A Mathematical Theory for Vibrational Levels Associated with Hydrogen Bonds
II: The Non–Symmetric Case

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Abstract

We propose an alternative to the usual time–independent Born–Oppenheimer approximation that is specifically designed to describe molecules with non–symmetrical hydrogen bonds. In our approach, the masses of the hydrogen nuclei are scaled differently from those of the heavier nuclei, and we employ a specialized form for the electron energy level surface. As a result, the different vibrational modes appear at different orders of approximation.

Although we develop a general theory, our analysis is motivated by an examination of the $F\,H\,Cl^-$ ion. We describe our results for it in detail.

We prove the existence of quasimodes and quasienergies for the nuclear vibrational and rotational motion to arbitrary order in the Born–Oppenheimer parameter ϵ. When the electronic motion is also included, we provide simple formulas for the quasienergies up to order ϵ^3 that compare well with experiment and numerical results.

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1 Introduction

This is the second in a series of articles devoted to the study of vibrational levels associated with hydrogen bonds. The first paper [5] deals with stretching vibrations of the hydrogen bond in the symmetric case in which the hydrogen binds two identical atoms or molecules. Our prototypical example is FHF^-, which displays strong anharmonic effects, coupling between vibrational modes, and a low frequency for the vibration of the hydrogen along the F–F axis. This second paper deals with all the vibrations and rotations in the non–symmetric situation. Our canonical example is $F\,H\,Cl^-$, which displays weaker anharmonic effects and a high frequency for the vibration of the hydrogen along the F–Cl axis.

Both of our papers contain two main new ideas. The first is the same for both papers. Standard Born–Oppenheimer approximations keep the electron masses fixed while all the nuclear masses are taken proportional to ϵ^{-4}. We take the hydrogen mass proportional to ϵ^{-3} while keeping the heavier atoms' masses proportional to ϵ^{-4}. This is physically appropriate for many molecules of interest: If the mass of an electron is 1 and ϵ is defined so the mass of a carbon C^{12} nucleus is ϵ^{-4}, then $\epsilon = 0.0821$,and the mass of a H^1 nucleus is $1.015\,\epsilon^{-3}$.

The second novel idea is to exploit the smallness of certain derivatives of the electron energy level surface for the molecule being studied. Here our two papers are completely different, and they are motivated by examinations of numerically computed electron energy level surfaces using Gaussian 2003 software [3]. In the symmetric case, the second derivative associated with moving the H along the axis of $A\,H\,A$ is small, and we could allow it to be small and negative if the H nucleus felt a double well potential. In the non–symmetric case, if the H is more weakly bound to the B in $A\,H\,B$, we assume all the derivatives associated with moving the B relative to $A\,H$ in $A\,H\,B$ are small. We assume all derivatives associated with stretching the distance between A and H not to be small.

To describe the smallness of the small derivatives, we could have introduced another small parameter. Instead, we have elected to let ϵ play a second role. We take all the small derivatives to be proportional to ϵ. For the choice of $\epsilon = 0.0821$ indicated above, that is again appropriate for our $F\,H\,F^-$ and $F\,H\,Cl^-$ examples. The small derivatives are on the order of ϵ in units where the non–small derivatives are on the order of 1.

We shall now restrict our attention to triatomic non–symmetrical hydrogen bonded molecules $A\,H\,B$, and assume the H is more strongly bound to the A. We do an asymptotic expansion for small ϵ, and our main results are the following:

1. To their respective leading orders, the vibrational levels are described by three independent harmonic oscillators in appropriate Jacobi coordinates: two separate one–dimensional harmonic oscillators and one two–dimensional isotropic harmonic oscillator. This is in contrast to the usual Born–Oppenheimer theory in which one obtains one coupled four–dimensional harmonic oscillator. Our technique does not require going through the diagonalization process to separate the normal modes. The different modes appear at different orders of the expansion, in contrast to the Born–Oppenheimer situation, where all vibrations are of order ϵ^2.
2. The highest frequency vibrational states have energy of order $\epsilon^{3/2}$. These are the stretching oscillations of the A–H bond with the B approximately sitting still.
3. The next highest frequency vibrations are the two degenerate bending modes. They are of order ϵ^2.
4. The lowest vibrational energies are of order $\epsilon^{5/2}$. They are the stretching oscillations of the weak bond between the $A\,H$ and the B.

For the specific case of $F\,H\,Cl^-$, we have the following comparison of results, where vibrational energies are measured in cm^{-1}. The experimental results come from [2]. We note that the experiments were not done in the "gas phase," so they may not accurately represent results for the isolated ions. All the Gaussian 2003 results presented in this paper are obtained by using the MP2 technique with the aug-cc-pvdz basis set. The software implements the standard Born–Oppenheimer approximation. The results for our model come from approximating the ground state electron energy surface with Gaussian 2003 and then applying our techniques.

Mode	**Experiment**	**Gaussian '03**	**Our Model**
$F-H$ stretch	2710	2960	2960
bends (degenerate)	843	875	871
$FH-Cl$ stretch	275	246	251

Remarks

1. It is not surprising that the results for our model are close to those obtained by Gaussian since we have used the same electron energy surface. The Gaussian software deals with the full 4–dimensional harmonic oscillator, whereas our technique deals with two 1–dimensional harmonic oscillators and one isotropic 2–dimensional harmonic oscillator. Evidently the Jacobi coordinates we have chosen are very close to the normal mode coordinates for the 4–dimensional oscillator.

2. The results from Gaussian and our model are just leading order (harmonic) calculations. Including higher order terms from the expansions might bring these into better agreement with experiment. Also, we again emphasize that the experimental results were not obtained for isolated ions.

A recent chemistry article [9] contains data for vibrations of eighteen hydrogen bonded molecules in the gas phase. It also contains an idea for quantifying how symmetric or non–symmetric a hydrogen bond is. Its conclusions are consistent with the analysis in our two papers. Figure 2 of that article plots the vibrational frequency of the $A-H$ stretch versus the difference in the "proton affinities" of A and B for a molecule $A\,H\,B$. When A and B are identical, the frequency is low (800–1000 cm^{-1}), and when they attract the proton very differently, the frequency is high (1600–3500 cm^{-1}). In our symmetric analysis, this vibrational energy is of order ϵ^2, whereas in our non–symmetric analysis, it is of order $\epsilon^{3/2}$, which is roughly 3.5 times larger when $\epsilon = 0.0821$.

Remarks

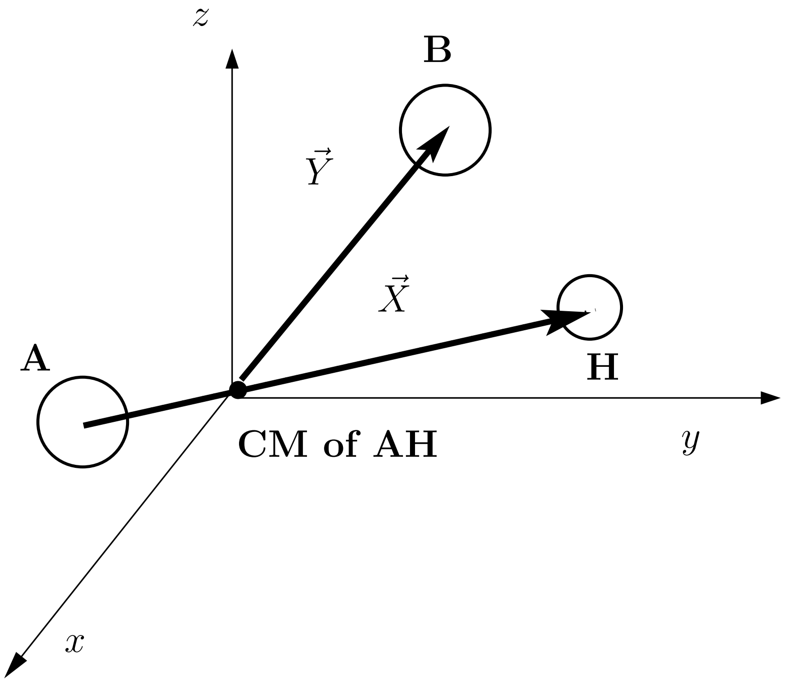
1. We assume that the ground state electron energy level we are considering is non–degenerate for all nuclear configurations of interest. Thus, we do not consider situations that exhibit the Renner–Teller effect [8, 10, 6].
2. Since our analysis includes rotations of the whole molecule, some small effects show up in the calculations. For example, l–type doubling [7] occurs for terms that have non–zero eigenvalues of the $L_{z'}$ operator at low order. ($L_{z'}$ is the nuclear angular momentum around the $A-B$ axis.) States corresponding to $L_{z'}$ eigenvalue $\pm k$ with $k \geq 1$ generically have their degeneracy in energy split at order ϵ^{2+3k} in our model.

The paper is organized as follows: In Section 2, we describe our model in detail. In Section 3, we do the semiclassical expansion to all orders for the nuclei. In Section 4 we include the electrons. However, when we include the electrons, we just show that the energy expansion is valid through order ϵ^3. Going to higher order is extremely complicated.

2 Semiclassical Analysis for the Effective Nuclear Hamiltonian

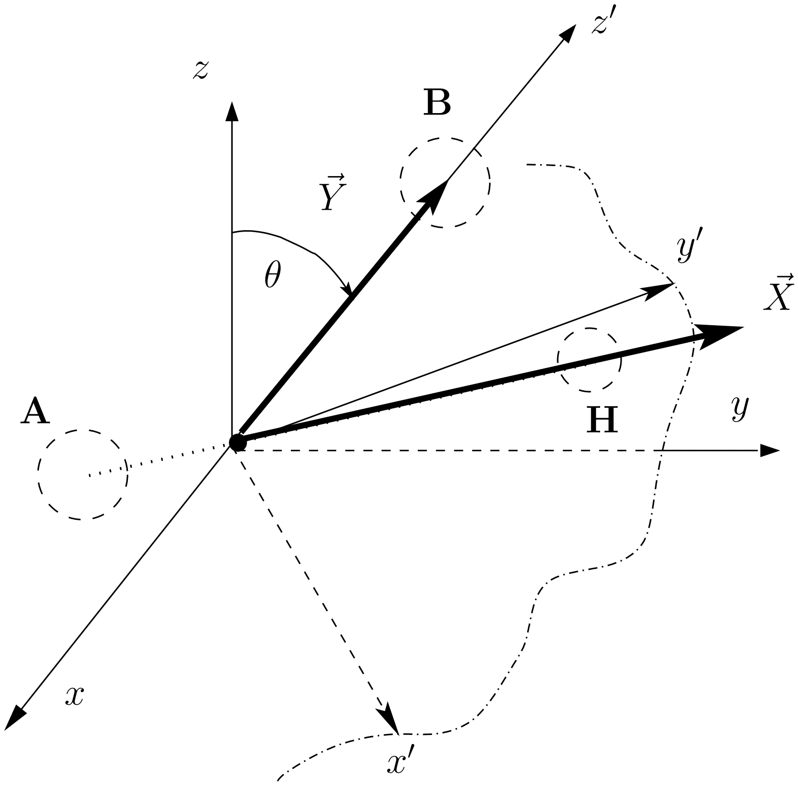
In this section, we give a precise description of the Hamiltonian for the nuclei. As mentioned above, we consider a molecular system $A\,H\,B$ in which the hydrogen is much more tightly bound to the A than to the B.

We construct the coordinate system we use in two steps, as illustrated in the figures below. The first step is to choose a standard Jacobi coordinate system for the nuclei in their center of mass frame of reference. The first three coordinates are the components X_1, X_2, and X_3 of the vector $\vec{X}$ from the A nucleus to the H nucleus. The fourth, fifth, and sixth coordinates Y_1, Y_2, and Y_3 are the components of the vector $\vec{Y}$ from the center of mass of the A and H nuclei to the B nucleus.

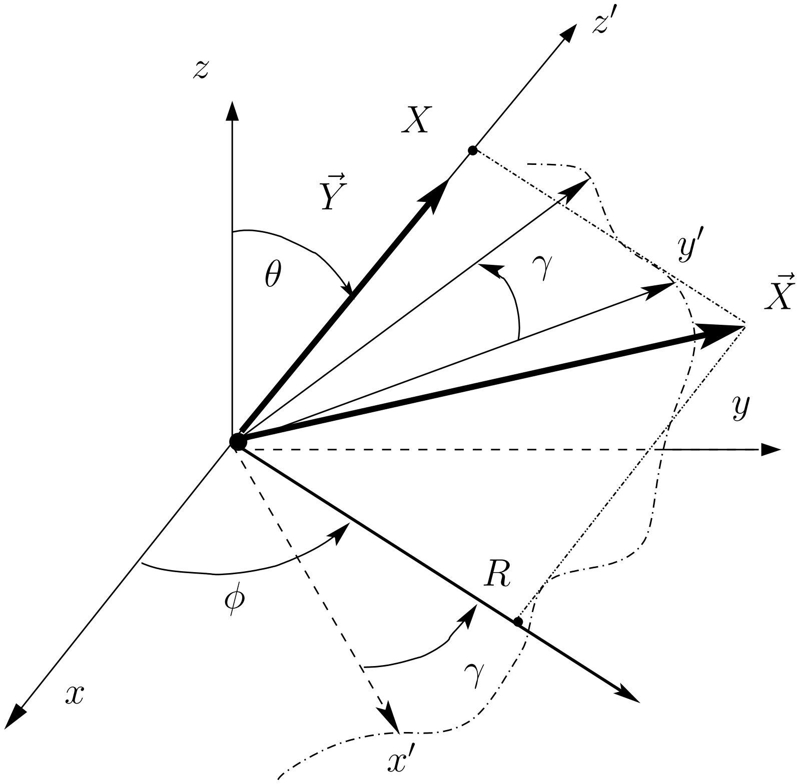


Jacobi coordinates for the molecule

We now change from these coordinates to new ones that we call (Y, θ, ϕ, R, γ, X). The (Y, θ, ϕ) are spherical coordinates for the vector described by (Y_1, Y_2, Y_3) in the original center of mass frame of reference. The (R, γ, X) are cylindrical coordinates for the vector (X_1, X_2, X_3) in a frame of reference that rotates so that the axis for these coordinates is in the direction of the vector described by (Y_1, Y_2, Y_3). The precise definition is below.



Jacobi coordinates fixed at the origin



The final coordinate system

One reason for using these coordinates is that the potential energy surface depends only on Y, X, and R. A second reason is that in these coordinates, we can separate the total angular momentum J^2 and its z component J_z from the other motions easily. Also, to low order in perturbation theory, the angular momentum $L_{z'}$ conjugate to γ (which is the angular momentum in the direction of (Y_1, Y_2, Y_3), gives another convenient quantum number. Note that $L_{z'}$ does not commute with the full Hamiltonian.

The drawback to using this coordinate system is that the kinetic energy expression is quite messy. The complication comes from the Laplacian in the (Y, θ, ϕ) variables. The Laplacian in (R, γ, X) is simply the usual cylindrical Laplacian.

These coordinates are closely related to ones used in [4] to deal with Born–Oppenheimer approximations for diatomic Coulomb systems. There is a minus sign error in the expression for $L \cdot J$ term on page 32 of that paper.

