{j=1}^{n} p_j^2 \,.$$

*Furthermore, $S(t)$ is uniformly bounded for $t$ in compact subsets of $I\!R^n$.*

**Proof:**

Let $||t|| \,=\, \left[\sum_{j=1}^n \, t_j^2\right]^{1/2}$, $||p\,|| \,=\, \left[\sum_{j=1}^n \, p_j^2\right]^{1/2}$. We prove the Lemma with $S(t) = 1 + 4\,||t||\,,\ \tilde{K} = 7/16$, and $K = 17/16$.

We first show that for this choice of $S(t)$, $K = 17/16$:

$$\begin{aligned}
\left| \sum_{j=1}^{n} (p_j + it_j)^2 \right| \;&\leq\; \sum_{j=1}^{n} |p_j + it_j|^2 \\
&=\; \sum_{j=1}^{n} (\, p_j^2 + t_j^2 \,) \\
&=\; ||p\,||^2 \left[ 1 \,+\, \frac{||t||^2}{||p\,||^2} \right] \\
&\leq\; ||p\,||^2 \left[ 1 \,+\, \frac{||t||^2}{(1 + 4\,||t||)^2} \right] \\
&\leq\; ||p\,||^2 \left( \frac{17}{16} \right).
\end{aligned}$$

In particular notice that this argument also shows

$$||\,p\,||^{\,2} \,+\, ||\,t\,||^{\,2} \,\leq\, \frac{17}{16}\,||\,p\,||^{\,2}\,. \tag{3.0.9}$$

Now we show that for this choice of $S(t)$, $\tilde{K} = 7/16$:

$$\begin{aligned}
\left|\sum_{j=1}^{n}(p_j + it_j)^2\right| &= \left[\left(\sum_{j=1}^{n}(p_j^2 - t_j^2)\right)^2 + \left(2\sum_{j=1}^{n} p_j\,t_j\right)^2\right]^{1/2} \\
&\geq \left|\;\left|\sum_{j=1}^{n}(p_j^2 - t_j^2)\right| - 2\left|\sum_{j=1}^{n} p_j\,t_j\right|\;\right| \\
&\geq \sum_{j=1}^{n}(p_j^2 - t_j^2) \,-\, 2\sum_{j=1}^{n}|p_j\,|\,|t_j\,| \\
&\geq \sum_{j=1}^{n}(p_j^2 - t_j^2) \,-\, 2\,||p\,||\;||t\,|| \\
&= ||p\,||^2\left(1 \,-\, \frac{||t\,||^2}{||p\,||^2} \,-\, 2\,\frac{||t\,||}{||p\,||}\right) \\
&\geq ||p\,||^2\left(1 \,-\, \frac{||t\,||^2}{(1+4\,||t||)^2} \,-\, \frac{2\;||t\,||}{1+4\,||t||}\right) \\
&\geq ||p\,||^2\left(\frac{7}{16}\right).
\end{aligned} \tag{3.0.10}$$

□

**Proposition 3.0.7.** *Let* $\Psi = \begin{pmatrix} f \\ \\ g \end{pmatrix} \in \mathcal{H}$ *be a solution of* $\mathbb{H}_2\Psi = E\Psi$, *with* $E > 0$. *Then, for any* $\gamma > 0$, *and any* $\alpha \in \mathbb{N}^2$, $D^\alpha f,\ D^\alpha g \in D(e^{\gamma\langle x\rangle})$, *where* $D^\alpha = \partial_X^{\alpha_1}\,\partial_Y^{\alpha_2}$.

**Proof:**

We use the Paley-Wiener Theorem, Theorem IX.13 of [22]:

Let $\phi \in L^2(I\!R^n)$. Then $e^{\gamma|x\,|}\,\phi \in L^2(I\!R^n)$ for all $\gamma < \gamma'$ if and only if $\hat{\phi}$ has an analytic continuation to the set $\{p \,:\, |\mathrm{Im}\, p\,| < \gamma'\}$ with the property that for each $t \in I\!R^n$ with $|t| < \gamma'$, $\hat{\phi}(\cdot + it) \in L^2(I\!R^n)$, and for any $\gamma < \gamma'$, $\sup_{|t|\leq\gamma'} \left|\left|\hat{\phi}(\cdot + it)\right|\right|_2 < \infty$.

If a function $\hat{\phi}$ satisfies the conditions in this theorem we will say that $\hat{\phi}$ is "P-W."

Let $p_j = -i\,\partial_{x_j}$. We present the proof for general $n$. In our case we have $n = 2$ with $x_1 = X$ and $x_2 = Y$.

Proposition 4 shows that $\hat{f}$ and $\hat{g}$ are P-W for any $\gamma' > 0$. In particular we know that $\hat{f},\ \hat{g}$ are analytic everywhere. So the analyticity condition will be a non-issue in the course of the proof. $\widehat{\nabla f},\ \widehat{\nabla g},\ \widehat{\Delta f},\ \widehat{\Delta g}$ are also P-W for any $\gamma' > 0$. So $p \mapsto p_j\,\hat{f}(p)$, $p \mapsto p_j\,\hat{g}(p)$, $p \mapsto \sum_{j=1}^n p_j^2\,\hat{f}(p)$, and $p \mapsto \sum_{j=1}^n p_j^2\,\hat{g}(p)$ are P-W for all $\gamma' > 0$.

Let $S(t) = 1 + 4\,||t\,||$ and $B_S$ be a ball of radius $S$ centered at the origin. Since $\sum_{j=1}^n p_j^2\,\hat{f}(p)$ is P-W, with (3.0.10) we have

$$\begin{aligned}\int_{I\!R^n\setminus B_{S(t)}} ||p\,||^4\ |\hat{f}(p+it)\,|^2\,dp \;&\leq\; \left(\frac{16}{7}\right)^2 \int_{I\!R^n\setminus B_{S(t)}} \left|\sum_{j=1}^n (p_j + it_j)^2\right|^2 |\hat{f}(p+it)\,|^2\,dp \\ &<\; \infty \qquad (3.0.11)\end{aligned}$$

uniformly for $t$ in compact subsets of $I\!R^n$. We only show results involving $f$. The same results hold with $f$ replaced by $g$.

Note that since $S(t)$ and $\left|\left|\hat{f}(\cdot + it)\right|\right|_2$ are uniformly bounded for $t$ in compact subsets of $\mathbb{R}^n$, we only need to prove estimates for $||p\,|| \geq S(t)$. All of the integral estimates that follow hold uniformly for $t$ in compact subsets of $\mathbb{R}^n$. From (3.0.9) and (3.0.11) we have

$$\begin{aligned}
&\int_{\mathbb{R}^n \setminus B_{S(t)}} |p_j + it_j\,|^2\,|p_k + it_k\,|^2\,|\hat{f}(p+it)\,|^2\,dp \\
&\qquad \leq \int_{\mathbb{R}^n \setminus B_{S(t)}} \left(||p\,||^2 + ||t\,||^2\right)^2 |\hat{f}(p+it)\,|^2\,dp \\
&\qquad \leq \left(\frac{17}{16}\right)^2 \int_{\mathbb{R}^n \setminus B_{S(t)}} ||p\,||^4\;|\hat{f}(p+it)\,|^2\,dp \\
&\qquad < \infty\ .
\end{aligned}$$

It follows that $\partial_{x_j}\,\partial_{x_k}\,f \in D(e^{\gamma\langle x\rangle})$ for any $\gamma > 0$. Again the same will hold for $g$.

We now start an induction on the length $|\alpha|$ in $D^\alpha f$ and $D^\alpha g$. Assume that $D^\beta f,\ D^\beta g \in D(e^{\gamma\langle x\rangle})$ for any $\gamma > 0$ and any $|\beta| \leq m-1$. It suffices to prove that $D^\alpha f \in D(e^{\gamma\langle x\rangle})$ for any $\gamma > 0$ and any $|\alpha\,| = m$.

Following the notation in the proof of Proposition 4, the eigenvalue equation gives us

$$\begin{aligned}
\Delta\,f &= V_{12}\,g + (V_{11} - E)\,f\ , \\
\Delta\,g &= V_{21}\,f + (V_{22} - E)\,g\ .
\end{aligned}$$

where $V_{11},\ V_{12} = V_{21}$, and $V_{22}$ are polynomials in $x_j$. Let $|\alpha'\,| = m-2$. Since the $V_{ij}$ are polynomial, our induction hypothesis gives us $D^{\alpha'}\Delta\,f \in D(e^{\gamma\langle x\rangle})$ for any $\gamma > 0$. It follows that for $j_k \in \{1, 2, \cdots, n\}$

$$\int_{\mathbb{R}^n \setminus B_{S(t)}} |p_{j_1} + it_{j_1}\,|^2\,|p_{j_2} + it_{j_2}\,|^2 \cdots |p_{j_{m-2}} + it_{j_{m-2}}\,|^2 \left|\sum_{j=1}^n (p_j + it_j)^2\right|^2 |\hat{f}(p+it)\,|^2\,dp < \infty\ ,$$

and from (3.0.10) we have

$$\int_{I\!R^n \setminus B_{S(t)}} |p_{j_1} + it_{j_1}|^2 |p_{j_2} + it_{j_2}|^2 \cdots |p_{j_{m-2}} + it_{j_{m-2}}|^2 \, ||p||^4 \, |\hat{f}(p+it)|^2 dp < \infty .$$

Since the $j_k$ are arbitrary, we have

$$\begin{aligned}
&\infty > \\
&\sum_{j_1, j_2, \cdots, j_{m-2}=1}^{n} \int_{I\!R^n \setminus B_{S(t)}} |p_{j_1} + it_{j_1}|^2 |p_{j_2} + it_{j_2}|^2 \cdots |p_{j_{m-2}} + it_{j_{m-2}}|^2 \, ||p||^4 \, |\hat{f}(p+it)|^2 dp \\
&= \sum_{j_1, j_2, \cdots, j_{m-2}=1}^{n} \int_{I\!R^n \setminus B_{S(t)}} (p_{j_1}^2 + t_{j_1}^2)(p_{j_2}^2 + t_{j_2}^2) \cdots (p_{j_{m-2}}^2 + t_{j_{m-2}}^2) \, ||p||^4 \, |\hat{f}(p+it)|^2 dp \\
&= \int_{I\!R^n \setminus B_{S(t)}} (||p||^2 + ||t||^2)^{m-2} \, ||p||^4 \, |\hat{f}(p+it)|^2 dp \\
&\geq \int_{I\!R^n \setminus B_{S(t)}} ||p||^{2(m-2)} \, ||p||^4 \, |\hat{f}(p+it)|^2 dp \\
&= \int_{I\!R^n \setminus B_{S(t)}} ||p||^{2m} \, |\hat{f}(p+it)|^2 dp
\end{aligned}$$

Then using (3.0.9), we have for any $j_k \in \{1, 2, \cdots, n\}$

$$\begin{aligned}
&\int_{I\!R^n \setminus B_{S(t)}} |p_{j_1} + it_{j_1}|^2 |p_{j_2} + it_{j_2}|^2 \cdots |p_{j_m} + it_{j_m}|^2 |\hat{f}(p+it)|^2 dp \\
\leq \; &\int_{I\!R^n \setminus B_{S(t)}} (||p||^2 + ||t||^2)^m |\hat{f}(p+it)|^2 dp \\
\leq \; &\left(\frac{17}{16}\right)^m \int_{I\!R^n \setminus B_{S(t)}} ||p||^{2m} \, |\hat{f}(p+it)|^2 dp \\
< \; &\infty .
\end{aligned}$$

So, for arbitrary $j_k \in \{1, 2, \cdots n\}$, $p \mapsto p_{j_1} p_{j_2} \cdots p_{j_m} \hat{f(p)}$ is P-W and it follows that $D^\alpha f \in D(e^{\gamma\langle x \rangle})$ for any $\gamma > 0$ and any $|\alpha| = m$. The same argument will work with $f$

replaced by $g$ and the proposition is proved. $\square$

**Lemma 3.0.8.** *Let* $\Psi = \begin{pmatrix} f \\ \\ g \end{pmatrix}$, $R(\lambda) = (\mathbb{H}_2 - \lambda)^{-1}$ *for* $\lambda \in \rho(\mathbb{H}_2)$, *and* $r(E) = (\mathbb{H}_2 - E)_r^{-1}$ *be the reduced resolvent at* $E$. *If* $f,\ g \in C^\infty$ *and* $(D^\alpha \otimes I_2)\,\Psi \in D(e^{\gamma\langle x\rangle} \otimes I_2)$, *for all* $\alpha \in \mathbb{N}^2$ *and any* $\gamma > 0$, *then* $(D^\alpha \otimes I_2)\,R(\lambda)\Psi,\ (D^\alpha \otimes I_2)\,r(E)\Psi \in D(e^{\gamma\langle x\rangle} \otimes I_2)$, *for all* $\alpha \in \mathbb{N}^2$ *and any* $\gamma > 0$.

**Proof:**

First note that for any $\gamma_1 > \gamma_2 > 0$ and $j, k = 0, 1, 2, \cdots$, there exists $M > 0$ such that

$$\left|\left| e^{\gamma_2\langle x\rangle}\, X^j\, Y^k\, \phi \right|\right| \;\leq\; M\ ||\phi\,||\ +\ \left|\left| e^{\gamma_1\langle x\rangle}\, \phi \right|\right|.$$

This relative bound implies that if $\phi \in D(e^{\gamma\langle x\rangle})$ for all $\gamma > 0$, then $X^j\, Y^k\, \phi \in D(e^{\gamma\langle x\rangle})$ for all $\gamma > 0$, and arbitrary $j, k = 0, 1, 2, \cdots$.

By an argument similar to the one by which we obtained $f,\ g \in C^\infty(I\!R^2)$ in the proof of Proposition 3.0.4, $R(\lambda)$ and $r(E)$ map functions from $C^\infty(I\!R^2) \oplus C^\infty(I\!R^2)$ to $C^\infty(I\!R^2) \oplus C^\infty(I\!R^2)$.

The following identity holds as long as the terms on the right hand side are in $L^2(I\!R^2) \oplus \text{L}^2(I\!R^2)$:

$$(\partial_X \otimes I_2)\,R(\lambda)\,\Phi \;=\; R(\lambda)\,(\partial_X \otimes I_2)\,\Phi \;-\; R(\lambda)\,[(\partial_X \otimes I_2)(V)]\,R(\lambda)\,\Phi, \qquad (3.0.12)$$

where $[(\partial_X \otimes I_2)(V)] = \begin{pmatrix} (a+b)\,X & b\,Y \\ b\,Y & (a-b)\,X \end{pmatrix}$. To see this, let $R(\lambda)\,\Phi = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}$ and we compute $[\,\partial_X \otimes I_2,\ R(\lambda)\,]$:

$$\{(\partial_X \otimes I_2)\,R(\lambda) - R(\lambda)\,(\partial_X \otimes I_2)\}\,\Phi$$

$$= (\partial_X \otimes I_2) \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} - R(\lambda)\,(\partial_X \otimes I_2)\,(\mathbb{H}_2 - \lambda) \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}$$

$$= \begin{pmatrix} \partial_X\,\psi_1 \\ \partial_X\,\psi_2 \end{pmatrix} - R(\lambda) \begin{pmatrix} \partial_X & 0 \\ 0 & \partial_X \end{pmatrix} \left[ \begin{pmatrix} (-\frac{1}{2}\,\Delta - \lambda)\,\psi_1 \\ (-\frac{1}{2}\,\Delta - \lambda)\,\psi_2 \end{pmatrix} + \begin{pmatrix} V_{11}\,\psi_1 + V_{12}\,\psi_2 \\ V_{21}\,\psi_1 + V_{22}\,\psi_2 \end{pmatrix} \right]$$

$$= \begin{pmatrix} \partial_X\,\psi_1 \\ \partial_X\,\psi_2 \end{pmatrix} - R(\lambda) \left[ \begin{pmatrix} (-\frac{1}{2}\,\Delta - \lambda)\,\partial_X\,\psi_1 \\ (-\frac{1}{2}\,\Delta - \lambda)\,\partial_X\,\psi_2 \end{pmatrix} + \begin{pmatrix} \partial_X(V_{11})\,\psi_1 + \partial_X(V_{12})\,\psi_2 \\ \partial_X(V_{21})\,\psi_1 + \partial_X(V_{22})\,\psi_2 \end{pmatrix} \right.$$

$$\left. + \begin{pmatrix} V_{11}\,\partial_X(\psi_1) + V_{12}\,\partial_X(\psi_2) \\ V_{21}\,\partial_X(\psi_1) + V_{22}\,\partial_X(\psi_2) \end{pmatrix} \right]$$

$$= \begin{pmatrix} \partial_X\,\psi_1 \\ \partial_X\,\psi_2 \end{pmatrix} - R(\lambda) \left[ (\mathbb{H}_2 - \lambda) \begin{pmatrix} \partial_X\,\psi_1 \\ \partial_X\,\psi_2 \end{pmatrix} + [(\partial_X \otimes I_2)(V)] \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} \right]$$

$$= -\,R(\lambda)\,[(\partial_X \otimes I_2)(V)] \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}$$

$$= -\,R(\lambda)\,[(\partial_X \otimes I_2)(V)]\,R(\lambda)\,\Phi.$$

Clearly (3.0.12) holds with $X$ replaced by $Y$.

