Lecture 7 July 8, '24

Today, we want to go over non-adiabatic physics in some more detail, focusing on the non-adiabatic coupling matrices, their properties, and dynamics in this coupled system.

Recall: we have established the coupled-channel formalism

$$\sum_{\nu} \left(-\frac{1}{2} \frac{d^2}{dR^2} - E \right) \delta_{\mu\nu} F_{\nu}(R) + \sum_{\nu} V_{\mu\nu} F_{\nu}(R) = 0$$

where

$$\psi(R, \Omega) = \sum_{\mu} \Phi_{\mu}(\Omega) F_{\mu}(R).$$

Recall: this was the outcome of turning an ND Schrö EQ into one $(N-1)$D Schrö. EQ (the one $H_e(\Omega) \Phi_\mu(\Omega) = E_\mu \Phi_\mu(\Omega)$) and infinitely many coupled 1D Schrö. EQs. (And typically the $(N-1)$D Schrö EQ is already solved, or is separable, or both — think about Sph-Harmonics etc...)

It does remain an important question how to determine the best Φ_μ for our problem!

→ Example from Ryd-Mols. We could choose (for the simplest spin-indep. model)

$$\Phi_\mu(r) = \frac{u_{nl}(r)}{r} Y_{lm}(\hat{r})$$

such that our coupled channel equations become, in the perturbative limit that n is fixed,

$$\sum_l \left(-\frac{1}{2}\frac{d^2}{dR^2} - \frac{1}{2(n-\mu_l)^2} - E \right) \delta_{l'l} F_l(R) + \sum_l 2\pi a_s \Phi^*_{nl'}(R) \Phi_{nl}(R) \cdot F_l(R) = 0.$$

This is easy to write down, but very hard to solve - especially for $l \gg 1$ where the states are highly degenerate!

→ The off-diagonal couplings $V_{ll'}$ become as large as V_{ll} and don't decrease with $|l-l'|$!

That motivated the introduction of a new representation - the <u>adiabatic</u> representation - where $U_{\ell\ell'}$ is diagonal!

$$U_{\ell\ell'}\,\chi_{\ell}'(r;R) = U_{\ell}(R)\,\chi_{\ell}(r;R)$$

This gives the coupled adiabatic channel eqns

$$\sum_{\nu}\left\{\left[-\frac{1}{2m}\frac{d^2}{dR^2} + U(R) - U_{\nu}(R) - E\right]\delta_{\mu\nu}F_{\nu}(R) + \frac{1}{2m}\left[2P_{\mu\nu}\frac{d}{dR} + Q_{\mu\nu}\right]F_{\nu}(R)\right\} = 0$$

NA coupling matrices!

bottom line = 0 in BO approx!

Properties of $\underline{P}$ and $\underline{Q}$:

i) $P_{\mu\nu} = \langle \phi_{\mu} | {}^{d}/_{dR} | \phi_{\nu} \rangle$ is anti-symmetric!

Proof: $0 = \frac{d}{dR}\langle \phi_{\mu} | \phi_{\nu}\rangle = \langle \phi_{\mu} | \phi_{\nu}' \rangle + \langle \phi_{\mu}' | \phi_{\nu} \rangle$

$\rightarrow$ $\underline{P_{\mu\nu} = -P_{\nu\mu}}$

2) $$\frac{dP_{\mu\nu}}{dR} = \langle \phi_\mu' | \phi_\nu' \rangle + \langle \phi_\mu | \phi_\nu'' \rangle$$

?

$= Q$ matrix!

$$= \sum_q \underbrace{\langle \phi_\mu' | \phi_q \rangle}_{(P^\dagger)_{\mu q}} \underbrace{\langle \phi_q | \phi_\nu' \rangle}_{P_{q\nu}} = \underline{P^2}$$

$$\rightarrow \underline{Q} = \frac{dP_{\mu\nu}}{dR} - P^2$$

That's a useful identity to avoid 2nd derivatives!