As mentioned above, (Y, θ, ϕ) are just standard spherical coordinates. To describe the other three coordinates precisely, we first define the rotation

$$\mathcal{R}_1(\theta,\,\phi)\;=\;\begin{pmatrix}\cos(\theta)\,\cos(\phi) & -\sin(\phi) & \sin(\theta)\,\cos(\phi)\\ \cos(\theta)\,\sin(\phi) & \cos(\phi) & \sin(\theta)\,\sin(\phi)\\ -\sin(\theta) & 0 & \cos(\theta)\end{pmatrix}.$$

It maps the vector $\begin{pmatrix}0\\0\\1\end{pmatrix}$ to the unit vector in the direction of $\begin{pmatrix}Y_1\\Y_2\\Y_3\end{pmatrix}$. We then define coordinates $(\xi_1,\,\xi_2,\,\xi_3)$ by

$$\begin{pmatrix}\xi_1\\ \xi_2\\ \xi_3\end{pmatrix}\;=\;[\,\mathcal{R}_1(\theta,\,\phi)\,]^{-1}\;\begin{pmatrix}X_1\\X_2\\X_3\end{pmatrix}.$$

Next, we define another rotation

$$\mathcal{R}_2(\gamma)\;=\;\begin{pmatrix}\cos(\gamma) & -\sin(\gamma) & 0\\ \sin(\gamma) & \cos(\gamma) & 0\\ 0 & 0 & 1\end{pmatrix},$$

where, for generic vectors ξ, γ is defined by requiring the second component of $[\,\mathcal{R}_2(\gamma)\,]^{-1}\,\xi$ to be 0 and its first component to be positive. We then define coordinates X and R by

$$\begin{pmatrix}R\\0\\X\end{pmatrix}\;=\;[\,\mathcal{R}_2(\gamma)\,]^{-1}\;\begin{pmatrix}\xi_1\\ \xi_2\\ \xi_3\end{pmatrix}.$$

Our Hamiltonian has kinetic energy

$$-\,\frac{\epsilon^3}{2\,\mu_1(\epsilon)}\;\Delta_{(X_1,\,X_2,\,X_3)}\;-\;\frac{\epsilon^4}{2\,\mu_2(\epsilon)}\;\Delta_{(Y_1,\,Y_2,\,Y_3)},$$

where $\mu_1(\epsilon)$ and $\mu_2(\epsilon)$ are modified reduced masses that we describe in detail below. Since Laplacians are rotationally invariant, under our coordinate changes, the first term simply becomes the usual cylindrical Laplacian

$$-\,\frac{\epsilon^3}{2\,\mu_1(\epsilon)}\;\left(\frac{\partial^2}{\partial R^2}\;+\;\frac{1}{R}\,\frac{\partial}{\partial R}\;+\;\frac{1}{R^2}\,\frac{\partial^2}{\partial\gamma^2}\;+\;\frac{\partial^2}{\partial X^2}\right).$$

By a very tedious calculation, the second term in the kinetic energy is

$$-\,\frac{\epsilon^4}{2\,\mu_2(\epsilon)}\;\left(\frac{\partial^2}{\partial Y^2}\;+\;\frac{2}{Y}\,\frac{\partial}{\partial Y}\;-\;\frac{1}{Y^2}\;\left\{\,J^2\;-\;2\,L\cdot J\;+\;L^2\,\right\}\right),$$

where

$$J^2\;=\;-\,\frac{\partial^2}{\partial\theta^2}\;-\;\cot\,\theta\;\frac{\partial}{\partial\theta}\;-\;\frac{1}{\sin^2\,\theta}\;\left(\frac{\partial^2}{\partial\phi^2}+\frac{\partial^2}{\partial\gamma^2}\right)\;+\;\frac{2\,\cos\,\theta}{\sin^2\,\theta}\;\frac{\partial^2}{\partial\phi\,\partial\gamma},\tag{2.1}$$

is the total angular momentum operator,

$$L\cdot J \;=\; \left(R\,\sin\gamma\,\frac{\partial}{\partial X}\,-\,X\,\sin\gamma\,\frac{\partial}{\partial R}\,-\,\frac{X}{R}\,\cos\gamma\,\frac{\partial}{\partial\gamma}\right)\left(\frac{1}{\sin\theta}\,\frac{\partial}{\partial\phi}\,-\,\cot\theta\,\frac{\partial}{\partial\gamma}\right)$$
$$+\;\;\left(R\,\cos\gamma\,\frac{\partial}{\partial X}\,-\,X\,\cos\gamma\,\frac{\partial}{\partial R}\,+\,\frac{X}{R}\,\sin\gamma\,\frac{\partial}{\partial\gamma}\right)\frac{\partial}{\partial\theta}$$

and

$$L^2 \;=\; -\,R^2\,\frac{\partial^2}{\partial X^2}\,+2\,X\,R\,\frac{\partial^2}{\partial X\,\partial R}\,-\,X^2\,\frac{\partial^2}{\partial R^2}\,-\,\frac{X^2}{R^2}\,\frac{\partial^2}{\partial\gamma^2}\,+\left(R-\frac{X^2}{R}\right)\frac{\partial}{\partial R}\,+2\,X\,\frac{\partial}{\partial X}\,+\,\frac{\partial^2}{\partial\gamma^2}.$$

The modified reduced masses are $\mu_1(\epsilon)\;=\;\epsilon^3\;\frac{\epsilon^{-4}m_A\,\epsilon^{-3}m_H}{\epsilon^{-4}m_A+\epsilon^{-3}m_H}$ and $\mu_2(\epsilon)=\epsilon^4\;\frac{(\epsilon^{-4}m_A\,\epsilon^{-3}m_H)\,\epsilon^{-4}m_B}{\epsilon^{-4}m_A+\epsilon^{-3}m_H+\epsilon^{-4}m_B}$, where the three nuclei have masses $\epsilon^{-4}m_A$, $\epsilon^{-3}m_H$, and $\epsilon^{-4}m_B$. The modified reduced masses have limits as ϵ tends to zero. To isolate the leading behavior, we abuse notation and define $\mu_1\;=\;\lim_{\epsilon\to 0}\,\mu_1(\epsilon)\;=\;m_H$ and $\mu_2\;=\;\lim_{\epsilon\to 0}\,\mu_2(\epsilon)\;=\;\frac{m_A\,m_B}{m_A+m_B}$. Then we have

$$\frac{\epsilon^3}{2\,\mu_1(\epsilon)}\;=\;\frac{\epsilon^3}{2\,\mu_1}\;+\;\frac{\epsilon^4}{2\,m_A}.$$

Similarly,

$$\frac{\epsilon^4}{2\,\mu_2(\epsilon)}\;=\;\frac{\epsilon^4}{2\,\mu_2}\;-\;\frac{\epsilon^5}{2\,m_A\,(m_A\;+\;2\,\epsilon\,m_H)}.$$

We define the operator

$$\epsilon^4\;D(\epsilon)\;=\;-\;\frac{\epsilon^4}{2\,m_A}\;\Delta_{(X_1,\,X_2,\,X_3)}\;+\;\frac{\epsilon^5}{2\,m_A\,(m_A\;+\;2\,\epsilon\,m_H)}\;\Delta_{(Y_1,\,Y_2,\,Y_3)},$$

written in the new variables, so that the kinetic energy can be expressed as

$$-\;\frac{\epsilon^3}{2\,\mu_1}\;\Delta_{(X_1,\,X_2,\,X_3)}\;-\;\frac{\epsilon^4}{2\,\mu_2}\;\Delta_{(Y_1,\,Y_2,\,Y_3)}\;+\;\epsilon^4\;D(\epsilon),$$

all written in terms of $(Y,\,\theta,\,\phi,\,R,\,\gamma,\,X)$.

The quantum fluctuations of the nuclei around their equilibrium positions occur on short length scales, so we now do the appropriate rescaling of variables. We assume the ground state electron energy surface has a minimum at $Y=Y_0$, $R=0$ (because the Hydrogen bond is linear), and $X=X_0$. Under the rescaling, the angles θ, ϕ and γ remain unchanged, but we replace Y, R, and X by

$$y\;=\;(Y-Y_0)/\epsilon^{3/4},\qquad r\;=\;R/\epsilon^{1/2},\qquad \text{and}\qquad x\;=\;(X-X_0)/\epsilon^{3/4}.$$

Under this rescaling, the total kinetic energy operator becomes

$$
\begin{aligned}
&-\frac{\epsilon^{3/2}}{2\,\mu_1}\frac{\partial^2}{\partial x^2} - \frac{\epsilon^2}{2\,\mu_1}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \gamma^2}\right) - \frac{\epsilon^{5/2}}{2\,\mu_2}\frac{\partial^2}{\partial y^2} \qquad (2.2)\\
&\quad - \frac{\epsilon^{13/4}}{\mu_2\,(Y_0+\epsilon^{3/4}y)}\frac{\partial}{\partial y} + \frac{\epsilon^4}{2\,\mu_2\,(Y_0+\epsilon^{3/4}y)^2}\left\{\,J^2 - 2\,L\cdot J + L^2\,\right\} + \epsilon^4\,D(\epsilon),
\end{aligned}
$$

where J^2 is still given by (2.1), but $L\cdot J$ and L^2 are now given by the ϵ–dependent expressions

$$
\begin{aligned}
L\cdot J \;=\;& \left(\epsilon^{-1/4}\,r\,\sin\gamma\,\frac{\partial}{\partial x} - \epsilon^{-1/2}(X_0+\epsilon^{3/4}x)\,\sin\gamma\,\frac{\partial}{\partial r} - \epsilon^{-1/2}\,\frac{X_0+\epsilon^{3/4}x}{r}\,\cos\gamma\,\frac{\partial}{\partial \gamma}\right)\\
&\times\left(\frac{1}{\sin\theta}\frac{\partial}{\partial \phi} - \cot\theta\,\frac{\partial}{\partial \gamma}\right)\\
&+\left(\epsilon^{-1/4}r\,\cos\gamma\,\frac{\partial}{\partial x} - \epsilon^{-1/2}(X_0+\epsilon^{3/4}x)\,\cos\gamma\,\frac{\partial}{\partial r} + \epsilon^{-1/2}\frac{X_0+\epsilon^{3/4}x}{r}\,\sin\gamma\,\frac{\partial}{\partial \gamma}\right)\\
&\times\frac{\partial}{\partial \theta}
\end{aligned}
$$

and

$$
\begin{aligned}
L^2 \;=\;& -\,\epsilon^{-1/2}r^2\,\frac{\partial^2}{\partial x^2} + 2\,\epsilon^{-3/4}\,(X_0+\epsilon^{3/4}x)\,r\,\frac{\partial^2}{\partial x\,\partial r} - \epsilon^{-1}(X_0+\epsilon^{3/4}x)^2\,\frac{\partial^2}{\partial r^2}\\
&-\frac{\epsilon^{-1}\,(X_0+\epsilon^{3/4}x)^2}{r^2}\,\frac{\partial^2}{\partial \gamma^2} + \epsilon^{-1}\left(\epsilon\,r - \frac{(X_0+\epsilon^{3/4}x)^2}{r}\right)\frac{\partial}{\partial r}\\
&+ 2\,\epsilon^{-3/4}\,(X_0+\epsilon^{3/4}x)\,\frac{\partial}{\partial x} + \frac{\partial^2}{\partial \gamma^2}.
\end{aligned}
$$

Remarks

1. The operator $L\cdot J$ can be rewritten as

$$
\begin{aligned}
L\cdot J \;=\;& \epsilon^{-1/4}\,\frac{r}{2}\,\frac{\partial}{\partial x}\left(L_{+'} - L_{-'}\right) - \epsilon^{-1/2}\,\frac{X_0+\epsilon^{3/4}\,x}{2}\,\frac{\partial}{\partial r}\left(L_{+'} - L_{-'}\right)\\
&- i\,\epsilon^{-1/2}\,\frac{X_0+\epsilon^{3/4}\,x}{2\,r}\,\frac{\partial}{\partial \gamma}\left(L_{+'} + L_{-'}\right), \qquad (2.3)
\end{aligned}
$$

where

$$
L_{\pm'} \;=\; e^{\pm i\gamma}\left(\pm\frac{\partial}{\partial \theta} + i\,\cot\theta\,\frac{\partial}{\partial \gamma} - i\,\frac{1}{\sin\theta}\,\frac{\partial}{\partial \phi}\right).
$$

By explicit computation, one can verify that $L_{+'}$ and $L_{-'}$ commute with both J^2 and J_z. The operators $L_{+'}$ and $L_{-'}$ are raising and lowering operators for the eigenstates of $L_{z'}$.

2. The dominant order terms in the expressions in $L \cdot J$ and L^2 are the ones of order ϵ^{-1} in L^2. Because of the overall factor of ϵ^4 that multiplies these operators in the Hamiltonian, they are not relevant until the order ϵ^3 perturbation calculations.

Motivated by numerical calculations for the $FHCl^-$ ion, we assume the ground state electron energy surface near its minimum depends only weakly on R and Y. To exploit this, we decompose the potential energy surface as

$$V_1(X) \;+\; \epsilon\, V_2(X,\, R,\, Y), \tag{2.4}$$

where V_1 and V_2 have Taylor expansions of the forms

$$V_1(X) \;\sim\; a_0 \;+\; \sum_{j=2}^{\infty} a_j\,(X-X_0)^j, \qquad \text{and} \tag{2.5}$$

$$V_2(X,\, R,\, Y) \;\sim\; \sum_{\substack{j+k+l\geq 2\\ k+l\geq 1\\ k \text{ even}}} b_{j,\,k,\,l}\,(X-X_0)^j\,R^k\,(Y-Y_0)^l. \tag{2.6}$$

The restrictions on the indices in V_2 are obtained requiring all pure X dependence to be V_1 and by requiring V_2 to be even in R (because of the symmetry).

We now can state our results for the semiclassical analysis of the bound states for the nuclei.

Theorem 2.1 *Consider the Hamiltonian*

$$H(\epsilon) \;=\; -\,\frac{\epsilon^3}{2\,\mu_1(\epsilon)}\,\Delta_{(X_1,\,X_2,\,X_3)} \;-\; \frac{\epsilon^4}{2\,\mu_2(\epsilon)}\,\Delta_{(Y_1,\,Y_2,\,Y_3)} \;+\; V_1(X) \;+\; \epsilon\, V_2(X,\,R,\,Y),$$

rewritten in terms of the variables $(X,\, R,\, Y,\, \theta,\, \phi,\, \gamma)$. *Assume* V_1 *and* V_2 *are* C^∞ *functions that satisfy (2.5) and (2.6). Assume* V_1 *has a unique global minimum* a_0 *at* $X = X_0 > 0$, *with* $a_2 > 0$ *in (2.5), and that* $\liminf_{|X|\to\infty} V(X) > a_0$. *Assume* V_2 *has a unique global minimum of* 0 *at* $X = X_0$, $R = 0$, *and* $Y = Y_0 > 0$, *with* $b_{0,2,0} > 0$ *and* $b_{0,0,2} > 0$ *in (2.6). Given any integer* $N > 0$, *there exist a quasimode* $\Psi_{N/4}(\epsilon) = \sum_{l=0}^{N} \epsilon^{l/4}\,\psi_{l/4}$ *and a* *quasienergy* $E_{N/4}(\epsilon) = \sum_{l=0}^{N} \epsilon^{l/4}\,\mathcal{E}_{l/4}$, *such that* $\|\psi_{l/4}\| = O(1)$ *for each* l, $\mathcal{E}_{l/4} = O(1)$ *for each* l, *and*

$$\left\| \Big(H(\epsilon) - E_{N/4}(\epsilon) \Big)\, \Psi_{N/4}(\epsilon) \right\| \quad \leq \quad C_N\, \epsilon^{(N+1)/4},$$

for some C_N *that depends on the choices of* n, k, m, *and* p *below.*
Furthermore,

$$\mathcal{E}_0 = a_0, \qquad \mathcal{E}_{1/4} = \mathcal{E}_{2/4} = \mathcal{E}_{3/4} = \mathcal{E}_{4/4} = \mathcal{E}_{5/4} = \mathcal{E}_{7/4} = \mathcal{E}_{9/4} = \mathcal{E}_{11/4} = 0,$$

$$\mathcal{E}_{6/4} = \sqrt{2\,a_2/\mu_1}\ \left(n + \frac{1}{2}\right), \qquad \text{for} \quad n = 0, 1, \cdots,$$

$$\mathcal{E}_{8/4} = \sqrt{2\,b_{0,2,0}/\mu_1}\ (2m + |k| + 1), \qquad \text{for an integer} \quad k, \quad \text{and} \quad m = 0, 1, \cdots,$$

$$\mathcal{E}_{10/4} = \sqrt{2\,b_{0,0,2}/\mu_2}\ \left(p + \frac{1}{2}\right), \qquad \text{for} \quad p = 0, 1, \cdots,$$

and $\mathcal{E}_{12/4}$ *is given by the expression (3.7). The rotational energy first appears in* $\mathcal{E}_{16/4}$*. For fixed angular momentum quantum numbers* j *and* j_z*, for order* $N \geq 12$*, the states with* $k = 0$ *are non-degenerate, and the states with* $|k| > 0$ *have multiplicity at most 2.*

Remark Theorem 2.1 is stated with global hypotheses and without growth conditions on the potential. When the electronic motion is also included, the potential energy surface may only exist locally. The cutoff functions that are introduced in Proposition 3.2 allow us to obtain analogous results with only local assumptions.

For the $FHCl^-$ ion, we have calculated values for the first few coefficients in the expansion for V, based on numerically differentiating results from Gaussian 2003. Here distances are measured in Angstroms, energies are in Hartrees, and we have used $\epsilon = 0.0821$.

$$\begin{aligned} a_0 &= -560.160 \\ a_2 &= 0.567 \\ b_{0,2,0} &= 0.597 \\ b_{1,0,1} &= 0.853 \\ b_{0,0,2} &= 0.664 \end{aligned}$$

The ϵ in (2.4) reflects the weakness of the hydrogen bond, and also that the molecule can bend easily. The $FHCl^-$ ion essentially looks like a slightly deformed FH molecule with a

Cl^- ion quite a long way from the FH. Gaussian 2003 assigns charges associated with each atom, and it obtains:

F	-0.58
H	0.51
Cl	-0.93

The calculated F–H distance is 0.98 Angstrom, and the H–Cl distance is 1.91 Angstroms. (For HF alone, the charges are ±0.33, the H–F distance is 0.925 Angstrom, and the calculated vibrational frequency is 4083 cm^{-1}.)