From the hypotheses on $\Psi$ and Corollary 3.0.5, we know that for all $\gamma > 0$, $R(\lambda)\,(\partial_X \otimes I_2)\,\Psi \in D(e^{\gamma\langle x\rangle} \otimes I_2) \subset L^2(I\!R^2) \oplus L^2(I\!R^2)$. From Corollary 3.0.5 and the note above, we know that $R(\lambda)\,[(\partial_X \otimes I_2)(V)]\,R(\lambda)\,\Psi \in D(e^{\gamma\langle x\rangle} \otimes I_2) \subset L^2(I\!R^2) \oplus L^2(I\!R^2)$ for all $\gamma > 0$. From this we see that (3.0.12) holds when applied to $\Psi$ and therefore $(\partial_X \otimes I_2)\,R(\lambda)\,\Phi \in D(e^{\gamma\langle x\rangle} \otimes I_2)$ for all $\gamma > 0$. Similarly, $(\partial_Y \otimes I_2)\,R(\lambda)\,\Phi \in D(e^{\gamma\langle x\rangle} \otimes I_2)$ for all $\gamma > 0$.

By applying (3.0.12) repeatedly, we see that $(D^\alpha \otimes I_2)\,R(\lambda)\,\Psi$ is a linear combination of terms of the form

$$R(\lambda)\,[(D^{\alpha_1} \otimes I_2)(V)]\,R(\lambda)\,[(D^{\alpha_2} \otimes I_2)(V)]\,\cdots\,R(\lambda)\,[(D^{\alpha_{m-1}} \otimes I_2)(V)]\,R(\lambda)\,(D^{\alpha_m} \otimes I_2)\,\Psi,$$

where $\sum_{j=1}^{m} |\alpha_j| = |\alpha|$. Since the $[(D^{\alpha_j} \otimes I_2)(V)]$ are matrices with polynomial entries, we use Corollary 3.0.5 and the note above to obtain $(D^\alpha \otimes I_2)\,R(\lambda)\,\Psi \in D(e^{\gamma\langle x\rangle} \otimes I_2)$ for all $\alpha \in \mathbb{N}^2$ and $\gamma > 0$. The conclusion involving $(D^\alpha \otimes I_2)\,r(E)\,\Psi$ follows from (3.0.8). $\square$

**Theorem 3.0.9.** *For $k \geq 2$, let $\Psi^{(k-2)} = \begin{pmatrix} f^{(k-2)} \\ \\ g^{(k-2)} \end{pmatrix}$, and $\psi_\perp^{(k)}$ be determined by the perturbation formulas of chapter 2. Then, $f^{(k-2)}$, $g^{(k-2)}$, $\psi_\perp^{(k)} \in C^\infty(I\!R^2)$, $f^{(k-2)}$, $g^{(k-2)}$, $\left|\left|\psi_\perp^{(k)}\right|\right|_{el} \in L^2(I\!R^2)$ and $f^{(k-2)}$, $g^{(k-2)}$, $\left|\left|\psi_\perp^{(k)}\right|\right|_{el} \in D(e^{\gamma\langle x\rangle})$, for any $\gamma > 0$. In addition, $D^\alpha f^{(k-2)}$, $D^\alpha g^{(k-2)}$, $\left|\left|D^\alpha \psi_\perp^{(k)}\right|\right|_{el} \in D(e^{\gamma\langle x\rangle})$ for all $\alpha \in \mathbb{N}^2$ and any $\gamma > 0$.*

**Proof:**

We refer to a function in $D(e^{\gamma\langle x\rangle})$ (or $D(e^{\gamma\langle x\rangle} \otimes I_2)$) for any $\gamma > 0$, as exponentially decaying with arbitrary $\gamma$. We first note that from the proof of lemma 3.0.8, multiplication by polynomials in $X$ and $Y$ preserves exponential decay with arbitrary $\gamma$.

Since $\Psi^{(0)} = \begin{pmatrix} f^{(0)} \\ \\ g^{(0)} \end{pmatrix}$ is determined at second order in $\epsilon$ as an eigenfunction of $\mathbb{H}_2$, we already know from propositions 3.0.4 and 3.0.7 that $\Psi^{(0)}$ satisfies the conclusion.

The $f^{(1)}$ and $g^{(1)}$ given by equation (2.0.10) are determined by $\mathbb{H}_3$ followed by a projection $Q_\perp$, and reduced resolvent $\mathbb{H}_2 - E^{(2)}$, acting on $\Psi^{(0)}$. By corollary 3.0.5 we know that the reduced resolvent preserves exponential decay with arbitrary $\gamma$. The projection $Q_\perp$ was the projection in $\mathcal{H}$ onto the subspace perpendicular to the eigenspace of the eigenvalue $E^{(2)}$ of $\mathbb{H}_2$. From proposition 3.0.4, we know that the eigenvectors of $\mathbb{H}_2$ have exponential decay with arbitrary $\gamma$, and so it follows that $Q_\perp$ will preserve exponential decay with arbitrary $\gamma$. Since the matrix entries of $\mathbb{H}_3$ only contain polynomials and derivatives in $X$ and $Y$, we know from lemma 3.0.8 that $(\mathbb{H}_3\,\Psi^{(0)})$ will have exponential decay with arbitrary $\gamma$. It follows that $\Psi^{(1)}$ will have exponential decay with arbitrary $\gamma$. By a similar argument, $\Psi^{(1)} \in C^\infty \oplus C^\infty$. From the definition of $Q_\perp$ along with proposition 3.0.7, we see that all of the derivatives of $Q_\perp\,\mathbb{H}_3\,\Psi^{(0)}$ are exponentially decaying with arbitrary $\gamma$. It then follows from lemma 3.0.8 that all of the derivatives of $\Psi^{(1)}$ are exponentially decaying with arbitrary $\gamma$.

Recall that $\psi_\perp^{(0)} = \psi_\perp^{(1)} = \psi_\perp^{(2)} = 0$. From equation (2.0.11) we know that

$$\begin{aligned}
\left|\left|\psi_\perp^{(3)}\right|\right|_{el} \;\leq\; & \left|\left| \left[(h\,P_\perp)^{(0)}\right]_r^{-1} \; P_\perp^{(0)} \left(\frac{\partial \Psi_1}{\partial x}\right)^{(0)} \right|\right|_{el} \left| \frac{\partial f^{(0)}}{\partial X} \right| \\
& + \left|\left| \left[(h\,P_\perp)^{(0)}\right]_r^{-1} \; P_\perp^{(0)} \left(\frac{\partial \Psi_1}{\partial y}\right)^{(0)} \right|\right|_{el} \left| \frac{\partial f^{(0)}}{\partial Y} \right| \\
& + \left|\left| \left[(h\,P_\perp)^{(0)}\right]_r^{-1} \; P_\perp^{(0)} \left(\frac{\partial \Psi_2}{\partial x}\right)^{(0)} \right|\right|_{el} \left| \frac{\partial f^{(0)}}{\partial X} \right| \\
& + \left|\left| \left[(h\,P_\perp)^{(0)}\right]_r^{-1} \; P_\perp^{(0)} \left(\frac{\partial \Psi_2}{\partial y}\right)^{(0)} \right|\right|_{el} \left| \frac{\partial f^{(0)}}{\partial Y} \right|.
\end{aligned}$$

By assumption, $\left(\frac{\partial \Psi_1}{\partial x}\right)^{(0)} \in \mathcal{H}_{el}$, and $\left[(h\,P_\perp)^{(0)}\right]_r^{-1}$ and $P_\perp^{(0)}$ are bounded operators on $\mathcal{H}_{el}$. So we have

$$\left|\left|\psi_\perp^{(3)}\right|\right|_{el} \;\leq\; A \left| \frac{\partial f^{(0)}}{\partial X} \right| \;+\; B \left| \frac{\partial f^{(0)}}{\partial Y} \right|,$$

for some positive real numbers $A$ and $B$ and $\left|\left|\psi_\perp^{(3)}\right|\right|_{el}$ is exponentially decaying for arbitrary $\gamma$ by proposition 3.0.7. Also, $\psi_\perp^{(3)} \in C^\infty(\mathbb{R}^2)$ since its $(X, Y)$ dependence comes strictly from derivatives of $f^{(0)}$ and $g^{(0)}$. By a similar argument, we see that $\left|\left| D^\alpha \psi_\perp^{(3)} \right|\right|_{el}$ is exponentially decaying with arbitrary $\gamma$, from proposition 3.0.7.

We now use induction on $k$ to show the conclusion. For the induction hypothesis, assume that $\Psi^{(k-3)}$ and $\psi_\perp^{(k-1)}$ given by the perturbation formulas of chapter 2 satisfy the conclusions. Using equations (2.0.17) and (2.0.18) to determine $\Psi^{(k-2)}$ and $\psi_\perp^{(k)}$, we argue the conclusions hold for these functions. We know from above that the reduced resolvent $\mathbb{H}_2 - E^{(2)}$ and the projection $Q_\perp$ can be ignored for our purposes. The matrix entries of the $\mathbb{H}_j$ operators arising in equation (2.0.17) only contain polynomials and derivatives in $X$ and $Y$, and by

the induction hypothesis, will preserve exponential decay with arbitrary $\gamma$. We know that $\Psi_1^{(j-2)}$ is a linear combination of terms of the form $\psi\, X^l\, Y^{j-2-l}$, where $\psi \in \mathcal{H}_{el}$. Then, we have

$$\begin{aligned} \left| \langle\, \Psi_1^{(j-2)},\ \psi_\perp^{(k-j)} \,\rangle_{el} \right| &\leq \left|\left| \Psi_1^{(j-2)} \right|\right|_{el} \left|\left| \psi_\perp^{(k-j)} \right|\right|_{el} \\ &\leq \sum_{l=0}^{j-2} A_l \left|X\right|^l \left|Y\right|^{j-2-l} \left|\left| \psi_\perp^{(k-j)} \right|\right|_{el}. \end{aligned}$$

We see that these terms also have exponential decay with arbitrary $\gamma$. Then, $\Psi^{(k-2)}$ will have exponential decay with arbitrary $\gamma$. We also see that $\Psi^{(k-2)}$ will be smooth. By a similar argument, $D^\alpha\, \Psi^{(k-2)}$ has exponential decay with arbitrary $\gamma$.

For $\psi_\perp^{(k)}$, the know that $\left[(\, h\ P_\perp)^{(0)}\right]_r^{-1}$, $P_\perp^{(j)}$, and $(\, h\, P_\perp)^{(j)}$ are bounded operators in $\mathcal{H}_{el}$ with only polynomial dependence in $(X, Y)$. The $(\Delta_{x,\,y}\ \Psi_1)^{(j)}$ and $\left(\frac{\partial \Psi_1}{\partial x}\right)^{(j)}$ are linear combinations of functions in $\mathcal{H}_{el}$ with polynomial dependence in $(X, Y)$. By an argument similar to the $\psi_\perp^{(3)}$ case above, it follows that $\psi_\perp^{(k)}$ is exponentially decaying with arbitrary $\gamma$. The $C^\infty$ conclusions follow similarly, as does $\left|\left| D^\alpha\, \psi_\perp^{(k)} \right|\right|_{el} \in D(e^{\gamma\langle x\rangle})$ for all $\alpha \in \mathbb{N}^2$ and any $\gamma > 0$.

□

# Chapter 4

# The Eigenstates of the Leading Order Hamiltonian

We adopt the following notation throughout:

1. The operator of nuclear angular momentum about the z-axis is denoted by $L_z^{nuc} = -i\dfrac{\partial}{\partial\phi}$. The operator of total electronic angular momentum about the z-axis is denoted by $L_z^{el}$. The operator of total angular momentum about the z-axis is denoted by $L_z^{TOT} = (L_z^{nuc} \otimes I) + (I \otimes L_z^{el})$.

2. We let $L_n^k(x)$ be the associated Laguerre polynomials, as defined in [25].

The first non-vanishing terms in our perturbation expansion are $E^{(2)},\ f^{(0)}(X,\,Y),\ g^{(0)}(X,\,Y)$ arising from the eigenvalue equation

$$\mathbb{H}_2 \begin{pmatrix} f^{(0)} \\ \\ g^{(0)} \end{pmatrix} \quad = \quad E^{(2)} \begin{pmatrix} f^{(0)} \\ \\ g^{(0)} \end{pmatrix},$$

where

$$\mathbb{H}_2 \ = -\ \frac{1}{2}\ \Delta_{X,\,Y} \otimes I_2 \ + \begin{pmatrix} \dfrac{a+b}{2}\ X^2 \ + \ \dfrac{a-b}{2}\ Y^2 & b\,X\,Y \\ \\ b\,X\,Y & \dfrac{a-b}{2}\ X^2 \ + \ \dfrac{a+b}{2}\ Y^2 \end{pmatrix}.$$

Let $(\rho, \phi)$ be the usual polar coordinates associated with $(X, Y)$. Define the unitary operators $U,\ Z\ :\ \mathcal{H} \rightarrow \mathcal{H}$ by:

$$U = \begin{pmatrix} \cos(\phi) & -\sin(\phi) \\ \\ \sin(\phi) & \cos(\phi) \end{pmatrix} \qquad \text{and} \qquad Z = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ \\ i & -i \end{pmatrix}.$$

We have

$$U^{-1}\,\mathbb{H}_2\,U \;=\; \left(\left(-\frac{1}{2}\,\frac{\partial^2}{\partial\rho^2} \;-\; \frac{1}{2\rho}\,\frac{\partial}{\partial\rho} \;+\; \frac{a}{2}\,\rho^2 \;+\; \frac{(L_z^{nuc})^2+1}{2\rho^2}\right)\otimes\, I_2\right) + \begin{pmatrix} \dfrac{b}{2}\,\rho^2 & \dfrac{i}{\rho^2}\,L_z^{nuc} \\ -\dfrac{i}{\rho^2}\,L_z^{nuc} & -\dfrac{b}{2}\,\rho^2 \end{pmatrix}$$

$$(UZ)^{-1}\,\mathbb{H}_2\,(UZ) \;=\; \left(\left(-\frac{1}{2}\,\frac{\partial^2}{\partial\rho^2} \;-\; \frac{1}{2\rho}\,\frac{\partial}{\partial\rho} \;+\; \frac{a}{2}\,\rho^2\right)\otimes\, I_2\right) + \begin{pmatrix} \dfrac{(L_z^{nuc}-1)^2}{2\rho^2} & \dfrac{b}{2}\,\rho^2 \\ \dfrac{b}{2}\,\rho^2 & \dfrac{(L_z^{nuc}+1)^2}{2\rho^2} \end{pmatrix}.$$

We note that $(U^{-1}\,\mathbb{H}_2\,U)\Psi \;=\; E\,\Psi$ was the leading order equation obtained by Renner [3], which is unitarily equivalent to our leading order equation $\mathbb{H}_2\,\Psi \;=\; E\,\Psi$. Renner showed that some of the eigenvalues can be solved for exactly, and used regular perturbation theory up to second order to approximate the other eigenvalues. These equations have been studied by several other authors, for example see [19, 24]. We will repeat some of Renner's results here, but we will calculate the perturbation series to much higher orders and show that many of the series likely have small radii of convergence and are diverging inside much of the region of interest. We also illustrate that there is likely a crossing involving the ground state eigenvalue of $\mathbb{H}_2$ near $b \approx 0.925a$. The ground state appears to be degenerate for $0 < b < 0.925a$ and non-degenerate for $0.925a < b < a$.

Let $r = a^{1/4}\,\rho,\ \tilde{b} = \dfrac{b}{a}$, and

$$\begin{aligned} H_U &= \frac{1}{\sqrt{a}}\,U^{-1}\,\mathbb{H}_2\,U \\ &= \left(\left(-\frac{1}{2}\frac{\partial^2}{\partial r^2} - \frac{1}{2r}\frac{\partial}{\partial r} + \frac{1}{2}\,r^2 + \frac{(L_z^{nuc})^2+1}{2r^2}\right)\otimes I_2\right) + \begin{pmatrix} \dfrac{\tilde{b}}{2}\,r^2 & \dfrac{i}{r^2}\,L_z^{nuc} \\ -\dfrac{i}{r^2}\,L_z^{nuc} & -\dfrac{\tilde{b}}{2}\,r^2 \end{pmatrix} \\ H_{UZ} &= \frac{1}{\sqrt{a}}\,(UZ)^{-1}\,\mathbb{H}_2\,(UZ) \\ &= \left(\left(-\frac{1}{2}\frac{\partial^2}{\partial r^2} - \frac{1}{2r}\frac{\partial}{\partial r} + \frac{1}{2}\,r^2\right)\otimes I_2\right) + \begin{pmatrix} \dfrac{(L_z^{nuc}-1)^2}{2r^2} & \dfrac{\tilde{b}}{2}\,r^2 \\ \dfrac{\tilde{b}}{2}\,r^2 & \dfrac{(L_z^{nuc}+1)^2}{2r^2} \end{pmatrix}. \end{aligned}$$

Both $H_U$ and $H_{UZ}$ commute with $L_z^{nuc}\otimes I_2$. So, we search for eigenfunctions of these operators of the form $\begin{pmatrix} e^{\pm i|l|\phi}\,\psi_1(r) \\ e^{\pm i|l|\phi}\,\psi_2(r) \end{pmatrix},\ |l| = 0, 1, 2, \cdots$

We warn the reader that although $l$ arises here as an eigenvalue of $L_z^{nuc}$, at this point we should not associate any physical meaning to $l$. Here we are dealing with the operators $H_U$ and $H_{UZ}$, which are related to $\mathbb{H}_2$ by the operations of $U$ and $Z$. The physical meaning of $l$ will later become apparent in theorem 5.0.1.

