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High order corrections to the time-independent Born-Oppenheimer approximation. — I. Smooth potentials

by

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ABSTRACT. — We study the bound states of quantum mechanical systems which consist of some particles of large mass and some particles of small mass. We prove that if the potentials are smooth and the large masses are proportional to ε^{-4}, then certain eigenvalues and eigenvectors of the Hamiltonian have asymptotic expansions to arbitrarily high order in powers of ε, as $\varepsilon \searrow 0$. The zeroth through fourth order terms in the expansions for the eigenvalues are those of the well-known Born-Oppenheimer approximation.

RÉSUMÉ. — On étudie les états liés de systèmes quantiques formés de quelques particules de masse élevée et de quelques particules de faible masse. On montre que, si les potentiels sont réguliers et les masses élevées proportionnelles à ε^{-4}, alors certaines valeurs propres et certains vecteurs propres du Hamiltonien admettent des développements asymptotiques à des ordres arbitrairement élevés en ε. Les termes d'ordre zéro à quatre dans les développements des valeurs propres sont ceux de l'approximation bien connue de Born-Oppenheimer.

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§ 1. INTRODUCTION

In 1927, Born and Oppenheimer [1] studied the time independent Schrödinger equation for molecular systems. The central idea of their work was to exploit the fact that the ratio ε^4 of the electron mass to the nuclear mass was small. They formally showed that molecular energy levels had asymptotic expansions through the fourth order in ε, and that the non-zero terms in the expansions had direct physical interpretations.

In the present paper we prove that these expansions can be extended to arbitrarily high order in the çase of smooth potentials. Unfortunately, the high order terms do not have simple physical interpretations. They involve complicated couplings between motions of the large mass and small mass particles.

The physical intuition behind the Born-Oppenheimer approximation is the following: The small mass electrons move very rapidly compared to the large mass nuclei. As a result, the adiabatic approximation fairly accurately describes the electron motion, i. e., on a short time scale, the electrons hardly notice the motion of the nuclei, and on a large time scale, they rapidly adjust their motion in response to the changing positions of the nuclei. In addition, the nuclear motion is approximately semiclassical due to the large nuclear masses.

The disparity between the periods for the electronic and nuclear motions leads to a separation in the energies of these motions. Roughly speaking, as ε tends to zero, the energy terms decompose as follows: The electronic energy is $0(1)$; the molecular vibrational energy is $0(\varepsilon^2)$; and the molecular rotational energy is $0(\varepsilon^4)$. There are additional $0(\varepsilon^4)$ terms (anharmonic corrections to the nuclear vibrational energies, and the lowest order term involving the coupling of electronic and nuclear motions). As we shall see below, the terms of orders ε^1, ε^3, and ε^5 all vanish. The terms of order ε^6 and higher involve complicated interactions between the electronic and nuclear motions. Although we have not computed the ε^7 terms in any specific examples, we believe that they are generically non-zero. In particular, we see no reason for all the odd order terms to vanish.

From the above discussion and the discussion in most physics text books on the subject, one would be led to believe that the disparity between time scales is the basis for the validity of the Born-Oppenheimer approximation. This is *not* the proper intuition, even in the time dependent approximation [6]. The crucial ingredient is a disparity in spatial scales. In the time that it takes the electrons to move a unit distance, the nuclei move a distance of order ε. As a result, the appropriate technique for analyzing the motion is the « method of multiple scales » applied to the appropriate spatial variables. In fact, if one looks carefully at the original work of Born and Oppenheimer [1], it is clear that they were well aware of the role of spatial scaling, but did not have a clean formalism for dealing with more than one scale in the same variable.

Despite the importance of the Born-Oppenheimer approximation to chemistry, there has been very little rigorous mathematical work concerning its validity until recently. During the last ten years or so, Seiler [9] has worked out a simple exactly soluble Born-Oppenheimer type model involving coupled harmonic oscillators, and Aventini, Combes, Duclos, Grossman, and Seiler [2] [3] [4] have rigously proved the results of [1]. The only other related mathematical work on this subject (of which we are aware) is the author's own work on the time dependent Born-Oppenheimer approximation [5] [6], and his brief summary of the present paper [7].

The papers [3] [4] of Combes, Duclos, and Seiler involve some very clever techniques for analyzing the discrete spectrum of a molecular Hamiltonian. In particular, by using a Feshbach projection technique, they have developed a method for computing rigorous upper and lower bounds for the eigenvalues. As $\varepsilon \searrow 0$, the upper and lower bounds asymptotically agree through fourth order, and the asymptotics of the lowest finitely many eigenvalues can be computed. Unfortunately, the estimates are not uniform, in the sense that as one looks at higher and higher eigenvalues, the estimates become poorer. Thus, only the bottom of the spectrum is completely described. The estimates do guarantee the presence of eigenvalues near certain higher energies, but do not preclude the possibility that eigenvalues with other asymptotics might be present above the first finitely many eigenvalues.

We regard the papers [3] [4] as being very deep, careful analyses of the low-lying spectrum in a very singular perturbation problem. In addition, the techniques are capable of handling the technical problems associated with Coulomb potentials. The crucial arguments of [3] [4] employ some clever non-linear techniques to establish the lower bounds. As a result, some rather unusual ideas must be used, and it is not clear how to proceed to higher order.

