

The Born-Oppenheimer Approximation for Triatomic Molecules with Large Angular Momentum in Two Dimensions

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(ABSTRACT)

We study the Born-Oppenheimer approximation for a symmetric linear triatomic molecule in two space dimensions. We compute energy levels up to errors of order ϵ^5 , uniformly for three bounded vibrational quantum numbers n_1 , n_2 , and n_3 ; and nuclear angular momentum quantum number $\ell \leq k\epsilon^{-3/4}$ for $k > 0$. Here the small parameter ϵ is the fourth root of the ratio of the electron mass to an average nuclear mass.

Dedication

Dedicated to my mother.

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Contents

1	Introduction	1
1.1	Our Results	3
2	Statement of the Problem	6
2.1	The Nuclear Angular Momentum	8
2.2	The Electron Energy Surface	11
3	The Multiple Scales Calculation	14
3.1	Order 0	20
3.2	Orders $1/4$ through $7/4$	21
3.3	Order 2	21
3.4	An Aside – “Weird” Powers of ϵ	24
3.5	Order $9/4$	26
3.6	Order $5/2$	27
3.7	Order $11/4$	27
3.8	Order 3	27
3.9	Order $13/4$	30
3.10	Order $7/2$	31
3.11	Order $15/4$	32

3.12 Order 4	32
3.13 Order 17/4	34
3.14 Order 9/2	36
4 Final Results	39
4.1 The Error in the Approximate Energy	40
Bibliography	43

List of Figures

2.1	The nuclear geometry.	7
2.2	The original domain of the variables θ_1 and θ_2	10
2.3	The naively rotated region, indicating lack of unitarity of the change of variables.	11
2.4	The correctly scaled and rotated region, showing the manipulation. The two right triangles are moved from the fourth quadrant to the first quadrant as indicated. The boundary condition in θ are thus the standard ones we expect. Note that area is preserved.	12
3.1	A (two-dimensional) illustration of the validity of the assumption $\psi_0 \perp \psi_\nu$. The circle depicted is the unit circle $\{\ \psi\ = 1\}$. By proceeding in this way, we obtain a vector ψ_ϵ which is not a unit vector but is instead some multiple of the unit vector $\hat{\psi}_\epsilon$	20
3.2	An illustration of the normal modes	23

Chapter 1

Introduction

In a seminal paper of 1927 ([1]), Max Born and Robert Oppenheimer presented results, motivated by (the then relatively new) quantum theory, that underpin much of what is known about molecular bound states – that is, bound states of some particles of small mass (electrons) and some particles of large mass (nuclei). Their results centered on a small, dimensionless parameter, which they took to be the fourth root of the ratio of the electron mass to an average nuclear mass associated with the molecule. In the present work, we denote this parameter by ϵ . The authors showed that one could perform an asymptotic expansion of the molecular energy levels to fourth order in ϵ , with the coefficients in the expansion having simple, and remarkable, physical interpretations:

- The coefficient of ϵ^0 represents the electronic energy near the optimal nuclear configuration;
- the coefficient of ϵ^2 represents the vibrational nuclear energy; and
- the coefficient of ϵ^4 represents the rotational nuclear energy, along with several corrections to the lower order terms (e.g., anharmonic vibrational corrections).

The coefficients of ϵ^1 and ϵ^3 were found to be identically zero. The physical intuition underlying their method was the fact that the nuclear masses are several orders of magnitude larger than the electron masses. Using this fact, an approximate solution to the time-independent Schrödinger equation for the molecule can be developed by (1) solving the *electronic* problem for a fixed configuration of the nuclei and then (2) solving the *nuclear* problem by letting

the energy eigenvalue of the electronic problem (which depends parametrically on the nuclear positions) act as an effective potential for the nuclei. An approximate wave function for the entire molecule can then be written as a product of the nuclear and electronic wave functions.

Born and Oppenheimer argued ingeniously for what they thought the molecular energy should look like, but their work was not rigorously verified for a realistic physical model until many years later by, among others, Combes, Duclos, and Seiler [2, 3]. The proper intuition underlying the time-independent Born-Oppenheimer approximation – that of the disparity between the *spatial* scales of the nuclear and electronic motions – was formalized in [5] by George Hagedorn using the *method of multiple scales*. He showed that, assuming smooth interaction potentials, energy eigenvalue and eigenfunction expansions exist to arbitrarily high orders in ϵ for Hamiltonians H of the form $H = -\frac{\epsilon^4}{2}\Delta + h$, where h contains interaction potential terms and terms related to the electronic kinetic energy. He provided a recipe for calculating the approximate energy eigenvalues and eigenfunctions (“quasimodes”). The work of Klein, Martinez, Seiler, and Wang [14] relaxed the smoothness assumption and demonstrated that expansions to all orders in ϵ exist for Coulomb potentials (which are singular at the origin) as well. Quite recently, Hagedorn and Toloza [9, 10] considered molecular models in which the nuclei had only one degree of freedom and certain restrictions were placed on the electron Hamiltonian. They used the method of “optimal truncation” to obtain *exponentially* accurate approximate energies.

In [16], Vania Sordoni studied diatomic molecules with large nuclear angular momentum (she allowed the angular momentum quantum number ℓ to grow as $\epsilon \rightarrow 0$) using techniques similar to those employed in [14] but very different from those used in [5]. She obtained error estimates for the approximate energies that were *uniform* for bounded nuclear vibrational quantum numbers n and ℓ satisfying $\ell < \epsilon^{-1}$. She proved the existence of energy expansions to arbitrary orders in ϵ , but did not provide explicit formulae for these energies. Most recently, in the Virginia Tech Ph.D. dissertation [12] and the paper [13], Sharon Hughes used the techniques developed in [5] to expand upon Sordoni’s work by providing formulae for the approximate energies of diatomic molecules with $\ell \leq \kappa\epsilon^{-3/2}$. She also provided error estimates for these energies that were $\mathcal{O}(\epsilon^5)$ and uniform in ℓ and n .

1.1 Our Results

In this work, we consider a simplified model of a triatomic molecule with an arbitrary finite number of electrons in *two dimensions*, appropriate for molecules whose equilibrium configuration is linear and symmetric. As was done in [16] and [12], we allow the nuclear angular momentum of our molecule to grow arbitrarily large as we make the parameter ϵ small. We obtain uniform, $\mathcal{O}(\epsilon^5)$ error estimates for an approximate energy level $E(\epsilon)$ of such a molecule for vibrational quantum numbers $n_1, n_2, n_3 \leq \mathcal{N}$ for some $\mathcal{N} \in \mathbb{N}_0 = \mathbb{N} \cup \{0\}$ (we confront *three* of these in the present work) and all ℓ satisfying $\ell = \kappa \epsilon^{-3/4}$, where κ is a real constant kept inside some compact interval $[0, k]$. We also obtain a quasimode Ψ_ϵ which satisfies $\|(H_\epsilon - E(\epsilon))\Psi_\epsilon\| = \mathcal{O}(\epsilon^5)$ for the molecular Hamiltonian H_ϵ . For a particular electron energy surface, we prove that $E(\epsilon)$ has the form

$$E(\epsilon) = \epsilon^2 f_2(N, \ell) + \epsilon^4 f_4(N, \ell) + \epsilon^6 f_6(N, \ell).$$

More specifically, letting $N = (n_1, n_2, n_3)$, where the n_j are nonnegative integers, there is an *exact* energy level $E_{N, \ell}$ of the molecule such that

$$E_{N, \ell} = \epsilon^2 \left\{ \left(n_1 + \frac{1}{2} \right) + \left(n_2 + \frac{1}{2} \right) \sqrt{3} + \left(n_3 + \frac{1}{2} \right) \sqrt{2} \right\} \quad (1.1)$$

$$+ \epsilon^4 \left\{ \frac{\ell^2}{4} - \frac{39}{224} - \frac{\sqrt{2}}{7} \left(n_1 + \frac{1}{2} \right) \left(n_3 + \frac{1}{2} \right) \right. \quad (1.2)$$

$$\left. + \frac{1}{\sqrt{6}} \left(n_2 + \frac{1}{2} \right) \left(n_3 + \frac{1}{2} \right) + \frac{1}{56} \left(n_3 + \frac{1}{2} \right)^2 + T_4(1, 1, \pi) \right\} \quad (1.3)$$

$$+ \epsilon^6 \ell^2 \left\{ \frac{3}{4} \left(n_1 + \frac{1}{2} \right) + \frac{7}{4\sqrt{3}} \left(n_2 + \frac{1}{2} \right) - \frac{1}{\sqrt{2}} \left(n_3 + \frac{1}{2} \right) \right\} \quad (1.4)$$

$$+ \mathcal{O}(\epsilon^5), \quad (1.5)$$

We make the following remarks about the above result:

- The term $T_4(1, 1, \pi)$ in (1.3) represents the *diagonal Born-Oppenheimer correction*.
- There is a slight abuse of notation above: It may seem strange to precede “ $\mathcal{O}(\epsilon^5)$ ” with a term that has coefficient ϵ^6 . But ℓ can grow to be as large as $k\epsilon^{-3/4}$, so the expression in brackets in (1.4) can be on the order of $\epsilon^6 \cdot \epsilon^{-3/2} = \epsilon^{9/2}$.
- The vibrational quantum numbers n_1 , n_2 , and n_3 correspond to the normal modes associated with the nuclear vibration. For our particular model, which fixes the central nucleus at the origin, these correspond to the symmetric stretch (n_1), the asymmetric stretch (n_2), and the bending (n_3) modes.
- We no longer see decoupling between the vibrational and rotational degrees of freedom for terms that are $\mathcal{O}(\epsilon^6)$. In the classic Born-Oppenheimer approximation, where the angular momentum and vibrational quantum numbers are held *fixed* as $\epsilon \rightarrow 0$, such coupling is absent. That there should, in general, be coupling between ℓ and n goes back to the work of Dunham (see [4], as well as the discussion in Herzberg’s book [11]), who suggested that there should be energy expansions of the form

$$\sum_{i,j} A_{ij}(\epsilon) \left(n + \frac{1}{2}\right)^i (\ell(\ell + 1))^j$$

for *diatomic* molecules with large angular momentum.

- In two dimensions, the linearity of the molecule is not so important – we treat the linear case in this work for simplicity’s sake. In three dimensions, however, linear molecules are very different from nonlinear ones. Rotations of *linear* molecules in \mathbb{R}^3 are described by two angles, whereas rotations for *nonlinear* molecules require three angles.
- That the absolute error

$$\mathcal{E} = |E_{N,\ell} - E(\epsilon)|$$

is $\mathcal{O}(\epsilon^5)$ (as $\epsilon \rightarrow 0$) of course implies that there exists a constant C and a $\delta > 0$ such that if $0 < \epsilon < \delta$, we have $|\mathcal{E}| \leq C\epsilon^5$. But we emphasize that this constant C actually depends on κ and N : $C = C_{N,\kappa}$. In other words, for fixed $N \in \mathbb{N}_0$ and $\kappa \in [0, k]$, our expression $E(\epsilon)$ differs from an exact energy level $E_{N,\kappa}$ of the molecule (subject to our assumptions) as follows:

$$\mathcal{E} = |E(\epsilon) - E_{N,\kappa}| \leq C_{N,\kappa}\epsilon^5$$

Uniform estimates follow from the fact that κ is kept inside a compact set, and the constant $C_{N,\kappa}$ depends continuously (polynomially, in fact) on κ . (We have used $E_{N,\kappa}$ instead of $E_{N,\ell}$ above because the crucial observation for uniformity is that the κ is kept in a compact set. But ℓ and κ are interchangeable, since $\ell = \kappa\epsilon^{-3/4}$.)

Chapter 2

Statement of the Problem

We consider the following two-dimensional model of a triatomic molecule: Let the central nucleus have infinite mass and be fixed at the origin. Suppose the two outer nuclei both have mass M . Let their position vectors be R_1 and R_2 . Consider, in addition, n electrons of mass m_e with position vectors $\xi_1, \xi_2, \dots, \xi_n \in \mathbb{R}^2$. Because of the assumption we've placed on the central nucleus, the center of mass for the system is the origin in \mathbb{R}^2 . In units (e.g., Hartree atomic units) where \hbar and m_e have numerical value 1, the total non-relativistic (spin-free) molecular Hamiltonian has the form

$$H_0 = -\frac{1}{2M}\Delta_{R_1} - \frac{1}{2M}\Delta_{R_2} - \frac{1}{2}\sum_{i=1}^n \Delta_{\xi_i} + U(R_1, R_2, \xi_1, \dots, \xi_n), \quad (2.1)$$

where Δ is the Laplacian operator, and we assume U is a smooth¹ potential that captures the details of how the nuclei and electrons interact with one another. The nuclear geometry of this model is depicted in Figure 2.1.

Now, let $\epsilon = M^{-1/4}$, and write $R_1 = (r_1, \theta_1)$ and $R_2 = (r_2, \theta_2)$ in their polar representations. Also, let $\Xi = (\xi_1, \dots, \xi_n) \in \mathbb{R}^{2n}$ denote the totality of the electronic coordinates. Since the polar Laplacian takes the form

$$\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} = \frac{\partial^2}{\partial r_i^2} + \frac{1}{r_i} \frac{\partial}{\partial r_i} + \frac{1}{r_i^2} \frac{\partial^2}{\partial \theta_i^2},$$

¹We are placing smoothness assumptions on the interaction potentials that are not satisfied if the potentials in question are Coulombic. However, we have reason to believe that similar results can be obtained (though after considerably more effort) for such potentials – see, for example, [14] and [6].

