Molecular propagation through crossings and avoided crossings of electron energy levels

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

Abstract

The time–dependent Born–Oppenheimer approximation describes the quantum mechanical motion of molecular systems. This approximation fails if a wavepacket propagates through an electron energy level crossing or "avoided crossing." We discuss the various types of crossings and avoided crossings and describe what happens when molecular systems propagate through them.

It is not practical to solve the time–dependent Schrödinger equation for molecular systems, but one can obtain useful information by using the time–dependent Born–Oppenheimer approximation. Although it is extremely useful, this approximation fails under certain circumstances. The simplest failures occur at crossings and avoided crossings of the electron energy levels.

In this note we briefly summarize the results of [2, 3, 4, 5, 6]. These papers classify crossings and avoided crossings and analyze what happens when molecular systems propagate through them.

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The standard Born–Oppenheimer approximation exploits the smallness of the parameter ϵ, where ϵ^4 is the ratio of the mass of an electron to the average of the masses of the nuclei in the molecular system. The largest value of ϵ that occurs in a real molecule is approximately 0.15.

The time–dependent Schrödinger equation for a molecule can be written in the form

$$i\,\epsilon^2\,\frac{\partial\psi}{\partial t} \;=\; -\,\frac{\epsilon^4}{2}\,\Delta_X\,\psi \;+\; h(X)\,\psi, \tag{1}$$

where $h(X)$ is a family of self-adjoint operators on the electron Hilbert space $\mathcal{H}_{el}$ that depends paramterically on the nuclear configuration variable $X \in I\!R^n$. The variable X describes the positions of all the nuclei, and the dimension n is $3k$, where k is the number of nuclei.

The Born–Oppenheimer approximation [1] provides an algorithm for approximately solving this equation for small values of ϵ. We briefly describe this algorithm in the simplest situation where the electron state is non-degenerate. The details can be found, *e.g.*, in [1] or [3].

The first step is to solve the eigenvalue problem $h(X)\,\Phi(X) \;=\; E(X)\,\Phi(X)$ for the electron Hamiltonian $h(X)$ for each X. We assume $E(X) \in I\!R$ and $\Phi(X) \in \mathcal{H}_{el}$ are chosen to depend continuously on X. In elementary situations, $E(X)$ is a simple, isolated eigenvalue of $h(X)$ for each X.

The second step is to solve for the semiclassical motion of the nuclei with the electron energy level $E(\cdot)$ playing the role of an effective potential. To do this, we solve Hamilton's equations

$$\begin{aligned}
\dot{a}(t) \;&=\; \eta(t) \\
\dot{\eta}(t) \;&=\; -\,(\nabla E)(a(t)),
\end{aligned}$$

with some initial position $a(0)$ and initial momentum $\eta(0)$. We then compute the classical action

$$S(t) \;=\; \int_0^t \left(\frac{\eta(s)^2}{2} \;-\; E(a(s))\right) ds,$$

and compute two matrices

$$\begin{aligned}
A(t) \;&=\; \frac{\partial a(t)}{\partial a(0)}\,A(0) \;+\; i\,\frac{\partial a(t)}{\partial \eta(0)}\,B(0) \\
B(t) \;&=\; \frac{\partial \eta(t)}{\partial \eta(0)}\,B(0) \;-\; i\,\frac{\partial \eta(t)}{\partial a(0)}\,B(0).
\end{aligned}$$

Here $A(0)$ and $B(0)$ are $n \times n$ invertible complex matrices that satisfy

$$A^* B + B^* A = 2 I$$

$$A^t B - B^t A = 0.$$

It follows that $A(t)$ and $B(t)$ also satisfy these conditions.

The third step is to solve a simple differential equation for a real phase function $\theta(X,t)$, so that $\Phi(X,t) = e^{i\theta(X,t)}\,\Phi(X)$ satisfies $\left(\dfrac{\partial}{\partial t} + \eta(t)\cdot\nabla_X\right)\Phi(X,t) = 0$.

