Chapter 6: Adiabatic approximation

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1 Introduction

1.1 Adiabatic approximation in Classical Mechanics

Let's go back to classical mechanics, with a harmonic oscillator performing motion but with $\omega(t)$ not constant. The hamiltonian of the system would be

$$H(x,p,\omega(t)) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2(t)x^2 \tag{1.1}$$

where x and p are going to be functions of time.
In general

$$\frac{dH}{dt} = \frac{\partial H}{\partial x}\dot{x} + \frac{\partial H}{\partial p}\dot{p} + \frac{\partial H}{\partial t}\,. \tag{1.2}$$

Hamilton's equation of motion read

$$\frac{\partial H}{\partial p} = \dot{x}\,, \qquad \frac{\partial H}{\partial x} = -\dot{p}\,. \tag{1.3}$$

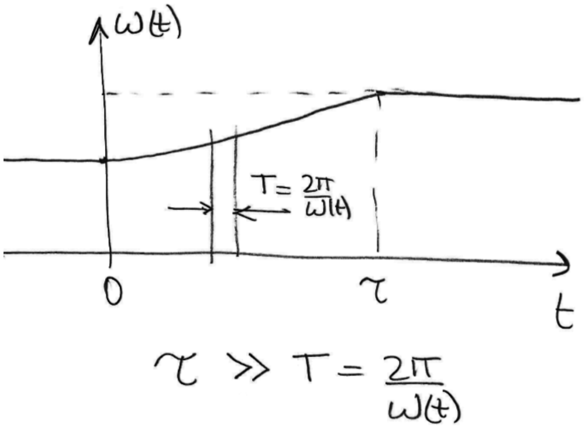
Even if you are not familiar with these, you probably know well their quantum analogs:

$$\begin{aligned} i\hbar\frac{d\langle x\rangle}{dt} &= \langle [x,H]\rangle = \left\langle i\hbar\frac{\partial H}{\partial p}\right\rangle \quad \rightarrow \quad \frac{d\langle x\rangle}{dt} = \left\langle \frac{\partial H}{\partial p}\right\rangle \\ i\hbar\frac{d\langle p\rangle}{dt} &= \langle [p,H]\rangle = \left\langle -i\hbar\frac{\partial H}{\partial x}\right\rangle \quad \rightarrow \quad \frac{d\langle p\rangle}{dt} = -\left\langle \frac{\partial H}{\partial x}\right\rangle \end{aligned} \tag{1.4}$$

At any rate, equations (1.3) imply that the first two terms in the right-hand side of (1.2) vanish and we have

$$\frac{dH}{dt} = \frac{\partial H}{\partial t} = m\omega\dot{\omega}x^2\,. \tag{1.5}$$

We have an *adiabatic* change if the time scale τ for change is much greater than time scale of the oscillation, $T = \frac{2\pi}{\omega(t)}$.



What remains roughly constant as $\omega(t)$ changes adiabatically?

$$\textbf{Claim:}\qquad I(t) \equiv \frac{H(t)}{\omega(t)} \qquad \text{is almost constant in adiabatic changes of } \omega. \tag{1.6}$$

$I(t)$ is called *the adiabatic invariant.*
Let us see why this is so:

$$\begin{aligned} \frac{dI}{dt} &= \frac{1}{\omega^2}\Big(\omega\frac{dH}{dt} - H(t)\dot{\omega}\Big) = \frac{1}{\omega^2}\Big(\omega\left(m\omega\dot{\omega}x^2\right) - \left(\frac{p^2}{2m} + \tfrac{1}{2}m\omega^2(t)x^2\right)\dot{\omega}\Big) = \\ &= \frac{\dot{\omega}}{\omega^2}\left(\tfrac{1}{2}m\omega^2(t)x^2 - \frac{p^2}{2m}\right) = \frac{\dot{\omega}}{\omega^2}\left(V(t) - K(t)\right)\,, \end{aligned} \tag{1.7}$$

where V and K are the potential and kinetic energies, respectively. We want to understand why this right-hand side is small. Clearly, $\frac{\dot{\omega}}{\omega^2}$ is slowly varying if $\dot{\omega}$ is slowly varying, but the term in parenthesis is actually quickly varying. Indeed, with

$$x = A\sin\omega t \quad \text{and} \quad p = Am\omega\cos\omega t$$

then the parenthesis goes like

$$\left(\tfrac{1}{2}m\omega^2x^2 - \frac{p^2}{2m}\right) \sim \tfrac{1}{2}m\omega^2(\sin^2\omega t - \cos^2\omega t) \sim -\tfrac{1}{2}m\omega^2\cos 2\omega t\,, \tag{1.8}$$

which is a fast variation. Let us see, however, how much $I(t)$ changes over one period

$$I(t+T) - I(t) = \int_t^{t+T} \frac{dI}{dt'} dt' = \int_t^{t+T} \frac{\dot{\omega}}{\omega^2}(t') \big(V(t') - K(t')\big)\, dt' \tag{1.9}$$

Since $\omega(t)$ is slowly varying, it changes very little over a period T and we can take the factor $\dot{\omega}/\omega$ out of the integral:

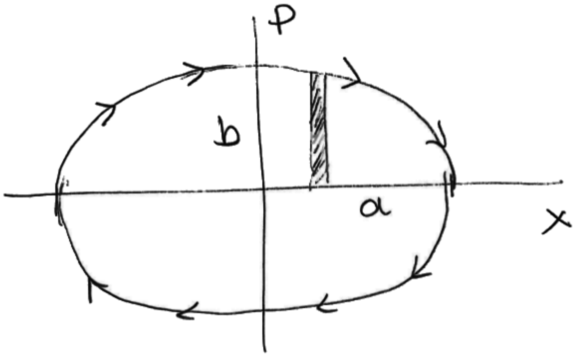
$$I(t+T) - I(t) \simeq \frac{\dot{\omega}}{\omega^2}(t) \int_t^{t+T} \left(V(t) - K(t)\right) dt' \tag{1.10}$$

In harmonic motion with ω constant, the *average* over a period of the potential energy $V(t)$ is exactly equal to the average of the kinetic energy $K(t)$, and the two terms above would cancel exactly. When ω is slowly changing they roughly cancel

$$I(t+T) - I(t) \simeq \frac{\dot{\omega}(t)}{\omega^2} \cdot 0 \simeq 0 \tag{1.11}$$

What is the geometrical interpretation of the adiabatic invariant E/ω? For this we consider the motion of a classical oscillator in phase space (x, p) where periodic oscillations trace the ellipse defined by energy conservation:

$$\frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2 = E \qquad\qquad (\omega, E, \text{constants})$$



We quickly see that the semi-major and semi-minor axes have lengths

$$a = \sqrt{\frac{2E}{m\omega^2}} \quad \text{and} \quad b = \sqrt{2mE} \tag{1.12}$$

Therefore

$$\text{Area of the ellipse } = \pi a b = 2\pi \frac{E}{\omega} \tag{1.13}$$

The adiabatic invariant is proportional to the area of the ellipse. That's neat! We can rewrite the area as an integral that takes a familiar form:

$$\text{Area of the ellipse } = \oint p\, dx$$

where we integrate over the *whole* closed trajectory with the orientation shown in the picture so that the area above the x axis is obtained as we go from left to right and the area under the x axis is obtained as we go from right to left. In this example

$$\oint p\, dx = 2\pi I\,. \tag{1.14}$$

More generally, for other systems the left-hand side is an adiabatic invariant. The value of the invariant is different for different systems, for the oscillator it is $2\pi E/\omega$.

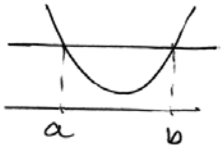
1.2 Quantum mechanics systems

What does it suggest for quantum mechanics?
First, for the harmonic oscillator

$$\frac{E}{\omega} = \frac{\hbar\omega\left(n+\frac{1}{2}\right)}{\omega} = \hbar\left(n+\tfrac{1}{2}\right) \tag{1.15}$$

Fixed $\frac{E}{\omega}$ is fixed quantum number! This suggests that in QM the quantum number doesn't tend to change under adiabatic changes. Indeed, we get the same intuition from WKB: consider a potential with two turning points a, b. We have the Bohr-Sommerfield quantization condition

$$\frac{1}{\hbar}\int_a^b p(x)dx = \left(n+\tfrac{1}{2}\right)\pi$$



rewritten as

$$\oint p(x)dx = 2\pi\hbar\left(n+\tfrac{1}{2}\right) \tag{1.16}$$

The left hand side, as noted before is an adiabatic invariant, so in the semiclassical approximation for *arbitrary* potential we find that the quantum number may not change under adiabatic changes! We will see that indeed that is the case.

