A Mathematical Theory for Vibrational Levels Associated with Hydrogen Bonds
I : The Symmetric Case

George A. Hagedorn[*]   Alain Joye

Abstract

We propose an alternative to the usual time–independent Born–Oppenheimer approximation that is specifically designed to describe molecules with 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. Consequently, anharmonic effects play a role in the leading order calculations of vibrational levels.

Although we develop a general theory, our analysis is motivated by an examination of symmetric bihalide ions, such as FHF^- or $ClHCl^-$. We describe our approach for the FHF^- ion in detail.

Keywords: Hydrogen Bonds, Vibrational Levels, Born-Oppenheimer Approximation.

Résumé

Nous proposons une alternative à l'approximation de Born-Oppenheimer indépendante du temps spécifiquement adaptée à la description de molécules possédant des liaisons hydrogènes symétriques. Dans notre approche, les masses des noyaux d'hydrogène sont échelonnées différemment de celles des noyaux plus lourds et nous employons une forme spécialisée de surface d'énergie électronique. En conséquence, les effets anharmoniques jouent un rôle dans le terme dominant du calcul des niveaux de vibration. Bien que nous développions une théorie générale, notre analyse est motivée par un examen des ions bihalides, tels FHF- ou ClHCl-. Nous détaillons notre approche pour le ion FHF-.

Mots-clés : hydrogènes symétriques, niveaux de vibration, approximation de Born-Oppenheimer.

---

1 Introduction

In standard Born–Oppenheimer approximations, the masses of the electrons are held fixed, and the masses of the nuclei are all assumed to be proportional to ϵ^{-4}. Approximate solutions to the molecular Schrödinger equation are then sought as expansions in powers of ϵ. For the time–independent problem, the electron energy level surface is also assumed to behave asymptotically like a quadratic function of the nuclear variables near a local minimum.

In this paper and in a future one [4], we propose an alternative approximation for molecules that contain Hydrogen atoms as well as some heavier atoms, such as Carbon, Nitrogen, or Oxygen. Our motivation is to develop an approach that is specifically tailored to describe the phenomenon of Hydrogen bonding.

In this paper, we examine the specific case of systems with symmetric Hydrogen bonds, such as FHF^-. In [4], we plan to study non–symmetric cases, where the structure of the typical electron energy surface is very different. The mathematical analysis of that situation is consequently completely different.

The model we present here differs from the usual Born–Oppenhimer model in two ways:

1. We scale the masses of the Hydrogen nuclei as ϵ^{-3} instead of ϵ^{-4}. This is physically appropriate. If the mass of an electron is 1, and we define ϵ^{-4} to be the mass of a C^{12} nucleus, then $\epsilon = 0.0821$, and the mass of a H^1 nucleus is $1.015\,\epsilon^{-3}$.

2. We do not assume that the electron energy level is well approximated by an ϵ–independent quadratic function near a local minimum. Instead, we allow it to depend on ϵ and to take a particular form that we specify below. The particular form we have chosen is motivated by a detailed examination of the lowest electronic potential energy surfaces for FHF^- and $ClHCl^-$.

Although symmetric bihalide ions are quite special, our approach is flexible enough to describe more general phenomena. For example, the lowest electron energy surface for FHF^- has a single minimum with the Hydrogen nucleus mid–way between the two Fluorines. Our model can handle situations with single or double wells in the coordinates for a Hydrogen nucleus that paticipates in Hydrogen bonding. We hope that the ideas in this paper and [4] might provide some insight into some properties of Hydrogen bonded systems.

Our model leads to a different expansion from the usual Born–Oppenheimer approximation. For Hydrogen nuclei not involved in Hydrogen bonding, the vibrational energies are of order $\epsilon^{3/2}$, while the vibrational energies for the other nuclei and the Hydrogen nuclei involved in the symmetric Hydrogen bonding are of order ϵ^2. Furthermore, anharmonic effects must be taken into account for a Hydrogen nucleus involved in Hydrogen bonding at their leading order, ϵ^2. In the standard Born–Oppenheimer model, all vibrational energies appear in a harmonic approximation at order ϵ^2. Anharmonic corrections enter at order ϵ^4.

We present our ideas only in the simplest possible situation. In that situation, there are only 3 nuclei, and they are constrained to move along a fixed line. We plan to study more general possibilities, such as bending of the molecule, in the future.

The paper is organized as follows: In Section 2, we present the formal expansion. In Section 3 we state our rigorous results as Theorems 3.6 and 3.7. The proofs of some technical results are presented in Section 4.

2   Description of the Model

We study a triatomic system with two identical heavy nuclei A and B, and one light (Hydrogen) nucleus C. We begin by describing the Hamiltonian for this system in Jacobi coordinates. We let x_A and x_B be the positions of the heavy nuclei, and let x_C be the position of the light nucleus C. We let their masses be $m_A = m_B$ and m_C. We let $R = \dfrac{m_A x_A + m_B x_B + m_C x_C}{m_A + m_B + m_C}$ denote the center of mass of all three nuclei, and let $x_{AB} = \dfrac{x_A + x_B}{2}$ denote the center of mass of the heavy nuclei. We let $W = x_B - x_A$ be the vector from nucleus A to nucleus B and let $Z = x_C - x_{AB}$ be the vector from the center of mass of A and B to C. We assume the electronic Hamiltonian h_e only depends on the vectors between the nuclei, and we set $m_{AB} = m_A + m_B$ and $M = m_A + m_B + m_C$. In the original variables, the Hamiltonian has the form

$$- \frac{1}{2\,m_A}\,\Delta_{x_A} \,-\, \frac{1}{2\,m_B}\,\Delta_{x_B} \,-\, \frac{1}{2\,m_C}\,\Delta_{x_C} \,+\, h_e(x_B - x_A,\, x_C - x_A,\, x_C - x_B).$$

In these Jacobi coordinates, it has the form

$$- \frac{1}{2\,M}\,\Delta_R \,-\, \frac{m_{AB}}{2\,m_A\,m_B}\,\Delta_W \,-\, \frac{M}{2\,m_{AB}\,m_C}\,\Delta_Z \,+\, h_e(W,\, Z + W/2,\, Z - W/2).$$

Since we are interested in bound states, we discard the kinetic energy of the center of mass. We take the electron mass to be 1, and the masses of the heavy nuclei to be $m_A = m_B = \epsilon^{-4}\mu$, for some fixed μ. The mass of the light nucleus is $m_C = \epsilon^{-3}\nu$, for some fixed ν. The electronic Hamiltonian h_e then becomes $h_e(W, Z + W/2, Z - W/2) \equiv h(W, Z)$, so that the Hamiltonian of interest is

$$- \frac{\epsilon^4}{\mu}\,\Delta_W \,-\, \frac{\epsilon^3}{2\,\nu}\,\left(1 + \frac{\epsilon\,\nu}{2\,\mu} \right)\,\Delta_Z \,+\, h(W,\, Z).$$

This computation is exact and valid in any dimension.

To simplify the exposition, we drop the term $\dfrac{\epsilon\,\nu}{2\,\mu}$ in the factor that multiplies Δ_Z. It gives rise to uninteresting, regular perturbation corrections. Also, for simplicity, we assume $\mu = 2$ and $\nu = 1$. This can always be accomplished by trivial rescalings of W and Z.

To describe our ideas in the simplest situation, we restrict W and Z to one dimension. Thus, we are not allowing rotations or bending of the molecule. Furthermore, we introduce ϵ dependence of the electronic Hamiltonian to model the pecularities of symmetric Hydrogen bonds that we describe below.

These considerations lead us to study the Hamiltonian

$$H_1(\epsilon) \;=\; -\,\frac{\epsilon^4}{2}\,\frac{\partial^2}{\partial W^2} \;-\; \frac{\epsilon^3}{2}\,\frac{\partial^2}{\partial Z^2} \;+\; h(\epsilon,\,W,\,Z). \tag{2.1}$$

The electron Hamiltonian $h(\epsilon,\,W,\,Z)$ is an operator in the electronic Hilbert space that depends parametrically on $(\epsilon,\,W,\,Z)$ and includes the nuclear repulsion terms. For convenience, we assume that $h(\epsilon,\,W,\,Z)$ is a real symmetric operator.

We now describe the specific ϵ dependence of $h(\epsilon,\,W,\,Z)$ that we assume. Although the electron Hamiltonian does not depend on nuclear masses, the parameter ϵ is dimensionless, and thus may play more than one role. The dependence of h on ϵ we allow is motivated by the smallness of a particular Taylor series coefficient we observed in numerical computations for the ground state electron energy level for the real system FHF^-. We allow only the ground state *eigenvalue* to depend on ϵ. Otherwise, our electron Hamiltonian is ϵ–independent. With the physical value of ϵ inserted in our Hamiltonian, we obtain the true physical Hamiltonian.

From numerical computations of $E(W,\,Z)$ for FHF^-, we observed that the Z^2 coefficient in the Taylor expansion about the minimum $(W_0,\,0)$ of the ground state potential energy surface had a small numerial value, on the order of the value of $\epsilon = \epsilon_0$, where ϵ_0 was defined by setting ϵ_0^{-4} equal to the nuclear mass of the C^{12} isotope of Carbon.

The value of ϵ_0 is roughly 0.0821. We define a_2 so that the true Z^2 Taylor series term is $a_2\,\epsilon_0\,Z^2$. We then obtain $h(\epsilon,\,W,\,Z)$ by adding $(\epsilon - \epsilon_0)\,a_2\,Z^2$ to the ground state eigenvalue $E(W,\,Z)$. We make no other alterations to the electron Hamiltonian. When $\epsilon = \epsilon_0$, our $h(\epsilon,\,W,\,Z)$ equals the true physical electron Hamiltonian $h(\epsilon_0,\,W,\,Z)$.

Thus, we assume the ground state electron level has the specific form

$$E_1(\epsilon,\,W,\,Z) \;=\; E_0 + a_1\,(W - W_0)^2 + \left(\,a_2\,\epsilon \,-\, a_3\,(W - W_0)\right)Z^2 + a_4\,Z^4 + \cdots, \tag{2.2}$$

with $a_j = O(1)$. As we shall see, the leading order behavior of the energy and the wave functions for the molecule are determined from the terms written explicitly in (2.2). The terms not explicitly displayed are of orders $(W - W_0)^\alpha\,Z^{2\beta}$, where α and β are non-negative integers that satisfy $\alpha + \beta \geq 3$. They play no role to leading order, but contribute to higher order corrections.

We assume a_1, a_3, and a_4 are positive, but that a_2 can be positive, zero, or negative. When a_2 is negative, $E_1(\epsilon,\,W,\,Z)$ has a closely spaced double well near $(W_0,\,0)$ instead of a single local minimum.

To ensure that the leading part of $E_1(\epsilon,\,W,\,Z)$,

$$\widetilde{E}_1(\epsilon,\,W,\,Z) \;=\; E_0 + a_1\,(W - W_0)^2 + \left(\,a_2\,\epsilon \,-\, a_3\,(W - W_0)\right)Z^2 + a_4\,Z^4,$$

is bounded below, we assume that either

$$a_3^2 \;<\; 4\,a_1\,a_4, \tag{2.3}$$

or

$$a_3^2 \;=\; 4\,a_1\,a_4 \qquad \text{and} \qquad a_2 \;\geq\; 0. \tag{2.4}$$

These conditions are equivalent to the property $\widetilde{E}_1(\epsilon, W, Z) \geq -C$ for some C, since we can write

$$\widetilde{E}_1(\epsilon, W, Z) \;=\; a_1 \left((W - W_0) - \frac{a_3}{2a_1} Z^2 \right)^2 \;+\; \left(a_4 - \frac{a_3^2}{4a_1} \right) Z^4 \;+\; a_2 \, \epsilon \, Z^2.$$

By rescaling with $w = (W - W_0)/\epsilon$ and $z = Z/\epsilon^{1/2}$, we see that the Hamiltonian

$$-\frac{\epsilon^4}{2} \frac{\partial^2}{\partial W^2} \;-\; \frac{\epsilon^3}{2} \frac{\partial^2}{\partial Z^2} \;+\; \widetilde{E}_1(\epsilon, W, Z)$$

is unitarily equivalent to ϵ^2 times the ϵ–independent Normal Form Hamiltonian

$$H_{\mathrm{NF}} \;=\; -\frac{1}{2} \frac{\partial^2}{\partial w^2} \;-\; \frac{1}{2} \frac{\partial^2}{\partial z^2} \;+\; E_{\mathrm{NF}}(w, z), \tag{2.5}$$

where

$$E_{\mathrm{NF}}(w, z) \;=\; a_1 \, w^2 \;+\; \left(a_2 \,-\, a_3 \, w \right) z^2 \;+\; a_4 \, z^4. \tag{2.6}$$

Remark Although we do not use it, further scaling shows that H_{NF} is essentially a three–parameter model, since the change of variables $w = \alpha \, s$, $z = \alpha \, t$, yields

$$H_{\mathrm{NF}} \;\simeq\; \alpha^{-2} \left(-\frac{1}{2} \frac{\partial^2}{\partial s^2} \;-\; \frac{1}{2} \frac{\partial^2}{\partial t^2} \;+ \alpha_1 \, s^2 + \alpha_2 \, t^2 - \alpha_3 \, s \, t^2 + t^4 \right),$$

with

$$\alpha = a_4^{-1/6}, \quad \alpha_1 = \frac{a_1}{a_4^{2/3}}, \quad \alpha_2 = \frac{a_2}{a_4^{2/3}}, \quad \text{and} \quad \alpha_3 = \frac{a_3}{a_4^{5/6}}.$$

Under conditions (2.3) or (2.4), H_{NF} is essentially self-adjoint on $C_0^\infty(I\!\!R^2)$ and has purely discrete spectrum. This last property is easy to verify under condition (2.3), or condition (2.4) with $a_2 > 0$, because $E_{\mathrm{NF}}(w, z)$ tends to infinity as $\| (w, z) \| \to \infty$. When (2.4) is satisfied with $a_2 = 0$, the result is more subtle because $E_{\mathrm{NF}}(w, z)$ attains its minimum value of zero along a parabola in (w, z). In that case we prove that the spectrum is discrete in Proposition 3.1.