## 4.1 The Exactly Solvable $l = 0$ States

The $l = 0$ states (no angular dependence) are exactly solvable. In this case $H_U$ reduces to

$$H_U^{[l=0]} = \begin{pmatrix} -\frac{1}{2}\frac{\partial^2}{\partial r^2} - \frac{1}{2r}\frac{\partial}{\partial r} + \frac{1+\tilde{b}}{2}r^2 + \frac{1}{2r^2} & 0 \\ 0 & -\frac{1}{2}\frac{\partial^2}{\partial r^2} - \frac{1}{2r}\frac{\partial}{\partial r} + \frac{1-\tilde{b}}{2}r^2 + \frac{1}{2r^2} \end{pmatrix}.$$

We recognize that the component equations are of the same form as the radial equation for angular momentum 1 states of the two dimensional Isotropic Harmonic Oscillator. From the first component equation, the eigenvalues and eigenfunctions (non-normalized) are

$$E_{N_+} = (2N_+ + 2)\sqrt{1+\tilde{b}}\,, \quad \begin{pmatrix} \tilde{r_+}\, L^1_{N_+}(\tilde{r_+}^2)\, e^{-\tilde{r_+}^2/2} \\ 0 \end{pmatrix}, \quad N_+ = 0, 1, 2, \cdots$$

where $\tilde{r_+} = (1+\tilde{b})^{1/4} r$. From the second component equation, the eigenvalues and eigenfunctions (non-normalized) are

$$E_{N_-} = (2N_- + 2)\sqrt{1-\tilde{b}}\,, \quad \begin{pmatrix} 0 \\ \tilde{r_-}\, L^1_{N_-}(\tilde{r_-}^2)\, e^{-\tilde{r_-}^2/2} \end{pmatrix}, \quad N_- = 0, 1, 2, \cdots$$

where $\tilde{r_-} = (1-\tilde{b})^{1/4} r$.

Since $\mathbb{H}_2$ is unitarily equivalent to $\sqrt{a}\, H_U$, we see these states give rise to eigenvalues and eigenfunctions of $\mathbb{H}_2$ given by

$$\begin{aligned} E_{N_-} &= (2N_- + 2)\sqrt{a-b} \\ \Psi^{[l=0]}_{N_-}(\rho,\phi) &= \begin{pmatrix} -\tilde{r_-}\, \sin(\phi)\, L^1_{N_-}(\tilde{r_-}^2)\, e^{-\tilde{r_-}^2/2} \\ \tilde{r_-}\, \cos(\phi)\, L^1_{N_-}(\tilde{r_-}^2)\, e^{-\tilde{r_-}^2/2} \end{pmatrix}, \quad N_- = 0, 1, 2, \cdots \end{aligned} \tag{4.1.1}$$

where $\tilde{r_-} = (a-b)^{1/4}\,\rho$, and

$$\begin{aligned} E_{N_+} &= (2N_+ + 2)\,\sqrt{a+b} \\ \Psi_{N_+}^{[l=0]}(\rho,\phi) &= \begin{pmatrix} \tilde{r_+}\,\cos(\phi)\,L_{N_+}^1(\tilde{r_+}^2)\,e^{-\tilde{r_+}^2/2} \\ \\ \tilde{r_+}\,\sin(\phi)\,L_{N_+}^1(\tilde{r_+}^2)\,e^{-\tilde{r_+}^2/2} \end{pmatrix}, \quad N_+ = 0,1,2,\cdots \end{aligned} \tag{4.1.2}$$

where $\tilde{r_+} = (a+b)^{1/4}\,\rho$.

## 4.2 The Perturbation Calculation For the $l \neq 0$ States

In this case, $H_{UZ}$ reduces to

$$H_{UZ}^{[\pm|l|]} =$$

$$\begin{pmatrix} -\frac{1}{2}\frac{\partial^2}{\partial r^2} - \frac{1}{2r}\frac{\partial}{\partial r} + \frac{1}{2}r^2 + \frac{(\pm|l|-1)^2}{2r^2} & 0 \\ 0 & -\frac{1}{2}\frac{\partial^2}{\partial r^2} - \frac{1}{2r}\frac{\partial}{\partial r} + \frac{1}{2}r^2 + \frac{(\pm|l|+1)^2}{2r^2} \end{pmatrix}$$

$$+ \frac{\tilde{b}}{2}r^2 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$= \begin{pmatrix} -\frac{1}{2}\frac{\partial^2}{\partial r^2} - \frac{1}{2r}\frac{\partial}{\partial r} + \frac{1}{2}r^2 + \frac{(|l|\mp 1)^2}{2r^2} & 0 \\ 0 & -\frac{1}{2}\frac{\partial^2}{\partial r^2} - \frac{1}{2r}\frac{\partial}{\partial r} + \frac{1}{2}r^2 + \frac{(|l|\pm 1)^2}{2r^2} \end{pmatrix}$$

$$+ \frac{\tilde{b}}{2}r^2 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

Denote the eigenfunctions of $H_{UZ}^{[\pm|l|]}$ by $\begin{pmatrix} f^{[\pm|l|]}(r) \\ g^{[\pm|l|]}(r) \end{pmatrix}$. It is clear that if $\begin{pmatrix} f^{[|l|]}(r) \\ g^{[|l|]}(r) \end{pmatrix}$ is an eigenfunction of $H_{UZ}^{[|l|]}$ with eigenvalue $E$, then $\begin{pmatrix} f^{[-|l|]}(r) \\ g^{[-|l|]}(r) \end{pmatrix} = \begin{pmatrix} g^{[|l|]}(r) \\ f^{[|l|]}(r) \end{pmatrix}$ is an eigenfunction of $H_{UZ}^{[-|l|]}$ with eigenvalue $E$. So we only need to find the eigenfunctions and eigenvalues

of the $H_{UZ}^{[|l|]}$.

We have not been able to solve for the eigenvalues and eigenfunctions in this case exactly. We use regular perturbation theory with perturbation parameter $\tilde{b}$, letting $H_{UZ}^{[|l|]} = H_0^{[|l|]} + \tilde{b}\tilde{V}$, where

$$H_0^{[|l|]} = \begin{pmatrix} -\frac{1}{2}\frac{\partial^2}{\partial r^2} - \frac{1}{2r}\frac{\partial}{\partial r} + \frac{1}{2}r^2 + \frac{(|l|-1)^2}{2r^2} & 0 \\ 0 & -\frac{1}{2}\frac{\partial^2}{\partial r^2} - \frac{1}{2r}\frac{\partial}{\partial r} + \frac{1}{2}r^2 + \frac{(|l|+1)^2}{2r^2} \end{pmatrix}$$

$$\tilde{V} = \frac{1}{2}r^2 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}.$$

We note that by the relative bound found in equation (3.0.2), it follows that

$$\begin{aligned} \left|\left|\tilde{V}\Psi\right|\right|_{\mathcal{H}} &= \left|\left|(e^{-i|l|\phi} \otimes I_2)(UZ)^{-1} V (UZ)(e^{i|l|\phi} \otimes I_2)\Psi\right|\right|_{\mathcal{H}} \\ &= \left|\left|V (UZ)(e^{i|l|\phi} \otimes I_2)\Psi\right|\right|_{\mathcal{H}} \\ &\leq \left|\left|H_{HO}(UZ)(e^{i|l|\phi} \otimes I_2)\Psi\right|\right|_{\mathcal{H}} + \left|\left|(UZ)(e^{i|l|\phi} \otimes I_2)\Psi\right|\right|_{\mathcal{H}} \\ &= \left|\left|(e^{-i|l|\phi} \otimes I_2)(UZ)^{-1} H_{HO}(UZ)(e^{i|l|\phi} \otimes I_2)\Psi\right|\right|_{\mathcal{H}} + ||\Psi||_{\mathcal{H}} \\ &= \left|\left|H_0^{[|l|]}\Psi\right|\right|_{\mathcal{H}} + ||\Psi||_{\mathcal{H}}. \end{aligned}$$

So, we know that in terms of $\tilde{b}$, $H_{UZ}^{[|l|]}$ is an analytic family of type A for small $\tilde{b}$ [21]. Therefore, the eigenvalues and eigenfunctions will be analytic functions of $\tilde{b}$ in a neighborhood of $\tilde{b} = 0$.

We expand the eigenvalues and eigenfunctions of $H_{UZ}^{[|l|]}$ in a series in $\tilde{b}$:

$$E^{N,|l|}(\tilde{b}) \;=\; \sum_{k=0}^{\infty} E_k^{N,|l|}\,\tilde{b}^k, \qquad\qquad \Psi^{N,|l|}(\tilde{b}) \;=\; \sum_{k=0}^{\infty} \Psi_k^{N,|l|}\,\tilde{b}^k \tag{4.2.3}$$

and solve for the coefficients $E_k^{N,|l|}$, $\Psi_k^{N,|l|}$ recursively. Here $N$ indexes the energy levels of $H_{UZ}^{[|l|]}$ for fixed $|l|$. Again from the two-dimensional isotropic oscillator, the eigenfunctions of $H_0^{[|l|]}$ are known exactly. The lowest state is non-degenerate, with eigenvalue and eigenfunction given by

$$E_0^{0,|l|} = |l|, \quad \Psi_0^{0,|l|} \;=\; \begin{pmatrix} r^{|l|-1}\,e^{-r^2/2} \\ \\ 0 \end{pmatrix}. \tag{4.2.4}$$

The rest of the states are two-fold degenerate, with eigenvalues and eigenfunctions given by

$$\begin{aligned} E_0^{N,|l|} &= 2N + |l|, \\ \Psi_{0,\,up}^{N,|l|} &= \begin{pmatrix} r^{|l|-1}\,L_N^{|l|-1}(r^2)\,e^{-r^2/2} \\ \\ 0 \end{pmatrix}, \\ \Psi_{0,\,dwn}^{N,|l|} &= \begin{pmatrix} 0 \\ \\ r^{|l|+1}\,L_{N-1}^{|l|+1}(r^2)\,e^{-r^2/2} \end{pmatrix}, \; N = 1, 2, \cdots \end{aligned} \tag{4.2.5}$$

The functions $\{e^{i\,l\,\phi}\,r^{|l|}\,L_K^{|l|}(r^2)\,e^{-r^2/2}\}_{\substack{l\in\mathbb{Z} \\ K=0,1,2,\cdots}}$ are the eigenfunctions of a self-adjoint operator with purely discrete spectrum and eigenvalues accumulating at infinity. Hence they form a basis for $L^2(\mathbb{R}^2)$ by theorem XIII.64 of [21]. Then for fixed $l \in \mathbb{Z}$, the functions $\{r^{|l|}\,L_K^{|l|}(r^2)\,e^{-r^2/2}\}_{K=0,1,2,\cdots}$ form a basis for the projection of $L^2(\mathbb{R}^2)$ onto $r$-dependent multi-

ples of $e^{i\,l\,\phi}$. We can then use the following orthonormal basis for the perturbation expansion:

$$\left\{ \left( \begin{array}{c} B_{N,|l|-1}\, r^{|l|-1}\, L_N^{|l|-1}(r^2)\, e^{-r^2/2} \\ \\ 0 \end{array} \right), \left( \begin{array}{c} 0 \\ \\ B_{N,|l|+1}\, r^{|l|+1}\, L_N^{|l|+1}(r^2)\, e^{-r^2/2} \end{array} \right) \right\}_{N=0,1,2,\cdots}$$

where the $B_{N,|l|}$ are constants of normalization.

We think of two component functions written in terms of this basis as two column vectors of infinite length. The first column stores the coefficients of the first component and the second column stores the coefficients of the second component. For example, if

$$\Psi \;=\; \left( \begin{array}{c} \displaystyle\sum_{N=0}^{\infty} a_N\; B_{N,|l|-1}\; r^{|l|-1}\; L_N^{|l|-1}(r^2)\; e^{-r^2/2} \\ \\ \displaystyle\sum_{N=0}^{\infty} b_N\; B_{N,|l|+1}\; r^{|l|+1}\; L_N^{|l|+1}(r^2)\; e^{-r^2/2} \end{array} \right),$$

then we write

$$\Psi \;=\; \left( \left( \begin{array}{c} a_0 \\ a_1 \\ a_2 \\ \cdot \\ \cdot \end{array} \right), \left( \begin{array}{c} b_0 \\ b_1 \\ b_2 \\ \cdot \\ \cdot \end{array} \right) \right). \tag{4.2.6}$$

Since the perturbation $\tilde{V}$ is off-diagonal, the relevant matrix elements are

$$(V_{odd})_{N,K} \;=\; \left\langle \; B_{N,|l|-1}\; r^{|l|-1}\; L_N^{|l|-1}(r^2)\; e^{-r^2/2} \;\middle|\; \frac{r^2}{2} \;\middle|\; B_{K,|l|+1}\; r^{|l|+1}\; L_K^{|l|+1}(r^2)\; e^{-r^2/2} \; \right\rangle_{r\,dr}$$

Define $V_{even} \;=\; (V_{odd})^T$. Then, if $\Psi$ is given by (4.2.6), then $\tilde{V}\Psi$ is given in terms our basis

as

$$\tilde{V}\Psi \;=\; \left( \begin{array}{c} V_{odd} \left( \begin{array}{c} b_0 \\ b_1 \\ b_2 \\ \cdot \\ \cdot \end{array} \right) \\ \\ , \; V_{even} \left( \begin{array}{c} a_0 \\ a_1 \\ a_2 \\ \cdot \\ \cdot \end{array} \right) \end{array} \right) .$$

### 4.2.1 Evaluation of the Matrix Elements

The matrix elements of $V_{odd}$ and $V_{even}$ can be found exactly. Utilizing the formulas we will find saves us significant computing time when solving for the perturbation coefficients.

For fixed $l$, we know that $\frac{B_{N,|l|}}{\sqrt{2\pi}}\, e^{i|l|\phi}\, r^{|l|}\, L_N^{|l|}(r^2)\, e^{-r^2/2}$ is a normalized (with respect to measure $rdrd\phi$) eigenfunction of the two-dimensional isotropic harmonic oscillator $-\frac{1}{2}\,\Delta_{r,\,\phi} \;+\; \frac{1}{2}\,r^2$ with eigenvalue $E_{N,|l|} = 2N + |l| + 1$, for $N = 0, 1, 2, \cdots$.

We have

$$(V_{odd})_{N,K} \;= \tag{4.2.7}$$

$$\left\langle \; B_{N,|l|-1}\; r^{|l|-1}\; L_N^{|l|-1}(r^2)\; e^{-r^2/2} \;\middle|\; \frac{r^2}{2} \;\middle|\; B_{K,|l|+1}\; r^{|l|+1}\; L_K^{|l|+1}(r^2)\; e^{-r^2/2} \;\right\rangle_{r\,dr} =$$

$$\left\langle \; \frac{B_{N,|l|-1}}{\sqrt{2\pi}}\; r^{|l|-1}\; L_N^{|l|-1}(r^2)\; e^{-r^2/2} \;\middle|\; \frac{r^2}{2} \;\middle|\; \frac{B_{K,|l|+1}}{\sqrt{2\pi}}\; r^{|l|+1}\; L_K^{|l|+1}(r^2)\; e^{-r^2/2} \;\right\rangle_{r\,dr\,d\phi} =$$

$$\left\langle \; \frac{B_{N,|l|-1}}{\sqrt{2\pi}}\, e^{i(|l|-1)\phi}\, r^{|l|-1}\, L_N^{|l|-1}(r^2)\, e^{-r^2/2} \;\middle|\; (\frac{r^2}{2}\, e^{-2i\phi})\, \frac{B_{K,|l|+1}}{\sqrt{2\pi}}\, e^{i(|l|+1)\phi}\, r^{|l|+1}\, L_K^{|l|+1}(r^2)\, e^{-r^2/2} \;\right\rangle_{r\,dr\,d\phi}$$

We will use raising and lowering operators to evaluate this last expression.

Let $(\tilde{X},\,\tilde{Y}) = (a^{1/4}\,X,\,a^{1/4}\,Y)$ and define

$$A_{\pm} \,=\, \frac{1}{2}\,[\tilde{X} \pm p_{\tilde{Y}} + i(p_{\tilde{X}} \mp \tilde{Y})] \,=\, \frac{1}{2}\,e^{\mp i\phi}(r + \frac{\partial}{\partial r} \pm \frac{L}{r})$$

$$A_{\pm}^{\dagger} \,=\, \frac{1}{2}\,[\tilde{X} \pm p_{\tilde{Y}} - i(p_{\tilde{X}} \mp \tilde{Y})] \,=\, \frac{1}{2}\,e^{\pm i\phi}(r - \frac{\partial}{\partial r} \pm \frac{L}{r}). \tag{4.2.8}$$

The operators $A_{\pm}, A_{\pm}^{\dagger}$ satisfy the commutation relations:

$$[A_+, A_-] = [A_+^{\dagger}, A_-^{\dagger}] = [A_+, A_-^{\dagger}] = [A_-, A_+^{\dagger}] = 0$$

$$[A_+, A_+^{\dagger}] = [A_-, A_-^{\dagger}] = 1$$

It can be shown that the eigenfunctions can be constructed using these raising and lower operators [25]. We have

$$\frac{B_{N,|l|}}{\sqrt{2\pi}}\,e^{i|l|\phi}\,r^{|l|}\,L_N^{|l|}(r^2)\,e^{-r^2/2} \,=\, (-1)^N\,\frac{1}{\sqrt{\pi}}\,\frac{1}{\sqrt{(N+|l|)!\,N!}}\,(A_+^{\dagger})^{N+|l|}\,(A_-^{\dagger})^N\,e^{-r^2/2}.$$

Let $m_N^+ = N + |l|$, $m_N^- = N$, and

$$|\,m_N^+, m_N^-\,\rangle \,=\, \frac{1}{\sqrt{\pi}}\,\frac{1}{\sqrt{m_N^+!\,m_N^-!}}\,(A_+^{\dagger})^{m_N^+}\,(A_-^{\dagger})^{m_N^-}\,e^{-r^2/2},$$

so that $\frac{B_{N,|l|}}{\sqrt{2\pi}}\,e^{i|l|\phi}\,r^{|l|}\,L_N^{|l|}(r^2)\,e^{-r^2/2} \,=\, (-1)^{m_N^-}\,|\,m_N^+, m_N^-\,\rangle$. It can be shown [25], that

$$A_+^{\dagger}\,|\,m^+, m^-\,\rangle \,=\, \sqrt{m^+ + 1}\,\,|\,m^+ + 1, m^-\,\rangle, \qquad A_-^{\dagger}\,|\,m^+, m^-\,\rangle \,=\, \sqrt{m^- + 1}\,\,|\,m^+, m^- + 1\,\rangle,$$

$$A_+\,|\,m^+, m^-\,\rangle \,=\, \sqrt{m^+}\,\,|\,m^+ - 1, m^-\,\rangle, \qquad A_-\,|\,m^+, m^-\,\rangle \,=\, \sqrt{m^-}\,\,|\,m^+, m^- - 1\,\rangle. \tag{4.2.9}$$

We see from (4.2.7), we need to evaluate

$$\frac{(-1)^{m_N^- + m_K^-}}{2}\,\langle\,m_N^+ - 1, m_N^-\,|\,\nu\,\rangle, \tag{4.2.10}$$

where $|\,\nu\,\rangle \,=\, (r\,e^{-i\phi})^2\,|\,m_K^+ + 1, m_K^-\,\rangle$.

