The Born Oppenheimer wave function near level crossing

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Abstract

The standard Born Oppenheimer theory does not give an accurate description of the wave function near points of level crossing. We give such a description near an isotropic conic crossing, for energies close to the crossing energy. This leads to the study of two coupled second order ordinary differential equations whose solution is described in terms of the generalized hypergeometric functions of the kind ${}_0F_3(;a,b,c;z)$. We find that, at low angular momenta, the mixing due to crossing is surprisingly large, scaling like $\mu^{1/6}$, where μ is the electron to nuclear mass ratio.

1 Introduction

In 1927, in a landmark paper, Born and Oppenheimer [2] paved the way to applying quantum mechanics to molecular spectra. In their paper they introduced an approximation that greatly simplified the treatment of quantum mechanical spectral problems in which the particles can be divided into heavy and light. Molecules are an example since the nuclei are much heavier than the electrons. We shall denote by μ the small parameter of the theory. In molecules $\mu \sim 10^{-4}$, the electron to nucleon mass ratio. Since the light particles are associated with the fast degrees of freedom and the heavy particles with the slow degrees of freedom, the Born Oppenheimer approximation is related to the adiabatic approximation [1, 4, 13]. At the same time, the Born

Oppenheimer method can be viewed as a generalized semi-classical approximation where the small parameter μ plays the role of $\hbar^2$. This is a reflection of the fact that the electrons and nuclei also live on different spatial scales, the electronic wave function is spread and is far from the semi-classical limit, while the nuclear wave function is tight and close to semiclassical.

The procedure put forward by Born and Oppenheimer is to first solve the electronic spectral problem with fixed nuclei, and view the nuclear coordinates as parameters. To the leading order in μ, and far from crossings, the heavy degrees of freedom in Born Oppenheimer theory are described by a (scalar) Schrödinger operator in the semiclassical limit with $\hbar^2 = \mu$ and where the electronic energy surface serves as a potential.

Born-Oppenheimer theory developed into two distinct directions. The main direction has been the application to various systems and the development of effective and accurate methods of calculations [8, 9, 10, 11]. The second direction has been the development of the theory as a tool of rigorous spectral theory [3, 4, 5] . Our work falls into the first class.

Points where electronic energy surfaces cross are singular points of the Born Oppenheimer theory. In certain cases, these points can affect spectral properties [8]. In this work we focus on the behaviour of eigenfunctions near crossing. There is surprising little that is known about this. It is not known if the function has finite values at the crossing; how the amplitude of the wave function near the crossing scales with μ. Since crossing controls the mixing of electronic levels, the knowledge of the wave function near crossing is important. Of course, these questions are interesting in the case that the crossing lies in the classically allowed region.

In this work we address these issues for conical (i.e. linear) crossing of two levels where the Born Oppenheimer problem reduces to two coupled Schrödinger equations. In the isotropic case the analysis reduces further to the study of two coupled, second order, ordinary differential equations. We obtain the nuclear wave function analytically, to leading order in μ, close to the crossing. It is related to the generalized hypergeometric functions of the kind ${}_0F_3$. This function takes the ordinary Born Oppenheimer nuclear wave functions, which are a good approximation far from the crossing, all the way to the crossing, where the nuclear wave function mixes the two electronic levels. We find that the nuclear wave function with total angular momentum[1]

[1] We do not actually mean here the physical angular momentum, but a quantum number reminiscent to it, see Eq. (12).

$m = \pm\frac{1}{2}$ is *nonzero* at the crossing point. Moreover, for low momenta, the wave function has a large amplitude near the crossing, of order $\mu^{-1/4}$. We find appreciable mixing of the two levels at distances that are smaller than $\mu^{1/3}$ and the total weight that is mixed between levels scales like $\mu^{1/6}$ which is remarkably large.

2 The Born-Oppenheimer approximation

This section is a brief introduction to the basic and elementary elements of Born Oppenheimer theory.

2.1 The basic model

A prototype of the Born-Oppenheimer problem, and the one we study here is [8]:

$$H = -\mu\Delta_x + H_e(x) \tag{1}$$

where μ is a small parameter. $H_e(x)$ is an operator valued function that acts in the Hilbert space of the light degrees of freedom. Since the eigenvalues of $H_e(x)$ repel [15], one does not expect crossing in the case of one heavy coordinate x. If $H_e(x)$ is time reversal invariant, then stable crossing will occur if there are two heavy coordinates. We therefore assume that $x \in \mathbb{R}^2$. For the sake of simplicity we have taken identical masses for the two heavy degrees of freedom[2]. Two degrees of freedom is the simplest case that is still rich enough to cover the phenomena we are interested in.

There are several ways to motivate H. The most direct is to think of H as a phenomenological quantization of the molecular vibration. For example, in the case of molecular trimers the two heavy modes are the antisymmetric stretching and bending of the molecule, see fig 1.

Alternatively, one can start with the Schrödinger equation for a molecule, which indeed has the form of Eq. (1) where $H_e(x)$ includes the Coulumb potential of the nuclei and the electrons and the electronic kinetic energy. Often, and this is the case in molecules, H, is invariant under Gallilean translation and rigid rotation. The symmetry gives three quantum numbers $\{P, J, m\}$ and the spectral analysis of $H_{P,J,m}$ is now restricted to the "internal" nuclear coordinates. In [8] one can find a detailed description of this procedure for a

[2] There is no loss here, for by scaling some of the x-directions this can always be achieved

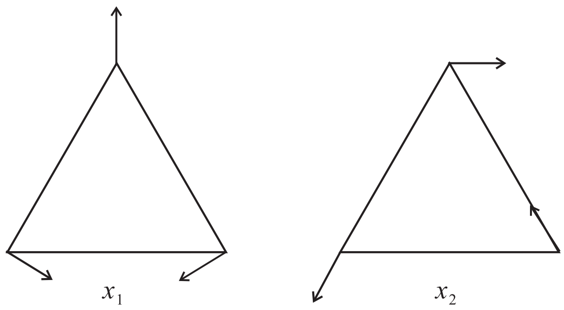

Figure 1: Two degenerate modes in triangular molecules.

triatomic molecule. $H_{P,J,m}$ has a more complicated expression than H: Fixing the center of mass at the origin and restricting to an angular momentum subspace replaces the kinetic energy $-\mu\,\Delta$ by a more general quadratic function of the of the momenta. However, locally near the crossing this expression reduces to [8] Eq. (1).