Explicit Computations for FHF⁻ The expression (2.2) is clearly special. Our computations for FHF^- that motivate this expression have roughly the following values, where distances are measured in Angstroms and energies are measured in Hartrees:

$W_0 = 2.287,$

$E_0 = -200.215,$

$a_1 = 0.26,$

$a_2 = 1.22 \qquad (\text{if} \quad \epsilon \;=\; 0.0821),$
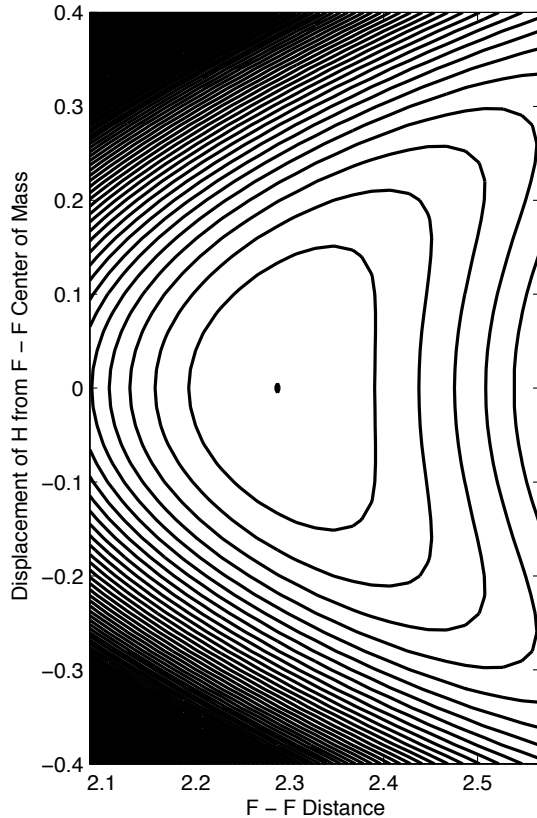
$a_3 = 1.29,$

$a_4 = 1.62.$

Figure 1: Contour plot of the ground state electronic potential energy surface in the Jacobi coordinates (W, Z). It is obviously not well approximated by a quadratic. Our technique exploits the flatness of the surface in the Z direction near the minimum.

These results came from fitting the output from Gaussian 2003 using second order Moller–Plesset theory with the aug–cc–pvtz basis set. We observed that the process of fitting the data was numerically quite unstable, and that condition (2.3) was barely satisfied by these a_j.

The experimentally observed values [9] for the excitation energies to the first symmetric stretching vibrational mode and the first asymmetric vibrational mode of FHF^- are $583.05 \, \mathrm{cm}^{-1}$ and $1331.15 \, \mathrm{cm}^{-1}$, respectively. With the values of a_j above, the leading order calculation from our model predicts $600 \, \mathrm{cm}^{-1}$ and $1399 \, \mathrm{cm}^{-1}$. By leading order, we mean $E_0 + \epsilon^2 \, \mathcal{E}_2$ in the expansion we present below. These values depend sensitively on precisely how we fit the potential energy surface, which itself depends sensitively on the electron structure calculations. By comparison, Gaussian 2003 with the aug-cc-pvdz basis set predicts harmonic frequencies of $608 \, \mathrm{cm}^{-1}$ and $1117 \, \mathrm{cm}^{-1}$. We could not obtain frequencies for the aug-cc-pvtz basis set from Gaussian because of our computer limitations.

For some very recent numerical results for vibrational frequencies of FHF^- that appeared as we were finishing this paper, see [2].

We now mimic the technique of [3] to obtain an expansion for the solution to the eigenvalue problem for (2.1). We could have used the technique of [5], but that would have led to more complicated formulas.

For convenience, we replace the variable W by $W - W_0$, so that henceforth, $W_0 = 0$.

The technique of [3] uses the method of multiple scales. Instead of searching directly for an eigenvector $\Psi(\epsilon, W, Z)$ for (2.1), we first search for an eigenvector $\psi(\epsilon, W, Z, w, z)$ for an operator that acts in more variables. When we have determined ψ, we obtain Ψ by setting

$$\Psi(\epsilon, W, Z) \;=\; \psi(\epsilon, W, Z, W/\epsilon, Z/\epsilon^{1/2}).$$

This is motivated physically by the following observation: The dependence of the electrons on the nuclear coordinates occurs on the length scale of (W, Z), while the semiclassical quantum fluctuations of the nuclei occur on the length scale of (w, z). To leading order in ϵ, these effects behave independently.

The equation for ψ is formally

$$H_2(\epsilon)\, \psi(\epsilon, W, Z, w, z) \quad=\quad \mathcal{E}(\epsilon)\, \psi(\epsilon, W, Z, w, z), \tag{2.7}$$

where

$$H_2(\epsilon) \;=\; -\,\frac{\epsilon^4}{2}\,\frac{\partial^2}{\partial W^2} \;-\; \epsilon^3\,\frac{\partial^2}{\partial W\,\partial w} \;-\; \frac{\epsilon^2}{2}\,\frac{\partial^2}{\partial w^2} \;-\; \frac{\epsilon^3}{2}\,\frac{\partial^2}{\partial Z^2} \;-\; \epsilon^{5/2}\,\frac{\partial^2}{\partial Z\,\partial z} \;-\; \frac{\epsilon^2}{2}\,\frac{\partial^2}{\partial z^2}$$

$$+\;\; [\, h(\epsilon, W, Z) - E(\epsilon, W, Z)\,] \;+\; E(\epsilon, \epsilon\, w, \epsilon^{1/2} z)$$

$$+\;\; \sum_{m=6}^{\infty}\, \epsilon^{m/2}\, \Big(\, T_{m/2}(W, Z) - T_{m/2}(\epsilon\, w, \epsilon^{1/2} z)\,\Big). \tag{2.8}$$

The functions $T_{m/2}$ in this expression will be chosen later. Different choices yield equally valid expansions for $\Psi(\epsilon, W, Z)$, although they alter the expressions for $\psi(\epsilon, W, Z, w, z)$ by converting (W, Z) dependence into (w, z) dependence.

In (2.8), we expand both $E(\epsilon, \epsilon w, \epsilon^{1/2} z)$ and $T_{m/2}(\epsilon w, \epsilon^{1/2} z)$ in Taylor series in powers of $\epsilon^{1/2}$. We then make the Ansatz that (2.7) has formal solutions of the form

$$\psi(\epsilon, W, Z, w, z) \;=\; \psi_0(W, Z, w, z) \;+\; \epsilon^{1/2}\,\psi_{1/2}(W, Z, w, z) \;+\; \epsilon^1\,\psi_1(W, Z, w, z) \;+\; \cdots, \tag{2.9}$$

with

$$\mathcal{E}(\epsilon) \;=\; \mathcal{E}_0 \;+\; \epsilon^{1/2}\,\mathcal{E}_{1/2} \;+\; \epsilon^1\,\mathcal{E}_1 \;+\; \cdots. \tag{2.10}$$

We substitute these expressions into (2.7) and solve the resulting equation order by order in powers of $\epsilon^{1/2}$.

Note: The description in this section is purely formal. In particular, it does not take into account the cutoffs that are necessary for rigorous results. The mathematical details are dealt with in the next section.

Order 0   The order ϵ^0 terms require

$$[\, h(\epsilon, W, Z) - E(\epsilon, W, Z)\,]\, \psi_0 \;+\; E_0\,\psi_0 \;=\; \mathcal{E}_0\,\psi_0.$$

We solve this by choosing

$$\mathcal{E}_0 \;=\; E_0,$$

and

$$\psi_0(W, Z, w, z) \;=\; f_0(W, Z, w, z)\,\Phi(W, Z),$$

where $\Phi(W, Z, \cdot)$ is a normalized ground state eigenvector of $h(\epsilon, W, Z)$. Under our assumptions, we can choose $\Phi(W, Z, \cdot)$ to be real, smooth in (W, Z), and independent of ϵ. This choice satisfies

$$\langle\, \Phi(W, Z, \cdot),\ \nabla_{W,Z}\Phi(W, Z, \cdot)\,\rangle_{\mathcal{H}_{el}} \;=\; 0, \tag{2.11}$$

where the inner product is in the electronic Hilbert space. We assume that $f_0(W, Z, w, z)$ is not identically zero.

Order 1/2   The order $\epsilon^{1/2}$ terms require

$$[\,h(\epsilon, W, Z) - E(\epsilon, W, Z)\,]\,\psi_{1/2} \;+\; E_0\,\psi_{1/2} \;=\; \mathcal{E}_0\,\psi_{1/2} \;+\; \mathcal{E}_{1/2}\,\psi_0.$$

The components of this equation in the $\Phi(W, Z)$ direction in the electronic Hilbert space require

$$\mathcal{E}_{1/2} \;=\; 0.$$

The components of the equation orthogonal to $\Phi(W, Z)$ in the electronic Hilbert space require

$$[\,h(\epsilon, W, Z) - E(\epsilon, W, Z)\,]\,\psi_{1/2} \;=\; 0,$$

so

$$\psi_{1/2}(W, Z, w, z) \;=\; f_{1/2}(W, Z, w, z)\,\Phi(W, Z).$$

Orders 1 and 3/2   By similar calculations, the order ϵ^1 and $\epsilon^{3/2}$ terms yield

$$\mathcal{E}_1 \;=\; \mathcal{E}_{3/2} \;=\; 0,$$

$$\psi_1(W, Z, w, z) \;=\; f_1(W, Z, w, z)\,\Phi(W, Z), \qquad \text{and}$$

$$\psi_{3/2}(W, Z, w, z) \;=\; f_{3/2}(W, Z, w, z)\,\Phi(W, Z).$$

Order 2   The order ϵ^2 terms that are multiples of $\Phi(W, Z)$ in the electronic Hilbert space require

$$-\,\frac{1}{2}\,\frac{\partial^2 f_0}{\partial w^2}(W, Z, w, z) \;-\; \frac{1}{2}\,\frac{\partial^2 f_0}{\partial z^2}(W, Z, w, z) \;+\; E_{\mathrm{NF}}(w, z)\,f_0(W, Z, w, z)$$

$$=\; \mathcal{E}_2\,f_0(W, Z, w, z), \tag{2.12}$$

where $E_{\mathrm{NF}}(w, z)$ is given by (2.6).

Because of the form of $E_{\mathrm{NF}}(w, z)$, (2.12) does not separate into two ODE's. We do not know $\mathcal{E}_2$ or f_0 exactly, although accurate numerical approximations can be found easily. These eigenvalues and eigenfunctions describe the coupled anharmonic vibrational motion of all three nuclei in the molecule. As we commented earlier, hypotheses (2.3) or (2.4)

guarantee that the eigenvalues $\mathcal{E}_2$ are discrete and bounded below, with normalized bound states $f_0(W, Z, w, z)$ in (w, z) for any (W, Z).

Later in the expansion, we choose the operator T_3 so that f_0 has no (W, Z) dependence. With this in mind, equation (2.12) determines $\mathcal{E}_2$ and a normalized function $f_0(w, z)$ (up to a phase) for any given vibrational level.

