Adiabatic Theory. Berry Phase. Born - Oppenheimer Approximation

Selected chapter of lecture notes on Quantum Mechanics

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Contents

1 Introduction

In this Chapter we will mainly discuss various theoretical developments which evolved from the problem of how to describe a time development of a quantum system when its Hamiltonian changes in time somehow "slowly". Formally this means devising approximations for solving the time dependent Schrödinger equation

$$i\hbar\frac{\partial\Psi(q,t)}{\partial t} = H(\hat{p},\hat{q};\mathbf{R}(t))\Psi(q,t) \tag{1}$$

for a system with, say, N degrees of freedom,

$$q = q_1, ..., q_N$$

governed by a Hamiltonian which depends on time via M "slowly changing" parameters

$$\mathbf{R}(t) = R_1(t), ..., R_M(t)\ .$$

We will understand below what "slowly" means.

2 An aside. Fast changing Hamiltonians. Sudden approximation

In order the better understand and actually contrast the physics of a system with slowly changing Hamiltonian we start with the opposite case - the Hamiltonian $\hat{H}$ which changes rapidly. We will discuss a particular case when $\hat{H}$ was time independent $\hat{H} = \hat{H}_0$ before a rapid change to $\hat{H}_1$ and stayed time independent $\hat{H} = \hat{H}_1$ after the change.

For simplicity we assume that just before the change the system was in the eigenstate $|\phi_0\rangle$ of $\hat{H}_0$. By the rapid change we mean that it can be assumed that the wave function $|\phi_0\rangle$ does not change and "finds itself" governed by the new Hamiltonian $\hat{H}_1$ after the change. This assumption is called **the sudden approximation**.

The time evolution of the system after the change is given by the Schrödinger equation

$$i\hbar\frac{\partial|\Psi(t)\rangle}{\partial t} = \hat{H}_1|\Psi(t)\rangle \tag{2}$$

with the initial condition

$$|\Psi(t = t_0)\rangle = |\phi_0\rangle$$

where t_0 is the time "just after" the rapid change of the Hamiltonian. Since $\hat{H}_1$ is time independent after t_0 we can write the time evolution of $|\Psi\rangle$ for $t > t_0$ as

$$|\Psi(t)\rangle = \sum_n C_n|\psi_n\rangle e^{-(i/\hbar)E_n t} \tag{3}$$

in terms of the eigenfunctions $|\psi_n\rangle$ and eigenenergies E_n of $\hat{H}_1$. The coefficients C_n are obviously given by overlaps

$$C_n = \langle\psi_n|\phi_0\rangle \tag{4}$$

A classic problem treated by this method is the excitation and ionization of an atom the nucleus of which undergoes a beta decay. An concrete practical example is the beta decay of tritium, in which one of the neutrons of the tritium nucleus emits an electron and an anti neutrino converting into hellium-3. The original one-electron tritium atom had its atomic electron in a 1s ground state for this Z = 1 nucleus. The electron emitted in the beta decay traverses the atomic dimension so rapidly the original atomic electron will still have the wave function of an 1s Z = 1 atom, even though it now "finds itself" in the Coulomb field of a Z = 2 nucleus. This state

will thus be a linear combination of the eigenstates of a one-electron He ion with probabilities simply given by the overlaps (4) of the original and the new states

When is this approximation valid? Very crude arguments are as follows. The time scale τ of the change from $\hat{H}_0$ to $\hat{H}_1$ must be much shorter than the relevant evolutions times of ϕ_0. These are given by the $\hbar/\Delta E^{(0)}_{m0}$ with energy differences $E^{(0)}_m$ between relevant (i.e. of interest or dominating, etc) eigenstates of $\hat{H}_0$ and $E^{(0)}_0$.

$$\tau \ll \frac{\hbar}{E^{(0)}_m - E^{(0)}_0} \tag{5}$$

A more refined arguments should examine under which conditions the time evolution operator $U(t_f, t_i)$ acting on $|\phi_0\rangle$ during the time τ can be approximated by just a unit operator, i.e. $U(t_0 + \tau, t_0)|\phi_0\rangle \approx |\phi_0\rangle$.

To conclude this section we notice that the rapid change of the Hamiltonian between two values is obviously not the only possible fast change which can happen but we will not consider these other options.

3 Slowly changing Hamiltonians

We now return to the equation (1) with slowly changing Hamiltonian. In contrast to the rapid change discussed above we may expect that under a slow evolution the wave function "has time" to evolve together with the Hamiltonian.

3.1 Adiabatic basis

To understand this better and more precisely we consider the instantaneous eigenbasis of the time dependent Hamiltonian in Eq.(1)

$$H(\hat{p}, \hat{q}; \mathbf{R})\phi_n(q, \mathbf{R}) = E_n(\mathbf{R})\phi_n(q, \mathbf{R}) \tag{6}$$

For every value of the parameters $\mathbf{R}$ (more precisely, set of values $\{R_1, ..., R_M\}$) we have complete orthonormal sets $\{\phi_n(q; \mathbf{R})\}$ forming a continuous array of bases in the Hilbert space of the system. This construction is called **adiabatic basis**.

A simple illustrative example to have in mind are coordinate systems along some path on a curved surface, e.g. Earth, cf., Fig. 1. Imagine moving "slowly" between such systems with the systems axes pointing into the correspondingly North, East and Up directions and longitude and latitude angles playing the role of the parameters.

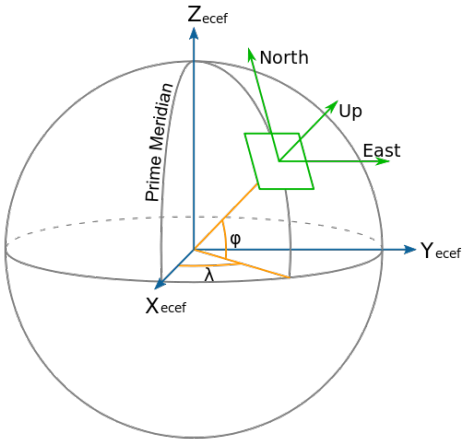

Figure 1: Coordinate system on the Earth surface. This figure is from Ref.[1]

3.2 Transforming the Schrödinger equation

Let us rewrite the equation (1) in the adiabatic basis defined by Eq. (6). To this end we expand the time dependent wave function as

$$\Psi(q,t) = \sum_n C_n(t)\phi_n(q;\mathbf{R}(t)) \exp\left(-\frac{i}{\hbar}\int_{t_0}^{t} E_n[\mathbf{R}(t')]dt'\right) \tag{7}$$

Note that the expansion basis changes with time in accordance with the time dependence of the parameters $\mathbf{R}(t)$ as they enter the Hamiltonian in Eq.(1). It is also important to note that the expansion coefficients C_n in general depend on time. And lastly note that for later convenience we have "pulled out" of $C_n(t)$ the exponential factors

$$\exp\left(-\frac{i}{\hbar}\int_{t_0}^{t} E_n[\mathbf{R}(t')]dt'\right)$$

where t_0 denotes some initial time. These exponentials are simply generalizations of the familiar factors $\exp(-iE_n(t-t_0)/\hbar)$ in the time independent case.

Let us now insert the (exact) expansion (7) in the equation (1). We have

$$\begin{aligned} i\hbar\frac{\partial\Psi(q,t)}{\partial t} &= \sum_n \left[i\hbar\frac{dC_n(t)}{dt}\phi_n(q;\mathbf{R}(t)) + C_n(t)\, i\hbar\frac{\partial\phi_n(q;\mathbf{R}(t))}{\partial t} + \right. \\ &+ \left. C_n\phi_n(q,\mathbf{R}(t))E_n(\mathbf{R}(t)] \exp\left(-\frac{i}{\hbar}\int_{t_0}^{t} E_n[\mathbf{R}(t')]dt'\right) \right. \end{aligned}$$

and

$$H(\hat{p},\hat{q};\mathbf{R}(t))\Psi(q,t)=\sum_n C_n(t)E_n(\mathbf{R}(t))\phi_n(q;\mathbf{R}(t))\exp\left(-\frac{i}{\hbar}\int_{t_0}^{t}E_n[\mathbf{R}(t')]dt'\right)$$

Inserting this into Eq.(1) we find

$$\sum_n\left[\frac{dC_n(t)}{dt}\phi_n(q;\mathbf{R}(t))+C_n(t)\frac{\partial\phi_n(q;\mathbf{R}(t))}{\partial t}\right]\exp\left(-\frac{i}{\hbar}\int_{t_0}^{t}E_n[\mathbf{R}(t')]dt'\right)=0 \quad (8)$$

We use the orthonormality of the set $\phi_n(q;\mathbf{R})$ and project the above equality on $\phi_m(q;\mathbf{R}(t))$, i.e. we multiply it by $\phi_m^*(q;\mathbf{R}(t))$ and integrate over q. We obtain

$$\frac{dC_m(t)}{dt}=-\sum_n\langle\phi_m|\frac{\partial}{\partial t}|\phi_n\rangle C_n(t)\exp\left(-\frac{i}{\hbar}\int_{t_0}^{t}[E_n(\mathbf{R}(t'))-E_m(\mathbf{R}(t')]dt'\right) \quad (9)$$

where we have switched to the Dirac notations and multiplied both sides by the exponential $\exp[(i/\hbar)\int_{t_0}^{t}E_m(\mathbf{R}(t'))dt']$.

It is important to note that the expression $\langle\phi_m|\partial/\partial t|\phi_n\rangle$ is not a matrix element of an operator $\partial/\partial t$ (it is not an operator in the space of functions $\phi(q;\mathbf{R})$). Rather it is an overlap between $\phi_n^*(q;\mathbf{R})$ and the change of $\phi_n(q;\mathbf{R})$ with time

$$\langle\phi_m|\frac{\partial}{\partial t}|\phi_n\rangle\equiv\langle\phi_m|\frac{\partial\phi_n}{\partial t}\rangle\equiv\int\phi^*(q;\mathbf{R}(t))\frac{\partial\phi(q;\mathbf{R}(t))}{\partial t}\,d^Nq \quad (10)$$

This can be written as

$$\langle\phi_m|\frac{\partial}{\partial t}|\phi_n\rangle=\frac{d\mathbf{R}}{dt}\cdot\int\phi^*(q;\mathbf{R}(t))\nabla_{\mathbf{R}}\phi(q;\mathbf{R}(t))\,d^Nq=\frac{d\mathbf{R}}{dt}\cdot\langle\phi_m(\mathbf{R})|\nabla_{\mathbf{R}}|\phi_n(\mathbf{R})\rangle \quad (11)$$

where we used an obvious notation dot $\cdot$ for the scalar product and $\nabla_{\mathbf{R}}$ for the "gradient" in the space of the parameters $\mathbf{R}$. We stress that as with $\langle\phi_m|\partial/\partial t|\phi_n\rangle$ the derivatives $\nabla_{\mathbf{R}}$ are not operators in the space of functions $\phi(q;\mathbf{R})$. We also note that another useful form of the expression $\langle\phi_m(\mathbf{R})|\nabla_{\mathbf{R}}|\phi_n(\mathbf{R})\rangle$ can be obtained by differentiating Eq.(6) with respect to $\mathbf{R}$. The details are found in the Appendix.

3.3 What is the meaning of the "slow" change?

3.3.1 Integral form of the evolution equations

Equations (9) represent a set of coupled equations for all the coefficients C_n. These equations are exact. Given initial condition $\Psi(q,t_0)$ at an initial time t_0 one should

expand it in the adiabatic basis of states $\phi_n(q;\mathbf{R}(t_0))$ according to Eq. (7) and find the initial values of all $C_n(t_0)$'s for the set (9)). An easy example to visualise is to assume that $\Psi(q,t_0)$ coincides with one of the states of the adiabatic basis at t_0, say $\phi_k(q,\mathbf{R}(t_0))$, so that $C_n(t_0) = \delta_{nk}$. As time evolves the non diagonal terms in Eqs. (9) will cause "branching out" of the $C_k(t_0) = 1$ amplitude to other states of the adiabatic basis leading to non zero values of the other amplitudes at later times $t > t_0$, cf. Fig. 2. These are called transitions between adiabatic levels or simply adiabatic transitions.