Using (4.2.8), we can write $(r\,e^{-i\phi})^2$ in terms of the raising and lowering operators:

$$(r\,e^{-i\phi})^2 \,=\, (A_+ \,+\, A_-^\dagger)^2 \,=\, (A_+)^2 \,+\, (A_-^\dagger)^2 \,+\, 2\,A_+\,A_-^\dagger\,.$$

Then, with (4.2.9) we have

$$\begin{aligned}
|\,\nu\,\rangle \;&=\; \Big(\,(A_+)^2 \,+\, (A_-^\dagger)^2 \,+\, 2\,A_+\,A_-^\dagger\,\Big)\,|\,m_K^+ + 1, m_K^-\,\rangle \\
&=\; \Big(\,\sqrt{(m_K^+ + 1)(m_K^+)}\,|\,m_K^+ - 1, m_K^-\,\rangle \,+\, \sqrt{(m_K^- + 1)(m_K^- + 2)}\,|\,m_K^+ + 1, m_K^- + 2\,\rangle \\
&\qquad\qquad +\, 2\,\sqrt{(m_K^+ + 1)(m_K^- + 1)}\,|\,m_K^+, m_K^- + 1\,\rangle\,\Big)
\end{aligned}$$

Now from (4.2.7) and (4.2.10), we have

$$\begin{aligned}
&(V_{odd})_{N,K} \\
&=\, \frac{(-1)^{m_N^- + m_K^-}}{2}\,\langle\, m_N^+ - 1, m_N^-\,|\,\nu\,\rangle \\
&=\, \frac{(-1)^{m_N^- + m_K^-}}{2}\,\langle\, m_N^+ - 1, m_N^-\,|\,\Big(\,\sqrt{(m_K^+ + 1)(m_K^+)}\,|\,m_K^+ - 1, m_K^-\,\rangle \\
&\quad +\, \sqrt{(m_K^- + 1)(m_K^- + 2)}\,|\,m_K^+ + 1, m_K^- + 2\,\rangle \,+\, 2\,\sqrt{(m_K^+ + 1)(m_K^- + 1)}\,|\,m_K^+, m_K^- + 1\,\rangle\,\Big) \\
&=\, \frac{(-1)^{m_N^- + m_K^-}}{2}\,\Big(\,\sqrt{(m_K^+ + 1)(m_K^+)}\;\delta_{m_N^+, m_K^+}\;\delta_{m_N^-, m_K^-} \\
&\quad +\, \sqrt{(m_K^- + 1)(m_K^- + 2)}\;\delta_{m_N^+ - 1, m_K^+ + 1}\;\delta_{m_N^-, m_K^- + 2} \\
&\quad +\, 2\,\sqrt{(m_K^+ + 1)(m_K^- + 1)}\;\delta_{m_N^+ - 1, m_K^+}\;\delta_{m_N^-, m_K^- + 1}\,\Big)\,.
\end{aligned}$$

Using the definitions of $m_N^+$, and $m_N^-$, we write this last expression in terms of $N,\ K$, and $|l|$:

$$(V_{odd})_{N,K} = \frac{1}{2}\sqrt{(K+|l|+1)(K+|l|)}\,\delta_{N,K} + \frac{1}{2}\sqrt{(K+1)(K+2)}\,\delta_{N,K+2} - \sqrt{(K+|l|+1)(K+1)}\,\delta_{N,K+1}.$$

### 4.2.2 The Non-Degenerate Perturbation Calculation

Recall from (4.2.4), for fixed $|l| \neq 0$, the lowest lying eigenvalue of $H_0^{[|l|]}$ is $E_0^{0,|l|} = |l|$. It is non-degenerate, with eigenfunction written in terms of our basis as

$$\Psi_0^{0,|l|} = \left( \begin{pmatrix} 1 \\ 0 \\ 0 \\ . \\ . \end{pmatrix}, \begin{pmatrix} 0 \\ 0 \\ 0 \\ . \\ . \end{pmatrix} \right).$$

This eigenvalue and eigenvector serve as the zeroth order coefficients in our perturbation series given by (4.2.3). Plugging the expansions in (4.2.3) into the equation

$$(H_0^{|l|} + \tilde{b}\,\tilde{V})\,\Psi^{0,|l|}(\tilde{b}) = E^{0,|l|}(\tilde{b})\,\Psi^{0,|l|}(\tilde{b})$$

and equating orders of $\tilde{b}$ gives the usual perturbation equations. Since the matrix elements of $V_{odd}$ and $V_{even}$ vanish except near the diagonal, we are able to calculate the exact perturbation coefficients, even to high orders. Using the *Mathematica* software package, we easily

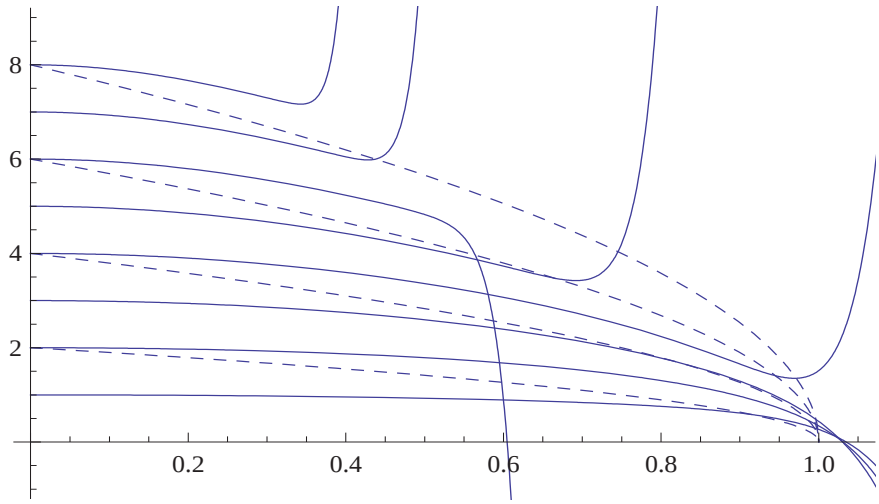


Figure 4.1: A plot of the perturbation series versus $\tilde{b}$, of the non-degenerate, lowest lying eigenvalue of $H_{UZ}^{[|l|]}$ up to order 28, for $|l| = 1, 2, \cdots, 8$. The dashed curves are $(2N+2)\sqrt{1-\tilde{b}}$, for $N = 0, 1, 2, 3$, which are the $l = 0$ states that we have solved for exactly.

computed the exact perturbation coefficients up to 28th order for the non-degenerate, lowest lying eigenvalue $E^{0,|l|}$, for several values of $|l|$ (See Figure 4.1).

Recall that we are concerned with the case where $0 < b < a$, so that $0 < \tilde{b} = \frac{b}{a} < 1$. The functions $E^{0,|l|}(\tilde{b})$ likely do not exist as eigenvalues of $H_{UZ}^{[|l|]}$ if $\tilde{b} \geq 1$. Seemingly the radii of convergence of the series are smaller as $|l|$ increases. It appears that for $|l| = 1, 2$, and 3 the radius of convergence is likely close to 1 (if not larger). For $|l| > 4$, the series are behaving erratically for values of $\tilde{b} < 1$. The $|l| = 4$ case appears to be borderline, with radius of convergence possibly only slightly smaller than 1. This divergent behavior was seen even from the low order coefficients for the larger values of $|l|$. The singularities are likely caused by avoided crossings between two states with the same value of $|l|$, as suggested in [3, 19, 24].

We highlight the crossing between the $|l| = 1$ state and the lowest lying $l = 0$ state near $\tilde{b} = 0.925$. Recall that for $l \neq 0$, the eigenvalue $E^{J,|l|}$ of $H_{UZ}^{[|l|]}$ is also an eigenvalue of $H_{UZ}^{[-|l|]}$. Together these states correspond to a degenerate eigenvalue of the original operator $\mathbb{H}_2$. The $l = 0$ states are all non-degenerate for $b > 0$. So, this crossing implies that the ground state of $\mathbb{H}_2$ is degenerate for approximately $0 < b < 0.925a$ and non-degenerate for $0.925a < b < 1$.

### 4.2.3 The Degenerate Perturbation Calculation

Recall from (4.2.4), that only the ground state of $H_0^{[|l|]}$ is non-degenerate if $|l| \neq 0$. In the perturbation calculation described in section 4.2.2, we used regular non-degenerate perturbation theory to obtain the perturbation coefficients for these eigenvalues. From (4.2.5), we have that for fixed $|l| \neq 0$, $H_0^{[|l|]}$ also has two-fold degenerate eigenvalues of $E_0^{N,|l|} = 2N + |l|$ for $N = 1, 2, \cdots$ So we must use degenerate perturbation theory to calculate the perturbation coefficients of these eigenvalues. Recall from (4.2.5), the degenerate pair of eigenfunctions corresponding to $E_0^{N,|l|}$ are given by $\Psi_{0,up}^{N,|l|}$ and $\Psi_{0,dwn}^{N,|l|}$. Written in terms of our basis as in (4.2.6), these functions are given by

$$\Psi_{0,up}^{N,|l|} : \qquad a_k = \begin{cases} 1, \text{ if } k = N \\ 0, \text{ otherwise} \end{cases}, \qquad b_k = 0 \text{ for all } k$$

and

$$\Psi_{0,dwn}^{N,|l|} : \qquad a_k = 0 \text{ for all } k, \qquad b_k = \begin{cases} 1, \text{ if } k = N-1 \\ 0, \text{ otherwise} \end{cases}.$$

Employing degenerate perturbation theory in the usual manner, we find there is splitting that

occurs at first order. One of the correct linear combinations of the zeroth order eigenfunctions is:

$$a_k^- = \begin{cases} \frac{1}{\sqrt{2}}\ , \text{ if } k = N \\ \\ 0, \text{ otherwise} \end{cases}\ , \qquad b_k^- = \begin{cases} \frac{1}{\sqrt{2}}\ , \text{ if } k = N-1 \\ \\ 0, \text{ otherwise} \end{cases}\ ,$$

with corresponding first order energy coefficient

$$E_1^{N,|l|} \ = \ \frac{1}{2}\left(V_{odd}\right)_{N,N-1} \ + \ \frac{1}{2}\left(V_{even}\right)_{N-1,N} \ = \ -\sqrt{N(N+|l|)}\ .$$

The other correct linear combination of the zeroth order eigenfunctions is

$$a_k^+ = \begin{cases} \frac{1}{\sqrt{2}}, \text{ if } k = N \\ \\ 0, \text{ otherwise} \end{cases}\ , \qquad b_k^+ = \begin{cases} -\frac{1}{\sqrt{2}}, \text{ if } k = N-1 \\ \\ 0, \text{ otherwise} \end{cases}\ ,$$

with corresponding first order energy coefficient

$$E_1^{N,|l|} \ = \ -\frac{1}{2}\left(V_{odd}\right)_{N,N-1} \ - \ \frac{1}{2}\left(V_{even}\right)_{N-1,N} \ = \ \sqrt{N(N+|l|)}\ .$$

Armed with the proper linear combinations we can now proceed as in the non-degenerate case. Using the *Mathematica* software package, we easily computed the exact perturbation coefficients up to 12th order for the first few eigenvalues $E^{N,|l|}$ that are degenerate at zeroth order, for several values of $|l|$ (See Figures 4.2, 4.3, 4.4).

While the splitting is nicely illustrated, we see that all of the series likely have radii of convergence well below 1. The radius of convergence appears to decrease as $|l|$ or $N$ increase. The divergent behavior was seen even at low orders of the perturbation coefficients.

We also used an elementary finite difference scheme to approximate the eigenvalues at several values of $\tilde{b}$, for $0 < \tilde{b} < 1$. The results are given in Figure 4.5. The plot was generated by

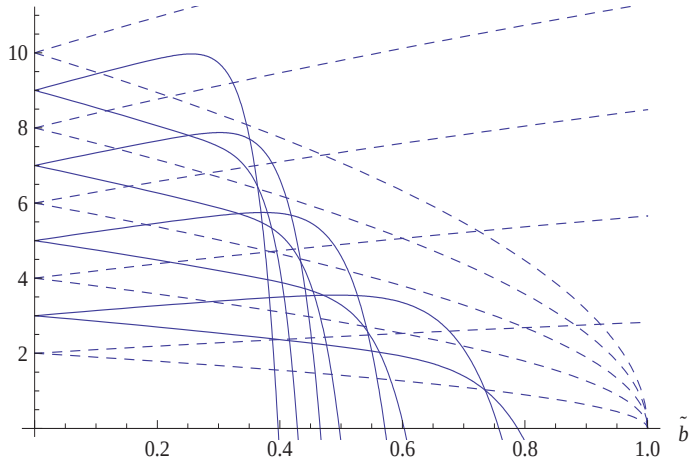


Figure 4.2: A plot of the perturbation series versus $\tilde{b}$ up to order 12, of the first 8 eigenvalues of $H_{UZ}^{[|l|]}$ that are degenerate at zeroth order, for $|l| = 1$. The dashed curves are $(2N+2)\sqrt{1-\tilde{b}}$ and $(2N+2)\sqrt{1+\tilde{b}}$, for $N = 0, 1, 2, 3, 4$, which are the $l = 0$ states that we have solved for exactly.

approximating the lowest lying 17 eigenvalues for a fixed $\tilde{b}$ value, then the value of $\tilde{b}$ was changed and the lowest 17 eigenvalues were calculated again. This was repeated at steps of $\Delta\tilde{b} = .01$ from $0 \leq \tilde{b} < .99$. Recall that the $l = 0$ states were exactly solvable. For comparison, the exact values of the lowest lying $l = 0$ states were plotted as dotted curves. We see that the finite difference scheme approximates these eigenvalues so well that the dotted curve are hardly distinguishable from the finite difference approximation of these eigenvalues. Near $\tilde{b} = 0$, the 17 eigenvalues that are being approximated can be identified by their values at $\tilde{b} = 0$:

1. The curve that has value 1 at $\tilde{b} = 0$ is actually two overlapping eigenvalues of $\mathbb{H}_2$

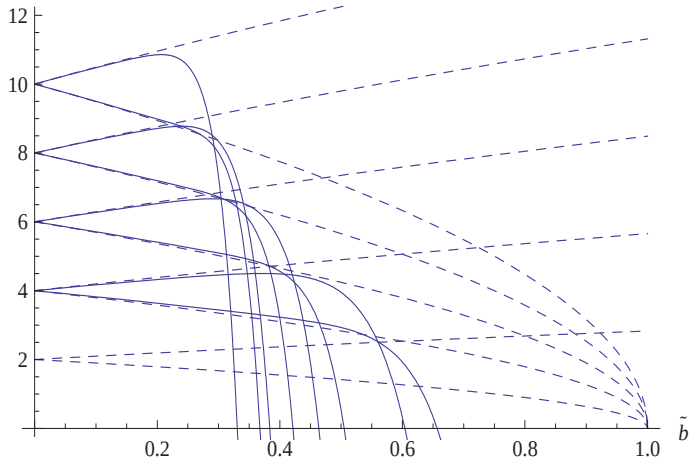


Figure 4.3: A plot of the perturbation series versus $\tilde{b}$ up to order 12, of the first 8 eigenvalues of $H_{UZ}^{[|l|]}$ that are degenerate at zeroth order, for $|l| = 2$. The dashed curves are $(2N+2)\sqrt{1-\tilde{b}}$ and $(2N+2)\sqrt{1+\tilde{b}}$, for $N = 0, 1, 2, 3, 4$, which are the $l = 0$ states that we have solved for exactly.

corresponding to the degenerate pair of lowest lying $|l| = 1$ states, one for $l = 1$ and $l = -1$.

2. There are three curves that have value 2 at $\tilde{b} = 0$. Two of the curves are the non-degenerate $l = 0$ states (one increases with $\tilde{b}$ and one decreases with $\tilde{b}$). The other curve is two overlapping eigenvalues corresponding to the degenerate pair of lowest lying $|l| = 2$ states, one for $l = 2$ and $l = -2$. These curves together account for four eigenvalues of $\mathbb{H}_2$.