The terms of order 2 that are orthogonal to $\Phi(W, Z)$ require

$$[h(\epsilon, W, Z) - E(\epsilon, W, Z)] \, \psi_2 \ = \ 0,$$

Thus,

$$\psi_2 \ = \ f_2(W, Z, w, z) \, \Phi(W, Z).$$

We split the scalar functions $f_\alpha(W, Z, w, z)$ with $\alpha > 0$ into two contributions

$$f_\alpha(W, Z, w, z) \ = \ f_\alpha^{\|}(W, Z, w, z) \ + \ f_\alpha^{\perp}(W, Z, w, z)$$

where for each fixed W and Z, $f_\alpha^{\|}(W, Z, \cdot, \cdot)$ is a multiple of $f_0(\cdot, \cdot)$, and $f_\alpha^{\perp}(W, Z, \cdot, \cdot)$ perpendicular to $f_0(\cdot, \cdot)$ in $L^2(\mathbb{R}^2, \, dw \, dz)$. Furthermore, we choose the operators $T_{3+m/2}$ later in the expansion so that $f_\alpha^{\|}(W, Z, \cdot, \cdot)$ has no (W, Z) dependence. We will not precisely normalize our approximate eigenfunctions, so we henceforth assume $f_\alpha^{\|}(W, Z, w, z) = 0$ for all $\alpha > 0$.

Order m/2 with m > 4   We equate the terms of order $m/2$ and then separately examine the projections of the resulting equation into the $\Phi(W, Z)$ direction in the electron Hilbert space and into the direction perpendicular to $\Phi(W, Z)$.

From the terms in the $\Phi(W, Z)$ direction, we obtain the value of $\mathcal{E}_{m/2}$ and an expression for $f_{(m-4)/2}(W, Z, w, z) = f_{(m-4)/2}^{\perp}(W, Z, w, z)$. When $m = 6$ we choose T_3 so that f_0 can be chosen independent of (W, Z). When $m > 6$, we choose $T_{m/2}$, so that $f_{(m-6)/2}^{\|}$ can be taken to be zero.

The terms orthogonal to $\Phi(W, Z)$ in the electronic Hilbert space give rise to an equation for $[h(\epsilon, W, Z) - E(\epsilon, W, Z)] \, \psi_{m/2}$. This equation has a solution of the form

$$\psi_{m/2}(W, Z, w, z) \ = \ \left(f_{m/2}^{\|}(W, Z, w, z) \ + \ f_{m/2}^{\perp}(W, Z, w, z) \right) \, \Phi(W, Z)$$

$$+ \ \psi_{m/2}^{\perp}(W, Z, w, z),$$

where $\psi_{m/2}^{\perp}$ is obtained by applying the reduced resolvent operator

$$[h(\epsilon, W, Z) - E(\epsilon, W, Z)]_r^{-1}$$

to the right hand side of the equation.

In the next section, we prove that this procedure yields a quasimode whose approximate eigenvalue and eigenvector each have asymptotic expansions to all orders in $\epsilon^{1/2}$.

3 Mathematical Considerations

In this section we present a mathematically rigorous version of the expansion of Section 2. This involves inserting cutoffs and proving that many technical conditions are satisfied at each order of the expansion.

Proposition 3.1 *Assume (2.3) or (2.4).*

Then, the spectrum of $H_{NF} = -\dfrac{1}{2}\dfrac{\partial^2}{\partial w^2} - \dfrac{1}{2}\dfrac{\partial^2}{\partial z^2} + E_{NF}(w,z)$ is purely discrete.

Proof We use Persson's Theorem (see, *e.g.*, [6]) to show that the essential spectrum of H_{NF} is empty. This theorem says that if $V \in L^p(I\!\!R^n) + L^\infty(I\!\!R^n)$, with $p = 2$ if $n \leq 3$, $p > 2$ if $n = 4$, and $p \geq n/2$ if $n \geq 5$, then the bottom of the essential spectrum of $H = -\Delta + V$ is characterized by the behavior of the operator at infinity. More precisely,

$$\inf\ \sigma_{\mathrm{ess}}(H) \ = \ \sup_{\substack{K \in \mathbf{R}^n \\ K\ \mathrm{compact}}}\ \inf_{\varphi \neq 0}\ \left\{ \frac{\langle \varphi,\, H\,\varphi \rangle}{\|\varphi\|^2}\ :\ \varphi \in C_0^\infty(I\!\!R^n \setminus K) \right\}.$$

Since E_{NF} does not satisfy the hypotheses, we replace it with a cut off potential

$$E_T(w,z) = \begin{cases} E_{NF}(w,z), & \text{if } E_{NF}(w,z) \leq T, \\[2mm] T, & \text{otherwise.} \end{cases}$$

The operator $H_T = -\Delta + E_T$ is self-adjoint on the domain of $-\Delta$. Because C_0^∞ is a core for both H_{NF} and H_F, and $\langle \varphi,\, H_{NF}\,\varphi \rangle \geq \langle \varphi,\, H_T\,\varphi \rangle$, for any $\varphi \in C_0^\infty$, the min-max principle shows that

$$\inf\ \sigma_{\mathrm{ess}}(H_{NF}) \ \geq\ \inf\ \sigma_{\mathrm{ess}}(H_T). \tag{3.1}$$

Under hypothesis (2.3) or (2.4) with $a_2 > 0$, E_{NF} is arbitrarily large for all large arguments. Persson's Theorem easily shows that $\inf\ \sigma_{\mathrm{ess}}(H_T) = T$ for all large positive T. Inequality (3.1) immediately implies the proposition.

Thus, we need only consider the case of hypothesis (2.4) with $a_2 = 0$. Since $E_T \leq T$, we see that $\inf\ \sigma_{\mathrm{ess}}(H_T) \leq T$. We shall use Persson's Theorem to prove the reverse inequality.

Consider a square $K(R)$ of side $2R > 0$, centered at the origin, and let $\varphi \in C_0^\infty(I\!\!R^n \setminus K(R))$. We observe that $E_{NF}(w,z) = T$ on the set $L_R = \{w \leq -R\} \cup \{|z| \geq R, |w| \leq R\}$, for $R > 2a_1/a_3$, provided $T \leq a_1 R^2$. Therefore,

$$\int_{L_R} \overline{\varphi(w,z)}\ \left(-\partial_w^2/2 - \partial_z^2/2 + E_T(w,z)\right)\ \varphi(w,z)\ dw\,dz \ \geq\ \int_{L_R} T\ |\varphi(w,z)|^2\ dw\,dz.$$

For $w \geq R$, we estimate the integral as follows

$$\int_{\{w \geq R, \ z \in \mathbb{R}\}} \overline{\varphi(w, z)} \ \left(-\partial_w^2/2 - \partial_z^2/2 + E_T(w, z)\right) \varphi(w, z) \ dw \, dz$$

$$\geq \int_{w \geq R} \int_{z \in \mathbb{R}} \overline{\varphi(w, z)} \ \left(-\partial_z^2/2 + E_T(w, z)\right) \varphi(w, z) \ dz \, dw$$

$$\equiv \int_{w \geq R} \langle \varphi(w, \cdot), h_T(w) \, \varphi(w, \cdot) \rangle_z \ dw. \tag{3.2}$$

For each value of $w \geq R$, the operator $h_T(w)$ is a one-dimensional Schrödinger operator with potential given by a (cut off) symmetric quartic double well. Hence $h_T(w)$ always has a ground state below T, for any large T. We shall show that the ground state converges to T as $w \to \infty$.

To do this, we show that $h_T(w) \to -\partial_z^2/2 + T$ in the norm resolvent sense. By the resolvent identity, this follows if we show that $\|(E_T(w, z) - T)(-\partial_z^2/2 + T)^{-1}\|$ tends to zero as $w \to \infty$. To show this we use the following claim:
There exists $c(T)$, such that,

$$\| V \, (-\partial_z^2 + T)^{-1} \|_{L^2(\mathbb{R}) \to L^2(\mathbb{R})} \ \leq \ c(T) \, \| V \|_2,$$

for all $V \in L^2(\mathbb{R})$.

By Theorem IX.28 in [11], given any $a > 0$, there exists $b \geq 0$, such that $\|\varphi\|_\infty \ \leq \ a \, \|(-\partial_z^2)\varphi\|_2 \ + \ b \, \|\varphi\|_2$, for any φ in the domain of $-\partial_z^2$. This implies that

$$\| V \, (-\partial_z^2 + T)^{-1} \|_{L^2(\mathbb{R}) \to L^2(\mathbb{R})} \ \leq \ \| V \|_{L^\infty(\mathbb{R}) \to L^2(\mathbb{R})} \, \| (-\partial_z^2 + T)^{-1} \|_{L^2(\mathbb{R}) \to L^\infty(\mathbb{R})}$$

$$\leq \ c(T) \, \| V \|_2,$$

for some finite $c(T)$. This proves the claim.

In our case, this yields

$$\| (E_T(w, \cdot) - T) \, (-\partial_z^2/2 + T)^{-1} \| \ \leq \ c(T) \, \| (E_T(w, \cdot) - T) \|_2,$$

where $c(T)$ is independent of w.

Under the assumption that $R \geq \sqrt{T/a_1}$, we have

$$\| (E_T(w, \cdot) - T) \|_2^2 \ \leq \ \int_{|w - z^2 a_3/(2a_1)| \leq \sqrt{T/a_1}} T^2 \ dz$$

$$= \ 2 \, T^2 \, \sqrt{\frac{2a_1}{a_3}} \, \left(\sqrt{w + \sqrt{T/a_1}} \ - \ \sqrt{w - \sqrt{T/a_1}} \right)$$

$$\leq \ T^2 \, \sqrt{\frac{2T}{a_3}} \ \frac{1}{\sqrt{w - \sqrt{T/a_1}}}$$

$$\simeq \ \tilde{c}(T) \, \frac{1}{\sqrt{w}}, \quad \text{as} \quad w \to \infty.$$

Thus by the resolvent formula and Theorem VIII.19 of [10], $h_T(w)$ converges in norm resolvent sense to $(-\partial_z^2/2 + T)$.

We let $P_\Delta(H)$ be the spectral projector on the interval $\Delta \in I\!\!R$ for a self-adjoint operator H. Then Theorem VIII.23 of [10] implies that for any positive $a < b < T$,

$$\lim_{w\to\infty} \| P_{(a,b)}(h_T(w)) - P_{(a,b)}(-\partial_z^2/2 + T) \| = \lim_{w\to\infty} \|P_{(a,b)}(h_T(w))\| = 0,$$

since $\sigma(-\partial_z^2/2 + T) = [T, \infty)$. Therefore, the bottom of the spectrum of $h_T(w)$ satisfies

$$T \geq b_T(w) \equiv \inf \sigma(h_T(w)) \to T \quad \text{as} \quad w \to \infty.$$

Using this in (3.2), we obtain

$$\int_{\{w\geq R, \; z\in I\!\!R\}} \overline{\varphi(w,z)} \, (-\partial_w^2/2 - \partial_z^2/2 + E_T(w,z)) \, \varphi(w,z) \, dw \, dz$$

$$\geq \inf_{v\geq R} b_T(v) \int_{\{w\geq R, z\in I\!\!R\}} |\varphi(w,z)|^2 \, dw \, dz.$$

Combining all the estimates, we see that for any $\varphi \in C_0^\infty(I\!\!R^n \setminus K(R))$

$$\langle \varphi, \, H_T \, \varphi \rangle \geq \inf_{v\geq R} b_T(v) \, \| \varphi \|^2,$$

provided $a_1 R^2 \geq T$. Thus,

$$\inf \sigma_{\text{ess}}(H_T) \geq \sup_{R\geq \sqrt{\frac{T}{a_1}}} \inf_{v\geq R} b_T(v) = T.$$

Since T is arbitrarily large, this implies the proposition. ∎

In the usual Born–Oppenheimer approximation, the semiclassical expansion for the nuclei is based on Harmonic oscillator eigenfunctions. They have many well-known properties. Our expansion relies on the analogous properties for eigenfunctions of H_{NF}. The following proposition establishes some of the properties we need in an even more general setting.

Proposition 3.2 *Let V be a non-negative polynomial, such that $H = -\Delta + V$ has purely discrete spectrum. Let $\varphi(x)$ be an eigenvector of H, i.e., an $L^2(\mathbb{R}^n)$ solution of $H\varphi = \mathcal{E}\varphi$, where $\mathcal{E} > 0$. Then, $\varphi \in C^\infty(I\!\!R^n)$ and $\nabla\varphi \in L^2(I\!\!R^n)$. Moreover, for any $a > 0$,*

$$\varphi \in D(e^{a\langle x\rangle}), \quad \nabla\varphi \in D(e^{a\langle x\rangle}), \quad \text{and} \quad \Delta\varphi \in D(e^{a\langle x\rangle}),$$

where $\langle x \rangle = \sqrt{1 + \sum_{j=1}^n x_j^2}$, and $D(e^{a\langle x\rangle})$ denotes the domain of multiplication by $e^{a\langle x\rangle}$.

Proof Since $V \in C^\infty$, elliptic regularity arguments (see *e.g.*, [7], Thm 7.4.1) show that all eigenfunctions are C^∞.