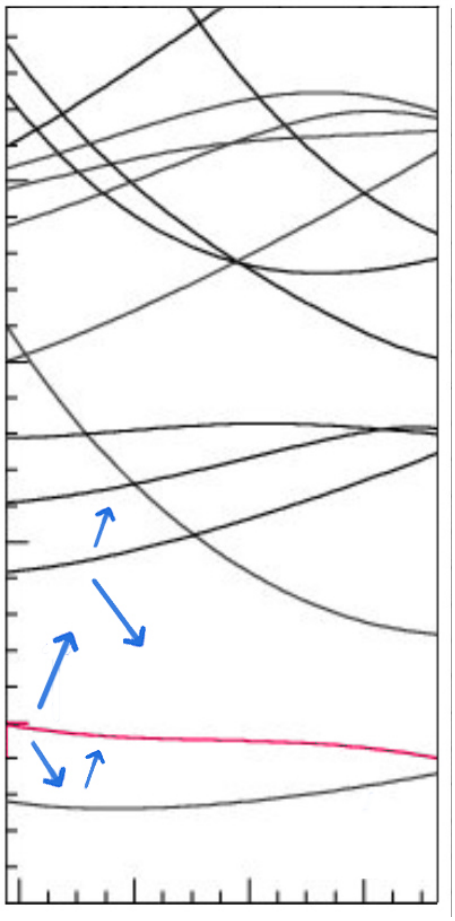

Figure 2: Example of adiabatic levels. The initial level is denoted by red and arrows schematically denote transitions between the levels

We want to explore what simplifications are introduced by the fact that the change

in time of the parameters $\mathbf{R}$ is slow. It is the easiest to discuss this by transforming (9) into integral form by integrating both its sides in time from t_0 to some current time t

$$C_m(t) = C_m(t_0) - \sum_n \int_{t_0}^{t} dt' \langle \phi_m | \frac{\partial}{\partial t'} | \phi_n \rangle C_n(t') \times \tag{12}$$
$$\times \exp\left[-\frac{i}{\hbar} \int_{t_0}^{t'} [E_n(\mathbf{R}(t'')) - E_m(\mathbf{R}(t'')] dt'' \right]$$

Let us now rewrite the integrals in the expression above as line integrals in the parameter space, i.e. integrals along the contour $\mathbf{R}'(t)$ in the parameter space which the parameters follow as they change in time from the initial value $\mathbf{R}(t_0) = \mathbf{R}_0$ to $\mathbf{R} = \mathbf{R}(t)$

$$C_m(t) = C_m(t) - \sum_n \int_{\mathbf{R}_0}^{\mathbf{R}} d\mathbf{R}' \cdot \langle \phi_m(\mathbf{R}') | \nabla_{\mathbf{R}'} | \phi_n(\mathbf{R}') \rangle C_n(\mathbf{R}'(t')) \times \tag{13}$$
$$\times \exp\left[-\frac{i}{\hbar} \int_{\mathbf{R}_0}^{\mathbf{R}'} [E_n(\mathbf{R}'') - E_m(\mathbf{R}''] \frac{|d\mathbf{R}''|}{|d\mathbf{R}''|/dt''} \right]$$

We used (11) together with the replacement

$$dt'' = \frac{|d\mathbf{R}''|}{|d\mathbf{R}''|/dt''} \, .$$

of the time differential dt'' in the exponential integrals by the differential of the length $|d\mathbf{R}''|$ along the contour $\mathbf{R}''(t)$ divided by the speed $|d\mathbf{R}''|/dt''$ of traversing this contour.

We note that although the "speed" with which the parameters $\mathbf{R}$ change enters the overlaps (11) it gets absorbed into $d\mathbf{R}'$ in the integral over $\mathbf{R}'$ above. Where it does appear (and with "vengeance") is in the denominator of the integrands in the integrals in the exponentials. When the parameters $\mathbf{R}$ change slowly, i.e. $|d\mathbf{R}|/dt$ is small these integrals are very large. This provided the corresponding adiabatic energy levels do not become too close, i.e. the differences

$$E_n(\mathbf{R}) - E_m(\mathbf{R})$$

do not get too small as the contour $\mathbf{R}(t)$ is traversed. Under these conditions, i.e. for such levels the exponential will oscillate rapidly as $\mathbf{R}'$ (the upper limit in its integral) is changing so that the integral over $\mathbf{R}'$ gets very small. The adiabatic transitions can be neglected for such levels.

3.3.2 More detailed discussion

More quantitatively the condition for this approximation can be discussed as following. Let us focus for simplicity on the adiabatic level E_m and transitions to the neighboring level E_{m+1}. Consider the corresponding term in the sum in Eq. (13) and choose an arbitrary point $\mathbf{R}$ on the integration contour in the integral in this term. Using for brevity the notation $\exp[-(i/\hbar)\sigma(\mathbf{R}')]$ for the exponential in this integral let us expand $\sigma(\mathbf{R}')$ in a small section $|\Delta\mathbf{R}|$ around $\mathbf{R}$

$$\sigma(\mathbf{R}+\Delta\mathbf{R}) = \sigma(\mathbf{R}) + \frac{\Delta E}{\mathcal{W}}|\Delta\mathbf{R}| + o(|\Delta\mathbf{R}|) \tag{14}$$

where we denoted by ΔE the energy "distance" $E_{m+1}(\mathbf{R}) - E_m(\mathbf{R})$ at $\mathbf{R}$ and by $\mathcal{W}$ the "speed" $|d\mathbf{R}|/dt$ at this point. Let us consider the magnitude of $|\Delta\mathbf{R}|$ such that the higher terms in the above expansion can be neglected. That defines a neighborhood of $\mathbf{R}$ in which the function (14) is linear so that the condition that the corresponding exponential oscillates fast is

$$\frac{\Delta E|\Delta\mathbf{R}|}{\hbar\mathcal{W}} \gg 1 \quad \rightarrow \quad \frac{|\Delta\mathbf{R}|}{\mathcal{W}} \gg \frac{\hbar}{\Delta E} \tag{15}$$

The second form of the above inequality as written on the right expresses a possible physical interpretation of the adiabaticity condition that the dynamical time $|\Delta\mathbf{R}|/\mathcal{W}$ of the system's motion must be much longer than the transition time $\hbar/\Delta E$ to the neighboring energy levels.

One concludes that for a given adiabatic basis the "velocity" $\mathcal{W}$ is the parameter controlling the approximation, i.e. it must be small enough for the adiabatic transitions to be negligible. This provided the above inequality holds for all the points along the time evolution contour $\mathbf{R}(t)$ in the Schrödinger equation Eq. (1). From the example of adiabatic levels in Fig. 2 we observe that levels can get close to each other and cross. Clearly the inequality (15) will be violated at and close to the crossing points. One should expects that the transitions between the levels will be concentrated in such "level crossing" regions of the parameters space. We will devote the Section 4 below to discuss this and related issues.

It is useful and instructive to note that the nature of the adiabatic limit in time dependent problems is **formally** similar to the semiclassical limit of quantum mechanics. In both cases it is not an expansion in powers of a small parameter but fast oscillating phases with a small parameter in the denominator which are the key elements. The small parameter $\mathcal{W}$ in the denominator of the adiabatic phase finds its parallel in the Plank constant $\hbar$ appearing similarly in semiclassical phases. Landau

used this analogy in his treatment of what is now called Landau-Zener transitions which will be discussed below.

3.4 The adiabatic approximation

When the conditions (15) hold we can neglect the coupling between different adiabatic levels in (12). In the differential version (9) this means that the equations for the coefficients become decoupled

$$\frac{dC_m(t)}{dt} = -\langle\phi_m|\frac{\partial}{\partial t}|\phi_m\rangle C_m(t) \tag{16}$$

with the solution

$$C_m(t) = C_m(t_0)\exp\left(-\int_{t_0}^{t}\langle\phi_m|\frac{\partial}{\partial t'}|\phi_m\rangle dt'\right) \tag{17}$$

Let us note that the overlap $\langle\phi_m|\frac{\partial}{\partial t}|\phi_m\rangle$ is pure imaginary. This follows from the simple fact that $|\phi_m(\mathbf{R}(t))\rangle$ are normalized *for all values of the parameters* $\mathbf{R}$. The details of the proof are given in the Appendix and we have

$$\langle\phi_m|\frac{\partial}{\partial t}|\phi_m\rangle = iIm\langle\phi_m|\frac{\partial}{\partial t}|\phi_m\rangle$$

so that we can write (17) as

$$\begin{aligned} C_m(t) &= C_m(t_0)\exp\left(-i\int_{t_0}^{t} Im\langle\phi_m|\frac{\partial}{\partial t'}|\phi_m\rangle dt'\right) = \\ &= C_m(\mathbf{R}_0)\exp\left(-i\int_{\mathbf{R}_0}^{\mathbf{R}} Im\langle\phi_m|\nabla_{\mathbf{R}'}|\phi_m\rangle\cdot d\mathbf{R}'\right) \end{aligned} \tag{18}$$

where in the last equality we used the relation Eq. (11) to transform the time integral into the line integral in parameter space. We also identified $C_m(t_0) \equiv C_m(\mathbf{R}_0)$.

The expression above shows that in the extreme adiabatic limit the probabilities of occupation of the adiabatic levels are independent of time but the corresponding amplitudes may have time dependent phases. These phases are called the geometrical or Berry phases. We will discuss these phases in detail in Section 5.

In the particular case of the initial wave function coinciding with one of the functions, say $\phi_k(q;\mathbf{R}(t_0))$, of the adiabatic basis, i.e. for $C_m(t_0) = \delta_{mk}$ we have the

time dependent wave function

$$\Psi_k(q,t) \approx \phi_k(q;\mathbf{R}(t)) \exp\left(-i\int_{t_0}^{t} Im\langle\phi_k|\frac{\partial}{\partial t'}|\phi_k\rangle dt'\right) \times$$
$$\times \exp\left(-i/\hbar\int_{t_0}^{t} dt' E_k(t')dt'\right) \tag{19}$$

Apart of the adiabatically evolving $\phi_k(q;\mathbf{R}(t))$ this expression has two phases - the geometrical Berry phase and dynamical phase - the generalization of the usual $\exp(-iE_k(t-t_0)/\hbar)$.

4 Avoided level crossings

As was shown in Section 3.3 the adiabatic approximation is expected to be violated when the adiabatic level under considerations approaches and possibly crosses its neighboring levels in the space of parameter $\mathbf{R}$. In this section we will discuss several important aspects of how this happens.

Let us begin by reviewing Fig. 3. The adiabatic levels shown in this figure appear to experience a strange "repulsion" when they approach a neighboring level (from above or below) too closely. One calls this phenomenon "avoided level crossings". Let us discuss why and when this happens.