3. There are three curves that have value 3 at $\tilde{b} = 0$. Two of the curves are overlapping degenerate $|l| = 1$ states, (one degenerate pair increases with $\tilde{b}$ and one degenerate

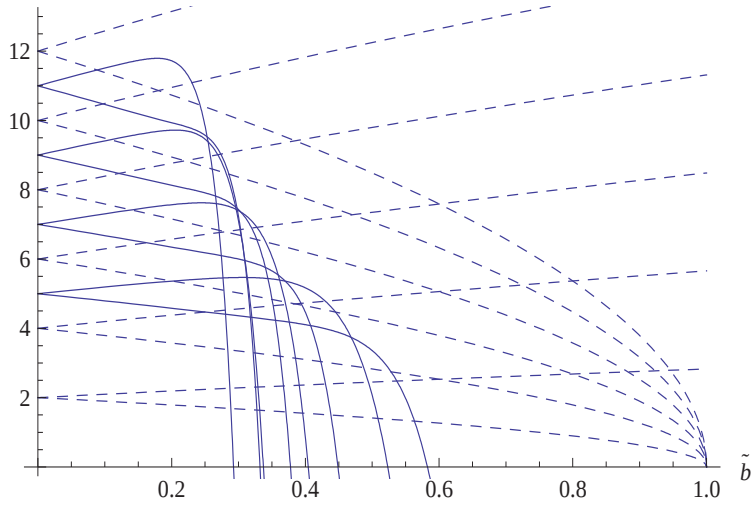


Figure 4.4: A plot of the perturbation series versus $\tilde{b}$ up to order 12, of the first 8 eigenvalues of $H_{UZ}^{[|l|]}$ that are degenerate at zeroth order, for $|l| = 3$. The dashed curves are $(2N+2)\sqrt{1-\tilde{b}}$ and $(2N+2)\sqrt{1+\tilde{b}}$, for $N = 0, 1, 2, 3, 4, 5$, which are the $l = 0$ states that we have solved for exactly.

pair decreases with $\tilde{b}$). The other curve an overlapping degenerate pair of lowest lying $|l| = 2$ states. These curves together account for six eigenvalues of $\mathbb{H}_2$.

4. There are three curves that have value 4 at $\tilde{b} = 0$. One of the curves is a non-degenerate $l = 0$ state, one is a degenerate pair of $|l| = 2$ states, and one is a degenerate pair of $|l| = 4$ states. Together these curves account for five eigenvalues of $\mathbb{H}_2$.

This plot supports the claim that a crossing occurs involving the ground state near $\tilde{b} = 0.925$. While the finite difference scheme is crude, we are inclined to trust the qualitative features of the results considering the lowest of the exactly solvable $l = 0$ eigenvalues were so well

approximated, even near $\tilde{b} = 1$ as seen in the figure. We note that as $\tilde{b}$ increases from zero, avoided crossings involving states with the same value of $|l|$ occur, as well as crossings involving states with different values of $|l|$. When the uppermost curve is involved with such a phenomenon it will appear to change behavior suddenly without reason, but this is only because we can only see the lowest 17 eigenvalues at each $\tilde{b}$.

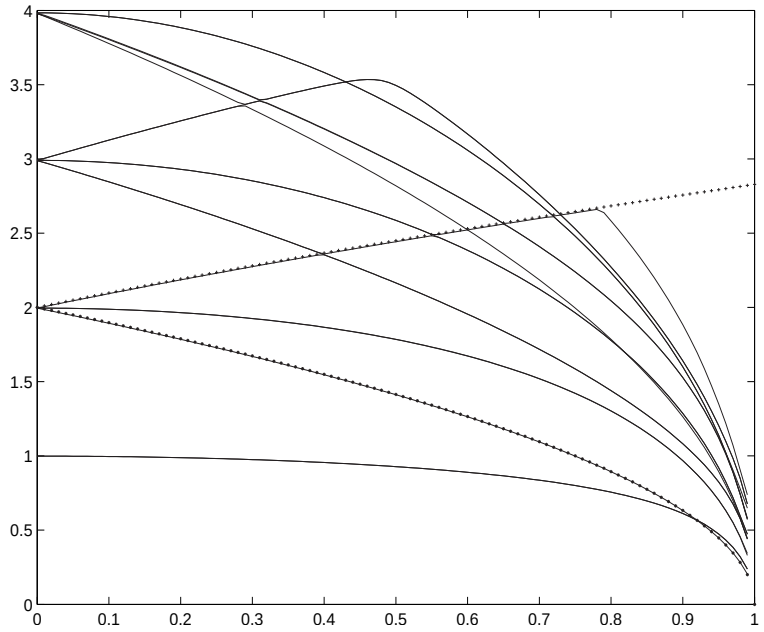


Figure 4.5: A plot of lowest 17 eigenvalues of $\mathbb{H}_2$ as a function of $\tilde{b}$, on $0 < \tilde{b} < 1$, as approximated by a finite difference scheme. The dotted curves are $2\sqrt{1-\tilde{b}}$ and $2\sqrt{1+\tilde{b}}$, which are the lowest of the $l = 0$ states that we have solved for exactly.

# Chapter 5

# Degeneracy of the Quasimode Energies

The eigenfunctions of $\mathbb{H}_2$ provide the zeroth order states for the quasimode expansion. Recall that if $\begin{pmatrix} f^{(0)} \\ g^{(0)} \end{pmatrix}$ is an eigenfunction of $\mathbb{H}_2$, we have derived perturbation formulas in chapter 2 that determine the functions $f^{(k)}(X, Y)$, $g^{(k)}(X, Y)$, and $\psi_{\perp}^{(k)}(X, Y)$ that enter in equation

(2.0.1) as the asymptotic series

$$\Phi_\epsilon \;=$$

$$\Psi_1(\epsilon\, X,\, \epsilon\, Y)\, \sum_{k=0}^{\infty} f^{(k)}(X,\, Y)\, \epsilon^k \;+\; \Psi_2(\epsilon\, X,\, \epsilon\, Y)\, \sum_{k=0}^{\infty} g^{(k)}(X,\, Y)\, \epsilon^k \;+\; \sum_{k=0}^{\infty} \psi_\perp^{(k)}(X,\, Y)\, \epsilon^k$$

$$= \sum_{k=0}^{\infty} \epsilon^k \left( \sum_{j=0}^{k} \left( \Psi_1^{(j)}(X,\, Y)\, f^{(k-j)}(X,\, Y) \;+\; \Psi_2^{(j)}(X,\, Y)\, g^{(k-j)}(X,\, Y) \right) \;+\; \psi_\perp^{(k)}(X,\, Y) \right),$$

$$=: \sum_{k=0}^{\infty} \epsilon^k\, \Phi_k,$$

where $\{\Psi_1(\epsilon\, X,\, \epsilon\, Y),\ \Psi_2(\epsilon\, X,\, \epsilon\, Y)\}$ is the electronic eigenfunction basis. The $f^{(k)}$ and $g^{(k)}$ have no electronic dependence (they are scalar functions) and $\psi_\perp^{(k)}$ has both electronic and nuclear dependence.

Recall that for $|l| \neq 0$, if $\begin{pmatrix} f^{[|l|]}(r) \\ \\ g^{[|l|]}(r) \end{pmatrix}$ is an eigenfunction of $H_{UZ}^{[|l|]}$ with eigenvalue $E$, then

$\begin{pmatrix} f^{[-|l|]}(r) \\ \\ g^{[-|l|]}(r) \end{pmatrix} = \begin{pmatrix} g^{[|l|]}(r) \\ \\ f^{[|l|]}(r) \end{pmatrix}$ is an eigenfunction of $H_{UZ}^{[-|l|]}$ with eigenvalue $E$. So if $|l| \neq 0$, we have two-fold degenerate eigenfunctions of $\mathbb{H}_2$ of the form (recall $r = a^{1/4}\rho$)

$$\begin{pmatrix} F^{(0)} \\ \\ G^{(0)} \end{pmatrix} \;=:\; U\, Z \begin{pmatrix} e^{i|l|\phi}\, f^{[|l|]}(r) \\ \\ e^{i|l|\phi}\, g^{[|l|]}(r) \end{pmatrix}$$

$$= \frac{1}{\sqrt{2}} \begin{pmatrix} e^{i(|l|-1)\phi}\, f^{[|l|]}(r) \;+\; e^{i(|l|+1)\phi}\, g^{[|l|]}(r) \\ \\ i\, \left( e^{i(|l|-1)\phi}\, f^{[|l|]}(r) \;-\; e^{i(|l|+1)\phi}\, g^{[|l|]}(r) \right) \end{pmatrix} \qquad (5.0.1)$$

and

$$U\,Z\begin{pmatrix} e^{-i|l|\phi}\,g^{[|l|]}(r) \\ \\ e^{-i|l|\phi}\,f^{[|l|]}(r) \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} e^{-i(|l|-1)\phi}\,f^{[|l|]}(r) + e^{-i(|l|+1)\phi}\,g^{[|l|]}(r) \\ \\ -i\left(e^{-i(|l|-1)\phi}\,f^{[|l|]}(r) - e^{-i(|l|+1)\phi}\,g^{[|l|]}(r)\right) \end{pmatrix}$$
$$= \begin{pmatrix} \overline{F^{(0)}} \\ \\ \overline{G^{(0)}} \end{pmatrix} \tag{5.0.2}$$

By taking appropriate linear combinations, these degenerate zeroth order functions lead to two orthogonal quasimodes using the perturbation formulas of chapter 2, possibly degenerate (no splitting) or non-degenerate (splitting).

We adopt the following nomenclature: We refer to the eigenfunctions of $\mathbb{H}_2$ that arise from the eigenfunctions of $H_{UZ}^{[|l|]}$, where $|l| \neq 0$, as $+|l|$ states. We refer to the eigenfunctions of $\mathbb{H}_2$ that arise from the eigenfunctions of $H_{UZ}^{[-|l|]}$, where $|l| \neq 0$, as $-|l|$ states. We refer to the eigenfunctions of $\mathbb{H}_2$ that arise from the eigenfunctions of $H_U^{[|l|=0]}$ as $|l| = 0$ states.

**Theorem 5.0.1.** *Let $L_z^{TOT}$ be the operator of total angular momentum around the z-axis and $0 < \tilde{b} < 1$. Then:*

1. *For $l \neq 0$, each $+|l|$ state generates a quasimode $\Phi_\epsilon^A$ of $H(\epsilon)$ that satisfies $L_z^{TOT}\,\Phi_\epsilon^A = |l|\,\Phi_\epsilon^A$. The corresponding degenerate $-|l|$ state generates a quasimode $\Phi_\epsilon^B$ that satisfies $\Phi_\epsilon^B = \overline{\Phi}_\epsilon^A$ and $L_z^{TOT}\,\Phi_\epsilon^B = -|l|\,\Phi_\epsilon^B$. The $\Phi_\epsilon^A$ and $\Phi_\epsilon^B$ quasimodes are orthogonal, and asymptotic to two-fold degenerate eigenfunctions of $H(\epsilon)$. We see that linear combinations of the these two-fold degenerate $\pm|l|$ states also generate valid quasimodes.*

2. *Each $|l| = 0$ state generates a quasimode that is asymptotic to a non-degenerate eigenfunction of $H(\epsilon)$.*

*In either case, the zeroth order of the electronic eigenfunction basis vectors $\Psi_1(0,0)$ and $\Psi_2(0,0)$ are linear combinations of eigenfunctions of $L_z^{el}$ with eigenvalues $\pm 1$.*

Remark:

The physical meaning of $l$ is now apparent. It corresponds to the total angular momentum about the z-axis of the wave function being approximated. From the proof to follow, it will be clear that the zeroth order $\Phi_0$ of a quasimode, can be constructed to satisfy $L_z^{TOT}\,\Phi_0 = l_z^{TOT}\,\Phi_0$. In this case it is a linear combination of two states of the form

$$\Xi_{l_z^{TOT}-1}(\vec{r}_{nuc})\,\tilde{\Psi}_+(\vec{r}_{el}) \quad \text{and} \quad \Xi_{l_z^{TOT}+1}(\vec{r}_{nuc})\,\tilde{\Psi}_-(\vec{r}_{el}),$$

where

$$L_z^{el}\,\tilde{\Psi}_+ = \tilde{\Psi}_+, \qquad L_z^{el}\,\tilde{\Psi}_- = -\tilde{\Psi}_-,$$

$$L_z^{nuc}\,\Xi_{l_z^{TOT}-1} = (l_z^{TOT}-1)\,\Xi_{l_z^{TOT}-1}, \qquad L_z^{nuc}\,\Xi_{l_z^{TOT}+1} = (l_z^{TOT}+1)\,\Xi_{l_z^{TOT}+1}.$$

**Proof:**

Since $[H(\epsilon),\ L_z^{TOT}] = 0$, we know that the true eigenfunctions $\Psi(\epsilon)$ of $H(\epsilon)$ can be constructed to satisfy $L_z^{TOT}\,\Psi(\epsilon) = l_z^{TOT}\,\Psi(\epsilon)$, at each $\epsilon$ in a neighborhood of 0, for some $l_z^{TOT} \in \mathbb{Z}$. This implies that $L_z^{TOT}\,\overline{\Psi(\epsilon)} = -\,l_z^{TOT}\,\overline{\Psi(\epsilon)}$, since $\overline{L_z^{TOT}\,\Psi(\epsilon)} = -\,L_z^{TOT}\,\overline{\Psi(\epsilon)}$. We can therefore arrange so that the asymptotic series $\Phi_\epsilon = \sum_{k=0}^{\infty}\epsilon^k\Phi_k$ satisfies $L_z^{TOT}\,\Phi_\epsilon = l_z^{TOT}\,\Phi_\epsilon$

at each order of $\epsilon$. We then know that each order $\Phi_k$ of the quasimode, and its complex conjugate, are eigenfunctions of $L_z^{TOT}$ with eigenvalues $l_z^{TOT}$ and $-l_z^{TOT}$ respectively.

We now separate into two cases:

**Case 1:** $|l| \neq 0$

In this case, we have degenerate zeroth order states of the form in (5.0.1) and (5.0.2). Regardless of whether splitting occurs, assume that we depart from zeroth order with a correct linear combination $\begin{pmatrix} f^{(0)} \\ \\ g^{(0)} \end{pmatrix} = \alpha \begin{pmatrix} F^{(0)} \\ \\ G^{(0)} \end{pmatrix} + \beta \begin{pmatrix} \overline{F^{(0)}} \\ \\ \overline{G^{(0)}} \end{pmatrix}$, so that this leads to a valid quasimode, which satisfies $L_z^{TOT}\,\Phi_\epsilon = l_z^{TOT}\,\Phi_\epsilon$. Then the zeroth order $\Phi_0$ must also be an eigenfunction of $L_z^{TOT}$ with eigenvalue $l_z^{TOT}$. The $\Phi_0$ function is given by

$$\begin{aligned}
\Phi_0 &= \Psi_1(0,0)\,f^{(0)} + \Psi_2(0,0)\,g^{(0)} \\
&= \Psi_1(0,0)\left(\alpha\,F^{(0)} + \beta\,\overline{F^{(0)}}\right) + \Psi_2(0,0)\left(\alpha\,G^{(0)} + \beta\,\overline{G^{(0)}}\right) \\
&= \alpha\left[e^{i(|l|-1)\phi}\,f^{[|l|]}\,(\Psi_1(0,0) + i\,\Psi_2(0,0)) + e^{i(|l|+1)\phi}\,g^{[|l|]}\,(\Psi_1(0,0) - i\,\Psi_2(0,0))\right] \\
&+ \beta\left[e^{-i(|l|-1)\phi}\,f^{[|l|]}\,(\Psi_1(0,0) - i\,\Psi_2(0,0)) + e^{-i(|l|+1)\phi}\,g^{[|l|]}\,(\Psi_1(0,0) + i\,\Psi_2(0,0))\right].
\end{aligned}$$

We now plug this into the equation $L_z^{TOT}\,\Phi_0 \,-\, l_z^{TOT}\,\Phi_0 \,=\, 0$:

$$\begin{aligned}
0 \,=\, \alpha\, \Big\{\, e^{i(|l|-1)\phi}\, f^{[|l|]}\, \Big[L_z^{el}\, \left(\Psi_1(0,0) \,+\, i\,\Psi_2(0,0)\right) \\
+ \left(l - 1 - l_z^{TOT}\right) \left(\Psi_1(0,0) \,+\, i\,\Psi_2(0,0)\right)\Big] \\
+\, e^{i(|l|+1)\phi}\, g^{[|l|]}\, \Big[L_z^{el}\, \left(\Psi_1(0,0) \,-\, i\,\Psi_2(0,0)\right) \\
+ \left(l + 1 - l_z^{TOT}\right) \left(\Psi_1(0,0) \,-\, i\,\Psi_2(0,0)\right)\Big]\Big\} \\
+\, \beta\, \Big\{\, e^{-i(|l|-1)\phi}\, f^{[|l|]}\, \Big[L_z^{el}\, \left(\Psi_1(0,0) \,-\, i\,\Psi_2(0,0)\right) \\
+ \left(-l + 1 - l_z^{TOT}\right) \left(\Psi_1(0,0) \,-\, i\,\Psi_2(0,0)\right)\Big] \\
+\, e^{-i(|l|+1)\phi}\, g^{[|l|]}\, \Big[L_z^{el}\, \left(\Psi_1(0,0) \,+\, i\,\Psi_2(0,0)\right) \\
+ \left(-l - 1 - l_z^{TOT}\right) \left(\Psi_1(0,0) \,+\, i\,\Psi_2(0,0)\right)\Big]\Big\}
\end{aligned} \tag{5.0.3}$$

For $|l| \geq 2$, we take projections of (5.0.3) along $e^{i(|l|-1)\phi}\, f^{[|l|]}$, $e^{i(|l|+1)\phi}\, g^{[|l|]}$, $e^{-i(|l|-1)\phi}\, f^{[|l|]}$, and $e^{-i(|l|+1)\phi}\, g^{[|l|]}$, and obtain the following four equations:

$$L_z^{el}\, \left(\Psi_1(0,0) \,+\, i\,\Psi_2(0,0)\right) \,=\, \left(l_z^{TOT} - |l| + 1\right) \left(\Psi_1(0,0) \,+\, i\,\Psi_2(0,0)\right) \tag{5.0.4}$$

$$L_z^{el}\, \left(\Psi_1(0,0) \,-\, i\,\Psi_2(0,0)\right) \,=\, \left(l_z^{TOT} - |l| - 1\right) \left(\Psi_1(0,0) \,-\, i\,\Psi_2(0,0)\right) \tag{5.0.5}$$

$$L_z^{el}\, \left(\Psi_1(0,0) \,-\, i\,\Psi_2(0,0)\right) \,=\, \left(l_z^{TOT} + |l| - 1\right) \left(\Psi_1(0,0) \,-\, i\,\Psi_2(0,0)\right) \tag{5.0.6}$$

$$L_z^{el}\, \left(\Psi_1(0,0) \,+\, i\,\Psi_2(0,0)\right) \,=\, \left(l_z^{TOT} + |l| + 1\right) \left(\Psi_1(0,0) \,+\, i\,\Psi_2(0,0)\right) \tag{5.0.7}$$