We first show that the $\nabla\varphi$ is L^2. Since $V \geq 0$, the quadratic form defined by

$$h(\varphi,\,\psi) \;=\; \langle\,\nabla\varphi,\,\nabla\psi\,\rangle \;+\; \langle\,\sqrt{V}\,\varphi,\,\sqrt{V}\,\psi\,\rangle$$

on $Q(h) = Q(-\Delta) \cap Q(V)$, is closed and positive. Here $Q(A)$ means the quadratic form domain of the operator A. Since $D(H) \subset Q(h)$, any eigenvector of H belongs to

$$Q(-\Delta) \;=\; \{\,\varphi \in L^2(I\!\!R^n) \;:\; \|\,\nabla\varphi\,\| \,<\, \infty\,\}.$$

Thus, $\nabla\varphi \in L^2$.

Next, we prove $\varphi \in D(e^{a\langle x\rangle})$, for any $a > 0$ by a Combes–Thomas argument, as presented in Theorem XII.39 of [12]. We describe the details for completeness. Let $\alpha \in I\!\!R$, and let v denote x_j for any $j \in \{1,\cdots,n\}$. We consider the unitary group $W(\alpha) = e^{i\alpha v}$ for $\alpha \in I\!\!R$, and compute

$$H(\alpha) \;=\; W(\alpha)\,(-\Delta + V)\,W(\alpha)^{-1} \;=\; H \,+\, i\,\alpha\,\partial_v \,+\, \alpha^2.$$

The operator $i\partial_v$ is H-bounded, with arbitrary small relative bound, since $V \geq 0$. Thus $\{H(\alpha)\}$ extends a self-adjoint, entire analytic family of type A, defined on $D(H)$. We note that since $H(0) = H$ has purely discrete spectrum, its resolvent, $R_0(\lambda)$ is compact, for any $\lambda \in \rho(H) \equiv \mathbb{C} \setminus \sigma(H)$. Hence, $R_\alpha(\lambda) = (H(\alpha) - \lambda)^{-1}$ is compact for any $\alpha \in I\!\!R$, and hence, for all $\alpha \in \mathbb{C}$, if $\lambda \in \rho(H(\alpha))$. It is jointly analytic in α and λ. The eigenvalues of $H(\alpha)$ are thus analytic in α, except at crossing points, where they may have algebraic singularities. Since for α real, $W(\alpha)$ is unitary, the eigenvalues are actually independent of α, and $\sigma(H(\alpha)) = \sigma(H)$, for any α.

Let P be the finite rank spectral projector corresponding to an eigenvalue $\mathcal{E}$ of H_{NF}. Then, for $\alpha \in I\!\!R$, $P(\alpha) = W(\alpha)PW(\alpha)^{-1}$ is the spectral projector corresponding to the eigenvalue $\mathcal{E}$ of $H(\alpha)$. By Riesz's formula and the properties of the resolvent, $P(\alpha)$ extends to an entire analytic function that satisfies

$$W(\alpha_0)P(\alpha)W(\alpha_0)^{-1} = P(\alpha_0 + \alpha).$$

for any $\alpha_0 \in I\!\!R$.

By O'Connor's Lemma (Sect. XIII.11 of [12]), this yields information about the eigenvectors. If $\varphi = P\varphi$, the vector $\varphi^\alpha = W(\alpha)\varphi$, defined for $\alpha \in I\!\!R$ has an analytic extension to the whole complex plane, and is an analytic vector for the operator v. Therefore, $\varphi \in D(e^{a|v|})$, for any $a > 0$. By taking all possible x_j's for v, and noting that $D(e^{a\langle x\rangle}) = D(e^{a(\sum_j |x_j|)})$, we see that $\varphi \in D(e^{a\langle x\rangle})$.

From this, it follows that $\Delta\varphi \in D(e^{a\langle x\rangle})$ for any $a > 0$ as well, since for any $\delta > 0$,

$$\int_{I\!\!R^n} e^{2a\langle x\rangle}\,|\Delta\varphi(x)|^2\,dx$$

$$=\; \int_{I\!\!R^n} e^{2a\langle x\rangle}\,|\,(V(x) - \mathcal{E})\,\varphi(x)\,|^2\;dx$$

$$\leq\; \|\,(V - \mathcal{E})^2\,e^{-\delta\langle\cdot\rangle}\,\|_\infty\;\|\,e^{(a+\delta/2)\langle\cdot\rangle}\,\varphi(\cdot)\,\|^2$$

$$<\; \infty.$$

Finally, Lemma 3.3 below shows that $\nabla \varphi \in D(e^{a\langle x \rangle})$. To apply this Lemma in our situation, we let $p(x) = e^{a\langle x \rangle}$ and note that for any $a > 0$,

$$(\nabla e^{a\langle x \rangle})/e^{a\langle x \rangle} \;=\; a\nabla\langle x \rangle \;=\; ax/\langle x \rangle$$

is uniformly bounded. ■

Lemma 3.3 requires some notation. Letting $p(x)$ be a positive weight function, we introduce the space

$$F_w^2 \;=\; \left\{ f \;:\; \|f\|_{F_w^2}^2 \;=\; \int_{\mathbb{R}^n} \left(|f(x)|^2 + |\Delta f(x)|^2 \right) \, p(x) \, dx \;<\; \infty \right\}.$$

We write $\|f\|_w^2 \;=\; \int_{\mathbb{R}^n} |f(x)|^2 \, p(x)\, dx$, for any $f \in L^2(\mathbb{R}^n, p(x)dx)$, and $\|f\|^2 = \int_{\mathbb{R}^n} |f(x)|^2\, dx$ when the weight is one.

Lemma 3.3 *Let $p \in C^1$ be positive, and assume that there exists a constant $C < \infty$, such that $|(\nabla p(x))/p(x)| \leq 2\,C$ for all $x \in \mathbb{R}^n$. Then, for any $f \in F_w^2$*

$$\|\nabla f\|_w \;\leq\; C\, \|f\|_w \;+\; \sqrt{\|f\|_w\, \|\Delta f\|_w \;+\; C^2\, \|f\|_w^2}. \tag{3.3}$$

We present the proof of this technical lemma in Section 4.

We now state and prove the following Corollary to Proposition 3.2:

Corollary 3.4 *Assume the hypotheses of Proposition 3.2. Let $R(\lambda)$ be the resolvent of $H = -\Delta + V$ for $\lambda \notin \sigma(H)$, and let $P_{\mathcal{E}}$ be the finite dimensional spectral projector of H on $\mathcal{E}$. Let $r(\mathcal{E}) = \left((H - \mathcal{E})|_{(\mathbb{I} - P_{\mathcal{E}})L^2} \right)^{-1}$ be the reduced resolvent at $\mathcal{E}$. Then, $e^{a\langle x \rangle}\, R(\lambda)\, e^{-a\langle x \rangle}$ and $e^{a\langle x \rangle}\, r(\mathcal{E})\, e^{-a\langle x \rangle}$ are bounded on $L^2(\mathbb{R}^n)$.*

Proof We use the notation of the proof of Proposition 3.2. We know that $R_\alpha(\lambda)$ is compact and analytic in $\alpha \in \mathbb{C}$, if $\lambda \notin \sigma(H)$. Hence, for any $\psi_1,\, \psi_2 \in C_0^\infty$, the map from $\mathbb{R} \times \rho(H)$ to $\mathbb{C}$ given by

$$(a, \lambda) \;\mapsto\; \langle\, \psi_1,\, e^{av}\, R_0(\lambda)\, e^{-av}\, \psi_2 \,\rangle$$

is uniformly bounded by $C\, \|\psi_1\|\, \|\psi_2\|$ on any given compact set of $\mathbb{R} \times \rho(H)$ for some C. From this we infer that for any $a > 0$, $e^{a\langle x \rangle}\, R(\lambda)\, e^{-a\langle x \rangle}$ is bounded in $L^2(\mathbb{R}^n)$, uniformly for λ in compact sets of $\rho(H)$. Since the reduced resolvent $r(\mathcal{E})$ can be represented as

$$r(\mathcal{E}) \;=\; \frac{1}{2\pi i}\, \int_{C_{\mathcal{E}}} R_0(\lambda)\, \frac{1}{\lambda - \mathcal{E}}\, d\lambda, \tag{3.4}$$

where $C_{\mathcal{E}}$ is a loop in the resolvent set encircling only $\mathcal{E}$, the boundedness of $e^{a\langle x \rangle}\, r(\mathcal{E})\, e^{-a\langle x \rangle}$ follows. ■

To show that the terms of our formal expansion all belong to L^2, we use the following generalization of Proposition 3.2. We present its proof in Section 4.

Proposition 3.5 *Assume the hypotheses of Proposition 3.2 and let φ be an L^2 solution of $(-\Delta + V - \mathcal{E})\, \varphi = 0$. Then, for any $a > 0$, and any multi-index $\alpha \in \mathbb{N}^n$, $D^\alpha \varphi \in D(e^{a\langle x \rangle})$, where $D^\alpha = \partial_{x_1}^{\alpha_1} \partial_{x_2}^{\alpha_2} \cdots \partial_{x_n}^{\alpha_n}$.*

We now prove that our formal expansion leads to rigorous quasimodes for the Hamiltonian $H_1(\epsilon)$ given by (2.1). Theorem 3.6 summarizes this result for the leading order, while Theorem 3.7 handles the arbitrary order results.

Theorem 3.6 *Let $h(\epsilon, W, Z)$ be defined as in Section 2 with W shifted so that $W_0 = 0$. We assume $h(\epsilon, W, Z)$ on $\mathcal{H}_{el}$ is C^2 in the strong resolvent sense for (W, Z) near the origin. We assume its non-degenerate ground state is given by*

$$
\begin{aligned}
E_1(\epsilon, W, Z) &= E_0 + a_1 W^2 + \left(a_2 \epsilon - a_3 W \right) Z^2 + a_4 Z^4 + S(\epsilon, W, Z) \\
&\equiv E_0 + \tilde{E}(\epsilon, W, Z) + S(\epsilon, W, Z),
\end{aligned}
\tag{3.5}
$$

under hypothesis (2.3) or (2.4), and we denote the corresponding normalized eigenstate by $\Phi(W, Z)$. Suppose the remainder term S is uniformly bounded below by some $r > -\infty$ and that $|S|$ satisfies a bound of the form

$$
|S(\epsilon, W, Z)| \leq C \sum_{\alpha+\beta \geq 3} |W^\alpha Z^{2\beta}|
\tag{3.6}
$$

for (W, Z) in a neighborhood of the origin. Here C is independent of ϵ, the sum is finite, and α and β are non-negative integers. Let $f_0(w, z)$ be a normalized non-degenerate eigenvector of H_{NF}, i.e.,

$$
(-\partial_w^2/2 - \partial_z^2/2 + E_{NF}(w, z))\, f_0 = \mathcal{E}_2\, f_0,
$$

with

$$
E_{NF}(w, z) = a_1\, w^2 + \left(a_2 - a_3\, w \right) z^2 + a_4\, z^4.
$$

Then, for small enough ϵ, there exists an eigenvalue $\mathcal{E}(\epsilon)$ of $H_1(\epsilon)$ which satisfies

$$
\mathcal{E}(\epsilon) = E_0 + \epsilon^2 \mathcal{E}_2 + O(\epsilon^\xi),
$$

for some $\xi > 2$ as $\epsilon \to 0$.

Remarks   1.   At this level of approximation, it is not necessary to require the eigenvector Φ to satisfy condition (2.11) or to require $h(\epsilon, W, Z)$ be real symmetric.
2.   We have stated our results for the electronic ground state, but the analogous results would be true for any non-degenerate state that had the same type of dependence on ϵ.