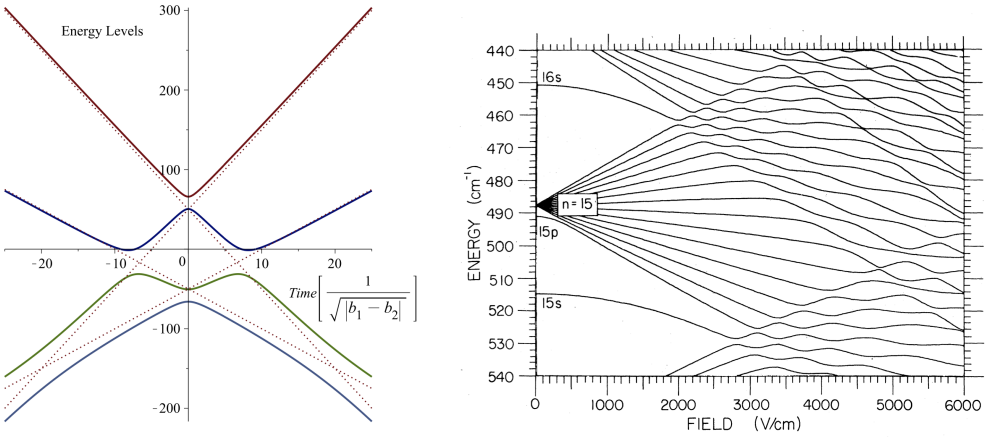

Figure 3: Examples of adiabatic levels. The left figure shows energy levels of two coupled qubits, i.e. of two coupled spin 1/2 systems with the parameters of the model Hamiltonian changing in time, Ref. [3]. The figure on the right shows electronic levels of lithium atom in a constant electric field as a function of the field strength, Ref. [4]

4.1 Level repulsion

4.1.1 What is the chance that two close levels cross?

This section discusses and proves what is known as von Neumann–Wigner theorem, cf., Ref. [2]. Let us consider a point $\mathbf{R}_0$ in the parameter space $\mathbf{R}$ for which some pair of adiabatic levels are very close to each other. Let us denote these levels $E_1(\mathbf{R}_0)$ and $E_2(\mathbf{R}_0)$,

$$H_{op}(\mathbf{R}_0)\phi_i(\mathbf{R}_0) = E_i(\mathbf{R}_0)\phi_i(\mathbf{r}_0) \ , \ \ i = 1, 2$$

Close to each other means that their energies difference $\Delta E(\mathbf{R}_0) = E_1(\mathbf{R}_0) - E_2(\mathbf{R}_0)$ is much smaller than the "distances" in energies to all other levels.

If now we change the system parameters from $\mathbf{R}_0$ to $\mathbf{R} = \mathbf{R}_0 + \Delta\mathbf{R}$ could we find $\Delta\mathbf{R}$ at which the two levels will cross? I.e. for which the difference $\Delta E(\mathbf{R}) = E_1(\mathbf{R}) - E_2(\mathbf{R})$ of the energies $E_1(\mathbf{R})$ and $E_2(\mathbf{R})$ of the new Hamiltonian $H_{op}(\mathbf{R}) \equiv H_{op}(\mathbf{R}_0 + \Delta\mathbf{R})$ will vanish? Since we assumed that at $\mathbf{R}_0$ the levels energies were close and we are looking at when they cross we can write approximate the corresponding wave functions at $\mathbf{R}$ as linear combinations of $\phi_i(\mathbf{R}_0),\ i = 1, 2$, i.e. we need to solve

$$H_{op}(\mathbf{R})\phi(\mathbf{R}) = E(\mathbf{r})\phi(\mathbf{R}) \ , \ \ \phi(R) = C_1(\mathbf{R})\phi_1(\mathbf{R}_0) + C_2(\mathbf{R})\phi_2(\mathbf{R}_0) \tag{20}$$

A more detailed explanation of the above approach is to make a parallel to the perturbation treatment of degenerate states. There too the first step is to diagonalize the perturbed Hamiltonian within the limited basis of the degenerate subspace. Similar to $\phi_i(\mathbf{R}_0),\ i = 1, 2$ here. Higher order corrections will come from the "outside" states $\phi_n(\mathbf{R}_0),\ n \neq 1, 2$ with coefficients

$$C_{ni} \approx \langle\phi_n(\mathbf{R}_0)|H_{op}(\mathbf{R})|\phi_i(\mathbf{R}_0)/(E_n - E_i) \ , \ \ i = 1, 2, \ \ n \neq i$$

which are small due to the assumed large energy difference with the $n \neq i$ states.

In a standard way Eq. (20) is transformed into a 2×2 matrix problem for the coefficients C_1 and C_2

$$\begin{pmatrix} H_{11}(\mathbf{R}) & H_{12}(\mathbf{R}) \\ H^*_{12}(\mathbf{R}) & H_{22}(\mathbf{R}) \end{pmatrix} \begin{pmatrix} C_1(\mathbf{R}) \\ C_2(\mathbf{R}) \end{pmatrix} = E(\mathbf{R}) \begin{pmatrix} C_1(\mathbf{R}) \\ C_2(\mathbf{R}) \end{pmatrix} \tag{21}$$

with the notation

$$H_{ij}(\mathbf{R}) = \langle\phi_i(\mathbf{R}_0|H(\mathbf{R})|\phi_j(\mathbf{R}_0\rangle \tag{22}$$

The new energies $E_1(\mathbf{R}), E_2(\mathbf{R})$ are solutions of

$$\det \begin{pmatrix} H_{11}(\mathbf{R}) - E & H_{12}(\mathbf{R}) \\ H^*_{12}(\mathbf{R}) & H_{22}(\mathbf{R}) - E \end{pmatrix} = 0$$

and it is straightforward to find their difference

$$\begin{aligned} \Delta E(\mathbf{R}) &= E_1(\mathbf{R}) - E_2(\mathbf{R}) = \\ &= \left\{ [H_{11}(\mathbf{R}) - H_{22}(\mathbf{R})]^2 + 4[ReH_{12}(\mathbf{R})]^2 + 4[ImH_{12}(\mathbf{R})]^2 \right\}^{1/2} \end{aligned} \tag{23}$$

This is the central result of this subsection. It shows that $\Delta E(\mathbf{R})$ is a square root of a sum of three positive terms so that to make it vanish requires three conditions

$$H_{11}(\mathbf{R}) = H_{22}(\mathbf{R}) \ , \ \ \mathrm{Re}\, H_{12}(\mathbf{R}) = \mathrm{Im}\, H_{12}(\mathbf{R}) = 0 \tag{24}$$

Let us discuss how these conditions can be realized for different Hamiltonians.

1.Complex Hamiltonians H.

Majority of Hamiltonians are not only Hermitian but also real. Complex Hamiltonian occurs when e.g. there is an external magnetic field or spin-orbit coupling. In this case all three conditions above give independent restrictions so at least three parameters $\mathbf{R}$ are required in order to satisfy them. If there are exactly 3 parameters then the level crossing is an isolated point. If there are $M > 3$ parameters then the conditions (24) are satisfied on an $M - 3$ dimensional manifold. For example for $M = 4$ there is a line at which the two levels cross. One says that for complex Hamiltonians level crossings have codimension three.

2.Real Hamiltonians.

In this most common case the last two equations in (24) reduce to one leaving only two conditions. In this case for $M = 2$ the level cross at a point. One can show (see below) that in this case if one draws the levels as surfaces in three dimensional space they forms a conical intersection, Fig. 4. This "diabolo" like geometry of level crossings is referred to as "diabolical points". We note that for $M > 2$ the crossing occurs in this case at $M - 2$ manifold. E.g. for $M = 3$ it is a line.

3. Different symmetry states.

If $\phi_1(\mathbf{R}_0)$ and $\phi_2(\mathbf{R}_0)$ belong to different symmetries (like different angular momenta or parity) then $H_{12} = \langle \phi_1(\mathbf{R}_0)|H|\phi_2(\mathbf{R}_0) >$ will vanish and only one condition remains $H_{11}(\mathbf{R}) = H_{22}(\mathbf{R})$. This can be satisfied by changing only one parameter so level crossing in such cases happens even for problems with just one parameter $M = 1$.

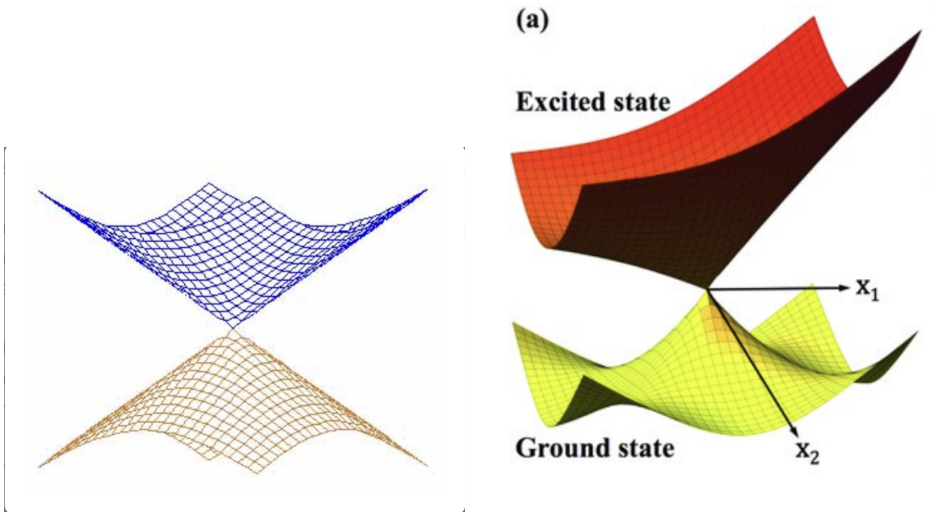

Figure 4: Examples of conical intersection of adiabatic levels, cf., Ref. [5]

4.1.2 How strong do levels repel?

In the previous section we used expression Eq. (23) to find conditions for adiabatic Hamiltonian to have two of its levels cross, i.e. for ΔE to vanish. It is instructive and useful to generalize this discussion for Hamiltonians to have a given energy difference ΔE between two neighboring levels. For simplicity we will limit ourselves to the values of ΔE which are much smaller than the energy difference to other levels. This will allow us to continue using the two levels approximation, i.e limit ourselves to 2×2 Hamiltonian matrices as in Eq. (21).

Let us begin by noticing that the conditions Eq. (24) for vanishing ΔE define a unique 2×2 matrix which is proportional to a unit matrix. This is easy to understand if one recalls the general representation of any 2×2 matrix with eigenvalues E_1 and E_2 as a unitary transformation of the corresponding diagonal matrix

$$H = U \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} U^+$$

Changing the unitary matrix U in this parametrization generates the complete set of 2×2 Hamiltonians with the given eigenvalues. The $E_1 = E_2$ case is a singular point of this "polar" representation with the same diagonal H proportional to the unit matrix for all the U's. This is analogous to the $r = 0$ value of the radial component in spherical coordinates denoting the same space point for all values of the angles.

One can make the above spherical coordinates analogy more precise by defining the following combinations of the matrix elements of H

$$S_0 = \frac{1}{2}(H_{11} + H_{22}) \ , \ \ S_1 = Re\, H_{12} \ , \ \ S_2 = -ImH_{12} \ , \ \ S_3 = \frac{1}{2}[H_{11} - H_{22}] \qquad (25)$$

It can be shown that under a unitary transformation of the Hamiltonian $H' = UHU$ the three components S_1, S_2, S_3 transform like components of a three dimensional vector while S_0 remains invariant. The details of the proof and formal aspects of this result are discussed in Appendix, Section 7.2. Let us just point out that it reflects the equivalence of the adjoint representation of the SU(2) group of the unitary transformations of H and the fundamental representation of the group of rotations O(3).

To use this equivalence in our context of closed levels let us introduce the space of all possible 2×2 Hamiltonian matrices with a (naturally defined) "volume" element

$$d\mu(H) \equiv dH_{11}\, dH_{22}\, dReH_{12}\, dImH_{12}$$

Given the transformation (25) we can view this space as the four dimensional space of "vectors" with components $S_0, \mathbf{S}$ and correspondingly

$$d\mu(H) \to d\mu(S) = (1/2) dS_0 dS_1 dS_2 dS_3$$

where the $1/2$ factor is the Jacobian.