The zeroth order time–dependent Born–Oppenheimer approximation to the solution to (1) is

$$\psi_j(X,t) = e^{i\,S(t)/\epsilon^2}\,\phi_j(A(t),B(t),\epsilon^2,a(t),\eta(t),X)\;\Phi(X,t) \tag{2}$$

Here j is an n-dimensional multi-index, and ϕ_j is a normalized vector in $L^2(I\!R^n)$ that is concentrated within a distance $\sqrt{|j|+1/2}\;\|A(t)\|\,\epsilon$ of $a(t)$. As j ranges over all multi-indices, the vectors $\phi_j(A,B,\epsilon^2,a,\eta,\cdot)$ form an orthonormal basis of $L^2(I\!R^n)$. For each j, ψ_j agrees with an exact solution to (1) up to an error whose norm is bounded by a j-dependent constant times ϵ, uniformly for t in a compact interval. For detailed statements and proofs, see, *e.g.*, [3].

This result breaks down if $E(X)$ does not stay isolated from the rest of the spectrum of $h(X)$.

The simplest type of breakdown occurs at a electron energy level crossings. We say that two eigenvalues $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ have a crossing on a proper submanifold $\Gamma \subset I\!R^n$ if they are isolated from the rest of the spectrum of $h(X)$ for all X, and are not equal to one another, except when $X \in \Gamma$. The codimension of the crossing is defined to be the codimension of Γ (which is n minus the dimension of Γ).

Since $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ are eigenvalues of $h(X)$, they are not just any two functions, and their behavior and the behavior of the associated eigenfunctions $\Phi_{\mathcal{A}}$ and $\Phi_{\mathcal{B}}$ can be complicated near a crossing. Generic, minimal multiplicity crossings are classified in [2]. There are 11 distinct types, and their structures depend on the action of the symmetry group for $h(X)$. The various types have codimensions 1, 2, 3, and 5.

Codimension 1 crossings occur generically only under certain symmetry situations. If $h(X)$ has a codimension 1 crossing, then the restriction of $h(X)$ to its spectral subspace associated to the two levels $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ can be diagonalized in a basis that depends smoothly on X. For example, if $E_{\mathcal{A}}(X)$ and $E_{\mathcal{B}}(X)$ are simple eigenvalues of $h(X)$

away from Γ, then we can choose a basis $\{\, \Phi_{\mathcal{A}}(X),\, \Phi_{\mathcal{B}}(X) \,\}$ of eigenvectors that depend smoothly on X, such that the matrix elements of $h(X)$ in this basis are

$$\begin{pmatrix} E_{\mathcal{A}}(X) & 0 \\ 0 & E_{\mathcal{B}}(X) \end{pmatrix}.$$

A codimension 1 crossing has no effect on the zeroth order Born–Oppenheimer approximation. However, during a temporal boundary layer as the zeroth order wave packet moves through the crossing, a correction term of order ϵ is produced. This correction term persists and propagates according to the dynamics associated with the other electron energy level. For example, suppose that the system is initially in the standard Born–Oppenheimer wave packet

$$e^{i\,S_{\mathcal{A}}(t)/\epsilon^2}\;\phi_0(A_{\mathcal{A}}(t), B_{\mathcal{A}}(t), \epsilon^2, a_{\mathcal{A}}(t), \eta_{\mathcal{A}}(t), X)\;\Phi_{\mathcal{A}}(X,t) \;+\; O(\epsilon)$$

associated with $E_{\mathcal{A}}$, and that $a_{\mathcal{A}}(t)$ first encounters Γ as time approaches $t = 0$. Then for positive times that are large compared to ϵ, the full wave function will have the form

$$\begin{aligned} & e^{i\,S_{\mathcal{A}}(t)/\epsilon^2}\;\phi_0(A_{\mathcal{A}}(t), B_{\mathcal{A}}(t), \epsilon^2, a_{\mathcal{A}}(t), \eta_{\mathcal{A}}(t), X)\;\Phi_{\mathcal{A}}(X,t) \\ +\quad & K\,\epsilon\; e^{i\,S_{\mathcal{B}}(t)/\epsilon^2}\;\phi_0(A_{\mathcal{B}}(t), B_{\mathcal{B}}(t), \epsilon^2, a_{\mathcal{B}}(t), \eta_{\mathcal{B}}(t), X)\;\Phi_{\mathcal{B}}(X,t) \\ +\quad & o(\epsilon). \end{aligned}$$

The value of K can be computed, but depends on the details of the situation [3].