3) Feynman-Hellman Thm:

$$P_{\mu\nu} = \frac{\langle \phi_\mu | \frac{dH}{dR} | \phi_\nu \rangle}{U_\nu - U_\mu}$$

Pf: $H|\phi_\nu\rangle = U_\nu |\phi_\nu\rangle$

$$\rightarrow \frac{dH}{dR}|\phi_\nu\rangle + H|\phi_\nu'\rangle = U_\nu'|\phi_\nu\rangle + U_\nu|\phi_\nu'\rangle$$

$$= \omega_\mu \langle \phi_\mu | \phi_\nu' \rangle = \omega_\mu P_{\mu\nu}$$

$$\rightarrow \langle \phi_\mu | \frac{dH}{dR} | \phi_\nu \rangle + \langle \phi_\mu | H | \phi_\nu' \rangle$$

$$= \omega_\nu' \underbrace{\langle \phi_\mu | \phi_\nu \rangle}_{=0} + \omega_\nu \underbrace{\langle \phi_\mu | \phi_\nu' \rangle}_{= P_{\mu\nu}}$$

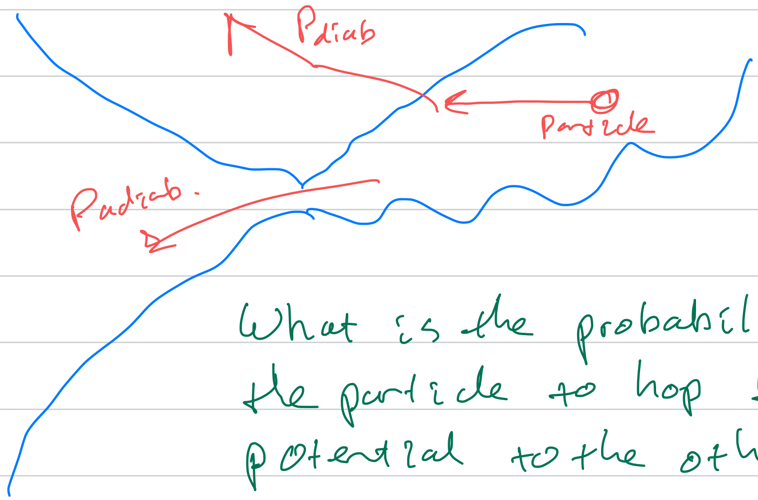
So: $\langle \phi_\mu | \frac{dH}{dR} | \phi_\nu \rangle = [\omega_\nu - \omega_\mu] P_{\mu\nu}$

And QED: $$P_{\mu\nu} = \frac{\langle \phi_\mu | \frac{dH}{dR} | \phi_\nu \rangle}{\omega_\nu - \omega_\mu}$$

And this is super useful as it gives very accurate values for the P-matrix without any numerical differentiation!

In the lecture, we discussed trilobite and butterfly molecules here. I will try to write this all up as a separate example later. We used supersymmetry to compute PECs, show that there are avoided crossings, and then this motivated...

the LANDAU - ZENER formula!!



What is the probability for the particle to hop from one potential to the other?

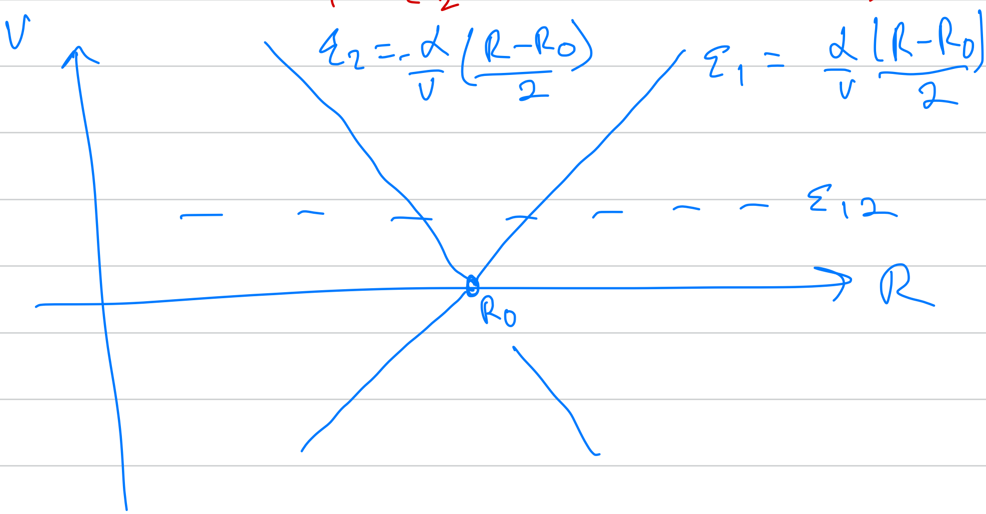
Landau Zener:

Let's consider first the approach of Clark.
We start with a diabatic Hamiltonian:

$$H\begin{pmatrix}\phi_1\\ \phi_2\end{pmatrix} = \begin{pmatrix}\varepsilon_1 & \varepsilon_{12}\\ \varepsilon_{12} & \varepsilon_2\end{pmatrix}\begin{pmatrix}\phi_1\\ \phi_2\end{pmatrix}$$

where ε_{12} is constant and

$$\varepsilon_1 - \varepsilon_2 = \alpha t = \alpha(R-R_0)/v$$



Landau-Zener formula results in

$$P_{na} = e^{-2\pi\gamma}, \quad \gamma = \varepsilon_{12}^2/\alpha.$$

Can we sketch out this derivation?

Let's go for it, semiclassically. That means we replace the dependence on R with just a parametric dependence on t: $R - R_0 = vt$. We use this to write our time-dep. Schrö eq:

$\beta = V_{12}$

$$i\hbar \frac{d}{dt}\begin{pmatrix} \psi_1(t) \\ \psi_2(t) \end{pmatrix} = \underbrace{\begin{pmatrix} \alpha t & \beta \\ \beta & -\alpha t \end{pmatrix}}_{\text{"}H^{el}\text{"}} \begin{pmatrix} \psi_1(t) \\ \psi_2(t) \end{pmatrix}$$

slope defined slightly diff.

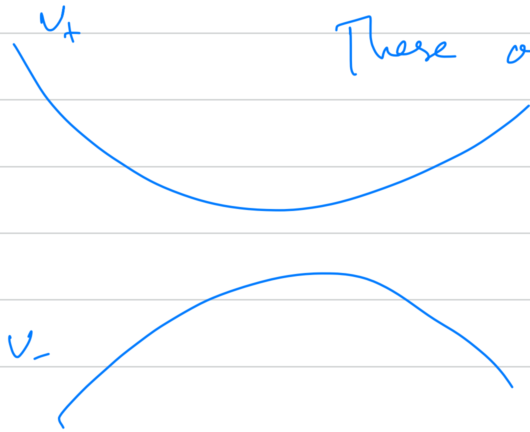
Step 1: go to adiabatic rep:

$$X^{\dagger} H_d X = H_{ad}$$

$$\rightarrow \begin{pmatrix} \overset{\alpha_1 t}{\alpha t} & \beta \\ \beta & \underset{\alpha_2 t}{-\alpha t} \end{pmatrix} X = X \begin{pmatrix} V_+(t) & 0 \\ 0 & V_-(t) \end{pmatrix}$$

$$V_{\pm}(t) = \frac{1}{2}\left[(\alpha_1 + \alpha_2)t \pm \sqrt{(\alpha_1 - \alpha_2)^2 t^2 + 4\beta^2}\right.$$

or: $= \pm \sqrt{\alpha^2 t^2 + \beta^2}$



These are the adiabatic potentials!

When we transform the S.E. we get:

$$X^\dagger \nearrow \quad i\hbar \frac{d}{dt} X \underbrace{X^\dagger \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}}_{\begin{matrix}\varphi_1 \\ \varphi_2\end{matrix}} = \nearrow X^\dagger \begin{pmatrix} \alpha t & \beta \\ \beta & -\alpha t \end{pmatrix} X \underbrace{X^\dagger \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}}_{= \begin{pmatrix} \varphi_1 \\ \varphi_2 \end{pmatrix}}$$

$$\rightarrow i\hbar \left(X^\dagger \frac{d}{dt} X \right) \begin{pmatrix} \varphi_1 \\ \varphi_2 \end{pmatrix} + i\hbar \begin{pmatrix} \varphi_1' \\ \varphi_2' \end{pmatrix} = \begin{pmatrix} V_+ & 0 \\ 0 & V_- \end{pmatrix} \begin{pmatrix} \varphi_1 \\ \varphi_2 \end{pmatrix}$$