Proof: In the course of the proof, we denote all generic non-negative constants by the same symbol c.
    Our candidate for the construction of a quasimode is

$$
\Psi_Q(\epsilon, W, Z) = F(W/\epsilon^{\delta_1})\, F(Z/\epsilon^{\delta_2})\, f_0(W/\epsilon, Z/\sqrt{\epsilon})\, \Phi(W, Z),
\tag{3.7}
$$

where $F : \mathbb{R} \to [0, 1]$ is a smooth, even cutoff function supported on $[-2, 2]$ which is equal to 1 on $[-1, 1]$. One should expect the introduction of these cutoffs not to affect the expansion at any finite order because the eigenvectors of $H_1(\epsilon)$ are localized near the

minimum of $E_1(\epsilon, W, Z)$. Thus, the properties of the electronic Hamiltonian for large values (W, Z) should not matter. The choice of a different cutoff for each variable is required because these variables have different scalings in ϵ. We determine the precise values of the positive exponents δ_1 and δ_2 in the course of the proof. We also use the notation

$$\mathcal{F}(\epsilon, W, Z) \quad = \quad F(W/\epsilon^{\delta_1}) \; F(Z/\epsilon^{\delta_2}). \tag{3.8}$$

We first estimate the norm of Ψ_Q.

$$\|\Psi_Q\|^2 \quad = \quad \int_{\mathbb{R}^2} \; |\mathcal{F}(\epsilon, W, Z) \; f_0(W/\epsilon, Z/\sqrt{\epsilon})|^2 \; \|\Phi(W, Z)\|^2_{\mathcal{H}_{\mathrm{el}}}$$

$$= \quad \int_{\mathbb{R}^2} \; |f_0(W/\epsilon, Z/\sqrt{\epsilon})|^2 \; dW \, dZ$$

$$- \int_{\mathbb{R}^2} \; (1 - \mathcal{F}^2(\epsilon, W, Z)) \; |f_0(W/\epsilon, Z/\sqrt{\epsilon})|^2 \; dW \, dZ.$$

The first term of the last expression equals $\epsilon^{3/2}$, by scaling, since f_0 is normalized. If $\delta_1 < 1$ and $\delta_2 < 1/2$, the negative of the second term is bounded above by

$$\int_{\substack{|W| \geq \epsilon^{\delta_1} \\ |Z| \geq \epsilon^{\delta_2}}} \; |f_0(W/\epsilon, Z/\sqrt{\epsilon})|^2 \; dW \, dZ$$

$$= \quad \epsilon^{3/2} \int_{\substack{|w| \geq \epsilon^{1-\delta_1} \\ |z| \geq \epsilon^{1/2-\delta_2}}} \; e^{-2a(|w|+|z|)} \; e^{2a(|w|+|z|)} \; |f_0(w, z)|^2 \; dw \, dz$$

$$\leq \quad \epsilon^{3/2} \; e^{-2a(1/\epsilon^{(1-\delta_1)}+1/\epsilon^{(1-\delta_2)})} \; \|e^{a(|\cdot|+|\cdot|)} f_0\|^2$$

$$= \quad O(\epsilon^\infty),$$

since $f_0 \in D(e^{a\langle(W,Z)\rangle})$. Hence,

$$\|\Psi_Q\| \quad = \quad \epsilon^{3/4} \; (1 + O(\epsilon^\infty)), \quad \text{where the } O(\epsilon^\infty) \text{ correction is non-positive.} \tag{3.9}$$

Next we compute

$$(H_1(\epsilon) - (E_0 + \epsilon^2 \mathcal{E}_2)) \; \Psi_Q(\epsilon, W, Z)$$
$$= \quad S(\epsilon, W, Z) \; f_0(w, z)|_{W,Z} \; \mathcal{F}(\epsilon, W, Z) \; \Phi(W, Z)$$
$$- \left(\left(\frac{\epsilon^4}{2} \partial_W^2 + \frac{\epsilon^3}{2} \partial_Z^2 \right) \mathcal{F}(\epsilon, W, Z) \; \Phi(W, Z) \right) \; f_0(w, z)|_{W,Z}, \tag{3.10}$$
$$- \quad \epsilon^3 \; (\partial_w f_0(w, z)|_{W,Z}) \; \partial_W(\mathcal{F}(\epsilon, W, Z)\Phi(W, Z))$$
$$- \quad \epsilon^{5/2} \; (\partial_z f_0(w, z)|_{W,Z}) \; \partial_Z(\mathcal{F}(\epsilon, W, Z)\Phi(W, Z)),$$

where we have introduced the shorthand $f_0(w, z)|_{W,Z} = f_0(W/\epsilon, Z/\sqrt{\epsilon})$ and used the identity

$$\tilde{E}(\epsilon, W, Z) \; - \; \epsilon^2 \, E_{NF}(W/\epsilon, Z/\sqrt{\epsilon}) \; \equiv \; 0.$$

Also

$$\partial_W \mathcal{F}(\epsilon, W, Z) \;=\; \frac{1}{\epsilon^{\delta_1}} \; F'(W/\epsilon^{\delta_1}) \; F(Z/\epsilon^{\delta_2})$$

$$\partial_Z \mathcal{F}(\epsilon, W, Z) \;=\; \frac{1}{\epsilon^{\delta_2}} \; F(W/\epsilon^{\delta_1}) \; F'(Z/\epsilon^{\delta_2})$$

and, by assumption, $\|\partial_W^\mu \partial_Z^\nu \Phi(W, Z)\|_{\mathcal{H}_{\mathrm{el}}}$ is continuous and of order ϵ^0 in a neighborhood of the origin, for $\mu + \nu \leq 2$. Therefore,

$$
\begin{aligned}
\sup_{\mathbb{R}^2} \;\; \| \, \partial_W \left(\mathcal{F}(\epsilon, W, Z) \Phi(W, Z) \right) \|_{\mathcal{H}_{\mathrm{el}}} \;&\leq\; \frac{c}{\epsilon^{\delta_1}} \\[4pt]
\sup_{\mathbb{R}^2} \;\; \| \, \partial_Z \left(\mathcal{F}(\epsilon, W, Z) \Phi(W, Z) \right) \|_{\mathcal{H}_{\mathrm{el}}} \;&\leq\; \frac{c}{\epsilon^{\delta_2}} \\[4pt]
\sup_{\mathbb{R}^2} \;\; \| \, \partial_W^2 \left(\mathcal{F}(\epsilon, W, Z) \Phi(W, Z) \right) \|_{\mathcal{H}_{\mathrm{el}}} \;&\leq\; \frac{c}{\epsilon^{2\delta_1}} \\[4pt]
\sup_{\mathbb{R}^2} \;\; \| \, \partial_Z^2 \left(\mathcal{F}(\epsilon, W, Z) \Phi(W, Z) \right) \|_{\mathcal{H}_{\mathrm{el}}} \;&\leq\; \frac{c}{\epsilon^{2\delta_2}},
\end{aligned}
\tag{3.11}
$$

where all vectors are supported in $\{ (W, Z) \,:\, |W| \leq 2/\epsilon^{\delta_1}, |Z| \leq 2/\epsilon^{\delta_2} \}$. Each of these vectors appears in (3.10), multiplied by one of the scalar functions $f_0(w, z)|_{W,Z}$, $(\partial_w f_0(w, z))|_{W,Z}$, or $(\partial_z f_0(w, z))|_{W,Z}$. In turn, each of these functions belongs to $L^2(\mathbb{R}^2)$ by Proposition 3.2, and each one has norm of order $\epsilon^{3/4}$ because of scaling, *e.g.*,

$$\left(\int_{\mathbb{R}^2} |\, (\partial_w f_0)(W/\epsilon, \, Z/\sqrt{\epsilon}) \,|^2 \; dW \, dZ \right)^{1/2} \;=\; \epsilon^{3/4} \, \| \, \partial_w f_0 \, \|_{L^2(\mathbb{R}^2)}.$$

Therefore, the norms of the last three vectors in (3.10) are of order $\epsilon^{3/4}$ times the corresponding power of ϵ stemming from (3.11).

We now estimate the norm of the term that arises from the error term S. From our hypothesis on the behavior of S, we have

$$
\begin{aligned}
\| \, S \, \mathcal{F} \, f_0 \, \Phi \, \|^2 \;&=\; \int_{\substack{|W| \leq 2/\epsilon^{\delta_1} \\ |Z| \leq 2/\epsilon^{\delta_2}}} \; |f_0(W/\epsilon, \, Z/\sqrt{\epsilon}) \, S(W, Z)|^2 \; dW \, dZ \\[6pt]
&\leq\; c \sum_{\alpha + \beta \geq 3} \int_{\substack{|W| \leq 2/\epsilon^{\delta_1} \\ |Z| \leq 2/\epsilon^{\delta_2}}} \; |f_0(W/\epsilon, \, Z/\sqrt{\epsilon})|^2 \, \left| W^\alpha Z^{2\beta} \right|^2 \; dW \, dZ \\[6pt]
&\leq\; c \sum_{\alpha + \beta \geq 3} \epsilon^{2(\alpha \delta_1 + 2\beta \delta_2)} \int_{\mathbb{R}^2} \; |f_0(W/\epsilon, \, Z/\sqrt{\epsilon})|^2 \; dW \, dZ \\[6pt]
&=\; c \sum_{\alpha + \beta \geq 3} \epsilon^{2(\alpha \delta_1 + 2\beta \delta_2)} \, \epsilon^{3/2},
\end{aligned}
$$

where the sums are finite.

Collecting these estimates and inserting the allowed values of α and β, we obtain

$$\| \, (H_1(\epsilon) - (E_0 + \epsilon^2 \mathcal{E}_2)) \; \Psi_Q \, \|$$

$$\leq\; c \, \epsilon^{3/4} \left(\epsilon^{3\delta_1} + \epsilon^{2(\delta_1 + \delta_2)} + \epsilon^{\delta_1 + 4\delta_2} + \epsilon^{6\delta_2} + \epsilon^{4 - 2\delta_1} + \epsilon^{3 - 2\delta_2} + \epsilon^{3 - \delta_1} + \epsilon^{5/2 - \delta_2} \right).$$

We further note that $\delta_1 < 1$ and $\delta_2 < 1/2$ imply $\epsilon^{4-2\delta_1} \ll \epsilon^{3-\delta_1}$ and $\epsilon^{3-2\delta_2} \ll \epsilon^{5/2-\delta_2}$. This, together with (3.9), shows that for small enough ϵ,

$$\frac{\| \left(H_1(\epsilon) - (E_0 + \epsilon^2 \mathcal{E}_2)\right) \Psi_Q \|}{\| \Psi_Q \|} \quad \leq \quad c \, \left(\epsilon^{3\delta_1} + \epsilon^{2(\delta_1+\delta_2)} + \epsilon^{\delta_1+4\delta_2} + \epsilon^{6\delta_2} + \epsilon^{3-\delta_1} + \epsilon^{5/2-\delta_2}\right)$$

We still must show that all terms in the parenthesis above can be made asymptotically smaller than ϵ^2. This can be done if there exist choices of δ_1 and δ_2 such that all exponents in the parenthesis above are strictly larger than 2. The inequalities to be satisfied are

$$0 < \delta_1 < 1, \quad \delta_1 > 2/3, \quad \delta_1 + \delta_2 > 1, \quad 0 < \delta_2 < 1/2, \quad \delta_2 > 1/3, \quad \delta_1 + 4\delta_2 > 2.$$

Satisfying these is equivalent to satisfying

$$\begin{cases} 2/3 < \delta_1 < 1 \\ 1/3 < \delta_2 < 1/2 \end{cases}$$

which defines the set of allowed values. The best value,

$$\xi \quad = \quad \max_{\substack{0<\delta_1<1 \\ 0<\delta_2<1/2}} \min \left\{ 3\delta_1, \; 2(\delta_1 + \delta_2), \; \delta_1 + 4\delta_2, \; 6\delta_2, \; 3 - \delta_1, \; 5/2 - \delta_2 \right\} \quad > \quad 0,$$

is obtained by straighforward optimization and is given by $\xi = 15/7$, obtained for $5/7 < \delta_1 < 6/7$ and $\delta_2 = 5/14$. With such a choice, there exists an eigenvalue $\mathcal{E}(\epsilon)$ of $H_1(\epsilon)$ that satisfies

$$\mathcal{E}(\epsilon) \quad = \quad E_0 \; + \; \epsilon^2 \mathcal{E}_2(\epsilon) \; + \; O(\epsilon^\xi),$$

with $\xi = 2 + 1/7$. $\blacksquare$

We now turn to the construction of a complete asymptotic expansion for the energy level $\mathcal{E}(\epsilon)$ of $H_1(\epsilon)$, as $\epsilon \to 0$.

Theorem 3.7 *Assume the hypotheses of Theorem 3.6 with the additional condition that $h(\epsilon, W, Z)$ on $\mathcal{H}_{el}$ is C^∞ in the strong resolvent sense in the variables (ϵ, W, Z). Then the energy level $\mathcal{E}(\epsilon)$ of $H_1(\epsilon)$ admits a complete asymptotic expansion in powers of $\epsilon^{1/2}$. The same conclusion is true for the corresponding quasimode eigenvector.*

Proof Our candidate for the quasimode is again the formal expansion (2.9) truncated at order $\epsilon^{N/2}$ and multiplied by the cutoff function (3.8), *i.e.*,

$$\Psi_Q(\epsilon, W, Z) \quad = \quad \mathcal{F}(\epsilon, W, Z) \; \sum_{j=0}^{N} \epsilon^{j/2} \, \psi_{j/2}(W, Z, W/\epsilon, Z/\sqrt{\epsilon}).$$

We shall determine $\psi_{j/2}$ and $T_{j/2}$ in (2.8) explicitly, but first we introduce some notation for certain Taylor series. Expanding in powers of $\epsilon^{1/2}$, we write

$$\begin{aligned} T_{j/2}(W, Z) \; &- \; T_{j/2}(\epsilon w, \epsilon^{1/2} z) \\ &= T_{j/2}(W, Z) - T_{j/2}(0,0) - \epsilon^{1/2} \partial_Z T_{j/2}(0,0) \\ &\quad + \epsilon \left(\partial_W T_{j/2}(0,0)w + \partial_{Z^2} T_{j/2}(0,0)w^2/2\right) + \cdots \\ &\equiv T_{j/2}(W, Z) \; - \; T_{j/2}(0,0) \; + \; \sum_{k=1}^{\infty} \tau_{j/2}^{(k/2)}(w, z) \, \epsilon^{k/2}. \end{aligned}$$

Next, our hypotheses imply that the function $S(\epsilon, W, Z)$ in (3.5)

$$E_1(\epsilon, W, Z) \quad = \quad E_0 \; + \; \tilde{E}(\epsilon, W, , Z) \; + \; S(\epsilon, W, Z)$$

is C^∞ in (ϵ, W, Z). Using (3.6), we write

$$E_1(\epsilon, \, \epsilon w, \, \epsilon^{1/2} z) \quad = \quad E_0 \; + \; \epsilon^2 \, E_{NF}(w, z) \; + \; \sum_{m \geq 6}^{\infty} \epsilon^{m/2} \, S_{m/2}(w, z).$$

Note Because we have assumed $E_1(\epsilon, W, Z)$ is even in Z, $S_{m/2}(w, z) = 0$ when m is odd, but the notation is somewhat simpler if we include these terms.