Equations (5.0.4) and (5.0.5) hold as long as $\alpha \neq 0$ and equations (5.0.6) and (5.0.7) hold as long as $\beta \neq 0$. By combining (5.0.4) and (5.0.7) we obtain $l_z^{TOT} - |l| + 1 = l_z^{TOT} + |l| + 1$ which

contradicts our assumption that $|l| \neq 0$. So, either $\alpha = 0$ or $\beta = 0$. Assume that $\beta = 0$ and take $\alpha = 1$, so that equations (5.0.4) and (5.0.5) still hold. Since $L_z^{TOT}\,\Phi_0 = l_z^{TOT}\,\Phi_0$, we know that $L_z^{TOT}\,\overline{\Phi_0} = -l_z^{TOT}\,\overline{\Phi_0}$. Using this equation and projecting along $e^{-i(|l|-1)\phi}\,f^{[|l|]}$ and $e^{-i(|l|+1)\phi}\,g^{[|l|]}$, we obtain equations similar to (5.0.6) and (5.0.7), but with $l_z^{TOT}$ replaced by $-l_z^{TOT}$:

$$L_z^{el}\,(\Psi_1(0,0) - i\,\Psi_2(0,0)) = (-l_z^{TOT} + |l| - 1)\,(\Psi_1(0,0) - i\,\Psi_2(0,0)) \tag{5.0.8}$$

$$L_z^{el}\,(\Psi_1(0,0) + i\,\Psi_2(0,0)) = (-l_z^{TOT} + |l| + 1)\,(\Psi_1(0,0) + i\,\Psi_2(0,0))\,. \tag{5.0.9}$$

By combining (5.0.4) and (5.0.9) we obtain $l_z^{TOT} = |l|$ and these equations now reduce to

$$L_z^{el}\,(\Psi_1(0,0) - i\,\Psi_2(0,0)) = -\,(\Psi_1(0,0) - i\,\Psi_2(0,0)) \tag{5.0.10}$$

$$L_z^{el}\,(\Psi_1(0,0) + i\,\Psi_2(0,0)) = \Psi_1(0,0) + i\,\Psi_2(0,0). \tag{5.0.11}$$

By repeating the argument with $\alpha = 0,\ \beta = 1$, we would instead find $l_z^{TOT} = -|l|$. From this analysis we see that $\alpha = 1,\ \beta = 0$ and $\alpha = 0,\ \beta = 1$ are correct linear combinations that will generate two orthogonal quasimodes $\Phi_\epsilon^A$ and $\Phi_\epsilon^B$ respectively. These quasimodes satisfy $L_z^{TOT}\,\Phi_\epsilon^A = |l|\Phi_\epsilon^A$ and $L_z^{TOT}\,\Phi_\epsilon^B = -|l|\,\Phi_\epsilon^B$ and that they are asymptotic to eigenfunctions of $H(\epsilon)$. We note that $\Phi_0^B = \overline{\Phi}_0^A$. Since $H(\epsilon)$ commutes with complex conjugation, we have that $\overline{\Phi}_\epsilon^A$ is also asymptotic to an eigenfunction with the same eigenvalue as $\Phi_\epsilon^A$. Since quasimodes are determined by their zeroth order eigenfunctions through the perturbation formulas of chapter 2, this imples that $\Phi_\epsilon^B = \overline{\Phi}_\epsilon^A$ since $\Phi_0^B = \overline{\Phi}_0^A$. So, the $\Phi_\epsilon^A$ and $\Phi_\epsilon^B$ correspond to a degenerate pair and we see that no splitting occurs in the perturbation expansion. As a

result, any linear combination would be a correct one. The $\Phi_\epsilon^A$ and $\Phi_\epsilon^B = \overline{\Phi}_\epsilon^A$ generated by the combinations $\alpha = 1,\ \beta = 0$ and $\alpha = 0,\ \beta = 1$ respectively, are the quasimodes that satisfy $L_z^{TOT}\,\Phi_\epsilon^A = |l|\,\Phi_\epsilon^A$ and $L_z^{TOT}\,\Phi_\epsilon^B = -|l|\,\Phi_\epsilon^B$.

If $|l| = 1$, we take projections of (5.0.3) along $f^{[1]}$, $e^{2i\phi}\,g^{[1]}$, and $e^{-2i\phi}\,g^{[|1|]}$, and obtain the following three equations:

$$0 = \left(L_z^{el} - l_z^{TOT}\right)\left[\alpha\,(\Psi_1(0,0) + i\,\Psi_2(0,0)) + \beta\,(\Psi_1(0,0) - i\,\Psi_2(0,0))\right] \tag{5.0.12}$$

$$L_z^{el}\,(\Psi_1(0,0) - i\,\Psi_2(0,0)) = (l_z^{TOT} - 2)\,(\Psi_1(0,0) - i\,\Psi_2(0,0)) \tag{5.0.13}$$

$$L_z^{el}\,(\Psi_1(0,0) + i\,\Psi_2(0,0)) = (l_z^{TOT} + 2)\,(\Psi_1(0,0) + i\,\Psi_2(0,0)) \tag{5.0.14}$$

Equation (5.0.13) holds as long as $\alpha \neq 0$ and equation (5.0.14) holds as long as $\beta \neq 0$. If we assume both $\alpha$ and $\beta$ are non-zero and plug (5.0.13) and (5.0.14) into equation (5.0.12), we obtain

$$0 = 2\left[\alpha\,(\Psi_1(0,0) + i\,\Psi_2(0,0)) - \beta\,(\Psi_1(0,0) - i\,\Psi_2(0,0))\right].$$

By taking the projection of this equation in $\mathcal{H}_{el}$ along $\Psi_1(0,0) + i\,\Psi_2(0,0)$, we find that $\alpha = 0$ which is a contradiction. So, either $\alpha$ or $\beta$ must be zero. By proceeding in a similar manner to the analysis in the $|l| \geq 2$ case above, we would obtain $l_z^{TOT} = 1$ if $\alpha = 1,\ \beta = 0$ and $l_z^{TOT} = -1$ if $\alpha = 0,\ \beta = 1$. In either case, we would obtain (5.0.10) and (5.0.11) and the desired results follow as in the $|l| \geq 2$ case above.

**Case 2:** $|l| = 0$

If $|l| = 0$, we have non-degenerate eigenfunctions of $\mathbb{H}_2$ of the form in equations (4.1.1) or (4.1.2). The zeroth order of the quasimode $\Phi_0$ takes the form

$$\begin{aligned}\Phi_0 &= (\Psi_1(0,0)\cos(\phi) + \Psi_2(0,0)\sin(\phi))\, F(\rho) \\ &= \frac{1}{2} F(\rho)\left[e^{i\phi}\,(\Psi_1(0,0) - i\,\Psi_2(0,0)) + e^{-i\phi}\,(\Psi_1(0,0) + i\,\Psi_2(0,0))\right] \qquad (5.0.15)\end{aligned}$$

or

$$\begin{aligned}\Phi_0 &= (-\Psi_1(0,0)\sin(\phi) + \Psi_2(0,0)\cos(\phi))\, G(\rho) \\ &= \frac{i}{2} G(\rho)\left[e^{i\phi}\,(\Psi_1(0,0) - i\,\Psi_2(0,0)) - e^{-i\phi}\,(\Psi_1(0,0) + i\,\Psi_2(0,0))\right]. \qquad (5.0.16)\end{aligned}$$

In either case, we see that $\Phi_0$ is real. Then from $L_z^{TOT}\,\Phi_0 = l_z^{TOT}\,\Phi_0$ and $L_z^{TOT}\,\overline{\Phi}_0 = -l_z^{TOT}\,\overline{\Phi}_0$, it is clear that $l_z^{TOT} = 0$ in this case. By plugging either (5.0.15) or (5.0.16) into $L_z^{TOT}\,\Phi_0 = 0$ and taking projections along $e^{i\phi}$ and $e^{-i\phi}$ in a manner similar to the $|l| \neq 0$ case, we obtain the same relations for the electronic basis vectors at zeroth order given by equations (5.0.10) and (5.0.11). □

**Corollary 5.0.2.** *For all $\tilde{b}$ in some interval $(0, \delta)$, if $\epsilon$ is sufficiently small, the ground state of $H(\epsilon)$ (corresponding to the R-T pair of states we are considering) is degenerate.*

**Proof:**

From our perturbation analysis, we have that for all $\tilde{b}$ in some interval $(0, \delta)$, the ground state of $\mathbb{H}_2$ is degenerate, arising from the $l = \pm 1$ states of $H_{UZ}$. The previous theorem tells us that these generate a degenerate pair of quasimodes $\Phi_\epsilon^A$ and $\Phi_\epsilon^B$ that satisfy $L_z^{TOT}\,\Phi_\epsilon^A = \Phi_\epsilon^A$,

$\Phi_\epsilon^B = \overline{\Phi}_\epsilon^A$ and $L_z^{TOT}\,\Phi_\epsilon^B = -\,\Phi_\epsilon^B$. If the quasimode energy lies below the essential spectrum, then this will correspond to the lowest lying eigenvalue of $H(\epsilon)$ corresponding to the R-T pair. $\square$

Our perturbation calculations suggest that there is a crossing involving this eigenvalue with the lowest lying $l = 0$ eigenvalue, somewhere near $\tilde{b} = 0.925$. The ground state seemingly corresponds to these $l = \pm 1$ states for $0 < \tilde{b} < 0.925$ and corresponds to the non-degenerate, lowest lying $l = 0$ state for $0.925 < \tilde{b} < 1$. We now prove that the ground state of $\mathbb{H}_2$ cannot arise from any other $|l|$ states.

**Proposition 5.0.3.** *Let $0 < \tilde{b} < 1$. Then the ground state of $H_{UZ}$ is either an $|l| = 1$ state or an $l = 0$ state.*

**Proof:**

As previously mentioned, since $[H_{UZ}, L_z^{nuc}] = 0$ we assume $\Psi = \begin{pmatrix} e^{\pm i|l|\phi}\,\psi_1(r) \\ \\ e^{\pm i|l|\phi}\,\psi_2(r) \end{pmatrix}$ and then $H_{UZ}$ reduces to

$$H_{UZ}^{[\pm|l|]} = \begin{pmatrix} -\frac{1}{2}\frac{\partial^2}{\partial r^2} - \frac{1}{2r}\frac{\partial}{\partial r} + \frac{1}{2}r^2 + \frac{(|l| \mp 1)^2}{2r^2} & 0 \\ \\ 0 & -\frac{1}{2}\frac{\partial^2}{\partial r^2} - \frac{1}{2r}\frac{\partial}{\partial r} + \frac{1}{2}r^2 + \frac{(|l| \pm 1)^2}{2r^2} \end{pmatrix} + \frac{\tilde{b}}{2}\,r^2 \begin{pmatrix} 0 & 1 \\ \\ 1 & 0 \end{pmatrix}.$$

We can write $H_{UZ}^{[\pm|l|]}$ in the form

$$H_{UZ}^{[\pm|l|]} = H_{UZ}^{[0]} + \frac{1}{2r^2}\begin{pmatrix} |l|^2 \mp 2|l| & 0 \\ 0 & |l|^2 \pm 2|l| \end{pmatrix}. \tag{5.0.17}$$

We now show that $H_{UZ}^{[0]}$ must have an eigenvalue below the eigenvalues of $H_{UZ}^{[\pm|l|]}$ if $|l| \geq 2$.

Recall that $\sigma\left(H_{UZ}^{[|l|]}\right) = \sigma\left(H_{UZ}^{[-|l|]}\right)$, so we only consider $H_{UZ}^{[|l|]}$. Since $\frac{1}{2r^2}\left(|l|^2 \pm 2|l|\right) > 0$ for $|l| > 2$, we know from (5.0.17) that $H_{UZ}^{[|l|]} > H_{UZ}^{[0]}$ for all $|l| > 2$. It easily follows that the lowest eigenvalue of $H_{UZ}^{[0]}$ must lie below the eigenvalues of $H_{UZ}^{[\pm|l|]}$ for all $|l| > 2$.

The presence of the off-diagonal terms in $H_{UZ}^{[|l|]}$ when $\tilde{b} \neq 0$, implies that both components of the eigenvectors must be non-vanishing. Let $\Psi$ be the eigenvector corresponding to the lowest lying eigenvalue of $H_{UZ}^{[2]}$. Then,

$$\begin{aligned} \left\langle \Psi,\, H_{UZ}^{[2]}\,\Psi \right\rangle &= \left\langle \Psi,\, H_{UZ}^{[0]}\,\Psi \right\rangle + \left\langle \Psi,\, \frac{1}{2r^2}\begin{pmatrix} 0 & 0 \\ 0 & 8 \end{pmatrix}\Psi \right\rangle \\ &> \left\langle \Psi,\, H_{UZ}^{[0]}\,\Psi \right\rangle \\ &\geq \inf\,\sigma\left(H_{UZ}^{[0]}\right). \end{aligned}$$

We see that $H_{UZ}^{[0]}$ has at least one eigenvalue below the eigenvalues of $H_{UZ}^{[2]}$. So, the ground state of $H_{UZ}$ must correspond to the ground state of $H_{UZ}^{[0]}$ or $H_{UZ}^{[\pm 1]}$. $\square$

# Chapter 6

# The Vanishing of the Odd Order Energy Coefficients

We now argue that the odd terms in the $E(\epsilon)$ series must be zero.

The Hamiltonian of interest in terms of the scaled nuclear coordinates $(X, Y) = (x/\epsilon, y/\epsilon)$ was given by

$$H(\epsilon) \;=\; \frac{-\epsilon^2}{2}\,\Delta_{X,Y} \;+\; h(\epsilon X, \epsilon Y),$$

where $h(x, y)$ is the electronic hamiltonian that also contains the nuclear repulsion terms. If $E(\epsilon)$ is an eigenvalue of $H(\epsilon)$, then $E(-\epsilon)$ is an eigenvalue of

$$H(-\epsilon) \;=\; \frac{-\epsilon^2}{2}\,\Delta_{X,Y} \;+\; h(-\epsilon X, -\epsilon Y).$$

Under the unitary change $\tilde{X} = -X$, $\tilde{Y} = -Y$, we see that $H(-\epsilon)$ becomes

$$H(-\epsilon) \;=\; \frac{-\epsilon^2}{2}\,\Delta_{\tilde{X},\tilde{Y}} \;+\; h(\epsilon\tilde{X}, \epsilon\tilde{Y}).$$

It is clear that $H(\epsilon)$ and $H(-\epsilon)$ share the same eigenvalues. This does not immediately imply $E(\epsilon) = E(-\epsilon)$, since there could be a pair of eigenvalues related by $E_A(\epsilon) = E_B(-\epsilon)$. However, this would imply that $E_A^{(2)} = E_B^{(2)}$, and then the results of theorem 5.0.1 tell us that $E_A(\epsilon) = E_B(\epsilon)$. Therefore, $E(\epsilon) = E(-\epsilon)$, and as a result the odd terms in the expansion must vanish.

We prove the same using our perturbation formulas. We know from the first few orders that $E^{(0)} = E^{(1)} = 0$ and $\psi_\perp^{(0)} = \psi_\perp^{(1)} = \psi_\perp^{(2)} = 0$. Also, we know from the results of chapter 4 that $f^{(0)}$ and $g^{(0)}$ can take the form

$$\begin{pmatrix} f^{(0)} \\ \\ g^{(0)} \end{pmatrix} = \alpha \left[ e^{i(|l|-1)\phi} \begin{pmatrix} F_1(\rho) \\ \\ i\,F_1(\rho) \end{pmatrix} + e^{i(|l|+1)\phi} \begin{pmatrix} F_2(\rho) \\ \\ -i\,F_2(\rho) \end{pmatrix} \right]$$

$$+ \beta \left[ e^{-i(|l|-1)\phi} \begin{pmatrix} F_1(\rho) \\ \\ -i\,F_1(\rho) \end{pmatrix} + e^{-i(|l|+1)\phi} \begin{pmatrix} F_2(\rho) \\ \\ i\,F_2(\rho) \end{pmatrix} \right],$$

for some non-zero integer $|l|$, functions $F_1,\ F_2$, and $\alpha,\ \beta \in \mathbb{C}$. The other possibility is when $l = 0$, and in this case we can have

$$\begin{pmatrix} f^{(0)} \\ \\ g^{(0)} \end{pmatrix} = e^{i\,\phi} \begin{pmatrix} G_1(\rho) \\ \\ -i\,G_1(\rho) \end{pmatrix} + e^{-i\,\phi} \begin{pmatrix} G_1(\rho) \\ \\ i\,G_1(\rho) \end{pmatrix}$$

or

$$\begin{pmatrix} f^{(0)} \\ \\ g^{(0)} \end{pmatrix} = e^{i\,\phi} \begin{pmatrix} i\,G_2(\rho) \\ \\ G_2(\rho) \end{pmatrix} + e^{-i\,\phi} \begin{pmatrix} -i\,G_2(\rho) \\ \\ G_2(\rho) \end{pmatrix}$$

for some functions $G_1$ and $G_2$.

We now make several definitions and observations:

A function $f(\rho, \phi)$ is said to have *odd parity* if it can be written as a linear combination of functions of the form $e^{ik\phi}F(\rho)$, where $k$ is odd. We say functions in $L^2 \otimes \mathbb{C}^2$ have odd parity if their vector components have odd parity.