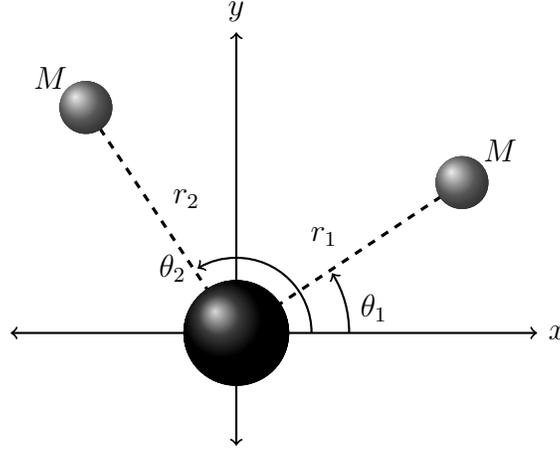


Figure 2.1: The nuclear geometry.

it follows that $H_0 = T_0 + h$, where

$$T_0 = -\frac{\epsilon^4}{2} \left(\frac{\partial^2}{\partial r_1^2} + \frac{1}{r_1} \frac{\partial}{\partial r_1} + \frac{1}{r_1^2} \frac{\partial^2}{\partial \theta_1^2} + \frac{\partial^2}{\partial r_2^2} + \frac{1}{r_2} \frac{\partial}{\partial r_2} + \frac{1}{r_2^2} \frac{\partial^2}{\partial \theta_2^2} \right).$$

is the nuclear kinetic energy operator, and

$$h(r_1, r_2, \theta_1, \theta_2) = -\frac{1}{2} \sum_{i=1}^n \Delta_{\xi_i} + U(r_1, \theta_1, r_2, \theta_2, \Xi).$$

We refer to h as the *electron* Hamiltonian. Note that it depends parametrically on the nuclear coordinates, though it is a differential operator in the electronic coordinates Ξ . The eigenvalue equation for this Hamiltonian reads $H_0 \Psi(r_1, r_2, \theta_1, \theta_2, \Xi) = E \Psi(r_1, r_2, \theta_1, \theta_2, \Xi)$. We can simplify our calculations by making a standard change of dependent variable and writing $\Psi = (r_1 r_2)^{-1/2} \psi$. In terms of the new dependent variable ψ , the eigenvalue equation reads

$$H_0 \left[\frac{\psi}{\sqrt{r_1 r_2}} \right] = E \left(\frac{\psi}{\sqrt{r_1 r_2}} \right).$$

After some algebra, we multiply both sides of this equation by $\sqrt{r_1 r_2}$ and find we are considering a new eigenvalue equation (with the same eigenvalues) $H_1 \psi = E \psi$, where H_1 takes the form

$$H_1 = -\frac{\epsilon^4}{2} \left(\frac{\partial^2}{\partial r_1^2} + \frac{1}{4r_1^2} + \frac{1}{r_1^2} \frac{\partial^2}{\partial \theta_1^2} + \frac{\partial^2}{\partial r_2^2} + \frac{1}{4r_2^2} + \frac{1}{r_2^2} \frac{\partial^2}{\partial \theta_2^2} \right) + h(r_1, r_2, \theta_1, \theta_2).$$

We make an additional change of variables: Let $\theta = \frac{1}{2}(\theta_1 + \theta_2)$ and $\phi = \theta_2 - \theta_1$. (The necessity of the factor of one half in the definition of θ is somewhat interesting and is discussed in more detail below.) The Chain Rule confirms that in terms of these new variables, $\frac{\partial}{\partial \theta_1} = \frac{1}{2} \frac{\partial}{\partial \theta} - \frac{\partial}{\partial \phi}$ and $\frac{\partial}{\partial \theta_2} = \frac{1}{2} \frac{\partial}{\partial \theta} + \frac{\partial}{\partial \phi}$. Letting $R = (r_1, r_2, \theta, \phi)$ denote the totality of the new nuclear coordinates (a convention we will adopt for the remainder of this paper), we write the total molecular Hamiltonian $H(\epsilon)$ as

$$H(\epsilon) = -\frac{\epsilon^4}{2} \left(\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} + \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \left(\frac{1}{4} \frac{\partial^2}{\partial \theta^2} + \frac{\partial^2}{\partial \phi^2} + \frac{1}{4} \right) + \left(\frac{1}{r_2^2} - \frac{1}{r_1^2} \right) \frac{\partial}{\partial \theta} \frac{\partial}{\partial \phi} \right) + h(R). \quad (2.2)$$

2.1 The Nuclear Angular Momentum

We first determine the form of the total nuclear angular momentum in terms of the original polar angles θ_1 and θ_2 . In our units ($\hbar = 1$), the angular momentum L_j of the j th nucleus (for $j = 1, 2$) takes the form

$$L_j = x_j p_{y_j} - y_j p_{x_j} = -i \left(x_j \frac{\partial}{\partial y_j} - y_j \frac{\partial}{\partial x_j} \right).$$

By the Chain Rule,

$$\begin{aligned} \frac{\partial}{\partial x_j} &= \frac{\partial}{\partial r_j} \frac{\partial r_j}{\partial x_j} + \frac{\partial}{\partial \theta_j} \frac{\partial \theta_j}{\partial x_j} = \frac{\cos \theta_j}{r_j} \frac{\partial}{\partial r_j} - \frac{\sin \theta_j}{r_j} \frac{\partial}{\partial \theta_j}, & \text{so } y_j \frac{\partial}{\partial x_j} &= \sin \theta_j \cos \theta_j \frac{\partial}{\partial r_j} - \sin^2 \theta_j \frac{\partial}{\partial \theta_j}. \\ \frac{\partial}{\partial y_j} &= \frac{\partial}{\partial r_j} \frac{\partial r_j}{\partial y_j} + \frac{\partial}{\partial \theta_j} \frac{\partial \theta_j}{\partial y_j} = \frac{\sin \theta_j}{r_j} \frac{\partial}{\partial r_j} + \frac{\cos \theta_j}{r_j} \frac{\partial}{\partial \theta_j}, & \text{so } x_j \frac{\partial}{\partial y_j} &= \sin \theta_j \cos \theta_j \frac{\partial}{\partial r_j} + \cos^2 \theta_j \frac{\partial}{\partial \theta_j}. \end{aligned}$$

This proves $L_j = -i \frac{\partial}{\partial \theta_j}$. The *total* nuclear angular momentum L , which is the sum of the angular momenta of the individual nuclei, is then given by

$$L = L_1 + L_2 = -i \left(\frac{\partial}{\partial \theta_1} + \frac{\partial}{\partial \theta_2} \right) = -i \left(\frac{1}{2} \frac{\partial}{\partial \theta} - \frac{\partial}{\partial \phi} + \frac{1}{2} \frac{\partial}{\partial \theta} + \frac{\partial}{\partial \phi} \right) = -i \frac{\partial}{\partial \theta}.$$

This operator has the familiar normalized eigenfunction

$$\Theta_\ell(\theta) = \frac{e^{i\ell\theta}}{\sqrt{2\pi}}$$

We will see that continuity of the eigenfunction in θ demands that $\Theta_\ell(\theta) = \Theta_\ell(\theta + 2\pi)$; or, $\ell = 0, \pm 1, \pm 2, \dots$. Note that L commutes with the nuclear kinetic energy operator

$$T(\epsilon) = -\frac{\epsilon^4}{2} \left(\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} + \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \left(\frac{1}{4} \frac{\partial^2}{\partial \theta^2} + \frac{\partial^2}{\partial \phi^2} + \frac{1}{4} \right) + \left(\frac{1}{r_2^2} - \frac{1}{r_1^2} \right) \frac{\partial}{\partial \theta} \frac{\partial}{\partial \phi} \right),$$

so we can simultaneously diagonalize $T(\epsilon)$ and L .

We have taken the time to elucidate the form of the nuclear angular momentum here because, in what follows, we will only be considering states with a specific form for the nuclear angular momentum. This will be made precise below.

We now take a moment to explain the factor of $1/2$ in the definition of θ . Figure 2.2 shows the original (gray) region in which θ_1 and θ_2 live. Periodic boundary conditions are imposed on θ_1 and θ_2 such that the dotted lines match up with the solid lines. If we make a naïve choice of coordinate change given by $\theta = \theta_1 + \theta_2$, $\phi = \theta_2 - \theta_1$, we obtain the region shown in Figure 2.3. Notice that the area of the region in which these new variables live (in the $\theta - \phi$ plane) is *twice* that of the original region (in the $\theta_1 - \theta_2$ plane). Hence the measure has changed; the transformation from (θ_1, θ_2) to (θ, ϕ) is *not* unitary. Another way to see this is to consider the matrix T of the transformation from (θ_1, θ_2) -space to (θ, ϕ) -space:

$$\begin{bmatrix} \theta \\ \phi \end{bmatrix} = \begin{bmatrix} 1 & 1 \\ -1 & 1 \end{bmatrix} \begin{bmatrix} \theta_1 \\ \theta_2 \end{bmatrix}$$

Then $\det T = 2$. Ideally, we would like the variables θ and ϕ to live in a nice rectangular region such that the measure $d\theta d\phi$ is identical to $d\theta_1 d\theta_2$. We remedy this as follows:

1. Define a *different* change of variables:

$$\theta = \frac{1}{2}(\theta_1 + \theta_2), \quad \phi = \theta_2 - \theta_1. \quad (2.3)$$

Under this change, the original domain of θ_1 and θ_2 is mapped to the region shown in Figure 2.4a.

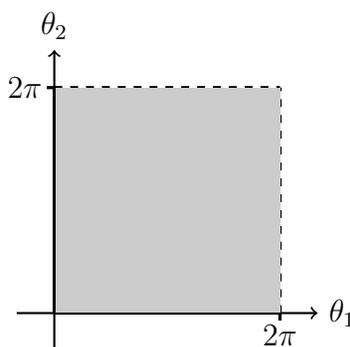


Figure 2.2: The original domain of the variables θ_1 and θ_2 .

2. The new change of variables has the advantage of preserving the area ($A = 4\pi^2$) of the original region. In other words, the transformation (2.3) preserves the measure. Also, note that the new transformation is unitary:

$$\begin{bmatrix} \theta \\ \phi \end{bmatrix} = \begin{bmatrix} \frac{1}{2} & \frac{1}{2} \\ -1 & 1 \end{bmatrix} \begin{bmatrix} \theta_1 \\ \theta_2 \end{bmatrix}, \quad \text{and} \quad \begin{vmatrix} \frac{1}{2} & \frac{1}{2} \\ -1 & 1 \end{vmatrix} = 1.$$

3. One can use the periodicity in the original polar variables to chop the isosceles triangle in the fourth quadrant of Figure 2.4a into two right triangles and move them to the first quadrant as indicated in Figure 2.4b. We then have the desired boundary conditions (2π periodicity) in θ for any given ϕ .
4. We note that the boundary conditions in ϕ for this new region (Figure 2.4b) are very strange. However, we will choose an electron energy surface for which ϕ will be highly localized (near π), so we won't need to worry too much about this.

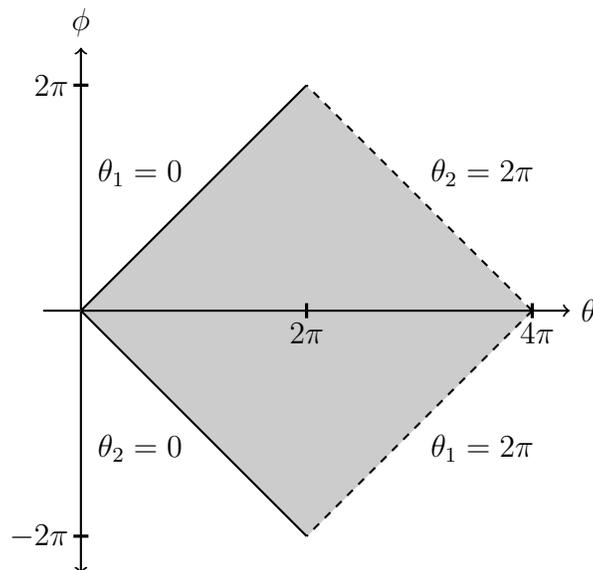


Figure 2.3: The naively rotated region, indicating lack of unitarity of the change of variables.

2.2 The Electron Energy Surface

As discussed in the introduction, one of the hallmarks of the Born-Oppenheimer approximation is the simplification of solving the electronic eigenvalue problem while holding the nuclear coordinates fixed. A solution to the eigenvalue problem for a fixed configuration of the nuclei is called an *electron energy surface*. In the calculation that follows in the next chapter, we assume we have found a *real* solution $\Phi(\Xi|R)$ (an assumption we are free to make, since h is a real operator), normalized in the Hilbert space $L^2(d\Xi)$ (such that $\|\Phi(\Xi|R)\| = 1$), to the electronic eigenvalue problem:

$$h(R) \Phi(\Xi|R) = V(r_1, r_2, \phi) \Phi(\Xi|R).$$

The notation “ $(\Xi|R)$ ” indicates that the nuclear variables enter the solution only as parameters – i.e., Φ is determined for a *given* set of nuclear coordinates. Note we are free to assume that the eigenvalue V has no θ dependence, since we need the potential to be invariant under a rotation of the entire system (electrons + nuclei) when the other variables are held fixed. In particular, we assume $V(r_1, r_2, \phi)$ takes the specific form

$$V(r_1, r_2, \phi) = \frac{1}{2}(r_1 - 1)^2 + \frac{1}{2}(r_2 - 1)^2 + \frac{1}{2}(r_1^2 + r_2^2 + 2r_1r_2 \cos \phi).$$

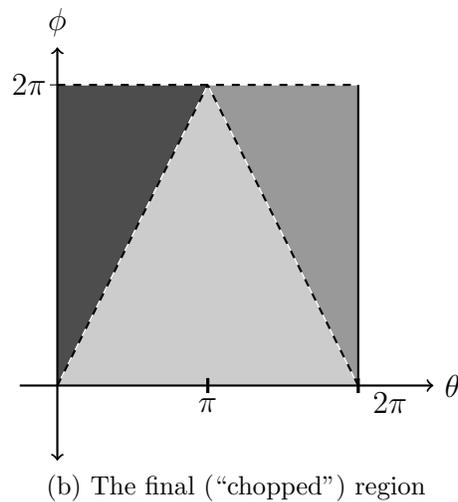
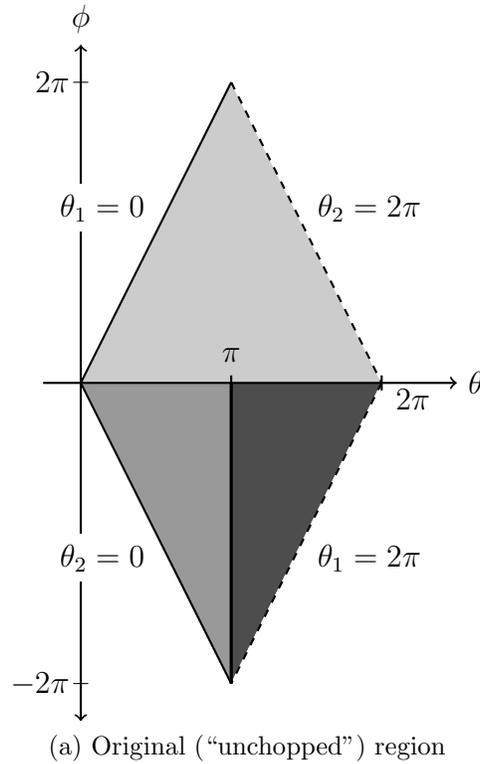


Figure 2.4: The correctly scaled and rotated region, showing the manipulation. The two right triangles are moved from the fourth quadrant to the first quadrant as indicated. The boundary condition in θ are thus the standard ones we expect. Note that area is preserved.

One sees immediately that this strictly nonnegative potential has a minimum at $r_1 = r_2 = 1$, $\phi = \pi$. It is therefore appropriate for a symmetric linear triatomic molecule of the form $A - B - A$ (e.g., CO_2). We assume this eigenvalue is isolated in the sense that there is a neighborhood about the minimum $(1, 1, \pi)$ such that, in this neighborhood, V does not intersect the continuous spectrum of h . We also assume V has multiplicity one.

Chapter 3

The Multiple Scales Calculation

The method of multiple scales is a technique that finds wide application in applied mathematics. As the name of the method indicates, it becomes important in perturbation theory problems that simultaneously involve very different length scales; for example, r and ϵr , where ϵ is a dimensionless parameter. The problem is solved by introducing a *new* variable $s = \epsilon r$ and treating the variables r and s as independent (as they are, to a good approximation, when ϵ is very small). The higher dimensional problem is then solved, with the replacement $s = \epsilon r$ made in the final solution.

We are presented with such a problem here, though it is slightly more complicated than the example mentioned above because we are dealing with several different variables. The different length scales in our problem are as follows:

- The (parametric) dependence of the electronic wavefunction Φ on the nuclear positions is $\mathcal{O}(1)$ (since the electronic Hamiltonian has the form $h(r_1, r_2, \theta, \phi)$); whereas
- There are *quantum* fluctuations of the nuclei about their optimal configuration that are $\mathcal{O}(\epsilon)$. More will be said about precisely *why* this is the correct scale to use below.

So we will need to play the game of multiple scales in the *three* nuclear variables r_1 , r_2 , and ϕ . Recall that the total molecular Hamiltonian $H(\epsilon)$ reads

$$H(\epsilon) = -\frac{\epsilon^4}{2} \left(\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} + \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \left(\frac{1}{4} \frac{\partial^2}{\partial \theta^2} + \frac{\partial^2}{\partial \phi^2} + \frac{1}{4} \right) + \left(\frac{1}{r_2^2} - \frac{1}{r_1^2} \right) \frac{\partial}{\partial \theta} \frac{\partial}{\partial \phi} \right) + h(R), \quad (3.1)$$

where we refer to $h(R)$ as the electronic Hamiltonian. We remind the reader that

$$h(R) = -\frac{1}{2}\Delta_{\Xi} + U(R, \Xi).$$

Again, we emphasize that h depends only *parametrically* on the nuclear variables $R = (r_1, r_2, \theta, \phi)$, but acts as a differential operator in $L^2(d\Xi)$.