Experimental values [2] for the vibrational frequencies of $FHCl^-$ (in cm^{-1}) are

275	FH oscillates relative to the Cl
843	bends (2 degenerate modes)
2710	FH oscillates

Gaussian 2003 calculates the harmonic vibrational frequencies (in cm^{-1}) to be

246	FH oscillates relative to the Cl
875	bends (2 degenerate modes)
2960	FH oscillates

To leading order, our model has these frequencies proportional to $\epsilon^{3/2}$, ϵ^2, and $\epsilon^{5/2}$ respectively. The specific harmonic frequencies that we obtain for $FHCl^-$ are

251	FH moves relative to the Cl
871	bends (2 degenerate modes)
2960	FH oscillates

3 The Perturbation Expansion for the Nuclei

We now do the perturbation expansion for the semiclassical motion of the nuclei under the global hypotheses of Theorem 2.1. When the hypotheses are satisfied only locally, see Proposition 3.2.

The perturbation expansion describes the small ϵ dependence of the eigenvalue problem for the following differential operator

$$\begin{aligned} &-\frac{\epsilon^{3/2}}{2\,\mu_1}\,\frac{\partial^2}{\partial x^2} - \frac{\epsilon^2}{2\,\mu_1}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\,\frac{\partial}{\partial r} + \frac{1}{r^2}\,\frac{\partial^2}{\partial \gamma^2}\right) - \frac{\epsilon^{5/2}}{2\,\mu_2}\,\frac{\partial^2}{\partial y^2} \qquad (3.1)\\ &\qquad - \frac{\epsilon^{13/4}}{\mu_2\,(Y_0+\epsilon^{3/4}y)}\,\frac{\partial}{\partial y} + \frac{\epsilon^4}{2\,\mu_2\,(Y_0+\epsilon^{3/4}y)^2}\,\left\{\,J^2 - 2\,L\cdot J + L^2\,\right\},\\ &\qquad + a_0 + \sum_{j=2}^{\infty} a_j\,\epsilon^{3j/4}\,x^j + \sum_{\substack{j+k+l\geq 2\\ k+l\geq 1\\ k\ \text{even}}} b_{j,\,k,\,l}\,\epsilon^{1+\frac{3(j+l)+2k}{4}}\,x^j\,r^k\,y^l. \end{aligned}$$

At this point we should make the Ansatz that the eigenvalue and eigenfunction have expansions of the forms

$$\mathcal{E} \;=\; \sum_{l=0}^{\infty} \nu_l(\epsilon)\, \mathcal{E}_{q_l} \qquad \text{and} \qquad \psi(x,\, r,\, y,\, \theta,\, \phi,\, \gamma) \;=\; \sum_{l=0}^{\infty} \nu_l(\epsilon)\, \psi_{q_l}(x,\, r,\, y,\, \theta,\, \phi,\, \gamma).$$

Here, $\nu_0(\epsilon) = 1$, ψ_0 is non-trivial, and $\nu_{l+1}(\epsilon)/\nu_l(\epsilon) \to 0$ as $\epsilon \to 0$.

However, one learns that every $\nu_l(\epsilon)$ that occurs is some power of $\epsilon^{1/4}$, so it is somewhat simpler just to take $\nu_l(\epsilon) = \epsilon^{l/4}$, *i.e.*,

$$\mathcal{E} \;=\; \sum_{l=0}^{\infty} \epsilon^{l/4}\, \mathcal{E}_{l/4} \qquad \text{and} \qquad \psi(x,\, r,\, y,\, \theta,\, \phi,\, \gamma) \;=\; \sum_{l=0}^{\infty} \epsilon^{j/4}\, \psi_{l/4}(x,\, r,\, y,\, \theta,\, \phi,\, \gamma).$$

Our Hamiltonian, J^2, and J_z all commute with one another, so we can simultaneously diagonalize these three operators. The eigenvalues of J^2 are $j(j+1)$, where $j = 0,\, 1,\, 2,\, \ldots$, and for a given j, they have degeneracy $(2j+1)^2$. We henceforth use the specific basis for the eigenspace for fixed j that is given in Section 4.7 of [1]:

$$\{\, |\, j,\, j_z,\, k\,\rangle \;:\; j_z = -j,\, -j+1,\, \ldots\,,\, j;\;\; k = -j,\, -j+1,\, \ldots\,,\, j\,\},$$

where

$$J_z\; |\, j,\, j_z,\, k\,\rangle \;=\; j_z\; |\, j,\, j_z,\, k\,\rangle \qquad \text{and} \qquad L_{z'}\; |\, j,\, j_z,\, k\,\rangle \;=\; k\; |\, j,\, j_z,\, k\,\rangle,$$

where $J_z = -\, i\, \dfrac{\partial}{\partial \phi}$ and $L_{z'} = -\, i\, \dfrac{\partial}{\partial \gamma}$. Note that although J^2, J_z, and $L_{z'}$ all commute with one another, $L_{z'}$ does not commute with the Hamiltonian.

For future reference, we note also that the operators in (2.3) have

$$L_{+'}\; |\, j,\, j_z,\, k\,\rangle \;=\; \alpha_{+,j,j_z,k}\; |\, j,\, j_z,\, k+1\,\rangle \qquad \text{and} \qquad L_{-'}\; |\, j,\, j_z,\, k\,\rangle \;=\; \alpha_{-,j,j_z,k}\; |\, j,\, j_z,\, k-1\,\rangle,$$

for some $\alpha_{\pm,j,j_z,k}$. When $|k| = j$, $\alpha_{+,j,j_z,j} = 0$ and $\alpha_{-,j,j_z,-j} = 0$.

By restricting attention to given values of j and j_z, the wave functions in our expansion can now be regarded (with some abuse of notation) as

$$\psi_{l/4}(x,\, r,\, y,\, \theta,\, \phi,\, \gamma) \;=\; \sum_{k=-j}^{j} \psi_{l/4}(x,\, r,\, y,\, k)\; |\, j,\, j_z,\, k\,\rangle.$$

We now substitute the Ansatz into the eigenvalue equation and equate terms order by order. We do not worry about normalization, but produce a quasimode that is $O(1)$ as ϵ

tends to 0. To simplify some of the discussion, we take $\psi_{l/4}$ orthogonal to ψ_0 for $l > 0$. The results of these computations yield the formal expansions of Theorem 2.1.

Order $\epsilon^{\mathbf{0}}$ These terms simply require $a_0\,\psi_0 \;=\; \mathcal{E}_0\,\psi_0$. So,

$$\mathcal{E}_0 \;=\; a_0.$$

Order $\epsilon^{\mathbf{l/4}}$ for $\mathbf{1 \le l \le 5}$ The terms of these orders successively require $a_0\,\psi_{l/4} \;=\; \mathcal{E}_0\,\psi_{l/4} + \mathcal{E}_{l/4}\,\psi_0$. So,

$$\mathcal{E}_{l/4} \;=\; 0.$$

Order $\epsilon^{\mathbf{6/4}}$ These terms require $-\,\dfrac{1}{2\mu_1}\,\dfrac{\partial^2\psi_0}{\partial x^2} \;+\; a_2\,x^2\,\psi_0 \;=\; \mathcal{E}_{6/4}\,\psi_0$.

This forces

$$\mathcal{E}_{6/4} \;=\; \left(n+\frac{1}{2}\right)\,\sqrt{2\,a_2/\mu_1} \qquad \text{for some} \quad n \;=\; 0,\,1,\,\cdots,$$

and

$$\psi_0(x,\,r,\,y,\,k) \;=\; f_0(r,\,y,\,k)\;\Phi_1(x),$$

where

$$\Phi_1(x) \;=\; (2\,a_2\,\mu_1)^{1/8}\;\pi^{-1/4}\;2^{-n/2}\;(n!)^{-1/2}\;H_n(x')\;e^{-x'^2/2}$$

with $x' = (2\,a_2\,\mu_1)^{1/4}\,x$. The function f_0 is not yet determined.

Order $\epsilon^{\mathbf{7/4}}$ We introduce the notation

$$H_{0,x} \;=\; -\,\frac{1}{2\mu_1}\,\frac{\partial^2}{\partial x^2} \;+\; a_2\,x^2.$$

Then the $\epsilon^{7/4}$ terms require $[H_{0,x} - \mathcal{E}_{6/4}]\;\psi_{1/4} \;=\; \mathcal{E}_{7/4}\;\psi_0$.
We first examine the components of this equation that are multiples of $\Phi_1(x)$. These $\|_x$ components require

$$\mathcal{E}_{7/4} \;=\; 0.$$

We then examine the components that are perpendicular to $\Phi_1(x)$ in the x variables. These $\perp_x$ components require

$$\psi_{1/4}(x,\,r,\,y,\,k) \;=\; f_{1/4}(r,\,y,\,k)\;\Phi_1(x),$$

where the function $f_{1/4}$ is not yet determined.

Order $\epsilon^{8/4}$ These terms require

$$[H_{0,x} - \mathcal{E}_{6/4}]\ \psi_{2/4}\ -\ \frac{1}{2\mu_1}\ \left(\frac{\partial^2\psi_0}{\partial r^2}\ +\ \frac{1}{r}\ \frac{\partial\psi_0}{\partial r}\ +\ \frac{1}{r^2}\ \frac{\partial^2\psi_0}{\partial\gamma^2}\right)\ +\ b_{0,2,0}\ r^2\ \psi_0\ =\ \mathcal{E}_{8/4}\ \psi_0.$$

The $\|_x$ components of this equation require

$$H_{0,r,\gamma}\ \psi_0\ =\ \mathcal{E}_{8/4}\ \psi_0,$$

where

$$H_{0,r,\gamma}\ =\ -\ \frac{1}{2\mu_1}\ \left(\frac{\partial^2}{\partial r^2}\ +\ \frac{1}{r}\ \frac{\partial}{\partial r}\ +\ \frac{1}{r^2}\ \frac{\partial^2}{\partial\gamma^2}\right)\ +\ b_{0,2,0}\ r^2.$$

This is a standard isotropic two dimensional Harmonic oscillator problem that one can solve by separating variables. In our context, the angular operator $L_{z'}\ =\ -\,i\,\dfrac{\partial\psi_0}{\partial\gamma}$ has eigenvalues $k = 0,\ \pm1,\ \pm2,\ \cdots,\ \pm j$ and eigenfunctions $e^{i\,k\,\gamma}$. For each such k, the radial operator

$$-\ \frac{1}{2\mu_1}\ \left(\frac{\partial^2}{\partial r^2}\ +\ \frac{1}{r}\ \frac{\partial}{\partial r}\ -\ \frac{k^2}{r^2}\right)\ +\ b_{0,2,0}\ r^2$$

has eigenvalues

$$\mathcal{E}_{8/4}\ =\ (\,2\,m\ +\ |k|\ +\ 1\,)\ \sqrt{2\,b_{0,2,0}/\mu_1},\qquad \text{where}\quad m\ =\ 0,\ 1,\ \cdots.$$

The corresponding normalized eigenfunctions are

$$\sqrt{\frac{2\ (m!)}{(m+|k|)!}}\ \ (\,2\,b_{0,2,0}\,\mu_1\,)^{1/4}\ \ (r')^{|k|}\ L_m^{|k|}(r'^2)\ e^{-r'^2/2},$$

where, $r' = (2\,b_{0,2,0}\,\mu_1)^{1/4}\,r$, $m \ge 0$, and $L_m^{|k|}$ is a Laguerre polynomial.

We permanently fix one such value of $\mathcal{E}_{8/4}$. Since different pairs $(m,\,k)$ can occur, we define

$$K\ =\ \{\,k \in \mathbb{Z}\ :\ |k| \le j,\ \text{and}\ m(k) \ge 0\,\}.$$

where

$$m(k)\ =\ \frac{1}{2}\ \left(\mathcal{E}_{8/4}\Big/\sqrt{2\,b_{0,2,0}/\mu_1}\ -\ |k|\ -\ 1\right).$$

One can easily show that K is non-empty and has at most $j+1$ elements.

For $k \in K$, we define the normalized wave functions

$$\Phi_2(|k|,\,r)\ =\ \sqrt{\frac{2\ (m(k)!)}{(m(k)+|k|)!}}\ \ (\,2\,b_{0,2,0}\,\mu_1\,)^{1/4}\ \ (r')^{|k|}\ L_{m(k)}^{|k|}(r'^2)\ e^{-r'^2/2}$$

and take

$$f_0(r,\,y,\,k) \;=\; \begin{cases} g_0(y,\,k)\;\Phi_2(|k|,\,r) & \text{if} \quad k \in K \\ 0 & \text{otherwise.} \end{cases}$$

The functions $g_0(y,\,k)$ for $k \in K$ are not yet determined. However, we now have

$$\psi_0(x,\,r,\,y,\,\theta,\,\phi,\,\gamma) \;=\; \sum_{k\in K}\; g_0(y,\,k)\;\Phi_1(x)\;\Phi_2(|k|,\,r)\;|\,j,\,j_z,\,k\,\rangle.$$

For future reference, we let Z_1 denote the subspace spanned by

$$\{\,\Phi_1(x)\;\Phi_2(|k|,\,r)\;|\,j,\,j_z,\,k\,\rangle \;:\; k \in K\,\}\,.$$

The $\perp_x$ terms at this order require $[H_{0,x} - \mathcal{E}_{6/4}]\;\psi_{2/4} \;=\; 0$, which simply forces

$$\psi_{2/4} \;=\; f_{2/4}(r,\,y,\,k)\;\Phi_1(x).$$

Order $\epsilon^{9/4}$ These terms require

$$[H_{0,x} - \mathcal{E}_{6/4}]\;\psi_{3/4} \;+\; [H_{0,r,\gamma} - \mathcal{E}_{8/4}]\;\psi_{1/4} \;+\; a_3\;x^3\;\psi_0$$

$$=\;\; \mathcal{E}_{9/4}\;\psi_0. \tag{3.2}$$

The $\|_x$ components of this equation require

$$[H_{0,r,\gamma} - \mathcal{E}_{8/4}]\;\psi_{1/4} \;=\; \mathcal{E}_{9/4}\;\psi_0. \tag{3.3}$$

We first examine the components of this equation that belong to the subspace Z_1. These $\|_x\,\|_{Z_1}$ components require

$$\mathcal{E}_{9/4} \;=\; 0.$$

Next, the $\|_x \perp_{Z_1}$ components of (3.3) that are orthogonal to Z_1 require $[H_{0,r,\gamma} - \mathcal{E}_{8/4}]\;\psi_{1/4} \;=\; 0$. This forces us to choose

$$f_{1/4}(r,\,y,\,k) \;=\; \begin{cases} g_{1/4}(y,\,k)\;\Phi_2(|k|,\,r) & \text{if} \quad k \in K \\ 0 & \text{otherwise.} \end{cases}$$

The $\perp_x$ components of (3.2) require $[H_{0,x} - \mathcal{E}_{6/4}]\;\psi_{3/4} \;+\; a_3\;x^3\;\psi_0 \;=\; 0$. We solve this equation by applying the reduced resolvent operator $[H_{0,x} - \mathcal{E}_{6/4}]_r^{-1}$. The result is

$$\psi_{3/4}(x,\,r,\,y,\,k) \;\;=\;\; -\,a_3\;\sum_{k\in K}\;g_0(y,\,k)\;\Phi_2(|k|,\,r)\;[H_{0,x} - \mathcal{E}_{6/4}]_r^{-1}\;\left(x^3\;\Phi_1(x)\right)$$

$$+\quad f_{3/4}(r,\,y,\,k)\;\Phi_1(x). \tag{3.4}$$

Order $\epsilon^{10/4}$

$$\begin{aligned}&[H_{0,x}-\mathcal{E}_{6/4}]\ \psi_{4/4}\ +\ [H_{0,r,\gamma}-\mathcal{E}_{8/4}]\ \psi_{2/4}\\ &\qquad -\ \frac{1}{2\mu_2}\ \frac{\partial^2\psi_0}{\partial y^2}\ +\ a_3\ x^3\psi_{1/4}\ +\ b_{0,0,2}\ y^2\ \psi_0\ +\ b_{1,0,1}\ x\,y\,\psi_0\ \ =\ \ \mathcal{E}_{10/4}\ \psi_0.\end{aligned} \tag{3.5}$$

The $\|_x\,\|_{Z_1}$ components require $-\ \dfrac{1}{2\mu_2}\ \dfrac{\partial^2\psi_0}{\partial y^2}\ +\ b_{0,0,2}\ y^2\ \psi_0\ =\ \mathcal{E}_{10/4}\ \psi_0$. This forces us to choose

$$\mathcal{E}_{10/4}\ =\ \left(p+\frac{1}{2}\right)\ \sqrt{2\,b_{0,0,2}/\mu_2}\qquad \text{where}\quad p\ =\ 0,\ 1,\ \cdots,$$

and

$$g_0(y,\,k)\ =\ c_{0,k}\ \Phi_3(y)\qquad \text{if}\quad k\in K, \tag{3.6}$$

where

$$\Phi_3(y)\ =\ (2\,b_{0,0,2}\,\mu_2)^{1/8}\ \pi^{-1/4}\ 2^{-p/2}\ (p!)^{-1/2}\ H_p(y')\ e^{-{y'}^2/2}$$

with $y'=(2\,b_{0,0,2}\,\mu_2)^{1/4}\,y$.