The formula for transitions at first order in perturbation theory gives complementary intuition:

$$P_{f\leftarrow i}(t) = \left|\int_0^t e^{i\omega_{fi}t}\,\frac{\widetilde{\delta H}_{fi}(t')}{i\hbar}\,dt'\right|^2 \tag{1.17}$$

For constant perturbations, $\widetilde{\delta H}_{fi}$ is time-independent and

$$P_{f\leftarrow i}(t) = \frac{|\widetilde{\delta H}_{fi}|^2}{\hbar^2}\left|\int_0^t e^{i\omega_{fi}t}\,dt'\right|^2 = \frac{|\widetilde{\delta H}_{fi}|^2}{\hbar^2}\,\frac{\left|e^{i\omega_{fi}T}-1\right|^2}{\omega_{fi}^2}\,. \tag{1.18}$$

- If the spectrum is discrete, it is hard to jump a big energy gap because of the $\frac{1}{\omega_{fi}^2}$ suppression.
- For slowly varying perturbations (compared to ω_{fi}) the $\frac{1}{\omega_{fi}^2}$ suppression will remain.

So it is difficult in general to change state with constant or slow perturbations, suggesting again that quantum numbers are adiabatic invariants. That is why transitions to the continuum with constant perturbations essentially conserve energy. And why you need oscillatory perturbations for efficient transitions between energy levels.

2 Adiabatic Evolution

Suppose you have found a $\psi(t)$ such that

$$H(t)|\psi(t)\rangle = E(t)|\psi(t)\rangle \tag{2.1}$$

we'll call $|\psi(t)\rangle$, defined by (2.1), an **instantaneous eigenstate**. I'd like to emphasize from the start that, in general, an instantaneous eigenstate *is not a solution* of the time dependent Schrödinger equation. As it turns out, it is a useful tool to construct approximate solutions to the Schrödinger equation.

Let us try to understand the relation between $|\psi(t)\rangle$ and $|\Psi(t)\rangle$, the solution to the Schrödinger equation

$$i\hbar\partial_t|\Psi(t)\rangle = H(t)|\Psi(t)\rangle\,. \tag{2.2}$$

Let us try an ansatz, building the solution $|\Psi(t)\rangle$ using the instantaneous eigenstate:

$$|\Psi(t)\rangle = c(t)\exp\left(\frac{1}{i\hbar}\int_0^t E(t')dt'\right)|\psi(t)\rangle\,, \tag{2.3}$$

with $c(t)$ a function of time to be determined and where we have included a familiar time dependent phase. There is *no guarantee* this ansatz will work but it seems a good try.

The LHS of the Schrödinger equation then looks like

$$i\hbar\partial_t|\Psi(t)\rangle = \dot{c}\,(t)\exp\left(\frac{1}{i\hbar}\int_0^t E(t')dt'\right)|\psi(t)\rangle + E(t)|\Psi(t)\rangle + c(t)\exp\left(\frac{1}{i\hbar}\int_0^t E(t')dt'\right)|\dot{\psi}(t)\rangle \tag{2.4}$$

For the RHS, using the instantaneous eigenstate equation, we have

$$H(t)|\Psi(t)\rangle = c(t)\exp\left(\frac{1}{i\hbar}\int_0^t E(t')dt'\right)H(t)|\psi(t)\rangle \;=\; E(t)|\Psi(t)\rangle\,. \tag{2.5}$$

Equating the two sides, we get

$$\dot{c}(t)\exp\left(\frac{1}{i\hbar}\int_0^t E(t')dt'\right)|\psi(t)\rangle + c(t)\exp\left(\frac{1}{i\hbar}\int_0^t E(t')dt'\right)|\dot{\psi}(t)\rangle = 0$$

and canceling the two exponentials we have

$$\boxed{\dot{c}(t)\,|\psi(t)\rangle \;=\; -c(t)\,|\dot{\psi}(t)\rangle\,.} \tag{2.6}$$

Multiply by $\langle\psi(t)|$ we get a differential equation for $c(t)$:

$$\dot{c}(t) \;=\; -c(t)\;\langle\psi(t)|\dot{\psi}(t)\rangle\,, \tag{2.7}$$

which happily we can solve. Letting $c(t=0)=1$ we can write

$$c(t) = \exp\left(-\int_0^t \langle\psi(t')|\dot{\psi}(t')\rangle dt'\right)\,. \tag{2.8}$$

The above exponential is a phase because the bracket in the integrand is actually purely imaginary:

$$
\begin{aligned}
\langle\psi(t)|\dot{\psi}(t)\rangle = & \int dx\ \psi^* \frac{d\psi}{dt} = \int dx\ \frac{d}{dt}(\psi^*\psi) - \int dx\ \frac{d\psi^*}{dt}\psi \\
= & \frac{d}{dt}\int dx\ \psi^*\psi - \langle\dot{\psi}(t)|\psi(t)\rangle
\end{aligned}
\tag{2.9}
$$

Since the wavefunction is normalized we have

$$
\langle\psi(t)|\dot{\psi}(t)\rangle = -\langle\dot{\psi}(t)|\psi(t)\rangle = -\langle\psi(t)|\dot{\psi}(t)\rangle^* \tag{2.10}
$$

showing that indeed $\langle\psi(t)|\dot{\psi}(t)\rangle$ is purely imaginary. To emphasize this fact we write

$$
c(t) = \exp\left(i\int_0^t i\langle\psi(t')|\dot{\psi}(t')\rangle dt'\right) \tag{2.11}
$$

Having apparently solved for $c(t)$ we now return to our ansatz (2.3), we get

$$
\boxed{|\Psi(t)\rangle \simeq c(0)\exp\left(i\int_0^t i\langle\psi(t')|\dot{\psi}(t')\rangle dt'\right)\exp\left(\frac{1}{i\hbar}\int_0^t E(t')dt'\right)|\psi(t)\rangle\,.} \tag{2.12}
$$

But there is a mistake in this analysis. We really did not solve the Schrödinger equation! That's why we put a $\simeq$ instead of an equality.

The equation we had to solve, (2.6), is a vector equation, and forming the inner product with $\langle\psi(t)|$ gives a necessary condition for the solution, but not a sufficient one. We must check the equation forming the overlap with a full basis set of states. Indeed since $|\psi(t)\rangle$ is known, the equation can only have a solution if the two vectors $|\dot{\psi}(t)\rangle$ and $|\psi(t)\rangle$ are parallel. This does not happen in general. So we really did not solve equation (2.6). The conclusion is that, ultimately, the ansatz in (2.3) is not good enough!

We can see the complication more formally. At $t = 0$ equation (2.6) reads

$$
\dot{c}(0)|\psi(0)\rangle = -c(0)|\dot{\psi}(0)\rangle\,. \tag{2.13}
$$

Using Gram-Schmidt we can construct an orthonormal basis $\mathcal{B}$ for the state space with the choice $|\psi(0)\rangle$ for the first basis vector:

$$
\mathcal{B} = \Big\{\ |1\rangle = |\psi(0)\rangle,\ |2\rangle,\ |3\rangle\,,\ldots\ \Big\}\,. \tag{2.14}
$$

Equation (2.13) requires

$$
\langle n|\dot{\psi}(0)\rangle = 0 \qquad n = 2,\,3,\,\ldots \tag{2.15}
$$

This will not hold in general. The key insight, however, is that (2.12) is a fairly accurate solution if the Hamiltonian is slowly varying. Making the definitions:

$$
\theta(t) \equiv -\frac{1}{\hbar}\int_0^t E(t')dt'\,, \qquad \nu(t) \equiv i\langle\psi(t)|\dot{\psi}(t)\rangle\,, \quad \gamma(t) \equiv \int_0^t \nu(t')dt' \tag{2.16}
$$

so that θ, ν and γ are all real, the state reads

$$
|\Psi(t)\rangle \simeq c(0)\exp\left(i\gamma(t)\right)\exp(i\theta(t))|\psi(t)\rangle\,. \tag{2.17}
$$

The phase $\theta(t)$ is called the *dynamical* phase and the phase $\gamma(t)$ is called the *geometric phase*.

Comment: Instantaneous eigenstates are rather ambiguous. If one has the $|\psi(t)\rangle$, they can be modified by the multiplication by an arbitrary phase:

$$|\psi(t)\rangle \to |\psi'(t)\rangle = e^{-i\chi(t)}|\psi(t)\rangle \,. \tag{2.18}$$

3 Systematic approach

Must use a basis to see the error terms and get a more general picture. We will do this now systematically. But first let us state precisely the idea in adiabatic approximation. Consider a family of instantaneous eigenstates:

$$H(t)|\psi_n(t)\rangle = E_n(t)|\psi_n(t)\rangle \tag{3.1}$$

with $E_1(t) < E_2(t) < \ldots$, so that there are no degeneracies.
Adiabatic approximation: If at $t = 0$ $|\Psi(0)\rangle = |\psi_n(0)\rangle$ for some n, then if $H(t)$ is slowly varying for $0 \leq t \leq T$ then at time T we have $|\psi(T)\rangle \simeq |\psi_n(T)\rangle$ up to a calculable phase.

Key facts:

1. The probability to jump to another state $|\psi_k(t)\rangle$ with $k \neq n$ is highly suppressed.
2. The phases can sometimes be relevant and have geometric meaning. An overall phase cannot be observed but if we have a superposition

   $$|\Psi(0)\rangle = c_1|\psi_1(0)\rangle + c_2|\psi_2(0)\rangle + \ldots \tag{3.2}$$

   the relative phases acquired by $|\psi_1(0)\rangle$ and $|\psi_2(0)\rangle$ after time evolution can matter.