We use this notation and substitute the formal series (2.9) and (2.10) into the eigenvalue equation (2.7), with H_2 given by (2.8). For orders $n/2$ with $n \leq 4$, we find exactly what we obtained in Section 2. When $n \geq 5$, we have to solve

$$
\begin{aligned}
&[h(\epsilon, \, W, \, Z) - E_1(\epsilon, \, W, \, Z)] \; \psi_{n/2} \\
&\quad + E_{NF}(w,z)\psi_{(n-4)/2} + S_{6/2}(w,z)\psi_{(n-6)/2} + S_{7/2}(w,z)\psi_{(n-7)/2} + \cdots + S_{n/2}(w,z)\psi_0 \\
&\quad + (T_{\frac{n}{2}}(W,Z) - T_{\frac{n}{2}}(0,0))\psi_0 - \tau_{\frac{n-1}{2}}^{(\frac{1}{2})}(w,z)\psi_0 - \tau_{\frac{n-2}{2}}^{(\frac{2}{2})}(w,z)\psi_0 - \cdots - \tau_{\frac{6}{2}}^{(\frac{n-6}{2})}(w,z)\psi_0 \\
&\quad + (T_{\frac{n-1}{2}}(W,Z) - T_{\frac{n-1}{2}}(0,0))\psi_{1/2} - \tau_{(n-2)/2}^{(1/2)}(w,z)\psi_{1/2} - \cdots - \tau_{\frac{6}{2}}^{(\frac{n-7}{2})}(w,z)\psi_{1/2} \\
&\qquad\qquad \vdots \\
&\quad + (T_{\frac{7}{2}}(W,Z) - T_{\frac{7}{2}}(0,0))\psi_{\frac{n-7}{2}} - \tau_{\frac{6}{2}}^{(\frac{1}{2})}(w,z)\psi_{(n-7)/2} \\
&\quad + (T_{\frac{6}{2}}(W,Z) - T_{\frac{6}{2}}(0,0))\psi_{(n-6)/2} \\
&\quad - \frac{1}{2}\Delta_{w,z}\psi_{(n-4)/2} - \partial_{Z,z}^2 \psi_{(n-5)/2} - \partial_{W,w}^2 \psi_{(n-6)/2} - \frac{1}{2}\partial_{Z,Z}^2 \psi_{(n-6)/2} - \frac{1}{2}\partial_{W,W}^2 \psi_{(n-8)/2} \\
&\quad = \mathcal{E}_2 \, \psi_{(n-4)/2} \; + \; \mathcal{E}_{5/2} \, \psi_{(n-5)/2} \; + \; \cdots \; + \; \mathcal{E}_{n/2}\psi_0,
\end{aligned}
$$
$$(3.12)$$

with the understanding that the quantities S, T and τ that appear with indices lower than those allowed in their definitions are equal to zero.

We solve (3.12 by induction on n. We assume that

$$
\begin{cases}
\mathcal{E}_{j/2}, \quad \psi_{j/2}^{\perp}(W, Z, w, z), \quad T_{j/2}(W, Z) & \text{for} \quad j \leq n - 1, \qquad \text{and} \\
f_{j/2}(W, Z, w, z) & \text{for} \quad j \leq n - 5
\end{cases}
$$

have already been determined, with $f_{j/2}^{\parallel}(W, Z, w, z) = 0$, for $j \geq 1$.

We project (3.12) into the $\Phi(W, Z)$ direction and the orthogonal direction in the electronic Hilbert space to obtain two equations that must each be solved.

First, we take the scalar product of (3.12) with $\Phi(W, Z)$ in the electronic Hilbert space to obtain

$$E_{NF}(w, z)f_{(n-4)/2} + S_{6/2}(w, z)f_{(n-6)/2} + S_{7/2}(w, z)f_{(n-7)/2} + \cdots + S_{n/2}(w, z)f_0$$

$$+ (T_{\frac{n}{2}}(W, Z) - T_{\frac{n}{2}}(0, 0))f_0 - \tau_{\frac{n-1}{2}}^{(\frac{1}{2})}(w, z)f_0 - \tau_{\frac{n-2}{2}}^{(\frac{2}{2})}(w, z)f_0 - \cdots - \tau_{\frac{6}{2}}^{(\frac{n-6}{2})}(w, z)f_0$$

$$+ (T_{\frac{n-1}{2}}(W, Z) - T_{\frac{n-1}{2}}(0, 0))f_{1/2} - \tau_{(n-2)/2}^{(1/2)}(w, z)f_{1/2} - \cdots - \tau_{\frac{6}{2}}^{(\frac{n-7}{2})}(w, z)f_{1/2}$$

$$\vdots$$

$$+ (T_{\frac{7}{2}}(W, Z) - T_{\frac{7}{2}}(0, 0))\ f_{\frac{n-7}{2}} - \tau_{\frac{6}{2}}^{(\frac{1}{2})}(w, z)\ f_{(n-7)/2}$$

$$+ (T_{\frac{6}{2}}(W, Z) - T_{\frac{6}{2}}(0, 0))\ f_{(n-6)/2}$$

$$- \frac{1}{2}\,\Delta_{w,z}f_{(n-4)/2} - \langle\Phi(W, Z), \partial_{Z,z}^2\psi_{(n-5)/2}\rangle_{\mathcal{H}_{el}} - \langle\Phi(W, Z), \partial_{W,w}^2\psi_{(n-6)/2}\rangle_{\mathcal{H}_{el}}$$

$$- \frac{1}{2}\,\langle\Phi(W, Z), \partial_{Z,Z}^2\psi_{(n-6)/2}\rangle_{\mathcal{H}_{el}} - \frac{1}{2}\,\langle\Phi(W, Z), \partial_{W,W}^2\psi_{(n-8)/2}\rangle_{\mathcal{H}_{el}}$$

$$= \mathcal{E}_2\ f_{(n-4)/2} + \mathcal{E}_{5/2}\ f_{(n-5)/2} + \cdots + \mathcal{E}_{n/2}\ f_0.$$

$$(3.13)$$

We further project (3.13) into the f_0 direction and the orthogonal direction in $L^2(I\!R^2)$ to obtain two equations that must each be solved.

We take the scalar product of (3.13) with f_0 in $L^2(\mathbb{R}^2)$. Using $f_{j/2}^\| = 0$ for $j \geq 1$ and $(-\frac{1}{2}\Delta_{w,z} + E_{NF}(w, z))\,f_0 = \mathcal{E}_2\,f_0$, we obtain

$$\mathcal{E}_{n/2} = T_{\frac{n}{2}}(W, Z) - T_{\frac{n}{2}}(0, 0)$$

$$+ \sum_{j=6}^{n} \langle\, f_0,\, S_{j/2}\ f_{(j-6)/2}\,\rangle_{L^2(\mathbb{R}^2)} \sum_{k=0}^{n-7}\sum_{j=1}^{n-6-k} \langle\, f_0,\, \tau_{j/2}^{(n-(j+k))/2)}\ f_{k/2}\,\rangle_{L^2(\mathbb{R}^2)}$$

$$- \Big\langle\, f_0,\, \Big\{\langle\,\Phi(W, Z), \partial_{Z,z}^2\psi_{(n-5)/2}\rangle_{\mathcal{H}_{el}} + \langle\Phi(W,Z), \partial_{W,w}^2\psi_{(n-6)/2}\rangle_{\mathcal{H}_{el}}$$

$$+ \frac{1}{2}\langle\Phi(W, Z), \partial_{Z,Z}^2\psi_{(n-6)/2}\rangle_{\mathcal{H}_{el}} + \frac{1}{2}\ \langle\Phi(W, Z), \partial_{W,W}^2\psi_{(n-8)/2}\rangle_{\mathcal{H}_{el}}\Big\}\Big\rangle_{L^2(\mathbb{R}^2)}.$$

$$(3.14)$$

We can solve this equation for $\mathcal{E}_{n/2}$ if the right hand side is independent of (W, Z). This will be true, if we choose

$$T_{\frac{n}{2}}(W, Z) = -\sum_{j=6}^{n} \langle\, f_0,\, S_{j/2}\ f_{(j-6)/2}\,\rangle_{L^2(\mathbb{R}^2)} + \sum_{k=0}^{n-7}\sum_{j=1}^{n-6-k} \langle\, f_0,\, \tau_{j/2}^{(n-(j+k))/2)}\ f_{k/2}\,\rangle_{L^2(\mathbb{R}^2)}$$

$$+ \Big\langle\, f_0,\, \Big\{\langle\Phi(W, Z), \partial_{Z,z}^2\psi_{(n-5)/2}\rangle_{\mathcal{H}_{el}} + \langle\Phi(W, Z), \partial_{W,w}^2\psi_{(n-6)/2}\rangle_{\mathcal{H}_{el}}$$

$$+ \frac{1}{2}\langle\Phi(W, Z), \partial_{Z,Z}^2\psi_{(n-6)/2}\rangle_{\mathcal{H}_{el}} + \frac{1}{2}\ \langle\Phi(W, Z), \partial_{W,W}^2\psi_{(n-8)/2}\rangle_{\mathcal{H}_{el}}\Big\}\Big\rangle_{L^2(\mathbb{R}^2)}$$

We then are forced to take

$$\mathcal{E}_{n/2} = - T_{\frac{n}{2}}(0, 0).$$

The first non-zero $T_{j/2}(W, Z)$ is

$$T_{6/2}(W, Z) = \frac{1}{2} \langle \Phi(W, Z), \partial_Z^2 \Phi(W, Z) \rangle_{\mathcal{H}_{el}} - \langle f_0, S_3 f_0 \rangle_{L^2(\mathbb{R}^2)}. \tag{3.15}$$

So,

$$\mathcal{E}_3 = \langle f_0, S_3 f_0 \rangle_{L^2(\mathbb{R}^2)} - \frac{1}{2} \langle \Phi(0, 0), (\partial_Z^2 \Phi)(0, 0) \rangle_{\mathcal{H}_{el}}.$$

We next equate the components on the two sides of (3.13) that are orthogonal to f_0 in $L^2(\mathbb{R}^2)$. The resulting equation can be solved by applying the reduced resolvent $r_{NF}(\mathcal{E}_2)$, which is the inverse of the restriction of $(-\frac{1}{2}\Delta_{w,z} + E_{NF} - \mathcal{E}_2)$ to the subspace orthogonal to f_0. We thus obtain

$$
\begin{aligned}
f_{(n-4)/2} = r_{NF}(\mathcal{E}_2) \Bigg[&\sum_{j=1}^{n-5} \mathcal{E}_{(n-j)/2} f_{j/2}^{\perp} - \sum_{j=6}^{n} (S_{j/2}(w, z) f_{(j-6)/2})^{\perp} \\
+ &\sum_{k=0}^{n-7} \sum_{j=1}^{n-6-k} (\tau_{j/2}^{(n-(j+k))/2}(w, z) f_{k/2})^{\perp} + \sum_{j=1}^{n-6} (T_{(n-j)/2}(0,0) - T_{(n-j)/2}(W, Z)) f_{j/2}^{\perp} \\
+ &\langle \Phi(W, Z), \partial_{Z,z}^2 \Psi_{(n-5)/2} \rangle_{\mathcal{H}_{el}}^{\perp} + \langle \Phi(W, Z), \partial_{W,w}^2 \Psi_{(n-6)/2} \rangle_{\mathcal{H}_{el}}^{\perp} \\
+ &\langle \Phi(W, Z), \partial_{Z,Z}^2 \Psi_{(n-6)/2} \rangle_{\mathcal{H}_{el}}^{\perp} + \langle \Phi(W, Z), \partial_{W,W}^2 \Psi_{(n-8)/2} \rangle_{\mathcal{H}_{el}}^{\perp} \Bigg],
\end{aligned}
$$