So far, the $c_{0,k}$ in (3.6) are arbitrary for $k\in K$, but we henceforth assume they satisfy the normalization condition

$$\sum_{k\in K}\,|\,c_{0,k}\,|^2\ =\ 1.$$

For future reference, we let Z_2 denote the subspace spanned by

$$\{\,\Phi_1(x)\ \Phi_2(|k|,\,r)\ \Phi_3(y)\ |\,j,\,j_z,\,k\,\rangle\ :\ k\in K\,\}\,.$$

The $\|_x\,\perp_{Z_1}$ components require

$$f_{2/4}(r,\,y,\,k)\ =\ \begin{cases} g_{2/4}(y,\,k)\ \Phi_2(|k|,\,r) & \text{if}\quad k\in K\\ \qquad 0 & \text{otherwise.}\end{cases}$$

The $\perp_x$ components require $[H_{0,x}-\mathcal{E}_{6/4}]\ \psi_{4/4}\ +\ a_3\ x^3\psi_{1/4}\ +\ b_{1,0,1}\ x\,y\ \psi_0\ =\ 0$. We apply the reduced resolvent of $H_{0,x}$ to obtain

$$\begin{aligned}\psi_{4/4}(x,\,r,\,y,\,k)\ \ =\ \ &-\ a_3\ g_{1/4}(y,\,k)\ \Phi_2(|k|,\,r)\ [H_{0,x}-\mathcal{E}_{6/4}]_r^{-1}\ \bigl(x^3\,\Phi_1(x)\bigr)\\ &-\ b_{1,0,1}\ c_{0,k}\ y\ \Phi_3(y)\ \Phi_2(|k|,\,r)\ [H_{0,x}-\mathcal{E}_{6/4}]_r^{-1}\ \bigl(x\ \Phi_1(x)\bigr)\\ &+\ f_{4/4}(r,\,y,\,k)\ \Phi_1(x).\end{aligned}$$

Note that the first two terms are zero if $k\notin K$.

Remarks

1. At this point, we have completely determined ψ_0, except for the values of $c_{0,k}$ for $k \in K$. Restoring the angular dependence in the notation, we have

$$\psi_0 \;=\; \sum_{k \in K} c_{0,k}\ \Phi_1(x)\ \Phi_2(|k|,\,r)\ \Phi_3(y)\ \ |\,j,\,j_z,\,k\,\rangle.$$

Since j and j_z are fixed, this is a linear combination of at most $j+1$ linearly independent states.

2. As we shall see, the degeneracy generically partially splits at order $\epsilon^{12/4}$. At that point, states with different values of $|k|$ have different energy, but two states with $k = \pm\lambda$ for $\lambda > 0$ have the same $\mathcal{E}_{12/4}$. In terms of the energy, the degeneracy of these two states generically splits completely at order $\epsilon^{2+3\lambda}$. When $\lambda = 1$, this splitting has long been observed in the spectra of linear polyatomic molecules. It is called l–type doubling [7].

3. We have determined the dominant terms for the eigenvalue:

$$\mathcal{E}_0 \;+\; \epsilon^{3/2}\left(n+\frac{1}{2}\right)\sqrt{2\,a_2/\mu_1} \;+\; \epsilon^2\ (2m(k)+|k|+1)\ \sqrt{2\,b_{0,2,0}/\mu_1} \;+\; \epsilon^{5/2}\left(p+\frac{1}{2}\right)\sqrt{2\,b_{0,0,2}/\mu_2}.$$

This quantity does not depend on the quantum numbers j, j_z, or $k \in K$.

The dominant contribution to the energy from the total angular momentum is $\dfrac{j(j+1)\,\epsilon^4}{2\,\mu_2\,Y_0^2}$, so it enters at order 16/4.

4. Below we impose the condition that every $\psi_{l/4}$ with $l > 0$ be orthogonal to the subspace Z_2.

5. At the next order, the pattern emerges for how to do all higher order formal perturbation calculations. For $l \geq 11$, we have the following:

- the $\|_x\,\|_{Z_1}\,\|_y$ terms determine $\mathcal{E}_{l/4}$,
- the $\|_x\,\|_{Z_1}\,\perp_y$ terms determine the y–dependence of $g_{(l-10)/4}(y,\,k)$
- the $\|_x\,\perp_{Z_1}$ terms determine the r and k dependence of $f_{(l-8)/4}(r,\,y,\,k)$, and
- the $\perp_x$ terms determine the x–dependence of $\psi_{(l-6)/4}(x,\,r,\,y,\,k)$.

Since the general pattern occurs at the next order, we present full calculations for only one more order explicitly.

Order $\epsilon^{11/4}$

$$[H_{0,x}-\mathcal{E}_{6/4}]\,\psi_{5/4}\;+\;[H_{0,r,\gamma}-\mathcal{E}_{8/4}]\,\psi_{3/4}\;+\;[H_{0,y}-\mathcal{E}_{10/4}]\,\psi_{1/4}$$

$$+\,a_3\,x^3\psi_{2/4}\;+\;b_{1,0,1}\,x\,y\,\psi_{1/4}\;+\;b_{0,2,1}\,r^2\,y\,\psi_0\;+\;b_{1,2,0}\,x\,r^2\,\psi_0$$

$$=\quad\mathcal{E}_{11/4}\,\psi_0.$$

The $\|_x\,\|_{Z_1}\,\|_y$ terms require

$$\mathcal{E}_{11/4}\;=\;0.$$

The $\|_x\,\|_{Z_1}\,\perp_y$ terms require

$$g_{1/4}(y,\,k)\quad=\quad-\,b_{0,2,1}\,c_{0,k}\,\left\langle\,\Phi_2(|k|,\,r),\,r^2\,\Phi_2(|k|,\,r)\,\right\rangle_r\;[H_{0,y}-\mathcal{E}_{10/4}]_r^{-1}\,\left(\,y\,\Phi_3(y)\,\right).$$

for $k\in K$. This is the first place in the perturbation calculations where different values of $|k|$ yield different results. Note that we could add $c_{1/4,k}\,\Phi_3(y)$ to $g_{1/4}(y,\,k)$ when $k\in K$, but we have chosen $c_{1/4,k}=0$ to impose the condition that $\psi_{1/4}$ be orthogonal to the subspace Z_2. See Remark 4 above.

The $\|_x\,\perp_{Z_1}$ terms require

$$[H_{0,r,\gamma}-\mathcal{E}_{8/4}]\,f_{3/4}\;+\;P_{\perp_{Z_1}}\,[H_{0,y}-\mathcal{E}_{10/4}]\,f_{1/4}\;+\;b_{0,2,1}\,y\,P_{\perp_{Z_1}}\,r^2\,f_0\;=\;0,$$

where $P_{\perp_{Z_1}}$ denotes the projection onto functions orthogonal to the subspace Z_1. We have already seen that the non-zero $f_{1/4}(r,\,y,\,k)$ belong to the subspace Z_1, so $P_{\perp_{Z_1}}\,[H_{0,y}-\mathcal{E}_{10/4}]\,f_{1/4}\;=\;0$. Thus, applying the reduced resolvent of $H_{0,r,\gamma}$ (which is zero on Z_1), we obtain

$$f_{3/4}(r,\,y,\,k)\;=\;-\;b_{0,2,1}\,c_{0,k}\,y\,\Phi_3(y)\,[H_{0,r}(|k|)-\mathcal{E}_{8/4}]_r^{-1}\,P_{\perp_{Z_1}}\,r^2\,\Phi_2(|k|,\,r)$$

$$+\quad g_{3/4}(y,\,k)\,\Phi_2(|k|,\,r)\qquad\text{if}\quad k\in K,\qquad\text{and}$$

$$f_{3/4}(r,\,y,\,k)\;=\quad 0\qquad\text{if}\quad k\notin K.$$

Here, we have used the notation

$$H_{0,r}(|k|)\;=\;-\,\frac{1}{2}\,\frac{\partial^2}{\partial r^2}\;-\;\frac{1}{2\,r}\,\frac{\partial}{\partial r}\;+\;\frac{k^2}{2\,r^2}$$

and the direct sum decomposition

$$[H_{0,r,\gamma}-\mathcal{E}_{8/4}]_r^{-1}\quad=\quad\bigoplus_{|k|\le j}\;[H_{0,r}(|k|)-\mathcal{E}_{8/4}]_r^{-1}$$

which results from $H_{0,r,\gamma}$ commuting with $L_{z'}$.

The $\perp_x$ terms require

$$[H_{0,x} - \mathcal{E}_{6/4}]\ \psi_{5/4}\ +\ [H_{0,r,\gamma} - \mathcal{E}_{8/4}]\ \psi_{3/4}^{\perp_x}$$

$$+\quad a_3\ x^3\ \psi_{2/4}\ +\ b_{1,0,1}\ x\,y\ \psi_{1/4}\ +\ b_{1,2,0}\ x\,r^2\ \psi_0\ =\ 0,$$

where $\psi_{3/4}^{\perp_x}$ denotes the component of $\psi_{3/4}$ orthogonal to $\Phi_1(x)$ in the x variables. By combining this with (3.4) and (3.6), we have

$$\psi_{3/4}^{\perp_x}(x,\,r,\,y,\,k)\ =\ \begin{cases} -\ a_3\ c_{0,k}\ \Phi_3(y)\ \Phi_2(|k|,\,r)\ [H_{0,x} - \mathcal{E}_{6/4}]_r^{-1}\ \left(x^3\,\Phi_1(x)\right) & \text{if}\quad k \in K \\ 0 & \text{if}\quad k \notin K. \end{cases}$$

So, we see that $[H_{0,r} - \mathcal{E}_{8/4}]\ \psi_{3/4}^{\perp_x}\ =\ 0$. Thus, we have

$$\begin{aligned} \psi_{5/4}(x,\,r,\,y,\,k)\ \ =\ \ -\ \ & a_3\ g_{2/4}(y,\,k)\ \Phi_2(|k|,\,r)\ \left([H_{0,x} - \mathcal{E}_{6/4}]_r^{-1}\ \left(x^3\,\Phi_1(x)\right)\right) \\ -\ \ & b_{1,0,1}\ y\ g_{1/4}(y,\,k)\ \Phi_2(|k|,\,r)\ \left([\,H_{0,x} - \mathcal{E}_{6/4}]_r^{-1}\ \left(x\ \Phi_1(x)\right)\right) \\ -\ \ & b_{1,2,0}\ c_{0,k}\ \Phi_3(y)\ r^2\,\Phi_2(|k|,\,r)\ \left([H_{0,x} - \mathcal{E}_{6/4}]_r^{-1}\ (x\ \Phi_1(x))\right) \\ +\ \ & f_{5/4}(r,\,y,\,k)\ \Phi_1(x) \qquad\qquad \text{if}\quad k \in K. \end{aligned}$$

For $k \notin K$,

$$\psi_{5/4}(x,\,r,\,y,\,k)\quad =\quad f_{5/4}(r,\,y,\,k)\ \Phi_1(x).$$

Note that only $g_{2/4}(y,\,k)$ (for $k \in K$) and $f_{5/4}(r,\,y,\,k)$ in these expressions have not yet been determined.

Remarks

1. Amazingly, $\psi_{1/4} \neq 0$. This component of the wave function involves an anharmonic correction related to the bending and AH–B stretching modes. Restoring the angular dependence to the notation, we have

   $\psi_{1/4}(x,\,r,\,y,\,\theta,\,\phi,\,\gamma)$

   $$=\ -\ b_{0,2,1}\ \sum_{k \in K}\ c_{0,k}\ \left\langle\,\Phi_2(|k|,\,r),\ r^2\,\Phi_2(|k|,\,r)\,\right\rangle_r$$

   $$\times\quad \Phi_1(x)\ \Phi_2(|k|,\,r)\ [H_{0,y} - \mathcal{E}_{10/4}]_r^{-1}\ \left(y\ \Phi_3(y)\right)\ \ |\,j,\,j_z,\,k\,\rangle.$$

2. Although we do not present the full calculations at order $\epsilon^{12/4}$, we do calculate $\mathcal{E}_{12/4}$ explicitly. It is generically contains non-zero anharmonic corrections.

Before going further with the expansion, we present a summary of what has been determined so far.

$$\mathcal{E} \;=\; \mathcal{E}_0 \,+\, \epsilon^{3/2}\,\left(n+\frac{1}{2}\right)\,\sqrt{2\,a_2/\mu_1} \quad+\quad \epsilon^2\,\left(2m(k)+|k|+1\right)\,\sqrt{2\,b_{0,2,0}/\mu_1}$$

$$+\quad \epsilon^{5/2}\,\left(p+\frac{1}{2}\right)\,\sqrt{2\,b_{0,0,2}/\mu_2} \quad+\quad O(\epsilon^{12/4}).$$

The last information for $\mathcal{E}$ came from order $11/4$, $\|_x \,\|_{Z_1}\,\|_y$.

$$\psi_0 \quad=\quad \sum_{k\in K} c_{0,k}\;\Phi_1(x)\;\Phi_2(|k|,\,r)\;\Phi_3(y)\;\;|\,j,j_z,k\,\rangle.$$

This was completely determined at order $10/4$, $\|_x\,\|_{Z_1}$.

$$\psi_{1/4} \quad=\quad -\,b_{0,2,1}\sum_{k\in K} c_{0,k}\;\left\langle\,\Phi_2(|k|,\,r),\;r^2\,\Phi_2(|k|,\,r)\,\right\rangle_r$$

$$\times\quad \Phi_1(x)\;\Phi_2(r)\;[H_{0,y}-\mathcal{E}_{10/4}]_r^{-1}\;\big(y\,\Phi_3(y)\big)\;|\,j,j_z,k\,\rangle$$

This was completely determined at order $11/4$, $\|_x\,\|_{Z_1}\,\perp_y$.

$$\psi_{2/4} \quad=\quad \sum_{k\in K} g_{2/4}(y,\,k)\;\Phi_1(x)\;\Phi_2(|k|,\,r)\;|\,j,j_z,k\,\rangle.$$

The last information came from order $10/4$, $\|_x\,\perp_{Z_1}$.

$$\psi_{3/4} \quad=\quad -\quad b_{0,2,1}\sum_{k\in K} c_{0,k}\;\Phi_1(x)\;\;(y\;\Phi_3(y))$$

$$\times\quad [H_{0,r}(|k|)-\mathcal{E}_{8/4}]_r^{-1}\;\left(P_{\perp_{Z_1}}\;r^2\;\Phi_2(|k|,\,r)\right)\;|\,j,j_z,k\,\rangle$$

$$+\quad \sum_{k\in K} g_{3/4}(y,\,k)\;\Phi_1(x)\;\Phi_2(|k|,\,r)\;|\,j,j_z,k\,\rangle.$$

The last information came from order $11/4$, $\|_x\,\perp_{Z_1}$.

$$
\begin{aligned}
\psi_{4/4} \;=\;& a_3\, b_{0,2,1}\, [H_{0,y} - \mathcal{E}_{10/4}]_r^{-1} \, \big(y\, \Phi_3(y)\big)\, [H_{0,x} - \mathcal{E}_{6/4}]_r^{-1}\, \big(x^3\, \Phi_1(x)\big) \\
& \qquad\qquad \times \sum_{k \in K} c_{0,k}\, \big\langle\, \Phi_2(|k|,\, r),\ r^2\, \Phi_2(|k|,\, r)\, \big\rangle_r\ \Phi_2(|k|,\, r) |\, j, j_z, k\,\rangle \\
& - \ b_{1,0,1}\, \big(\, y\ \Phi_3(y)\,\big)\, [H_{0,x} - \mathcal{E}_{6/4}]_r^{-1}\, \big(x\ \Phi_1(x)\big) \sum_{k \in K} c_{0,k}\, \Phi_2(|k|,\, r)\, |\, j, j_z, k\,\rangle \\
& + \sum_{k=-j}^{j} f_{4/4}(r,\, y,\, k)\ \Phi_1(x)\, |\, j, j_z, k\,\rangle.
\end{aligned}
$$

The last information came from order 10/4, $\perp_x$
(coupled with 11/4, $\|_x \|_{Z_1} \perp_y$, because of $g_{1/4}$).

$$
\begin{aligned}
\psi_{5/4} \;=\; & - \ a_3 \sum_{k \in K} g_{2/4}(y,\, k)\ \Phi_2(|k|,\, r)\, \Big([H_{0,x} - \mathcal{E}_{6/4}]_r^{-1}\, \big(x^3\, \Phi_1(x)\big) \Big)\, |\, j, j_z, k\,\rangle \\
& - \ b_{1,0,1}\, b_{0,2,1} \sum_{k \in K} c_{0,k}\, \big\langle\, \Phi_2(|k|,\, r),\ r^2\, \Phi_2(|k|,\, r)\, \big\rangle_r\, \Big([H_{0,x} - \mathcal{E}_{6/4}]_r^{-1}\, (x\, \Phi_1(x)) \Big) \\
& \qquad\qquad \times\ \Phi_2(|k|,\, r)\, \Big(y\ [H_{0,y} - \mathcal{E}_{10/4}]_r^{-1}\, \big(y\, \Phi_3(y)\big)\Big) |\, j, j_z, k\,\rangle \\
& - \ b_{1,2,0} \sum_{k \in K} c_{0,k}\, \Phi_3(y)\, r^2\, \Phi_2(|k|,\, r)\, \Big([H_{0,x} - \mathcal{E}_{6/4}]_r^{-1}\, \big(x\ \Phi_1(x)\big) \Big)\, |\, j, j_z, k\,\rangle \\
& + \sum_{k=-j}^{j} f_{5/4}(r,\, y,\, k)\ \Phi_1(x)\, |\, j, j_z, k\,\rangle.
\end{aligned}
$$

The last information came from order 11/4, $\perp_x$.