We will be interested in finding approximate solutions, or *quasimodes*, for the eigenvalue problem given by the time-independent Schrödinger equation for the entire molecule:

$$H_0 \Upsilon(R, \Xi) = E \Upsilon(R, \Xi).$$

If we let $\Upsilon(R, \Xi) = \frac{\Psi(R, \Xi)}{\sqrt{r_1 r_2}}$, we are then seeking approximate solutions to the time-independent Schrödinger equation corresponding to the Hamiltonian $H(\epsilon)$ in (2.2):

$$H(\epsilon)\Psi(R, \Xi) = E\Psi(R, \Xi).$$

We will attempt to find $\Psi_{\epsilon}(R, \Xi)$ (the ϵ subscript reminds us that we are considering an *approximate*, not an exact, solution to the eigenvalue problem) and $E(\epsilon)$ such that for all ϵ sufficiently small,

$$\|(H(\epsilon) - E(\epsilon))\Psi_{\epsilon}\| \leq C\epsilon^5$$

for some positive constant $C \in \mathbb{R}$. Note that, because of the θ dependence in the electronic Hamiltonian h , the nuclear angular momentum operator $L = -i\frac{\partial}{\partial\theta}$ does *not*, in general, commute with $H(\epsilon)$, in which case the nuclear angular momentum ℓ is not a conserved quantity. We will find, however, that it will provide us with a convenient way to label our states.

To find Ψ_{ϵ} using the method of multiple scales, we will first seek a solution to a higher-dimensional problem, presented as follows (more details are provided in the paper [5]): Define variables x_i, y_i such that $x_1 = r_1$, $x_2 = r_2$, and $x_3 = \phi$. For the y_i 's, let

$$y_1 = \frac{r_1 - 1}{\epsilon}, \quad y_2 = \frac{r_2 - 1}{\epsilon}, \quad y_3 = \frac{\phi - \pi}{\epsilon}.$$

Henceforth, let $X \in \mathbb{R}^3$ denote the vector (x_1, x_2, x_3) and $Y \in \mathbb{R}^3$ denote the vector

(y_1, y_2, y_3) . We now set

$$\Psi_\epsilon(X, \theta, \Xi) = \psi_\epsilon(X, Y, \theta, \Xi),$$

where ψ_ϵ is our higher-dimensional solution.

Some rearrangement of terms in (3.1) gives

$$\begin{aligned} H(\epsilon) = & -\frac{\epsilon^4}{2} \left\{ \frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} + \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \frac{\partial^2}{\partial \phi^2} \right. \\ & \left. + \frac{1}{4} \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \left(\frac{\partial^2}{\partial \theta^2} + 1 \right) + \left(\frac{1}{r_2^2} - \frac{1}{r_1^2} \right) \frac{\partial}{\partial \theta} \frac{\partial}{\partial \phi} \right\} \\ & + h(R). \end{aligned} \tag{3.2}$$

The Chain Rule confirms that in terms of the variables x_1 and y_1 , the differential operators above take the form

$$\begin{aligned} \frac{\partial^2}{\partial r_i^2} &= \frac{\partial^2}{\partial x_i^2} + \frac{2}{\epsilon} \frac{\partial}{\partial x_i} \frac{\partial}{\partial y_i} + \frac{1}{\epsilon^2} \frac{\partial^2}{\partial y_i^2}, \\ \frac{\partial}{\partial \phi} &= \frac{\partial}{\partial x_3} + \frac{1}{\epsilon} \frac{\partial}{\partial y_3}, \\ \frac{\partial^2}{\partial \phi^2} &= \frac{\partial^2}{\partial x_3^2} + \frac{2}{\epsilon} \frac{\partial}{\partial x_3} \frac{\partial}{\partial y_3} + \frac{1}{\epsilon^2} \frac{\partial^2}{\partial y_3^2}. \end{aligned}$$

We now make a judicious choice of whether to replace the original nuclear variables with the x_i or y_i 's in the expression for $H(\epsilon)$. Since the nuclear kinetic energy derives principally from quantum effects, we let $r_i = 1 + \epsilon y_i$ for $i = 1, 2$ for r_i in the nuclear kinetic energy operator. We will also introduce an operator T_4 into the Hamiltonian $H(\epsilon)$, which will have the job of removing the X dependence of certain functions that will show up in our calculations. We find that T_4 allows us to treat the variables X and Y as if they are independent, even though they really aren't. (See [5] for more details about this.) The Hamiltonian in terms

of the variables X and Y is then

$$\begin{aligned}
H(\epsilon) = & -\frac{\epsilon^4}{2} \frac{\partial^2}{\partial x_1^2} - \epsilon^3 \frac{\partial^2}{\partial x_1 \partial y_1} - \frac{\epsilon^2}{2} \frac{\partial^2}{\partial y_1^2} \\
& -\frac{\epsilon^4}{2} \frac{\partial^2}{\partial x_2^2} - \epsilon^3 \frac{\partial^2}{\partial x_2 \partial y_2} - \frac{\epsilon^2}{2} \frac{\partial^2}{\partial y_2^2} \\
& + \left(\frac{1}{(1 + \epsilon y_1)^2} + \frac{1}{(1 + \epsilon y_2)^2} \right) \left(-\frac{\epsilon^4}{2} \frac{\partial^2}{\partial x_3^2} - \epsilon^3 \frac{\partial^2}{\partial x_3 \partial y_3} - \frac{\epsilon^2}{2} \frac{\partial^2}{\partial y_3^2} \right) \\
& + \frac{1}{8} \left(\frac{1}{(1 + \epsilon y_1)^2} + \frac{1}{(1 + \epsilon y_2)^2} \right) \left(-\epsilon^4 \frac{\partial^2}{\partial \theta^2} - \epsilon^4 \right) \\
& + \frac{1}{2} \left(\frac{1}{(1 + \epsilon y_2)^2} - \frac{1}{(1 + \epsilon y_1)^2} \right) \left(-\epsilon^4 \frac{\partial}{\partial x_3} - \epsilon^3 \frac{\partial}{\partial y_3} \right) \frac{\partial}{\partial \theta} \\
& + [h(x_1, x_2, x_3, \theta) - V(x_1, x_2, x_3)] + V(1 + \epsilon y_1, 1 + \epsilon y_2, \pi + \epsilon y_3) \\
& + \epsilon^4 [T_4(1 + \epsilon y_1, 1 + \epsilon y_2, \pi + \epsilon y_3) - T_4(X)].
\end{aligned}$$

We expand $V(1 + \epsilon y_1, 1 + \epsilon y_2, \pi + \epsilon y_3)$ and all other terms that feature $1 + \epsilon y_i$ or $\pi + \epsilon y_3$ in their Taylor series about $\epsilon = 0$. Since

$$\begin{aligned}
V(1 + \epsilon y_1, 1 + \epsilon y_2, \pi + \epsilon y_3) = & \left(y_1^2 + y_2^2 - y_1 y_2 + \frac{1}{2} y_3^2 \right) \epsilon^2 + \left(\frac{1}{2} y_1 y_3^2 + \frac{1}{2} y_2 y_3^2 \right) \epsilon^3 \\
& + \left(\frac{1}{2} y_1 y_2 y_3^2 - \frac{1}{24} y_3^2 \right) \epsilon^4 + \mathcal{O}(\epsilon^5)
\end{aligned}$$

and

$$\frac{1}{(1 + \epsilon y_i)^2} = 1 - 2\epsilon y_i + 3\epsilon^2 y_i^2 - 4\epsilon^3 y_i^3 + 5\epsilon^4 y_i^4 + \mathcal{O}(\epsilon^5),$$

it follows that $H(\epsilon)$ takes the form:

$$\begin{aligned}
H(\epsilon) = & -\frac{\epsilon^4}{2} \frac{\partial^2}{\partial x_1^2} - \epsilon^3 \frac{\partial}{\partial x_1} \frac{\partial}{\partial y_1} - \frac{\epsilon^2}{2} \frac{\partial^2}{\partial y_1^2} \\
& -\frac{\epsilon^4}{2} \frac{\partial^2}{\partial x_2^2} - \epsilon^3 \frac{\partial}{\partial x_2} \frac{\partial}{\partial y_2} - \frac{\epsilon^2}{2} \frac{\partial^2}{\partial y_2^2} \\
& + (2 - 2\epsilon(y_1 + y_2) + 3\epsilon^2(y_1^2 + y_2^2) - 4\epsilon^3(y_1^3 + y_2^3) + \mathcal{O}(\epsilon^4)) \left(-\frac{\epsilon^4}{2} \frac{\partial^2}{\partial x_3^2} - \epsilon^3 \frac{\partial}{\partial x_3} \frac{\partial}{\partial y_3} - \frac{\epsilon^2}{2} \frac{\partial^2}{\partial y_3^2} \right) \\
& + \left(\frac{1}{4} - \frac{1}{4}\epsilon(y_1 + y_2) + \frac{3}{8}\epsilon^2(y_1^2 + y_2^2) - \frac{1}{2}\epsilon^3(y_1^3 + y_2^3) + \mathcal{O}(\epsilon^4) \right) \left(-\epsilon^4 \frac{\partial^2}{\partial \theta^2} - \epsilon^4 \right) \\
& + \left((y_1 - y_2) - \frac{3}{2}\epsilon(y_1^2 - y_2^2) + 2\epsilon^2(y_1^3 - y_2^3) + \mathcal{O}(\epsilon^3) \right) \left(-\epsilon^5 \frac{\partial}{\partial x_3} \frac{\partial}{\partial \theta} - \epsilon^4 \frac{\partial}{\partial y_3} \frac{\partial}{\partial \theta} \right) \\
& + h(X, \theta) - V(X) \\
& + \epsilon^2 \left(y_1^2 - y_1 y_2 + y_2^2 + \frac{y_3^2}{2} \right) + \epsilon^3 \left(\frac{1}{2} y_3^2 (y_1 + y_2) \right) + \epsilon^4 \left(\frac{1}{2} y_3^2 \left(y_1 y_2 - \frac{y_3^2}{12} \right) \right) + \mathcal{O}(\epsilon^5) \\
& + \epsilon^4 [T_4(1 + \epsilon y_1, 1 + \epsilon y_2, \pi + \epsilon y_3) - T_4(X)].
\end{aligned}$$

Collecting like powers of ϵ , we can formally write $H(\epsilon)$ as

$$H(\epsilon) = H_0 + \epsilon^2 H_2 + \epsilon^3 H_3 + \epsilon^4 H_4 + \mathcal{O}(\epsilon^5),$$

where

$$\begin{aligned}
H_0 &= h(X, \theta) - V(X), \\
H_2 &= -\frac{1}{2} \frac{\partial^2}{\partial y_1^2} - \frac{1}{2} \frac{\partial^2}{\partial y_2^2} - \frac{\partial^2}{\partial y_3^2} + y_1^2 + y_2^2 + \frac{1}{2} y_3^2 - y_1 y_2, \\
H_3 &= -\frac{\partial}{\partial x_1} \frac{\partial}{\partial y_1} - \frac{\partial}{\partial x_2} \frac{\partial}{\partial y_2} - 2 \frac{\partial}{\partial x_3} \frac{\partial}{\partial y_3} + (y_1 + y_2) \left(\frac{\partial^2}{\partial y_3^2} + \frac{1}{2} y_3^2 \right), \\
H_4 &= -\frac{1}{2} \frac{\partial^2}{\partial x_1^2} - \frac{1}{2} \frac{\partial^2}{\partial x_2^2} - \frac{\partial^2}{\partial x_3^2} + 2(y_1 + y_2) \frac{\partial}{\partial x_3} \frac{\partial}{\partial y_3} - \frac{3}{2} (y_1^2 + y_2^2) \frac{\partial^2}{\partial y_3^2} \\
& - \frac{1}{4} - \frac{1}{4} \frac{\partial^2}{\partial \theta^2} - (y_1 - y_2) \frac{\partial}{\partial y_3} \frac{\partial}{\partial \theta} + \frac{1}{2} y_3^2 \left(y_1 y_2 - \frac{y_3^2}{12} \right) \\
& + T_4(1 + \epsilon y_1, 1 + \epsilon y_2, \pi + \epsilon y_3) - T_4(X).
\end{aligned}$$

It will also be important to account for operators of order 5 and 6 in the Hamiltonian that

contain $\partial/\partial\theta$ and $\partial^2/\partial\theta^2$. These are:

$$H_5 = \frac{1}{4}(y_1 + y_2)\frac{\partial^2}{\partial\theta^2} - (y_1 - y_2)\frac{\partial}{\partial x_3}\frac{\partial}{\partial\theta} + \frac{3}{2}(y_1^2 - y_2^2)\frac{\partial}{\partial y_3}\frac{\partial}{\partial\theta},$$

$$H_6 = -\frac{3}{8}(y_1^2 + y_2^2)\frac{\partial^2}{\partial\theta^2} + \frac{3}{2}(y_1^2 - y_2^2)\frac{\partial}{\partial x_3}\frac{\partial}{\partial\theta} - 2(y_1^3 - y_2^3)\frac{\partial}{\partial y_3}\frac{\partial}{\partial\theta}.$$

Since we are interested in angular momentum quantum numbers ℓ that can be as large as $\kappa\epsilon^{-3/4}$, these operators actually produce terms of order *lower* than ϵ^5 , as we will soon see.

We now study the perturbation problem

$$H(\epsilon)(\epsilon^{\nu_0}\psi_{\nu_0} + \epsilon^{\nu_1}\psi_{\nu_1} + \epsilon^{\nu_2}\psi_{\nu_2} + \dots) = (\epsilon^{\nu_0}E_{\nu_0} + \epsilon^{\nu_1}E_{\nu_1} + \epsilon^{\nu_2}E_{\nu_2} + \dots)(\epsilon^{\nu_0}\psi_{\nu_0} + \epsilon^{\nu_1}\psi_{\nu_1} + \epsilon^{\nu_2}\psi_{\nu_2} + \dots),$$

where the ν_i allow for the fact that we might have weird (that is, non-integer) powers of ϵ in the expansions of ψ and E because of the $\epsilon^{-3/4}$. We will determine what the ν 's are as we go along. Because of this, we make the ansatz that only *quarter* powers of ϵ will appear in the wavefunction and energy expansions; i.e., ψ and E will have the form

$$\psi = \psi_0 + \sum_{n=1}^{19} \epsilon^{n/4}\psi_{n/4} + \mathcal{O}(\epsilon^5),$$

$$E = E_0 + \sum_{n=1}^{19} \epsilon^{n/4}E_{n/4} + \mathcal{O}(\epsilon^5),$$

with $\psi_{n/4}$ and $E_{n/4}$ possibly being equal to zero for certain values of n . In fact, we will find that the wavefunction will look (formally) like

$$\begin{aligned} \psi_\epsilon = & \psi_0 + \epsilon \psi_1 + \epsilon^{5/4}\psi_{5/4} + \epsilon^{3/2}\psi_{3/2} + \epsilon^2\psi_2 + \epsilon^{9/4}\psi_{9/4} \\ & + \epsilon^{5/2}\psi_{5/2} + \epsilon^3\psi_3 + \epsilon^{13/4}\psi_{13/4} + \epsilon^{17/4}\psi_{17/4} + \epsilon^{9/2}\psi_{9/2}, \end{aligned} \tag{3.3}$$

with each of the ψ_ν above not equal to zero. We will make the following additional assumption on the ψ_ν :

$$\psi_\nu \perp \psi_0 \quad \text{for } \nu > 0. \tag{3.4}$$

By considering Figure 3.1, one sees that at each order this can be done, though the eigenvector of $H(\epsilon)$ thereby obtained will not necessarily be normalized.