We shall assume that $H_e(x)$ has discrete spectrum and has smooth dependence on the coordinates[3]. In addition, since we shall use the Born Oppenheimer theory as a calculational tool, rather than a tool of spectral analysis, we shall assume that the problem has benign qualitative spectral features. For example, we shall assume that the spectrum of H in the energy range of interest is discrete, and that the associated wave functions are localized in space in the classically allowed region, and that this region is connected. Subtleties associated with tunneling and other exponentially small phenomena will not concern us here.

Since the small parameter μ multiplies the leading derivative in the x variable, the Born-Oppenheimer problem is a version of semiclassical problem where the operator $H_e(x)$ replaces the scalar potential $V(x)$.

In molecules there is a second small parameter, $1/c \approx 1/137$, which governs relativistic effects. In particular, spin-orbit interactions, are of order $1/c^2$. The lowest order of Born Oppenheimer theory gives an energy scale of $\sqrt{\mu}$ which is comparable to $1/c$ but is much larger than $1/c^2$. It is therefore consistent when discussing Born Oppenheimer to leading order to disregard spin orbit. This is also the reason why we shall not go beyond the leading

[3]Both assumptions are not realistic; The electronic Hamiltonian has continuous spectrum at high energy, and because of Coulombic singularities there is no smoothness in the x dependence. Fortunately, both problems are, by now, well understood and may be viewed as a technical complication that, for our purposes, can be left out.

order.

2.2 Partial Diagonalization

The starting point of the Born Oppenheimer method is to consider H in the basis that diagonalizes the fast (electronic) degrees of freedom.

We assume that the electronic Hamiltonian is real, which is the case in the absence of external magnetic fields. Let $O(x)$ be the orthogonal transformation that diagonalizes $H_e(x)$. If $H_e(x)$ has simple (non-degenerate) spectrum in the vicinity of x then $O(x)$ is uniquely determined up to multiplication by a diagonal matrix with ± 1 on the diagonal. Locally, one can choose $O(x)$ so that it inherits the smoothness properties of $H_e(x)$ [17]. It follows that in the basis that diagonalizes $H_e(x)$, Eq. (1) takes the form

$$O^\dagger H O = \mu(-i\nabla_x - A(x))^2 + E(x), \tag{2}$$

where $E(x)$ is a diagonal matrix whose entries $E_j(x)$ are the electronic energy surfaces and $A(x) = iO^\dagger(x)\nabla O(x)$ is a (matrix) gauge field. Since $O(x)$ is real, A is *antisymmetric* and hermitian. A is responsible to the coupling between electronic energy levels.

One can associate to a crossing point n indices, $\{i_1, \dots, i_n\}$, where $n = dim\ H_e$ and $i_j = \pm 1$. Let us take a closed curve around a crossing point. After such a cycle $O(x)$ must return to itself up to up to multiplication by a diagonal matrix with entries ± 1 on the diagonal. These entries are the indices of the crossing. It is known [7] that for a conic crossing between the $j-th$ and $j+1$ eigenvalues of $H_e(x)$ give $i_j = i_{j+1} = -1$ and all other indices are, of course, $+1$.

For conic (linear) crossing $O(x)$ flips signs on a circle of radius $|x|$ [7]. Therefore its gradient must be of order $1/|x|$. This makes A of order $1/|x|$. It follows that the coupling between electronic states diverges like a simple pole near crossing.

This completes the local description of the theory. The problem also has an interesting global aspect. Since $H_e(x)$ is a real symmetric matrix, the Wigner von Neumann crossing rule [15] says that $H_e(x),\ x \in \mathbb{R}^2$ has, generically, isolated crossing points. As a consequence, with points of crossing being removed the plane becomes multiply connected (see fig. 2)

We can now describe the boundary conditions associated with Eq. (2). The general case of several crossing points can be complicated but in the

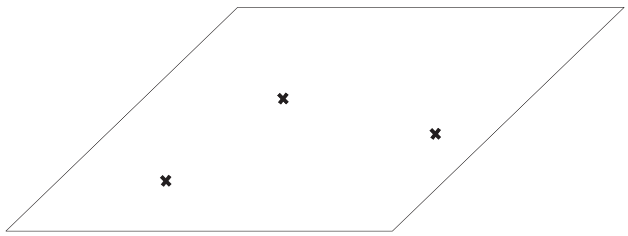

Figure 2: With points of crossing removed the plane becomes multiply connected.

case of at most one point of crossing the situation is simple. In that case, cut the plane from the crossing point to infinity. On the cut plane $O(x)$ is uniquely defined in a continuous way. Then the boundary condition on the j-th component of the wave function associated with Eq. (2) is periodic or anti-periodic according to the index i_j.