Let us now notice that the expression (23) shows that the radial coordinate in the 3 dimensional subspace of vectors $\mathbf{S} \equiv \{S_1, S_2, S_3\}$ is proportional to the distance between the energy levels of the matrices H which are represented by $\mathbf{S}$

$$|\mathbf{S}| = \sqrt{S_1^2 + S_2^2 + S_3^2} = 2\Delta E = 2|E_1 - E_2| \qquad (26)$$

What this means is that if we work with spherical coordinates in the space of vectors $\mathbf{S}$ the volume element can be written as

$$d\mu(S) = (1/2) dS_0\, dS_1\, dS_2\, dS_3 = (1/2)|\mathbf{S}|^2 d|\mathbf{S}| d\Omega dS_0 = 4(\Delta E)^2\, d(\Delta E)\, d\Omega\, dS_0 \qquad (27)$$

where by $d\Omega$ we have denoted the angular part of the volume element in the S_1, S_2, S_3 vector space similar to the ordinary coordinate space expression $d^3r = r^2 dr d\Omega$.

4.1.3 Ensembles of Hamiltonian matrices

To appreciate the meaning of the above result let us ask what is the distribution of level spacings ΔE in the ensemble of 2×2 H's given by some distribution $W(H)$

$$W(H) \equiv W(H_{11}, H_{22}, ReH_{11}, ImH_{12})$$

such that probability to find H in the "volume" element $d\mu(H)$ is given by

$$dP = W(H)d\mu(H)$$

In the discussion which led to Eq. (23) such an ensemble was the distribution of $H(\mathbf{R})$'s in the vicinity of the point $\mathbf{R}_0$ in the parameter space. For our discussion the explicit form of $W(H)$ will not be essential apart of assuming it to be a smooth positive function of its arguments.

To find the distribution of ΔE's in such or similar ensemble let us go to the variables Eq. (25) and then express the resulting $W(S_0, \mathbf{S})$ in spherical components of $\mathbf{S}$, i.e.

$$W(H) \to W(S_0, \mathbf{S}) \to W(S_0, |\mathbf{S}|, \Omega)$$

The distribution of level spacings ΔE is then given by

$$\frac{dP(\Delta E)}{d(\Delta E)} = 4(\Delta E)^2 \int W\left(|\mathbf{S}| = 2\Delta E, \theta, \phi, S_0\right) d\Omega dS_0 \tag{28}$$

We thus see that for any smooth distribution of complex Hamiltonian matrices $W(H)$ the distribution of the energy level spacings $\Delta E = |E_1 - E_2|$ has *UNIVERSAL* behaviour $\sim (\Delta E)^2$ at small ΔE. In other words the probability to find a matrix in such an ensemble with small level spacing is vanishing as $(\Delta E)^2$ as $\Delta E \to 0$. This result goes under the name "level repulsion".

We note that for real H, i.e. when $S_3 = -ImH_{12}$ vanishes identically the volume element is

$$d\mu(S) = (1/2)dS_1\, dS_2\, dS_0 = (1/2)|\mathbf{S}|d|\mathbf{S}|d\Omega dS_0 = 4(\Delta E)d(\Delta E)d\Omega dS_0 \tag{29}$$

since we have two dimensional space of the vectors $\mathbf{S}$. Therefore for small ΔE the probability of the level spacing ΔE will have a linear dependence

$$\frac{dP(\Delta E)}{d(\Delta E)} \sim \Delta E \tag{30}$$

MENTION HOW THIS "LEVEL REPULSION" WAS SEEN (PROBABLY FOR THE FIRST TIME) IN SLOW NEUTRON SCATTERING RESONANCES OF NUCLEI. ALSO MORE RECENTLY IN LEVEL DISTRIBUTION IN CLASSICALLY CHAOTIC SYSTEMS.

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One of the first studied and best examples of the "level repulsion" phenomenon is a heavy nucleus. Experimental data has been amassed for thousands of energy levels but they do not appear to follow any simple mathematical form, such as the Rydberg formula in atoms, etc. Instead it appears that the levels are quite random and can be well characterized statistically (Ref. Shriner J, Mitchell G and Von Egidy T 1991 Z. Phys. A 338 309). In 1955, Wigner (Ref. Wigner E P 1993 The Collected Works of Eugene Paul Wigner (Berlin: Springer) pp 524–40) proposed using random matrices to understand the distribution of energy levels found experimentally, which turned out to be an extremely deep and insightful approach to adopt. His reasoning was quite general, and had nothing to do with the precise form of interactions in the nucleus, as QCD was unknown at the time.

==========

In the so called Gaussian ensemble one assumes that

$$W(H) = \frac{1}{Z}\exp\{-\frac{1}{2}TrH^2\} = \frac{1}{Z}\exp\{-\frac{1}{2}\sum_{i,j=1}^{2}|H_{ij}|^2\}$$

where $1/Z$ is normalization constant but as already remarked our discussion will not depend on a particular form of $W(H)$.

4.2 What happens at avoided crossings - the Landau-Zener transitions

Let us now discuss quantitatively the deviations from the extreme adiabatic evolution as the physical system passes through the regions of avoided level crossings. We will assume for simplicity that such regions are isolated (at least along the evolution contour $\mathbf{R}(t)$) so that one can discuss each one separately. One need to calculate the probability (probability amplitude) of not remaining in the level the system was before it approached an avoided crossing but making a transition to the level which came close. Such transitions are called Landau-Zener transitions after the scientists who first discussed them. Since as we have seen in the previous Section the description of a given avoided crossing if fairly universal also the Landau-Zener results have quite universal character. Landau arguments are short but hard to follow while Zener's are

relatively straightforward and can be found in Ref. [7]. We will follow the framework of the latter.

4.2.1 Isolating two-level evolution

As we have seen in the previous section in the vicinity of the avoided crossing one can isolate just the two levels which came close and consider only the corresponding 2×2 part of the Hamiltonian. We will further simplify this approach and consider a very simple time dependent Hamiltonian

$$H(t) = \begin{pmatrix} -\epsilon(t) & \Delta \\ \Delta^* & \epsilon(t) \end{pmatrix} \tag{31}$$

To understand the meaning of the evolution which this H produces let us first find its adiabatic basis, i.e. the instantaneous eigenvalues and eigenfunctions of the above matrix. We need to solve

$$H(t)\phi(t) = E(t)\phi(t) \quad , \quad \phi(t) = A_1(t) \begin{pmatrix} 1 \\ 0 \end{pmatrix} + A_2(t) \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{32}$$

which gives

$$\begin{array}{rcrcl} -\epsilon(t)A_1 & + & \Delta\, A_2 & = & EA_1 \\ \Delta^*\, A_1 & + & \epsilon(t)A_2 & = & EA_2 \end{array} \tag{33}$$

Starting with eigenvalues we have

$$Det \begin{pmatrix} -\epsilon(t) - E & \Delta \\ \Delta^* & \epsilon(t) - E \end{pmatrix} = 0 \quad \rightarrow \quad E_\pm(t) = \pm\sqrt{\epsilon(t)^2 + |\Delta|^2} \tag{34}$$

Let us now choose the simplest form of $\epsilon(t)$

$$\epsilon(t) = \alpha t \quad , \quad \alpha > 0 \tag{35}$$

for which the adiabatic energies

$$E_\pm(t) = \pm\sqrt{(\alpha t)^2 + |\Delta|^2} \tag{36}$$

have the shape of hyperbolas, Fig. 5.

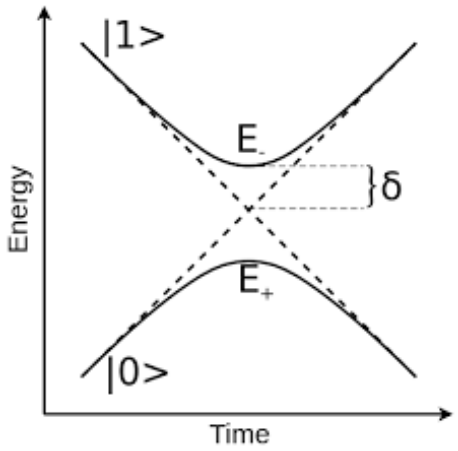

Figure 5: Avoided crossing of adiabatic levels $E_{\pm}(t)$

a) Asymptotically $E_{\pm}(t)$ tend to the lines $\pm\alpha t$ as follows

$$E_{\pm}(t \to -\infty) \to \mp\alpha t = \pm\alpha|t| \quad \text{but} \quad E_{\pm}(t \to \infty) \to \pm\alpha t$$

so that $E_{\pm}(t)$ describe respectively the upper and the lower adiabatic energy levels in Fig. 5.

b) The parameter α controls the speed of the evolution while Δ controls the magnitude of the smallest energy difference

$$\min(E_+(t) - E_-(t)) = 2\Delta \quad \text{at} \quad t = 0.$$

Let us note that this example offers a simple illustration of our discussion in Section 4. Viewing the energies $E_{\pm}$ as the function of two parameters t and Δ we clearly see that the levels cross at a single point $t = 0, \Delta = 0$ in the two dimensional parameter space and the expression Eq.(34) viewed as a function of t and Δ describes a conical intersection in the 3 dimensional space of E, t, Δ. Let us also observe that for complex valued Δ the expression (34) will be

$$E_{\pm}(t) = \pm\sqrt{\alpha^2 t^2 + |\Delta|^2} = \pm\sqrt{\alpha^2 t^2 + (Re\Delta)^2 + (Im\Delta)^2}$$

so we would have three parameters, $t, Re\Delta$ and $Im\Delta$ on which the energies $E_{\pm}$ dependent. The level crossing occurs at one point in this parameter space $t = Re\Delta = Im\Delta = 0$.

Returning to our problem with real Δ we find that the two eigenfunctions corresponding to $E_\pm(t)$ (i.e. the adiabatic basis set) are

$$\phi_\pm(t) = \mathcal{N}'_\pm(t) \begin{pmatrix} 1 \\ \frac{E_\pm(t)+\alpha t}{\Delta} \end{pmatrix} = \mathcal{N}''_\pm(t) \begin{pmatrix} \frac{E_\pm(t)-\alpha t}{\Delta} \\ 1 \end{pmatrix} \tag{37}$$

where $\mathcal{N}'_\pm(t)$ and $\mathcal{N}''_\pm(t)$ are appropriate normalizations. Here we used first the upper then the lower of the equations (33) to obtain the two equivalent forms of $\phi_\pm$.

It is important to examine the $t \to \pm\infty$ limits of the adiabatic states. This is made easier by our use of two equivalent forms for each $\phi_\pm(t)$ states. We have for $t \to -\infty$ $\frac{E_+(t)+\alpha t}{\Delta} \to 0$ and $\frac{E_-(t)+\alpha t}{\Delta} \to \infty$ so

$$\phi_+(t \to -\infty) \to \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad , \quad \phi_-(t \to -\infty) \to \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

while for $t \to +\infty$ we have $\frac{E_+(t)-\alpha t}{\Delta} \to 0$ and $\frac{E_-(t)-\alpha t}{\Delta} \to -\infty$ so

$$\phi_+(t \to +\infty) \to \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad , \quad \phi_-(t \to +\infty) \to \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

It is also useful to record these states at $t = 0$

$$\phi_+(t=0) = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad , \quad \phi_-(t=0) = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

In the "spin" language one can view $\phi_-(t)$ state as describing "spin down" (with respect to an imagined z-axis) at $t \to -\infty$, then rotating and becoming parallel to the x-axis at $t = 0$ and finally ending "spin up" at $t \to \infty$.