Calculation:

$$|\Psi(t)\rangle = \sum_n c_n(t)|\psi_n(t)\rangle \tag{3.3}$$

Schrödinger equation :

$$i\hbar \sum_n \Big(\dot{c_n}|\psi_n(t)\rangle + c_n|\dot{\psi_n(t)}\rangle \Big) = \sum_n c_n(t)E_n(t)|\psi_n(t)\rangle \tag{3.4}$$

act with $\langle\psi_k(t)|$ from the left:

$$\begin{aligned} i\hbar\dot{c_k} &= E_k c_k - i\hbar\sum_n \langle\psi_k|\dot{\psi_n}\rangle c_n \\ i\hbar\dot{c_k} &= \Big(E_k - i\hbar\langle\psi_k|\dot{\psi_k}\rangle c_k\Big) - i\hbar\sum_{n\neq k}\langle\psi_k|\dot{\psi_n}\rangle c_n \end{aligned} \tag{3.5}$$

We can relate $\langle\psi_k|\dot{\psi_n}\rangle$ to a matrix element of $H(t)$ in the space of instantaneous eigenvectors

$$H(t)|\psi_n\rangle = E_n(t)|\psi_n\rangle \tag{3.6}$$

take time derivative

$$\dot{H(t)}|\psi_n\rangle + H(t)|\dot{\psi_n}\rangle = \dot{E_n}(t)|\psi_n\rangle + E_n(t)|\dot{\psi_n}\rangle \tag{3.7}$$

multiplty by $\langle\psi_k(t)|$ with $k \neq n$

$$\langle\psi_k(t)|\dot{H(t)}|\psi_n\rangle + E_k(t)\langle\psi_k(t)|\dot{\psi_n}\rangle = \dot{E}_n(t)\langle\psi_k(t)|\dot{\psi_n}\rangle \tag{3.8}$$

hence

$$\langle\psi_k(t)|\dot{\psi_n}\rangle = \frac{\langle\psi_k(t)|\dot{H(t)}|\psi_n\rangle}{E_n(t) - E_k(t)} \equiv \frac{\dot{H}_{kn}}{E_n - E_k} \tag{3.9}$$

We can use plug (3.9) back in Eq.(3.5) to get

$$\boxed{i\hbar\dot{c_k} = \Big(E_k - i\hbar\langle\psi_k|\dot{\psi_k}\rangle c_k\Big) - i\hbar\sum_{n\neq k}\frac{\dot{H}_{kn}}{E_n - E_k}c_n} \tag{3.10}$$

Note that if the term proportional to $\frac{\dot{H}_{kn}}{E_n - E_k}$ vanishes, then $|c_k| = 1$, hence if you start in $|\psi_k\rangle$ you stay in $|\psi_k\rangle$.

If we ignore the extra term:

$$\begin{aligned} c_k(t) &= c_k(0)\exp\left[\frac{1}{i\hbar}\int_0^t \Big(E_k(t') - i\hbar\langle\psi_k|\dot{\psi_k}\rangle\Big)\,dt'\right] \\ &= c_k(0)\exp\left(\frac{1}{i\hbar}\int_0^t E_k(t')dt'\right)\exp\left(i\int_0^t i\langle\psi_k|\dot{\psi_k}\rangle dt'\right) \\ &= c_k(0)e^{i\theta_k(t)}e^{i\gamma_k(t)} \end{aligned} \tag{3.11}$$

where

$$\theta_k(t) = -\frac{1}{\hbar}\int_0^t E_k(t')dt' \tag{3.12}$$

$$\nu_k(t) = i\langle\psi_k(t)|\dot{\psi_k}(t)\rangle \tag{3.13}$$

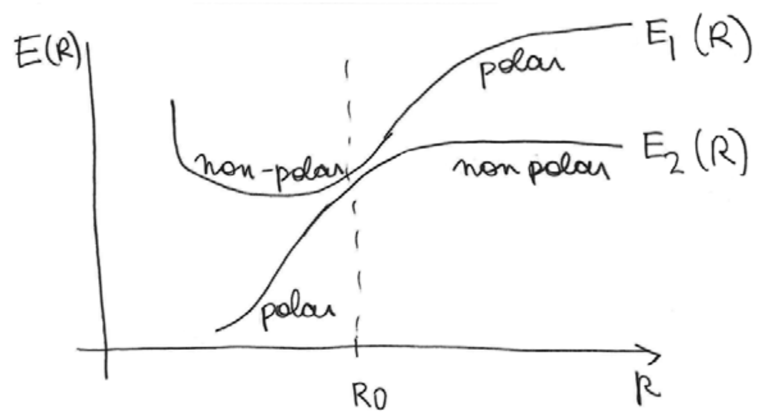
$$\gamma(t)_k = \int_0^t \nu_k(t')dt' \tag{3.14}$$

4 Landau-Zener transitions

Take $\psi_1(x;R)$ and $\psi_2(x;R)$ to be the electronic configurations of a molecule with fixed nuclei separated at a distance R.

We have

$$H(R)\psi_i(x;R) = E_i(R)\psi_i(x;R) \tag{4.1}$$



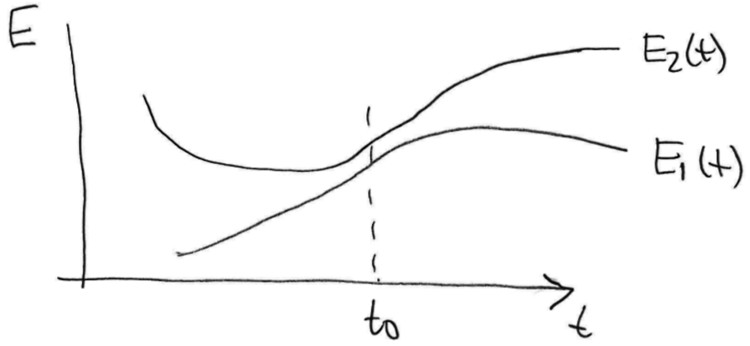
Depending on R the states are polar or non polar changing characteristic near $R = R_0$. If R changes slowly, ψ_1 remains ψ_1 or ψ_2 will remain ψ_2. But if R varies quickly, then $\psi_1 \to \psi_2$ near R_0. This would be a non-adiabatic transition. Thinking of R as a function of time, we have a time dependent hamiltonian

$$H\big(R(t)\big)$$

with instantaneous energy eigenstates

$$\psi_i\big(x;R(t)\big)\,, \qquad E_i\big(R(t)\big)$$

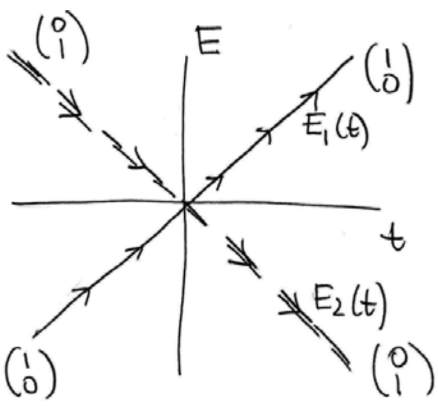
we can now plot the energies for constant velocity $\dot{R}$



We can sometimes think of this as a 2-level problem; if no other eigenstates are relevant.
So consider a slightly idealized 2×2 system

$$H(t) = \begin{pmatrix} \frac{\alpha t}{2} & 0 \\ 0 & -\frac{\alpha t}{2} \end{pmatrix}, \quad \alpha > 0 \qquad\qquad |1\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \text{ (spin up)}$$

$$E_1(t) = \frac{\alpha t}{2}, \quad E_2(t) = -\frac{\alpha t}{2} \qquad\qquad |2\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \text{ (spin down)} \tag{4.2}$$



The instantaneous eigenstates $|1\rangle$, $|2\rangle$ are actually time independent. Take

$$|\psi_1\rangle = \begin{pmatrix}1\\0\end{pmatrix} \qquad |\psi_2\rangle = \begin{pmatrix}0\\1\end{pmatrix} \tag{4.3}$$

then

$$|\psi_1(t)\rangle = \exp\left(\frac{1}{i\hbar}\int_0^t E_1(t')dt'\right)|1\rangle = \exp\left(-\frac{i\alpha t^2}{4\hbar}\right)|1\rangle \quad \text{solves the Schrödinger equation} \tag{4.4}$$

$$|\psi_2(t)\rangle = \exp\left(\frac{1}{i\hbar}\int_0^t E_2(t')dt'\right)|2\rangle = \exp\left(+\frac{i\alpha t^2}{4\hbar}\right)|2\rangle \quad \text{solves the Schrödinger equation} \tag{4.5}$$

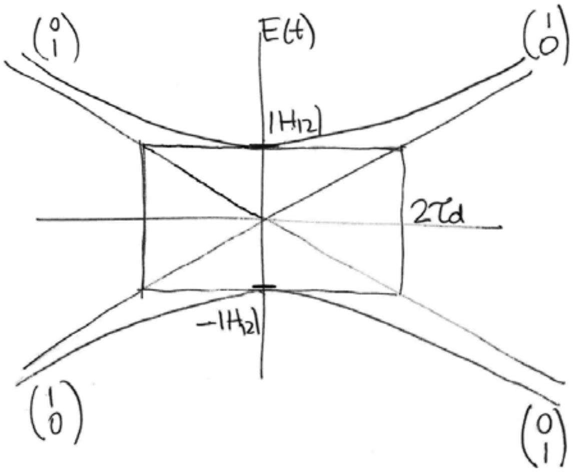
Time evolution is clear: if $|\psi\rangle = \begin{pmatrix}1\\0\end{pmatrix}$ at $t = -\infty$ it will remain in that state forever. Same for $|\psi\rangle = \begin{pmatrix}0\\1\end{pmatrix}$.