In contrast, we will restrict attention to nice potentials and use essentially linear methods to produce high order « quasimodes. » That is, we will produce solutions to the inequality

$$\| H(\varepsilon)\Psi(\varepsilon) - \mathcal{E}(\varepsilon)\Psi(\varepsilon) \| \leqslant C_N \varepsilon^N,$$

where N is arbitrarily large and C_N is appropriately chosen. The existence of such quasimodes quarantees that either $\mathcal{E}(\varepsilon)$ is in the spectrum of the self-adjoint operator $H(\varepsilon)$, or the norm of the resolvent is least ε^{-N}/C_N. Thus, $H(\varepsilon)$ must have some spectrum in the interval $[\mathcal{E}(\varepsilon) - \varepsilon^{-N}/C_N, \mathcal{E}(\varepsilon) + \varepsilon^{-N}/C_N]$. This proves the presence of spectrum near certain energies, but does not preclude the possibility that there is also other spectrum present. In addition, we have the same uniformity problem as [*3*] [*4*]. However, by combining our results with other results, more detailed information can be obtained. For example:

1. By combining our results with the HVZ Theorem [*8*], we can be sure that certain quasimodes correspond to discrete eigenvalues: The HVZ Theorem characterizes the bottom Σ of the essential spectrum. Quasimode estimates that guarantee spectrum below Σ, guarantee the presence of discrete eigenvalues.
2. By combining our results with those of [*3*] [*4*], it is easy to see that our high order quasimodes completely describe the asymptotics of the lowest finitely many eigenvalues to arbitrarily high order.

To simplify the exposition of the paper, we will only discuss the case of diatomic molecules. In the next section, we will precisely state our results in that case. In section 3, we will give a formal computation of the quasimodes by using the method of multiple scales. In the fourth section we will rigorously justify all the steps of the formal computation.

Remark. — We are not particularly fond of our proof, but have not been able to improve upon it. We believe there ought to be a proof similar to the one used in [*10*] to study semiclassical asymptotics. All of our attempts in this direction have been stymied by the presence of infinite degeneracies at low orders. Unless one goes to at least fourth order in the approximation, there are infinitely many orthogonal quasimode states with the same energy. By exploiting the rotational symmetry of the problem, one can approach the problem in a way which involves much more complicated formulas, but in which the infinite degeneracy is broken at second order instead of fourth order. Even using that approach, we do not know how to produce the type of proof we would like.

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§ 2. NOTATION AND RESULTS

The purpose of this section is to present a precise statement of our main theorem. For simplicity, we will restrict attention to the case of diatomic molecules.

We consider an N-body quantum mechanical system of particles whose masses are $M_1\varepsilon^{-4}$, $M_2\varepsilon^{-4}$, and m_j ($j = 2, 3, \ldots, N$). We refer to such a system a diatomic molecule. Particles 1 and 2 are called the nuclei;

particles 2, 3, . . ., N are called the electrons. The Hamiltonian for a diatomic molecule is

$$\tilde{H}(\varepsilon) = -\frac{\varepsilon^4}{2M_1}\Delta_1 - \frac{\varepsilon^4}{2M_2}\Delta_2 - \sum_{j=3}^{N}\frac{1}{2m_j}\Delta_j + \sum_{i<j} V_{ij}(|x_i - x_j|)$$

on $L^2(\mathbb{R}^{3N})$. We choose a Jacobi coordinate system [8] in which the first three coordinates are the vector X, from the first nucleus to the second. Then we remove the center of mass dependence [8] from $\tilde{H}(\varepsilon)$ to obtain

$$H(\varepsilon) = -\frac{\varepsilon^4}{2M}\Delta_X - \sum_{j=1}^{N-2}\frac{1}{2\nu_j(\varepsilon)}\Delta_{\zeta_j} + V(X, \zeta_1, \zeta_2, \ldots, \zeta_{N-2})$$

on $L^2(\mathbb{R}^{3N-3})$. The reduced masses $\nu_j(\varepsilon)$ are analytic in ε^4 and approach non-zero values μ_j as ε tends to zero. We assume that $M = 1$ (rescale X if necessary), and we define r to be the vector $(\zeta_1, \zeta_2, \ldots, \zeta_{N-2}) \in \mathbb{R}^{3N-6}$. We define the electron Hamiltonian $h(X)$ to be the operator valued function

$$h(X) = -\sum_{j=1}^{N-2}\frac{1}{2\mu_j}\Delta_{\zeta_j} + V(X, \zeta_1, \zeta_2, \ldots, \zeta_{N-2})$$

on $L^2(\mathbb{R}^{3N-6}, dr)$. By using the direct integral decomposition

$$L^2(\mathbb{R}^{3N-3} dX dr) = \int_{\mathbb{R}^3} \oplus\, L^2(\mathbb{R}^{3N-6}) dX,$$

we define h to be the operator on $L^2(\mathbb{R}^{3N-3} dX dr)$ which is the direct integral of the fiber operators $h(X)$. In addition, we define an operator $D(\varepsilon)$ by the relation

$$\varepsilon^4 D(\varepsilon) = -\sum_{j=1}^{N-2}\left(\frac{1}{2\nu_j(\varepsilon)} - \frac{1}{2\mu_j}\right)\Delta_{\zeta_j}.$$

Note that $D(\varepsilon)$ is a second order differential operator whose coefficients are analytic in ε^4. With this notation, we have

$$H(\varepsilon) = -\frac{\varepsilon^4}{2}\Delta_X + h + \varepsilon^4 D(\varepsilon).$$

The term $\varepsilon^4 D(\varepsilon)$ plays the uninteresting role of a regular perturbation because it is relatively bounded with respect to h. The interesting mathematics arises from the interplay of h and $-\frac{\varepsilon^4}{2}\Delta_X$, which involves a singular perturbation problem.

We will henceforth use the spherical coordinates $(\mathrm{R}, \theta, \varphi)$ to represent the vector X. Because of the isotropic nature of the problem, the spectrum of $h(\mathrm{R}, \theta, \varphi)$ is independent of θ and φ. We assume that $h(\mathrm{R}, \theta, \varphi)$ has an isolated non-degenerate eigenvalue $\mathrm{E(R)}$ for R in some open neighborhood U of some value $\mathrm{R}_0 > 0$. In addition, we assume that $\mathrm{E(R)}$ has a local minimum at R_0 with $\mathrm{E}''(\mathrm{R}_0)$ strictly positive. In many examples of interest, $\mathrm{E(R)}$ is the ground state energy (which is necessarily non-degenerate) of $h(\mathrm{R}, \theta, \varphi)$, and has a global minimum at some value R_0.