A function $f(\rho, \phi)$ is said to have *even parity* if it can be written as a linear combination of functions of the form $e^{ik\phi}F(\rho)$, where $k$ is even. We say functions in $L^2 \otimes \mathbb{C}^2$ have even parity if their vector components have even parity.

An operator $\Omega$ (defined on $L^2$ or $L^2 \otimes \mathbb{C}^2$) is said to be *parity preserving* (or just p.p.) if it maps functions of odd parity to functions of odd parity and functions of even parity to functions of even parity.

An operator $\Omega$ (defined on $L^2$ or $L^2 \otimes \mathbb{C}^2$) is said to be *parity switching* (or just p.s.) if it maps functions of odd parity to functions of even parity and functions of even parity to functions of odd parity.

We make several observations:

1. We see from the form of $f^{(0)}$ and $g^{(0)}$ above, that both have odd parity if $l$ is even, and both have even parity if $l$ is odd. We note that if two functions have opposite parity, then the angular dependence forces their inner product on $\langle \cdot\,, \cdot \rangle_{\rho d\rho d\phi}$ to be zero.

2. The structure of the p.p. and p.s. operators under composition is similar to adding even and odd integers. If $\Omega_1,\ \Omega_2$ are both p.p. or both p.s., then $(\Omega_1\,\Omega_2)$ is p.p. If $\Omega_1$

is p.p and $\Omega_2$ is p.s., then $(\Omega_1\,\Omega_2)$ and $(\Omega_2\,\Omega_1)$ are p.s.

3. If $\Omega_1,\ \Omega_2$ are both p.p., then $\Omega_1 + \Omega_2$ is p.p. If $\Omega_1,\ \Omega_2$ are both p.s., then $\Omega_1 + \Omega_2$ is p.s.

4. If $\Omega$ is polynomial in $(X, Y)$ of order $k$ (meaning it is a linear combination of terms of the form $X^j\,Y^{k-j}$ for $j = 0, 1, \cdots, k$), then $\Omega$ is p.p. when $k$ is even and p.s. when $k$ is odd. We see this from

$$\begin{aligned} X^j\,Y^{k-j} &= \rho^k\,\cos^j(\phi)\ \sin^{k-j}(\phi) \\ &\propto (e^{i\phi} + e^{-i\phi})^j\ (e^{i\phi} - e^{-i\phi})^{k-j} \\ &= \sum_{m=0}^{j} c_m\,e^{i\,m\,\phi}\,e^{-i\,(j-m)\,\phi} \sum_{n=0}^{k-j} d_n\,e^{i\,n\,\phi}\,e^{-i\,(j-k-n)\,\phi} \\ &= \sum_{m=0}^{j}\sum_{n=0}^{k-j} c_m\,d_n\,e^{i\,(2(m+n-j)+k)\,\phi} \end{aligned}$$

   It follows that, if $\Omega_1$ is polynomial in $(X, Y)$ of order $k$ and $\Omega_2$ is polynomial in $(X, Y)$ of order $j$, then $\Omega_1\,\Omega_2$ is p.p. if $j + k$ is even and p.s. if $j + k$ is odd.

5. The $\mathbb{H}_2$ operator is p.p. To see this, we note that the Laplacian $\Delta_{\rho,\phi}$ is p.p., and $X^2 - Y^2$ and $XY$ are polynomial in $(X, Y)$ of order 2 and thus p.p. by the observation above.

6. The reduced resolvent $r(E^{(2)}) = (\mathbb{H}_2 - E^{(2)})_r^{-1}$, defined on the orthogonal complement of the eigenspace of $E^{(2)}$, is p.p. To see this, we note that the eigenvectors of $\mathbb{H}_2$ form an orthonormal basis. Let the eigenspace of $E^{(2)}$ be spanned by $\Psi_1^{n_1,l_1}$ and $\Psi_2^{n_2,l_2}$.

Then, we can use the eigenvectors to form an orthonormal basis of the form (note that these basis vectors will no longer be eigenvectors)

$$\left\{\Phi_1^{n,l}\right\}_{\substack{n\in\mathbb{N}\\ l\in\mathbb{Z}}} \cup \left\{\Phi_2^{n,l}\right\}_{\substack{n\in\mathbb{N}\\ l\in\mathbb{Z}}} \cup \Psi_1^{n_1,l_1} \cup \Psi_2^{n_2,l_2},$$

where the basis vectors take the form

$$\Phi_1^{n,l} = \begin{pmatrix} e^{i\,l\,\phi}\,F^{n,l}(\rho) \\ \\ 0 \end{pmatrix},\ \Phi_2^{n,l} = \begin{pmatrix} 0 \\ \\ e^{i\,l\,\phi}\,G_2^{n,l}(\rho) \end{pmatrix}.$$

Let $\Psi$ be in the orthogonal complement of $E^{(2)}$ and have even parity (the argument with odd parity is the same). Let $r(E^{(2)})\,\Psi = \Phi$. Then, $\Phi$ is in the domain of $\mathbb{H}_2$ and in the orthogonal complement of $E^{(2)}$. So, $\Phi$ can be written in terms of the basis as

$$\Phi = \sum_{\substack{n\in\mathbb{N}\\ l\,even}} (a_{n,l}\,\Phi_1^{n,l} + b_{n,l}\,\Phi_2^{n,l}) + \sum_{\substack{n\in\mathbb{N}\\ l\,odd}} (c_{n,l}\,\Phi_1^{n,l} + d_{n,l}\,\Phi_2^{n,l})$$

From the observation above, we know that

$$(\mathbb{H}_2 - E^{(2)}) \sum_{\substack{n\in\mathbb{N}\\ l\,even}} (a_{n,l}\,\Phi_1^{n,l} + b_{n,l}\,\Phi_2^{n,l}) = \sum_{\substack{n\in\mathbb{N}\\ l\,even}} (A_{n,l}\,\Phi_1^{n,l} + B_{n,l}\,\Phi_2^{n,l}),$$

and

$$(\mathbb{H}_2 - E^{(2)}) \sum_{\substack{n\in\mathbb{N}\\ l\,odd}} (c_{n,l}\,\Phi_1^{n,l} + d_{n,l}\,\Phi_2^{n,l}) = \sum_{\substack{n\in\mathbb{N}\\ l\,odd}} (C_{n,l}\,\Phi_1^{n,l} + D_{n,l}\,\Phi_2^{n,l}),$$

for some constants $A_{n,l},\ B_{n,l},\ C_{n,l}$, and $D_{n,l}$. We have $\Psi = (\mathbb{H}_2 - E^{(2)})\,\Phi$ and since $\Psi$ has vector components with even parity, we know

$$\left\langle \begin{pmatrix} e^{i\,k\,\phi} \\ \\ 0 \end{pmatrix},\ \Psi \right\rangle_{d\phi} = 0, \quad \text{for } k \text{ odd}.$$

We see that $C_{n,k} = 0$ for $n \in \mathbb{N}$ and $k$ odd, and similarly $D_{n,k} = 0$ for $n \in \mathbb{N}$ and $k$ odd. Since the $\Phi_1^{n,l},\ \Phi_2^{n,l}$ basis vectors are not in the nullspace of $(\mathbb{H}_2 - E^{(2)})$, this forces $c_{n,k} = d_{n,k} = 0$ if $k$ is odd. We then have that $\Phi = r(E^{(2)})\,\Psi$ has vector components of even parity.

7. The derivative operators $\frac{\partial}{\partial X}$ and $\frac{\partial}{\partial Y}$ are p.s. This follows easily from writing the operators in terms of the polar coordinates $\rho$ and $\phi$.

8. The projection onto the orthogonal complement of the eigenspace of $E^{(2)}$, denoted by $Q_\perp$, is p.p. To see this, we note that $Q_\perp = I - |\,\Psi_1^{n_1,l_1}\,\rangle\langle\,\Psi_1^{n_1,l_1}\,| - |\,\Psi_2^{n_2,l_2}\,\rangle\langle\,\Psi_2^{n_2,l_2}\,|$, where $\Psi_1^{n_1,l_1}$ and $\Psi_2^{n_1,l_2}$ have the same parity. Then, if $\psi$ has opposite parity of $\Psi_1^{n_1,l_1}$ and $\Psi_2^{n_1,l_2}$, we know that $Q_\perp\psi = \psi$. If $\psi$ has the same parity as $\Psi_1^{n_1,l_1}$ and $\Psi_2^{n_1,l_2}$, we know that $Q_\perp\psi$ is a linear combination of $\psi,\ \Psi_1^{n_1,l_1}$, and $\Psi_2^{n_2,l_2}$. In either case, we see that $Q_\perp\psi$ has the same parity as $\psi$.

We are now ready to prove by induction that the odd terms in the expansion of $E(\epsilon)$ are zero:

Recall that $E^{(0)} = E^{(1)} = 0$ and also $\psi_\perp^{(0)} = \psi_\perp^{(1)} = \psi_\perp^{(2)} = 0$.

Fix integer $k \geq 3$. Assume that we know $E^{(j)}$ and $\psi_\perp^{(j)}$ for all $j = 0, 1, \cdots, k-1$, and that we know $f^{(j)}$, $g^{(j)}$ for all $j = 0, 1, \cdots, k-3$. Assume also that $E^{(j)} = 0$ for odd $j$ less than $k$ and that the known $f^{(j)}$, $g^{(j)}$, and $\psi_\perp^{(j)}$ are either zero or have the same parity as $f^{(0)}$ and $g^{(0)}$ if $j$ is even, and have opposite parity as $f^{(0)}$ and $g^{(0)}$ if $j$ is odd.

We show that $E^{(k)} = 0$ if $k$ is odd and that $f^{(k-2)}$, $g^{(k-2)}$, and $\psi_\perp^{(k)}$ have the same parity as

$f^{(0)}$ and $g^{(0)}$ if $k$ is even, and have opposite parity if $k$ is odd. It follows by induction that $E^{(k)} = 0$ for all odd $k$.

We will only present the details assuming $f^{(0)}$ and $g^{(0)}$ are of even parity, simply because it is easier to describe, and the other case is similar. If $f^{(0)}$ and $g^{(0)}$ are of even parity, then the induction hypothesis says that the known $f^{(j)}$, $g^{(j)}$, $\psi_{\perp}^{(j)}$ have the same parity as the number $j$ (meaning they are even parity when j is even, and of odd parity when j is odd).

Using the induction hypothesis, we first show that the inner products arising in equation (2.0.16) are zero if $k$ is odd. The terms $T_{mn}^{(j-4)}$ are polynomial in $(X, Y)$ of order $j-4$ and the terms $h_{mn}^{(j)}$ are polynomial in $(X, Y)$ of order $j$. We see that both are p.p. if $j$ is even and p.s. if $j$ is odd. The terms $A_{mn}^{(j-3)}$ and $B_{mn}^{(j-3)}$ are polynomial in $(X, Y)$ of order $j-3$ and thus p.s. if $j$ is even and p.p. if $j$ is odd. Since $\frac{\partial}{\partial X}$ and $\frac{\partial}{\partial Y}$ are p.s., we see that all of the entries in $\mathbb{H}_j$ are p.p. if $j$ is even and p.s. if $j$ is odd. Then, $\mathbb{H}_j \begin{pmatrix} f^{(k-j)} \\ \\ g^{(k-j)} \end{pmatrix}$ will have the same parity as the number $k - j + j = k$. Recalling that $E^{(j)} = 0$ for odd $j < k$, we see that $(\mathbb{H}_j - E^{(j)}) \begin{pmatrix} f^{(k-j)} \\ \\ g^{(k-j)} \end{pmatrix}$ will have the same parity as the number $k$. It follows that the first two terms of in equation (2.0.16) are zero if $k$ is odd, since in that case the terms are inner products of two functions with different parity.

To show the last term is zero, we note that the $\Psi_m^{(j-2)}$ are polynomial in $(X, Y)$ of order $j-2$ (and so has the same parity as the number $j-2$) and recall also that the Laplacian is p.p. It follows that $\langle\ \Psi_1^{(j-2)},\ \Delta_{X,Y}\ \psi_{\perp}^{(k-j)}\ \rangle$ has the same parity as the number $k-j+j-2 = k-2$

and so the same parity as $k$. We see that as before, the last term vanishes when $k$ is odd. So, $E^{(k)} = 0$ if $k$ is odd.

From the arguments we just made, we now see that equation (2.0.17) has $Q_\perp$ and the reduced resolvent acting on terms which have the same parity as the number $k$. Since $Q_\perp$ and the reduced resolvent are p.p., we know that $f^{(k-2)}$ and $g^{(k-2)}$ have the same parity as $k$ and thus $k-2$, which is what we wanted to show.

Equation (2.0.18) is treated in the same manner. The $\left[ (\, h \; P_\perp)^{(0)} \right]_r^{-1}$ operator is p.p. since it has no $(X, Y)$ dependence, and will thus be ignored. All of the operators and functions involved in this equation of the form $\Omega^{(j)}$, except for the $f$, $g$, and $\psi_\perp$ orders, are polynomial in $(X, Y)$ of order $j$, and thus p.p. if $j$ is even and p.s. if $j$ is odd. We consider each term individually as before, showing that every term that arises has the same parity as the number $k$.

The $P_\perp^{(j-2)} \left[ \, \Delta_{X,Y} \; \psi_\perp^{(k-j)} \, \right]$ term will have the same parity as the number $j-2+k-j = k-2$ and thus the same parity as $k$.

The $(\, h \, P_\perp)^{(j)} \;\; \psi_\perp^{(k-j)}$ term will have the same parity as the number $j + k - j = k$.

The terms similar to $P_\perp^{(j-l)} \left[ \, (\Delta_{x,\,y} \; \Psi_1)^{(l-4)} \, \right] \;\; f^{(k-j)}$ will have the same parity as the number $k - j + l - 4 + j - l = k - 4$ and thus the same parity as $k$.

The terms similar to

$$\left( P_\perp^{(j-l)} \left[ \left( \frac{\partial \Psi_1}{\partial x} \right)^{(l-3)} \right] \; \frac{\partial}{\partial X} \; + \; P_\perp^{(j-l)} \left[ \left( \frac{\partial \Psi_1}{\partial y} \right)^{(l-3)} \right] \; \frac{\partial}{\partial Y} \right) \; f^{(k-j)}$$

will have the same parity as the number $k - j + 1 + l - 3 + j - l = k - 2$ and thus the same parity as $k$.

The term $E^{(j)}\psi_{\perp}^{(k-j)}$ does not enter if $j$ is odd. If $j$ is even, it will have the same parity as the number $k - j$ and thus the same parity as $k$.

We see that the $\psi_{\perp}^{(k)}$ will have the same parity as $k$ and we have finished what we set out to do.

# Chapter 7

# Proof of the Main Theorem

Here we use the quasimode expansion constructed in Chapter 2 to sketch the proof of theorem 1.2.1. Our candidates for the approximate wave function and energy in the theorem are

$$\Phi_{\epsilon,K} \;=\; F(\epsilon\rho)\,\Psi_{\epsilon,K},$$

where

$$\Psi_{\epsilon,K} \;=\; \left(\sum_{j=0}^{K-2} \epsilon^j \,\left(\Psi_1(\epsilon X,\epsilon Y)\,f^{(j)}(X,Y) \;+\; \Psi_2(\epsilon X,\epsilon Y)\,g^{(j)}(X,Y)\right) \;+\; \sum_{j=0}^{K} \epsilon^j\,\psi_\perp^{(j)}(X,Y)\right)$$

and $E_{\epsilon,K} \;=\; \sum_{j=0}^{K} \epsilon^j\,E^{(j)}$, where the $f^{(j)},\; g^{(j)},\; \psi_\perp^{(j)}$, and $E^{(j)}$ are determined by the perturbation formulas in chapter 2. The cut-off function $F(\epsilon\rho)$ is needed to restrict the analysis to a neighborhood of the local minimum of the electronic eigenvalues $E_1(\tilde{\rho})$ and $E_2(\tilde{\rho})$ at $\tilde{\rho}=0$, where $E_1$ and $E_2$ are isolated from the rest of the spectrum of $h(\epsilon X,\epsilon Y)$ and also where the functions and operators that we have expanded into powers of $\epsilon$ (such as $\Psi_1(\epsilon X,\epsilon Y)$) have asymptotic expansions (recall that $(x,y)=(\epsilon X,\,\epsilon Y)$ and $\tilde{\rho}=\epsilon\rho$). We require that the

cut-off function $F(\tilde{\rho}) : I\!R^2 \rightarrow [0,1]$ be smooth in both variables $x$ and $y$. It has support in some neighborhood where $\tilde{\rho} < S$. Also, $F(\tilde{\rho}) = 1$ for $\tilde{\rho} \leq R$, where $0 < R < S$. So, the derivatives of $F(\tilde{\rho})$ with respect to $x$ and $y$ vanish outside the region $R \leq \tilde{\rho} \leq S$.

