Born-Oppenheimer Approximation near Level Crossing

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Abstract

We consider the Born-Oppenheimer problem near conical intersection in two dimensions. For energies close to the crossing energy we describe the wave function near an isotropic crossing and show that it is related to generalized hypergeometric functions ${}_0F_3$. This function is to a conical intersection what the Airy function is to a classical turning point. As an application we calculate the anomalous Zeeman shift of vibrational levels near a crossing.

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The Born-Oppenheimer problem [1] is concerned with the analysis of Schrödinger type operators where m_e/M, the small electron to nucleon mass ratio, plays the role of the semi-classical parameter $\hbar^2$ [2–8]. We shall henceforth write $\hbar^2 = m_e/M$. The theory identifies distinct energy scales: The electronic scale which, in atomic units, is of order one and the scale of nuclear vibrations which is of order $\hbar$ in these units. The identification of the electrons as the fast degrees of freedom is central to the theory.

The clean splitting between fast and slow degrees of freedom fails near eigenvalue crossing of the electronic Hamiltonian where there is strong mixing between electronic and vibrational modes. This lies at the boundary of the conventional Born-Oppenheimer theory. In particular, there is no description of the wave function near crossings for energies close to the energy at which the crossing occurs. We give such a description in the special case of isotropic conical crossing.

The strong mixing of the electronic and nuclear degrees of freedom near crossing leads to an emergence of a new scale of $\hbar^{1/3}$. This scale appears in the Zeeman shift of levels near the crossing energy. Normally, the Zeeman shift of vibrational levels is of the order of $\hbar^2 B$ in atomic units which is what one expects from nuclei whose magnetic moments are $\hbar^2$ smaller than the Bohr magneton. In contrast, for levels *near the crossing energy* the Zeeman shift is anomalously large and turns out to be

$$\Delta E(m) \approx \hbar^{1/3} \frac{g(m)}{T_c} B. \tag{1}$$

The sign $\approx$ means equality in the limit $\hbar \to 0$. m, a half odd integer, is the azimuthal quantum number, T_c is half a period of the classical motion, see Eq. (23) below. $g(m)$ is a universal dimensionless factor which is determined by the wave function near the crossing, see Eq. (20) below. As we shall see $g(m) = -g(-m)$ and numerical estimates of Eq. (20) give

$$g\left(\frac{1}{2}\right) = 0.961, \; g\left(\frac{3}{2}\right) = 0.543, \; g\left(\frac{5}{2}\right) = 0.396. \tag{2}$$

$g(m)$ is a molecular analog of the Landé g factor in atoms: So, while Langé g factor describes the Zeeman shift due to the mixing of spin and orbital degrees of freedom, $g(m)$ does it for the nuclear and electronic ones.

A simple model Hamiltonian that preserves the relevant key aspects of the problem is

$$H_{bo} = -\hbar^2 \Delta_x + H_e(x), \tag{3}$$

where $H_e(x)$, the electronic Hamiltonian, depends parameterically on the nuclear coordinates x. When time reversal is not broken, $H_e(x)$ is a real symmetric matrix for integral spin, and $H_e(x)$ is quaternionic real when the spin is half integral [9]. Wigner von Neumann crossing rule [10] says that $H_e(x)$ has generically a crossing point for two modes of vibrations, $x \in \mathbb{R}^2$, in the case of integer spin and for five vibrational modes, $x \in \mathbb{R}^5$, for half integer spin.

Here we shall consider the simple scenario where the spin is integral, $x \in \mathbb{R}^2$, and $H_e(x)$ is a 2×2 matrix. We shall assume that $H_e(x)$ has a single crossing point at $x = 0$, and set the crossing energy at 0. We further assume that the crossing is conic, that $H_e(x)$ is isotropic about the origin, and that the x dependence of $H_e(x)$ is smooth near the origin.

By isotropy we mean that H_{bo} commutes with $J_3 = L_3 + \frac{1}{2}\sigma_3$. We shall also assume that $H_e(x)$ has, at most, one negative eigenvalue.