If the potentials V_{ij} for our system are $\mathrm{C}^\infty(\mathbb{R}^3)$, then under the above assumptions, we can choose a real $\mathrm{C}^\infty(\mathrm{U} \times \mathrm{S}^2)$ eigenfunction $\Phi(\mathrm{R}, \theta, \varphi)$, so that

$$h(\mathrm{R}, \theta, \varphi)\Phi(\mathrm{R}, \theta, \varphi) = \mathrm{E(R)}\Phi(\mathrm{R}, \theta, \varphi).$$

With this notation, we can now state our main result:

THEOREM 2.1. — Assume the situation described above, with the V_{ij} smooth. Then given an arbitrary K, there exist quasimode energies

$\mathcal{E}_{n,l,m}(\varepsilon) = \sum_{k=0}^{\mathrm{K}} \varepsilon^k \mathrm{E}_{n,l,m;k}$ and quasimodes

$$\Psi_{\varepsilon,n,l,m}(\mathrm{R}, \theta, \varphi, \zeta_1, \zeta_2, \ldots, \zeta_{\mathrm{N}-2}) = \sum_{k=0}^{\mathrm{K}} \varepsilon^k \Psi_{\varepsilon,n,l,m;k}(\mathrm{R}, \theta, \varphi, \zeta_1, \zeta_2, \ldots, \zeta_{\mathrm{N}-2}),$$

so that

$$\| \mathrm{H}(\varepsilon)\Psi_{\varepsilon,n,l,m}(\mathrm{R}, \theta, \varphi, \zeta_1, \zeta_2, \ldots, \zeta_{\mathrm{N}-2}) - \mathcal{E}_{n,l,m}(\varepsilon)\Psi_{\varepsilon,n,l,m}(\mathrm{R}, \theta, \varphi, \zeta_1, \zeta_2, \ldots, \zeta_{\mathrm{N}-2}) \| \leqslant \mathrm{C}_{n,l,m;\mathrm{K}}\varepsilon^{\mathrm{K}+1},$$

for $n = 0, 1, 2, \ldots, l = 0, 1, 2, \ldots,$ and $m = -l, -l+1, \ldots, l-1, l$. The numbers $\mathrm{E}_{n,l,m;1}$, $\mathrm{E}_{n,l,m;3}$, and $\mathrm{E}_{n,l,m;5}$ are always zero. $\mathrm{E}_{n,l,m;0} = \mathrm{E}(\mathrm{R}_0)$ is the electronic contribution to the energy, and $\mathrm{E}_{n,l,m;2} = (n+1/2)\,[\mathrm{E}''(\mathrm{R}_0)]^{1/2}$ is the harmonic approximation to the nuclear vibrational energy. The formula for $\mathrm{E}_{n,l,m;4}$ is given in the remarks below. The zeroth order term in the quasimode is

$$\Psi_{\varepsilon,n,l,m;0}(\mathrm{R}, \theta, \varphi, \zeta_1, \zeta_2, \ldots, \zeta_{\mathrm{N}-2}) = \sum_{j=-l}^{l} c_{k,l,m;j}\mathrm{R}^{-1}\mathrm{H}_n\left(\frac{\mathrm{R}-\mathrm{R}_0}{\varepsilon}\right)e^{-(\mathrm{R}-\mathrm{R}_0)^2/2\varepsilon^2}\mathrm{Y}_{l,j}(\theta, \varphi)\Phi(\mathrm{R}, \theta, \varphi, r),$$

where $c_{k,l,m;j}$ are constants, H_n is the n^{th} degree Hermite polynomial, $\mathrm{Y}_{l,m}$ is the $(l, m)^{th}$ spherical harmonic function, and Φ is the electronic eigenfunction corresponding to $\mathrm{E(R)}$.

Remarks. — 1. There may be several different choices of E(R) and R_0, depending on the details of the electronic hamiltonian $h(R, \theta, \varphi)$.

2. If $\mathcal{E}_{n,l,m}(\varepsilon)$ lies below the essential spectrum of $H(\varepsilon)$ for all small ε, then it asymptotically corresponds to an eigenvalue of $H(\varepsilon)$. It is conceivable that there might be eigenvalues with asymptotics other than the various $\mathcal{E}_{n,l,m}(\varepsilon)$'s.

3. It is reasonable to conjecture that the quasimodes of the theorem whose energies lie in the essential spectrum of $H(\varepsilon)$ correspond to resonances of the molecule.

4. If E(R) is chosen to be the ground state energy of $h(R, \theta, \varphi)$, and if E(R) has a global minimum at R_0 with $E''(R_0) > 0$, then the asymptotics of the lowest lying eigenvalues of $H(\varepsilon)$ are completely described by the corresponding $\mathcal{E}_{n,l,m}(\varepsilon)$, i. e., there are no other low lying eigenvalue asymptotics. This is a result of [*2*] [*3*] [*4*].

5. The formula for $E_{n,l,m;4}$ depends on the electronic eigenfunction Φ, but we can still give a fairly explicit formula for it. Explicitly,

$$E_{n,l,m;4} = a_l + b + c_n,$$

where

$$a_l = \frac{l(l+1)}{2(R_0)^2}$$

is the dominant term in the angular momentum dependence of the molecule's energy;

$$b = \left\langle \Phi(R, \theta, \varphi, .), \left[-\frac{1}{2}\Delta_X + D_0 \right] \Phi(R, \theta, \varphi, .) \right\rangle_{L^2(dr)}$$

is the lowest order nontrivial coupling of the electronic and nuclear motions (D_0 is the constant term in the power series in ε^4 for $D(\varepsilon)$); and

$$c_n = -\left[\frac{E'''(R_0)}{E''(R_0)}\right]^2 \left(\frac{11}{288} + \frac{5n(n+1)}{48}\right) + \frac{E''''(R_0)}{E''(R_0)} \left(\frac{1}{32} + \frac{n(n+1)}{16}\right)$$

is the lowest anharmonic correction to the nuclear vibrational energy.