2.2.1 Born Oppenheimer theory near a non degenerate minimum

Let $x = 0$ be a minimizer of an electronic energy surface. Pick the origin so that the minimum is at zero energy (see Fig. 3). Upon scaling, $x = \mu^{1/4}\xi$,

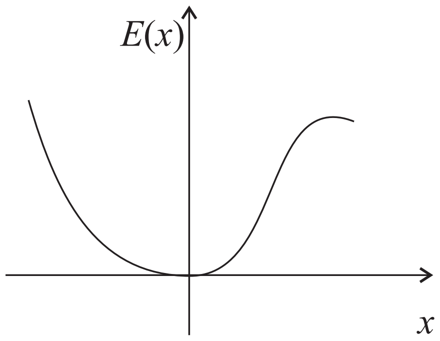

Figure 3: A potential energy surface near a nondegenerate minimum.

the Born Oppenheimer operator assumes the form

$$\sqrt{\mu}\left((-i\nabla_\xi - \varepsilon\, A(\varepsilon\xi))^2 + \frac{1}{\sqrt{\mu}}\, E(\varepsilon\xi)\right), \quad \varepsilon = \mu^{1/4}. \tag{3}$$

The (scaled, matrix) potential energy is $O(1)$ for the electronic energy surface near the minimum, and has gaps of order $\mu^{-1/2}$ to (scaled) "excited electronic states". Suppose first that there is no crossing. Then the coupling between electronic levels is small, $\varepsilon\, A(\varepsilon\xi) = O(\mu^{1/4})$, and a perturbation argument shows that the effect on eigenvalues is of order $O(\mu)$ (in unscaled energy) and of order $O(\mu^{3/4})$ for the wave function. It follows that the spectral analysis in an energy interval of order $o(1)$ near the minimum, reduces to an ordinary Schrödinger equation (not matrix valued) with no vector potential (since A vanishes on the diagonal). This accounts for $o(1/\mu)$ eigenvalues near the minimum in two dimensions.

Now, if there is a point of crossing, there are two possibilities. The first, and simplest, is that the crossing lies in the classically forbidden region, see Fig 4. Then the divergent vector potential is harmless, since the wave func-

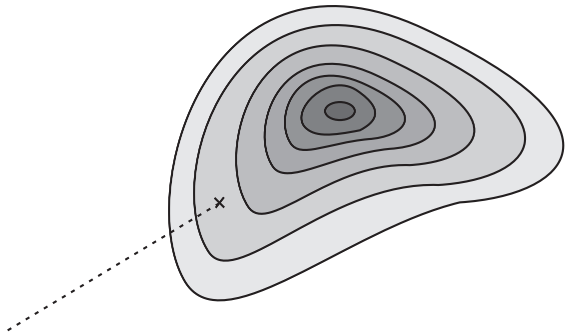

Figure 4: For a non-degenerate minimum, when the crossing falls in a classically forbidden region, the cut to infinity can be pushed to the classically forbidden zone, and one can forget about the crosing to leading order.

tion is $\exp(-\frac{1}{\sqrt{\mu}})$ near the crossing. The cut to infinity can be pushed to the classically forbidden zone, so the difference between periodic or antiperiodic boundary conditions is exponentially small, and one can forget about the crossing altogether. If the crossing point lies in the classically allowed region, it couples two nuclear Scrödinger equations and ruins the traditional Born-Oppenheimer approximation.

2.2.2 Born Oppenheimer theory near a degenerate minimizer

It can happen that the crossing must be taken into account although it lies at the classically forbidden zone. This happens when the cut can not be pushed to the classically forbidden zone. This is the case, for example, when the curve $\gamma \in \mathbb{R}^2$ is a minimizer of an electronic energy surface with zero energy [4] on γ. If γ encircles a crossing (see Fig. 5) then the cut necessarily

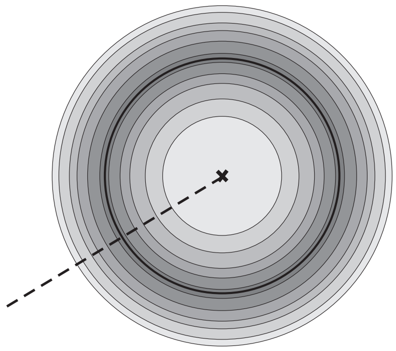

Figure 5: A degenerate minimum around a crossing. The solid circle represents γ. Although the crossing falls in the classically forbidden zone, it should be taken into account.

intersects γ and since γ lies in the classically accessible region, the wave function is large there and it matters if one imposes periodic or anti-periodic boundary conditions.

3 Born Oppenheimer theory near crossing

Consider now the spectral problem near crossing energy of two electronic energy surfaces. Let us set the crossing energy at 0 and assume that the crossing is conic. This is the generic situation.

Upon scaling, $x = \epsilon\xi,\ \epsilon = \mu^{1/3}$, the Born Oppenheimer operator assumes the form

$$\epsilon \left((-i\nabla_\xi - \epsilon\, A(\epsilon\xi))^2 + \frac{1}{\epsilon}\, E(\epsilon\xi) \right), \quad \epsilon = \mu^{1/3}. \tag{4}$$

The scaling increases the gaps between the electronic energy surfaces and decreases the coupling *of the crossing pair* to other levels since $\epsilon\, A_{ij}(\epsilon\xi) = O(\mu^{1/3})$ when i belongs to the pair and j to other levels. On the other hand, the crossing pair remains coupled, because the Coulombic singularity near the crossing says that $\epsilon A_{i,i'}(\epsilon\xi) = O\left(\frac{1}{|\xi|}\right)$, which is large when ξ is small. We see that a spectral problem in an interval of order $o(1)$ near the crossing

[4]Similar arguments apply if the energy associated with γ is sufficiently small

energy, reduces to a problem where $H_e(x)$ is a 2×2 matrix up to an error of order μ in the eigenvalues and of order $\mu^{2/3}$ in the eigenfunctions.

Our aim, in this work, is to describe the wave functions for states, located at an interval of width that is much smaller than $\mu^{1/3}$ near the crossing. Even though this is a small interval, it has lots of eigenvalues: By Weyl's rule there are many states, of order $\mu^{-2/3}$, in an interval of width $\mu^{1/3}$, in two dimensions. One can expect to find many states in the interval in question.