WE OBSERVE HERE THE TYPICAL ADIABATIC BASIS BEHAVIOR - ITS STATES i.e. THE ADIABATIC WAVE FUNCTIONS CHANGE DRASTICALLY WHEN ONE ("INFINITELY SLOWLY") MOVES ACROSS AN AVOIDED CROSSING. Namely the upper and the lower states of the avoided crossing exchange their "character". It is as if moving "infinitely slow" they have "enough time" to undergo this drastic change.

4.2.2 The transition amplitude

To understand the validity of the adiabatic approximation in this case we now indicate the steps and relevant results of the exact solution of this problem. We have to solve

$$i\hbar \frac{\partial \Psi(t)}{\partial t} = H_{op} \Psi(t)$$

with H_{op} given by Eq. (31). Representing $\Psi(t)$ in the fixed (!!!!) basis

$$\Psi(t) = C_1(t) \begin{pmatrix} 1 \\ 0 \end{pmatrix} + C_2(t) \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

we find coupled equations

$$i\hbar\dot{C}_1 = -\epsilon(t)C_1 + \Delta C_2 \quad ; \quad i\hbar\dot{C}_2 = \Delta C_1 + \epsilon(t)C_2$$

or in a more compact form

$$\left[i\hbar\frac{d}{dt} \pm \epsilon(t)\right] C_{1,2} = \Delta C_{2,1}$$

Now try to find decoupled equations for C_1 and C_2. For that apply $\left[i\hbar\frac{d}{dt} \mp \epsilon(t)\right]$ to both sides of the above equation

$$\left[i\hbar\frac{d}{dt} \mp \epsilon(t)\right] \left[i\hbar\frac{d}{dt} \pm \epsilon(t)\right] C_{1,2} = \left[i\hbar\frac{d}{dt} \mp \epsilon(t)\right] \Delta C_{2,1} = (\Delta)^2 C_{1,2}$$

which gives

$$\frac{d^2C_{1,2}}{dt^2} \mp \frac{i}{\hbar}\frac{d\epsilon(t)}{dt}C_{1,2} + \frac{1}{\hbar^2}[(\Delta)^2 + \epsilon^2(t)]C_{1,2} = 0$$

For the assumed linear dependence $\epsilon(t) = \alpha t$ have

$$\frac{d^2C_{1,2}}{dt^2} + \frac{1}{\hbar^2}\left[(\Delta)^2 \mp i\hbar\alpha + \alpha^2t^2\right] C_{1,2} = 0$$

One can express solutions of these equations in terms of the so called Weber functions (in quantum mechanics they appear as solutions for the INVERSE harmonic oscillator, i.e. parabolic barrier potential). Cf., the original Zener's paper for details, Ref. 2 in the References at the end of this Chapter.

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Final result is the probability amplitude of the Landau-Zener transition which is given by

$$a_+(t \to \infty) = -e^{-\pi/2\gamma} \quad , \quad \gamma = \frac{\hbar\alpha}{\Delta^2} \tag{38}$$

The notation here is for the amplitude of the solution in the adiabatic (NOT THE FIXED!!!) basis as given by Eq. (37)

$$\Psi(t) = a_-(t)\phi_-(t) + a_+(t)\phi_+(t) \tag{39}$$

under the initial condition that $|a_-(t \to -\infty)| = 1$ and $|a_+(t \to -\infty)| = 0$

Clearly the combination γ controls the smallness of the transition probability, i.e. must have

$$\frac{\hbar\alpha}{\Delta^2} \ll 1$$

at every avoided crossing to have the adiabatic approximation valid i.e. to remain in the same adiabatic level. The smallest energy 2Δ between the level must be large in relation to the combination $\sqrt{\hbar\alpha}$ which depends on the parameter α controlling the rate of change of the time dependence of the Hamiltonian in this model.

Note that characteristically the dependence of the transition probability upon α is the non analytic $\exp(-\alpha_0/\alpha)$ ($\alpha_0 \equiv \pi\Delta^2/2\hbar$) .

5 The Berry Phase

It is convenient to rewrite the (real valued) Berry phase in (18) as

$$\gamma_m(t) = i\int_{t_0}^{t}\langle\phi_m|\frac{\partial}{\partial t'}|\phi_m\rangle dt' = i\int_{\mathbf{R}_0}^{\mathbf{R}} d\mathbf{R}'\cdot\langle\phi_m(\mathbf{R}')|\nabla_{\mathbf{R}'}|\phi_m(\mathbf{R}')\rangle \tag{40}$$

where as before we used

$$\frac{\partial}{\partial t'} = \frac{d\mathbf{R}'}{dt'}\cdot\nabla_{\mathbf{R}'} \quad \text{and} \quad dt'\,\frac{d\mathbf{R}'}{dt'} = d\mathbf{R}'.$$

The last expression in Eq. (40) emphasyzes an important aspect of the Berry phase - it is a *GEOMETRICAL PHASE*, i.e. a phase which depends only the geometry (the shape) of the curve from $\mathbf{R}_0$ to $\mathbf{R}$ and not on the way (the speed with which) it is transversed.

5.1 The Berry connection

The (real) function

$$\mathcal{A}_m(\mathbf{R}) \equiv -i\langle\phi_m(\mathbf{R})|\nabla_{\mathbf{R}}|\phi_m(\mathbf{R})\rangle = Im\langle\phi_m(\mathbf{R})|\nabla_{\mathbf{R}}|\phi_m(\mathbf{R})\rangle \tag{41}$$

is called the Berry connection. It is induced in the parameter space by the parameter dependent wave function which is a solution of the eigenvalue problem for the parameter dependent Hamiltonian which itself "lives" in the wave functions' Hilbert space. By using the polar form of the wave function

$$\phi_m(q;\mathbf{R}) = |\phi_m(q;\mathbf{R})|\exp[i\xi_m(q;\mathbf{R})]$$

one has

$$\mathcal{A}_m(\mathbf{R}) = \int dq |\phi_m(q;\mathbf{R})|^2 \nabla_{\mathbf{R}} \xi_m(q;\mathbf{R}) \tag{42}$$

showing that the Berry connection is a weighted gradient with respect to the parameters $\mathbf{R}$ of the wave function phase.

The Berry connection is not uniquely defined. Indeed as is usual with wave functions the eigenvalue equations (6) do not define the overall phases of the eigenfunctions ϕ_m's. In other words the substitution

$$\phi_m(q;\mathbf{R}) \;\rightarrow\; \phi_m(q;\mathbf{R}) e^{i\chi(\mathbf{R})} \tag{43}$$

for an arbitrary $\chi(\mathbf{R})$ is also a solution of (6). Although this is a standard quantum mechanical ambiguity the new element here is that χ is not just an arbitrary number but it can be an arbitrary function of $\mathbf{R}$. Expression (42) shows that under the change (43) with smooth $\chi(\mathbf{R})$ the Berry connection changes as

$$\mathcal{A}_m(\mathbf{R}) \;\;\rightarrow\;\; \mathcal{A}_m(\mathbf{R}) + \nabla_{\mathbf{R}} \chi(\mathbf{R}) \tag{44}$$

The arbitrariness of $\chi(\mathbf{R})$ seems to suggest that it can be chosen so as to make $\mathcal{A}_m(\mathbf{R})$ vanish. But as was first realised by Berry if one considers a closed contour C, i.e. the one with $\mathbf{R}(t) = \mathbf{R}(t_0)$ then for any SINGLE VALUED $\chi(\mathbf{R})$

$$\gamma_m(C) \equiv \oint_C \mathcal{A}_m(\mathbf{R}) \cdot d\mathbf{R} \;\;\rightarrow\;\; \oint_C \mathcal{A}_m(\mathbf{R}) \cdot d\mathbf{R} + \chi(\mathbf{R}(t)) - \chi(\mathbf{R}(t_0)) = \gamma_m(C) \tag{45}$$

i.e. $\gamma_m(C)$ is not changing under (43), it is invariant under this (analogue of the) gauge transformation.

5.2 The Berry curvature

One can transform the contour integral in (45) into a surface integral over any surface S in parameter space whose boundary is C (M. Berry, Proc. R. Soc. Lond., A392 (1984) 45). For simplicity and in order to use the familiar results of the vector analysis let us consider the 3 dimensional parameter $\mathbf{R}$ space. This case is important also in applications. Using the Stokes theorem the closed contour integral in (45) can be written

$$\gamma_m(C) = \int_S d\mathbf{S} \cdot \nabla_{\mathbf{R}} \times \mathcal{A}_m(\mathbf{R}) \tag{46}$$

We calculate the curl (omitting for brevity the subscript $\mathbf{R}$)

$$\begin{aligned}\epsilon_{ijk}\nabla_j[\mathcal{A}_m]_k &= -\epsilon_{ijk}\nabla_j Im\langle\phi_m|\nabla_k\phi_m\rangle = -\epsilon_{ijk}Im\langle\nabla_j\phi_m|\nabla_k\phi_m\rangle = \\ &= -\epsilon_{ijk}Im\sum_{n\neq m}\langle\nabla_j\phi_m|\phi_n\rangle\langle\phi_n|\nabla_k\phi_m\rangle\end{aligned}$$

Here we inserted $1=\sum_n|\phi_n\rangle\langle\phi_n|$ and excluded $n=m$ since

$$\langle\nabla_j\phi_m|\phi_m\rangle\langle\phi_m|\nabla_k\phi_m\rangle = (iIm\langle\nabla_j\phi_m|\phi_m\rangle)(iIm\langle\phi_m|\nabla_k\phi_m\rangle)$$

is real.

We now use (68) in the Appendix to obtain

$$\gamma_m(C) = -\int_S d\mathbf{S}\cdot\mathbf{V}_m(\mathbf{R}) \tag{47}$$

with the "vector" field $\mathbf{V}_m(\mathbf{R})$ components defined as

$$[\mathbf{V}_m(\mathbf{R})]_i \equiv Im\sum_{n\neq m}\epsilon_{ijk}\frac{\langle\phi_m(\mathbf{R})|\nabla_j\hat{H}(\mathbf{R})|\phi_n(\mathbf{R})\rangle\langle\phi_n(\mathbf{R})|\nabla_k\hat{H}(\mathbf{R})|\phi_m(\mathbf{R})\rangle}{[E_n(\mathbf{R})-E_m(\mathbf{R})]^2} \tag{48}$$

or using vector product notation

$$\mathbf{V}_m(\mathbf{R}) \equiv Im\sum_{n\neq m}\frac{\langle\phi_m(\mathbf{R})|\nabla_{\mathbf{R}}\hat{H}(\mathbf{R})|\phi_n(\mathbf{R})\rangle\times\langle\phi_n(\mathbf{R})|\nabla_{\mathbf{R}}\hat{H}(\mathbf{R})|\phi_m(\mathbf{R})\rangle}{[E_n(\mathbf{R})-E_m(\mathbf{R})]^2} \tag{49}$$

DISCUSS. TALK ABOUT DEGENERACY POINTS. It is seen that $\mathbf{V}_m$ is singular at points in the parameter space where

$$E_m(\mathbf{R}) = E_n(\mathbf{R}) \tag{50}$$

for one of n's. One can show that such points serve as "sources" of the field $\mathbf{V}_m(\mathbf{R})$. More precisely one can show that they act as point monopole-like sources of $\mathbf{V}_m(\mathbf{R})$, cf.,next Section or Section 3 from the reference of M. Berry above. For a single monopole the Berry phase γ_m in (45) (cf., Eq. (46)) is just given by the flux of $\mathbf{V}_m(\mathbf{R})$ emanating from the monopole into the solid angle which the contour C subtends.