The higher codimension crossings are much more complicated [2]. However, the canonical examples of operator valued functions with codimension 2 and 3 crossings are (respectively) the 2×2 matrix operators

$$h_2(X) \;=\; \begin{pmatrix} X_1 & X_2 \\ X_2 & -X_1 \end{pmatrix} \qquad \text{and} \qquad h_3(X) \;=\; \begin{pmatrix} X_1 & X_2 + iX_3 \\ X_2 - iX_3 & -X_1 \end{pmatrix}.$$

Their respective eigenvalues are $\pm\sqrt{X_1^2 + X_2^2}$ and $\pm\sqrt{X_1^2 + X_2^2 + X_3^2}$, and they have crossings at the origin in $I\!R^2$ and $I\!R^3$, respectively. Because of the shapes of the graphs of these eigenvalues, the chemists call these "conical intersections." One can prove that the eigenvectors associated with levels involved in generic higher codimension crossings cannot be continuous in neighborhoods of the crossings.

If a standard Born–Oppenheimer wave packet propagates through higher codimension crossings, it gets split at zeroth order in ϵ into two pieces that propagate independently according to the two different levels. This yields a much stronger coupling between the

two levels than in codimension 1 crossings. The details are complicated, and the probabilities for the system to end up on each of the two levels depend on the detailed shape of the incident wave function. However, one can understand intuitively what is going on by applying a Landau–Zener formula "to each part of the incident wave packet." In the short time that the wave packet strongly interacts with the crossing, the Schrödinger equation is approximately hyperbolic. Different parts of the wave packet propagate along different characteristics and feel different size minimal gaps between the eigenvalues. Along different characteristics, different Landau–Zener formulas apply, and one can compute the transition probabilites by computing an integral [3].

A similar analysis has be done for avoided crossings in collaboration with Alain Joye [4, 5, 6]. In this analysis, an avoided crossing is defined to be a crossing that has been detuned by the change of another parameter. That is, we consider electron Hamiltonians $h(X, \delta)$, where $h(X, 0)$ has a crossing, but $h(X, \delta)$ does not whenever the detuning parameter δ is non-zero.

With this definition, generic, minimal multiplicity avoided crossings are classified in [4]. There turn out to be 6 distinct types, and two canonical examples of electron Hamiltonians that exhibit two different types are

$$\widetilde{h}_1(X,\delta) \;=\; \begin{pmatrix} X_1 & \delta \\ \delta & -X_1 \end{pmatrix} \qquad \text{and} \qquad \widetilde{h}_2(X,\delta) \;=\; \begin{pmatrix} X_1 & X_2 + i\delta \\ X_2 - i\delta & -X_1 \end{pmatrix}.$$

For these two examples, the eigenvalues are $\pm\sqrt{X_1^2 + \delta^2}$ and $\pm\sqrt{X_1^2 + X_2^2 + \delta^2}$, respectively.

For an avoided crossing to have a significant effect when ϵ is small, one intuitively expects that δ must have to be on the order of ϵ or smaller. The critical situation where $\delta = \epsilon$ is studied in [5, 6].

Two of the six types of avoided crossing have structures that are intuitively similar to the avoided crossing of $\widetilde{h}_1(X, \delta)$. Molecular propagation through such avoided crossings with $\delta = \epsilon$ is studied in [5]. The main result is that the Landau–Zener formula dictates coupling between the levels to zeroth order in ϵ. Here, every part of the wave function feels the same size gap, so this is what one might expect intuitively. However, the details of the proofs are extremely complicated.

Molecular propagation through the remain four types of avoided crossings with $\delta = \epsilon$ is analyzed in [6]. The details are again complicated, but one can again compute transition probabilities. The procedure for doing so is similar to the one described above

for higher codimension crossings. Each infinitesimal piece of the wave function follows a different characteristic, feels a different sized minimal gap, and has a different Landau–Zener formula. The full transition probability depends on the shape of the wave packet and is obtained by an integration, after the application of the appropriate Landau–Zener formula for each piece.

To summarize, one can classify all generic, minimal multiplicity crossings and avoided crossings. Furthermore, molecular propagation through all of the types of these crossings and avoided crossings (with $\delta = \epsilon$) can be analyzed through the order in ϵ to which the two electron energy levels are non-trivially coupled.

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