or: $$i\hbar \frac{d\vec{\varphi}}{dt} = \begin{pmatrix} V_+ & 0 \\ 0 & V_- \end{pmatrix} \vec{\varphi} - i\hbar \underline{P}(t),$$

$$\underline{P = X^\dagger \frac{d}{dt} X}$$

In the adiabatic approx,

$$\varphi_\lambda(t) = \varphi_\lambda(t_0)\, e^{-i/\hbar \int_{t_0}^{t} V_\lambda(t')\,dt'}$$

Landau realized: V_+, V_- are two branches of an analytic function in the complex t' plane. So if we follow the right path through complex t'-space, we can neglect β! (why? Maybe b/c we can do it arbitrarily slowly!)

→ If we want to go from $-$ to $+$, we need to follow the curve:

$-\infty < t < 0$: Real negative t values.

$0 \leq \mathrm{Im}\, t' \leq i\beta/\alpha$: to connect to the upper (and then back) surface

$0 < t' \to \infty$ Real positive t again!

So: $\psi(t\to\infty) = \psi(t_0)\, e^{-i\int_C v(t')\,dt'}$

$$\int_C v(t')\,dt' = \int_{t_0}^{0} v_-(t')\,dt' + \int_0^{i\beta/\alpha} v_-(t')\,dt'$$

$$+ \int_{i\beta/\alpha}^{0} v_+(t')\,dt' + \int_0^{t} v_+(t')\,dt'$$

These are both real integrals, and give only a phase.

$$\pm\int_0^{i\beta/\alpha} \sqrt{\alpha^2 t^2 + \beta^2}\,dt = \pm\int_0^{\beta/\alpha} i\sqrt{-\alpha^2 t^2 + \beta^2}\,dt$$

$$= \pm\, \beta^2 \pi / 4\alpha$$

$$\to \sqcup + -\sqcup = -\beta^2\pi/2\alpha$$

So: the amplitude changes by

$$e^{-\beta^2\pi/2\alpha}.$$

and thus too the probability:

$$P = e^{-\beta^2 \pi/\alpha} = e^{-\frac{2\pi V_{12}^2}{\frac{d}{dt}(V_{11}-V_{22})}}$$

$$= e^{-\frac{2\pi V_{12}^2}{\frac{d}{dR}(V_{11}-V_{22})\cdot\frac{dR}{dt}}} \checkmark$$

Now that we have P_{LZ}, let's return to Clark's paper. He also diagonalizes H:

$$H\,\phi_\pm(t) = \varepsilon_\pm\,\phi_\pm(t)$$

$$\varepsilon_\pm = \frac{1}{2}(\varepsilon_1+\varepsilon_2) \pm \sqrt{\frac{1}{4}(\varepsilon_1-\varepsilon_2)^2+\varepsilon_{12}^2}$$

$$\begin{pmatrix}\phi_+\\ \phi_-\end{pmatrix} = \underbrace{\begin{bmatrix}\cos\theta & \sin\theta\\ -\sin\theta & \cos\theta\end{bmatrix}}_{\theta \text{ is some complex } t\text{-dep func!}}\begin{pmatrix}\phi_1\\ \phi_2\end{pmatrix}$$

Now we need the P-matrix:

$$\langle\phi_-|\tfrac{d}{dt}\phi_+\rangle = \frac{\langle\phi_-|\frac{dH}{dt}|\phi_+\rangle}{\varepsilon_+-\varepsilon_-}$$

$$= \frac{\begin{pmatrix}\cos\theta\phi_1\\ \sin\theta\phi_2\end{pmatrix}^{+}\cdot\begin{pmatrix}\alpha & 0\\ 0 & -\alpha\end{pmatrix}\begin{pmatrix}-\sin\theta\phi_1\\ \cos\theta\phi_2\end{pmatrix}}{2\sqrt{1/4(\varepsilon_1-\varepsilon_2)^2+\varepsilon_{12}^2}}$$

(did not finish yet!)