Topological aspects of the Berry phase

The singularities at points of degeneracies (50) can be viewed as rendering non trivial topology for the parameter space. In a way it is similar to what we saw in the AB effect. There the presence of the flux tubes made the space multiply connected -

not all closed contours could be smoothly deformed into each other without crossing the flux tube. That led to a possible non zero AB phase.

In the Berry phase set up not all closed *surfaces* in the parameter space can be smoothly deformed into each other without crossing the singular degeneracy points. This leads to a possible non zero Berry phase as described above.

5.3 Level crossing induces magnetic monopole with Dirac string in a parameter space

We want to consider the effect of level crossing in a parameter space on the Berry phase. Consider two levels close to the point where they cross. By "close" we assume that all other levels are energetically much father away in this parameter region. One can then neglect these distant levels and consider a 2×2 submatrix of the full Hamiltonian which to a good approximation will account for the crossed levels of interest. The most general form of such a matrix is

$$H' = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \tag{51}$$

with real H_{11} and H_{22} and

$$H_{21} = H_{12}^* \, .$$

The indices here just serve to label the position of the numbers H_{ij} in the matrix.

It is convenient to write this matrix as

$$\frac{1}{2}(H_{11} + H_{22}) \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} \frac{1}{2}(H_{11} - H_{22}) & H_{12} \\ H_{12}^* & \frac{1}{2}(H_{22} - H_{11}) \end{pmatrix}$$

The part proportional to the unit matrix does not effect the eigenvectors and produces just an equal shift in eigenvalues. We are led to consider therefore the Hamiltonian

$$H = \begin{pmatrix} Z & X + iY \\ X - iY & -Z \end{pmatrix} \tag{52}$$

with the obvious notations for X, Y and Z variables. It has the eigenvalues

$$\det \begin{pmatrix} Z - E & X + iY \\ X - iY & -Z - E \end{pmatrix} \quad = 0 \quad \rightarrow \quad -(Z^2 - E^2) - X^2 - Y^2 = 0$$

$$E = \pm R \quad \equiv \pm\sqrt{X^2 + Y^2 + Z^2} \tag{53}$$

The eigenfunctions $\psi = (\psi_1, \psi_2)$ satisfy

$$(Z - E)\psi_1 + (X + iY)\psi_2 = 0 \quad \rightarrow \quad \psi_1 = \frac{X + iY}{E - Z}\psi_2$$

so for

$$E = R$$

have

$$|\psi_1|^2 + |\psi_2|^2 = \left[\frac{X^2 + Y^2}{(R - Z)^2} + 1\right]|\psi_2|^2 = 1 \quad \rightarrow \quad \frac{X^2 + Y^2 + R^2 + Z^2 - 2RZ}{(R - Z)^2}|\psi_2|^2 = 1$$

so up to an arbitrary phase

$$\begin{aligned}
\psi_2 &= \sqrt{\frac{(R - Z)^2}{2R(R - Z)}} = \sqrt{\frac{R - Z}{2R}} = \sqrt{\frac{1}{2}(1 - \cos\theta)} = \sin\theta/2 \\
\psi_1 &= \frac{X + iY}{\sqrt{2R(R - Z)}} = \frac{\sin\theta e^{i\phi}}{\sqrt{2(1 - \cos\theta)}} = \frac{2\sin\theta/2\cos\theta/2e^{i\phi}}{2\sin\theta/2} = \cos(\theta/2)e^{i\phi}
\end{aligned}$$

This result can be multiplied by an arbitrary phase

$$\psi \rightarrow \psi' = e^{i\chi(\phi,\theta)}\psi$$

For simplicity we explore only two simple cases of $\chi = 0$ and $\chi = -\phi$. In terms ψ's we consider $\psi_\pm$ with

$$\psi_+ = \begin{pmatrix} \cos(\theta/2)e^{i\phi} \\ \sin(\theta/2) \end{pmatrix} \quad , \quad \psi_- = \begin{pmatrix} \cos(\theta/2) \\ \sin(\theta/2)e^{-i\phi} \end{pmatrix} \tag{54}$$

Let us calculate the corresponding Berry connection

$$\mathcal{A}_\pm(\mathbf{R}) = i\langle\psi_\pm(\mathbf{R})|\nabla_{\mathbf{R}}|\psi_\pm(\mathbf{R})\rangle$$

In spherical coordinates

$$\begin{aligned}
\nabla_{\mathbf{R}}|\psi_+(\mathbf{R})\rangle &= \left(\mathbf{e}_R\frac{\partial}{\partial R} + \mathbf{e}_\theta\frac{1}{R}\frac{\partial}{\partial\theta} + \mathbf{e}_\phi\frac{1}{R\sin\theta}\frac{\partial}{\partial\phi}\right)\begin{pmatrix} \cos(\theta/2)e^{i\phi} \\ \sin(\theta/2) \end{pmatrix} \\
&= \mathbf{e}_\theta\frac{1}{2R}\begin{pmatrix} -\sin(\theta/2)e^{i\phi} \\ \cos(\theta/2) \end{pmatrix} + \mathbf{e}_\phi\frac{ie^{i\phi}\cos(\theta/2)}{R\sin\theta}\begin{pmatrix} 1 \\ 0 \end{pmatrix}
\end{aligned}$$

while

$$\begin{aligned}\nabla_{\mathbf{R}}|\psi_-(\mathbf{R})\rangle &= \left(\mathbf{e}_R\frac{\partial}{\partial R}+\mathbf{e}_\theta\frac{1}{R}\frac{\partial}{\partial\theta}+\mathbf{e}_\phi\frac{1}{R\sin\theta}\frac{\partial}{\partial\phi}\right)\begin{pmatrix}\cos(\theta/2)\\ \sin(\theta/2)e^{-i\phi}\end{pmatrix}\\ &= \mathbf{e}_\theta\frac{1}{2R}\begin{pmatrix}-\sin(\theta/2)\\ \cos(\theta/2)e^{-i\phi}\end{pmatrix}+\mathbf{e}_\phi\frac{-ie^{-i\phi}\sin(\theta/2)}{R\sin\theta}\begin{pmatrix}0\\1\end{pmatrix}\end{aligned}$$

so that

$$\begin{aligned}\mathcal{A}_+(\mathbf{R}) &= i\left(\cos(\theta/2)e^{-i\phi},\sin(\theta/2)\right)\left[\mathbf{e}_\theta\frac{1}{2R}\begin{pmatrix}-\sin(\theta/2)e^{i\phi}\\ \cos(\theta/2)\end{pmatrix}+\mathbf{e}_\phi\frac{ie^{i\phi}\cos(\theta/2)}{R\sin\theta}\begin{pmatrix}0\\1\end{pmatrix}\right]=\\ &= i\left\{\mathbf{e}_\theta\frac{1}{2R}\left[-\cos(\theta/2)\sin(\theta/2)+\sin(\theta/2)\cos(\theta/2)\right]+\mathbf{e}_\phi\frac{i\cos^2(\theta/2)}{R\sin\theta}\right\}=\\ &= -\mathbf{e}_\phi\frac{\cos^2(\theta/2)}{R\sin\theta}=-\mathbf{e}_\phi\frac{1+\cos\theta}{2R\sin\theta}\end{aligned}$$

and

$$\begin{aligned}\mathcal{A}_-(\mathbf{R}) &= i\left(\cos(\theta/2),\sin(\theta/2)e^{i\phi}\right)\left[\mathbf{e}_\theta\frac{1}{2R}\begin{pmatrix}-\sin(\theta/2)\\ \cos(\theta/2)e^{-i\phi}\end{pmatrix}+\mathbf{e}_\phi\frac{-ie^{-i\phi}\sin(\theta/2)}{R\sin\theta}\begin{pmatrix}0\\1\end{pmatrix}\right]=\\ &= i\left\{\mathbf{e}_\theta\frac{1}{2R}\left[-\cos(\theta/2)\sin(\theta/2)+\sin(\theta/2)\cos(\theta/2)\right]+\mathbf{e}_\phi\frac{-i\sin^2(\theta/2)}{R\sin\theta}\right\}=\\ &= \mathbf{e}_\phi\frac{\sin^2(\theta/2)}{R\sin\theta}=\mathbf{e}_\phi\frac{1-\cos(\theta)}{2R\sin\theta}\end{aligned}$$

Can write

$$\mathcal{A}_\pm(\mathbf{R})=-\mathbf{e}_\phi\frac{\pm1+\cos\theta}{2R\sin\theta} \tag{55}$$

Let us calculate the curl of this to get the Berry curvature. Since $\mathcal{A}$ has only A_ϕ component we obtain

$$\nabla\times\mathcal{A}_\pm=\frac{1}{R\sin\theta}\frac{\partial[(\sin\theta)A_{\phi,\pm}]}{\partial\theta}\mathbf{e}_R-\frac{1}{R}\frac{\partial(RA_{\phi,\pm})}{\partial R}\mathbf{e}_\theta=-\frac{1}{R\sin\theta}\frac{\partial}{\partial\theta}\left[\frac{\pm1+\cos\theta}{2R}\right]\mathbf{e}_R$$

which gives

$$\mathbf{V}_\pm(\mathbf{R})\equiv\nabla\times\mathcal{A}_\pm=\frac{1}{2R^2}\mathbf{e}_R \tag{56}$$

This result somehow (????) misses the Dirac string which for $\mathcal{A}_+$ ($\mathcal{A}_-$) stretches along the positive (negative) z-axis. This can be seen by calculating the circulation of $\mathcal{A}_\pm$ along a closed contour around the z-axis

$$\oint_C\mathcal{A}_\pm\cdot d\mathbf{l}=\int_0^{2\pi}A_{\phi,\pm}R\sin\theta d\phi=-\frac{\pm1+\cos\theta}{2R\sin\theta}2\pi R\sin\theta=-\pi(\pm1+\cos\theta)$$

This result holds for all contours which "lie" on the cone which a line emanating from the origin of the $\mathbf{R}$ space at angle θ spans if rotated around the z-axis. One observes that

a) For $\mathcal{A}_+$ it tends to -2π for $\theta \to 0$ (small contours around positive z) and to 0 for $\theta \to \pi$ (small contours along negative z).

b) For $\mathcal{A}_-$ it tends to 0 for $\theta \to 0$ (small contours around positive z) and to 2π for $\theta \to \pi$ (small contours along negative z).

CONCLUSIONS: For the Berry phase connection (i.e. the "vector potential" $\mathcal{A}(\mathbf{R})$) the level crossing of two levels plays the role of a "magnetic monopole" in the parameter space $\mathbf{R}$.

The monopole position is at the point of the level crossing and there is an analogue of the Dirac string stretching from this point to "infinity" and "feeding" the monopole.

The orientation of the string depends on the arbitrary phase of the adiabatic wave function (the "gauge choice" for $\mathcal{A}(\mathbf{R})$).

5.4 Chern number

EXPLAIN.