We first consider the norm of $\Phi_{\epsilon,K}$. The leading order contribution of $\Phi_{\epsilon,K}$ arises from

$$F(\epsilon\rho)\,\Psi_{0,K} \;=\; F(\epsilon\rho)\,\left(\Psi_1(0,0)\,f^{(0)}(X,Y) \;+\; \Psi_2(0,0)\,g^{(0)}(X,Y)\right).$$

Then, the leading order of $||\Phi_{\epsilon,K}||^2_{\mathcal{H}_{nuc}\otimes\mathcal{H}_{el}}$ arises from

$$\begin{aligned}
&\int_{I\!R^2} |\,F(\epsilon\rho)\,|^2\,\left(\left|\,f^{(0)}(X,Y)\,\right|^2 \;+\; \left|\,g^{(0)}(X,Y)\,\right|^2\right)dxdy \\
&\quad= \;\epsilon^2\left(\int_{I\!R^2} |\,F(\epsilon\rho)\,|^2\,\left(\left|\,f^{(0)}(X,Y)\,\right|^2 \;+\; \left|\,g^{(0)}(X,Y)\,\right|^2\right)dXdY\right) \\
&\quad\geq \;\epsilon^2\left(\int_{I\!R^2} \chi_{[\rho<R/\epsilon]}\,\left(\left|\,f^{(0)}(X,Y)\,\right|^2 \;+\; \left|\,g^{(0)}(X,Y)\,\right|^2\right)dXdY\right) \\
&\quad= \;\epsilon^2\left(\int_{I\!R^2} \left(\left|\,f^{(0)}(X,Y)\,\right|^2 \;+\; \left|\,g^{(0)}(X,Y)\,\right|^2\right)dXdY\right. \\
&\qquad\qquad\left. -\;\int_{[\rho>R/\epsilon]} \left(\left|\,f^{(0)}(X,Y)\,\right|^2 \;+\; \left|\,g^{(0)}(X,Y)\,\right|^2\right)dXdY\right) \\
&\quad= \;\epsilon^2\left(1 \;-\; \int_{[\rho>R/\epsilon]} \left(\left|\,f^{(0)}(X,Y)\,\right|^2 \;+\; \left|\,g^{(0)}(X,Y)\,\right|^2\right)dXdY\right) \\
&\quad= \;\epsilon^2\left(1 \;-\; \int_{[\rho>R/\epsilon]} e^{-2\gamma\langle x\rangle}\,e^{2\gamma\langle x\rangle}\,\left(\left|\,f^{(0)}(X,Y)\,\right|^2 \;+\; \left|\,g^{(0)}(X,Y)\,\right|^2\right)dXdY\right) \\
&\quad\geq \;\epsilon^2\left(1 \;-\; e^{-2\gamma\sqrt{1+R^2/\epsilon^2}}\int_{I\!R^2} e^{2\gamma\langle x\rangle}\,\left(\left|\,f^{(0)}(X,Y)\,\right|^2 \;+\; \left|\,g^{(0)}(X,Y)\,\right|^2\right)dXdY\right) \\
&\quad= \;\epsilon^2\left(1 \;-\; e^{-2\gamma\sqrt{1+R^2/\epsilon^2}}\right)\,C,
\end{aligned}$$

where C is a positive constant. Above, we have used that $\begin{pmatrix} f^{(0)} \\ g^{(0)} \end{pmatrix}$ is normalized and in

$D(e^{\gamma\langle x\rangle} \otimes I_2)$. We see that the leading order contribution has the form $\epsilon^2\,(1 - O(\epsilon^\infty))$. It follows that $||\Phi_{\epsilon,K}||_{\mathcal{H}_{nuc}\otimes\mathcal{H}_{el}}$ is asymptotic to $\epsilon$.

We have

$$(H(\epsilon) - E_{\epsilon,K})\,\Phi_{\epsilon,K} \;=\; F(\epsilon\rho)\,(H(\epsilon) - E_{\epsilon,K})\,\Psi_{\epsilon,K} \;-\; \frac{\epsilon^2}{2}\,[\,\Delta_{X,Y}\,,\,F(\epsilon\rho)\,]\;\Psi_{\epsilon,K}. \qquad (7.0.1)$$

From the estimate on the norm of $\Phi_{\epsilon,K}$, we need to show that both terms on the right hand side of (7.0.1) are finite linear combinations of the form $\epsilon^J\,G$, where $||G||_{\mathcal{H}_{nuc}\otimes\mathcal{H}_{el}} < \infty$ and $J \geq K + 2$. Recall from chapter 2 that $P_\perp$ was the projection in $\mathcal{H}_{el}$ onto $\{\Psi_1, \Psi_2\}^\perp$. We can write

$$(H(\epsilon) - E_{\epsilon,K})\,\Psi_{\epsilon,K} \;=\; \chi_1(\epsilon, X, Y)\,\Psi_1(\epsilon X, \epsilon Y) \;+\; \chi_2(\epsilon, X, Y)\,\Psi_2(\epsilon X, \epsilon Y) \;+\; \chi_\perp(\epsilon, X, Y),$$

where $\chi_\perp \;=\; P_\perp\,[(H(\epsilon) - E_{\epsilon,K})\,\Psi_{\epsilon,K}]$ (so $\chi_1$ and $\chi_2$ have no electronic dependence, but $\chi_\perp$ does have electronic dependence).

The analysis regarding $\chi_2$ and $\chi_\perp$ is similar to that of $\chi_1$ and will be omitted. Using (2.0.2) with our definition of $\Psi_{\epsilon,K}$, we have

$$\chi_1 \;=\; -\,\frac{\epsilon^2}{2}\,\Delta_{X,Y}\,\sum_{j=0}^{K-2}\epsilon^j\,f^{(j)} \;+\; h_{11}\,\sum_{j=0}^{K-2}\epsilon^j\,f^{(j)} \;+\; h_{12}\,\sum_{j=0}^{K-2}\epsilon^j\,g^{(j)}$$

$$-\,\frac{\epsilon^2}{2}\,\langle\,\Psi_1,\,\Delta_{X,Y}\,\psi_\perp\,\rangle_{el} \;-\; \frac{\epsilon^4}{2}\,\sum_{j=0}^{K-2}\epsilon^j\,f^{(j)}\,\langle\,\Psi_1,\,\Delta_{x,y}\,\Psi_1\,\rangle_{el} \;-\; \frac{\epsilon^4}{2}\,\sum_{j=0}^{K-2}\epsilon^j\,g^{(j)}\,\langle\,\Psi_1, \Delta_{x,y}\,\Psi_2\,\rangle_{el}$$

$$-\,\epsilon^3\left(\sum_{j=0}^{K-2}\epsilon^j\,\frac{\partial g^{(j)}}{\partial X}\,\langle\,\Psi_1,\,\frac{\partial\Psi_2}{\partial x}\,\rangle_{el} \;+\; \sum_{j=0}^{K-2}\epsilon^j\,\frac{\partial g^{(j)}}{\partial Y}\,\langle\,\Psi_1,\,\frac{\partial\Psi_2}{\partial y}\,\rangle_{el}\right) \;-\; \sum_{j=0}^{K}\epsilon^j\,E^{(j)}\,\sum_{l=0}^{K-2}\epsilon^l\,f^{(l)}.$$

To show $||F(\epsilon\rho)\,\chi_1\,\Psi_1||_{\mathcal{H}_{nuc}\otimes\mathcal{H}_{el}} \leq C\,\epsilon^{K+2}$, we can consider the terms in the above equation separately and use the triangle inequality. Analogous to equations (2.0.4) and (2.0.5), we

expand all functions with $(\epsilon X, \epsilon Y)$ dependence into powers of $\epsilon$, however, we truncate the series here and add an error term. For example, we can write $h_{11}(\epsilon X, \epsilon Y) = \sum_{j=0}^{K} \epsilon^j \, h_{11}^{(j)} + \epsilon^{K+1} \, h_{11}^{err}(X, Y)$, where we know $h_{11}^{err}(X, Y)$ is in $C^{\infty}(X, Y)$ and is bounded by a polynomial in $X$ and $Y$ of order $K+1$ on $\text{supp}(F(\epsilon\rho))$. If we do this, we know all terms of order $\epsilon^j$, for $j \leq K$, will cancel in the above equations, since the terms of $f$, $g$, $E$, and $\psi_{\perp}$ were chosen using the perturbation formulas. We show how to deal with the $h_{11}$ term arising in $F(\epsilon\rho) \, \chi_1 \, \Psi_1$ only, the rest of the terms are handled similarly. This term can be written (only expressions of order $\epsilon^{K+1}$ or higher are considered)

$$\begin{aligned} h_{11}(\epsilon X, \epsilon Y) \sum_{j=0}^{K-2} \epsilon^j \, f^{(j)} &= \left( \sum_{l=0}^{K} \epsilon^l \, h_{11}^{(l)} + \epsilon^{K+1} \, h_{11}^{err}(X, Y) \right) \sum_{j=0}^{K-2} \epsilon^j \, f^{(j)} \\ &= \sum_{\substack{0 \leq j \leq K-2 \\ 0 \leq l \leq K \\ j+l \geq K+1}} \epsilon^{l+j} \, h_{11}^{(l)} \, f^{(j)} + \sum_{j=0}^{K-2} \epsilon^{K+j+1} \, h_{11}^{err}(X, Y) \, f^{(j)} \end{aligned}$$

and then

$$
\begin{aligned}
&\left\| F(\epsilon\rho)\, h_{11}(\epsilon X, \epsilon Y) \sum_{j=0}^{K-2} \epsilon^j\, f^{(j)}\, \Psi_1(\epsilon X, \epsilon Y) \right\|_{\mathcal{H}_{nuc}\otimes\mathcal{H}_{el}} \\
\leq & \sum_{\substack{0\leq j\leq K-2 \\ 0\leq l\leq K \\ j+l\geq K+1}} \epsilon^{l+j} \left( \int_{I\!R^2} \left| F(\epsilon\rho)\, h_{11}^{(l)}(X,Y)\, f^{(j)}(X,Y) \right|^2 dxdy \right)^{1/2} \\
& + \sum_{j=0}^{K-2} \epsilon^{K+j+1} \left( \int_{I\!R^2} \left| F(\epsilon\rho)\, h_{11}^{err}(X,Y)\, f^{(j)}(X,Y) \right|^2 dxdy \right)^{1/2} \\
\leq & \sum_{\substack{0\leq j\leq K-2 \\ 0\leq l\leq K \\ j+l\geq K+1}} \epsilon^{l+j+1} \left( \int_{I\!R^2} \left| h_{11}^{(l)}(X,Y)\, f^{(j)}(X,Y) \right|^2 dXdY \right)^{1/2} \\
& + \sum_{j=0}^{K-2} \epsilon^{K+j+2} \left( \int_{I\!R^2} \left| h_{11}^{err}(X,Y)\, f^{(j)}(X,Y) \right|^2 dXdY \right)^{1/2} \\
\leq & \sum_{\substack{0\leq j\leq K-2 \\ 0\leq l\leq K \\ j+l\geq K+1}} \epsilon^{l+j+1} \left( \int_{I\!R^2} \left| \sum_{m=0}^{l} C_m\, X^m\, Y^{l-m} \right|^2 \left| f^{(j)}(X,Y) \right|^2 dXdY \right)^{1/2} \\
& + \sum_{j=0}^{K-2} \epsilon^{K+j+2} \left( \int_{I\!R^2} \left| \sum_{m=0}^{K+1} D_m\, X^m\, Y^{K+1-m} \right|^2 \left| f^{(j)}(X,Y) \right|^2 dXdY \right)^{1/2} \\
\leq & \sum_{\substack{0\leq j\leq K-2 \\ 0\leq l\leq K \\ j+l\geq K+1}} \epsilon^{l+j+1}\, C_{l,j} \;+\; \sum_{j=0}^{K-2} \epsilon^{K+j+2}\, D_{l,j},
\end{aligned}
$$

where $C_m$, $D_m$, $C_{l,j}$, $D_{l,j} \;<\; \infty$. Above we have used that $f^{(j)} \in D(e^{\gamma\langle x\rangle})$, which we know from the results of chapter 3. We see that this term is indeed of order greater or equal to $O(\epsilon^{K+2})$. All of the terms of $\chi_1$ and $\chi_\perp$ can be handled in a similar fashion using the results

of theorem 3.0.9.

The term involving the derivatives of $F$ in equation (7.0.1) are handled using theorem 3.0.9 as well. The derivatives of $F$ are supported away from the origin and the terms of $\Psi_{\epsilon,K}$ are exponentially decaying. We only show the terms involving derivatives with respect to $X$ since the same will hold with $X$ replaced by $Y$. Let $M$ be larger than $\sup_{\mathbb{R}^2} |\frac{\partial^2 F}{\partial x^2}|$ and $\sup_{\mathbb{R}^2} |\frac{\partial F}{\partial x}|$.

$$
\begin{aligned}
&\left|\left|\left[ \frac{\partial^2}{\partial X^2} \, , \, F(\epsilon\rho) \right] \, \Psi_{\epsilon,K} \right|\right|_{\mathcal{H}_{nuc}\otimes\mathcal{H}_{el}} \\
&\quad \leq \epsilon^2 \left|\left| \frac{\partial^2 F(\tilde{\rho})}{\partial x^2} \, \Psi_{\epsilon,K} \right|\right|_{\mathcal{H}_{nuc}\otimes\mathcal{H}_{el}} \; + \; 2\,\epsilon \left|\left| \frac{\partial F(\tilde{\rho})}{\partial x} \, \frac{\partial \Psi_{\epsilon,K}}{\partial X} \right|\right|_{\mathcal{H}_{nuc}\otimes\mathcal{H}_{el}} \\
&\quad \leq M \left( \epsilon^2 \left|\left| \chi_{[\rho>R/\epsilon]} \, \Psi_{\epsilon,K} \right|\right|_{\mathcal{H}_{nuc}\otimes\mathcal{H}_{el}} \; + \; 2\,\epsilon \left|\left| \chi_{[\rho>R/\epsilon]} \, \frac{\partial \Psi_{\epsilon,K}}{\partial X} \right|\right|_{\mathcal{H}_{nuc}\otimes\mathcal{H}_{el}} \right) \\
&\quad \leq M \, e^{-\gamma\sqrt{1+R^2/\epsilon^2}} \left( \epsilon^2 \left|\left| e^{\gamma\langle x\rangle} \, \Psi_{\epsilon,K} \right|\right|_{\mathcal{H}_{nuc}\otimes\mathcal{H}_{el}} \; + \; 2\,\epsilon \left|\left| e^{\gamma\langle x\rangle} \, \frac{\partial \Psi_{\epsilon,K}}{\partial X} \right|\right|_{\mathcal{H}_{nuc}\otimes\mathcal{H}_{el}} \right) \\
&\quad \leq O(\epsilon^{\infty}),
\end{aligned}
$$

where we have used that all terms of $\Psi_{\epsilon,K}$ and their derivatives are exponentially decaying from theorem 3.0.9. The conclusion of the theorem follows. $\square$

# Chapter 8

# Future Work

The model we have considered here contains various simplifications. Several degrees of freedom were restricted, potentials were assumed to be smooth functions of the nuclear coordinates, and spin interactions were not considered. An obvious next step would be to attempt a similar Born-Oppenheimer expansion in a mathematically rigorous framework using the model of this paper, but allowing for Coulomb potentials. Also, a less simplified model that allows all three nuclei to move in three dimensional space could be considered. This would account for the stretching and rotational modes of the molecule. Another possible direction may be to study the situation in cases (b) and (c) of Figure 1.1 with mathematical rigor.

To account for non-smooth Coulomb potentials, depending on the model, it is likely possible to change to a coordinate system in which the electronic hamiltonian is smooth in terms of

the new nuclear variables, as in [6]. This would allow for the asymptotic expansions that are needed to employ a Born-Oppenheimer expansion as in this paper. For example, consider the same model we have used here, with two nuclei clamped to the $z$-axis at positions $(0, 0, R_1)$ and $(0, 0, R_2)$, where $R_1 > 0$ and $R_2 < 0$. Again we allow the middle nucleus to move in the perpendicular plane with cartesian coordinates $(x, y, 0)$. For simplicity we only consider one electron with cartesian coordinates $\vec{r} = (r_1, r_2, r_3)$. Define $R = \min\{|R_1|, |R_2|\}$ and let $f(r_3) \in C^\infty(\mathbb{R})$ with range in $[0, 1]$ that satisfies

$$f(r_3) = \begin{cases} 1, \text{ if } |r_3| \leq R/3 \\ \\ 0, \text{ if } |r_3| \geq 2R/3 \end{cases}.$$

Now define the new coordinates $(\tilde{x}, \tilde{y}, \tilde{r}_1, \tilde{r}_2, \tilde{r}_3)$ by

$$\begin{aligned} \tilde{r}_1 &= r_1 - x\, f(r_3), \\ \tilde{r}_2 &= r_2 - y\, f(r_3), \\ \tilde{r}_3 &= x_3, \quad \tilde{x} = x, \quad \tilde{y} = y. \end{aligned}$$

In terms of these coordinates, the electronic hamiltonian will be smooth in the nuclear coordinates $\tilde{x}$ and $\tilde{y}$ since the singularity positions contained in the Coulomb potentials will not directly depend on $\tilde{x}$ and $\tilde{y}$. To see this, consider first the Coulomb term involving the electron and the middle nucleus in terms of the new coordinates:

$$|\vec{r} - (x,\, y,\, 0)|^2 = (\,\tilde{r}_1 - \tilde{x}\,(\,1 - f(\tilde{r_3})\,)\,)^2 + (\,\tilde{r}_2 - \tilde{y}\,(\,1 - f(\tilde{r_3})\,)\,)^2 + \tilde{r}_3^2.$$

The function $1 - f(\tilde{r_3})$ vanishes near $\tilde{r_3} = 0$ so the singularity in the Coulomb function occurs only at $(\tilde{r}_1, \tilde{r}_2, \tilde{r}_3) = (0, 0, 0)$. If we consider the Coulomb term involving the electron and

the upper nucleus in terms of the new coordinates:

$$|\vec{r} - (0, 0, R_2)|^2 = (\tilde{r}_1 + \tilde{x}\, f(\tilde{r_3}))^2 + (\tilde{r}_2 + \tilde{y}\, f(\tilde{r_3}))^2 + (\tilde{r}_3 - R_1)^2.$$

The function $f(\tilde{r_3})$ vanishes near $\tilde{r_3} = R_2$ so the singularity in the Coulomb function occurs only at $(\tilde{r}_1, \tilde{r}_2, \tilde{r}_3) = (0, 0, R_2)$.

This is just one example of a new coordinate system in which the electron hamiltonian will be smooth in terms of the nuclear coordinates. There may be a better choice of coordinates to handle the case of Coulomb potentials.

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