We now return to describing higher orders of the perturbation expansion. We determine $\mathcal{E}_{12/4}$, and explicitly write the equations that must be solved through order $\epsilon^{16/4}$. That is the order at which the angular momentum quantum number j appears, and the degeneracy due to rotations is split.

Order $\epsilon^{12/4}$

$$\begin{aligned}
& [H_{0,x} - \mathcal{E}_{6/4}]\ \psi_{6/4}\ +\ [H_{0,r,\gamma} - \mathcal{E}_{8/4}]\ \psi_{4/4}\ +\ [H_{0,y} - \mathcal{E}_{10/4}]\ \psi_{2/4}\ +\ a_3\ x^3\ \psi_{3/4} \\
& \qquad +\quad a_4\ x^4\ \psi_0\ +\ b_{1,0,1}\ x\, y\ \psi_{2/4}\ +\ b_{0,2,1}\ r^2\, y\ \psi_{1/4}\ +\ b_{1,2,0}\ x\, r^2\ \psi_{1/4} \\
& \qquad +\quad b_{0,4,0}\ r^4\ \psi_0\ +\ \frac{X_0^2}{2\,\mu_2\, Y_0^2}\ H_{0,r,\gamma}\ \psi_0 \\
& =\quad \mathcal{E}_{12/4}\ \psi_0.
\end{aligned}$$

From the $\|_x \|_{Z_1} \|_\gamma$ terms, we can easily solve for $\mathcal{E}_{12/4}$.

$$\begin{aligned}
\mathcal{E}_{12/4} \quad = \quad & -\quad a_3^2\ \langle\, \Phi_1(x),\ x^3\ [H_{0,x} - \mathcal{E}_{6/4}]_r^{-1}\ x^3\ \Phi_1(x)\,\rangle_x \\
& +\quad a_4\ \langle\, \Phi_1(x),\ x^4\ \Phi_1(x)\,\rangle_x \\
& -\quad b_{0,2,1}^2\ \langle\, \Phi_2(|k|,\, r),\ r^2\ \Phi_2(|k|,\, r)\,\rangle_r^2\quad \langle\, \Phi_3(y),\ y\ [H_{0,y} - \mathcal{E}_{10/4}]_r^{-1}\ y\ \Phi_3(y)\,\rangle_y \\
& +\quad b_{0,4,0}\ \langle\, \Phi_2(|k|,\, r),\ r^4\ \Phi_2(|k|,\, r)\,\rangle_r \\
& +\quad \frac{X_0}{2\,\mu_2\, Y_0^2}\quad \sqrt{2\, b_{0,2,0}/\mu_1}\quad (2m(k) + |k| + 1)
\end{aligned}$$

As long as $b_{0,4,0} \neq 0$, this expression yields different values for different $|k|$. To see this, first note that the factor

$$\langle\, \Phi_2(|k|,\, r),\ r^2\ \Phi_2(|k|,\, r)\,\rangle_r^2\ =\ \left(\frac{2m(k)\ +\ |k|\ +\ 1}{\sqrt{2\, b_{0,2,0}\, \mu_1}} \right)^2$$

does not depend on k, and the term

$$\frac{X_0}{2\,\mu_2\, Y_0^2}\quad \sqrt{2\, b_{0,2,0}/\mu_1}\quad (2m(k)\ +\ |k|\ +\ 1)$$

does not depend on k. In fact, the only term that has non-trivial dependence on k in $\mathcal{E}_{12/4}$ is

$$\langle\, \Phi_2(|k|,\, r),\ r^4\ \Phi_2(|k|,\, r)\,\rangle_r\ =\ \frac{(2 + 3|k| + k^2)\ +\ 6\,(|k| + 1)\, m(k)\ +\ 6\, m(k)^2}{2\, b_{0,2,0}\, \mu_1}$$

We now show that different values of k yield different values of this quantity.

Let $k_1 \geq 0$ and $k_2 \geq 0$ be two different values of $|k|$ that yield the same result. Simultaneously solving

$$(2 + 3k_1 + k_1^2) + 6(k_1 + 1)m(k_1) + 6m(k_1)^2 = (2 + 3k_2 + k_2^2) + 6(k_2 + 1)m(k_2) + 6m(k_2)^2$$

and

$$2m(k_1) + k_1 + 1 \;=\; 2m(k_2) + k_2 + 1$$

forces

$$\begin{aligned} m(k_1) \;&=\; (-3 \,-\, 5\,k_1 \,+\, k_2)/6 \\ m(k_2) \;&=\; (-3 \,+\, k_1 \,-\, 5k_2)/6. \end{aligned}$$

However, $m(k_1)$ and $m(k_2)$ must both be non-negative. There are no simultaneous non-negative solutions to

$$\begin{aligned} k_2 \;&>\; 3 \,+\, 5\,k_1 \\ k_2 \;&<\; (-3 \,+\, k_1)/5 \end{aligned}$$

since this would require $3 \,+\, 5\,k_1 \,<\, -3/5 \,+\, k_1/5$, which requires $24k_1 < -18$ or $k_1 < -3/4$. This contradicts $k_1 \geq 0$, so different values of $|k|$ must yield different values for $\mathcal{E}_{12/4}$.

Therefore, at this level of perturbation, the eigenvalues generically have multiplicity 1 when $k = 0$ and multiplicity 2 when $k \geq 1$.

Explicitly,

$$\begin{aligned} \mathcal{E}_{12/4} \;=\; &-\; \frac{1}{32\,\mu_1} \left(\frac{a_3}{a_2}\right)^2 \left(11 \,+\, 30\,n \,+\, 30\,n^2\right) \;+\; \frac{3\,a_4}{8\,a_2\,\mu_1} \left(1 \,+\, 2\,n \,+\, 2\,n^2\right) \\ &-\; \frac{b_{0,2,1}^2}{8\,b_{0,2,0}\,b_{0,0,2}\,\mu_1} \left(2\,m(k) \,+\, |k| \,+\, 1\right)^2 \\ &+\; \frac{b_{0,4,0}}{2\,b_{0,2,0}\,\mu_1} \left((2 \,+\, 3\,|k| \,+\, k^2) \,+\, 6\,(\,|k| \,+\, 1\,)\,m(k) \,+\, 6\,m(k)^2\right) \\ &+\; \frac{X_0}{\mu_2\,Y_0^2} \sqrt{\frac{b_{0,2,0}}{2\,\mu_1}} \;(\,2\,m(k) \,+\, |k| \,+\, 1\,). \end{aligned} \tag{3.7}$$

Order $\boldsymbol{\epsilon^{13/4}}$

$$\begin{aligned}
&[H_{0,x} - \mathcal{E}_{6/4}]\,\psi_{7/4} \;+\; [H_{0,r,\gamma} - \mathcal{E}_{8/4}]\,\psi_{5/4} \;+\; [H_{0,y} - \mathcal{E}_{10/4}]\,\psi_{3/4} \\
&\qquad -\;\frac{1}{2\,\mu_2\,Y_0}\,\frac{\partial\psi_0}{\partial y} \;+\; a_3\,x^3\,\psi_{4/4} \;+\; a_4\,x^4\,\psi_{1/4} \;+\; b_{1,0,1}\,x\,y\,\psi_{3/4} \;+\; b_{0,2,1}\,r^2\,y\,\psi_{2/4} \\
&\qquad +\;b_{1,2,0}\,x\,r^2\,\psi_{2/4} \;+\; b_{0,4,0}\,r^4\,\psi_{1/4} \;+\; b_{0,0,3}\,y^3\,\psi_0 \;+\; b_{1,0,2}\,x\,y^2\,\psi_0 \;+\; b_{2,0,1}\,x^2\,y\,\psi_0 \\
&\qquad +\;\frac{X_0^2}{2\,\mu_2\,Y_0^2}\,H_{0,r,\gamma}\,\psi_{1/4} \;+\; \frac{X_0}{\mu_2\,Y_0^2}\left(r\,\frac{\partial^2}{\partial x\,\partial r} \;+\; \frac{\partial}{\partial x}\right)\psi_0 \\
&=\;\; \mathcal{E}_{13/4}\,\psi_0 \;+\; \mathcal{E}_{12/4}\,\psi_{1/4}.
\end{aligned}$$

Order $\boldsymbol{\epsilon^{14/4}}$

$$\begin{aligned}
&[H_{0,x} - \mathcal{E}_{6/4}]\,\psi_{8/4} \;+\; [H_{0,r,\gamma} - \mathcal{E}_{8/4}]\,\psi_{6/4} \;+\; [H_{0,y} - \mathcal{E}_{10/4}]\,\psi_{4/4} \\
&\qquad -\;\frac{1}{2\,\mu_2\,Y_0}\,\frac{\partial\psi_{1/4}}{\partial y} \;+\; a_3\,x^3\,\psi_{5/4} \;+\; a_4\,x^4\,\psi_{2/4} \;+\; b_{1,0,1}\,x\,y\,\psi_{4/4} \;+\; b_{2,0,1}\,x^2\,y\,\psi_{1/4} \\
&\qquad +\;b_{0,2,1}\,r^2\,y\,\psi_{3/4} \;+\; b_{1,2,0}\,x\,r^2\,\psi_{3/4} \;+\; b_{0,4,0}\,r^4\,\psi_{2/4} \;+\; b_{0,0,3}\,y^3\,\psi_{1/4} \\
&\qquad +\;b_{1,0,2}\,x\,y^2\,\psi_{1/4} \;+\; b_{0,2,2}\,r^2\,y^2\,\psi_0 \;+\; b_{1,2,1}\,x\,r^2\,y\,\psi_0 \;+\; b_{2,2,0}\,x^2\,r^2\,\psi_0 \\
&\qquad +\;\frac{X_0^2}{2\,\mu_2\,Y_0^2}\,H_{0,r,\gamma}\,\psi_{2/4} \;+\; \frac{X_0}{\mu_2\,Y_0^2}\left(r\,\frac{\partial^2}{\partial x\,\partial r} \;+\; \frac{\partial}{\partial x}\right)\psi_{1/4} \;-\; \frac{r^2}{2\,\mu_2\,Y_0^2}\,\frac{\partial^2}{\partial x^2}\,\psi_0 \\
&\qquad +\;\frac{1}{\mu_2\,Y_0^2}\,\Bigg[\left(X_0\,\sin\gamma\,\frac{\partial}{\partial r} \;+\; \frac{X_0}{r}\,\cos\gamma\,\frac{\partial}{\partial\gamma}\right)\left(\frac{1}{\sin\theta}\,\frac{\partial}{\partial\phi} \;-\; \cot\theta\,\frac{\partial}{\partial\gamma}\right) \\
&\qquad\qquad\qquad +\;\left(X_0\,\cos\gamma\,\frac{\partial}{\partial r} \;-\; \frac{X_0}{r}\,\sin\gamma\,\frac{\partial}{\partial\gamma}\right)\frac{\partial}{\partial\theta}\Bigg]\,\psi_0 \\
&=\;\; \mathcal{E}_{14/4}\,\psi_0 \;+\; \mathcal{E}_{13/4}\,\psi_{1/4} \;+\; \mathcal{E}_{12/4}\,\psi_{2/4}.
\end{aligned}$$

Note: This is where we first encounter operators that mix the various different values of k. If we use (2.3) in the above expression and take ψ_0 to be a linear combination of the two degenerate states with $|k| = \lambda$, we see that the last term on the left hand side of the equation contains $L_{\pm'}\,|\,j,\,j_z,\,\lambda\,\rangle$ and $L_{\pm'}\,|\,j,\,j_z,\,-\lambda\,\rangle$, which are linear combinations of $|\,j,\,j_z,\,\lambda \pm 1\rangle$ and $L_{\pm'}\,|\,j,\,j_z,\,-\lambda \pm 1\,\rangle$, respectively. Thus, $\psi_{6/4}$ is the lowest order term that involves $k \neq \pm\lambda$.

Order $\boldsymbol{\epsilon^{15/4}}$

$$
\begin{aligned}
&[H_{0,x} - \mathcal{E}_{6/4}]\ \psi_{9/4} \ + \ [H_{0,r,\gamma} - \mathcal{E}_{8/4}]\ \psi_{7/4} \ + \ [H_{0,y} - \mathcal{E}_{10/4}]\ \psi_{5/4} \\
&\qquad - \ \frac{1}{2\,\mu_2\,Y_0}\ \frac{\partial \psi_{2/4}}{\partial y} \ + \ a_3\ x^3\ \psi_{6/4} \ + \ a_4\ x^4\ \psi_{3/4} \ + \ a_5\ x^5\ \psi_0 \ + \ b_{1,0,1}\ x\,y\ \psi_{5/4} \\
&\qquad + \ b_{0,2,1}\ r^2\,y\ \psi_{4/4} \ + \ b_{1,2,0}\ x\,r^2\ \psi_{4/4} \ + \ b_{0,4,0}\ r^4\ \psi_{3/4} \ + \ b_{0,0,3}\ y^3\ \psi_{2/4} \\
&\qquad + \ b_{2,0,1}\ x^2\,y\,\psi_{2/4} \ + \ b_{1,0,2}\ x\,y^2\ \psi_{2/4} \ + \ b_{0,2,2}\ r^2\,y^2\ \psi_{1/4} \ + \ b_{1,2,1}\ x\,r^2\,y\ \psi_{1/4} \\
&\qquad + \ b_{2,2,0}\ x^2\,r^2\ \psi_{1/4} \ + \ b_{0,4,1}\ r^4\,y\ \psi_0 \ + \ b_{1,4,0}\ x\,r^4\ \psi_0 \\
&\qquad + \ \frac{X_0^2}{2\,\mu_2\,Y_0^2}\ H_{0,r,\gamma}\ \psi_{3/4} \ + \ \frac{X_0}{\mu_2\,Y_0^2}\ \left(\ r\ \frac{\partial^2}{\partial x\,\partial r} \ + \ \frac{\partial}{\partial x}\ \right)\ \psi_{2/4} \ - \ \frac{r^2}{2\,\mu_2\,Y_0^2}\ \frac{\partial^2}{\partial x^2}\ \psi_{1/4} \\
&\qquad + \ \frac{1}{\mu_2\,Y_0^2}\ \Bigg[\ \left(X_0\ \sin\,\gamma\ \frac{\partial}{\partial r} \ + \ \frac{X_0}{r}\ \cos\,\gamma\ \frac{\partial}{\partial \gamma}\right)\left(\frac{1}{\sin\,\theta}\ \frac{\partial}{\partial \phi} \ - \ \cot\,\theta\ \frac{\partial}{\partial \gamma}\right) \\
&\qquad\qquad\qquad\qquad + \ \ \left(X_0\ \ \cos\,\gamma\ \frac{\partial}{\partial r} \ - \ \frac{X_0}{r}\ \ \sin\,\gamma\ \frac{\partial}{\partial \gamma}\right)\frac{\partial}{\partial \theta}\ \Bigg]\ \psi_{1/4} \\
&\qquad + \ \frac{X_0}{\mu_2\,Y_0^2}\ \left(\ x \ - \ \frac{X_0\,y}{Y_0}\right)\ \left(-\ \frac{\partial^2}{\partial r^2} \ - \ \frac{1}{r}\ \frac{\partial}{\partial r} \ + \ \frac{1}{r^2}\ L_{z'}^2\ \right)\ \psi_0 \\
&\qquad + \ \frac{1}{\mu_2\,Y_0^2}\ \Bigg[\ \left(-\ r\ \ \sin\,\gamma\ \frac{\partial}{\partial x}\ \right)\ \left(\ \frac{1}{\sin\,\theta}\ \frac{\partial}{\partial \phi} \ - \ \cot\,\theta\ \frac{\partial}{\partial \gamma}\ \right) \\
&\qquad\qquad\qquad\qquad\qquad\qquad - \ r\ \ \cos\,\gamma\ \ \frac{\partial^2}{\partial x\,\partial \theta}\ \Bigg]\ \psi_0 \\
&= \quad \mathcal{E}_{15/4}\ \psi_0 \ + \ \mathcal{E}_{14/4}\ \psi_{1/4} \ + \ \mathcal{E}_{13/4}\ \psi_{2/4} \ + \ \mathcal{E}_{12/4}\ \psi_{3/4}.
\end{aligned}
$$