We first recall how close to a crossing one can get with the standard Born-Oppenheimer theory. When $H_e(x)$ is symmetric it can be diagonalized by an *orthogonal* transformation $R(x)$. In the 2×2 case, and when $H_e(x)$ is non-degenerate, $R(x)$ is uniquely determined, up to an overall sign, by requiring $\det R(x) = 1$. Hence, away from crossing, H_{bo} is unitarily equivalent to

$$-\hbar^2 \Big(\nabla_x + R^T(x)\nabla_x R(x)\Big)^2 + \begin{pmatrix} E_1(x) & 0 \\ 0 & E_2(x) \end{pmatrix}, \tag{4}$$

where $E_{1,2}(x)$ are the two eigenvalues of $H_e(x)$. The vector potential $-iR^T(x)\nabla_x R(x)$ is purely off-diagonal. For linear crossing, $R(x) \to -R(x)$ as x surrounds the origin [4]. This forces a $1/|x|$ singularity of the vector potential for small x. Away from the origin, to leading order in $\hbar$, the two components of the wave function decouple and are given by

$$\Psi_{bo,j}(x) \approx \psi_{cl,j}(x) R(x) \begin{pmatrix} \delta_{j,1} \\ \delta_{j,2} \end{pmatrix}, \quad j = 1, 2, \tag{5}$$

where $\psi_{cl,j}$ is a semiclassical solution of the Schrödinger equation with potential $E_j(x)$ in the cut plane with antiperiodic boundary conditions [4,6]. This analysis holds provided $|x| >> \hbar^{2/3}$, see Eq. (11) below.

Our aim is to analyze the Born-Oppenheimer theory, to leading order in $\hbar$, near the crossing of H_e. In contrast with the usual situation in Born-Oppenheimer theory, the leading order behaviour does not reduce to the study of a scalar Schrödinger equation. The reason one can still hope to say something useful near the crossing is that the asymptotic form of H_{bo} near the crossing, i.e. for $|x| << 1$, is universal

$$H = -\hbar^2 \Delta_x + x_1\sigma_1 + x_2\sigma_2 \tag{6}$$

where σ are the Pauli matrices [11]. The eigenfunctions Ψ of the full Born-Oppenheimer Hamiltonian (3) for an eigenvalue ε near the crossing, solve an equation of the form $H\Psi = O(x^2\Psi) + O(\varepsilon\Psi)$, where the right hand side depends on details of the full problem. H always has an eigenvalue ε in a neighborhood $O(\hbar)$ of zero. By scaling Eq. (6), one shows that provided $|x| << \hbar^{1/3}$ the solution Ψ has a universal leading order (in $\hbar$) approximant $\mathcal{F}$ such that $H\mathcal{F} = 0$. The appropriate solutions of this equation are to a crossing point what the Airy function is to a classical turning point [12,13]: They interpolate between a region where the wave function is intrinsically a two component spinor, and a region where the wave function is highly oscillatory and merge with the standard Born-Oppenheimer form Eq. (5) away from the crossing.

Since H commutes with $J_3 = L_3 + \frac{1}{2}\sigma_3$, we consider solutions of the differential equation of the form

$$\mathcal{F}(\xi) = e^{im\theta} \begin{pmatrix} \varphi_1(\rho; m)e^{-i\theta/2} \\ \varphi_2(\rho; m)e^{i\theta/2} \end{pmatrix}, \quad \xi = \{\rho, \theta\}, \tag{7}$$

where $\xi_j = \hbar^{-2/3} x_j$ is the scaled variable and ρ, θ are the corresponding polar coordinates. m must be *half odd integer*, for the wave function to be single valued. Since H commutes with (time reversal) $T = *\sigma_2 I$ [14], where $Ix = -x$ while $TJ_3T = -J_3$, it is enough to consider $m \geq \frac{1}{2}$.

Separating variables, the radial equation, in the m-th sector, takes the form:

$$\left\{\mathcal{D}(m) + \begin{pmatrix} -\frac{m}{\rho^2} & \rho \\ \rho & \frac{m}{\rho^2} \end{pmatrix}\right\} \mathcal{F}(\rho; m) = 0, \tag{8}$$

where

$$\mathcal{D}(m) = -\frac{d^2}{d\rho^2} - \frac{1}{\rho}\frac{d}{d\rho} + \frac{m^2 + 1/4}{\rho^2}, \ \mathcal{F}(\cdot\,; m) = \begin{pmatrix} \varphi_1 \\ \varphi_2 \end{pmatrix}.$$

This ordinary differential equation has four linearly independent solutions. Two solutions diverge at the origin. This is because 0 is a regular-singular point [15] of (8), the roots of the corresponding incidal equation are $\pm(m + \frac{1}{2})$ for the lower component and $\pm(m - \frac{1}{2})$ for the upper component. For $m > \frac{1}{2}$, there are two negative roots, and therefore two solutions which are divergent at the origin. Although for $m = 1/2$ there is only one negative root (-1), the two degenerate zero roots force us to introduce a solution which includes $\ln(x)$, to be logarithmically divergent at the origin.