Close to the crossing $H_e(x)$ can be expanded in terms of the Pauli matrices and the unit matrix. We assume that asymptotically close to the crossing point $H_e(x)$ is isotropic and conic[5]:

$$H_e(x) = \sigma \cdot x + O(x^2). \tag{5}$$

We choose $\sigma_{1,2}$ real[6]:

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{6}$$

$O(x^2)$ accounts for the behaviour far from the crossing which is not universal, or isotropic.

How restrictive is the assumption that near the crossing $H_e(x)$ is isotropic? Molecules are never isotropic, although some may be approximately so. Nevertheless, isotropic conic intersections are, in fact, common. This is a known phenomenon in group theory: Discrete symmetry can force full continuous symmetry on tensors of finite rank [22]. For example, as shown by [9], the D_3 symmetry of trimers forces isotropy of the conics.

It follows from the above that if one is interested in the local behavior of eigenfunctions for eigenvalues that lie in an *energy range* that is small compared to $\mu^{1/3}$ and in a *spatial neighborhood* of the crossing, $|x| << 1$, the eigenfunctions satisfy, to leading order in μ, a *canonical system of partial differential equations*,

$$\Big(- \mu \, \Delta_{xx} + \sigma \cdot x \Big) \Psi = \mu^{1/3} \Big(- \, \Delta_{\xi\xi} + \sigma \cdot \xi \Big) \Psi = 0. \tag{7}$$

The rotational symmetry allows us to reduce the system Eq. (7), to a system of linear, *ordinary differential equation* parameterized by angular momentum

[5]Reality, isotropy and linearity would allow for an additional overall scale factor in H_e. This scale can be absorbed in a redefinition of μ.

[6]This is unconventional, but convenient.

$m \in \mathbb{Z} + \frac{1}{2}$ (see section 4.1):

$$\left\{ -\frac{d^2}{d\rho^2} - \frac{1}{\rho}\frac{d}{d\rho} + \frac{m^2 + 1/4}{\rho^2} + \begin{pmatrix} -\frac{m}{\rho^2} & \rho \\ \rho & \frac{m}{\rho^2} \end{pmatrix} \right\} \mathcal{F}_m = 0, \quad \rho = |\xi|. \tag{8}$$

For fixed m the space of solutions of the ODE is four dimensional. We shall see that there is a *one dimensional subspace of solutions* that is well behaved near the origin $\rho = 0$, and near infinity. As we shall explain, functions in this space describe the asymptotic behavior of eigenfunctions with energies near the crossing and spatially close to it. The explicit expression for these solutions, is described below.

3.1 The main result

We now describe our main result:

Theorem 3.1 *For $m \in \mathbb{Z} + \frac{1}{2}$, and $m \geq \frac{1}{2}$, let*

$$\begin{aligned} \mathcal{F}_m(\rho) &= \frac{3^{-\frac{1}{2}} 6^{-(\frac{5}{6}+\frac{2m}{3})} \rho^{m-\frac{1}{2}}}{\Gamma(\frac{2}{3})\Gamma(\frac{1}{2}+\frac{m}{3})\,\Gamma(\frac{7}{6}+\frac{m}{3})} \begin{pmatrix} {}_0F_3(;\frac{1}{3},\frac{1}{2}+\frac{m}{3},\frac{5}{6}+\frac{m}{3};\frac{\rho^6}{6^4}) \\ \frac{\rho^3}{6+4m}\, {}_0F_3(;\frac{4}{3},\frac{3}{2}+\frac{m}{3},\frac{5}{6}+\frac{m}{3};\frac{\rho^6}{6^4}) \end{pmatrix} \\ &- \frac{3^{-\frac{1}{2}}\, 6^{-(\frac{1}{6}+\frac{2m}{3})}\, \rho^{m+\frac{1}{2}}}{\Gamma(\frac{1}{3})\Gamma(\frac{1}{2}+\frac{m}{3})\Gamma(\frac{5}{6}+\frac{m}{3})} \begin{pmatrix} \frac{\rho^3}{12+8m}\, {}_0F_3(;\frac{5}{3},\frac{3}{2}+\frac{m}{3},\frac{7}{6}+\frac{m}{3};\frac{\rho^6}{6^4}) \\ {}_0F_3(;\frac{2}{3},\frac{1}{2}+\frac{m}{3},\frac{7}{6}+\frac{m}{3};\frac{\rho^6}{6^4}) \end{pmatrix} \end{aligned}$$

then

- *$\mathcal{F}_m(\rho)$, is a solution of the system of differential equations, Eq. (8).*
- *For small ρ*

$$\mathcal{F}_m(\rho) \to \frac{3^{-\frac{1}{2}} \rho^{m-\frac{1}{2}}}{\Gamma(\frac{1}{2}+\frac{m}{3}) 6^{\frac{4m+1}{6}}} \begin{pmatrix} \frac{1}{\Gamma(\frac{2}{3})\Gamma(\frac{7}{6}+\frac{m}{3})6^{\frac{2}{3}}} \\ -\frac{\rho}{\Gamma(\frac{1}{3})\Gamma(\frac{5}{6}+\frac{m}{3})} \end{pmatrix}. \tag{9}$$

  In particular, $\mathcal{F}_{\frac{1}{2}}(0) \neq 0$.