Now make the problem more interesting by perturbing the hamiltonian

$$H(t) = \begin{pmatrix}\frac{\alpha t}{2} & H_{12}\\ H_{12}^* & -\frac{\alpha t}{2}\end{pmatrix} \tag{4.6}$$

with H_{12} constant.

At $t = 0$ the energy eigenvalues are $\pm|H_{12}|$



$$H = \frac{\alpha t}{2}\sigma_z + \Re(H_{12})\sigma_x - \Im(H_{12})\sigma_y \tag{4.7}$$

$$E_{\pm}(t) = \pm\sqrt{|H_{12}|^2 + \frac{\alpha^2 t^2}{4}} \tag{4.8}$$

we can write H in a compact form by defining the vector

$$\mathbf{a} = \left(H_{12}, 0, \frac{\alpha t}{2}\right) = |\mathbf{a}|\mathbf{n} = E_+(t)\mathbf{n} \tag{4.9}$$

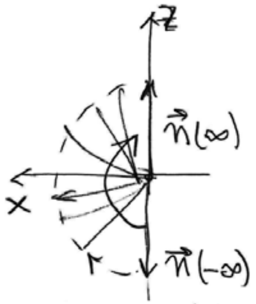
taking H_{12} to be real

so that

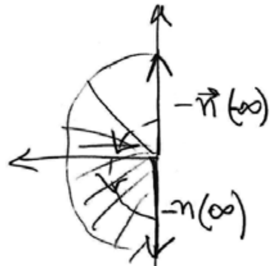
$$H = \mathbf{a}\cdot\boldsymbol{\sigma} \tag{4.10}$$

The instantaneous energy eigenstates are

$$\big|\pm\mathbf{n}(t)\big\rangle \quad \text{with energies} \quad E_{\pm}(t)$$



$$|n(-\infty)\rangle = \begin{pmatrix}0\\1\end{pmatrix}$$
$$|n(\infty)\rangle = \begin{pmatrix}1\\0\end{pmatrix}$$



$$|-n(-\infty)\rangle = \begin{pmatrix}1\\0\end{pmatrix}$$
$$|-n(\infty)\rangle = \begin{pmatrix}0\\1\end{pmatrix}$$

The instantaneous energy eigenstates change type

$$\begin{pmatrix}0\\1\end{pmatrix} \to \begin{pmatrix}1\\0\end{pmatrix} \qquad \text{(polar - non polar)}$$

$$\begin{pmatrix}1\\0\end{pmatrix} \to \begin{pmatrix}0\\1\end{pmatrix} \qquad \text{(non polar - polar)}$$

An adiabatic process will keep you there. Consider τ_d for the <u>duration</u> of the change $\frac{|H_{12}|}{|\alpha|} \equiv \tau_\alpha$, since

$$E_1 = \frac{\alpha t}{2} \to |H_{12}| = \frac{|\alpha| t}{2} \quad \text{(see fig)} \tag{4.11}$$

Also $\frac{|H_{12}|}{\hbar} \equiv \omega_{12}$ and it is called *Rabi frequency.* It's relevant for the transitions at $t = 0$ since $H(0) = \begin{pmatrix} 0 & H_{12} \\ H_{12} & 0 \end{pmatrix}$.

Process is adiabatic when

$$\boxed{\omega_{12}\tau_\alpha \gg 1} \implies \frac{|H_{12}|^2}{\hbar|\alpha|} \gg 1 \tag{4.12}$$

i.e.

$$\frac{2\pi}{\omega_{12}} = T_{12} \ll \tau_\alpha \tag{4.13}$$

hence, the adiabatic change is much slower than the natural time scale of the system.
Alternatively: The Hamiltonian should not vary much over the time scale T associated with the relevant energy difference ΔE

$$\left| T \frac{dH}{dt} \right| \ll H \tag{4.14}$$

Approximate $T = \frac{\hbar}{H}$ if $\Delta E \simeq H$

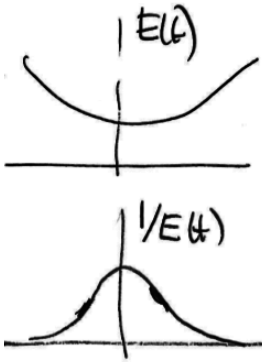
$$\left| \frac{\hbar}{H^2} \frac{dH}{dt} \right| \ll 1 \implies \left| \hbar \frac{d}{dt} \left(\frac{1}{H} \right) \right| \ll 1 \quad \text{or} \quad \left| \partial_t \left(\frac{\hbar}{E} \right) \right| \tag{4.15}$$

analog of $\left| \partial_x \left(\frac{\hbar}{p} \right) \right| \ll 1$ in WKB.
For our case

$$\left| \frac{d}{dt} \frac{\hbar}{\sqrt{|H_{12}|^2 + \frac{\alpha^2 t^2}{4}}} \right| \overset{?}{\ll} 1 \tag{4.16}$$

Let's check!

$$\begin{aligned} \left| \frac{d}{dt} \frac{\hbar}{\sqrt{|H_{12}|^2 + \frac{\alpha^2 t^2}{4}}} \right| &= \left| \frac{\hbar \alpha^2 t}{\left(|H_{12}|^2 + \frac{\alpha^2 t^2}{4} \right)^{3/2}} \right| = \hbar \alpha \left| \frac{\alpha t}{\left(|H_{12}|^2 + \frac{\alpha^2 t^2}{4} \right)^{3/2}} \right| \\ &\leq \max_t \ \hbar \alpha \left| \frac{\alpha t}{\left(|H_{12}|^2 + \frac{\alpha^2 t^2}{4} \right)^{3/2}} \right| \approx \frac{\hbar \alpha |H_{12}|}{|H_{12}|^3} = \frac{\hbar \alpha}{|H_{12}|^2} \ll 1 \quad \checkmark \end{aligned} \tag{4.17}$$



Max of $\frac{x}{(a^2+x^2)^{3/2}}$ happens for $x^2 = \frac{a^2}{2}$

Probability for a non-adiabatic transition

$$P_{n.ad.} = \exp\left(-2\pi \omega_{12} \tau_\alpha\right) = \exp\left(-2\pi \frac{|H_{12}|^2}{\hbar |\alpha|} \right) \tag{4.18}$$

5 Berry's phase

Adiabatic theorem: $|\psi(t=0)\rangle = |\psi_n(0)\rangle$ and with instantaneous eigenstates $|\psi_n(t)\rangle$ we find

$$|\psi(t)\rangle \simeq e^{i\theta_n(t)} e^{i\gamma_n(t)} |\psi_n(t)\rangle \tag{5.1}$$

with, as in (3.12)

$$\theta_n(t) = -\frac{1}{\hbar} \int_0^t E_n(t') dt' \tag{5.2}$$

$$\nu_n(t) = i \langle \psi_n(t) | \dot{\psi}_n(t) \rangle \tag{5.3}$$

$$\gamma_n(t) = \int_0^t \nu_n(t') dt' \tag{5.4}$$

We now understand the relevance of $\gamma_n(t)$, the *geometrical phase*:

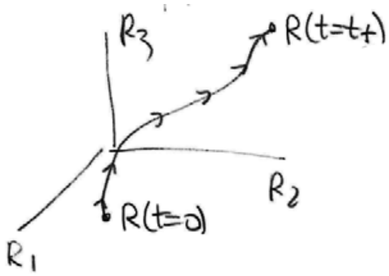
Assume H depends on a set of coordinates

$$\mathbf{R}(t) = (R_1(t),\, R_2(t), \ldots,\, R_N(t)) \tag{5.5}$$

several parameters that are tune dependent.

Instantaneous states

$$H(\mathbf{R})|\psi_n(\mathbf{R})\rangle = E(\mathbf{R})|\psi_n(\mathbf{R})\rangle \tag{5.6}$$



Evaluate the geometric phase. Start by computing

$$\nu_n(t) = i\ \psi_n(\mathbf{R}(t))\big|\frac{d}{dt}\big|\psi_n(\mathbf{R}(t))\big\rangle \tag{5.7}$$

we need $\frac{d}{dt}\big|\psi_n(\mathbf{R}(t))\big\rangle$

$$\frac{d}{dt}\big|\psi_n(\mathbf{R}(t))\big\rangle = \sum_{i=1}^{N} \frac{d}{d\mathbf{R}_i}\big|\psi_n(\mathbf{R}(t))\big\rangle \frac{d\mathbf{R}_i}{dt} = \vec{\nabla}_{\mathbf{R}}\big|\psi_n(\mathbf{R}(t))\big\rangle \cdot \frac{d\mathbf{R}(t)}{dt} \tag{5.8}$$

so that

$$\nu_n(t) = i\ \psi_n(\mathbf{R}(t))\big|\vec{\nabla}_{\mathbf{R}}\big|\psi_n(\mathbf{R}(t))\big\rangle \cdot \frac{d\mathbf{R}(t)}{dt} \tag{5.9}$$

and

$$\gamma_n(\tau) \equiv \int_0^\tau \nu_n(t)dt = \int_0^\tau i\ \psi_n(\mathbf{R}(t))\big|\vec{\nabla}_{\mathbf{R}}\big|\psi_n(\mathbf{R}(t))\big\rangle \cdot \frac{d\mathbf{R}(t)}{dt}dt \tag{5.10}$$

hence the geometrical phase $\gamma_n(t_f)$, also known as *Berry phase*, is

$$\boxed{\gamma_n(t_f) = \int_{\mathbf{R}_i}^{\mathbf{R}_f} i\ \psi_n(\mathbf{R})\big|\vec{\nabla}_{\mathbf{R}}\big|\psi_n(\mathbf{R})\big\rangle \cdot \mathrm{d}\mathbf{R}} \tag{5.11}$$

The integral depends on the path, but does not depend on time!! Whether you take a nano second or a year to make transition, the geometric phase is the same!