The fourth order differential equation for each component φ_j, are related to the differential equation that defines the generalized hypergeometric functions ${}_0F_3$. Namely, with $\zeta = \rho^6/6^4$, and $\mathrm{D} = \zeta\frac{d}{d\zeta}$:

$$\left\{\mathrm{D}(\mathrm{D} - \frac{1}{2} + \frac{(-1)^j}{6})(\mathrm{D} + \frac{m}{3} - \frac{1}{2})(\mathrm{D} + \frac{m}{3} + \frac{(-1)^j}{6}) - \zeta\right\} \zeta^{\frac{-m-(-1)^j/2}{6}} \varphi_j(\zeta) = 0. \tag{9}$$

The two linearly independent solutions that are regular at the origin are:

$$\mathcal{F}_1(\rho; m) = \begin{pmatrix} \rho^{m-\frac{1}{2}} {}_0F_3(;\frac{1}{3}, \frac{1}{2} + \frac{m}{3}, \frac{5}{6} + \frac{m}{3}; \frac{\rho^6}{6^4}) \\ \frac{\rho^{m+\frac{5}{2}}}{6+4m} {}_0F_3(;\frac{4}{3}, \frac{5}{6} + \frac{m}{3}, \frac{3}{2} + \frac{m}{3}; \frac{\rho^6}{6^4}) \end{pmatrix};$$
$$\mathcal{F}_2(\rho; m) = \begin{pmatrix} \frac{\rho^{m+\frac{7}{2}}}{12+8m} {}_0F_3(;\frac{5}{3}, \frac{7}{6} + \frac{m}{3}, \frac{3}{2} + \frac{m}{3}; \frac{\rho^6}{6^4}) \\ \rho^{m+\frac{1}{2}} {}_0F_3(;\frac{2}{3}, \frac{1}{2} + \frac{m}{3}, \frac{7}{6} + \frac{m}{3}; \frac{\rho^6}{6^4}) \end{pmatrix}, \tag{10}$$

where ${}_0F_3(;a, b, c; \rho)$ are the generalized hypergeometric functions [16,17].

To investigate the solutions for large value of ρ, $1 << \rho << \hbar^{-1/3}$, we rewrite the differential equation in the form:

$$\left\{\mathcal{D}(m) + \begin{pmatrix} -\rho & \frac{m}{\rho^2} \\ \frac{m}{\rho^2} & \rho \end{pmatrix}\right\} \begin{pmatrix} \varphi_1 - \varphi_2 \\ \varphi_1 + \varphi_2 \end{pmatrix} = 0 \tag{11}$$

For large values of ρ the matrix is asymptotically diagonal and the operator decouples into two scalar Schrödinger equations. The lower/upper component is a solution of a Schrödinger equation for a particle in a linearly increasing/decreasing potential $\pm\rho$. The asymptotic $(\rho >> 1)$ form of the solutions is therefore [12,13]:

$$\frac{1}{\rho^{3/4}}\left\{\left(A_+(m)e^z + A_-(m)e^{-z}\right)\begin{pmatrix} 1 \\ 1 \end{pmatrix} + C(m)\cos(z + \phi_m)\begin{pmatrix} 1 \\ -1 \end{pmatrix}\right\}, \quad z = \frac{2}{3}\rho^{3/2} \tag{12}$$

The four dimensional family of solutions to the differential equation can therefore be parameterized by A_+, A_-, C and ϕ. It follows that, up to normalization, there is a unique linear combination of the two solutions that are regular at the origin, $\mathcal{F}_1$ and $\mathcal{F}_2$, which decays at infinity. One can fix the normalization of this solution by fixing the amplitude $C = 1$.

$$\mathcal{F}_c(\rho; m) = A_1(m)\mathcal{F}_1(\rho; m) + A_2(m)\mathcal{F}_2(\rho; m). \tag{13}$$