This solution has $f_{(n-4)/2} = f_{(n-4)/2}^{\perp}$ orthogonal to f_0, as claimed in Section 2. The first non-trivial $f_{j/2}$, for $j \geq 1$ is

$$f_1^{\perp}(W, Z, w, z) = - r_{NF}(\mathcal{E}_2) (S_3(w, z) f_0(w, z))^{\perp}. \tag{3.16}$$

Next, we equate the components of (3.12) that are orthogonal to $\Phi(W, Z)$ in $\mathcal{H}_{el}$. We solve the resulting equation for $\psi_{n/2}^{\perp}$ by applying the reduced resolvent $r(W, Z)$ of $h(\epsilon, W, Z)$ at $E_1(\epsilon, W, Z)$. This yields

$$
\begin{aligned}
\psi_{n/2}^{\perp} = r(W, Z) \Bigg[&\sum_{j=1}^{n-5} \mathcal{E}_{(n-j)/2} \psi_{j/2}^{\perp} - \sum_{j=6}^{n} S_{j/2}(w, z) \psi_{(j-6)/2}^{\perp} \\
+ &\sum_{k=0}^{n-7} \sum_{j=1}^{n-6-k} \tau_{j/2}^{(n-(j+k))/2}(w, z) \psi_{k/2}^{\perp} + \sum_{j=1}^{n-6} (T_{(n-j)/2}(0,0) - T_{(n-j)/2}(W, Z)) \psi_{j/2}^{\perp} \\
+ &(\partial_{Z,z}^2 \psi_{(n-5)/2})^{\perp} + ((\partial_{W,w}^2 + \partial_{Z,Z}^2) \psi_{(n-6)/2})^{\perp} \\
+ &(\partial_{W,W}^2 \psi_{(n-8)/2})^{\perp} - (\frac{1}{2}\Delta_{w,z} + E_{NF}(w, z) - \mathcal{E}_2) \psi_{(n-4)/2}^{\perp} \Bigg].
\end{aligned}
$$

$$\tag{3.17}$$

The first non-zero component $\psi_{j/2}^{\perp}$ with $j \geq 0$, is

$$\psi_{5/2}^{\perp}(W, Z, w, z) \quad = \quad (\partial_z f_0)(w, z)\, r(W, Z)\, (\partial_Z \Phi)(W, Z). \tag{3.18}$$

Finally, Proposition 3.9 below shows that each $\psi_{j/2}$ in this expansion belongs to $D(e^{a(|W|/\epsilon + |Z|/\sqrt{\epsilon})})$. As a result, whenever a derivative acts on the cutoff, it yields a contribution whose L^2 norm is exponentially small. This way, we can neglect such terms. For example

$$(\partial_W \mathcal{F}(\epsilon, W, Z))\, \psi_{j/2}(W, Z, W/\epsilon, Z/\sqrt{\epsilon})$$
$$= \; \epsilon^{-\delta_1}\, F'(W/\epsilon^{\delta_1})\, F(Z/\epsilon^{\delta_2})\, \psi_{j/2}(W, Z, W/\epsilon, Z/\sqrt{\epsilon}).$$

The square of the L^2 norm of this term is bounded by a constant times

$$\epsilon^{-2\delta_1} \int_{|W|/\epsilon^{\delta_1} \geq 1,\, |Z|/\epsilon^{\delta_2} \leq 2} |\psi_{j/2}(W, Z, W/\epsilon, Z/\sqrt{\epsilon})|^2$$
$$e^{2a(|W|/\epsilon + |Z|/\sqrt{\epsilon})} e^{-2a(1/\epsilon^{1-\delta_1})} dW\, dZ \; = \; O(\epsilon^{\infty}).$$

Thus, we have constructed the non-zero quasimode (3.7) that satisfies the eigenvalue equation up to an arbitrary high power of $\epsilon^{1/2}$. ∎

The proof of Proposition 3.9 relies on the following lemma.

Lemma 3.8 *Let V be a polynomial that is bounded below, such that the spectrum of $H = -\frac{1}{2}\Delta + V$ purely discrete. Let $\varphi \in C^{\infty}(\mathbb{R}^n)$ satisfy $D^{\alpha}\varphi \in D(e^{a\langle x \rangle})$, for all $\alpha \in \mathbf{N}^n$ and any $a > 0$. If $R(\lambda)$ denotes the resolvent of H, then $D^{\alpha} R(\lambda)\varphi \in D(e^{a\langle x \rangle})$ for all $\alpha \in \mathbf{N}^n$ and all λ in $\rho(H)$. The same is true for $D^{\alpha} r(\mathcal{E})\varphi$, where $r(\mathcal{E})$ is the reduced resolvent at $\mathcal{E}$.*

Proof We first note that elliptic regularity implies that the resolvent $R(\lambda)$ maps C^{∞} functions to C^{∞} functions. Next, applied to smooth functions in L^2, we have the identity

$$[\,\partial_{x_j},\, R(\lambda)\,] \; = \; R(\lambda)\, (\partial_{x_j} V)\, R(\lambda).$$

We claim that the operators on the two sides of this equation have bounded extensions to all of L^2. To see this, note that $D^{\beta}V$ is relatively bounded with respect to V for any $\beta \in \mathbf{N}^n$, because V is a polynomial. Furthermore, since $H \geq V$, we see that $D^{\beta}V$ is relatively bounded with respect to H, which implies the claim. Hence, for φ as in the lemma, we have

$$\partial_{x_j} R(\lambda)\, \psi \; = \; R(\lambda)\, \partial_{x_j}\, \varphi \; + \; R(\lambda)\, (\partial_{x_j} V)\, R(\lambda)\, \varphi. \tag{3.19}$$

The first term on the right hand side of this equation belongs to $D(e^{a\langle x \rangle})$ since $R(\lambda)$ maps exponentially decaying functions to exponentially decaying functions (see Corollary 3.4). The same is true for the second term, with a possible arbitrarily small loss on the

exponential decay rate, due to the polynomial growth of $\partial_{x_j} V$. This provides the starting point for an induction on the order of the derivative that appears in the conclusion of the lemma.

We now assume that for some $\alpha \in \mathbf{N}^n$, $D^\alpha R(z)\varphi$ is a linear combination of smooth functions of the form $R(z)(D^{\gamma_1}V)R(z)\cdots R(z)(D^{\gamma_{j-1}}V)R(z)D^{\gamma_j}\varphi$ all of which belong to $D(e^{a\langle x\rangle})$, for any $a > 0$. We assume every γ that occurs here has $|\gamma| \leq |\alpha|$. Then $\partial_{x_j} D^\alpha R(z)\varphi$ is a linear combination of elements of the form

$$\partial_{x_j}(R(z)(D^{\gamma_1}V)R(z)\cdots R(z)(D^{\gamma_{j-1}}V)R(z)D^{\gamma_j}\varphi)$$

Applying (3.19) successively, we see that the structure is preserved. Since all $D^{\gamma_k}V$ are polynomial, Corollary 3.4 implies the result.

The statement for the reduced resolvent follows from the representation (3.4). ∎

Proposition 3.9 *Assume the hyptheses of Theorem 3.7. Let $\psi_{j/2}(W, Z, w, z)$ be determined by the construction above, where (W, Z) belongs to a closed neighborhood Ω of the origin and $(w, z) \in I\!\!R^2$. Then $\psi_{j/2}$ is C^∞, and the function*

$$G(w, z) = \sup_{(W,Z)\in\Omega} |\psi_{j/2}(W, Z, w, z)|$$

belongs to $D(e^{a\langle (w,z)\rangle})$.

Proof The hypothesis on the Hamiltonian and the properties of the normal form H_{NF} proven above imply that $\Phi(W, Z)$ and $r(W, Z)$ are smooth, and that $r_{NF}(\mathcal{E}_2)$ maps smooth functions to smooth functions. We also know that the non-degenerate eigenstate f_0 is smooth and belongs to $D(e^{a\langle (w,z)\rangle})$. The smoothness of $\psi_{j/2}(W, Z, w, z)$ follows trivially in $\Omega \times I\!\!R^2$.

Concerning the exponential decay, we observe that the (w, z) dependence of $\psi_{j/2}$ stems from the successive actions of derivatives, reduced resolvents, and multiplications by polynomials in (w, z), acting on the eigenstate f_0. Lemma 3.8 applied in conjunction with Proposition 3.5 shows that the exponential decay properties are preserved under such operations. ∎

4   Technicalities

In this section, we present the proofs of Lemma 3.3 and Proposition 3.5.

Proof of Lemma 3.3 We first note that the hypothesis on p implies $p(x) > 0$ for any $x \in \mathbb{R}^n$, and that

$$e^{-2C|x-y|} \leq p(x)/p(y) \leq e^{2C|x-y|}. \tag{4.1}$$

Let $B_R \in \mathbb{R}^n$ be a ball of radius $R > 0$. We first show that $f \in L^2(B_{R+1})$ and $\Delta f \in L^2(B_{R+1})$ imply $f \in H^2(B_R)$, where

$$H^2(B_R) = \{ f \in L^2(B_R), \ \nabla f \in L^2(B_R), \ \text{and} \ \Delta f \in L^2(B_R) \}.$$

We denote the usual $H^2(B_R)$ norm by $\|\cdot\|_{H^2(B_R)}$. We now show the existence of a constant $K(R) > 0$, which depends only on R, such that

$$\int_{B_R} |\nabla f|^2 \ \leq \ K(R) \int_{B_{R+1}} \left(|\Delta f|^2 + |f|^2 \right). \tag{4.2}$$

Note This estimate does not hold in general if the balls over which one integrates have the same radius.

We set $g = \Delta f$ on B_{R+1} and $g(x) = 0$ if $|x| > R + 1$. We can then decompose $f = f_1 + f_2$ with f_1 and f_2 solutions to

$$\begin{cases} \Delta f_1 = g, & f_1|_{\partial B_{R+3}} = 0 \\[2mm] \Delta f_2 = 0 & |x| \leq R + 1. \end{cases}$$

Thus, $f_1 \in H^2(B_{R+3})$, and there exists a constant $c_1(R)$, which depends only on R, such that

$$\|f_1\|_{H^2(B_{R+3})} \ \leq \ c_1(R) \, \|\Delta f_1\|_{L^2(B_{R+3})} \ = \ c_1(R) \, \|\Delta f\|_{L^2(B_{R+1})}, \tag{4.3}$$

so that

$$\|\nabla f_1\|_{L^2(B_{R+1})} \ \leq \ \|f_1\|_{H^2(B_{R+3})} \ \leq \ c_1(R) \, \|\Delta f\|_{L^2(B_{R+1})}.$$

By the mean value property for harmonic functions, f_2 also satisfies estimate (4.2), for some constant $K_2(R)$ with $\Delta f_2 = 0$ (see *e.g.*, Chapter 8 of [1]). Combining these arguments, we see that for $c_2(R) = c_1(R) + K_2(R)$,

$$\int_{B_R} |\nabla (f_1 + f_2)|^2 \ \leq \ c_2(R) \int_{B_{R+1}} \left(|\Delta f_1|^2 + |f_2|^2 \right) \ \leq \ c_2(R) \int_{B_{R+1}} \left(|\Delta f|^2 + 2(|f|^2 + |f_1|^2) \right).$$

But $\int_{B_{R+1}} |f_1|^2 \ \leq \ \|f_1\|^2_{H^2(B_{R+3})}$, so (4.3) implies that (4.2) holds for some constant $K(R)$.

Because of (4.1), we can insert the weight p into this estimate to establish the existence of another constant $\tilde{K}(R)$, which depends only on R, such that

$$\int_{B_R} p \, |\nabla f|^2 \ \leq \ \tilde{K}(R) \int_{B_{R+1}} p \, \left(|\Delta f|^2 + |f|^2 \right). \tag{4.4}$$

In other words, $p^{1/2} \, \nabla f \in L^2_{loc}$ if $f \in F^2_w$.