Order $\epsilon^{16/4}$

$$[H_{0,x} - \mathcal{E}_{6/4}]\,\psi_{10/4} \;+\; [H_{0,r,\gamma} - \mathcal{E}_{8/4}]\,\psi_{8/4} \;+\; [H_{0,y} - \mathcal{E}_{10/4}]\,\psi_{6/4}$$

$$- \;\frac{1}{2\,\mu_2\,Y_0}\,\frac{\partial \psi_{3/4}}{\partial y} \;+\; a_3\,x^3\,\psi_{7/4} \;+\; a_4\,x^4\,\psi_{4/4} \;+\; a_5\,x^5\,\psi_{1/4} \;+\; b_{1,0,1}\,x\,y\,\psi_{6/4}$$

$$+ \;b_{0,2,1}\,r^2\,y\,\psi_{5/4} \;+\; b_{1,2,0}\,x\,r^2\,\psi_{5/4} \;+\; b_{0,4,0}\,r^4\,\psi_{4/4} \;+\; b_{2,0,1}\,x^2\,y\,\psi_{3/4}$$

$$+ \;b_{0,0,3}\,y^3\,\psi_{3/4} \;+\; b_{1,0,2}\,x\,y^2\,\psi_{3/4} \;+\; b_{0,2,2}\,r^2\,y^2\,\psi_{2/4} \;+\; b_{1,2,1}\,x\,r^2\,y\,\psi_{2/4}$$

$$+ \;b_{2,2,0}\,x^2\,r^2\,\psi_{2/4} \;+\; b_{0,4,1}\,r^4\,y\,\psi_{1/4} \;+\; b_{1,4,0}\,x\,r^4\,\psi_{1/4} \;+\; b_{0,6,0}\,r^6\,\psi_0$$

$$+ \;b_{0,0,4}\,y^4\,\psi_0 \;+\; b_{1,0,3}\,x\,y^3\,\psi_0 \;+\; b_{2,0,2}\,x^2\,y^2\,\psi_0 \;+\; b_{3,0,1}\,x^3\,y\,\psi_0$$

$$+ \;\frac{X_0^2}{2\,\mu_2\,Y_0^2}\,H_{0,r,\gamma}\,\psi_{4/4} \;+\; \frac{X_0}{\mu_2\,Y_0^2}\left(r\,\frac{\partial^2}{\partial x\,\partial r} + \frac{\partial}{\partial x}\right)\psi_{3/4} \;-\; \frac{r^2}{2\,\mu_2\,Y_0^2}\,\frac{\partial^2}{\partial x^2}\,\psi_{2/4}$$

$$+ \;\frac{1}{\mu_2\,Y_0^2}\Bigg[\left(X_0\,\sin\gamma\,\frac{\partial}{\partial r} \;+\; \frac{X_0}{r}\,\cos\gamma\,\frac{\partial}{\partial \gamma}\right)\left(\frac{1}{\sin\theta}\,\frac{\partial}{\partial \phi} \;-\; \cot\theta\,\frac{\partial}{\partial \gamma}\right)$$

$$+ \;\left(X_0\,\cos\gamma\,\frac{\partial}{\partial r} \;-\; \frac{X_0}{r}\,\sin\gamma\,\frac{\partial}{\partial \gamma}\right)\frac{\partial}{\partial \theta}\Bigg]\,\psi_{2/4}$$

$$+ \;\frac{X_0}{\mu_2\,Y_0^2}\left(x \;-\; \frac{X_0\,y}{Y_0}\right)H_{0,r,\gamma}\,\psi_{1/4}$$

$$+ \;\frac{1}{\mu_2\,Y_0^2}\Bigg[\left(-\,r\,\sin\gamma\,\frac{\partial}{\partial x}\right)\left(\frac{1}{\sin\theta}\,\frac{\partial}{\partial \phi} \;-\; \cot\theta\,\frac{\partial}{\partial \gamma}\right)$$

$$-\,r\,\cos\gamma\,\frac{\partial^2}{\partial x\,\partial \theta}\Bigg]\,\psi_{1/4}$$

$$+ \;\Bigg[-\,\frac{2\,X_0\,y}{\mu_2\,Y_0^3}\left(\frac{\partial}{\partial x} \;+\; r\,\frac{\partial^2}{\partial x\,\partial r}\right)$$

$$+ \;\frac{1}{2\,\mu_2\,Y_0^2}\left(2\,x\,r\,\frac{\partial^2}{\partial x\,\partial r} \;+\; r\,\frac{\partial}{\partial r} \;+\; 2\,x\,\frac{\partial}{\partial x} \;-\; L_{z'}^2\right)\Bigg]\,\psi_0$$

$$+ \;\frac{j(j+1)}{2\,\mu_2\,Y_0^2}\,\psi_0 \;+\; \frac{1}{\mu_2\,Y_0^2}\,y\,\frac{\partial \psi_0}{\partial y} \;+\; D(0)\,\psi_0$$

$$= \;\mathcal{E}_{16/4}\,\psi_0 \;+\; \mathcal{E}_{15/4}\,\psi_{1/4} \;+\; \mathcal{E}_{14/4}\,\psi_{2/4} \;+\; \mathcal{E}_{13/4}\,\psi_{3/4} \;+\; \mathcal{E}_{12/4}\,\psi_{4/4}.$$

3.1 The Complete Asymptotic Expansion

We now prove the existence of a complete expansion in powers of $\epsilon^{1/4}$ for the quasienergies and the corresponding quasimodes under suitable hypotheses. The following proposition completes the proof of Theorem 2.1.

Proposition 3.1 *We assume the potential energy surface (2.4) is smooth, with Taylor series given by (2.5) and (2.6). Then, the eigenvalue problem for (3.1) can be solved by formal asymptotic expansions of the form*

$$\begin{aligned} \mathcal{E} &= \sum_{l=0}^{N} \epsilon^{l/4}\, \mathcal{E}_{l/4} \;+\; O(\epsilon^{(N+1)/4}), \\ \psi(x,\, r,\, y,\, \theta,\, \phi,\, \gamma) &= \sum_{l=0}^{N} \epsilon^{l/4}\, \psi_{l/4}(x,\, r,\, y,\, \theta,\, \phi,\, \gamma) \;+\; O(\epsilon^{(N+1)/4}), \end{aligned}$$

for any $N \in \mathbb{N}$.

Proof

Keeping the original variables (X, R, Y), we first make use of the invariant subspace $\mathcal{L}$ generated by the basis $\{|k\rangle\}_{k=-j,\cdots,j}$ of eigenvectors of $L_{z'}$, where we have dropped the fixed parameters j and j_z from the notation. In this basis, the operator $J^2 - 2L\cdot J + L^2$ can be represented by a matrix. Let $\mathbb{I}$ denote the identity matrix, A denote the matrix representation of $i\,\frac{\sin(\gamma)}{\sin(\theta)}\left(-i\,\frac{\partial}{\partial\phi} + i\,\cos(\theta)\frac{\partial}{\partial\gamma}\right) + \cos(\gamma)\frac{\partial}{\partial\theta}$, and B denote the matrix representation of $i\,\frac{\cos(\gamma)}{\sin(\theta)}\left(-i\,\frac{\partial}{\partial\phi} + i\,\cos(\theta)\frac{\partial}{\partial\gamma}\right) + \sin(\gamma)\frac{\partial}{\partial\theta}$. Note that these angular differential operators can be written as linear combinations of L'_+ and L'_-, which ensures that they leave $\mathcal{L}$ invariant.

With these definitions, we can write

$$\begin{aligned} &J^2 - 2L\cdot J + L^2 \\ = &\left(j(j+1) + \left(-R^2\frac{\partial^2}{\partial X^2} + 2XR\frac{\partial^2}{\partial RX} - X^2\frac{\partial^2}{\partial R^2} + \left(R - \frac{X^2}{R}\right)\frac{\partial}{\partial R} + 2X\frac{\partial}{\partial X}\right)\right)\mathbb{I} \\ &+ \left(\frac{X^2}{R^2} - 1\right)L_{z'}^2 - 2\left(R\frac{\partial}{\partial X} - X\frac{\partial}{\partial R}\right)A - 2\frac{X}{R}B. \end{aligned}$$

Then, going to the rescaled variables and dropping the symbol $\mathbb{I}$, the differential operator (3.1) takes the form

$$-\,\frac{\epsilon^{6/4}}{2\,\mu_1(\epsilon)}\,\frac{\partial^2}{\partial x^2} \;-\; \frac{\epsilon^{8/4}}{2\,\mu_1(\epsilon)}\left(\frac{\partial^2}{\partial r^2} \;+\; \frac{1}{r}\,\frac{\partial}{\partial r} \;-\; \frac{1}{r^2}\,L_{z'}^2\right) \;-\; \frac{\epsilon^{10/4}}{2\,\mu_2(\epsilon)}\,\frac{\partial^2}{\partial y^2}$$

$$
\begin{aligned}
&-\ \frac{\epsilon^{13/4}}{\mu_2(\epsilon)\,(Y_0+\epsilon^{3/4}y)}\ \frac{\partial}{\partial y}\ -\ \frac{\epsilon^{12/4}(X_0+\epsilon^{3/4}x)^2}{2\ \mu_2(\epsilon)\,(Y_0+\epsilon^{3/4}y)^2}\ \left\{\frac{\partial^2}{\partial r^2}+\frac{1}{r}\frac{\partial}{\partial r}-\frac{1}{r^2}\ L_{z'}^2\right\}\\
&+\ \frac{\epsilon^{13/4}(X_0+\epsilon^{3/4}x)}{\mu_2(\epsilon)\,(Y_0+\epsilon^{3/4}y)^2}\ \left\{r\frac{\partial^2}{\partial x\partial r}+\frac{\partial}{\partial x}\right\}\\
&+\ \frac{\epsilon^{14/4}(X_0+\epsilon^{3/4}x)}{\mu_2(\epsilon)\,(Y_0+\epsilon^{3/4}y)^2}\ \left\{\frac{\partial}{\partial r}\ A\ -\frac{1}{r}\ B\right\}-\ \frac{\epsilon^{14/4}}{2\ \mu_2(\epsilon)\,(Y_0+\epsilon^{3/4}y)^2}\ \left\{r^2\frac{\partial^2}{\partial x^2}\right\}\\
&-\ \frac{\epsilon^{15/4}}{\mu_2(\epsilon)\,(Y_0+\epsilon^{3/4}y)^2}\ \left\{r\frac{\partial}{\partial x}\ A\right\}+\ \frac{\epsilon^{16/4}}{2\,\mu_2(\epsilon)\,(Y_0+\epsilon^{3/4}y)^2}\ \left\{j(j+1)+r\frac{\partial}{\partial r}-L_{z'}^2\ \right\}\\
&\qquad\qquad +\ \ a_0\ +\ \sum_{j=2}^{\infty}\ a_j\ \epsilon^{3j/4}\ x^j\ +\ \sum_{\substack{j+k+l\geq 2\\ k+l\geq 1\\ k\ \text{even}}}\ b_{j,\,k,\,l}\ \epsilon^{1+\frac{3(j+l)+2k}{4}}\ x^j\, r^k\, y^l.
\end{aligned}
$$

We get a matrix valued differential operator given as a formal infinite series in powers of $\epsilon^{1/4}$ by expanding the reduced masses $\mu_j(\epsilon)$ and the denominators $(Y_0+\epsilon^{3/4})$ and $(Y_0+\epsilon^{3/4})^2$. Observe that in each term of the resulting expansion, the differential operators are at most of order two.

The r dependence of these operators is explicit, which will allow us to check that that the factors $1/r$ and $1/r^2$ do not cause divergences in the expressions that we encounter below. The measure in the r variable is $r\,dr$, so the only term that might yield a vector not in L^2 is the $L_{z'}/r^2$. In the eigenspace where $L_{z'}$ multiplies by zero, there is no problem. In the eigenspaces where $L_{z'}$ multiplies by something non-zero, the wave functions contain factors of r, so again, there is no problem.

We introduce the notation

$$
\Psi_{l/4}(x,r,y)\ \ =\ \ \sum_{k=-j}^{j}\psi_{l/4}(x,r,y,k)\,|k\rangle\ \ \equiv\ \ \begin{pmatrix}\psi_{l/4}(x,r,y,-j)\\ \psi_{l/4}(x,r,y,-j+1)\\ \vdots\\ \psi_{l/4}(x,r,y,j)\end{pmatrix}.
$$

We have already explicitly presented perturbation theory through order $\epsilon^{l/4}$ for $l\leq 11$. The equation we must solve at order $\epsilon^{l/4}$ with $l\geq 12$ now can be expressed as

$$
\begin{aligned}
&(H_{0,x}-\mathcal{E}_{6/4})\,\Psi_{(l-6)/4}\ +\ (H_{0,r,\gamma}-\mathcal{E}_{8/4})\,\Psi_{(l-8)/4}\ +\ (H_{0,y}-\mathcal{E}_{10/4})\,\Psi_{(l-10)/4}\\
&+a_3\,x^3\,\Psi_{(l-9)/4}\ +\ b_{1,0,1}\,x\,y\,\Psi_{(l-10)/4}\ +\ \sum_{q=11}^{l}\,D_q\,\Psi_{(l-q)/4}
\end{aligned}
$$

$$= \ \mathcal{E}_{l/4}\,\Psi_{0/4} \ + \ \cdots \ + \ \mathcal{E}_{12/4}\,\Psi_{(l-12)/4}, \tag{3.8}$$

where the symbols D_q denote at most second order differential operators in x, r, y with matrix valued coefficients whose entries are polynomials in these variables divided by r^p, with $p = 0, 1, 2$. We note also that $H_{0,r,\gamma}$ is now matrix–valued, because of the centrifugal term $L_{z'}^2/r^2$, whereas $H_{0,x}$ and $H_{0,y}$ are scalar differential operators multiplied by the identity matrix.

The point of this decomposition is to separate the vectors $\Psi_{q/4}$ of order less than or equal to $(l-11)/4$ from those of order $(l-10)/4$ to $(l-6)/4$.