- *For large ρ*

$$\mathcal{F}_c(\rho) \to \frac{1}{(2\pi)^{3/2}\rho^{3/4}} \cos\left(\frac{2}{3}\rho^{3/2} - \pi\left(\frac{m}{3} + \frac{1}{4}\right)\right) \begin{pmatrix} 1 \\ -1 \end{pmatrix} \tag{10}$$

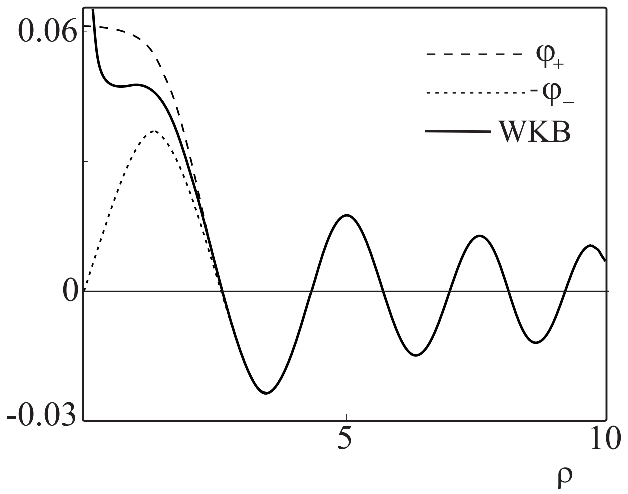

Figure 6: The components of $\mathcal{F}_m(\rho)$ for $m = \frac{1}{2}$ and their asymptotic form given by (10). The function is compared with the WKB Born Oppenheimer wave function.

Theorem 3.2 *For $m \in \mathbb{Z} + \frac{1}{2}$, and $m \geq \frac{1}{2}$, let*

$$\Psi_m(r,\theta) = \mu^{-1/4} e^{im\theta} \begin{pmatrix} e^{-i\theta/2} & ie^{i\theta/2} \\ ie^{-i\theta/2} & e^{i\theta/2} \end{pmatrix} \mathcal{F}_m(\mu^{-1/3} r) \tag{11}$$

then

- *Ψ_m is a solution of the system of PDE, Eq. (7) where $x = (r\cos\theta, r\sin\theta)$.*
- *The m-th component of an eigenfunction of Eq. (1) near crossing, i.e. with eigenvalue $|E| << \mu^{1/3}$ and for $x = (r\cos\theta, r\sin\theta)$, $r << 1$ is, to leading order, proportional to $\Psi_m(r,\theta)$.*
- *The amplitude of Ψ_m is independent of μ in the region $r >> \mu^{1/3}$.*
- *Near the crossing, $r \approx \mu^{1/3}$, the amplitude of the wave function $\Psi_m = O(\mu^{-1/4})$*

Remark 3.1 *The most interesting aspect of the solution is that the wave function has* large amplitude *at the crossing region in the limit of small μ. As we shall see, this result follows from arguments that do not rely on the explicit form of the solution, but do depend on the fact that in the non-mixing region, $r >> \mu^{1/3}$ the solution has a WKB form in the radial direction.*

Remark 3.2 *The function* Ψ_m does not *describe the behavior of wave functions in the far zone where* $r > 1$. *The behaviour in the far zone is not universal and depends on the details of the electronic energy surface . The far zone is described by standard Born Oppenheimer, so* Ψ_m *gives complementary information.*

Remark 3.3 *There are* $o\left(\mu^{-2/3}\right)$ *states in the relevant energy interval* $o\left(\mu^{1/3}\right)$ *near the crossing disregarding* m. *For a given* m *there are only* $\mu^{-1/6}$ *levels in this interval. This says that near the crossing* m *is bounded by order* $\mu^{-1/2}$.

Remark 3.4 *We shall actually only prove the theorem in the special case that* $H_e(x)$ *is rotationally symmetric. The symmetry decouples channels with different angular momenta. We believe that mixing of angular momenta in the far zone is only a technical complication and that the result also holds without rotational symmetry in the far zone.*

4 The Rotationally Symmetric Case

In the following we describe a derivation of the main result for a Born Oppenheimer model that is rotationally symmetric. With rotational symmetry we can reduce the spectral problem of a PDE to a spectral problem of an ODE. No real molecule is rotationally symmetric and the general case leads to mixing of m channels. We believe that this is only a technical complication.

We require invariance of $H_e(x)$ under infinitesimal rotations in the nuclear and electronic Hilbert spaces. Such a rotation is generated by

$$J_3 = L_3 + \frac{1}{2}\sigma_3 = -ix_1\frac{\partial}{\partial x_2} + ix_2\frac{\partial}{\partial x_1} + \frac{1}{2}\sigma_3, \tag{12}$$

with

$$\sigma_3 = \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}.$$

The L_3 part generates $SO(2)$ rotations in the nuclear Hilbert space ($x_1 - x_2$ plane), whereas the $\frac{1}{2}\sigma_3$ part generates a rotation in the electronic Hilbert space. J_3 does not have the meaning of total angular momentum since the Pauli matrices do not represent spin. Isotropy means that J_3 commutes with $H_e(x)$:

$$0 = [J_3, H_e(x)]$$

The most general form of $H_e(x)$ for a two level system that is rotationally symmetric and real is:

$$H_e(x) = Q_0(r) + Q_1(r)(x \cdot \sigma) + Q_2(r)(x \times \sigma), \quad r = |x| \tag{13}$$

An additional $Q_3(r)\sigma_3$ term in (13) is allowed by rotational invariance but it is forbidden by time reversal symmetry, since σ_3 is imaginary.

The energy surfaces of $H_e(x)$ are equal to

$$E_\pm(r) = Q_0(r) \pm q(r); \quad q(r) = r\sqrt{Q_1^2(r) + Q_2^2(r)} \tag{14}$$

We shall assume that $Q_{0,1,2}$ are smooth functions of r and that $Q_1(0) = 1$ while[7] $Q_{0,2}(r) = O(r^2)$ for small r. This gives conic intersection at zero with $E_\pm(r) = \pm r$, see Fig. 7.