$i\ \psi_n(\mathbf{R})\big|\vec{\nabla}_{\mathbf{R}}\big|\psi_n(\mathbf{R})\big\rangle$ is an $N-$component object that lives in the parameter space. It is called the *Berry connection* $\mathbf{A}_n(\mathbf{R})$, associated with $|\psi_n(t)\rangle$

$$\mathbf{A}_n(\mathbf{R}) = i\ \psi_n(\mathbf{R})\big|\vec{\nabla}_{\mathbf{R}}\big|\psi_n(\mathbf{R})\big\rangle \tag{5.12}$$

In this way we can rewrite the Berry phase as

$$\gamma_n = \int_{\mathbf{R}_i}^{\mathbf{R}_f} \mathbf{A}_n(\mathbf{R}) \cdot \mathrm{d}\mathbf{R} \tag{5.13}$$

If we redefine the instantaneous states by an overall phase

$$\big|\psi_n(\mathbf{R})\big\rangle \to |\widetilde{\psi_n}(\mathbf{R})\rangle = e^{-i\beta(\mathbf{R})}\big|\psi_n(\mathbf{R})\big\rangle \tag{5.14}$$

where $\beta(\mathbf{R})$ is an arbitrary real function, what happens to $\mathbf{A}_n(\mathbf{R})$?

$$\begin{aligned}
\widetilde{\mathbf{A}_n}(\mathbf{R}) &= i\ \widetilde{\psi_n}(\mathbf{R})\big|\vec{\nabla}_{\mathbf{R}}\big|\widetilde{\psi_n}(\mathbf{R})\big\rangle = \\
&= i\ \psi_n(\mathbf{R})\big|e^{i\beta(\mathbf{R})}\vec{\nabla}_{\mathbf{R}}e^{-i\beta(\mathbf{R})}\big|\psi_n(\mathbf{R})\big\rangle \\
&= i\left(-i\vec{\nabla}_{\mathbf{R}}\beta(\mathbf{R})\right)\underbrace{\langle\psi_n(\mathbf{R})|\psi_n(\mathbf{R})\rangle}_{1} + \mathbf{A}_n(\mathbf{R}) \qquad (5.15)
\end{aligned}$$

$$\widetilde{\mathbf{A}_n}(\mathbf{R}) = \mathbf{A}_n(\mathbf{R}) + \vec{\nabla}_{\mathbf{R}}\beta(\mathbf{R}) \qquad (5.16)$$

analogous to the vector potential in EM ($\vec{A'} \to \vec{A'} + \nabla E$).
What about the Berry phase?

$$\widetilde{\gamma_n}(\mathbf{R}_f) = \int_{\mathbf{R}_i}^{\mathbf{R}_f} \widetilde{\mathbf{A}_n}(\mathbf{R})\cdot \mathrm{d}\mathbf{R} = \gamma_n(\mathbf{R}_f) + \int_{\mathbf{R}_i}^{\mathbf{R}_f} \vec{\nabla}_{\mathbf{R}}\beta(\mathbf{R})\cdot\mathrm{d}\mathbf{R} \implies \qquad (5.17)$$

$$\widetilde{\gamma_n}(\mathbf{R}_f) = \gamma_n(\mathbf{R}_f) + \beta(\mathbf{R}_f) - \beta(\mathbf{R}_i) \qquad (5.18)$$

The geometrical phase is completely well defined for closed paths in parameter space.
<u>Comments</u>:

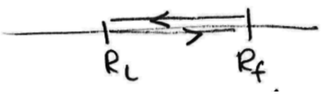
- If the $\psi_n(t)$ are real, then the Berry phase vanishes:

$$\begin{aligned}
\nu_n = i\langle\psi_n(t)|\dot{\psi}_n(t)\rangle &= i\int d\mathbf{x}\,\psi_n^*(t,\mathbf{x})\frac{d}{dt}\psi_n(t,\mathbf{x}) \\
&= i\int d\mathbf{x}\,\psi_n(t,\mathbf{x})\frac{d}{dt}\psi_n(t,\mathbf{x}) = \frac{i}{2}\int d\mathbf{x}\,\frac{d}{dt}\Big(\psi_n(t,\mathbf{x})\Big)^2 = \\
&= \frac{i}{2}\frac{d}{dt}\int d\mathbf{x}\,|\psi_n(t,\mathbf{x})|^2 = 0\,, \qquad (5.19)
\end{aligned}$$

  since the wavefunction is normalized. This should not be surprising. In general grounds we have seen that $\langle\psi_n(t)|\dot{\psi}_n(t)\rangle$ is purely imaginary. But if ψ_n is real this overlap cannot produce a complex number, so it can only be zero.

- If there is just one coordinate, i.e. $\mathbf{R} = R$, Berry's phase vanishes for a loop

$$\oint A_n(R)dR = 0 \qquad (5.20)$$



  In here the integral from R_i to R_f is cancelled by the integral back from R_f to R_i.

- In 3D we can make use of Stoke's theorem to simplify the calculation of $\gamma_n[C]$

$$\gamma_n[C] = \oint_C \mathbf{A}_n(\mathbf{R})\cdot\mathrm{d}\mathbf{R} = \iint_S \Big(\vec{\nabla}\times\mathbf{A}_n(\mathbf{R})\Big)\cdot d\vec{S} \equiv \iint_S \mathbf{D}_n\cdot d\vec{S} \qquad (5.21)$$

  where S is the surface with boundary C and we defined the *Berry curvature* $\mathbf{D}_n$

$$\mathbf{D}_n \equiv \vec{\nabla}\times\mathbf{A}_n(\mathbf{R}) \qquad (5.22)$$

If we think of the Berry connection as the vector potential, the Berry curvature is the associated magnetic field. Note that the curvature is invariant under phase redefinition

$$\begin{aligned}\mathbf{D}_n \;\to\; \mathbf{D}'_n =&\; \vec{\nabla}\times\widetilde{\mathbf{A}_n}(\mathbf{R}) = \vec{\nabla}\times\Big(\mathbf{A}_n(\mathbf{R}) + \vec{\nabla}\beta(\mathbf{R})\Big)\\ =&\; \vec{\nabla}\times\mathbf{A}_n(\mathbf{R}) + \cancel{\vec{\nabla}\times\vec{\nabla}\beta(\mathbf{R})} = \vec{\nabla}\times\mathbf{A}_n(\mathbf{R}) = \mathbf{D}_n\,.\end{aligned} \tag{5.23}$$

Example: Berry phase for an electron in a slowly varying magnetic field. Take a magnetic field with fixed intensity and slowly varying direction $\mathbf{B}(t) = B\vec{n}(t)$, put an electron inside this magnetic field, so that we get an interaction described by the hamiltonian

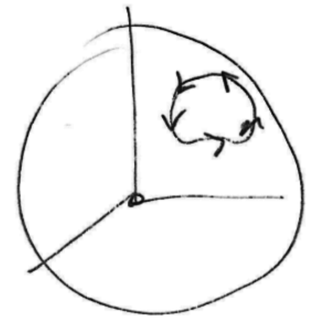
$$H(t) = -\boldsymbol{\mu}\cdot\mathbf{B}(t) = \mu_B B\vec{n}(t)\cdot\vec{\sigma} \tag{5.24}$$

The direction of the B field, $\vec{n}(t)$ swipes a closed loop C on the surface of an imaginary sphere of radius ρ in a time scale $T \gg \frac{\hbar}{\mu_B B}$. Think of the instantaneous eigenstates $\big|\chi_\pm\big(\mathbf{R}(t)\big)\big\rangle$ satisfying

$$H(t)\big|\chi_\pm\big(\mathbf{R}(t)\big)\big\rangle = \pm\mu_B B\big|\chi_\pm\big(\mathbf{R}(t)\big)\big\rangle \tag{5.25}$$

where

$$\mathbf{R}(t) = (\underbrace{r(t)}_{=\rho\text{ (fixed)}}\,,\,\theta(t)\,,\,\phi(t)) \tag{5.26}$$



We get

$$\vec{D}_\pm = \mp\frac{1}{2r^2}\hat{r} \implies \gamma_\pm[C] = \iint_S \vec{D}_\pm\cdot d\vec{S} = \mp\iint_S \frac{1}{2r^2}\hat{r}\cdot\hat{r}r^2 d\Omega = \mp\frac{1}{2}\iint_S d\Omega = \mp\frac{\Omega}{2} \tag{5.27}$$

6 Molecules and Born-Oppenheimer

Molecules are much harder to treat than atoms. Atoms are hard because even though the potential created by the nucleus is spherically symmetric, the Coulomb interactions between the electrons breaks the spherical symmetry. In molecules even ignoring Coulomb repulsion between electrons, the potential created by nuclei that are spatially separated is not spherically symmetric.