In what follows we will consider only states whose leading order term ψ_0 has the following

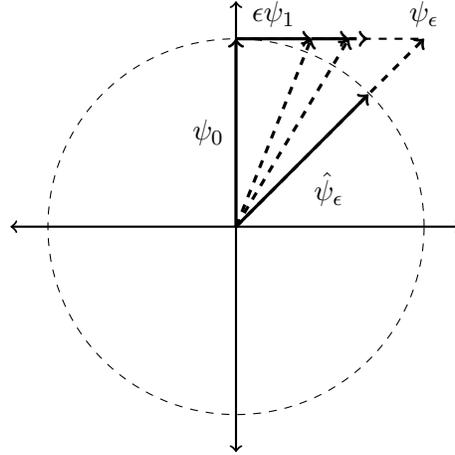


Figure 3.1: A (two-dimensional) illustration of the validity of the assumption $\psi_0 \perp \psi_\nu$. The circle depicted is the unit circle $\{|\psi| = 1\}$. By proceeding in this way, we obtain a vector ψ_ϵ which is not a unit vector but is instead some multiple of the unit vector $\hat{\psi}_\epsilon$.

form:

$$\psi_0(X, Y, \theta, \Xi) = \Theta_\ell(\theta)\Phi(\Xi|X)f(X, Y, \Xi), \quad (3.5)$$

where f is an arbitrary function with no θ dependence. In words, we assume that the θ dependence of ψ_0 enters *only* through the electronic eigenfunction Φ and the angular momentum eigenfunction $\Theta_\ell(\theta) = \frac{e^{i\ell\theta}}{\sqrt{2\pi}}$. This restricts the generality of our results, but it also prevents the calculations from becoming prohibitively complicated.

We now embark on the multiple scales perturbation calculation. We will use a number of Hilbert space tricks – predominantly properties of inner products – to simplify the expressions at each order. We begin with terms that multiply ϵ^0 .

3.1 Order 0

The leading order terms in $H(\epsilon)$ are the order zero terms. They require

$$[h(X, \theta) - V(X)]\psi_0(X, Y, \theta, \Xi) = E_0\psi_0(X, Y, \theta, \Xi).$$

This equation will be satisfied if we set $\underline{E_0 = 0}$ and allow ψ_0 to be a multiple of Φ in the Hilbert space $L^2(d\Xi)$. We therefore conclude that $\underline{\psi_0 = f_0(X, Y)\Phi(\Xi|X)\Theta_\ell(\theta)}$ for some function f_0 .

3.2 Orders 1/4 through 7/4

The next several orders in ϵ — namely, $\nu = n/4$ for $n = 1, 2, \dots, 7$ — are each treated as follows:

1. Since, inductively, $E_{\nu-1/4} = 0$, and there are no terms in the Hamiltonian of order $\nu \in (0, 2)$, the order ν terms require $H_0\psi_\nu = E_\nu\psi_0$, or

$$[h(X, \theta) - V(X)]\psi_\nu = E_\nu\psi_0. \quad (3.6)$$

2. We satisfy (3.6) by setting $\underline{E_\nu = 0}$ and writing $\underline{\psi_\nu = f_\nu(X, Y, \theta)\Phi(\Xi|X)}$, where the f_ν are arbitrary functions with no dependence on the electronic coordinates. We only expect ψ_1 , $\psi_{3/2}$, and $\psi_{5/4}$ to be nonzero.

3.3 Order 2

The next order terms acting on the wavefunction are of order ϵ^2 . At this order, we have

$$\begin{aligned} & [h(X, \theta) - V(X)]\psi_2 \\ & + \left(-\frac{1}{2} \frac{\partial^2}{\partial y_1^2} - \frac{1}{2} \frac{\partial^2}{\partial y_2^2} - \frac{\partial^2}{\partial y_3^2} + y_1^2 + y_2^2 + \frac{1}{2} y_3^2 - y_1 y_2 \right) \psi_0 = E_2 \psi_0. \end{aligned} \quad (3.7)$$

To satisfy this equation, we make the change of variables

$$z_1 = \frac{1}{\sqrt{2}}(y_1 + y_2), \quad z_2 = \frac{1}{\sqrt{2}}(y_1 - y_2), \quad z_3 = \frac{1}{\sqrt{2}}y_3. \quad (3.8)$$

In terms of these new variables, H_2 becomes a standard harmonic oscillator Hamiltonian in three dimensions with the three frequencies $\omega_1 = 1$, $\omega_2 = \sqrt{3}$, and $\omega_3 = \sqrt{2}$. These frequencies are *not* rationally related, so there is no degeneracy in the energies associated

with this oscillator. We write

$$H_{\text{osc}} = -\frac{1}{2} \frac{\partial^2}{\partial z_1^2} - \frac{1}{2} \frac{\partial^2}{\partial z_2^2} - \frac{1}{2} \frac{\partial^2}{\partial z_3^2} + \frac{1}{2} z_1^2 + \frac{3}{2} z_2^2 + z_3^2.$$

Then the ϵ^2 terms require $H_0\psi_2 + [H_{\text{osc}} - E_2]\psi_0 = 0$. We make one more change of variables: $\zeta_i = \omega_i^{1/2} z_i$. Considering the components of (3.7) parallel to Φ , we conclude that

$$\psi_0 = g_0(X) \Phi(\Xi|X) \Theta_\ell(\theta) \prod_{i=1}^3 \phi_{n_i}(\zeta_i), \quad (3.9)$$

where $g_0(X)$ is an arbitrary function of X , and we have defined $\phi_{n_i}(\zeta_i)$ as follows:

$$\phi_{n_i}(\zeta_i) = A_{n_i} H_{n_i}(\zeta_i) e^{-\zeta_i^2/2} \quad (3.10)$$

for $n_i = 0, 1, 2, \dots$, with $H_{n_i}(\zeta_i)$ the n_i th Hermite polynomial in the variable ζ_i and A_{n_i} the normalization constant that satisfies $\langle \phi_{n_i}, \phi_{n_i} \rangle_{z_i} = 1$; that is,

$$1 = A_{n_i}^2 \int_{-\infty}^{\infty} H_{n_i}^2(\omega_i^{1/2} z_i) e^{-(\omega_i^{1/2} z_i)^2} dz_i. \quad (3.11)$$

It follows that $A_{n_i} = 2^{-n_i/2} (n_i!)^{-1/2} \pi^{-1/4} \omega_i^{1/4}$. An appeal to the standard results for harmonic oscillators shows us that E_2 then takes the form

$$\underline{\underline{E_2 = \left(n_1 + \frac{1}{2} \right) + \left(n_2 + \frac{1}{2} \right) \sqrt{3} + \left(n_3 + \frac{1}{2} \right) \sqrt{2},}}$$

giving us the first nonzero contribution to the energy expansion. Since the product of harmonic oscillator eigenfunctions determined above will crop up later in a number of places, we simplify notation by letting $N = (n_1, n_2, n_3)$, $Z = (\zeta_1, \zeta_2, \zeta_3)$, and $\prod_1^3 A_{n_i} H_{n_i}(\zeta_i) e^{-\zeta_i^2/2} = \Omega_N(Z)$. In this new notation, ψ_0 takes the more manageable form

$$\psi_0 = g_0 \Theta_\ell(\theta) \Phi(\Xi|X) \Omega_N(Z).$$

Note that we have removed the X dependence from g_0 , which we will soon find we can do (see the discussion in Section 3.12) by making an appropriate choice for the operator T_4 . We find that no constraints fix the value of g_0 , so we set $g_0 = 1$. Then the *final* (normalized)

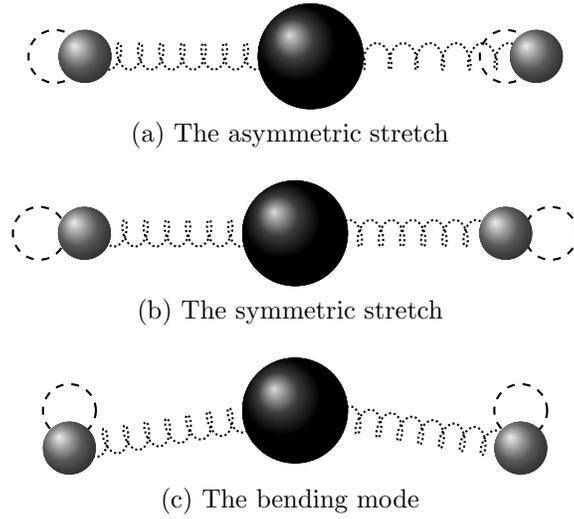


Figure 3.2: An illustration of the normal modes

form for ψ_0 is $\underline{\psi_0 = \Phi(\Xi|X)\Omega_N(Z)\Theta_\ell(\theta)}$.

We make a few remarks about the form of ψ_0 :

- It is not difficult to see that these frequencies correspond to the normal modes for a system of two oscillators free to move in two dimensions, as mentioned in the introduction. Obviously, n_3 corresponds to changing ϕ and keeping the r_i 's fixed – the bending mode. Since n_1 corresponds to keeping $r_1 - r_2$ and ϕ fixed while varying $r_1 + r_2$, this is the symmetric stretch. The quantum number n_2 corresponds to the asymmetric stretch. Figure 3.2 depicts these modes.
- It should now be apparent why the quantum fluctuations mentioned on page 14 occur on the order of ϵ^1 : Notice that our ψ_0 in (3.9) contains gaussians in the variables ζ_i , which look like

$$\exp\left(-\frac{\omega_i z_i^2}{2}\right) = \exp\left(-\frac{\omega_i (r_i - r_{\min})^2}{2\epsilon^2}\right).$$

One way to think of this expression is to view ϵ as the variance of the gaussian; then $\sqrt{\epsilon^2} = \epsilon$ represents the characteristic length. Alternatively, note that we have (for example)

$$r_1 - 1 = \frac{\epsilon}{\sqrt{2}}(z_1 + z_2).$$

Hence the quantum fluctuations of the nuclei about their equilibrium positions (e.g., $r_1 - 1$) really are on the order of ϵ .

- The observant reader will note that the harmonic oscillator Hamiltonian in the variable x is normally solved for $x \in (-\infty, \infty)$. However, $r_1, r_2 \in [0, \infty)$, and $\phi \in [0, 2\pi)$. We will remedy this by multiplying the entire wavefunction Υ_ϵ by a cut-off function $F(q)$ that restricts the domain of the wavefunction. (A similar strategy is employed in both [5] and [12].) In constructing F , we exploit the assumption that V is isolated to find a $\delta > 0$ such that F has the following properties:

1. F is C^∞ in all three variables.
2. F is symmetric about zero.
3. F satisfies

$$F(q) = \begin{cases} 1 & \text{if } |q| < \delta, \\ 0 & \text{if } |q| > 2\delta. \end{cases}$$

4. For $\delta \leq |q| \leq 2\delta$, we define F in such a way that the requirements (1) and (2) are satisfied and such that F only takes values in the range $[0, 1]$.

We will multiply our final solution by $F(r_1 - 1)F(r_2 - 1)F(\phi - \pi)$. This removes the ambiguity introduced by the implication in our definition of $\Omega_N(Z)$ that the z_i 's live everywhere. Calculations carried out in [12] demonstrate that L^2 norms of derivatives of the cut-off functions times the ϕ 's defined above are exponentially small, so we can carry out our perturbation theory calculations without taking the cut-off functions into account. It is also argued in [12] that the normalization constant derived in (3.11) still works, since the gaussians in the ϕ 's are highly localized, and the difference $\|\phi - F\phi\|$ (where $\|\cdot\|$ is the L^2 norm) is again exponentially small.

Considering the components of (3.7) perpendicular to Φ , we find $\psi_2 = f_2(X, Y, \theta)\Phi(\Xi|X)$ for some arbitrary function f_2 .

3.4 An Aside – “Weird” Powers of ϵ

Having obtained a particular form for ψ_0 in terms of $\Phi(\Xi|X)$, it will be important for us to consider the action of the operators H_4 , H_5 , and H_6 on ψ_0 . At present, we shall only be concerned with certain terms of these operators that contain partial derivatives in θ (for

reasons that will soon be apparent). To this end, define operators Λ_4 and Λ_6 as follows:

$$\Lambda_4 = -\frac{1}{4}\frac{\partial^2}{\partial\theta^2} - (y_1 - y_2)\frac{\partial}{\partial y_3}\frac{\partial}{\partial\theta}, \quad (3.12)$$

$$\Lambda_6 = -\frac{3}{8}(y_1^2 + y_2^2)\frac{\partial^2}{\partial\theta^2}. \quad (3.13)$$

These operators isolate the terms in H_4 and H_6 that contain partial derivatives in θ . We first look at $\Lambda_4\psi_0$ (where we have abbreviated the form of ψ_0 to $\psi_0 = \Phi\Theta\Omega$):

$$\begin{aligned} \epsilon^4\Lambda_4\psi_0 &= \epsilon^4 \left(-\frac{1}{4}\frac{\partial^2}{\partial\theta^2} - (y_1 - y_2)\frac{\partial}{\partial y_3}\frac{\partial}{\partial\theta} \right) \Phi\Theta\Omega \\ &= -\frac{\epsilon^4}{4}\Omega \left(\Theta\frac{\partial^2\Phi}{\partial\theta^2} + 2\frac{\partial\Phi}{\partial\theta}\frac{\partial\Theta}{\partial\theta} + \Phi\frac{\partial^2\Theta}{\partial\theta^2} \right) - \epsilon^4(y_1 - y_2)\frac{\partial\Omega}{\partial y_3} \left[\frac{\partial\Phi}{\partial\theta}\Theta + \frac{\partial\Theta}{\partial\theta}\Phi \right] \\ &= -\frac{\epsilon^4}{4}\Omega\Theta \left(\frac{\partial^2\Phi}{\partial\theta^2} + 2il\frac{\partial\Phi}{\partial\theta} - \ell^2\Phi \right) - \epsilon^4(y_1 - y_2)\Theta\frac{\partial\Omega}{\partial y_3} \left[\frac{\partial\Phi}{\partial\theta} + il\Phi \right]. \end{aligned}$$

After letting $\ell = \kappa\epsilon^{-3/4}$ and grouping like powers of ϵ , we find

$$\begin{aligned} \epsilon^4\Lambda_4\psi_0 &= -\epsilon^4 \left(\frac{1}{4}\Omega\Theta\frac{\partial^2\Phi}{\partial\theta^2} + (y_1 - y_2)\frac{\partial\Omega}{\partial y_3}\frac{\partial\Phi}{\partial\theta}\Theta \right) + \epsilon^{5/2}\frac{\kappa^2}{4}\psi_0 \\ &\quad - \epsilon^{13/4} \left(\frac{i\kappa}{2}\Omega\Theta\frac{\partial\Phi}{\partial\theta} + i\kappa(y_1 - y_2)\frac{\partial}{\partial y_3}\psi_0 \right). \end{aligned} \quad (3.14)$$