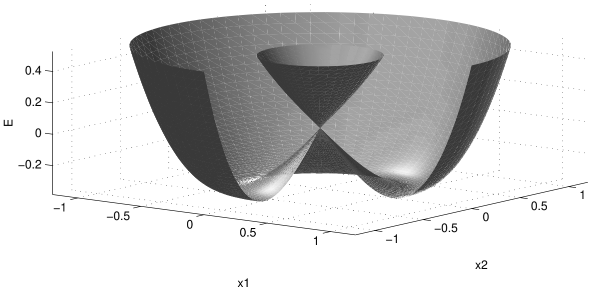

Figure 7: The electronic energy surfaces of $H_e(x)$

4.1 The radial Hamiltonian

The spectral subspace of J_3, with eigenvalue m is spanned by

$$e_1 = e^{-i(m+1/2)\theta}\begin{pmatrix}1\\ i\end{pmatrix} \qquad e_2 = e^{-i(m-1/2)\theta}\begin{pmatrix}i\\ 1\end{pmatrix} \tag{15}$$

m must be half odd integer for $e_{1,2}$ to be univalued, i.e. $m \in \mathbb{Z} + \frac{1}{2}$.

Since

$$-\Delta\, e_1 = \frac{(m+\frac{1}{2})^2}{r^2}\, e_1, \qquad -\Delta\, e_2 = \frac{(m-\frac{1}{2})^2}{r^2}\, e_2,$$

[7] $Q_2(0)$ can be always set to zero by an appropriate rotation in the x space only, i. e. by an appropriate choice of the heavy coordinates.

$$
\begin{aligned}
x \cdot \sigma\, e_1 &= ir\, e_2, &\qquad \sigma \cdot x\, e_2 &= r\, e_1, \\
x \times \sigma\, e_1 &= -ir\, e_2, &\qquad x \times \sigma\, e_2 &= ir\, e_1,
\end{aligned} \tag{16}
$$

in terms of the basis $\{e_1, e_2\}$ we obtain for the radial equation:

$$
H(m,\mu) = -\mu \left(\frac{d^2}{dr^2} + \frac{1}{r}\frac{d}{dr} - \frac{1}{4r^2} \right) + H_e(r,\mu,m) \tag{17}
$$

with

$$
H_e(r,\mu,m) = Q_0(r) + rQ_1(r)\sigma_1 + rQ_2(r)\sigma_3 - \frac{\mu}{r^2}\left(m\sigma_2 - m^2\right) \tag{18}
$$

Scaling $r = \mu^{1/3}\rho$ we get Eq. (8), to leading order in μ, for $0 \le \rho << \mu^{-1/3}$.

Remark 4.1 *The radial Hamiltonian, $H_e(m,\mu,r)$, actually has no level crossing. This, by itself, does not ameliorate the mixing of the two levels for now the gap in the spectrum of $H_e(m,\mu,r)$ is of order $\mu^{1/3}$. The smallness of this gap leads to mixing of the electronic levels.*

We shall restrict ourselves to $m > 0$. Since

$$
\sigma_1\, H_e^*(r,\mu,m)\sigma_1 = H_e(r,\mu,-m), \tag{19}
$$

$H(m,\mu)$ and $H(-m,\mu)$ are isospectral and the radial part of the function with $-m$ can be obtained from the one with $+m$ by interchanging upper and lower components and taking complex conjugates.

4.2 The Indicial equation

The origin, $\rho = 0$ is regular-singular point [20] of the equation. Substituting

$$
\begin{pmatrix} \rho^\alpha \\ \rho^\beta \end{pmatrix} (1 + O(\rho)) \tag{20}
$$

into (8) we obtain the roots $\alpha = \pm(m - \frac{1}{2})$ and $\beta = \pm(m + \frac{1}{2})$. Equation (8) therefore has four linearly independent solutions, which asymptotically near the origin, behave like

$$
\begin{pmatrix} \rho^{m-\frac{1}{2}} \\ 0 \end{pmatrix};\ \begin{pmatrix} \rho^{-m+\frac{1}{2}} \\ 0 \end{pmatrix};\ \begin{pmatrix} 0 \\ \rho^{m+\frac{1}{2}} \end{pmatrix};\ \begin{pmatrix} 0 \\ \rho^{-m-\frac{1}{2}} \end{pmatrix} \tag{21}
$$

(21) is correct only for $|m| \neq \frac{1}{2}$. The case $|m| = \frac{1}{2}$ requires special treatment, because of the two degenerate roots in the upper component. For $|m| = \frac{1}{2}$ the four linearly independent solutions behave asymptotically near the origin like [20]

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix}; \quad \begin{pmatrix} \ln(\rho) \\ 0 \end{pmatrix}; \quad \begin{pmatrix} 0 \\ \rho \end{pmatrix}; \quad \begin{pmatrix} 0 \\ 1/\rho \end{pmatrix} \tag{22}$$

We see that for any m there are always two solutions which are bounded near the origin and two others which are divergent. Since a smooth Hamiltonian can give rise to smooth eigenfunctions only [21] in the four dimensional space of solutions to the differential equation, there is a two dimensional subspace of admissible solutions, the ones which are well behaved at the origin.