In some approximation one can view a molecule as a system in which nuclei in classical equilibrium with well localized positions while the electrons move around in the Coulomb potential created by the nuclei. This approximation is reasonable since typically $\frac{m}{M} \simeq 10^{-4}$ where m is the electron mass and M the nuclear one. In this picture slow nuclear vibrations adiabatically deform the electronic states.

In order to make estimates, consider a molecule of size a, so that

$$p_{\text{electron}} \sim \frac{\hbar}{a} \quad\text{and}\quad E_{\text{electron}} \sim \frac{\hbar^2}{ma^2} \tag{6.1}$$

The positively charged nuclei repell each other but the electrons in between create an effective attraction that, at equilibrium, cancels the repulsive forces. There will be nuclear vibrations around the equilibrium configuration. Consider the nuclear oscillations governed by the nuclear Hamiltonian

$$H_N \;=\; \frac{P^2}{2M} + \tfrac{1}{2}\,kx^2 \tag{6.2}$$

The restoring force is determined by k, and it is due to the electron system, with no reference to the mass M. Since k has units of energy over length-square, we must have

$$k \;=\; \frac{\text{Energy}}{L^2} \;\sim\; \frac{\hbar^2}{ma^4}\,. \tag{6.3}$$

But $k = M\omega^2$, with ω the frequency of nuclear oscillations so we have

$$M\omega^2 \sim \frac{\hbar^2}{ma^4} \quad\to\quad \omega^2 \sim \frac{m}{M}\frac{\hbar^2}{m^2a^4} \quad\to\quad \hbar\omega \sim \sqrt{\frac{m}{M}}\,\frac{\hbar^2}{ma^2}\,. \tag{6.4}$$

We thus find that the nuclear vibrational energies are

$$\boxed{E_{\text{vibration}} \;\sim\; \sqrt{\frac{m}{M}}E_{\text{electron}}\;.} \tag{6.5}$$

There are also rotations and their energy E_{rot} is even smaller, as they involve essentially no distortion of the molecule

$$E_{rot} = \frac{L^2}{2I} \simeq \frac{\hbar^2\ell(\ell+1)}{Ma^2} \sim \frac{m}{M}\frac{\hbar}{ma^2} \;\Longrightarrow\; \boxed{E_{\text{rotation}} \simeq \frac{m}{M}E_{\text{electron}}} \tag{6.6}$$

Therefore we have the following hierarchy of energies

$$E_{\text{electron}} \,:\, E_{\text{vibration}} \,:\, E_{\text{rotation}} \;=\; 1 \,:\, \sqrt{\frac{m}{M}} \,:\, \frac{m}{M}\,. \tag{6.7}$$

6.1 Born-Oppenheimer approximation

Consider a molecule with N nuclei and n electrons. The Hamiltonian takes the form

$$H = \sum_{\alpha=1}^{N}\frac{\mathbf{P}_\alpha^2}{2M_\alpha} + V_{NN}(\mathbf{R}) + \sum_{i=1}^{n}\frac{\mathbf{p}_i^2}{2m} + V_{eN}(\mathbf{R},\mathbf{r}) + V_{ee}(\mathbf{r})\,, \tag{6.8}$$

where M_α with $\alpha = 1,\dots,N$ are the nuclear masses and

$\mathbf{P}_\alpha$, $\mathbf{R}_\alpha$: nuclei canonical variables

$\mathbf{p}_i$, $\mathbf{r}_i$: electron canonical variables

$\mathbf{R} \equiv (\mathbf{R}_1,\dots,\mathbf{R}_N)$

$\mathbf{r} \equiv (\mathbf{r}_1,\dots,\mathbf{r}_n)$

V_{NN} : nuclei-nuclei interaction

V_{ee} : electron-electron interaction

V_{eN} : electron-nuclei interaction

The wavefunction $\psi(\mathbf{R},\mathbf{r})$ for the molecule is, in position space, a function of all the nuclear positions and all the electron positions.

In the limit when $M_\alpha/m \to \infty$ the nuclear skeleton may be considered fixed, making the positions $\mathbf{R}$ are fixed. The electrons then move under the effect of the nuclear potential $V_{eN}(\mathbf{R},\mathbf{r})$ with fixed $\mathbf{R}$, and the electron-electron Coulomb repulsion. The relevant Hamiltonian H_e for the electrons is then

$$H_e(\mathbf{p},\mathbf{r};\mathbf{R}) = \sum_{i=1}^{n}\frac{\mathbf{p}_i^2}{2m} + V_{eN}(\mathbf{R},\mathbf{r}) + V_{ee}(\mathbf{r})\,. \tag{6.9}$$

This is a different Hamiltonian each time we change the positions $\mathbf{R}$ of the nuclei. The associated Schrödinger equation for the electrons is

$$\left[-\frac{\hbar^2}{2m}\sum_{i=1}^{n}\nabla^2_{\mathbf{r}_i} + V_{eN}(\mathbf{R},\mathbf{r}) + V_{ee}(\mathbf{r})\right]\phi^{(i)}_{\mathbf{R}}(\mathbf{r}) = E^{(i)}_e(\mathbf{R})\phi^{(i)}_{\mathbf{R}}(\mathbf{r})\,. \tag{6.10}$$

The wavefunction for the electrons, as expected, is a function of the position of the electrons $\mathbf{r}$, which appears as the argument of the wavefunction. Since the wavefunction depends on the nuclear positions, this dependence is included as a subscript. Finally, the superscript i labels the various wavefunctions that may appear as solutions of this equation. The associated energies $E^{(i)}_e(\mathbf{R})$ depend on the nuclear positions and the label i. If we calculated all the $\phi^{(i)}_{\mathbf{R}}(\mathbf{r})$ we would have a full basis of electronic configurations and we could write an ansatz for the full wavefunction of the molecule:

$$\psi(\mathbf{R},\mathbf{r}) = \sum_i \eta^{(i)}(\mathbf{R})\phi^{(i)}_{\mathbf{R}}(\mathbf{r})\,, \tag{6.11}$$

where the $\eta^{(i)}$ are the unknowns. Substitution into the full Schrödinger equation

$$H\psi(\mathbf{R},\mathbf{r}) = E\psi(\mathbf{R},\mathbf{r})\,, \tag{6.12}$$

gives an infinite set of coupled differential equations for $\eta^{(i)}(\mathbf{R})$. This is too difficult, so we try to make do with a single term:

$$\psi(\mathbf{R},\mathbf{r}) = \eta(\mathbf{R})\phi_{\mathbf{R}}(\mathbf{r})\,, \tag{6.13}$$

where we would generally use for $\phi_{\mathbf{R}}(\mathbf{r})$ the ground state wavefunction for the electrons in the frozen nuclear potential. If we have this wavefunction for all $\mathbf{R}$, as we now assume, we also know the value $E_e(\mathbf{R})$ of the associated energy.

We will do a variational analysis. For this we will compute the expectation value $\langle\psi|H|\psi\rangle$ using $\psi(\mathbf{R},\mathbf{r}) = \eta(\mathbf{R})\phi_{\mathbf{R}}(\mathbf{r})$. We will then utilize the known $\phi_{\mathbf{R}}(\mathbf{r})$ to integrate the electronic dependence in the expectation value

$$\begin{aligned}\langle H\rangle &= \int \mathrm{d}\mathbf{R}d\mathbf{r}\ \psi^*(\mathbf{R},\mathbf{r})H\,\psi(\mathbf{R},\mathbf{r}) = \int \mathrm{d}\mathbf{R}d\mathbf{r}\ \eta^*(\mathbf{R})\phi^*_{\mathbf{R}}(\mathbf{r})H\,\eta(\mathbf{R})\phi_{\mathbf{R}}(\mathbf{r})\\ &= \int \mathrm{d}\mathbf{R}\ \eta^*(\mathbf{R})H_{\text{eff}}\,\eta(\mathbf{R})\,,\end{aligned} \tag{6.14}$$

thus discovering the effective Hamiltonian H_{eff} for the nuclear degrees of freedom. We begin the calculation by rewriting the original Hamiltonian:

$$H = \hat{H}_N + \hat{H}_e\,, \qquad \hat{H}_N = \sum_{\alpha=1}^{N}\frac{\mathbf{P}^2_\alpha}{2M_\alpha} + V_{NN}(\mathbf{R})\,. \tag{6.15}$$