The leading term in the asymptotic ($\rho >> 1$) expansion of $\mathcal{F}_c$ is therefore *equal* to:

$$\frac{1}{\rho^{3/4}} \cos\left(\frac{2}{3}\rho^{3/2} + \phi_m\right)\begin{pmatrix} 1 \\ -1 \end{pmatrix}. \tag{14}$$

The coefficients $A_{1,2}(m)$ and the phase ϕ_m of Eq. (13) can be shown to be given by:

$$\begin{aligned} A_j(m) &= \frac{-(-1)^j 2\pi^{3/2} 6^{\frac{(-1)^j - 2m}{3}}}{3\Gamma(\frac{1}{2} + \frac{m}{3})\Gamma(\frac{1}{2} - \frac{(-1)^j}{6})\Gamma(1 + \frac{2m-(-1)^j}{6})}; \\ \phi_m &= -\pi\left(\frac{m}{3} + \frac{1}{4}\right). \end{aligned} \tag{15}$$

$\mathcal{F}_c(\rho; m)$ gives the radial components of the solution of Eq. (6) from which $\mathcal{F}_c(x)$, the full wave function can be easily constructed by Eq. (7). The solution is finite at the crossing point, and it propagates into the region $\rho >> 1$, far from the crossing, where it matches the Born-Oppenheimer wave function $\Psi_{bo,1}$ of Eq. (5). To see this matching in more detail note that the asymptotic form of Ψ_c, the full wave function obtained from $\mathcal{F}_c$, is

$$\begin{aligned} \Psi_c(\rho, \theta; m) &\approx \frac{e^{im\theta}}{\rho^{3/4}} \cos\left(\frac{2}{3}\rho^{3/2} + \phi_m\right) R(\theta)\begin{pmatrix} 1 \\ 0 \end{pmatrix}, \\ R(\theta) &= \frac{1}{\sqrt{2}}\begin{pmatrix} e^{i\theta/2} & e^{i\theta/2} \\ -e^{-i\theta/2} & e^{-i\theta/2} \end{pmatrix}. \end{aligned} \tag{16}$$

$R(\theta)$ is, indeed, the matrix that diagonalizes $H_e(x)$, with $x = \{r, \theta\}$, provided $|x| << 1$.

Let us now turn to the Zeeman shift. Consider

$$H_{bo}(B) = -\hbar^2\Delta_x + H_e(x) + B\sigma_3. \tag{17}$$

The $B\sigma_3$ term represents magnetic interaction which is mediated by the electrons. It removes the crossing in the electronic Hamiltonian. We have not minimally coupled the magnetic field directly to the vibrations for this is a weaker effect, of order $\hbar^2$, while the shift mediated by the electrons is $\hbar^{1/3}$, as we shall see. To avoid complications which have nothing to do with the crossing, let us assume that the eigenvalue $E_2(x)$ of $H_e(x)$ is always positive.

This model has, for $B = 0$, Kramers degeneracy, so every state is two fold degenerate. The magnetic field B breaks time reversal, $T\sigma_3 = -\sigma_3 T$ (recall that time reversal is $T = *\sigma_2 I$). Hence, the (Kramer) degeneracy for $B = 0$ is split. The splitting is twice the Zeeman shift in the energy for the two states $\pm m$ move in opposite directions.

Since isotropy is preserved by B, the Zeeman shift of the state m can be calculated by first order perturbation theory:

$$\Delta E(m) \approx B\,\frac{\int_0^\infty \rho\, d\rho\, (\psi_1^2(\rho; m) - \psi_2^2(\rho; m))}{\int_0^\infty \rho\, d\rho\, (\psi_1^2(\rho; m) + \psi_2^2(\rho; m))}, \tag{18}$$

where ψ_j are the radial components of the exact wave function of H_{bo} for $B = 0$.

We shall now show that in the numerator, the exact components ψ_j can be replaced, to leading order in $\hbar$, by the components φ_j of the canonical solution $\mathcal{F}_c$. While in the denominator, which fixes the overall normalization of the wave function, the components ψ_j can be replaced, again to leading order in $\hbar$, by ψ_{cl}, the Born-Oppenheimer approximation to the wave function far from the crossing.