→ Switching to Glasbrenner + Schleich paper

Typical LZ setup:

$$i\hbar \begin{pmatrix} \dot{\tilde{a}}(t) \\ \dot{\tilde{b}}(t) \end{pmatrix} = \hbar \begin{pmatrix} -\alpha t & \beta \\ \beta & \alpha t \end{pmatrix} \begin{pmatrix} \tilde{a}(t) \\ \tilde{b}(t) \end{pmatrix}$$

To solve: let

$$\tilde{a}(t) = e^{i\alpha t^2/2} a(t), \quad \tilde{b}(t) = e^{-i\alpha t^2/2} b(t)$$

Then:
$$\dot{\tilde{a}} = e^{i\alpha t^2/2}\dot{a}(t) + i\alpha t e^{i\alpha t^2/2} a(t)$$
$$\dot{\tilde{b}} = e^{-i\alpha t^2/2}\dot{b}(t) - i\alpha t e^{-i\alpha t^2/2} b(t)$$

$$\rightarrow i\begin{pmatrix} e^{i\cdots} & 0 \\ 0 & e^{-i\cdots} \end{pmatrix}\begin{pmatrix} \dot{a} \\ \dot{b} \end{pmatrix} + \begin{pmatrix} \cancel{-\alpha t} & 0 \\ 0 & \cancel{\alpha t} \end{pmatrix}\begin{pmatrix} \tilde{a} \\ \tilde{b} \end{pmatrix} = \begin{pmatrix} \cancel{-\alpha t} & \beta \\ \beta & \cancel{\alpha t} \end{pmatrix}\begin{pmatrix} \tilde{a} \\ \tilde{b} \end{pmatrix}$$

$$\rightarrow \dot{a} = -i\beta e^{-i\alpha t^2} b(t)$$
$$\dot{b} = -i\beta e^{i\alpha t^2} a(t)$$

Now solve for $b(t)$:

$$b = \int_{-\infty}^{t} \left(-i\beta e^{i\alpha t'^2} a(t')\right) dt'$$

$$\rightarrow \dot{a}(t) = -\beta^2 e^{-i\alpha t^2} \cdot \int_{-\infty}^{t} e^{i\alpha t'^2} a(t')\,dt'$$

Markov approx: $a(t)$ does not depend on initial conditions or its history!

$$\rightarrow \dot{a}(t) = -\beta^2 e^{-i\alpha t^2} a(t) \int_{-\infty}^{t} e^{i\alpha t'^2} dt'$$

So: $a(t) = e^{-\beta^2 \int_{-\infty}^{t} e^{-i\alpha p^2} \int_{-\infty}^{p} e^{i\alpha q^2} dq}$

To get $a(\infty)$ then requires evaluating

$$I = \int_{-\infty}^{\infty} e^{-i\alpha p^2} \int_{-\infty}^{p} e^{i\alpha q^2} dq$$

$$= \int_{-\infty}^{\infty} e^{-i\alpha p^2} \int_{-\infty}^{\infty} e^{i\alpha q^2} dq$$

$$- \int_{-\infty}^{\infty} e^{-i\alpha p^2} \int_{p}^{\infty} e^{i\alpha q^2} dq$$

same here

$p' \rightarrow p$

let $q' = -q$

$$= \int_{-\infty}^{\infty} e^{-i\alpha p^2} \int_{-\infty}^{\infty} e^{i\alpha q^2} dq \rightarrow \sqrt{\frac{\pi i}{\alpha}}$$

$\rightarrow dq' = -dq'$

$\infty \rightarrow -\infty$

$$+ -\int_{-\infty}^{\infty} e^{-i\alpha p'^2} \int_{-\infty}^{+p'} e^{i\alpha q'^2} dq'\,dp'$$

$p \rightarrow -p$

$$= \int_{-\infty}^{\infty} e^{-i\alpha p^2} \int_{-\infty}^{\infty} e^{i\alpha q^2} dq\, dp$$

$$+ I \rightarrow 2I = \int_{-\infty}^{\infty} e^{-i\alpha p^2} \int_{-\infty}^{\infty} e^{i\alpha q^2} dq$$

This is a product of 2 typical Gaussian integrals.

$$\rightarrow I = \frac{1}{2} \sqrt{i\pi/\alpha} \sqrt{-i\pi/\alpha} = \pi/2\alpha$$