As a warmup we calculate the expectation value of $\hat{H}_e$:

$$\begin{aligned}
\langle H_e \rangle &= \int d\mathbf{R}\, d\mathbf{r}\, \eta^*(\mathbf{R})\phi^*_{\mathbf{R}}(\mathbf{r})\hat{H}_e\eta(\mathbf{R})\phi_{\mathbf{R}}(\mathbf{r}) \\
&= \int d\mathbf{R}\, \eta^*(\mathbf{R}) \underbrace{\left[\int d\mathbf{r}\, \phi^*_{\mathbf{R}}(\mathbf{r})\hat{H}_e\phi_{\mathbf{R}}(\mathbf{r})\right]}_{E_e(\mathbf{R})} \eta(\mathbf{R}) \\
&= \int d\mathbf{R}\, \eta^*(\mathbf{R})E_e(\mathbf{R})\eta(\mathbf{R})\,. \qquad (6.16)
\end{aligned}$$

This term has contributed to the effective nuclear Hamiltonian the value of the $\mathbf{R}$ dependent electron energy. Now the nuclear term

$$\begin{aligned}
\left\langle \frac{\mathbf{P}^2_\alpha}{2M_\alpha} \right\rangle &= \frac{1}{2M_\alpha}\int d\mathbf{R}\, d\mathbf{r}\, \eta^*(\mathbf{R})\phi^*_{\mathbf{R}}(\mathbf{r})\mathbf{P}_\alpha\mathbf{P}_\alpha(\eta(\mathbf{R})\phi_{\mathbf{R}}(\mathbf{r})) \\
&= \frac{1}{2M_\alpha}\int d\mathbf{R}\, d\mathbf{r}\, \eta^*(\mathbf{R})\phi^*_{\mathbf{R}}(\mathbf{r})\mathbf{P}_\alpha\Big[\big(\mathbf{P}_\alpha\eta(\mathbf{R})\big)\phi_{\mathbf{R}}(\mathbf{r}) + \eta(\mathbf{R})\big(\mathbf{P}_\alpha\phi_{\mathbf{R}}(\mathbf{r})\big)\Big] \qquad (6.17)
\end{aligned}$$

We want to move $\phi^*_{\mathbf{R}}(\mathbf{r})$ closer to the other $\phi_{\mathbf{R}}(\mathbf{r})$ to be able to do the integrals. For that we use

$$\phi^*_{\mathbf{R}}(\mathbf{r})\mathbf{P}_\alpha = \mathbf{P}_\alpha\phi^*_{\mathbf{R}}(\mathbf{r}) - \big(\mathbf{P}_\alpha\phi^*_{\mathbf{R}}(\mathbf{r})\big)\,, \qquad (6.18)$$

where in the last term, as indicated by the parenthesis, the derivation is acting only on the field $\phi^*_{\mathbf{R}}(\mathbf{r})$. Hence

$$\begin{aligned}
\left\langle \frac{\mathbf{P}^2_\alpha}{2M_\alpha} \right\rangle = \frac{1}{2M_\alpha}\int d\mathbf{R}\, d\mathbf{r}\, \eta^*(\mathbf{R}) \Big\{ &\mathbf{P}_\alpha\Big[\phi^*_{\mathbf{R}}(\mathbf{r})\big(\mathbf{P}_\alpha\eta(\mathbf{R})\big)\phi_{\mathbf{R}}(\mathbf{r}) + \phi^*_{\mathbf{R}}(\mathbf{r})\eta(\mathbf{R})\big(\mathbf{P}_\alpha\phi_{\mathbf{R}}(\mathbf{r})\big)\Big] \\
&- \big(\mathbf{P}_\alpha\phi^*_{\mathbf{R}}(\mathbf{r})\big)\Big[\big(\mathbf{P}_\alpha\eta(\mathbf{R})\big)\phi_{\mathbf{R}}(\mathbf{r}) + \eta(\mathbf{R})\big(\mathbf{P}_\alpha\phi_{\mathbf{R}}(\mathbf{r})\big)\Big]\Big\} \qquad (6.19)
\end{aligned}$$

We can now move in the $d\mathbf{r}$ integral

$$\begin{aligned}
\left\langle \frac{\mathbf{P}^2_\alpha}{2M_\alpha} \right\rangle = \frac{1}{2M}\int d\mathbf{R}\, \eta^*(\mathbf{R}) \Big\{ &\mathbf{P}_\alpha\Big[\mathbf{P}_\alpha\eta(\mathbf{R})\int d\mathbf{r}\, \phi^*_{\mathbf{R}}(\mathbf{r})\phi_{\mathbf{R}}(\mathbf{r}) + \eta(\mathbf{R})\int d\mathbf{r}\, \phi^*_{\mathbf{R}}(\mathbf{r})\mathbf{P}_\alpha\phi_{\mathbf{R}}(\mathbf{r})\Big] \\
&- \big(\mathbf{P}_\alpha\eta(\mathbf{R})\big)\int d\mathbf{r}\, \big(\mathbf{P}_\alpha\phi^*_{\mathbf{R}}(\mathbf{r})\big)\phi_{\mathbf{R}}(\mathbf{r}) + \eta(\mathbf{R})\int d\mathbf{r}\, \big(\mathbf{P}_\alpha\phi^*_{\mathbf{R}}(\mathbf{r})\big)\big(\mathbf{P}_\alpha\phi_{\mathbf{R}}(\mathbf{r})\big)\Big\} \qquad (6.20)
\end{aligned}$$

It is now convenient to define

$$\boxed{\mathbf{A}_\alpha(\mathbf{R}) \equiv i\hbar\int d\mathbf{r}\, \phi^*_{\mathbf{R}}(\mathbf{r})\nabla_{\mathbf{R}_\alpha}\phi_{\mathbf{R}}(\mathbf{r}) = -\int d\mathbf{r}\, \phi^*_{\mathbf{R}}(\mathbf{r})\mathbf{P}_\alpha\phi_{\mathbf{R}}(\mathbf{r})} \qquad (6.21)$$

This is a Berry connection! We have a full Berry connection for each nucleus (thus the label α). The Berry connection arises from the electronic configuration. With this definition we have

$$\begin{aligned}
\left\langle \frac{\mathbf{P}^2_\alpha}{2M_\alpha} \right\rangle &= \frac{1}{2M}\int d\mathbf{R}\, \eta^*(\mathbf{R}) \Big\{\mathbf{P}^2_\alpha\eta(\mathbf{R}) - \mathbf{P}_\alpha\eta(\mathbf{R})A_\alpha(\mathbf{R}) - A_\alpha(\mathbf{R})\big(\mathbf{P}_\alpha\eta(\mathbf{R})\big) + \hbar^2\eta(\mathbf{R})\int d\mathbf{r}\, \big|\nabla_{\mathbf{R}_\alpha}\phi_{\mathbf{R}}(\mathbf{r})\big|^2\Big\} \\
&= \int d\mathbf{R}\, \eta^*(\mathbf{R}) \left\{\frac{(\mathbf{P}_\alpha - \mathbf{A}_\alpha)^2}{2M_\alpha} - \frac{\mathbf{A}^2_\alpha}{2M_\alpha} + \frac{\hbar^2}{2M_\alpha}\int d\mathbf{r}\, \big|\nabla_{\mathbf{R}_\alpha}\phi_{\mathbf{R}}\big|^2\right\}\eta(\mathbf{R}) \qquad (6.22)
\end{aligned}$$

Hence

$$\left\langle \sum_\alpha \frac{\mathbf{P}_\alpha^2}{2M_\alpha} \right\rangle = \int d\mathbf{R}\, \eta^*(\mathbf{R}) \left[\sum_\alpha \frac{(\mathbf{P}_\alpha - \mathbf{A}_\alpha)^2}{2M_\alpha} - \sum_\alpha \frac{\mathbf{A}_\alpha^2}{2M_\alpha} + \sum_\alpha \frac{\hbar^2}{2M_\alpha} \int d\mathbf{r} \left| \nabla_{\mathbf{R}_\alpha} \phi_{\mathbf{R}} \right|^2 \right] \eta(\mathbf{R}) \quad (6.23)$$

so that the total expression reads

$$\begin{aligned} \langle H \rangle &= \left\langle \sum_\alpha \frac{\mathbf{P}_\alpha^2}{2M_\alpha} + V_{NN}(\mathbf{R}) + H_e \right\rangle = \\ &= \int d\mathbf{R}\, \eta^*(\mathbf{R}) \left[\sum_\alpha \frac{(\mathbf{P}_\alpha - \mathbf{A}_\alpha)^2}{2M_\alpha} + V_{NN}(\mathbf{R}) + E_e(\mathbf{R}) - \sum_\alpha \frac{\mathbf{A}_\alpha^2}{2M_\alpha} + \sum_\alpha \frac{\hbar^2}{2M_\alpha} \int d\mathbf{r} \left| \nabla_{\mathbf{R}_\alpha} \phi_{\mathbf{R}} \right|^2 \right] \eta(\mathbf{R}) \end{aligned} \quad (6.24)$$

and separating $\langle H \rangle$ in kinematics and potential term

$$\langle H \rangle = \int d\mathbf{R}\, \eta^*(\mathbf{R}) \left[\sum_\alpha \frac{(\mathbf{P}_\alpha - \mathbf{A}_\alpha)^2}{2M_\alpha} + U(\mathbf{R}) \right] \eta(\mathbf{R}) \quad (6.25)$$

we can read from (6.24) the effective potential $U(\mathbf{R})$

$$\boxed{U(\mathbf{R}) \equiv V_{NN}(\mathbf{R}) + E_e(\mathbf{R}) + \sum_\alpha \frac{\hbar^2}{2M_\alpha} \int d\mathbf{r} \left| \nabla_{\mathbf{R}_\alpha} \phi_{\mathbf{R}} \right|^2 - \sum_\alpha \frac{\mathbf{A}_\alpha^2(\mathbf{R})}{2M_\alpha}} \quad (6.26)$$