6. The fourth order terms $\varepsilon^4 E_{n,l,m;4}$ break the infinite degeneracy, but through fourth order $\mathcal{E}_{n,l,m}(\varepsilon)$ remains finitely degenerate. The $\mathcal{E}_{n,l,m}(\varepsilon)$ have no m-dependence through fourth order, and so to that order, each quasimode energy corresponds to $2l + 1$ orthogonal quasimodes. Except for degeneracies due to symmetry, we expect the degeneracy to be completely broken at sixth order.

§ 3. FORMAL DERIVATION OF THE EXPANSION

In this section we give a formal derivation of the results that were stated in Section 2. These formal computations are based on the « method of multiple scales » applied to the variable R. This method is appropriate because of the presence of effects which occur in the variable R on length scales of order 1 and order ε.

As described in the previous sections, we wish to study the small ε asymptotics of the solutions to the equation

$$-\frac{\varepsilon^4}{2}\Delta_{\mathrm{R},\theta,\varphi}\eta_\varepsilon + h\eta_\varepsilon + \varepsilon^4\mathrm{D}(\varepsilon)\eta_\varepsilon = \mathcal{E}(\varepsilon)\eta_\varepsilon . \tag{3.1}$$

To simplify the radial Laplacian, we make a standard change of dependent variable and concentrate on $\Psi_\varepsilon(\mathrm{R}, \theta, \varphi, r) = \mathrm{R}\eta_\varepsilon(\mathrm{R}, \theta, \varphi, r)$. Then, rather than directly seeking $\Psi_\varepsilon(\mathrm{R}, \theta, \varphi, r)$, we will seek a solution $\psi_\varepsilon(x, y, \theta, \varphi, r)$ to a higher dimensional problem. We will then recover

$$\Psi_\varepsilon(\mathrm{R}, \theta, \varphi, r) = \psi_\varepsilon\left(\mathrm{R}, \frac{\mathrm{R}-\mathrm{R}_0}{\varepsilon}, \theta, \varphi, r\right).$$

This is the technique of « multiple scales. » It is useful for our problem because as $\varepsilon \to 0$, the variables $x = \mathrm{R}$ and $y = \dfrac{\mathrm{R}-\mathrm{R}_0}{\varepsilon}$ behave in a more or less independent fashion. Moreover, semiclassical effects occur in the variable y, and adiabatic effects occur in the variable x. Without the independent treatments of these variables, the two types of effects become intertwined and much more difficult to understand. The introduction of the two variables x and y allows one to do a separation of variables in the low orders of approximation. It also yields a clean formalism for splitting high order correction terms into adiabatic and semiclassical components. Without this clean splitting, the analysis is prohibitively complicated.

To obtain the equation that is satisfied by $\psi_\varepsilon(x, y, \theta, \varphi, r)$, we make a formal change of variables from $(\mathrm{R}, \theta, \varphi, r)$ to $(x, y, \theta, \varphi, r)$, with $x = \mathrm{R}$ and $y = \dfrac{\mathrm{R}-\mathrm{R}_0}{\varepsilon}$. We also make a careful choice of when to replace the variable R by x or $[\mathrm{R}_0 + \varepsilon y]$, and we introduce some operators T_j whose purpose is to change x dependence into y dependence. These operators simply do the bookkeeping associated with the fact that x and y are not actually independent. Without the operators T_j, one cannot treat x and y as though they were independent. The apparent independence is a consequence of a proper choice of the T_j's, and their choice provides a uniqueness criterion in the expansion.

The equation satisfied by $\psi_\varepsilon(x, y, \theta, \varphi, r)$ is the following:

$$\left[-\frac{\varepsilon^4}{2}\frac{\partial^2}{\partial x^2}-\varepsilon^3\frac{\partial^2}{\partial x\partial y}-\frac{\varepsilon^2}{2}\frac{\partial^2}{\partial y^2}+\varepsilon^4\frac{L^2}{2(R_0+\varepsilon y)^2}+\varepsilon^4 D(\varepsilon)\right.$$
$$+h(x,\theta,\varphi)-E(x)+E(R_0+\varepsilon y)$$
$$\left.+\sum_{j=4}\varepsilon^j[T_j(R_0+\varepsilon y)-T_j(x)]\right]\psi_\varepsilon(x,y,\theta,\varphi,r)=\mathcal{E}(\varepsilon)\psi_\varepsilon(x,y,\theta,\varphi),\qquad(3.2)$$

where L^2 denotes the usual quantum mechanical angular momentum operator. It is trivial to check that any solution $\psi_\varepsilon(x, y, \theta, \varphi, r)$ to equation (3.2) gives rise to a solution $\eta_\varepsilon(R, \theta, \varphi, r) = R\psi_\varepsilon\left(R, \dfrac{R - R_0}{\varepsilon}, \theta, \varphi, r\right)$ to equation (3.1), regardless of the choices of the T_j's. Our particular choices of the T_j's will be specified later in this section. They will be chosen to be certain operators on $L^2(\sin(\theta)d\theta d\varphi)$, and the choices will be made in order to make certain functions in the expansion independent of x. In Section 4 we will prove that our procedure gives rise to certain approximate solutions to equation (3.2), which in turn give rise to approximate solutions to equation (3.1).