Let P_x, P_y and $P_{r,\gamma}$ be the orthogonal projectors on the eigenstates $\Phi_1(x)$, $\Phi_3(y)$ and on the subspace $Z_0 = \text{span}\{\Phi_2(r,|k|)\ |k\rangle\}_{k\in K}$, respectively. We abuse notation and use the same symbols to denote the corresponding projectors when considered on $L^2(\mathbb{R}_x, dx) \otimes L^2(\mathbb{R}_r^+, rdr) \otimes L^2(\mathbb{R}_y, dy) \otimes \mathcal{L}$. Note that these operators commute with one another and that the following identity holds for any $q \in \mathbb{N}$:

$$P_x\, x^{2q+1} \ = \ P_x\, x^{2q+1}\, P_x^{\perp}, \qquad \text{where} \qquad P_x^{\perp} = \mathbb{I} - P_x. \tag{3.9}$$

Also, we have constructed $\Psi_{l/4}$ so that

$$\Psi_0 \ = \ P_x\, P_{r,\gamma}\, P_y\, \Psi_0 \quad \text{and} \quad P_x\, P_{r,\gamma}\, P_y\, \Psi_{l/4} \ = \ 0, \qquad \text{for all} \quad l \geq 1. \tag{3.10}$$

Hence, for $l \geq 1$,

$$\Psi_{l/4} \ = \ P_x^{\perp}\, \Psi_{l/4} + P_x\, P_{r,\gamma}^{\perp}\, \Psi_{l/4} \ + \ P_x\, P_{r,\gamma}\, P_y^{\perp}\, \Psi_{l/4}. \tag{3.11}$$

In terms of the quantities introduced in the explicit computations of the lower orders, we have in particular

$$\begin{aligned} P_x\, \Psi_{l/4} \ &= \ \sum_{k=-l}^{l} \Phi_1(x)\ f_{l/4}(r,y,k)\ |k\rangle \qquad (3.12) \\ P_x\, P_{r,\gamma}\, \Psi_{l/4} \ &= \ \sum_{k\in K} \Phi_1(x)\ \Phi_2(r,|k|)\ g_{l/4}(y,k)\ |k\rangle \\ P_x\, P_{r,\gamma}\, P_y\, \Psi_0 \ &= \ \sum_{k\in K} \Phi_1(x)\ \Phi_2(r,|k|)\ \Phi_3(y)\, c_{k,0}\ |k\rangle, \end{aligned}$$

where $c_{k,0} \in \mathbb{C}$ and $\sum_{k\in K} |c_{k,0}|^2 = 1$. Note that by virtue of (3.10),

$$g_{l/4}(y,k) \ = \ P_y^{\perp}\, g_{l/4}(y,k), \quad \text{for any } k \in K \text{ and any } l > 0. \tag{3.13}$$

We solve (3.8) by two independent steps. The first consists of determining the vectors $\Psi_{l/4}$ for any set of coefficients $\{c_{0,k}\}_{k\in K}$, and the other consists of solving an eigenvalue equation for $\mathcal{E}_{j/4}$ in $\mathbb{C}^{\#(K)}$ which may reduce the set of free coeffcients $\{c_{0,k}\}_{k\in K}$. It is only when we construct the actual quasimode that we restrict the values of the coefficients $\{c_{0,k}\}_{k\in K}$ to those given by the determination of the the $\mathcal{E}_{l/4}$'s.

We now formulate our induction hypothesis for $l \geq 12$.

IH: After solving equation (3.8) through order $\epsilon^{(l-1)/4}$ for vectors satisfying (3.10), we have:

- The following vectors are determined completely in terms of the coefficients $\{c_{0,k}\}_{k\in K}$ and depend linearly on $\{c_{0,k}\}_{k\in K}$:

$$\begin{array}{ll} \Psi_{q/4}, & \text{for} \quad q = 0,\, 1,\, \cdots,\, l-11, \\ (\mathbb{I} - P_x P_{r,\gamma})\, \Psi_{(l-10)/4}, & \\ (\mathbb{I} - P_x\, P_{r,\gamma})\, \Psi_{(l-9)/4}, & \\ (\mathbb{I} - P_x)\, \Psi_{(l-8)/4}, & \text{and} \\ (\mathbb{I} - P_x - P_x^{\perp}\, P_{r,\gamma})\, \Psi_{(l-7)/4}. & \end{array} \tag{3.14}$$

- The x dependence of the vector $P_x^{\perp}\, P_{r,\gamma}\, \Psi_{(l-7)/4}$ is determined and has the form

$$P_x^{\perp}\, P_{r,\gamma}\, \Psi_{(l-7)/4} \;=\; P_x^{\perp}\, P_{r,\gamma}\, \Psi_{(l-7)/4}(\{g_{(l-10)/4}\}), \tag{3.15}$$

  with linear dependence on $\{g_{(l-10)/4}(y,k)\}_{k\in K}$, the set of functions $\{g_{(l-10)/4}\}$ entailing the unknown y dependence.

- There exist vector spaces $W_q \subseteq \mathbb{C}^{\#(K)}$ satisfying

$$\mathbb{C}^{\#(K)} = W_0 \supseteq W_1 \supseteq \cdots \supseteq W_{l-1} \tag{3.16}$$

  such that $\mathcal{E}_{q/4}$ is determined by an eigenvalue equation in W_q, for $q = 0, 1, \cdots, l-1$.

Our explicit computations show that these properties are satisfied for $l = 12$, with $W_q = \mathbb{C}^{\#(K)}$, for $q = 0, \cdots, 11$. We now show that the induction hypothesis holds at order $\epsilon^{l/4}$.

Using (3.9) and (3.10) and applying $P_x\, P_{r,\gamma} P_y$ to equation (3.8) yields

$$\mathcal{E}_{l/4}\, \Psi_0 \;=\; P_x\, P_{r,\gamma}\, P_y \left(a_3 x^3 P_x^{\perp} \Psi_{(l-9)/4} + b_{1,0,1} xy P_x^{\perp} \Psi_{(l-10)/4} + \sum_{q=11}^{l} D_q \Psi_{(l-q)/4} \right).$$

We note that for $s = 9$, 10, the vectors $P_x^\perp \Psi_{(l-s)/4} = P_x^\perp (\mathbb{I} - P_x P_{r,\gamma}) \Psi_{(l-s)/4}$ are completely determined by **IH**. By **IH** again, the right hand side depends linearly on the set $\{c_{0,k}\}_{k\in K}$. Expressing the equation in the basis $\{\Phi_1(x)\Phi_2(|k|, r)\Phi_3(y)\}_{k\in K}$ of Z_2, we get a finite dimensional eigenvalue equation. Restricting attention to the subspace $W_{l-1} \subseteq \mathbb{C}^{\#(K)}$ of free coefficients, we get an eigenvalue equation in W_{l-1} which we solve to yield $\mathcal{E}_{l/4}$ and the subspace $W_l \subseteq W_{l-1}$ of free coefficients.

We now turn to the computation of the vectors. Application of $P_x\, P_{r,\gamma}\, P_y^\perp$ to equation (3.8) yields

$$\begin{aligned} & P_x\, P_{r,\gamma}\, P_y^\perp\, \Psi_{(l-10)/4} & (3.17) \\ = \; - \; & (H_{0,y} - \mathcal{E}_{10/4})_r^{-1} P_x P_{r,\gamma} P_y^\perp \left(a_3 x^3 P_x^\perp \Psi_{(l-9)/4} + b_{1,0,1} xy P_x^\perp \Psi_{(l-10)/4} + \sum_{q=11}^{l} \tilde{D}_q \Psi_{(l-q)/4} \right) \end{aligned}$$

where $\tilde{D}_q = D_q - \mathcal{E}_{q/4}$. The right hand side is known by **IH**, and since $P_x\, P_{r,\gamma}\, P_y^\perp\, \Psi_{(l-10)/4} = P_x\, P_{r,\gamma}\, \Psi_{(l-10)/4}$, (see (3.12), (3.13)), (3.11) implies that $\Psi_{(l-10)/4}$ is fully determined up to the coefficients $\{c_{0,k}\}_{k\in K}$. Since the dependence of $P_x\, P_{r,\gamma}\, \Psi_{(l-10)/4}$ is linear in the previously determined quantities, we get by **IH** that $\Psi_{(l-10)/4}$ depends linearly in the coefficients $\{c_{0,k}\}_{k\in K}$. Hence, the vector $P_x^\perp\, P_{r,\gamma}\, \Psi_{(l-7)/4}\, (\{g_{(l-10)/4}\})$ in **IH** is, in turn, fully determined, and it depends linearly on the $\{c_{0,k}\}_{k\in K}$'s. Thus, the same is true for $(\mathbb{I} - P_x)\, \Psi_{(l-7)/4}$.

Application of $P_x\, P_{r,\gamma}^\perp$ to equation (3.8) yields

$$\begin{aligned} P_x\, P_{r,\gamma}^\perp\, \Psi_{(l-8)/4} \; = \; & -\, (H_{0,r,\gamma} - \mathcal{E}_{8/4})_r^{-1}\, P_x\, P_{r,\gamma}^\perp \quad \times & (3.18) \\ & \left((H_{0,y} - \mathcal{E}_{10/4})\Psi_{(l-8)/4} + a_3 x^3 P_x^\perp \Psi_{(l-9)/4} + b_{1,0,1} xy P_x^\perp \Psi_{(l-10)/4} + \sum_{q=11}^{l} \tilde{D}_q \Psi_{l-q} \right), \end{aligned}$$

where, by the same arguments, the right hand side is fully determined up to the coefficients $\{c_{0,k}\}_{k\in K}$, on which it depends linearly. Now, from **IH** and the identity

$$P_x\, \Psi_{(l-8)/4} \; = \; P_x\, P_{r,\gamma}\, \Psi_{(l-8)/4} \; + \; P_x\, P_{r,\gamma}^\perp\, \Psi_{(l-8)/4}$$

we see that $(\mathbb{I} - P_x P_{r,\gamma})\, \Psi_{(l-8)/4}$ is fully determined and depends linearly on the coefficients $\{c_{0,k}\}_{k\in K}$.

Finally, application of $P_x^\perp$ to equation (3.8) yields

$$\begin{aligned} P_x^\perp \Psi_{(l-6)/4} \; = \; & -\, (H_{0,x} - \mathcal{E}_{6/4})_r^{-1}\, P_x^\perp \Bigg((H_{0,r,\gamma} - \mathcal{E}_{8/4})\, P_x^\perp\, \Psi_{(l-8)/4} + & (3.19) \\ & (H_{0,y} - \mathcal{E}_{10/4})\, P_x^\perp\, \Psi_{(l-10)/4} \; + \; a_3 x^3 \Psi_{(l-9)/4} \; + \; b_{1,0,1} xy \Psi_{(l-10)/4} \; + \; \sum_{q=11}^{l} \tilde{D}_q\, \Psi_{l-q} \Bigg), \end{aligned}$$

where, this time, the right hand side is not fully determined since there is no projector $P_x^\perp$ acting on $\Psi_{(l-9)/4}$. However, at this step, $\Psi_{(l-10)/4}$ and $P_x^\perp \Psi_{(l-8)/4} = P_x^\perp (\mathbb{I} - P_x P_{r,\gamma})\Psi_{(l-8)/4}$ are fully determined and linear in the $\{c_{0,k}\}_{k\in K}$, so that from **IH** we see that the only undetermined part comes from

$$P_x\, P_{r,\gamma}\, \Psi_{(l-9)/4} \;=\; \sum_{k\in K} \Phi_1(x)\, \Phi_2(r, |k|)\, g_{(l-9)/4}(y,k)\, c_{k,0}\; |k\rangle.$$

We conclude that the x dependence of the vector $P_x^\perp\, \Psi_{(l-6)/4}$ is determined, and that the undetermined part of this vector depends on the set of functions $\{g_{(l-9)/4}(y,k)\}_{k\in K}$ purely linearly.

Thus, we have reproduced the all the requirements of the induction hypothesis, which ends the proof. ■

3.2 The Expansion Around a Local Minimum

We now describe the construction of quasimodes of arbitrarily high order under assumptions that are only local. This construction uses the formal expansions of Proposition 3.1 and the insertion of cutoff functions. The construction is quite similar to that given in [5], so we refrain from presenting all details.

Let $N \geq 0$ be fixed and set

$$\begin{aligned}
\Psi^{(N)}(x,r,y,\theta,\phi,\gamma) &= \sum_{l=0}^{N} \epsilon^{l/4}\; \psi_{l/4}(x,r,y,\theta,\phi,\gamma),\\
\mathcal{E}^{(N)} &= \sum_{l=0}^{N} \epsilon^{l/4}\; \mathcal{E}_{l/4}, \qquad\qquad (3.20)\\
V^{(N)}(X,Y,R) &= \sum_{l\le (N+1)/3} a_l (X-X_0)^l + \epsilon \sum_{\substack{j+k+l\ge 2\\ k+l\ge 1\\ k \text{ even}\\ 4+3(j+l)+2k\le N}} b_{j,\,k,\,l}(X-X_0)^j\, R^k\, (Y-Y_0)^l,
\end{aligned}$$

where the vectors $\psi_{l/4}$ and the scalars $\mathcal{E}_{l/4}$ are defined in Proposition 3.1.

Then we introduce a cutoff function. Let $\mathcal{F} : I\!\!R \to [0,1]$ be C^∞ and such that supp $\mathcal{F} \subset [-2,2]$ with $\mathcal{F}(t) = 1$ for $t \in [-1,1]$. We set

$$\mathcal{F}_\epsilon(X,R,Y) \;=\; \mathcal{F}((X-X_0)/\epsilon^{\delta_1})\; \mathcal{F}(R/\epsilon^{\delta_2})\; \mathcal{F}((Y-Y_0)/\epsilon^{\delta_3}),$$

where $0 < \delta_1 < 3/4$, $0 < \delta_2 < 1/2$ and $0 < \delta_3 < 3/4$.

The quasimode $\Psi_Q^{(N)}$ is defined as

$$\begin{aligned} & \Psi_Q^{(N)}(X, R, Y, \theta, \phi, \gamma) \qquad (3.21) \\ = \quad & \epsilon^{-5/4}\ \mathcal{F}_\epsilon(X, R, Y)\ \Psi^{(N)}((X-X_0)/\epsilon^{3/4}, R/\epsilon^{1/2}, (Y-Y_0)/\epsilon^{3/4}, \theta, \phi, \gamma). \end{aligned}$$

The factor of $\epsilon^{-5/4}$ in this expression ensures asymptotic normalization of the quasimode because of the Jacobian factor in the integral for the L^2 norm.

Proposition 3.2 *Let*

$$H(\epsilon) \;=\; -\,\frac{\epsilon^3}{2\,\mu_1(\epsilon)}\,\Delta_{(X_1,\,X_2,\,X_3)} \;-\; \frac{\epsilon^4}{2\,\mu_2(\epsilon)}\,\Delta_{(Y_1,\,Y_2,\,Y_3)} \;+\; V_1(X) \;+\; \epsilon\, V_2(X,\,R,\,Y),$$

satisfy the hypotheses of Proposition 3.1. Then, for any $N \in \mathbb{N}$, there exists a constant C_N, such that the vector (3.21) and the scalar (3.20) satisfy $\|\Psi_Q^{(N)}\| = 1 + O(\epsilon^{1/4})$ *and*

$$\frac{\left\|H(\epsilon)\Psi_Q^{(N)} - \mathcal{E}^{(N)}\Psi_Q^{(N)}\right\|}{\left\|\Psi_Q^{(N)}\right\|} \;\le\; C_N\ \epsilon^{(N+1)/4}, \qquad \textit{as}\ \ \epsilon \to 0.$$

Proof

We begin by computing the norm of $\Psi_Q^{(N)}$. The vectors $\psi_{l/4}$, for $l = 0, \cdots, N$, are given as a finite linear combinations of angular functions $|k, j_z, j\rangle$, $(k = -j, \cdots, j)$, multiplied by Gaussians in x, r, y, times polynomials in these variables. Thus, they all belong to L^2.

In particular, by our choices for ψ_0, we have

$$\begin{aligned} & \int |\epsilon^{-5/4}\,\psi_0((X-X_0)/\epsilon^{3/4}, R/\epsilon^{1/2}, (Y-Y_0)/\epsilon^{3/4}, \theta, \phi, \gamma)|^2\ R\,dR\,dX\,dY\,d\Omega \\ = \quad & \int |\psi_0(x, r, y, \theta, \phi, \gamma)|^2\ r\,dr\,dx\,dy\,d\Omega \\ = \quad & 1, \end{aligned}$$

where $d\Omega$ denotes the solid angle element in the angular variables. The norms of the other $\psi_{l/4}$ are similarly $O(1)$.