And so: $\boxed{a(\infty) = e^{-\beta^2 \pi/2\alpha}}$

$$\rightarrow \underline{P = e^{-\beta^2 \pi/\alpha}}$$

(scratch work for Clark's derivation)

$$= \begin{pmatrix} \cos\theta\,\varphi_1 \\ \sin\theta\,\varphi_2 \end{pmatrix}^t \cdot \begin{pmatrix} -\alpha\sin\theta\,\varphi_1 \\ \alpha\cos\theta\,\varphi_2 \end{pmatrix}$$

(not yet done!!)

$$\frac{dH}{dt} = \begin{pmatrix} \alpha & 0 \\ 0 & -\alpha \end{pmatrix}$$

$$\rightarrow P = \begin{pmatrix} -\sin\theta\,\varphi_1 + \cos\theta\,\varphi_2 \end{pmatrix} \begin{pmatrix} \alpha & 0 \\ 0 & -\alpha \end{pmatrix} \begin{pmatrix} \cos\theta\,\varphi_1 + \sin\theta\,\varphi_2 \end{pmatrix}$$

$$P = \left(-\sin\theta \begin{pmatrix} 1 \\ 0 \end{pmatrix} \varphi_1 + \cos\theta \begin{pmatrix} 0 \\ 1 \end{pmatrix} \varphi_2 \right) \begin{pmatrix} \alpha & 0 \\ 0 & -\alpha \end{pmatrix} \left(\cos\theta \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \sin\theta \begin{pmatrix} 0 \\ 1 \end{pmatrix} \right)$$

$$= \left(-\sin\theta \right.$$

$$= \alpha \left(\cos\theta\sin\theta - \right.$$

$$= -2\alpha\cos\theta\sin\theta = -2\alpha\cos^2\theta\tan\theta$$

$$= -2\alpha\tan\theta / 1+\tan^2\theta$$

$$1+\tan^2\theta = \frac{\cos^2\theta + \sin^2\theta}{\cos^2\theta} = \frac{1}{\cos^2\theta}$$

So: $P_{LZ} = \dfrac{-2\alpha \tan\theta / 1+\tan^2\theta}{2\sqrt{\frac{1}{4}(\varepsilon_1-\varepsilon_2)^2+\varepsilon_{12}^2}}$

$= \dfrac{-2\alpha\tan\theta / 1+\tan^2\theta}{\underbrace{\sqrt{(\alpha t)^2+\Delta^2}}_{x}}$ $\quad \Delta = 2\varepsilon_{12}$

UMA: evecs: $1,\ -\dfrac{-\alpha t+\sqrt{4\varepsilon_{12}^2+(\alpha t)^2}}{2\varepsilon_{12}}$

$\Rightarrow \tan\theta = \dfrac{\Delta}{\alpha t+\sqrt{\Delta^2+(\alpha t)^2}}$

$= \dfrac{\Delta}{\alpha t+\Delta\sqrt{1+(\alpha/\Delta)^2t^2}}$

$= \dfrac{1}{y+\underbrace{\sqrt{1+y^2}}_{x}}$ $\quad y = \alpha t/\Delta$

$= \dfrac{1}{y+x}$

$\Rightarrow P_{LZ} = \dfrac{-2\alpha/\Delta \cdot \left(\frac{1}{y+x}\right) / \left(1+\frac{1}{(y+x)^2}\right)}{x}$

$= -\dfrac{2\alpha/\Delta}{x} \cdot \dfrac{1}{y+x} \cdot \dfrac{(y+x)^2}{1+(y+x)^2}$

$$= \frac{-2\alpha/\Delta}{x} \cdot \frac{y+x}{1+y+x}$$

$$\tan\sigma = -\frac{\Delta}{\alpha t - \sqrt{\Delta^2 + (\alpha t)^2}} = -\frac{1}{\alpha t/\Delta - \sqrt{1+(\alpha t/\Delta)^2}}$$

$$= -\frac{1}{y - \sqrt{1+y^2}}, \quad y = \alpha t/\Delta$$

$$\Rightarrow \quad 1 + \tan^2 = y^2 - 2y\sqrt{1+y^2} + 1 + y^2 - 1$$