In the numerator, write

$$\psi_1^2 - \psi_2^2 = (\psi_1 - \psi_2)(\psi_1 + \psi_2). \tag{19}$$

Far from the crossing, as we have seen, $(\psi_1 + \psi_2) \approx 0$ so the integrand lives near the crossing and therefore we can replace ψ_j by the canonical solution φ_j. The new integrand decays rapidly at infinity, therefore there is no harm in keeping the upper limit at infinity. If we take numerator as the definition of the gyromagnetic coefficient, then to leading order in $\hbar$,

$$g(m) = \int_0^\infty \rho\, d\rho\, (\varphi_{1c}^2(\rho; m) - \varphi_{2c}^2(\rho; m)). \tag{20}$$

From the invariance under T of $H_{bo}(0)$ it follows that $g(m) = -g(-m)$. For the denominator, write

$$\psi_1^2 + \psi_2^2 = \frac{1}{2}\Big((\psi_1 - \psi_2)^2 + (\psi_1 + \psi_2)^2\Big). \tag{21}$$

Clearly, the probability of finding the particle inside a circle of radius $\hbar^{2/3}$ around the crossing is arbitrarily small in the semiclassical limit. Most of the wave function is far from the crossing where, by the Born-Oppenheimer wave function, Eq. (5), $\psi_1 + \psi_2 \approx 0$ while $\frac{1}{2}(\psi_1 - \psi_2) \approx \psi_{cl}$.

By WKB, the wave function, in the classically allowed region, that fits with the canonical solution $\mathcal{F}_c$, is

$$\psi_{cl}(r; m) \approx \sqrt{\frac{\hbar}{r}}\, \frac{\cos(\hbar^{-1} \int^r \sqrt{-E_1(r')}dr' + \phi_m)}{(-E_1(r))^{1/4}} \tag{22}$$

where $E_1(x)$ is the negative eigenvalue of $H_e(x)$. The $\sqrt{\hbar}$ is due to the scaling back from ρ to r of (16). It follows that the normalization constant is related to the period of the classical oscillation in the potential $E_1(\rho)$:

$$2\hbar^{1/3} \int \rho\, d\rho\, \psi_{cl}^2(\rho; m) \approx \int dr \frac{1}{\sqrt{-E_1(r)}} = T_c, \tag{23}$$

where the integration is carried out over the classically allowed region. This concludes the derivation of Eq. (1).

One motivation for this work was an attempt to understand the different status of crossing in theory and experiment. Theory puts crossing and avoided crossing in distinct baskets: conic crossings come with fractional azimuthal quantum numbers while avoided crossings come with integral quantum numbers. In contrast, measurements of molecular spectra normally can not tell a crossing from near avoided crossing. Only with precision measurements

[18] and precision quantum mechanical calculations [19] can one tell when molecular spectra favor an interpretation in terms of crossing and half integral quantum numbers or avoided crossing with integral quantum numbers. The Zeeman shift appears to be an appropriate tool to study crossing. It serves as a magnifying glass sensitive to crossing and reveals crossings by their anomalously large Zeeman shift.

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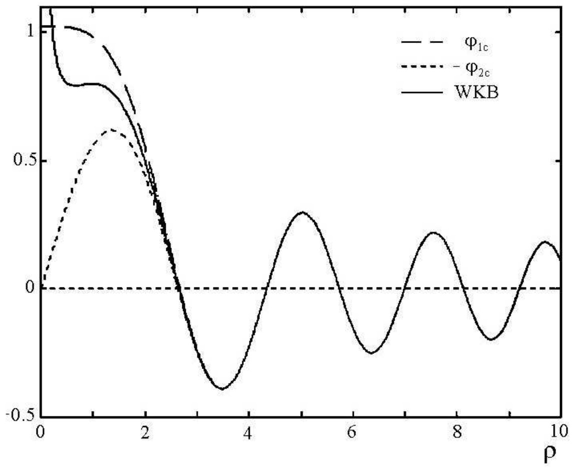
FIGURES



φ1c
φ2c
WKB
1
0.5
0
-0.5
0
2
4
6
8
10
ρ

FIG. 1. The components of $\mathcal{F}_c(m;\rho)$ for $m = \frac{1}{2}$ and their asymptotic form given by (14), which is also the Born-Oppenheimer wave function approximated by WKB, see Eq. (22).