To formally derive our approximate solutions to equation (3.2), we begin by assuming the hypotheses of Theorem 2.1 and making the ansatz that equation (3.2) possesses an approximate solution of the form

$$\psi_\varepsilon = (\psi_0 + \varepsilon\psi_1 + \varepsilon^2\psi_2 + \dots)F(x)\qquad(3.3a)$$

with

$$\mathcal{E}(\varepsilon) = \mathcal{E}_0 + \varepsilon\mathcal{E}_1 + \varepsilon^2\mathcal{E}_2 + \dots .\qquad(3.3b)$$

Here $F(x)$ is a function with compact support that is identically 1 on an open neighborhood of $x = R_0$, and has support inside the set where $E(x)$ is non-degenerate.

Remark. — The reader who is not interested in a detailed proof of Theorem 2.1 is encouraged to ignore the factor $F(x)$ in this ansatz, and to think of the open set U as all of $[0, \infty)$. The factor $F(x)$ is necessary for the proof that is given in Section 4. It provides some uniformity in the estimates and causes the proper boundary condition to be satisfied at $R = 0$, but it causes an extra complication in the formal computations. In particular, certain terms which occur below contain derivatives of F. In Section 4, these terms are proved to be basically irrelevant. Whenever we encounter one of these terms in this section, we will make a comment, drop the term, and refer the reader to Section 4 for the explanation of why the term can be dropped.

Heuristically, these terms can be dropped because derivatives of F(R) are supported in a region of configuration space where the wave function is exponentially small in ε as $\varepsilon \to 0$.

We now need to determine the functions ψ_n. Since $F(x) = 0$ for $x \notin U$, we can arbitrarily set $\psi_n(x, y, \theta, \varphi, r) = 0$ for all $x \notin U$. To determine these functions for $x \in U$ we substitute the expressions (3.3) into equation (3.2) and expand all ε dependence in its Taylor series in powers of ε. Then we multiply everything out and equate coefficients of like powers of ε on the two sides of the equation.

The zeroth order terms force us to take

$$[h(x, \theta, \varphi) - E(x) + E(R_0)]\psi_0 = \mathcal{E}_0\psi_0.$$

Since this is to be true for all $x \in U$, we are forced to take

$$\mathcal{E}_0 = E(R_0)$$

and

$$\psi_0(x, y, \theta, \theta, r) = h_0(x, y, \theta, \varphi)\Phi(x, \theta, \varphi, r),$$

where h_0 is (so far) arbitrary.

The first order terms force us to take

$$[h(x, \theta, \varphi) - E(x) + E(R_0)]\psi_1 + E'(R_0)y\psi_0 = \mathcal{E}_0\psi_1 + \mathcal{E}_1\psi_0.$$

Since this is to hold for all y and $x \in U$, we must have

$$\mathcal{E}_1 = E'(R_0) = 0,$$
$$\psi_1(x, y, \theta, \varphi, r) = h_1(x, y, \theta, \varphi)\Phi(x, \theta, \varphi, r),$$

where h_1 is (so far) arbitrary.

The second order terms require

$$[h(x, \theta, \varphi) - E(x)]\psi_2 + \left[-\frac{1}{2}\frac{\partial^2}{\partial y^2} + \frac{1}{2}E''(R_0)y^2 \right]\psi_0 = \mathcal{E}_2\psi_0.$$

To satisfy this equation, we recall that we have assumed $E''(R_0) > 0$. We let $z = y(E''(R_0))^{1/2}$, and take

$$\mathcal{E}_2 = \left(n + \frac{1}{2}\right)(E''(R_0))^{1/2},$$
$$\psi_0 = g_0(x, \theta, \varphi)H_n(z)e^{-z^2/2}\Phi(x, \theta, \varphi, r),$$

and

$$\psi_2(x, y, \theta, \varphi, r) = h_2(x, y, \theta, \varphi)\Phi(x, \theta, \varphi, r).$$

where g_0 and h_2 are (so far) arbitrary, and H_n denotes the n^{th} degree Hermite polynomial.

As we commented earlier, we have the freedom to choose the operator T_j, in order to impose uniqueness conditions on the ψ_n's. We will arbitrarily pick the first operator T_4 so that g_0 will have no dependence on the variable x.

(It is clear that we can impose such a condition on g_0. In our final answer, $g_0(x, \theta, \varphi)$ is equivalent to $g_0(R_0 + \varepsilon y, \theta, \varphi)$, and we can expand this last expression in its Taylor series in ε. We can then put the constant term in this series in ψ_0, and put all the other Taylor series terms in the higher order ψ_n's. We accomplish this by choosing T_4 appropriately.) So, we henceforth assume g_0 to be a function of θ and φ only.

With this assumption we now approach the third order terms. There is one third order term that contains a derivative of F. It makes no contribution to the expansion at any finite order (see section 4), so we will ignor it here. The remaining terms require

$$[h(x, \theta, \varphi) - E(x)]\psi_3 + \left[-\frac{1}{2}\frac{\partial^2}{\partial y^2} + \frac{1}{2}E''(R_0)y^2 - \mathcal{E}_2 \right]\psi_1 + \frac{1}{3}E'''(R_0)y^3\psi_0 - \frac{\partial^2}{\partial x \partial y}\psi_0 = \mathcal{E}_3\psi_0. \quad (3.4)$$

To satisfy this equation we introduce some new notation. We break $up\psi_n$ as

$$\psi_n = \psi_n^{\perp} + \psi_n^{\|\perp} + \psi_n^{\|\,\|},$$

where

$\psi_n^{\perp}$ is orthogonal to $\Phi(x, \theta, \varphi, r)$ in $L^2(dr)$;

$\psi_n^{\|\perp}$ is a multiple of $\Phi(x, \theta, \varphi, r)$,

but orthogonal to

$$H_n(z)e^{-z^2/2} \quad \text{in} \quad L^2(dy) ;$$

and

$\psi_n^{\|\,\|}$ is a multiple of $H_n(z)e^{-z^2/2}\Phi(x, \theta, \varphi)$.