Thus, because of the form we have chosen for the angular momentum quantum number ℓ , some terms that *appear* at first glance to be of order 4 are actually of order $4 - 3/4 = \underline{\underline{13/4}}$ or order $4 - 3/2 = \underline{\underline{5/2}}$. Now, we consider $H_5\psi_0$:

$$\begin{aligned} \epsilon^5 H_5\psi_0 &= \epsilon^5 \left(\frac{1}{4}(y_1 + y_2)\frac{\partial^2}{\partial\theta^2} - (y_1 - y_2)\frac{\partial}{\partial x_3}\frac{\partial}{\partial\theta} + \frac{3}{2}(y_1^2 - y_2^2)\frac{\partial}{\partial y_3}\frac{\partial}{\partial\theta} \right) \Phi\Theta\Omega \\ &= \frac{\epsilon^5}{4}(y_1 + y_2)\Omega \left(\Theta\frac{\partial^2\Phi}{\partial\theta^2} + 2\frac{\partial\Theta}{\partial\theta}\frac{\partial\Phi}{\partial\theta} + \Phi\frac{\partial^2\Theta}{\partial\theta^2} \right) \\ &\quad - \epsilon^5(y_1 - y_2)\Omega \left(\Theta\frac{\partial}{\partial\theta}\frac{\partial\Phi}{\partial x_3} + \frac{\partial\Phi}{\partial x_3}\frac{\partial\Theta}{\partial\theta} \right) + \frac{3\epsilon^5}{2}(y_1^2 - y_2^2)\frac{\partial\Omega}{\partial y_3} \left(\Theta\frac{\partial\Phi}{\partial\theta} + \Phi\frac{\partial\Theta}{\partial\theta} \right) \\ &= \frac{\epsilon^5}{4}(y_1 + y_2)\Omega\Theta \left(\frac{\partial^2\Phi}{\partial\theta^2} + 2il\frac{\partial\Phi}{\partial\theta} - \ell^2\Phi \right) \\ &\quad - \epsilon^5(y_1 - y_2)\Omega\Theta \left(\frac{\partial}{\partial\theta}\frac{\partial\Phi}{\partial x_3} + il\frac{\partial\Phi}{\partial x_3} \right) + \frac{3\epsilon^5}{2}(y_1^2 - y_2^2)\Theta\frac{\partial\Omega}{\partial y_3} \left(\frac{\partial\Phi}{\partial\theta} + il\Phi \right). \end{aligned}$$

Imposing $\ell = \kappa\epsilon^{-3/4}$ and grouping together powers of ϵ , we find

$$\begin{aligned} \epsilon^5 H_5 \psi_0 = & \epsilon^5 \Theta \left(\frac{1}{4}(y_1 + y_2)\Omega \frac{\partial^2 \Phi}{\partial \theta^2} - (y_1 - y_2)\Omega \frac{\partial}{\partial \theta} \frac{\partial \Phi}{\partial x_3} + \frac{3}{2}(y_1^2 - y_2^2) \frac{\partial \Omega}{\partial y_3} \frac{\partial \Phi}{\partial \theta} \right) \\ & + \epsilon^{17/4} \Theta \left(\frac{1}{2}i\kappa(y_1 + y_2)\Omega \frac{\partial \Phi}{\partial \theta} - i\kappa(y_1 - y_2)\Omega \frac{\partial \Phi}{\partial x_3} + \frac{3}{2}i\kappa(y_1^2 - y_2^2)\Phi \frac{\partial \Omega}{\partial y_3} \right) \\ & - \epsilon^{7/2} \frac{\kappa^2}{4}(y_1 + y_2)\psi_0. \end{aligned} \quad (3.15)$$

So we have terms that are of order $5 - 3/4 = \underline{\underline{17/4}}$ and $5 - 3/2 = \underline{\underline{7/2}}$. Finally, we consider $\Lambda_6 \psi_0$ when $\ell = \kappa\epsilon^{-3/4}$:

$$\begin{aligned} \epsilon^6 \Lambda_6 \psi_0 = & -\frac{3}{8}\epsilon^6(y_1^2 + y_2^2)\Omega \left(\Phi \frac{\partial^2 \Theta}{\partial \theta^2} + \Theta \frac{\partial^2 \Phi}{\partial \theta^2} + 2\frac{\partial \Theta}{\partial \theta} \frac{\partial \Phi}{\partial \theta} \right) \\ = & -\frac{3}{8}\epsilon^6(y_1^2 + y_2^2)\Omega \left(-\ell^2 \Phi \Theta + \Theta \frac{\partial^2 \Phi}{\partial \theta^2} + 2i\ell \Theta \frac{\partial \Phi}{\partial \theta} \right) \\ = & \epsilon^{9/2} \frac{3}{8}\kappa^2(y_1^2 + y_2^2)\psi_0 - \epsilon^6 \frac{3}{8}(y_1^2 + y_2^2)\Omega \Theta \frac{\partial^2 \Phi}{\partial \theta^2} - \epsilon^{21/4} \frac{3}{4}i\kappa(y_1^2 + y_2^2)\Omega \Theta \frac{\partial \Phi}{\partial \theta}. \end{aligned}$$

So, instead of showing up at order 6, as we might expect, terms show up at orders $6 - 3/2 = \underline{\underline{9/2}}$ and $6 - 3/4 = \underline{\underline{21/4}}$. These observations will be important as we move forward. We will need to do something similar once we obtain precise forms for higher-order ψ_ν 's.

3.5 Order 9/4

Terms multiplying $\epsilon^{9/4}$ require

$$[h(X, \theta) - V(X)]\psi_{9/4} = E_{9/4}\psi_0.$$

Our strategy for orders 1/4 through 7/4 works here as well. We conclude that $E_{9/4} = 0$ and

$$\psi_{9/4} = f_{9/4}(X, Y, \theta)\Phi(\Xi|X).$$

3.6 Order 5/2

The next order terms in the Hamiltonian acting on the wavefunction are of order 5/2 (see (3.14) above). They require

$$[h(X, \theta) - V(X)]\psi_{5/2} = \left(E_{5/2} - \frac{\kappa^2}{4} \right) \psi_0.$$

In analogy with the $\epsilon^{9/4}$ calculation, we satisfy this equation by setting $E_{5/2} = \kappa^2/4$ and taking

$$\psi_{5/2} = f_{5/2}(X, Y, \theta)\Phi(\Xi|X).$$

3.7 Order 11/4

We find the terms of order 11/4 require

$$[h(X, \theta) - V(X)]\psi_{11/4} = E_{11/4}\psi_0.$$

Again, we are reminded of our order 9/4 calculation. We conclude immediately, therefore, that $E_{11/4} = 0$, and that

$$\psi_{11/4} = f_{11/4}(X, Y, \theta)\Phi(\Xi|X).$$

3.8 Order 3

We next need to consider $H_3\psi_0 + H_2\psi_1 + H_0\psi_3 = E_2\psi_1 + E_3\psi_0$, or

$$\begin{aligned} & [h(X, \theta) - V(X)]\psi_3 + [H_{\text{osc}} - E_2]\psi_1 \\ & + \left((y_1 + y_2) \frac{\partial^2}{\partial y_3^2} + \frac{1}{2} y_3^2 (y_1 + y_2) - \frac{\partial}{\partial x_1} \frac{\partial}{\partial y_1} - \frac{\partial}{\partial x_2} \frac{\partial}{\partial y_2} - 2 \frac{\partial}{\partial x_3} \frac{\partial}{\partial y_3} \right) \psi_0 \\ & = E_3\psi_0. \end{aligned} \tag{3.16}$$

To assist with calculations for this and higher orders, we decompose the ψ_ν as follows: $\psi_\nu = \psi_\nu^\perp + \psi_\nu^{\parallel\perp} + \psi_\nu^{\parallel\parallel}$, where

- ψ_ν^\perp is orthogonal to $\Phi(\Xi|X)$ in the Hilbert space $L^2(d\Xi)$ (where, again, $\Xi \in \mathbb{R}^{2n}$),
- $\psi_\nu^{\parallel\perp}$ is a multiple of $\Phi(\Xi|R)$ but orthogonal to $\Omega_N(Z)$ in $L^2(dZ) = L^2(dz_1 dz_2 dz_3)$, and
- $\psi_\nu^{\parallel\parallel}$ is a multiple of $\Phi(\Xi|R)\Omega_N(Z)$.

This strategy enables us to make the following useful observations:

1. The assumption that $\psi_0 \perp \psi_\nu$ for $\nu > 0$ enables us to say that $\psi_\nu^{\parallel\parallel} = 0$ for $\nu > 0$. This means $\psi_\nu = \psi_\nu^\perp + \psi_\nu^{\parallel\perp}$ for $\nu > 0$.
2. If it is determined that ψ_ν has the form $f_\nu(X, Y, \theta)\Phi(\Xi|R)$ for some function f_ν , then $\psi_\nu^\perp = 0$, and it follows that $\psi_\nu = \psi_\nu^{\parallel\perp}$. In light of this observation and our previous computations, we conclude the following:
3. Note that since Φ is a unit vector in $L^2(d\Xi)$, we know $\frac{\partial\Phi}{\partial x_i} \perp \Phi$ and $\frac{\partial\Phi}{\partial\theta} \perp \Phi$ in $L^2(d\Xi)$.

Taking the inner product of both sides of (3.16) with $\Phi(\Xi|R)$ and $\Omega_N(Z)$, we find that $\underline{E_3 = 0}$. The components of either side of (3.16) in the direction of $\Phi(\Xi|R)$ but perpendicular to $\Omega_N(Z)$ must be equal. We therefore have

$$\psi_1 = \psi_1^{\parallel\perp} = \Theta_\ell(\theta)\Phi(\Xi|R)[H_{\text{osc}} - E_2]_r^{-1} \left[(y_1 + y_2) \left(-\frac{\partial^2}{\partial y_3^2} - \frac{1}{2}y_3^2 \right) \Omega_N(Z) \right], \quad (3.17)$$

where the reduced resolvent $[H_{\text{osc}} - E_2]_r^{-1}$ denotes the inverse of the restriction of the operator $[H_{\text{osc}} - E_2]$ to the subspace of $L^2(dZ)$ orthogonal to $\Omega_N(Z)$. We will need the explicit form of ψ_1 in later calculations, so we simplify it by letting

$$G_1(Y) = [H_{\text{osc}} - E_2]_r^{-1} \left[(y_1 + y_2) \left(-\frac{\partial^2}{\partial y_3^2} - \frac{1}{2}y_3^2 \right) \Omega_N(Z) \right] \quad (3.18)$$

It then follows that

$$\psi_1 = \Theta_\ell(\theta) \Phi(\Xi|R) G_1(Y). \quad (3.19)$$

Likewise, the components of both sides of (3.16) orthogonal to $\Phi(\Xi|R)$ must be equal, so

$$\psi_3^\perp = \Theta_\ell(\theta)[h(X, \theta) - V(X)]_r^{-1} \left(\frac{\partial \Omega_N}{\partial y_1} \frac{\partial \Phi}{\partial x_1} + \frac{\partial \Omega_N}{\partial y_2} \frac{\partial \Phi}{\partial x_2} + 2 \frac{\partial \Omega_N}{\partial y_3} \frac{\partial \Phi}{\partial x_3} \right),$$

where $[h(X, \theta) - V(X)]_r^{-1}$ is the restriction of the operator $[h(X, \theta) - V(X)]$ to the subspace of $L^2(d\Xi)$ orthogonal to Φ .

Having found an explicit form for ψ_1 in terms of the electron eigenfunction, we mimic what we did above for ψ_0 and consider what happens when the operators H_4 and H_5 act on ψ_1 . Again, we will only be concerned with terms involving partial derivatives in θ , for only these operators produce terms of strange (but relevant) orders. Retaining the definition of Λ_4 in (3.12), we find

$$\begin{aligned} \epsilon^5 \Lambda_4 \psi_1 &= -\epsilon^5 \left[\frac{1}{4} \frac{\partial^2}{\partial \theta^2} + (y_1 - y_2) \frac{\partial}{\partial y_3} \frac{\partial}{\partial \theta} \right] \Theta \Phi G_1 \\ &= -\frac{\epsilon^5}{4} G_1 \left(\Theta \frac{\partial^2 \Phi}{\partial \theta^2} + 2 \frac{\partial \Phi}{\partial \theta} \frac{\partial \Theta}{\partial \theta} + \Phi \frac{\partial^2 \Theta}{\partial \theta^2} \right) - \epsilon^5 (y_1 - y_2) \frac{\partial G_1}{\partial y_3} \left[\frac{\partial \Phi}{\partial \theta} \Theta + \frac{\partial \Theta}{\partial \theta} \Phi \right] \\ &= -\frac{\epsilon^5}{4} G_1 \left(\Theta \frac{\partial^2 \Phi}{\partial \theta^2} + 2i\ell \frac{\partial \Phi}{\partial \theta} \Theta - \ell^2 \Phi \Theta \right) - \epsilon^5 (y_1 - y_2) \frac{\partial G_1}{\partial y_3} \left[\frac{\partial \Phi}{\partial \theta} \Theta + i\ell \Theta \Phi \right], \end{aligned}$$

and after letting $\ell = \kappa \epsilon^{-3/4}$ and grouping like powers of ϵ , we find

$$\begin{aligned} \epsilon^5 \Lambda_4 \psi_1 &= -\epsilon^5 \left(\frac{1}{4} G_1 \Theta \frac{\partial^2 \Phi}{\partial \theta^2} + (y_1 - y_2) \frac{\partial G_1}{\partial y_3} \frac{\partial \Phi}{\partial \theta} \Theta \right) + \epsilon^{7/2} \frac{\kappa^2}{4} \psi_1 \\ &\quad - \epsilon^{17/4} \left(\frac{i\kappa}{2} G_1 \Theta \frac{\partial \Phi}{\partial \theta} + i\kappa (y_1 - y_2) \frac{\partial G_1}{\partial y_3} \Theta \Phi \right). \end{aligned} \tag{3.20}$$

Thus, our choice for the particular form taken by ℓ implies that what *appear* to be fifth-order terms are really terms of orders $7/2$ and $17/4$. We will similarly be concerned with what

happens when H_5 acts on ψ_1 :

$$\begin{aligned}
\epsilon^6 H_5 \psi_1 &= \epsilon^6 \left(\frac{1}{4}(y_1 + y_2) \frac{\partial^2}{\partial \theta^2} - (y_1 - y_2) \frac{\partial}{\partial x_3} \frac{\partial}{\partial \theta} + \frac{3}{2}(y_1^2 - y_2^2) \frac{\partial}{\partial y_3} \frac{\partial}{\partial \theta} \right) \Theta \Phi G_1 \\
&= \frac{\epsilon^6}{4} (y_1 + y_2) \Theta G_1 \left(\frac{\partial^2 \Phi}{\partial \theta^2} + 2i\ell \frac{\partial \Phi}{\partial \theta} - \ell^2 \Phi \right) \\
&\quad - \epsilon^6 (y_1 - y_2) G_1 \Theta \left(\frac{\partial}{\partial x_3} \frac{\partial \Phi}{\partial \theta} + i\ell \frac{\partial \Phi}{\partial x_3} \right) + \frac{3\epsilon^6}{2} (y_1^2 - y_2^2) \Theta \frac{\partial G_1}{\partial y_3} \left(\frac{\partial \Phi}{\partial \theta} + i\ell \Phi \right) \\
&= \epsilon^6 \left(\frac{1}{4}(y_1 + y_2) \Theta G_1 \frac{\partial^2 \Phi}{\partial \theta^2} - (y_1 - y_2) G_1 \Theta \frac{\partial}{\partial x_3} \frac{\partial \Phi}{\partial \theta} + \frac{3}{2}(y_1^2 - y_2^2) \Theta \frac{\partial G_1}{\partial y_3} \frac{\partial \Phi}{\partial \theta} \right) \\
&\quad + \epsilon^{21/4} \left(i\kappa \frac{1}{2}(y_1 + y_2) \Theta G_1 \frac{\partial \Phi}{\partial \theta} - i\kappa (y_1 - y_2) \Theta G_1 \frac{\partial \Phi}{\partial x_3} + \frac{3}{2} i\kappa (y_1^2 - y_2^2) \Theta \frac{\partial G_1}{\partial y_3} \Phi \right) \\
&\quad - \epsilon^{9/2} \frac{\kappa^2}{4} (y_1 + y_2) \psi_1.
\end{aligned}$$

The last term, of order $6 - 3/2 = \underline{9/2}$, will be relevant to us. The other terms are ignored, since they are of order larger than five.