5.5 A brief aside - Berry phase in solid state physics

Over the recent years it was found that Berry phase plays important role in many physical phenomena in solid state physics. DISCUSS BRIEFLY THE REASONS FOR THAT - NATURAL APPEARANCE OF PHYSICAL PROBLEMS WITH HAMILTONIANS WHICH DEPEND ON PARAMETERS. Common example - Hamiltnonian of the Bloch wavefunctions. RECALL- if have Hamiltonian which is periodic, e.g.

$$H_{op} = \frac{\mathbf{p}_{op}^2}{2m} + V(\mathbf{r}) \quad \text{, with} \quad V(\mathbf{r}+\mathbf{a}) = V(\mathbf{r})$$

where $\mathbf{a}$ are vectors of a periodic lattice, them according to the Bloch theorem the eigenfunctions of such H_{op} have the form

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) \quad \text{with} \quad u_{n\mathbf{k}}(\mathbf{r}+\mathbf{a}) = u_{n\mathbf{k}}(\mathbf{r})$$

Inserting this form into the Schrödinger equantion for $\psi_{n\mathbf{k}}(\mathbf{r})$ we obtain

$$H_{op}\psi_{n\mathbf{k}} = E_{n\mathbf{k}}\psi_{n\mathbf{k}} \quad \rightarrow \quad \left[\frac{(\mathbf{p}_{op}+\hbar\mathbf{k})^2}{2m} + V(\mathbf{r})\right] u_{n\mathbf{k}}(\mathbf{r}) = E_{n\mathbf{k}} u_{n\mathbf{k}}(\mathbf{r})$$

This common appearance of this eigenstate problem with the Hamiltonian depending on the parameters - the components of the Bloch momentum **k**, is the basis behind the widespread use of the Berry connection and the Berry curvature in condensed matter physics. Here is a quote from the book

Bernevig, B. Andrei, Topological Insulators and Topological Superconductors PRINCETON UNIVERSITY PRESS

"Although interesting in its own right, the Berry potential (connection - SL) and the Berry curvature became of widespread use in condensed matter physics because of their far-ranging consequences in the physics of electrons on a lattice. The manner in which the Berry phase and the Berry curvature enter in solid-state physics is strongly dependent on the dimensionality of the system and on whether the system is a metal or an insulator. In general, the Berry phase is the integral of the Berry potential over a closed curve (a 1-D manifold). As such, it is relevant for filled bands (insulators) in one spatial dimension (wires?) for which the closed curve could be the Bloch momentum $-\pi < kx < \pi$ .... . Other 1-D closed manifolds (curves) that we can envision in crystals are the (1-D) Fermi surfaces of 2-D metals. The Berry phase is relevant in these cases too. As a rule of thumb, the Berry phase is relevant for 1-D insulators or 1-D Fermi surfaces of 2-D metals.

The Berry field strength (curvature - SL) is a 2-form, which implies it should be relevant in the case of surfaces. Its integral over a surface (2-D manifold) is relevant in two cases. First it is relevant in filled bands in two dimensions, for which the surface could be the full 2-D Brillouin zone. In this case, the integral of the Berry curvature over the full (filled) Brillouin zone is related to the Hall conductance of the insulator ... and is identical to the Chern number of the filled band. Second, the Berry curvature is relevant for Fermi surfaces in 3-D metals. These are 2-D manifolds and are also characterized by a Chern number (integral of the Berry curvature over the 2-D Fermi surface)."

6 The Born-Oppenheimer approximation

We follow here J. Moody, A. Shapere and F. Wilczek paper in Ref. [9].

So far we have considered problems related to Hamiltonians of the type (1) which depend on "external" parameters **R**. The dependence of **R** on time was produced "externally". The resulting dynamics of the system degrees of freedom q did not have any "back reaction" on this time dependence. In this section we will consider physical systems in which **R** are part of the dynamics of the system with their Hamiltonian being a part of the Hamiltonian of the system. The slow "external" time evolution

of $\mathbf{R}$ will be replaced by the "slow" dynamics of their Hamiltonian.

6.1 Molecules as an example

The original problem where this was discussed was apparently the quantum mechanics of molecules in which the degrees of freedom are sharply separated into degrees of freedom of nuclei and electrons. The former are much heavier and are naturally considered as "slow" while the light electrons are "fast". In some sense while the nuclei barely move the electrons already have their wave functions "established". The approximation which is based on this intuitive notion is called the Born-Oppenheimer approximation. It is the subject of this Section.

The molecular Hamiltonian has the following obvious form

$$H_{\text{molecule}} = T_{\text{nucl}}(\mathbf{P}) + V_{\text{nucl}}(\mathbf{R}) + T_{\text{el}}(\mathbf{p}) + V_{\text{el}}(\mathbf{r}) + V_{\text{el-nucl}}(\mathbf{r}, \mathbf{R})$$

where the nuclear kinetic and potential energy operators and electronic potential and kinetic energy operators are (schematically and in the CGS units)

$$T_{\text{nucl}} = \sum_a \frac{\mathbf{P}_a^2}{2M_a} \ , \ V_{\text{nucl}} = \frac{1}{2}\sum_{a\neq b} \frac{Z_a Z_b e^2}{|\mathbf{R}_a - \mathbf{R}_b|} \ ; \ T_{\text{el}} = \sum_c \frac{\mathbf{p}_c^2}{2m} \ , \ V_{\text{el}} = \frac{1}{2}\sum_{c\neq d} \frac{e^2}{|\mathbf{r}_c - \mathbf{r}_d|}$$

and the electrons-nuclei interaction

$$V_{\text{el-nucl}} = -\sum_{a,c} \frac{Z_a e^2}{|\mathbf{r}_c - \mathbf{R}_a|}$$

6.2 Generic case

Following this example we consider a general case of the system described by the Hamiltonian

$$H(\mathbf{P}, \mathbf{R}; p.q) = H_0(\mathbf{P}, \mathbf{R}) + h(p, q; \mathbf{R}) \tag{57}$$

with the respective "fast" and "slow" coordinates $q = q_1, q_2, ..., q_N$ and $\mathbf{R} = R_1, ..., R_M$ and $p = p_1, ..., p_N$ and $\mathbf{P} = P_1, ..., P_M$ their corresponding momentum operators. We need to solve the stationary Schrödinger equation with this Hamiltonian

$$H(\mathbf{P}, \mathbf{R}; p.q)\Psi(\mathbf{R}, q) = E\Psi(\mathbf{R}, q) \tag{58}$$

We note that in the above Hamiltonian the part $h(p, q; \mathbf{R})$ is precisely analogous to the parameter dependent Hamiltonian in the adiabatic development we have discussed

earlier, Eq.(1). We follow the logic of that development and define the "adiabatic basis" which represents the complete set of solutions of

$$h(p,q;\mathbf{R})\phi_n(q;\mathbf{R}) = \epsilon_n(\mathbf{R})\phi_n(q;\mathbf{R}) \tag{59}$$

for values of the slow coordinate $\mathbf{R}$ as parameters. For a fixed $\mathbf{R}$ this set can be chosen as orthonormal

$$\int \phi^*_m(q;\mathbf{R})\phi_n(q;\mathbf{R})\; d^N q = \delta_{mn}$$

and is complete for expanding any function of q. We actually have a family of such sets, each for different $\mathbf{R}$ values.

We use the basis $\{\phi_n(q;\mathbf{R})\}$ and expand the wave function of the entire system as following

$$\Psi(\mathbf{R},q) = \sum_n \xi_n(\mathbf{R})\phi_n(q;\mathbf{R}) \tag{60}$$

We stress that we are expanding this function AS A FUNCTION OF q but for every $\mathbf{R}$ we use the matching complete set $\{\phi_n(q;\mathbf{R})\}$ as discussed just above. We accordingly denoted the expansion coefficients by $\xi_n(\mathbf{R})$. They clearly must in general depend on (be different for different) $\mathbf{R}$. In a vague sense $\xi_n(\mathbf{R})$ may be viewed as probability amplitudes of the fast degrees of freedom to be in a wave function $\phi_n(q;\mathbf{R})$ at given value $\mathbf{R}$ of the slow coordinates.

We now insert the above expansion into the Schroedinger equation for $\Psi(q,\mathbf{R})$. Using the assumed form of the full Hamiltonian (58) we obtain

$$H(\mathbf{P},\mathbf{R};p.q)\Psi(\mathbf{R},q) = \sum_n \left[H_0(\mathbf{P},\mathbf{R}) + h(p,q;\mathbf{R})\right]\xi_n(\mathbf{R})\phi_n(q;\mathbf{R}) =$$

$$= \sum_n \left[H_0(\mathbf{P},\mathbf{R}) + \epsilon_n(\mathbf{R})\right]\xi_n(\mathbf{R})\phi_n(q;\mathbf{R}) = E\sum_n \xi_n(\mathbf{R})\phi_n(q;\mathbf{R}). \tag{61}$$

We now want to project this equality on $\phi_m(q;\mathbf{R})$ i.e. multiply on the left by $\phi^*(q;\mathbf{R})$ and integrate over q. Before doing this we assume that $H_0(\mathbf{P},\mathbf{R})$ has the standard "kinetic plus potential energy" form. Schematically we write

$$H_0(\mathbf{P},\mathbf{R}) = -\frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}} + U(\mathbf{R}) \tag{62}$$

where for simplicity of notation we take all "heavy" masses to be equal. This can be easily corrected at the expense of less compact notation.

With this form of $H_0(\mathbf{P},\mathbf{R})$ we project (61) on ϕ_m and obtain using the Dirac nottaion

$$-\frac{\hbar^2}{2M}\sum_n \langle\phi_m(\mathbf{R})|\nabla^2_{\mathbf{R}}|\phi_n(\mathbf{R})\rangle\xi_n(\mathbf{R}) + [U(\mathbf{R})+\epsilon_m(\mathbf{R})]\xi_m(\mathbf{R}) = E\,\xi_m(\mathbf{R}) \qquad (63)$$

This set of coupled equations for $\xi_m(\mathbf{R})$ amplitudes is still exact. As we see the coupling is produced by the kinetic energy which is responsible for the motion of the "slow" degrees of freedom. The coupling terms have heavy masses in the denominator. The Born-Oppenheimer approximation uses this fact and assumes that the off diagonal terms can be neglected in the above set

$$-\frac{\hbar^2}{2M}\langle\phi_m(\mathbf{R})|\nabla^2_{\mathbf{R}}|\phi_m(\mathbf{R})\rangle\xi_m(\mathbf{R}) + [U(\mathbf{R})+\epsilon_m(\mathbf{R})]\xi_m(\mathbf{R}) = E\,\xi_m(\mathbf{R}) \qquad (64)$$

We will discuss the validity of this approximation below.

6.3 Equation for slow variables. Energy surfaces

At the moment let us concentrate on the first term in the above equation and note that $\nabla^2_{\mathbf{R}}$ in the above equation acts both on $|\phi_m(\mathbf{R})\rangle$ and $\xi_m(\mathbf{R})$. Using the standard formula for the second derivative of a product we have

$$\begin{aligned}\nabla^2_{\mathbf{R}}|\phi_m(\mathbf{R})\rangle\xi_m(\mathbf{R}) &= [\nabla^2_{\mathbf{R}}|\phi_m(\mathbf{R})\rangle]\xi_m(\mathbf{R}) + \\ &+ 2[\nabla_{\mathbf{R}}|\phi_m(\mathbf{R})\rangle]\nabla_{\mathbf{R}}\xi_m(\mathbf{R}) + |\phi_m(\mathbf{R})\rangle\nabla^2_{\mathbf{R}}\xi_m(\mathbf{R})\end{aligned}$$

so that

$$\begin{aligned}\langle\phi_m(\mathbf{R})|\nabla^2_{\mathbf{R}}|\phi_m(\mathbf{R})\rangle\xi_m(\mathbf{R}) &= [\langle\phi_m(\mathbf{R})|\nabla^2_{\mathbf{R}}|\phi_m(\mathbf{R})\rangle]\xi_m(\mathbf{R}) + \\ &+ 2[\langle\phi_m(\mathbf{R})|\nabla_{\mathbf{R}}|\phi_m(\mathbf{R})\rangle]\nabla_{\mathbf{R}}\xi_m(\mathbf{R}) + \nabla^2_{\mathbf{R}}\xi_m(\mathbf{R})\end{aligned} \qquad (65)$$

As a last step we use in the first term

$$\begin{aligned}&\langle\phi_m(\mathbf{R})|\nabla^2_{\mathbf{R}}|\phi_m(\mathbf{R})\rangle = \\ &= \sum_n \langle\phi_m(\mathbf{R})|\nabla_{\mathbf{R}}|\phi_n(\mathbf{R})\rangle\langle\phi_n(\mathbf{R})|\nabla_{\mathbf{R}}|\phi_m(\mathbf{R})\rangle \approx (\langle\phi_m(\mathbf{R})|\nabla_{\mathbf{R}}|\phi_m(\mathbf{R})\rangle)^2\end{aligned}$$

i.e. we neglect the off-diagonal terms which is consistent with what we did to arrive at (64).