With this notation, we can now satisfy equation (3.4) by looking at the components in the various directions in the Hilbert space:

The components on the two sides of equation (3.4) that are x, θ, and φ dependent multiples of $H_n(z)e^{-z^2/2}\Phi(x, \theta, \varphi, r)$ must be equal. From this we obtain

$$\mathcal{E}_3 = 0,$$

and

$$\psi_1^{\|\,\|} = g_1(x, \theta, \varphi)H_n(z)e^{-z^2/2}\Phi(x, \theta, \varphi, r)$$

where g_1 is (so far) arbitrary.

We assume T_5 will be chosen so that g_1 will not depend on x. The argument for why this may be done is the same as the one that allowed us to choose T_4 so that g_0 would be independent of x.

The components of equation (3.4) that are multiples of $\Phi(x, \theta, \varphi, r)$, but orthogonal to $H_n(z)e^{-z^2/2}$ must be equal on the two sides of the equation. So,

$$\psi_1^{\|\perp} = g_0(\theta, \varphi)\Phi(x, \theta, \varphi, r) . [H_{osc} - \mathcal{E}_2]_r^{-1}\left(-\frac{1}{6}E'''(R_0)y^3H_n(z)e^{-z^2/2} \right),$$

where $[\mathrm{H}_{\mathrm{osc}} - \mathcal{E}_2]_r^{-1}$ denotes the inverse of the restriction of

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial y^2} + \frac{1}{2}\mathrm{E}''(\mathrm{R}_0)y^2 - \mathcal{E}_2\right]$$

to the subspace of $\mathrm{L}^2(dy)$ orthogonal to $\mathrm{H}_n(z)e^{-z^2/2}$. We note that

$$\left(-\frac{1}{6}\mathrm{E}'''(\mathrm{R}_0)y^3\mathrm{H}_n(z)e^{-z^2/2}\right)$$

belongs to this subspace because of symmetries.

The components that are orthogonal to $\Phi(x, \theta, \varphi, r)$ in $\mathrm{L}^2(dr)$ must also be equal on the two sides of equation (3.4). So we have

$$\psi_3^{\perp} = g_0(\theta, \varphi)\left[\frac{\partial}{\partial y}\mathrm{H}_n(z)e^{-z^2/2}\right]\left[h(x, \theta, \varphi) - \mathrm{E}(x)\right]_r^{-1}\frac{\partial\Phi}{\partial x}(x, \theta, \varphi, r),$$

where $\left[h(x, \theta, \varphi) - \mathrm{E}(x)\right]_r^{-1}$ denotes the inverse of the restriction of $[h(x, \theta, \varphi) - \mathrm{E}(x)]$ to the subspace of $\mathrm{L}^2(dr)$ orthogonal to $\Phi(x, \theta, \varphi, r)$. Note that since $\Phi(x, \theta, \varphi, r)$ is a unit vector in $\mathrm{L}^2(dr)$, $\dfrac{\partial\Phi}{\partial x}(x, \theta, \varphi, r)$ is orthogonal to $\Phi(x, \theta, \varphi, r)$ in $\mathrm{L}^2(dr)$.

We now concentrate on the fourth order terms in equation (3.2). They require

$$\begin{aligned}
&[h(x, \theta, \varphi) - \mathrm{E}(x)]\psi_4 + \left[-\frac{1}{2}\frac{\partial^2}{\partial y^2} + \frac{1}{2}\mathrm{E}''(\mathrm{R}_0)y^2 - \mathcal{E}_2\right]\psi_2 \\
&\quad + \frac{1}{6}\mathrm{E}'''(\mathrm{R}_0)y^3\psi_1 + \frac{1}{24}\mathrm{E}''''(\mathrm{R}_0)y^4\psi_0 - \frac{\partial^2}{\partial x\partial y}\psi_1 \\
&\quad - \frac{1}{2}\frac{\partial^2}{\partial x^2}\psi_0 + \frac{\mathrm{L}^2}{2\mathrm{R}_0^2}\psi_0 + \mathrm{D}(0)\psi_0 + \mathrm{T}_4(\mathrm{R}_0)\psi_0 - \mathrm{T}_4(x)\psi_0 = \mathcal{E}_4\psi_0 \qquad (3.5)
\end{aligned}$$

We again ignor terms involving derivatives of F because they will be shown in Section 4 to not contribute at finite order. The components of equation (3.5) that are x, θ and φ dependent multiples of $\mathrm{H}_n(z)e^{-z^2/2}\Phi(x, \theta, \varphi, r)$ force us to have

$$\begin{aligned}
&\mathrm{H}_n(z)e^{-z^2/2}\frac{\mathrm{L}^2}{2\mathrm{R}_0^2}g_0(\theta, \varphi) - \frac{1}{36}(\mathrm{E}'''(\mathrm{R}_0))^2 g_0(\theta, \varphi)\mathrm{P}_y(y^3[\mathrm{H}_{\mathrm{osc}} - \mathcal{E}_2]_r^{-1}y^3\mathrm{H}_n(z)e^{-z^2/2}) \\
&\quad + \frac{1}{24}\mathrm{E}''''(\mathrm{R}_0)g_0(\theta, \varphi)\mathrm{P}_y(y^4\mathrm{H}_n(z)e^{-z^2/2}) + g_0(\theta, \varphi)\mathrm{H}_n(z)e^{-z^2/2} \\
&\quad \cdot\left\langle \Phi(x, \theta, \varphi, .), \left[-\frac{1}{2}\frac{\partial^2}{\partial x^2} + \frac{\mathrm{L}^2}{2\mathrm{R}_0^2} + \mathrm{D}(0)\right]\Phi(x, \theta, \varphi, .)\right\rangle_{\mathrm{L}^2(dr)} \\
&\quad - \mathrm{H}_n(z)e^{-z^2/2}\mathrm{T}_4(x)g_0(\theta, \varphi) + \mathrm{H}_n(z)e^{-z^2/2}\mathrm{T}_4(\mathrm{R}_0)g_0(\theta, \varphi) \\
&\quad = \mathcal{E}_4\mathrm{H}_n(z)e^{-z^2/2}g_0(\theta, \varphi), \qquad (3.6)
\end{aligned}$$