4.3 Solution to the ODE

Theorem 4.1 *The two solutions of (8) which are bounded at the origin are:*

$$\begin{aligned}
\mathcal{F}_m^{(1)}(\rho) &= \begin{pmatrix} \varphi_+^{(1)}(\rho) \\ \varphi_-^{(1)}(\rho) \end{pmatrix} = \begin{pmatrix} \rho^{m-\frac{1}{2}} {}_0F_3(;\frac{1}{3}, \frac{1}{2}+\frac{m}{3}, \frac{5}{6}+\frac{m}{3}; \frac{\rho^6}{6^4}) \\ \frac{\rho^{m+\frac{5}{2}}}{6+4m} {}_0F_3(;\frac{4}{3}, \frac{3}{2}+\frac{m}{3}, \frac{5}{6}+\frac{m}{3}; \frac{\rho^6}{6^4}) \end{pmatrix}; \\
\mathcal{F}_m^{(2)}(\rho) &= \begin{pmatrix} \varphi_+^{(2)}(\rho) \\ \varphi_-^{(2)}(\rho) \end{pmatrix} = \begin{pmatrix} \frac{\rho^{m+\frac{7}{2}}}{12+8m} {}_0F_3(;\frac{5}{3}, \frac{3}{2}+\frac{m}{3}, \frac{7}{6}+\frac{m}{3}; \frac{\rho^6}{6^4}) \\ \rho^{m+\frac{1}{2}} {}_0F_3(;\frac{2}{3}, \frac{1}{2}+\frac{m}{3}, \frac{7}{6}+\frac{m}{3}; \frac{\rho^6}{6^4}) \end{pmatrix},
\end{aligned} \tag{23}$$

where ${}_0F_3(;a,b,c;x)$ are the generalized hypergeometric functions of the kind ${}_0F_3$.

Proof: To show this we need to turn the two coupled second order equations (8) into one scalar fourth order equation. The equations obtained for φ_+ and φ_- can be written, with $\zeta = \rho^6/6^4$, and $\mathrm{D} = \zeta\frac{d}{d\zeta}$, in the form:

$$\begin{aligned}
&\left\{\mathrm{D}(\mathrm{D}-\frac{2}{3})(\mathrm{D}+\frac{m}{3}-\frac{1}{2})(\mathrm{D}+\frac{m}{3}-\frac{1}{6}) - \zeta\right\} \zeta^{\frac{-m+1/2}{6}} \varphi_+(\zeta) = 0 \\
&\left\{\mathrm{D}(\mathrm{D}-\frac{1}{3})(\mathrm{D}+\frac{m}{3}-\frac{1}{2})(\mathrm{D}+\frac{m}{3}+\frac{1}{6}) - \zeta\right\} \zeta^{\frac{-m-1/2}{6}} \varphi_+(\zeta) = 0
\end{aligned} \tag{24}$$

These equations are special cases of the generalized hypergeometric equation [24]:

$$\{\mathrm{D}(\mathrm{D}+a-1)(\mathrm{D}+b-1)(\mathrm{D}+c-1) - \zeta\}\, f(\zeta) = 0 \tag{25}$$

Which is solved by ${}_0F_3(;a,b,c;\zeta)$. These functions, parameterized by a, b, c, are always entire functions. Their definition appears in the appendix.

We shall now construct both solutions of (8). The first one, according to (24) and (25), has for the upper component

$$\varphi_+^{(1)}(\rho) = \rho^{m-\frac{1}{2}}{}_0F_3\left(;\frac{1}{3},\frac{1}{2}+\frac{m}{3},\frac{5}{6}+\frac{m}{3};\frac{\rho^6}{6^4}\right).$$

To find the corresponding $\varphi_-^{(1)}$ we apply to equation (8), which can give us the relation

$$\varphi_-^{(1)}(\rho) = \frac{\rho^{m-\frac{1}{2}}}{\rho^3}\left\{\rho\frac{d}{d\rho}\left(\rho\frac{d}{d\rho}+2m-1\right)\right\}\frac{\varphi_+^{(1)}(\rho)}{\rho^{m-\frac{1}{2}}} \tag{26}$$

With the identities [24, 26]

$$\begin{aligned}\left(\zeta\frac{d}{d\zeta}+c-1\right){}_0F_3(;a,b,c;\zeta) &= (c-1){}_0F_3(;a,b,c-1;\zeta)\\ \frac{d}{d\zeta}{}_0F_3(;a,b,c;\zeta) &= \frac{1}{abc}{}_0F_3(;a+1,b+1,c+1;\zeta)\end{aligned}$$

we obtain

$$\varphi_-^{(1)}(\rho) = \frac{1}{6+4m}\rho^{m+\frac{5}{2}}{}_0F_3\left(;\frac{4}{3},\frac{3}{2}+\frac{m}{3},\frac{5}{6}+\frac{m}{3};\frac{\rho^6}{6^4}\right).$$

The second solution to (8) is obtained from the second equation of (24). It gives for $\varphi_-^{(2)}$ the solution

$$\varphi_-^{(2)}(\rho) = \rho^{m+\frac{1}{2}}{}_0F_3(;\frac{2}{3},\frac{1}{2}+\frac{m}{3},\frac{7}{6}+\frac{m}{3};\frac{\rho^6}{6^4}),$$

and with a relation

$$\varphi_-^{(1)}(\rho) = \frac{\rho^{m+\frac{1}{2}}}{\rho^3}\left\{\rho\frac{d}{d\rho}\left(\rho\frac{d}{d\rho}+2m+1\right)\right\}\frac{\varphi_{+1}(m;\rho)}{\rho^{m+\frac{1}{2}}}$$

similar to (26) one computes the upper component of the second solution:

$$\varphi_+^{(2)}(\rho) = \frac{1}{12+8m}\rho^{m+\frac{7}{2}}{}_0F_3\left(;\frac{5}{3},\frac{3}{2}+\frac{m}{3},\frac{7}{6}+\frac{m}{3};\frac{\rho^6}{6^4}\right)\blacksquare$$

4.4 The well behaved solutions

We have seen that of the four dimensional family of solution of Eq.(8) there is a distinguished two dimensional family that is well behaved near the origin. We shall now show that there is a three dimensional family that is well behaved at infinity:

Theorem 4.2 • *In the four dimensional space of solutions of Eq. (8) there is a three dimensional family of solutions that vanish at infinity, and one dimensional subspace that diverges exponentially at infinity.*