Hence $\|\Psi_Q^{(N)}\|^2 = \|\Psi^{(N)} + (\mathcal{F}_\epsilon^2 - 1)\Psi^{(N)}\|^2$, where,

$$\begin{aligned} & \left\|(1-\mathcal{F}_\epsilon^2)\,\Psi^{(N)}\right\|^2 \qquad (3.22) \\ \le \quad & \int_{\substack{|X-X_0| \ge \epsilon^{\delta_1} \\ R \ge \epsilon^{\delta_2} \\ |Y-Y_0| \ge \epsilon^{\delta_3}}} |\Psi^{(N)}((X-X_0)/\epsilon^{3/4}, R/\epsilon^{1/2}, (Y-Y_0)/\epsilon^{3/4}, \theta, \phi, \gamma)|^2\,R\,dR\,dX\,dY\,d\Omega. \end{aligned}$$

The choice of exponents δ_j and the exponential decay of $\Psi^{(N)}$ imply that (3.22) is of order ϵ^∞, and we finally see that

$$\left\|\Psi_Q^{(N)}\right\| \;=\; 1 \;+\; O(\epsilon^{1/4}).$$

By construction, there exist $C > 0$ and $D > 0$, independent of ϵ, such that

$$\mathcal{R}^{(N)}(X,R,Y) \;=\; V_1(X) \;+\; \epsilon\, V_2(X,R,Y) \;-\; V^{(N)}(X,Y,R)$$

satisfies

$$|\mathcal{R}^{(N)}(X,R,Y)| \leq C(|X-X_0|^{(N+1)/3} + \epsilon|X-X_0|^a R^b |Y-Y_0|^c), \tag{3.23}$$

where $4+3(a+c)+2c \geq N+1$, if $(|X-X_0|+R+|Y-Y_0|) < D$. Consider now

$$\begin{aligned} V\,\Psi_Q^{(N)} \;&=\; V^{(N)}\,\Psi_Q^{(N)} \;+\; \mathcal{R}^{(N)}\,\Psi_Q^{(N)} \\ &=\; V^{(N)}\,\mathcal{F}_\epsilon\,\Psi^{(N)} \;+\; \mathcal{R}^{(N)}\,\mathcal{F}_\epsilon\,\Psi^{(N)}. \end{aligned}$$

Due to the support conditions imposed by the cutoff, we can estimate $\mathcal{F}_\epsilon\mathcal{R}^{(N)}$ by means of (3.23), and, after passing to the rescaled variables x, r, y, we obtain

$$\mathcal{F}_\epsilon(X,R,Y)\,|\mathcal{R}^{(N)}(X,R,Y)| \;\leq\; \mathcal{F}_\epsilon(X,R,Y)\,\epsilon^{(N+1)/4}\,C\,\left(|x|^{(N+1)/3} + |x|^a r^b |y|^c\right).$$

Once again using the Gaussian decay of $\Psi^{(N)}$, we finally get the L^2 estimate

$$\left\|\mathcal{R}^{(N)}\,\Psi_Q^{(N)}\right\| \;=\; O\left(\epsilon^{(N+1)/4}\right).$$

We now have estimated everything except the terms in which the kinetic energy acts on the cutoffs. First note that derivatives with respect to angular variables do not affect the cutoffs. Next, by the Leibniz formula, the first and second derivatives with respect to $x,\ y$, or r acting on $\mathcal{F}_\epsilon\,\Psi^{(N)}$ yield supplementary terms given by first and second derivatives of $\mathcal{F}_\epsilon$ multiplied by $\Psi^{(N)}$ or first derivatives of $\Psi^{(N)}$. By construction of the cutoff, the successive derivatives of $\mathcal{F}_\epsilon$ are supported away of the origin in at least one of the variables $x,\ y$, or r. Since $\Psi^{(N)}$ and its derivatives are Gaussian times polynomials in these variables, these supplementary terms are all of order ϵ^∞.

Finally, taking into account the formal expansions of Theorem 3.1, and the definition

$$H^{(N)}(\epsilon) \;=\; -\,\frac{\epsilon^3}{2\,\mu_1(\epsilon)}\,\Delta_{(X_1,\,X_2,\,X_3)} \;-\; \frac{\epsilon^4}{2\,\mu_2(\epsilon)}\,\Delta_{(Y_1,\,Y_2,\,Y_3)} \;+\; V^{(N)}(X,\,R,\,Y,),$$

we get the L^2 norm estimate

$$\begin{aligned} & \left\| H(\epsilon)\Psi_Q^{(N)} - \mathcal{E}^{(N)}\Psi_Q^{(N)} \right\| \\ = \ & \left\| H^{(N)}(\epsilon)\Psi_Q^{(N)} - \mathcal{E}^{(N)}\Psi_Q^{(N)} \right\| \ + \ O\left(\epsilon^{(N+1)/4}\right) \\ = \ & \left\| \mathcal{F}_\epsilon(H^{(N)}(\epsilon)\Psi^{(N)} - \mathcal{E}^{(N)}\Psi^{(N)}) \right\| \ + \ O\left(\epsilon^{(N+1)/4}\right) \ + \ O\left(\epsilon^{\infty}\right) \\ = \ & O\left(\epsilon^{(N+1)/4}\right). \end{aligned}$$

■

4 Inclusion of the Electrons

In this section we show that including the quantum mechanical treatment of the electrons does not change the expression for the energy up to an error of order ϵ^3.

We decompose the Hamiltonian for all the particles in the molecule as the sum of the nuclear kinetic energy plus a self-adjoint electron Hamiltonian $h_1(Y,\, \theta,\, \phi,\, R,\, \gamma,\, X)$. The electron Hamiltonian depends parametrically on $(Y,\, \theta,\, \phi,\, R,\, \gamma,\, X)$ and acts on functions of all of the electron variables, that we describe jointly with the single symbol Z. To avoid questions about Berry phases, we assume $h_1(Y,\, \theta,\, \phi,\, R,\, \gamma,\, X)$ commutes with complex conjugation, *i.e.*, it is a real symmetric operator.

Because of rotational symmetries, the electron Hamiltonian can be written as

$$h_1(Y,\, \theta,\, \phi,\, R,\, \gamma,\, X) \ = \ U(\theta,\, \phi,\, \gamma)\; h_2(X,\, R,\, Y)\; U(\theta,\, \phi,\, \gamma)^{-1},$$

where $U(\theta,\, \phi,\, \gamma)$ is unitary on the electron Hilbert space and depends smoothly on θ, ϕ, and γ. As a consequence, discrete eigenvalues of $h_1(Y,\, \theta,\, \phi,\, R,\, \gamma,\, X)$ do not depend on θ, ϕ, or γ.

We assume that the resolvent of $h_2(X,\, R,\, Y)$ depends smoothly on $(X,\, R,\, Y)$. As a result, all discrete eigenvalues of $h_1(Y,\, \theta,\, \phi,\, R,\, \gamma,\, X)$ depend smoothly on the nuclear configurations.

We assume further that the ground state eigenvalue $V(X,\, R,\, Y)$ of $h(Y,\, \theta,\, \phi,\, R,\, \gamma,\, X)$ is discrete and non-degenerate for each fixed value of $(Y,\, \theta,\, \phi,\, R,\, \gamma,\, X)$. We also assume that $V(X,\, R,\, Y)$ has a global minimum at $(X_0,\, 0,\, Y_0)$ with a strictly positive Hessian at that minimum. To ensure that we are approximating discrete eigenvalues for the full molecular Hamiltonian, we assume that the $V(X_0,\, 0,\, Y_0)$ is strictly below the bottom of the spectrum of $h_2(X,\, R,\, Y)$ for all $(X,\, R,\, Y)$ outside a small neighborhood of $(X_0,\, 0,\, Y_0)$.

We now introduce ϵ–dependence in h_2, and hence h_1. We choose functions $V_1(X)$ and $V_2(X,\, R,\, Y)$ that satisfy

$$V(X,\, R,\, Y) \;=\; V_1(X) \;+\; \epsilon_0\, V_2(X,\, R,\, Y)$$

and the restrictions imposed after expression (2.4). Here ϵ_0 is a fixed value of ϵ that we take to be the fourth root of the electron mass divided by the carbon C^{12} nuclear mass. We then define $h(\epsilon,\, Y,\, \theta,\, \phi,\, R,\, \gamma,\, X)$ by replacing $V(X,\, R,\, Y)$ by $V_1(X) + \epsilon\, V_2(X,\, R,\, Y)$ in the spectral decomposition of $h_1(Y,\, \theta,\, \phi,\, R,\, \gamma,\, X)$. Thus, we only introduce ϵ–dependence in this single eigenvalue and alter none of the eigenfunctions.

Remark To minimize technicalities, we have made assumptions for all $(X,\, R,\, Y)$. At the expense of inserting cut off functions, our assumptions need only be imposed for $(X,\, R,\, Y)$ in a neighborhood of $(X_0,\, 0,\, Y_0)$.

We shall write down an explicit quasimode with an $O(\epsilon^{12/4})$ energy error for the Schrödinger operator

$$H(\epsilon) \;=\; -\,\frac{\epsilon^3}{2\mu_1(\epsilon)}\,\Delta_{(X_1,X_2,X_3)} \;-\; \frac{\epsilon^4}{2\mu_2(\epsilon)}\,\Delta_{(Y_1,Y_2,Y_3)} \;+\; h(\epsilon,\, X_1,\, X_2,\, X_3,\, Y_1,\, Y_2,\, Y_3),$$

rewritten in terms of the variables $(Y,\, \theta,\, \phi,\, R,\, \gamma,\, X,\, Z)$.

The quasienergy will be

$$\mathcal{E}(\epsilon) \;=\; \mathcal{E}_0 \;+\; \epsilon^{6/4}\,\mathcal{E}_{6/4} \;+\; \epsilon^{8/4}\,\mathcal{E}_{8/4} \;+\; \epsilon^{10/4}\,\mathcal{E}_{10/4}, \tag{4.1}$$

but the quasimode will be somewhat complicated.

To specify the quasimode, we first let $\chi(Y,\, \theta,\, \phi,\, R,\, \gamma,\, X,\, Z)$ denote a normalized real ground state eigenfunction of $h(\epsilon,\, Y,\, \theta,\, \phi,\, R,\, \gamma,\, X)$ that depends continuously on its variables. Next, we let

$$\zeta(\epsilon,\, Y,\, \theta,\, \phi,\, R,\, \gamma,\, X) \;=\; \epsilon^{-5/4}\,\sum_{l=0}^{5}\,\epsilon^{l/4}\,\psi_{l/4}\left(\frac{X-X_0}{\epsilon^{3/4}},\, \frac{R}{\epsilon^{1/2}},\, \frac{Y-Y_0}{\epsilon^{3/4}},\, \theta,\, \phi,\, \gamma\right),$$

where the $\psi_{l/4}$ are the wave functions from Section 3 with $g_{2/4}(y,\, \pm\lambda) = g_{3/4}(y,\, \pm\lambda) = f_{4/4}(r,\, y,\, k) = f_{5/4}(r,\, y,\, k) = 0$. Note that when $\lambda = 0$ there is one linearly independent choice for ζ. When $\lambda > 0$, we have two linearly independent choices corresponding to $k = \pm\lambda$.

The quasimode is

$$
\begin{aligned}
&\Psi(\epsilon,\, Y,\, \theta,\, \phi,\, R,\, \gamma,\, X,\, Z)\\
=\quad & \mathcal{F}_\epsilon(X,\, R,\, Y)\, \zeta(\epsilon,\, Y,\, \theta,\, \phi,\, R,\, \gamma,\, X)\, \chi(Y,\, \theta,\, \phi,\, R,\, \gamma,\, X,\, Z)\\
&+\quad \frac{\epsilon^3}{2\,\mu_1}\, \mathcal{F}_\epsilon(X,\, R,\, Y)\, \Big[h(\epsilon,\, Y,\, \theta,\, \phi,\, R,\, \gamma,\, X)\, -\, V(\epsilon,\, X,\, R,\, Y) \Big]_r^{-1} \qquad (4.2)\\
&\qquad\times\quad \bigg(\frac{\partial\zeta}{\partial X}(\epsilon,\, Y,\, \theta,\, \phi,\, R,\, \gamma,\, X)\, \frac{\partial\chi}{\partial X}(Y,\, \theta,\, \phi,\, R,\, \gamma,\, X,\, Z)\\
&\qquad\qquad +\quad \frac{\partial\zeta}{\partial R}(\epsilon,\, Y,\, \theta,\, \phi,\, R,\, \gamma,\, X)\, \frac{\partial\chi}{\partial R}(Y,\, \theta,\, \phi,\, R,\, \gamma,\, X,\, Z) \bigg).
\end{aligned}
$$

Theorem 4.1 *There exists a constant C, such that the function $\Psi(\epsilon)$ given by (4.2) and quasienergy $\mathcal{E}(\epsilon)$ given by (4.1) satisfy*

$$\|\, \Psi(\epsilon)\, \| \;=\; 1 \;+\; O\left(\epsilon^{1/2}\right)$$

and

$$\left\| \Big(H(\epsilon)\, -\, \mathcal{E}(\epsilon) \Big)\, \Psi(\epsilon,\, \cdot) \right\| \;\leq\; C\, \epsilon^3 \qquad (4.3)$$

Proof The function $\Psi(\epsilon,\, \cdot)$ equals the normalized vector $\psi_0\, \chi$ plus terms that are orthogonal to $\psi_0\, \chi$. Since the largest of these orthogonal terms is $\epsilon^{1/4}\, \psi_{1/4}\, \chi$, we see that $\Psi(\epsilon)$ has norm $1 + O(\epsilon^{1/2})$.

To prove the second estimate of the theorem, we begin by noting that the electronic eigenfunction χ has the form

$$\chi(Y,\, \theta,\, \phi,\, R,\, \gamma,\, X,\, Z) \;=\; U(\theta,\, \phi,\, \gamma)\; \chi_0(Y,\, R,\, X,\, Z),$$

where $U(\theta,\, \phi,\, \gamma)$ is unitary.

We next compute

$$\Big(H(\epsilon)\, -\, \mathcal{E}(\epsilon) \Big)\, \mathcal{F}_\epsilon(X,\, R,\, Y)\, \zeta(\epsilon,\, \cdot)\, \chi(\cdot), \qquad (4.4)$$

where $H(\epsilon)$ is decomposed as

$$
\begin{aligned}
H(\epsilon) \quad = \quad & -\, \frac{\epsilon^3}{2\mu_1(\epsilon)}\, \Delta_{(X_1, X_2, X_3)} \;-\; \frac{\epsilon^4}{2\mu_2(\epsilon)}\, \Delta_{(Y_1, Y_2, Y_3)}\\
& +\quad \Big[h(\epsilon,\, X_1,\, X_2,\, X_3,\, Y_1,\, Y_2,\, Y_3) \;-\; V_1(X) \;-\; \epsilon\, V_2(X,\, R,\, Y) \Big]\\
& +\quad V_1(X) \;+\; \epsilon\, V_2(X,\, R,\, Y),
\end{aligned}
$$

with the two final terms expanded in their Taylor series of appropriate orders. We write the resulting expression in the variables $(Y,\, \theta,\, \phi,\, R,\, \gamma,\, X,\, Z)$. When the all the derivatives in $H(\epsilon)$ act on ζ, all terms that are larger than order ϵ^3 cancel because of Taylor series estimates and the choices of the $\psi_{l/4}$. When all the derivatives act on χ, all terms are $O(\epsilon^3)$ or smaller because χ is smooth and the cutoffs are zero the singularity at $Y=0$. When any derivatives act on $\mathcal{F}_\epsilon$, we obtain terms of order $O(\epsilon^q)$, for any q, due to the rapid fall off of the functions in ζ. The term that arises from $[h(\epsilon) - V_1 - \epsilon\, V_2]$ yields zero because it acts only on the χ.

The remaining terms in (4.4) contain terms in which a partial derivative acts on ζ and the same partial derivative acts on χ. All of these terms are $O(\epsilon^3)$ or smaller, except for

$$\begin{aligned} & \frac{\partial \zeta}{\partial X}(\epsilon,\, Y,\, \theta,\, \phi,\, R,\, \gamma,\, X)\, \frac{\partial \chi}{\partial X}(Y,\, \theta,\, \phi,\, R,\, \gamma,\, X,\, Z) \\ + \; & \frac{\partial \zeta}{\partial R}(\epsilon,\, Y,\, \theta,\, \phi,\, R,\, \gamma,\, X)\, \frac{\partial \chi}{\partial R}(Y,\, \theta,\, \phi,\, R,\, \gamma,\, X,\, Z). \end{aligned} \tag{4.5}$$

Thus, (4.4) yields (4.5) plus $O(\epsilon^3)$. However, when the $[h(\epsilon) - V_1 - \epsilon\, V_2]$ acts on the second term in (4.2), the terms that arise from (4.5) cancel, leaving us with $O(\epsilon^3)$ errors plus the kinetic energy and potential terms acting on the second term in (4.1). Because of the cutoff, the potential terms yield bounded operators times $O(\epsilon^3)$ terms. When the kinetic energy acts on these terms, we obtain terms of order $\epsilon^{9/2}$ or smaller, since everything is smooth, and the largest terms come from ϵ^6 and two X–derivatives acting on ζ.

Note that when computing the norm in (4.3), it is essential that χ be orthogonal to $\dfrac{\partial \chi}{\partial X}$ and $\dfrac{\partial \chi}{\partial R}$, or cross terms would yield terms of order greater than ϵ^3. This orthogonality is guaranteed by our hypothesis that the electron Hamiltonian $h(\epsilon,\, \cdot\,)$ be real symmetric and that we choose χ to be real. ■

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