where P_y denotes the orthogonal projection in $L^2(dy)$ onto the subspace generated by $H_n(z)e^{-z^2/2}$. This equation is to hold for all x, and we wish to have g_0 independent of x. So, we choose T_4 to be multiplication by

$$T_4(x) = \left\langle \Phi(x, \theta, \varphi, .), \left[-\frac{1}{2}\frac{\partial^2}{\partial x^2} + \frac{L^2}{2R_0^2} + D(0) \right] \Phi(x, \theta, \varphi, .) \right\rangle_{L^2(dr)} .$$

With this choice, the fourth and fifth terms on the left hand side of equation (3.6) cancel, and one is left with the familiar angular momentum operator eigenvalue problem. Thus, $g_0(\theta, \varphi)$ must be a superposition of spherical harmonics corresponding to one value of l, i. e.,

$$g_0(\theta, \varphi) = \sum_{m=-l}^{l} c_m Y_{l,m}(\theta, \varphi) .$$

The value of $\mathcal{E}_4$ depends on l and n, but not m, and is given in Remark 5 at the end of section 2.

From the components of equation (3.5) that are multiples of $\Phi(x, \theta, \varphi, r)$ but orthogonal to $H_n(z)e^{-z^2/2}$ we must have

$$\begin{aligned}
\psi_2^{\parallel\perp} = & -\frac{1}{6} E'''(R_0) g_1(\theta, \varphi)\Phi(x, \theta, \varphi, r)[H_{osc} - \mathcal{E}_2]_r^{-1} y^3 H_n(z)e^{-z^2/2} \\
& + \frac{1}{36}(E'''(R_0))^2 g_0(\theta, \varphi)\Phi(x, \theta, \varphi, r) \\
& \quad . [H_{osc} - \mathcal{E}_2]_r^{-1} Q_y y^3 [H_{osc} - \mathcal{E}_2]_r^{-1} y^3 H_n(z)e^{-z^2/2} \\
& - \frac{1}{24} E''''(R_0) g_0(\theta, \varphi)\Phi(x, \theta, \varphi, r) . [H_{osc} - \mathcal{E}_2]^{-1} Q_y y^4 H_n(z)e^{-z^2/2} ,
\end{aligned}$$

where Q_y denotes the orthogonal projection in $L^2(dy)$ onto the subspace orthogonal to $H_n(z)e^{-z^2/2}$.

The components of equation (3.5) that are orthogonal to $\Phi(x, \theta, \varphi, r)$ in $L^2(dr)$ force us to choose

$$\begin{aligned}
\psi_4^{\perp} = & g_1(\theta, \varphi)\left(\frac{\partial}{\partial y} H_n(z)e^{-z^2/2}\right)[h(x, h, \varphi) - E(x)]_r^{-1} \frac{\partial \Phi}{\partial x}(x, \theta, \varphi, r) \\
& + \frac{1}{6} E'''(R_0) g_0(\theta, \varphi)\left(\frac{\partial}{\partial y}[H_{osc} - \mathcal{E}_2]_r^{-1} y^3 H_n(z)e^{-z^2/2}\right)\frac{\partial \Phi}{\partial x}(x, \theta, \varphi, r) \\
& + g_0(\theta, \varphi) H_n(z)e^{-z^2/2} \\
& \quad . [h(x, \theta, \varphi) - E(x)]_r^{-1} Q_r \left(\frac{1}{2}\frac{\partial^2}{\partial x^2} - \frac{L^2}{2R_0^2} - D(0)\right)\Phi(x, \theta, \varphi, r) ,
\end{aligned}$$

where Q_r denotes the orthogonal projection in $L^2(dr)$ onto the subspace orthogonal to $\Phi(x, \theta, \varphi, r)$.

Thus, at fourth order, the infinite degeneracy is reduced to a finite degeneracy and ψ_0 is essentially determined.

From this point on, the k^{th} order terms from equation (3.2) yield formulas for $\mathcal{E}_k$, $\psi_{k-4}^{\|\,\|}$, $\psi_{k-2}^{\|\perp}$, and $\psi_k^{\perp}$. The operators T_k is chosen so that g_k is independent of x. These higher order calculations are straight-forward formal degenerate perturbation theory calculations. We will only present part of the fifth order calculation of the demonstrate that $\mathcal{E}_5 = 0$, since this result does not seem to be in the literature. We remind the reader that we believe $\mathcal{E}_6, \mathcal{E}_7, \mathcal{E}_8, \ldots$ are all generically non-zero. The symmetries that cause $\mathcal{E}_1$, $\mathcal{E}_3$, and $\mathcal{E}_5$ to be 0 are not present in the higher orders because of couplings between the electronic and nuclear motions.