We now resume the perturbation calculation.

3.9 Order 13/4

The next-highest order terms acting on the wavefunction give

$$\begin{aligned}
&[h(X, \theta) - V(X)]\psi_{13/4} + [H_{\text{osc}} - E_2]\psi_{5/4} \\
&\quad - i\kappa (y_1 - y_2) \frac{\partial \Omega_N}{\partial y_3} \Theta_\ell(\theta) \Phi - \frac{1}{2} i\kappa \Theta_\ell(\theta) \Omega_N(Z) \frac{\partial \Phi}{\partial \theta} = E_{13/4} \psi_0.
\end{aligned} \tag{3.21}$$

Taking inner products of both sides with $\Phi(\Xi|R)\Omega_N(Z)$, we conclude that $\underline{E_{13/4} = 0}$.

Looking on both sides of (3.21) at components parallel to $\Phi(\Xi|R)$ but orthogonal to $\Omega_N(Z)$, we find that

$$\begin{aligned}
\psi_{5/4} = \psi_{5/4}^{\perp\perp} &= i\kappa \Theta_\ell(\theta) \Phi(\Xi|R) [H_{\text{osc}} - E_2]_r^{-1} \left((y_1 - y_2) \frac{\partial \Omega_N}{\partial y_3} \right) \\
&= -\kappa \Theta_\ell(\theta) \Phi(\Xi|R) [H_{\text{osc}} - E_2]_r^{-1} \left((y_1 - y_2) \left(-i \frac{\partial \Omega_n}{\partial y_3} \right) \right).
\end{aligned} \tag{3.22}$$

All remaining terms are orthogonal to $\Phi(\Xi|R)$, so

$$\psi_{13/4}^\perp = \frac{1}{2} i\kappa \Theta_\ell(\theta)\Omega_N(Z)[h(X, \theta) - V(X)]_r^{-1} \frac{\partial\Phi}{\partial\theta}. \quad (3.23)$$

Again, we need to consider what happens when H_4 acts on $\psi_{5/4}$ to see what kind of weird powers of ϵ pop up. Retaining the definition of Λ_4 provided in (3.12) and simplifying notation by letting

$$G_{5/4}(Y) = [H_{\text{osc}} - E_2]_r^{-1} \left((y_1 - y_2) \frac{\partial\Omega_N}{\partial y_3} \right),$$

we have, after some algebra,

$$\begin{aligned} \epsilon^{21/4} \Lambda_4 \psi_{5/4} &= -\epsilon^{21/4} \left(\frac{1}{4} \frac{\partial^2}{\partial\theta^2} + (y_1 - y_2) \frac{\partial}{\partial y_3} \frac{\partial}{\partial\theta} \right) i\kappa \Theta \Phi G_{5/4} \\ &= -i\kappa \epsilon^{21/4} \left(\frac{1}{4} G_{5/4} \Theta \frac{\partial^2 \Phi}{\partial\theta^2} + (y_1 - y_2) \frac{\partial G_{5/4}}{\partial y_3} \frac{\partial \Phi}{\partial\theta} \Theta \right) + \epsilon^{15/4} \frac{\kappa^2}{4} \psi_{5/4} \\ &\quad + \epsilon^{9/2} \left(\frac{\kappa^2}{2} G_{5/4} \Theta \frac{\partial \Phi}{\partial\theta} + \kappa^2 (y_1 - y_2) \frac{\partial G_{5/4}}{\partial y_3} \Theta \Phi \right). \end{aligned} \quad (3.24)$$

3.10 Order 7/2

The next-highest order terms acting on the wavefunction are of order 7/2 (see (3.15) and (3.20)). They require, after some cancellation,

$$[h(X, \theta) - V(X)]\psi_{7/2} + [H_{\text{osc}} - E_2]\psi_{3/2} - \frac{\kappa^2}{4}(y_1 + y_2)\psi_0 = E_{7/2}\psi_0. \quad (3.25)$$

Taking the inner product of both sides with $\Phi(\Xi|R)\Omega_N(Z)$, we conclude that $\underline{\underline{E_{7/2} = 0}}$. And we find that $\underline{\underline{\psi_{7/2}^\perp = 0}}$ and $\underline{\underline{\psi_{3/2} = \psi_{3/2}^{\perp\perp} = \frac{\kappa^2}{4} \Theta_\ell(\theta) \Phi [H_{\text{osc}} - E_2]_r^{-1} ((y_1 + y_2) \Omega_N(Z))}}$. The form of $\psi_{3/2}$ will be important to us in later computations, but it's a bit messy as written. We will simplify things by letting

$$G_{3/2} = [H_{\text{osc}} - E_2]_r^{-1} ((y_1 + y_2) \Omega_N(Z)), \quad (3.26)$$

in which case the expression for $\psi_{3/2}$ becomes

$$\psi_{3/2} = \frac{\kappa^2}{4} \Theta_\ell(\theta) \Phi(\Xi|R) G_{3/2}. \quad (3.27)$$

3.11 Order 15/4

The terms multiplying $\epsilon^{15/4}$ require (see (3.24))

$$[h(X, \theta) - V(X)]\psi_{15/4} + \frac{\kappa^2}{4}\psi_{5/4} = E_{15/4}\psi_0 + E_{5/2}\psi_{5/4}.$$

But $(\kappa^2/4)\psi_{5/4} = E_{5/2}\psi_{5/4}$, so these terms cancel. Taking inner products of both sides with $\Phi(\Xi|R)\Omega_N(Z)$, we find $E_{15/4} = 0$ and $\psi_{15/4} = f_{15/4}(X, Y, \theta)\Phi(\Xi|X)$.

3.12 Order 4

We now move to the order 4 terms. The operator T_4 will appear at this order to remove the X dependence from the functions g_ν . The terms multiplying ϵ^4 then require, in part by what we unearthed in (3.14),

$$\begin{aligned} & [h(X, \theta) - V(X)]\psi_4 + [H_{\text{osc}} - E_2]\psi_2 \\ & + \left((y_1 + y_2) \left(\frac{\partial^2}{\partial y_3^2} + \frac{1}{2}y_3^2 \right) - \frac{\partial}{\partial x_1} \frac{\partial}{\partial y_1} - \frac{\partial}{\partial x_2} \frac{\partial}{\partial y_2} - 2 \frac{\partial}{\partial x_3} \frac{\partial}{\partial y_3} \right) \psi_1 \\ & + \left[-\frac{1}{2} \frac{\partial^2}{\partial x_1^2} - \frac{1}{2} \frac{\partial^2}{\partial x_2^2} - \frac{\partial^2}{\partial x_3^2} + 2(y_1 + y_2) \frac{\partial}{\partial x_3} \frac{\partial}{\partial y_3} - \frac{3}{2}(y_1^2 + y_2^2) \frac{\partial^2}{\partial y_3^2} \right. \\ & \left. - \frac{1}{4} + \frac{1}{2}y_3^2 \left(y_1 y_2 - \frac{y_3^2}{12} \right) \right] \psi_0 - \left(\frac{1}{4} \Omega \Theta \frac{\partial^2 \Phi}{\partial \theta^2} + (y_1 - y_2) \frac{\partial \Omega}{\partial y_3} \frac{\partial \Phi}{\partial \theta} \Theta \right) \\ & + T_4(1, 1, \pi)\psi_0 - T_4(X)\psi_0 = E_4\psi_0. \end{aligned} \quad (3.28)$$

We remind the reader that ψ_1 takes the form (3.17). Employing the definition of $G_1(Y)$ given in (3.18) and taking inner products of each side of (3.28) with $\Theta_\ell(\theta)\Phi(\Xi|X)$, we find

$$\begin{aligned}
& [H_{\text{osc}} - E_2] \langle \Theta, f_2 \rangle_\theta + (y_1 + y_2) \left(\frac{\partial^2}{\partial y_3^2} + \frac{1}{2} y_3^2 \right) G_1(Y) \\
& + \Omega_N(Z) \left\langle \Phi(\Xi|X), \left(-\frac{1}{2} \frac{\partial^2}{\partial x_1^2} - \frac{1}{2} \frac{\partial^2}{\partial x_2^2} - \frac{\partial^2}{\partial x_3^2} - \frac{1}{4} \frac{\partial^2}{\partial \theta^2} \right) \Phi(\Xi|X) \right\rangle \\
& - \frac{3}{2} (y_1^2 + y_2^2) \frac{\partial^2 \Omega_N}{\partial y_3^2} - \frac{1}{4} \Omega_N(Z) + \frac{1}{2} y_3^2 \left(y_1 y_2 - \frac{y_3^2}{12} \right) \Omega_N(Z) \\
& + \Omega_N(Z) T_4(1, 1, \pi) - \Omega_N(Z) T_4(X) = \Omega_N(Z) E_4.
\end{aligned} \tag{3.29}$$

If we set

$$T_4(X) = \left\langle \Phi(\Xi|X), \left(-\frac{1}{2} \frac{\partial^2}{\partial x_1^2} - \frac{1}{2} \frac{\partial^2}{\partial x_2^2} - \frac{\partial^2}{\partial x_3^2} - \frac{1}{4} \frac{\partial^2}{\partial \theta^2} \right) \Phi(\Xi|X) \right\rangle,$$

then there will be cancellation of two of the terms on the left-hand side. Then, taking the inner product of both sides of (3.29) with $\Omega_N(Z)$, we obtain an expression for E_4 :

$$\begin{aligned}
E_4 & = \left\langle \Omega_N(Z), (y_1 + y_2) \frac{\partial^2 G_1}{\partial y_3^2} \right\rangle + \frac{1}{2} \langle \Omega_N(Z), (y_1 + y_2) y_3^2 G_1(Y) \rangle \\
& - \frac{3}{2} \left\langle \Omega_N(Z), (y_1^2 + y_2^2) \frac{\partial^2 \Omega_N(Z)}{\partial y_3^2} \right\rangle \\
& - \frac{1}{4} + \frac{1}{2} \langle \Omega_N(Z), y_1 y_2 y_3^2 \Omega_N(Z) \rangle - \frac{1}{24} \langle \Omega_N(Z), y_3^4 \Omega_N(Z) \rangle + T_4(1, 1, \pi).
\end{aligned} \tag{3.30}$$

Writing this entirely in terms of the z_i 's and letting $p_3 = -i \frac{\partial}{\partial z_3}$, we find that

$$\begin{aligned}
E_4 & = -\frac{1}{\sqrt{2}} \langle \Omega_N, z_1 p_3^2 G_1 \rangle + \sqrt{2} \langle \Omega_N, z_1 z_3^2 G_1 \rangle + \frac{3}{4} \langle \Omega_N, (z_1^2 + z_2^2) p_3^2 \Omega_N \rangle \\
& + \frac{1}{2} \langle \Omega_N, (z_1^2 - z_2^2) z_3^2 \Omega_N \rangle - \frac{1}{6} \langle \Omega_N, z_3^4 \Omega_N \rangle - \frac{1}{4} + T_4(1, 1, \pi).
\end{aligned} \tag{3.31}$$

These inner products were computed in Mathematica – some sample code is provided in the

appendix, beginning on page 44. At the end of the day, we find

$$\begin{aligned}
E_4 = & -\frac{39}{224} - \frac{\sqrt{2}}{7} \left(n_1 + \frac{1}{2}\right) \left(n_3 + \frac{1}{2}\right) + \frac{1}{\sqrt{6}} \left(n_2 + \frac{1}{2}\right) \left(n_3 + \frac{1}{2}\right) \\
& + \frac{1}{56} \left(n_3 + \frac{1}{2}\right)^2 + T_4(1, 1, \pi).
\end{aligned} \tag{3.32}$$

The term $T_4(1, 1, \pi)$ is known as the diagonal Born-Oppenheimer correction. It clearly depends on the form of the electronic eigenfunction Φ , so we can say nothing further about it. We can, however, write down an expression for ψ_2 :

$$\begin{aligned}
\psi_2 = \psi_2^{\parallel\perp} = & [H_{\text{osc}} - E_2]_r^{-1} (y_1 + y_2) \left(-\frac{\partial^2}{\partial y_3^2} - \frac{1}{2}y_3^2\right) \psi_1 \\
& + \frac{3}{2} [H_{\text{osc}} - E_2]_r^{-1} (y_1^2 + y_2^2) \frac{\partial^2}{\partial y_3^2} \psi_0 - \frac{1}{2} [H_{\text{osc}} - E_2]_r^{-1} y_3^2 \left(y_1 y_2 - \frac{y_3^2}{12}\right) \psi_0.
\end{aligned} \tag{3.33}$$

3.13 Order 17/4

The next order we see in the Hamiltonian is 17/4. These terms give

$$\begin{aligned}
& [h(X, \theta) - V(X)]\psi_{17/4} + [H_{\text{osc}} - E_2]\psi_{9/4} \\
& - \frac{1}{2} i\kappa \Theta_\ell(\theta) G_1(Y) \frac{\partial \Phi}{\partial \theta} + i\kappa (y_1 - y_2) \frac{\partial}{\partial y_3} \psi_1
\end{aligned} \tag{3.34}$$

$$\begin{aligned}
& + \left((y_1 + y_2) \frac{\partial^2}{\partial y_3^2} + \frac{1}{2} y_3^2 (y_1 + y_2) - \frac{\partial^2}{\partial x_1 \partial y_1} - \frac{\partial^2}{\partial x_2 \partial y_2} - 2 \frac{\partial^2}{\partial x_3 \partial y_3} \right) \psi_{5/4} \\
& + \left(-i\kappa (y_1 - y_2) \frac{\partial}{\partial x_3} + \frac{3}{2} i\kappa (y_1^2 - y_2^2) \frac{\partial}{\partial y_3} \right) \psi_0 + \frac{1}{2} i\kappa (y_1 + y_2) \Theta_\ell(\theta) \Omega_N(Z) \frac{\partial \Phi}{\partial \theta} \\
& = E_{17/4} \psi_0.
\end{aligned} \tag{3.35}$$

The terms (3.34) and (3.35) above result from H_4 acting on ψ_1 and H_5 acting on ψ_0 , respectively. We take the inner product of ψ_0 with both sides. We get

$$E_{17/4} = \kappa \left\langle \Omega_N(Z), (y_1 - y_2) \left(-i \frac{\partial}{\partial y_3} \right) \Omega_N(Z) \right\rangle + \left\langle \Omega_N(Z), (y_1 + y_2) \frac{\partial^2}{\partial y_3^2} \psi_{5/4} \right\rangle \\ + \frac{1}{2} \left\langle \Omega_N(Z), (y_1 + y_2) y_3^2 \psi_{5/4} \right\rangle - \frac{3}{2} \kappa \left\langle \Omega_N(Z), (y_1^2 - y_2^2) \left(-i \frac{\partial}{\partial y_3} \right) \Omega_N(Z) \right\rangle.$$

Rewriting this in terms of the z_i 's, we get

$$E_{17/4} = \kappa \left\langle \Omega_N(Z), (y_1 - y_2) \left(-i \frac{\partial}{\partial y_3} \right) \Omega_N(Z) \right\rangle \quad (3.36)$$

$$+ \left\langle \Omega_N(Z), (y_1 + y_2) \frac{\partial^2}{\partial y_3^2} \psi_{5/4} \right\rangle \quad (3.37)$$

$$+ \frac{1}{2} \left\langle \Omega_N(Z), (y_1 + y_2) y_3^2 \psi_{5/4} \right\rangle \quad (3.38)$$

$$- \frac{3}{2} \kappa \left\langle \Omega_N(Z), (y_1^2 - y_2^2) \left(-i \frac{\partial}{\partial y_3} \right) \Omega_N(Z) \right\rangle, \quad (3.39)$$

where the inner products are computed in $L^2(dZ)$. Each of these inner products is zero. This is relatively obvious for (3.36) and (3.39), since $\langle z_j^{2n+1} \rangle$ and $\langle p_j^{2n+1} \rangle$ (the odd moments) vanish for all n in the harmonic oscillator eigenstates. Rewriting these inner products entirely in terms of the z_i 's, we find that (3.36) involves a computation of $\langle \phi_{n_1}(z_1), z_1 \phi_{n_1}(z_1) \rangle = 0$ and (3.39) involves $\langle \phi_{n_3}(z_3), p_3 \phi_{n_3}(z_3) \rangle = 0$. For the other two lines, we need to work a bit harder, since these inner products involve $[H_{\text{osc}} - E_2]_r^{-1}$. But since H_{osc} is an *even* operator, it preserves the parity of what it operates on. Using the form of $\psi_{5/4}$ in (3.22), we note that the second function in the inner products in both (3.37) and (3.38) is odd in z_1 (and z_2).