Since

$$\mathbf{P}_\alpha - \mathbf{A}_\alpha = \frac{\hbar}{i} \nabla_{\mathbf{R}_\alpha} - \mathbf{A}_\alpha = \frac{\hbar}{i} \left(\nabla_{\mathbf{R}_\alpha} - \frac{i}{\hbar} \mathbf{A}_\alpha \right), \quad (6.27)$$

the Schrödinger equation for nuclear motion is

$$\left[-\sum_\alpha \frac{\hbar^2}{2M_\alpha} \left(\nabla_{\mathbf{R}_\alpha} - \frac{i}{\hbar} \mathbf{A}_\alpha \right)^2 + U(\mathbf{R}) \right] \eta(\mathbf{R}) = E \eta(\mathbf{R}) \quad (6.28)$$

Berry's phases are not there if $\phi_{\mathbf{R}}(\mathbf{r})$ can be chosen to be real (note that we still have the $\int d\mathbf{r} \left| \nabla_{\mathbf{R}_\alpha} \phi_{\mathbf{R}} \right|^2$ term). Lowest order Born-Oppenheimer:

$$H = -\sum_\alpha \frac{\hbar^2}{2M_\alpha} \nabla^2_{\mathbf{R}_\alpha} + V_{NN}(\mathbf{R}) + E_e(\mathbf{R}) \quad (6.29)$$

6.2 Following the direct route

$$H = \hat{H}_N + \hat{H}_e = \hat{T}_N + \hat{V}_{NN} + \hat{H}_e \quad (6.30)$$

where

$$\hat{T}_N = \sum_\alpha \frac{\hbar^2}{2M_\alpha} \nabla^2_{\mathbf{R}_\alpha} \quad (6.31)$$

$$\hat{H}_e \phi^{(i)}_{\mathbf{R}} = E_e(\mathbf{R})^{(i)} \phi^{(i)}_{\mathbf{R}} \quad (6.32)$$

and

$$\psi = \sum_i \eta^{(i)}(\mathbf{R})\phi^{(i)}_{\mathbf{R}}(\mathbf{r})\,. \tag{6.33}$$

Therefore the eigenvalue equation $H\psi = E\psi$ looks like

$$\begin{aligned} H\psi &= \sum_i \hat{T}_N \eta^{(i)}(\mathbf{R})\phi^{(i)}_{\mathbf{R}}(\mathbf{r}) + \sum_i \eta^{(i)}(\mathbf{R})\left(\hat{V}_{NN} + \hat{H}_e\right)\phi^{(i)}_{\mathbf{R}}(\mathbf{r}) \\ &= \sum_i (\hat{T}_N + \hat{V}_{NN} + E^{(i)}_e(\mathbf{R}))\eta^{(i)}(\mathbf{R})\phi^{(i)}_{\mathbf{R}}(\mathbf{r}) - \sum_i\sum_\alpha \frac{\hbar^2}{2M_\alpha}\left[2\big(\nabla_{\mathbf{R}_\alpha}\eta^{(i)}(\mathbf{R})\big)\big(\nabla_{\mathbf{R}_\alpha}\phi^{(i)}_{\mathbf{R}}(\mathbf{r})\big) + \eta^{(i)}(\mathbf{R})\nabla^2_{\mathbf{R}_\alpha}\phi^{(i)}_{\mathbf{R}}(\mathbf{r})\right] \\ &= E\sum_i \eta^{(i)}(\mathbf{R})\phi^{(i)}_{\mathbf{R}}(\mathbf{r}) \end{aligned} \tag{6.34}$$

We now multiply by $\int d\mathbf{r}\,\phi^{*(j)}_{\mathbf{R}}(\mathbf{r})$

$$\left[\hat{T}_N + \hat{V}_{NN} + E^{(i)}_e(\mathbf{R})\right]\eta^{(j)} = E\eta^{(j)} + \sum_{i,\alpha}\frac{\hbar^2}{2M_\alpha}\left[2\big(\nabla_{\mathbf{R}_\alpha}\eta^{(i)}\big)\int d\mathbf{r}\,\phi^{*(j)}_{\mathbf{R}}(\mathbf{r})\nabla_{\mathbf{R}_\alpha}\phi^{(i)}_{\mathbf{R}}(\mathbf{r}) + \eta^{(i)}\int d\mathbf{r}\phi^{*(j)}_{\mathbf{R}}(\mathbf{r})\nabla^2_{\mathbf{R}_\alpha}\phi^{(i)}_{\mathbf{R}}(\mathbf{r})\right] \tag{6.35}$$

Suppose there was no sum over "i", so that $j = i$

$$\begin{aligned} &\sum_\alpha \frac{\hbar^2}{2M_\alpha}\left[2\nabla_{\mathbf{R}_\alpha}\eta^{(i)}\frac{1}{i\hbar}A_\alpha(\mathbf{R}) + \eta^{(i)}\int d\mathbf{r}\phi^{*(j)}_{\mathbf{R}}(\mathbf{r})\nabla^2_{\mathbf{R}_\alpha}\phi^{(i)}_{\mathbf{R}}(\mathbf{r})\right] \\ &= \nabla_{\mathbf{R}_\alpha}\left(\eta^{(i)}\int d\mathbf{r}\phi^{*(j)}_{\mathbf{R}}(\mathbf{r})\nabla_{\mathbf{R}_\alpha}\phi^{(i)}_{\mathbf{R}}(\mathbf{r})\right) - (\nabla_{\mathbf{R}_\alpha}\eta^{(i)})\frac{1}{i\hbar}A_\alpha(\mathbf{R}) - \eta^{(i)}\int d\mathbf{r}\nabla_{\mathbf{R}_\alpha}\phi^{*(j)}_{\mathbf{R}}(\mathbf{r})\nabla_{\mathbf{R}_\alpha}\phi^{(i)}_{\mathbf{R}}(\mathbf{r}) = \\ &= \frac{i}{\hbar}P_\alpha\left(\eta^i\frac{1}{i\hbar}A_\alpha\right) - \cancel{(\nabla_{\mathbf{R}_\alpha}\eta^{(i)})\frac{1}{i\hbar}A_\alpha}(\mathbf{R}) - \eta^{(i)}\int d\mathbf{r}\left|\nabla_{\mathbf{R}_\alpha}\phi^{(j)}_{\mathbf{R}}(\mathbf{r})\right|^2 \end{aligned} \tag{6.36}$$

Back

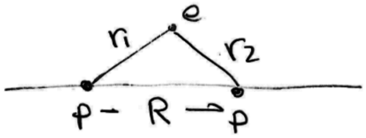
$$\sum_\alpha \frac{1}{2M_\alpha}P_\alpha\left(\eta^i A_\alpha\right) - A_\alpha\mathbf{P}_\alpha\eta^{(i)}\int - \eta^{(i)}\int d\mathbf{r}\left|\nabla_{\mathbf{R}_\alpha}\phi^{(j)}_{\mathbf{R}}(\mathbf{r})\right|^2 \tag{6.37}$$

would get perfect agreement!!

6.3 The H_2^+ ion

The electron Hamiltonian is

$$H_e = \underbrace{-\frac{\hbar^2}{2m}\nabla^2}_{\hat{T}_e}\underbrace{-e^2\left(\frac{1}{r_1} + \frac{1}{r_2}\right)}_{V_{Ne}} \tag{6.38}$$



Do a variational ansatz

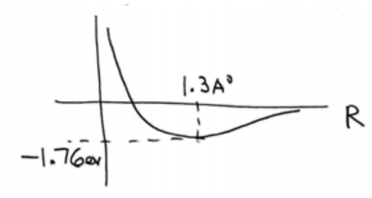
$$\psi = A[\psi_0(r_1) + \psi_0(r_2)] \qquad \psi_0(r) = \frac{1}{\sqrt{\pi a_0^3}}e^{-\frac{r}{a_0}} \tag{6.39}$$

Impose normalization of the wavefunction

$$|\psi|^2 = 1 \implies |A|^2 = \frac{1}{2(1+I)} \qquad \text{with} \qquad I \equiv e^{\frac{R}{a}}\left[1 + \frac{R}{a} + \frac{1}{3}\left(\frac{R}{a}\right)^2\right] \tag{6.40}$$

Since $\langle H_e \rangle \simeq E_e(R)$ the full potential is

$$E_e(R) + \underbrace{V_{NN}(R)}_{\frac{e^2}{R}} \tag{6.41}$$



Experimentally we have $R = 1.06\mathring{A}$ and $E = -2.8$ eV.
Ansatz is not very accurate, for small R wavefunction becomes ground state of Hydrogen atom not ground state of Helium, as it should.

8.06 Quantum Physics III
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