The fifth order terms in equation (3.2) require

$$\begin{aligned}
&[h(x, \theta, \varphi) - \mathrm{E}(x)]\psi_5 + \left[-\frac{1}{2}\frac{\partial^2}{\partial y^2} + \frac{1}{2}\mathrm{E}''(\mathrm{R}_0)y^2 - \mathcal{E}_2 \right]\psi_3 \\
&\qquad + \frac{1}{6}\mathrm{E}'''(\mathrm{R}_0)y^3\psi_2 + \frac{1}{24}\mathrm{E}''''(\mathrm{R}_0)y^4\psi_1 + \frac{1}{120}\mathrm{E}^{(5)}(\mathrm{R}_0)y^5\psi_0 \\
&\qquad - \frac{\partial^2}{\partial x \partial y}\psi_2 - \frac{1}{2}\frac{\partial^2}{\partial x^2}\psi_1 + \frac{\mathrm{L}^2}{2\mathrm{R}_0^2}\psi_1 + \mathrm{D}(0)\psi_1 - y\frac{\mathrm{L}^2}{\mathrm{R}_0^3}\psi^0 \\
&\qquad + \mathrm{T}_4(\mathrm{R}_0)\psi_1 - \mathrm{T}_4(x)\psi_1 + y\mathrm{T}_4'(\mathrm{R}_0)\psi_0 + \mathrm{T}_5(\mathrm{R}_0)\psi_0 - \mathrm{T}_5(x)\psi_0 \\
&\qquad = \mathcal{E}_4\psi_1 + \mathcal{E}_5\psi_0 .
\end{aligned} \tag{3.7}$$

We now concentrate on the terms of this equation which are x, θ, and φ dependent multiples of $\mathrm{H}_n(z)e^{-z^2/2}\Phi(x, \theta, \varphi, r)$. There is a cancellation of several terms on the left with $\mathcal{E}_4\psi_1$ on the right. After this cancellation, the remaining terms require

$$\left(\frac{\mathrm{L}^2}{2\mathrm{R}_0^2} - \frac{l(l+1)}{2\mathrm{R}_0^2}\right)g_1(\theta, \varphi) = (\mathrm{T}_5(\mathrm{R}_0) - \mathrm{T}_5(x) + \mathcal{E}_5)g_0(\theta, \varphi).$$

The two sides of this equation are orthogonal to one another for $x = \mathrm{R}_0$, and the only x dependence comes from the $\mathrm{T}_5(x)$. We therefore choose $\mathrm{T}_5(x) = 0$, and observe that $\mathcal{E}_5$ must be zero. In addition, $g_1(\theta, \varphi)$ must be a superposition of spherical harmonics of angular momentum l:

$$g_1(\theta, \varphi) = \sum_{m=-l}^{l} d_m \mathrm{Y}_{l,m}(\theta, \varphi),$$

where the numbers d_m are arbitrary. Nothing is gained by choosing g_1 to be non-zero, except for keeping the normalization of the wave function, so we arbitrarily choose $g_1(\theta, \varphi) = 0$. In fact, to impose uniqueness for the higher order terms, we impose the condition that all such secular (angular momentum l) terms in $g_k(\theta, \varphi)$ be set equal to zero for $k > 0$.

Since we have shown $\mathcal{E}_5 = 0$, we will not pursue the fifth order calculation further. Of course, the other components of the fifth order terms determine $\psi_3^{\|\perp}$ and $\psi_5^{\perp}$ uniquely.

Remark. — The sixth order terms which are x, θ, and φ dependent multiples of $H_n(z)e^{-z^2/2}\Phi(x, \theta, \varphi, r)$ require

$$\left(\frac{L^2}{2R_0^2} - \frac{l(l+1)}{2R_0^2}\right)g_2(\theta, \varphi) = (A(x) + T_6(R_0) - T_6(x) + \mathcal{E}_6)g_0(\theta, \varphi),$$

where $A(x)$ is a function with values in the operators on L^2 of the sphere. We choose $T_6(x) = A(x)$, and then look separately at the components of angular momentum l and those with angular momentum different from l. The terms with angular momentum different from l determine g_2 uniquely since we arbitrarily require that $g_n(\theta, \varphi)$ have no component of angular momentum l for $n > 0$. The terms of angular momentum l require

$$P_l\,[T_6(R_0) + \mathcal{E}_6\,]g_0(\theta, \varphi) = 0\,.$$

This is a matrix eigenvalue problem that should generically split the remaining degeneracies that are not required by symmetries.

The higher order terms are dealt with in a similar fashion.

§ 4. PROOF OF THE MAIN THEOREM

Since we are only constructing quasimodes, the proof of the theorem consists in checking that the formally constructed quasimodes actually are rigorous quasimodes. This task is more or less trivial.

It is easy to check that the formal calculations of section 3 can be done to arbitrarily high order. If one has done these calculations through order $K \geqslant 4$, then

$$\psi_\varepsilon = \sum_{n=0}^{K-4} \varepsilon^n \psi_n + \sum_{n=K-3}^{K-2} \varepsilon^n \psi_n^{\|\perp} + \sum_{n=K-3}^{K} \varepsilon^n \psi_n^{\perp}$$

and

$$\mathcal{E}(\varepsilon) = \sum_{n=0}^{K} \varepsilon^n \mathcal{E}_n$$

have been determined. We define

$$\Psi_\varepsilon(R, \theta, \varphi, r) = \psi_\varepsilon\left(R, \frac{R - R_0}{\varepsilon}, \theta, \varphi, r\right)F(R)$$

and compute

$$\{\,H(\varepsilon) - \mathcal{E}(\varepsilon)\,\}\,\Psi_\varepsilon(R, \theta, \varphi, r)\,.$$

This quantity contains two types of terms. The first type involves derivatives of F. The R dependence of these terms involves products of bounded functions of R with support away from R_0, times polynomials in $\frac{R - R_0}{\varepsilon}$, times $e^{-(R-R_0)^2/2\varepsilon^2}$. Such functions are easily seen to have norms that are smaller than ε^j for any j. The second type of term has the form of a function whose norm is bounded as ε tends to zero, times ε^n, for some $n \geqslant K$. Thus, by the triangle inequality, the norm of

$$\{ H(\varepsilon) - \mathcal{E}(\varepsilon) \} \Psi_\varepsilon(R, \theta, \varphi, r).$$

is bounded by a multiple of ε^{K+1}, and Ψ_ε is a quasimode of order K. This proves the theorem.

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