Hence $\underline{E_{17/4}} = 0$. We also find

$$\begin{aligned}
\psi_{17/4}^\perp &= \frac{1}{2} i\kappa \Theta_\ell(\theta) [H_{\text{osc}} - E_2]_r^{-1} \left[(y_1 + y_2) \left(-\frac{\partial^2}{\partial y_3^2} - \frac{1}{2} y_3^2 \right) \Omega_N(Z) \right] [h(X, \theta) - V(X)]_r^{-1} \frac{\partial \Phi}{\partial \theta} \\
&\quad - \kappa \Theta_\ell(\theta) \frac{\partial}{\partial y_1} \left([H_{\text{osc}} - E_2]_r^{-1} \left[(y_1 - y_2) \left(-i \frac{\partial}{\partial y_3} \right) \Omega_N(Z) \right] \right) [h(X, \theta) - V(X)]_r^{-1} \frac{\partial \Phi}{\partial x_1} \\
&\quad - \kappa \Theta_\ell(\theta) \frac{\partial}{\partial y_2} \left([H_{\text{osc}} - E_2]_r^{-1} \left[(y_1 - y_2) \left(-i \frac{\partial}{\partial y_3} \right) \Omega_N(Z) \right] \right) [h(X, \theta) - V(X)]_r^{-1} \frac{\partial \Phi}{\partial x_2} \\
&\quad - 2\kappa \Theta_\ell(\theta) \frac{\partial}{\partial y_3} \left([H_{\text{osc}} - E_2]_r^{-1} \left[(y_1 - y_2) \left(-i \frac{\partial}{\partial y_3} \right) \Omega_N(Z) \right] \right) [h(X, \theta) - V(X)]_r^{-1} \frac{\partial \Phi}{\partial x_3} \\
&\quad + i\kappa (y_1 - y_2) \Theta_\ell(\theta) \Omega_N(Z) [h(X, \theta) - V(X)]_r^{-1} \frac{\partial \Phi}{\partial x_3} \\
&\quad + \frac{1}{2} i\kappa (y_1 + y_2) \Theta_\ell(\theta) \Omega_N(Z) [h(X, \theta) - V(X)]_r^{-1} \frac{\partial \Phi}{\partial \theta}.
\end{aligned}$$

We also see that

$$\begin{aligned}
\psi_{9/4}^{\parallel\perp} &= \psi_{9/4} = \\
& 2\kappa [H_{\text{osc}} - E_2]_r^{-1} \left[(y_1 - y_2) \left(-i \frac{\partial}{\partial y_3} \right) [H_{\text{osc}} - E_2]_r^{-1} \left((y_1 + y_2) \left(-\frac{\partial^2}{\partial y_3^2} - \frac{1}{2} y_3^2 \right) \Omega_N(Z) \right) \right] \\
& + 2\kappa [H_{\text{osc}} - E_2]_r^{-1} \left[(y_1 + y_2) \left(-\frac{\partial^2}{\partial y_3^2} \right) [H_{\text{osc}} - E_2]_r^{-1} \left((y_1 - y_2) \frac{\partial}{\partial y_3} \Omega_N(Z) \right) \right] \\
& + \kappa [H_{\text{osc}} - E_2]_r^{-1} \left[y_3^2 (y_1 + y_2) \left(-\frac{\partial^2}{\partial y_3^2} \right) [H_{\text{osc}} - E_2]_r^{-1} \left((y_1 - y_2) \frac{\partial}{\partial y_3} \Omega_N(Z) \right) \right] \\
& - 3\kappa [H_{\text{osc}} - E_2]_r^{-1} \left[(y_1^2 - y_2^2) \left(-i \frac{\partial}{\partial y_3} \right) \right].
\end{aligned}$$

3.14 Order 9/2

The terms multiplying $\epsilon^{9/2}$ give

$$\begin{aligned}
& [h(X, \theta) - V(X)] \psi_{9/2} + [H_{\text{osc}} - E_2] \psi_{5/2} \\
& + \left((y_1 + y_2) \frac{\partial^2}{\partial y_3^2} + \frac{1}{2} y_3^2 (y_1 + y_2) - \frac{\partial}{\partial x_1} \frac{\partial}{\partial y_1} - \frac{\partial}{\partial x_2} \frac{\partial}{\partial y_2} - 2 \frac{\partial}{\partial x_3} \frac{\partial}{\partial y_3} \right) \psi_{3/2} \\
& + \kappa^2 (y_1 - y_2) \frac{\partial G_{5/4}}{\partial y_3} \Theta \Phi - \frac{\kappa^2}{4} (y_1 + y_2) \psi_1 + \frac{3}{8} \kappa^2 (y_1^2 + y_2^2) \psi_0 + \frac{\kappa^2}{2} \Theta G_{5/4}(Y) \frac{\partial \Phi}{\partial \theta} \\
& = E_{9/2} \psi_0
\end{aligned} \tag{3.40}$$

It follows that

$$\begin{aligned}
E_{9/2} &= \left\langle \Omega_N, (y_1 + y_2) \frac{\partial^2}{\partial y_3^2} \psi_{3/2} \right\rangle + \frac{1}{2} \langle \Omega_N, (y_1 + y_2) y_3^2 \psi_{3/2} \rangle \\
&\quad + \kappa^2 \left\langle \Omega_N, (y_1 - y_2) \frac{\partial}{\partial y_3} G_{5/4} \right\rangle - \frac{\kappa^2}{4} \langle \Omega_N, (y_1 + y_2) \psi_1 \rangle \\
&\quad + \frac{3}{8} \kappa^2 \langle \Omega_N, (y_1^2 + y_2^2) \psi_0 \rangle.
\end{aligned} \tag{3.41}$$

Again, this computation was carried out in Mathematica, where it was determined that

$$E_{9/2} = \frac{3}{4} \kappa^2 \left(n_1 + \frac{1}{2} \right) + \frac{7}{4\sqrt{3}} \kappa^2 \left(n_2 + \frac{1}{2} \right) - \frac{1}{\sqrt{2}} \kappa^2 \left(n_3 + \frac{1}{2} \right).$$

The relevant code can be found in the Appendix. We also have

$$\begin{aligned}
\psi_{9/2}^\perp &= \frac{\kappa^2}{4} \Theta \frac{\partial}{\partial y_1} \left([H_{\text{osc}} - E_2]_r^{-1} ((y_1 + y_2) \Omega_N) \right) [h(X, \theta) - V(X)]_r^{-1} \frac{\partial \Phi}{\partial x_1} \\
&\quad + \frac{\kappa^2}{4} \Theta \frac{\partial}{\partial y_2} \left([H_{\text{osc}} - E_2]_r^{-1} ((y_1 + y_2) \Omega_N) \right) [h(X, \theta) - V(X)]_r^{-1} \frac{\partial \Phi}{\partial x_2} \\
&\quad + \frac{\kappa^2}{2} \Theta \frac{\partial}{\partial y_3} \left([H_{\text{osc}} - E_2]_r^{-1} ((y_1 + y_2) \Omega_N) \right) [h(X, \theta) - V(X)]_r^{-1} \frac{\partial \Phi}{\partial x_3} \\
&\quad - \frac{\kappa^2}{2} \Theta [H_{\text{osc}} - E_2]_r^{-1} \left((y_1 - y_2) \frac{\partial \Omega_N}{\partial y_3} \right) [h(X, \theta) - V(X)]_r^{-1} \frac{\partial \Phi}{\partial \theta},
\end{aligned} \tag{3.42}$$

and

$$\begin{aligned}
\psi_{5/2}^{\parallel\perp} &= -\frac{\kappa^2}{4} \Theta \Phi [H_{\text{osc}} - E_2]_r^{-1} \left[(y_1 + y_2) \frac{\partial^2}{\partial y_3^2} [H_{\text{osc}} - E_2]_r^{-1} ((y_1 + y_2) \Omega_N) \right] \\
&\quad - \frac{\kappa^2}{8} \Theta \Phi [H_{\text{osc}} - E_2]_r^{-1} \left[y_3^2 (y_1 + y_2) [H_{\text{osc}} - E_2]_r^{-1} ((y_1 + y_2) \Omega_N) \right] \\
&\quad + \kappa \Theta \Phi [H_{\text{osc}} - E_2]_r^{-1} \left[(y_1 - y_2) \left(-i \frac{\partial}{\partial y_3} \right) [H_{\text{osc}} - E_2]_r^{-1} \left((y_1 - y_2) \left(-i \frac{\partial}{\partial y_3} \right) \Omega_N \right) \right] \\
&\quad + \frac{\kappa^2}{4} \Theta \Phi [H_{\text{osc}} - E_2]_r^{-1} \left[(y_1 + y_2) [H_{\text{osc}} - E_2]_r^{-1} \left((y_1 + y_2) \left(-\frac{\partial^2}{\partial y_3^2} - \frac{1}{2} y_3^2 \right) \Omega_N \right) \right] \\
&\quad - \frac{3}{8} \kappa^2 \Theta \Phi [H_{\text{osc}} - E_2]_r^{-1} ((y_1^2 + y_2^2) \Omega_N).
\end{aligned} \tag{3.43}$$

The remaining terms in the expansion are $\mathcal{O}(\epsilon^5)$, so we've reached the goal, though in

principle it should be possible to work in a similar fashion to proceed to arbitrarily high orders in ϵ .

Chapter 4

Final Results

We have obtained an approximate energy of the form

$$\begin{aligned} E(\epsilon) = & \epsilon^2 \left\{ \left(n_1 + \frac{1}{2} \right) + \left(n_2 + \frac{1}{2} \right) \sqrt{3} + \left(n_3 + \frac{1}{2} \right) \sqrt{2} \right\} \\ & + \epsilon^{5/2} \left\{ \frac{\kappa^2}{4} \right\} \\ & + \epsilon^4 \left\{ -\frac{39}{224} - \frac{\sqrt{2}}{7} \left(n_1 + \frac{1}{2} \right) \left(n_3 + \frac{1}{2} \right) + \frac{1}{\sqrt{6}} \left(n_2 + \frac{1}{2} \right) \left(n_3 + \frac{1}{2} \right) \right. \\ & \left. + \frac{1}{56} \left(n_3 + \frac{1}{2} \right)^2 + T_4(1, 1, \pi) \right\} \\ & + \epsilon^{9/2} \kappa^2 \left\{ \frac{3}{4} \left(n_1 + \frac{1}{2} \right) + \frac{7}{4\sqrt{3}} \left(n_2 + \frac{1}{2} \right) - \frac{1}{\sqrt{2}} \left(n_3 + \frac{1}{2} \right) \right\} \end{aligned} \quad (4.1)$$

when $\ell = \kappa\epsilon^{-3/4}$. If we make this replacement in the above result, we obtain the result on page 3. We've also built up an approximate eigenvector as we've gone along. In the interest of aesthetics, though, we refrain from reproducing it in its entirety here!

4.1 The Error in the Approximate Energy

It is a well-known (though by no means trivial) result from operator theory (see, for example, [15]) that if H is a Hermitian operator on a Hilbert space \mathcal{H} and $E \in \mathbb{R}$, then

$$\|(H - E)^{-1}\|_o = \frac{1}{\text{dist}(E, \sigma(H))},$$

where $\sigma(H)$ is the set of eigenvalues of H (so we necessarily have $\sigma(H) \subset \mathbb{R}$, since H is assumed Hermitian), $\text{dist}(E, \sigma(H)) = \inf_{s \in \sigma(H)} |E - s|$, and

$$\|T\|_o = \sup_{\substack{x \in \mathcal{H} \\ \|x\|=1}} \|Tx\| \quad (4.2)$$

is the operator norm on the set of bounded operators on \mathcal{H} . Consider the vector Ψ_ϵ given by

$$\Psi_\epsilon(R, \Xi) = F(r_1 - 1)F(r_2 - 1)F(\phi - \pi) \sum_{\nu \in N} \Psi_\nu(R, \Xi),$$

where N is the set of ν 's for which ψ_ν was computed to be nonzero in Chapter 3, F is our cut-off function, and

$$\Psi_\nu(R, \Xi) = \Psi_\nu(r_1, r_2, \theta, \phi, \Xi) = \psi_\nu \left(r_1, r_2, \phi, \frac{r_1 - 1}{\epsilon}, \frac{r_2 - 1}{\epsilon}, \frac{\phi - \pi}{\epsilon}, \theta, \Xi \right),$$

In other words, we obtain Ψ_ϵ by replacing all the x_i 's and y_i 's in our multiple scales solution with their expressions in terms of the r_i 's. Though the notation may have concealed it, the wavefunctions Ψ_ν are elements of the Hilbert space

$$\mathcal{H} = L^2(dR) \otimes L^2(d\Xi) \quad \text{with norm} \quad \|\cdot\|.$$

They involve gaussians, or derivatives of gaussians, whose decay compensates for any growth from derivatives of the Hermite polynomials. Hence they are still square-integrable. It follows that $\Psi_\epsilon \in \mathcal{H}$ and satisfies (by construction)

$$\|(H(\epsilon) - E(\epsilon))\Psi_\epsilon\| = \mathcal{O}(\epsilon^5)$$

for $H(\epsilon)$ in (2.2) and $E(\epsilon)$ in (4.1). Clearly, we have

$$\|\Psi_0\| = \|\Theta_\ell(\theta)\Phi(\Xi|R)\Omega_N(R)\| = 1.$$

Also, note that $\|\Psi_\epsilon\| = \|\Psi_0 + \Psi_\perp\|$, where

$$\Psi_\perp = \sum_{\substack{\nu \in N \\ \nu \neq 0}} \epsilon^\nu \Psi_\nu$$

By construction, $\langle \Psi_0, \Psi_\perp \rangle = 0$, so we can apply the Pythagorean theorem to conclude

$$\|\Psi_\epsilon\| = \sqrt{\|\Psi_0\|^2 + \|\Psi_\perp\|^2} \geq 1.$$

We therefore have

$$\begin{aligned} \frac{1}{\text{dist}(\sigma(H(\epsilon)), E(\epsilon))} &= \|(H - E)^{-1}\| \\ &\geq \left\| (H(\epsilon) - E(\epsilon))^{-1} \frac{(H(\epsilon) - E(\epsilon))\Psi_\epsilon}{\|(H(\epsilon) - E(\epsilon))\Psi_\epsilon\|} \right\| \\ &= \frac{\|\Psi_\epsilon\|}{\|(H(\epsilon) - E(\epsilon))\Psi_\epsilon\|} \\ &\geq \frac{1}{\mathcal{O}(\epsilon^5)} \\ &= \mathcal{O}(\epsilon^{-5}). \end{aligned}$$

Hence $\text{dist}(\sigma(H(\epsilon)), E(\epsilon)) \leq \mathcal{O}(\epsilon^5)$, meaning that we can find a real constant $D > 0$ and an $E_{N,\ell}$ in the spectrum of the full molecular Hamiltonian $H(\epsilon)$ (of course, it will depend on the values we fix for these constants) such that

$$|E_{N,\ell} - E(\epsilon)| \leq D_{N,\kappa} \epsilon^5.$$

when ϵ is sufficiently small. This proves the result that was stated in the introduction: Uniformity of this estimate follows from the fact that we are considering only finitely many N 's (i.e., we are keeping the vibrational quantum numbers n_i bounded) and are keeping our $\kappa = \ell\epsilon^{3/4}$ in a compact set. It can be shown that the constant D has a polynomial dependence

on what κ is chosen to be, allowing us to invoke continuity of D in κ to choose a $D_{\max, N}$ that works for every value of κ in the interval $[0, k]$. One then chooses $D = \max_N D_{\max, N}$, and D becomes the uniform bound.