Introducing the notation (41) for the Berry connection we can use this and further write for (65)

$$\begin{aligned}\langle\phi_m(\mathbf{R})|\nabla^2_{\mathbf{R}}|\phi_m(\mathbf{R})\rangle\xi_m(\mathbf{R}) &\approx \\ &= \nabla^2_{\mathbf{R}}\xi_m(\mathbf{R}) - 2i\mathcal{A}_m(\mathbf{R})\nabla_{\mathbf{R}}\xi_m(\mathbf{R}) - \mathcal{A}^2_m(\mathbf{R})\xi_m(\mathbf{R}) = \\ &= [\nabla_{\mathbf{R}} - i\mathcal{A}_m(\mathbf{R})]^2\xi_m(\mathbf{R})\end{aligned}$$

HAVE A PROBLEM WITH THE COMMUTATOR OF $\nabla_{\mathbf{R}}$ AND $\mathcal{A}_m(\mathbf{R})$ - VALID AWAY FROM POINTS WHERE $\nabla_{\mathbf{R}} \cdot \mathcal{A}_m(\mathbf{R}) \neq 0$.

Using this in Eq. (64) we obtain

$$\frac{1}{2M}\left[-i\hbar\nabla_{\mathbf{R}} - \mathcal{A}_m(\mathbf{R})\right]^2 \xi_m(\mathbf{R}) + [U(\mathbf{R}) + \epsilon_m(\mathbf{R})]\xi_m(\mathbf{R}) = E\,\xi_m(\mathbf{R}) \tag{66}$$

This is is the final form of the Bohr-Oppenheimer (BO) equation for the slow degrees of freedom. It has two contributions from the fast degrees of freedom dynamics - the "adiabatic energy" level $\epsilon_m(\mathbf{R})$ and the Berry connection $\mathcal{A}_m(\mathbf{R})$. The energy $\epsilon_m(\mathbf{R})$ appears as the contribution to the potential energy added to the original $U(\mathbf{R})$. The Berry connection appears as a vector potential as if an effective magnetic field is acting on the slow degrees of freedom on the part of the fast ones.

We note that the entire BO equation are for a particular state index m, i.e. for a particular value of the quantum numbers set of the fast degrees of freedom. The potential energy $U(\mathbf{R}) + \epsilon_m(\mathbf{R})$ and the vector potential $\mathcal{A}_m(\mathbf{R})$ depend on m. In molecular physics BO potential energies with different m's are often called "potential energy surfaces" or "electronic surfaces" since the fast degrees of freedom are electronic.

DRAW ROUGH EXAMPLES (SAY WITH AVOIDED LEVEL CROSSING) FOR SAY DIATOMIC MOLECULE. EXPLAIN VERY BRIEFLY WHAT ARE VIBRATIONAL AND ROTATIONAL BANDS IN THIS SCHEME.

For each fixed m the solutions of the BO equations will themselves form an infinite set labelled by, say, quantum numbers M. Thus the entire set of eigenfuctions will be labeled by the double set of indices $\{m, M\}$ as in fact is expected. Each eigenfunction solution of the exact Eq.(58) in the BO apparoximation is

$$\Psi_{Mm}(\mathbf{R}, q) = \xi_{Mm}(\mathbf{R})\phi_m(q; \mathbf{R}) \tag{67}$$

Condition for the validity of the Born-Oppenheimer approximation

ADD HERE.

7 Appendix

7.1 Differentiating with respect to parameters

A useful form of the expression $\langle\phi_m(\mathbf{R})|\nabla_{\mathbf{R}}|\phi_n(\mathbf{R})\rangle$ is found by differentiating Eq.(6) with respect to the parameters $\mathbf{R}$. Using the Dirac notation we obtain

$$[\nabla_{\mathbf{R}}\hat{H}(\mathbf{R})]|\phi_n(\mathbf{R})\rangle + \hat{H}(\mathbf{R})\nabla_{\mathbf{R}}|\phi_n(\mathbf{R})\rangle = [\nabla_{\mathbf{R}}E_n(\mathbf{R})]|\phi_n(\mathbf{R})\rangle + E_n(\mathbf{R})\nabla_{\mathbf{R}}|\phi_n(\mathbf{R})\rangle$$

Multiplying this equality from the left with (i.e. projecting on) $\langle\phi_m(\mathbf{R})|$ we obtain for $m \neq n$

$$\langle\phi_m(\mathbf{R})|\nabla_{\mathbf{R}}|\phi_n(\mathbf{R})\rangle = \frac{\langle\phi_m(\mathbf{R})|\nabla_{\mathbf{R}}\hat{H}(\mathbf{R})|\phi_n(\mathbf{R})\rangle}{E_n(\mathbf{R}) - E_m(\mathbf{R})} \quad ; \quad m \neq n \tag{68}$$

For $m = n$ one obtains what is called Feynman-Hellmann relation

$$\nabla_{\mathbf{R}}E_n(\mathbf{R}) = \langle\phi_n(\mathbf{R})|\nabla_{\mathbf{R}}\hat{H}(\mathbf{R})]|\phi_n(\mathbf{R})\rangle \tag{69}$$

Note that the expressions (68) and (69) are directly related to the familiar perturbation theory results for small changes

$$|\phi_n\rangle \to |\phi_n\rangle + |\delta\phi_n\rangle \ , \ \ E_n \to E_n + \delta E_n$$

of an eigenfunction and of the corresponding energy under the perturbation $\hat{H} \to \hat{H} + \delta\hat{H}$

$$|\delta\phi_n\rangle = \sum_{m\neq n} |\phi_m\rangle \frac{\langle\phi_m|\delta\hat{H}|\phi_n\rangle}{E_n - E_m} \ , \ \ \delta E_n = \langle\phi_n|\delta\hat{H}|\phi_n\rangle$$

Let us now address the diagonal $\langle\phi_n(\mathbf{R})|\nabla_{\mathbf{R}}|\phi_n(\mathbf{R})\rangle$. To match the discussion after Eq. (17) let us work with the time derivative

$$\begin{aligned}
\langle\phi_m(\mathbf{R}(t)|\phi_m(\mathbf{R}(t))\rangle &= 1 \ \to \ \frac{\partial}{\partial t}\langle\phi_m(\mathbf{R}(t)|\phi_m(\mathbf{R}(t))\rangle = \\
= \langle\frac{\partial\phi_m(\mathbf{R}(t)}{\partial t}|\phi_m(\mathbf{R}(t))\rangle &+ \langle\phi_m(\mathbf{R}(t)|\frac{\partial\phi_m(\mathbf{R}(t))}{\partial t}\rangle = \\
= \langle\phi_m(\mathbf{R}(t)|\frac{\partial\phi_m(\mathbf{R}(t))}{\partial t}\rangle^* &+ \langle\phi_m(\mathbf{R}(t)|\frac{\partial\phi_m(\mathbf{R}(t))}{\partial t}\rangle = \\
&= 2Re\langle\phi_m(\mathbf{R}(t)|\frac{\partial\phi_m(\mathbf{R}(t))}{\partial t}\rangle = 0
\end{aligned}$$

which of course also means that

$$Re\langle\phi_n(\mathbf{R})|\nabla_{\mathbf{R}}|\phi_n(\mathbf{R})\rangle = 0$$

7.2 From matrices to vectors

The discussion in this appendix relies to a large extent on the formal developments presented in Section 4.2 of the Chapter "Open Systems in Quantum Mechanics". Using the results in that Chapter let us expand an arbitrary 2×2 Hamiltonian matrix

$$H = S_0\, I + \sum_{i=1}^{3} S_i \sigma_i \tag{70}$$

where I and $\sigma_1, \sigma_2, \sigma_3$ are respectively the unit and the Pauli matrices

$$I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad \sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} .$$

Since the expansion matrices are hermitian the coefficients S_0 and S_i are real. Using $Tr\sigma_i = 0$ and $Tr\sigma_i\sigma_j = 2\delta_{ij}$ it is straightforward to find

$$S_0 = \frac{1}{2} Tr\, H \qquad , \qquad S_i = \frac{1}{2}\, Tr\, \sigma_i\, H$$

which gives the relations (25). To recheck

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{12}^* & H_{22} \end{pmatrix} = \begin{pmatrix} S_0 + S_3 & S_1 - iS_2 \\ S_1 + iS_2 & S_0 - S_3 \end{pmatrix} =$$

$$= S_0 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} S_3 & S_1 - iS_2 \\ S_1 + iS_2 & -S_3 \end{pmatrix} = S_0\, I + \sum_{i=1}^{3} S_i \sigma_i$$

Under unitary rotations

$$UHU^+ = S_0\, I + \sum_{i=1}^{3} S_i\, U\sigma_i U^+ = S_0\, I + \sum_{i=1}^{3} S_i' \sigma_i \;\text{ with }\; S_i' = \sum_{j=1}^{3} S_j A_{ji} \tag{71}$$

where we have reexpanded $U\sigma_i U^+$ in σ_j's

$$U\sigma_i U^+ = \sum_{j=1}^{3} A_{ij}\sigma_j \tag{72}$$

We now use the relations proved in Section 4.2 of the Chapter "Open Systems in Quantum Mechanics" that the 3×3 matrix A_{ij} is real and orthogonal

$$AA^T = A^T A = 1 \tag{73}$$

This shows that under unitary rotations of H the coefficient S_0 in the expansion (70) remains invariant while the S_i's transform like components of a 3 dimensional vector,

$$H = S_0\, I + \mathbf{S} \cdot \boldsymbol{\sigma} \tag{74}$$

7.3 Landau-Zener transitions - details of the derivation

Consider the 2nd integral in the Eq.(9) of Ref. [8] and split it into two parts

$$\int_{-\infty}^{\infty} dt\, e^{-i\alpha t^2/2} \int_0^t dt' e^{i\alpha t'/2} \quad = \tag{75}$$

$$= \quad \int_{-\infty}^{0} dt\, e^{-i\alpha t^2/2} \int_0^t dt' e^{i\alpha t'/2} + \int_0^{\infty} dt\, e^{-i\alpha t^2/2} \int_0^t dt' e^{i\alpha t'/2}$$

Consider the 1st part and change in it $t \to -t$. Have $dt \to -dt$, and the integral from $\int_{-\infty}^{0} dt$ change to

$$-\int_{\infty}^{0} dt.... = \int_0^{\infty} ...dt$$

So the 1st part becomes

$$\int_{-\infty}^{0} dt\, e^{-i\alpha t^2/2} \int_0^t dt' e^{i\alpha t'/2} = \int_0^{\infty} dt\, e^{-i\alpha t^2/2} \int_0^{-t} dt' e^{i\alpha t'/2}$$

with the inner integral having $-t$ as an upper limit. Need to change this to compare with the second term in Eq. (75). So change $t' \to -t'$ in the inner integral. Using $dt' \to -dt'$ this gives

$$\int_0^{-t} dt' e^{i\alpha t'/2} \ \to -\int_0^t dt' e^{i\alpha t'/2}$$

Thus the 1st part in Eq. (75) becomes

$$\int_0^{\infty} dt\, e^{-i\alpha t^2/2} \int_0^{-t} dt' e^{i\alpha t'/2} = -\int_0^{\infty} dt\, e^{-i\alpha t^2/2} \int_0^t dt' e^{i\alpha t'/2}$$

which is negative of the 2nd part in this relation.

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