A second step consists in showing that $p^{1/2} \, \nabla f$ is in $L^2(\mathbb{R}^n)$ and satisfies (3.3). Let $\chi_R \in C^\infty(\mathbb{R}^n)$ be a truncation function such that $0 \leq \chi_R \leq 1$, with $\chi_R(x) = 1$ if $|x| \leq R$, and $\chi_R(x) = 0$ if $|x| \geq R + 1$. We can take χ_R so that $\|\nabla \chi_R\|_\infty$ is independent of R. Let $f \in F^2_w$, and set $f_R = \chi_R f$. Since $\nabla f_R = \chi_R \nabla f + f \nabla \chi_R$, we see that $\|p^{1/2} \, \nabla f_R\|_{L^2(B_R)} = \|p^{1/2} \, \nabla f\|_{L^2(B_R)}$, and

$$\lim_{R \to \infty} \|p^{1/2} \, (f_R - f)\|_{L^2(\mathbb{R}^n)} \to 0,$$

by Lebesgue dominated convergence. By the same argument with $\Delta f_R = \chi_R \Delta f + f \Delta \chi_R + 2 \nabla \chi_R \nabla f$,

$$\lim_{R \to \infty} \|p^{1/2} \, (\Delta f - (\chi_R \Delta f + f \Delta \chi_R))\|_{L^2(\mathbb{R}^n)} \ = \ 0.$$

We have the estimate $\|p^{1/2}\nabla\chi_R\nabla f\|^2_{L^2(B_{R+1})} \leq c_2 \int_{B_{R+1}\setminus B_R} p^{1/2} |\nabla f|^2$, for some constant c_2, independent of R. We can cover the set $B_{R+1}\setminus B_R$ by a finite set of balls $\{B_1(j)\}_{j=1,\cdots,N(R)}$, of radius 1, centered at points x_j such that $|x_j| = R + 1/2$. In each of these balls $B_1(j)$, we can apply (4.4) (with a constant $\tilde{K}_1$, independent of R), to see that

$$\int_{B_{R+1}\setminus B_R} p\,|\nabla f|^2 \leq c_2\,\tilde{K}_1 \sum_{j=1}^{N(R)} \int_{B_2(j)} p\,(|\Delta f|^2 + |f|^2),$$

where $B_2(j)$ has radius 2 instead of 1. Using $\cup_{j=1}^{N(R)} B_2(j) \subset B_{R+3}\setminus B_{R-3}$, and taking into account that certain points are counted (uniformly) finitely many times in the integral, we eventually obtain

$$\|p^{1/2}\nabla\chi_R\nabla f\|^2_{L^2(\mathbb{R}^n)} \leq c_3 \int_{B_{R+1}\setminus B_R} p\,(|\Delta f|^2 + |f|^2),$$

where c_3 is uniform in R. By the dominated convergence theorem again, this integral goes to zero as R goes to infinity. So, we finally obtain

$$\lim_{R\to\infty} \|p^{1/2}(\Delta f - \Delta f_R))\|_{L^2(\mathbb{R}^n)} = 0.$$

Since f_R belongs to $H^2_c(\mathbb{R}^n)$, the set of compactly supported functions in H^2, we compute

$$\nabla\cdot\left(p\,\bar{f}_R\,\nabla f_R\right) = p\,\bar{f}_R\,\Delta f_R + |\nabla f_R|^2\,p + \bar{f}_R\,\nabla p\,\nabla f_R.$$

Since f_R has compact support, Stokes Theorem and our hypotheses on ∇p show that

$$\int p\,|f_R|^2 = \left| \int \bar{f}_R\,\Delta f_R\,p + \int \bar{f}_R\,\nabla p\,\nabla f_R \right|$$
$$\leq \left(\int |\Delta f_R|^2 p\right)^{1/2}\left(\int |f_R|^2 p\right)^{1/2} + 2C\left(\int |f_R|^2 p\right)^{1/2}\left(\int |\nabla f_R|^2 p\right)^{1/2},$$

or, in other words,

$$\|\nabla f_R\|^2_p \leq \|\Delta f_R\|_w\,\|f_R\|_w + 2C\,\|\nabla f_R\|_w\,\|f_R\|_w.$$

This estimate implies (3.3) for f_R. The right hand side of that estimate has a finite limit as $R\to\infty$ with f in place of f_R on the right hand side. Since

$$\int_{B_R} p\,|\nabla f|^2 \leq \int p\,|\nabla f_R|^2,$$

we deduce that $p\,|\nabla f|^2 \in L^1(\mathbb{R}^n)$ and satisfies (3.3). ∎

Proof of Proposition 3.5 We use the following Paley–Wiener theorem, Theorem IX.13 of [11]:

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

We refer to the conditions on $\widehat{f}$ in this theorem as "the Paley–Wiener conditions."

Since $e^{a|x|}\varphi \in L^2(I\!\!R^n)$ is equivalent to $\varphi \in D(e^{a\langle x\rangle})$, Proposition 3.2 shows that $\widehat{\varphi}$ is analytic everywhere and satisfies the Paley–Wiener conditions. The functions $p \mapsto p_j\,\widehat{\varphi}(p)$ and $p \mapsto \sum_j p_j^2\,\widehat{\varphi}(p)$ also satisfy these conditions.

As a preliminary remark, we note that for any fixed $t \in I\!\!R^n$, there exist $K(t) > \widetilde{K}(t) > 0$ and $R(t) > 0$, such that if $p \in I\!\!R^n$ satisfies $\sum_j p_j^2 \geq R(t)$, then

$$\widetilde{K}(t) \sum_{j=1}^{n} p_j^2 \;\leq\; \left| \sum_{j=1}^{n} (p_j + it_j)^2 \right| \;\leq\; K(t) \sum_{j=1}^{n} p_j^2. \tag{4.5}$$

So, if B_R is a ball of radius R with center at the origin, $-\widehat{\Delta\varphi}$ satisfies

$$\int_{I\!\!R^n \setminus B_{R(t)}} \left(\sum_{j=1}^{n} p_j^2 \right)^2 |\hat{\varphi}(p+it)|^2 \, dp < \infty, \tag{4.6}$$

uniformly for t in compact sets of $I\!\!R^n$.

We now start an induction on the length $|\alpha|$ of the multi-index α in $D^\alpha\varphi$. We first show that $p \mapsto p_j\,p_k\,\widehat{\varphi}(p)$ satisfies the Paley–Wiener conditions for any $j,k \in \{1,\cdots,n\}$. Note that we only need to prove estimates for large values of the $|p_j|$'s. Also, note that if $\sum_{j=1}^{n} p_j^2 \geq R(t) > 1$, there exists a constant $C(t) > 0$ such that

$$|\,(p_j + it_j)\,(p_k + it_k)\,| \;\leq\; C(t) \sum_{j=0}^{n} p_j^2, \tag{4.7}$$

Therefore, (4.6) implies that

$$\int_{I\!\!R^n \setminus B_{R(t)}} |\,(p_j + it_j)\,(p_k + it_k)\,|^2 \, |\widehat{\varphi}(p+it)|^2 \, dp$$

$$\leq\; C^2(t) \int_{I\!\!R^n \setminus B_{R(t)}} \left(\sum_{j=1}^{n} p_j^2 \right)^2 |\widehat{\varphi}(p+it)|^2 \, dp$$

$$<\; \infty,$$

uniformly for t in compact sets of $I\!\!R^n$. Hence, $\partial_{x_j}\partial_{x_k}\varphi \in D(e^{a\langle x\rangle})$ for any $a > 0$.

We next turn to third order derivatives. Consider the derivative of $-\Delta\varphi + (V-\mathcal{E})\varphi = 0$. For any $j \in \{1,\cdots,n\}$,

$$\partial_{x_j} \Delta\varphi \;=\; (\partial_{x_j}V)\varphi \;+\; (V - \mathcal{E})\,\partial_{x_j}\varphi.$$

Since V is a polynomial, Proposition (3.2) shows that $\partial_{x_j}\Delta\varphi \in D(e^{a\langle x\rangle})$, for any $a > 0$. Thus, the function $p \mapsto p_j\,(\sum_{j=0}^{n} p_j^2)\,\widehat{\varphi}(p)$ satisfies the Paley–Wiener conditions.

Consider now any triple of indices j,k,l. For $\sum_{j=0}^{n} p_j^2 \geq R(t)$, we have

$$|\,(p_j + it_j)\,(p_k + it_k)\,(p_l + it_l)\,| \;\leq\; C(t)\,|p_j + it_j| \sum_{j=0}^{n} p_j^2.$$

Hence, using this estimate with (4.6), we deduce that

$$\int_{\mathbb{R}^n \setminus B_{R(t)}} |\,(p_j + it_j)\,(p_k + it_k)\,(p_l + it_l)\,|^2 \ |\widehat{\varphi}(p + it)|^2 \ dp$$

$$\leq \ C^2(t) \int_{\mathbb{R}^n \setminus B_{R(t)}} |p_j + it_j|^2 \left(\sum_{j=1}^{n} p_j^2\right)^2 \ |\widehat{\varphi}(p + it)|^2 \ dp$$

$$< \ \infty,$$

uniformly for t in compact sets of $\mathbb{R}^n$. Therefore, the Paley–Wiener Theorem asserts that $\partial_{x_j}\,\partial_{x_k}\,\partial_{x_l}\,\varphi \in D(e^{a\langle x\rangle})$, for any $a > 0$.

We now proceed by assuming $D^\beta\varphi \in D(e^{a\langle x\rangle})$, for any $a > 0$ and any β, such that $|\beta| \leq m$. Let α have $|\alpha| = m+1$. Let $\tilde{\alpha}$ be any multi-index of length $m-1$. Differentiating the eigenvalue equation again, Leibniz's formula yields

$$D^{\tilde{\alpha}}\Delta\varphi \ = \ \sum_{0 \leq \gamma \leq \tilde{\alpha}} C_\gamma^{\tilde{\alpha}} \ \left(D^{\tilde{\alpha}-\gamma}(V - \mathcal{E})\right) \ D^\gamma\varphi, \tag{4.8}$$

where the $C_\gamma^{\tilde{\alpha}}$ are multinomial coefficients. The induction hypothesis and the assumption that V is a polynomial show that $D^{\tilde{\alpha}} \ \Delta\varphi \in L^2(\mathbb{R}^n)$. Therefore, $p \mapsto p^{\tilde{\alpha}} \left(\sum_{j=1}^{n} p_j^2\right) \widehat{\varphi}(p)$ satisfies the Paley–Wiener conditions. In α, there are two indices, α_j and α_k, not necessarily distinct, which are larger or equal to one, such that we can write

$$(p + it)^\alpha \tag{4.9}$$

$$= \ (p_1 + it_1)^{\alpha_1} \cdots (p_j + it_j)^{\alpha_j - 1} \cdots (p_k + it_k)^{\alpha_k - 1} \cdots (p_n + it_n)^{\alpha_n} \ (p_j + it_j) \ (p_k + it_k).$$

Estimating the absolute value of the last two factors by (4.7) and using that $\tilde{\alpha} = (\alpha_1, \cdots, \alpha_j - 1, \cdots, \alpha_k - 1, \cdots, \alpha_n)$ has length $m-1$, we see that $p \mapsto p^\alpha \ \widehat{\varphi}(p)$ satisfies the Paley–Wiener conditions. Hence, $D^\alpha\varphi \in D(e^{a\langle x\rangle})$ for any $a > 0$. ∎

References

[1] Axler, S., Bourdon, P., Ramey, W.: *Harmonic Function Theory*, Springer 2001.

[2] Elghobashi, N. and González, L.: A Theoretical Anharmonic Study of the Infrared Absorption Spectra of FHF^-, FDF^-, OHF^-, and ODF^- Ions. *J. Chem. Phys.* **124**, article 174308 (2006).

[3] Hagedorn, G.A.: High Order Corrections to the Time-Independent Born-Oppenheimer Approximation I: Smooth Potentials. *Ann. Inst. H. Poincaré Sect. A.* **47**, 1–16 (1987).

[4] Hagedorn, G.A. and Joye, A.: A Mathematical Theory for Vibrational Levels Associated with Hydrogen Bonds II: The Non–Symmetric Case. (in preparation).

[5] Hagedorn, G.A. and Toloza, J.H.: Exponentially Accurate Quasimodes for the Time–Independent Born–Oppenheimer Approximation on a One–Dimensional Molecular System. *Int. J. Quantum Chem.* **105**, 463–477 (2005).

[6] Hislop, P. and Sigal, M.: *Introduction to Spectral Theory with Applications to Schrodinger Operators*, Applied Mathematics Sciences, Volume **113**, New York, Springer, 1996.

[7] Hörmander, L.: *Linear Partial Differential Operators*, Berlin, Göttingen, Heidelberg, Springer, 1964.

[8] Kato, T.: *Perturbation Theory for Linear Operators*, Springer, 1980.

[9] Kawaguchi, K. and Hirota, E.: Diode Laser Spectroscopy of the ν_3 and ν_2 Bands of FHF^- in 1300 cm^{-1} Region. *J. Chem. Phys.* **87**, 6838–6841 (1987).

[10] Reed, M. and Simon, B.: *Methods of Modern Mathematical Physics I. Functional Analysis*, New York, London, Academic Press, 1972.

[11] Reed, M. and Simon, B.: *Methods of Modern Mathematical Physics II. Fourier Analysis, Self-Adjointness*, New York, London, Academic Press, 1975.

[12] Reed, M. and Simon, B.: *Methods of Modern Mathematical Physics IV. Analysis of Operators*, New York, London, Academic Press, 1978.

George A. Hagedorn
Department of Mathematics and
Center for Statistical Mechanics and Mathematical Physics
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061-0123, U.S.A.

Alain Joye
Institut Fourier
Unité Mixte de Recherche CNRS-UJF 5582
Université de Grenoble I
BP 74
38402 Saint Martin d'Hères Cedex, France
and
Laboratoire de Physique et Modélisation des Milieux Condensés
UMR CNRS-UJF 5493, Université de Grenoble I
BP 166
38042 Grenoble, France