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Appendix A

Mathematica Computations

The (approximate) energy expression on page 3 was obtained after taking various inner products of the harmonic oscillator eigenstates first defined in (3.10). These were carried out in Mathematica by using raising and lowering operators as defined in [7]. The code used to obtain these results is reproduced, in part, below.

Recall that, after performing a suitable change of variables (see (3.8)), we were able to write the $\mathcal{O}(\epsilon^2)$ terms in the Hamiltonian $H(\epsilon)$ as a sum of three noninteracting harmonic oscillators: $H_{\text{osc}} = \sum_{j=1}^3 H_{z_j}$, where

$$H_{z_1} = \frac{p_1^2}{2} + \frac{1}{2}z_1^2, \tag{A.1}$$

$$H_{z_2} = \frac{p_2^2}{2} + \frac{3}{2}z_2^2, \tag{A.2}$$

$$H_{z_3} = \frac{p_3^2}{2} + z_3^2, \tag{A.3}$$

and we have let $p_j = -i\frac{\partial}{\partial z_j}$. In [7], techniques are provided for defining ladder operators for quadratic Hamiltonians like these. Specifically, for a Hamiltonian of the form $H = \frac{p^2}{2} + \frac{1}{2}\omega^2 x^2$ (where $\omega \in \mathbb{R}$), one sees we can define a *raising* operator a^\dagger and a *lowering* operator a as

follows:

$$a^\dagger = \frac{x - ip}{\sqrt{2\omega}}, \quad (\text{A.4})$$

$$a = \frac{x + ip}{\sqrt{2\omega}}. \quad (\text{A.5})$$

There is an additional factor of $\hbar^{-1/2}$ multiplying each of these operators in [7], but we remind the reader that \hbar has numerical value 1 here. It follows that, in terms of these ladder operators,

$$x = \frac{1}{\sqrt{2\omega}}(a^\dagger + a), \quad (\text{A.6})$$

$$p = i\sqrt{\frac{\omega}{2}}(a^\dagger - a). \quad (\text{A.7})$$

It is then straightforward to show that $H = \frac{\omega}{2}(a^\dagger a + a a^\dagger)$. The matrix of the Hamiltonian H is diagonal in a basis of $L^2(dx)$ given by $\{\phi_k(x)\}_{k=0}^\infty$, where $\phi_0(x) = \pi^{-1/4}\omega^{-1/4} \exp\left(-\frac{\omega x^2}{2}\right)$ and we define $\phi_{k+1}(x)$ recursively for $k \geq 0$ by $\phi_{k+1}(x) = \frac{a^\dagger \phi_k(x)}{\sqrt{k+1}}$. In [7], it is also shown that the ϕ_k behave as expected with respect to a : that is, $a\phi_k = \sqrt{k}\phi_{k-1}$.

Now to the problem: At fourth order in ϵ , we are faced with evaluating the inner products in (3.31), which we reproduce for convenience here:

$$\begin{aligned} E_4 = & -\frac{1}{\sqrt{2}} \langle \Omega_N, z_1 p_3^2 G_1 \rangle + \sqrt{2} \langle \Omega_N, z_1 z_3^2 G_1 \rangle + \frac{3}{4} \langle \Omega_N, (z_1^2 + z_2^2) p_3^2 \Omega_N \rangle \\ & + \frac{1}{2} \langle \Omega_N, (z_1^2 - z_2^2) z_3^2 \Omega_N \rangle - \frac{1}{6} \langle \Omega_N, z_3^4 \Omega_N \rangle - \frac{1}{4} + T_4(1, 1, \pi), \end{aligned} \quad (\text{A.8})$$

where $G_1(Y) = [H_{\text{osc}} - E_2]_r^{-1} \left[(y_1 + y_2) \left(-\frac{\partial^2}{\partial y_3^2} - \frac{1}{2} y_3^2 \right) \Omega_N(Z) \right]$. The first thing we need to do is write G_1 entirely in terms of the z_i 's:

$$G_1(Z) = \sqrt{2} [H_{\text{osc}} - E_2]_r^{-1} \left[z_1 \left(\frac{1}{2} p_3^2 - z_3^2 \right) \Omega_N(Z) \right],$$

where of course $p_3^2 = -\frac{\partial^2}{\partial z_3^2}$ and the inner products are computed in $L^2(dZ)$. We plug this into (10) where appropriate and find that the inner product we need to evaluate then looks

like

$$\begin{aligned}
E_4 = & -\frac{1}{2} \langle \Omega_N, z_1 p_3^2 [H_{\text{osc}} - E_2]_r^{-1} z_1 p_3^2 \Omega_N(Z) \rangle \\
& + \langle \Omega_N, z_1 p_3^2 [H_{\text{osc}} - E_2]_r^{-1} z_1 z_3^2 \Omega_N(Z) \rangle \\
& + \langle \Omega_N, z_1 z_3^2 [H_{\text{osc}} - E_2]_r^{-1} z_1 p_3^2 \Omega_N(Z) \rangle \\
& - 2 \langle \Omega_N, z_1 z_3^2 [H_{\text{osc}} - E_2]_r^{-1} z_1 z_3^2 \Omega_N \rangle \\
& + \frac{3}{4} \langle \Omega_N, (z_1^2 + z_2^2) p_3^2 \Omega_N \rangle \\
& + \frac{1}{2} \langle \Omega_N, (z_1^2 - z_2^2) z_3^2 \Omega_N \rangle \\
& - \frac{1}{6} \langle \Omega_N, z_3^4 \Omega_N \rangle \\
& - \frac{1}{4} + T_4(1, 1, \pi).
\end{aligned} \tag{A.9}$$

We take a moment to remind the reader that $\Omega_N(Z) = \phi_{n_1}(z_1)\phi_{n_2}(z_2)\phi_{n_3}(z_3)$. In light of this, for $j = 1, 2, 3$, we define

$$\begin{aligned}
a_j^\dagger &= (2\omega_j)^{-1/2}(z_j - ip_j), \\
a_j &= (2\omega_j)^{-1/2}(z_j + ip_j), \text{ so} \\
H_{z_j} &= \frac{\omega_j}{2}(a_j^\dagger a_j + a_j a_j^\dagger).
\end{aligned}$$

We are now interested in computing the matrix elements $[z_j]_{k,k'} = \langle \phi_k(z_j), z_j \phi_{k'}(z_j) \rangle$:

$$\langle \phi_k, z_j \phi_{k'} \rangle = \frac{1}{\sqrt{2\omega_j}} \langle \phi_k, (a + a^\dagger) \phi_{k'} \rangle = \frac{1}{\sqrt{2\omega_j}} \left(\sqrt{k'+1} \delta_{k,k'+1} + \sqrt{k'} \delta_{k,k'-1} \right),$$

where $\delta_{i,j}$ is the Kronecker delta. It follows that

$$[z_j]_{k,k-1} = \sqrt{\frac{k}{2\omega_j}}, \quad [z_j]_{k,k+1} = \sqrt{\frac{k+1}{2\omega_j}},$$

with all other entries being zero. Similarly, for $[p_3]_{k,k'}$, we have (since $\omega_3 = \sqrt{2}$)

$$\langle \phi_k, p_3 \phi_{k'} \rangle = i \sqrt{\frac{\omega_3}{2}} \langle \phi_k, (a^\dagger - a) \phi_{k'} \rangle = i 2^{-1/4} \left(\sqrt{k'+1} \delta_{k,k'+1} - \sqrt{k'} \delta_{k,k'-1} \right),$$

from which it follows that

$$[p_3]_{k,k-1} = i 2^{-1/4} \sqrt{k}, \quad [p_3]_{k,k+1} = -i 2^{-1/4} \sqrt{k+1}, \quad (\text{A.10})$$

with all other entries being zero. We also find that

$$\langle \phi_k, H_{z_j} \phi_{k'} \rangle = \frac{\omega_j}{2} \langle \phi_k, (a^\dagger a + a a^\dagger) \phi_{k'} \rangle = \omega_j (k' + 1/2) \delta_{kk'}.$$

This implies $[H_{z_i}]_{k,k} = \omega_j (k + 1/2)$, with all other entries zero; i.e., the matrix is diagonal, as expected. The matrices $[z_j]$ and $[p_3]$ are (of course) infinite dimensional, but because of the particular form of the inner products we want to compute, we will only need to focus on smaller submatrices.

Below, we show how we define the matrix $[z_1]$ in Mathematica. The energy eigenstates in this variable are indexed by the nonnegative integer n_1 . The matrices $[z_2]$ and $[z_3]$ are defined similarly.

```
 $\gamma 1 = 1;$ 
 $\omega 1 = \text{Sqrt}[\gamma 1];$ 
 $A 1 = \text{Sqrt}[1/\omega 1];$ 
 $Z 1 = \text{Table}[0, \{a, 1, 13\}, \{b, 1, 13\}];$ 
 $\text{For}[a = 1, a \leq 12, a++, Z 1[[a, a + 1]] = \text{Sqrt}[1/(2\omega 1)(a - 6 + n 1)];$ 
 $Z 1[[a + 1, a]] = \text{Sqrt}[1/(2\omega 1)(a - 6 + n 1)]$ 
```

Note that the only states we have been concerned with in this definition are the ones indexed by $n_1 - 6, n_1 - 5, \dots, n_1 + 6$. One can see that these are (at most) the ones that enter into the perturbation theory calculation if we start in the state $\phi_{n_1}(z_1)$.

We define the matrix for the operator p_3 as follows, using (12):

```
 $P 3[[a, a + 1]] =$ 
 $-I * \text{Sqrt}[\omega 3/2] \text{Sqrt}[n 3 - 6 + a];$ 
 $P 3[[a + 1, a]] =$ 
 $I * \text{Sqrt}[\omega 3/2] \text{Sqrt}[n 3 - 6 + a]$ 
```

Now, we must construct the harmonic oscillator reduced resolvent $[H_{\text{osc}} - E_2]_r^{-1}$, which figures prominently in the calculation in (11). First comes H_{osc} , which we define as follows: First, we write an array to correspond to H_{z_j} for each j (the code for $j = 1$ is shown here):

```
H1 = Table[0, {a, 1, 13}, {b, 1, 13}];
For[a = 1, a ≤ 13, a++,
H1[[a, a]] = ω1 * (n1 + a - 7 + 1/2)]
```

We then define the “big” Hamiltonian H_{osc} as follows:

```
BigH =
KroneckerProduct[H1, IdentityMatrix[13], IdentityMatrix[13]]+
KroneckerProduct[IdentityMatrix[13], H2, IdentityMatrix[13]]+
KroneckerProduct[IdentityMatrix[13], IdentityMatrix[13], H3];
```

Similar “big” definitions need to be made for the operators z_j and p_j . The reduced resolvent $[H_{\text{osc}} - E_2]_r^{-1}$ can then be entered as follows:

```
BigRResolvent = Table[0, {a, 1, 13^3}, {b, 1, 13^3}];
For[a = 1, a ≤ 13^3, a++, If[ Simplify[BigH[[a, a]] - ((n1 + 1/2)ω1 + (n2 + 1/2)ω2 +
(n3 + 1/2)ω3)] != 0,
BigRResolvent[[a, a]] = 1 / (BigH[[a, a]] - ((n1 + 1/2)ω1 + (n2 + 1/2)ω2 + (n3 + 1/2)ω3) )]]
```

These operators will need to act on the vector

```
psi0 = {0, 0, 0, 0, 0, 0, 1, 0, 0, 0, 0, 0};
Psi0 = Flatten[KroneckerProduct[Flatten[KroneckerProduct[psi0, psi0]], psi0]];
```

which involves a Kronecker product of vectors corresponding to the state indexed by (n_1, n_2, n_3) . This puts us in a position to evaluate the inner products in (11), which we do with the following code:

```
E4 = -1/4 + Simplify[3/4 * Psi0.BigZ1.BigZ1.BigP3.BigP3.Psi0] +
Simplify[3/4 * Psi0.BigZ2.BigZ2.BigP3.BigP3.Psi0] +
Simplify[1/2 * Psi0.BigZ1.BigZ1.BigZ3.BigZ3.Psi0] -
Simplify[1/2 * Psi0.BigZ2.BigZ2.BigZ3.BigZ3.Psi0] -
Simplify[1/6 * Psi0.BigZ3.BigZ3.BigZ3.BigZ3.Psi0] -
Simplify[1/2 * Psi0.BigZ1.BigP3.BigP3.BigRResolvent.BigZ1.BigP3.BigP3.Psi0] +
Simplify[Psi0.BigZ1.BigP3.BigP3.BigRResolvent.BigZ1.BigZ3.BigZ3.Psi0] +
Simplify[Psi0.BigZ1.BigZ3.BigZ3.BigRResolvent.BigZ1.BigP3.BigP3.Psi0] -
Simplify[2 * Psi0.BigZ1.BigZ3.BigZ3.BigRResolvent.BigZ1.BigZ3.BigZ3.Psi0]
```

Simplification of the result of this command gives the result (3.32). Similarly, we need to

rewrite the expression for $E_{9/2}$ contained in (3.41) entirely in terms of the z_j 's. We find

$$\begin{aligned}
E_{9/2} = & -\frac{\kappa^2}{4} \langle \Omega_N, z_1 p_3^2 [H_{\text{osc}} - E_2]_r^{-1} z_1 \Omega_N \rangle \\
& + \frac{\kappa^2}{2} \langle \Omega_N, z_1 z_3^2 [H_{\text{osc}} - E_2]_r^{-1} z_1 \Omega_N \rangle \\
& - \kappa^2 \langle \Omega_N, z_2 p_3 [H_{\text{osc}} - E_2]_r^{-1} z_2 p_3 \Omega_N \rangle \\
& - \frac{\kappa^2}{4} \langle \Omega_N, z_1 [H_{\text{osc}} - E_2]_r^{-1} z_1 p_3^2 \Omega_N \rangle \\
& + \frac{\kappa^2}{2} \langle \Omega_N, z_1 [H_{\text{osc}} - E_2]_r^{-1} z_1 z_3^2 \Omega_N \rangle \\
& + \frac{3}{4} \kappa^2 \langle \Omega_N, (z_1^2 + z_2^2) \Omega_N \rangle.
\end{aligned} \tag{A.11}$$

This is computed similarly to obtain the result (3.41).