- *The solutions of (8) for $\rho >> 1$ are (asymptotically) spanned by the four dimensional family :*

$$\begin{aligned} &\rho^{-3/4}\exp\left(-\frac{2}{3}\rho^{3/2}\right)\begin{pmatrix}1\\1\end{pmatrix}; \qquad &&\rho^{-3/4}\exp\left(\frac{2}{3}\rho^{3/2}\right)\begin{pmatrix}1\\1\end{pmatrix};\\ &\rho^{-3/4}\cos\left(\frac{2}{3}\rho^{3/2}\right)\begin{pmatrix}1\\-1\end{pmatrix}; \qquad &&\rho^{-3/4}\sin\left(\frac{2}{3}\rho^{3/2}\right)\begin{pmatrix}1\\-1\end{pmatrix}. \end{aligned} \tag{27}$$

- *The exponential blow up of $\mathcal{F}_m^{(1,2)}$ of Eq. (8) is given by*

$$\begin{aligned} 2\mathcal{F}_m^{(1)}(\rho) &\to \Gamma\left(\frac{1}{3}\right)\Gamma\left(\frac{1}{2}+\frac{m}{3}\right)\Gamma\left(\frac{5}{6}+\frac{m}{3}\right)6^{\frac{1}{6}+\frac{2m}{3}}\rho^{-3/4}\exp\left(\frac{2}{3}\rho^{3/2}\right)\begin{pmatrix}1\\1\end{pmatrix}\\ 2\mathcal{F}_m^{(2)}(\rho) &\to \Gamma\left(\frac{2}{3}\right)\Gamma\left(\frac{1}{2}+\frac{m}{3}\right)\Gamma\left(\frac{7}{6}+\frac{m}{3}\right)6^{\frac{5}{6}+\frac{2m}{3}}\rho^{-3/4}\exp\left(\frac{2}{3}\rho^{3/2}\right)\begin{pmatrix}1\\1\end{pmatrix} \end{aligned}$$

- *The solution to Eq (8) that vanishes at the origin and at infinity is a multiple of*

$$\Gamma\left(\frac{2}{3}\right)\Gamma\left(\frac{1}{2}+\frac{m}{3}\right)\Gamma\left(\frac{7}{6}+\frac{m}{3}\right)6^{\frac{5}{6}}\,\mathcal{F}_m^{(1)}(\rho)-$$
$$\Gamma\left(\frac{1}{3}\right)\Gamma\left(\frac{1}{2}+\frac{m}{3}\right)\Gamma\left(\frac{5}{6}+\frac{m}{3}\right)6^{\frac{1}{6}}\,\mathcal{F}_m^{(2)}(\rho).$$

Proof: $H_e(\rho,\mu,m)$ for Eq. (8) is, for $\rho >> 1$,

$$H_e(\rho,\mu,m)=\frac{m^2+1/4}{\rho^2}+\begin{pmatrix}-\frac{m}{\rho^2} & \rho\\ \rho & \frac{m}{\rho^2}\end{pmatrix}\approx\begin{pmatrix}0 & \rho\\ \rho & 0\end{pmatrix} \tag{28}$$

With eigenvalues $\pm\rho$. It follows that the solution for large ρ reduces to the study of two uncoupeld equations:

$$\left(-\frac{d^2}{d\rho^2} - \frac{1}{\rho}\frac{d}{d\rho} \pm \rho\right)\psi = 0. \tag{29}$$

Since ρ is large, these can be solved by WKB to give the first part of the theorem. The blow up of the solutions at infinity can be obtained from the relation [23] (omitting the exponentially decaying part)

$${}_0F_3(;a,b,c;x) \to \frac{\Gamma(a)\Gamma(b)\Gamma(c)}{2(2\pi)^{3/2}} x^\gamma \left(e^{4x^{\frac{1}{4}}} + 2\cos(4x^{\frac{1}{4}} + 2\pi\gamma)\right),$$

with $\gamma = -\frac{a+b+c-3/2}{4}$. From this the rest follows, as well as the proof of theorem 3.1. ■

It remains to explain how eigenvectors are related to these well behaved solutions. The point is that the canonical differential equation approximates the eigenvalue equation only for $r << 1$, or, equivalently, for $\rho << \mu^{-1/3}$. Consider an eigenfunction. Far from the crossing this eigenfunction can be approximated by a WKB solution, and it is clear that this WKB solution can be approximated by WKB solution of the canonical problem in the interval $\mu^{-1/3} >> \rho >> 1$. The component that blows up must have an exponentially small amplitude, of order $\exp(-\frac{2}{3\sqrt{\mu}})$, and, to leading order can be neglected near the crossing.

5 Anomalous Mixing

The basic and fundamental observation of the Born-Oppenheimer theory is the emergence of the energy scale $\sqrt{\mu}$ in molecular spectra associated with vibrations. Perhaps the most interesting observation that results from the analysis of the Born-Oppenheimer theory near crossing, is that emergence of the scale, $\mu^{1/6}$, associated with mixing at crossing. $\mu^{1/6}$ is normally not a small number: In molecules $\mu^{1/6} \sim .2$.

Classically, a uniform density on the energy shell, $\delta(p^2+V(x)-E)$ implies that, in two dimensions, the spatial density is also uniform on the classically allowed region. The region where there is substantial mixing between the two electronic energy surfaces has linear dimensions that scale like $\mu^{1/3}$. For a crossing point in two dimension the volume characterizing the mixing therefore scales like $\mu^{2/3}$. The semi-classical expectation is therefore that mixing near crossing should scale like the area $\mu^{2/3}$.

For isotropic crossing we found that the wave function has anomalously *large* amplitude in the mixing region for values of azymuthal quantum numbers that are small compares to $\mu^{-1/2}$. For these, from theorem 3.2, the amplitude in the near zone scales like $\mu^{-1/4}$. This implies that the total mixing weight scales like $\mu^{1/6}$.

It would be interesting to have a more complete picture of the mixing near non-isotropic crossing and also for chaotic systems.

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