Adiabatic motion in classical Physics

Key concept: the pendulum will keep swinging regularly parallel to the same plane if external condition change little during an oscillation. In Quantum Mechanics the Born-Oppenheimer approximation is somewhat similar.

From Griffiths *Introduction to Quantum Mechanics*
Adiabatic theorem (Kato 1949)

Basic for perturbation theory, Berry phase etc

\[ i\hbar \frac{\partial}{\partial t} \psi_n(t) = H[R(t)]\psi_n(t) \]

\[ \psi_n(t = 0) = a_n[R(0)] \]

At \( t = 0 \) system in eigenstate, but \( R = R(t) \) adiabatically in \((0, T)\), \( T \to \infty \)

Formal expansion over instantaneous complete set of eigenstates of \( H[R(t)] \) treated as static:

\[ \psi_n(t) = c_n(t)a_n[R(t)] + \sum_{m \neq n} c_m(t)a_m[R(t)] \]

\[ c_n(0) = 1 \]
Adiabatic theorem:
Let $H[R]$ have discrete spectrum with no degeneracy.
⇒ For slow enough changes
\[ H[R]a_n[R] = E_n[R]a_n[R] \]
$c_m = 0$ for $m \neq n$ in adiabatic limit.

Tosio Kato (from family photo album).
Adiabatic Theorem (see Griffiths, Meccanica Quantistica)

Time-dependent part of $H$

$$H'(t) = Vf(t)$$

$$H'(\infty) = V$$

$\psi_m^f = \text{final Hamiltonian stationary states}$

$$(H + V)\psi_m^f = E_m^f \psi_m^f$$

Initial state $\Psi(t = 0) = \psi_n^i \equiv \psi_n$

**Temporary assumption:** for the moment assume $V$ very small, too

This enables first-order time-independent perturbation theory for final stationary states

$$\psi_m^f = \psi_m + \sum_{k \neq m} \frac{V_{km}}{E_m - E_k} \psi_k$$

Assumptions: $T$ very long, $f(t)$ gradual, discrete spectrum, → no level crossing
For $t=0$ system in level $n$: initial state $\Psi(t=0) = \psi_n^i \equiv \psi_n$.

Use time-dependent perturbation theory, too, to evaluate $\Psi(T)$ in terms of the initial eigenstates.

$$\Psi(t) = \sum_m c_m(t) \psi_m(t) \quad \text{where} \quad \psi_m(t) = \psi_i(0)e^{-i\frac{E_m t}{\hbar}}.$$ 

Recalling time-dependent part of $H$: $H'(t) = Vf(t)$

Amplitude of $n \rightarrow m$  
$$c_m(t) = \frac{-i}{\hbar} V_{mn} \int_0^t dt' f(t') e^{i\frac{(E_m - E_n) t'}{\hbar}}, l \neq n.$$  

Amplitude of remaining in initial state:

$$n \rightarrow n \quad c_n(t) = 1 - \frac{-i}{\hbar} V_{nn} \int_0^t dt' f(t')$$
Trick to exploit the smallness of $\frac{d}{dt} f(t)$

Amplitude of $n \to m$ 

$$c_m(t) = \frac{-i}{\hbar} V_{mn} \int_0^t dt' f(t') e^{\frac{i(E_m - E_n)t'}{\hbar}}$$, \(l \neq n\).

Insert identity $e^{\frac{i(E_m - E_n)t'}{\hbar}} = \frac{-i\hbar}{E_m - E_n} \frac{d}{dt'} e^{\frac{i(E_m - E_n)t'}{\hbar}}$

$$c_m(t) = \frac{-i\hbar}{E_m - E_n} \frac{-i}{\hbar} V_{ln} \int_0^t dt' f(t') \frac{d}{dt'} e^{\frac{i(E_m - E_n)t'}{\hbar}}$$

by parts 

$$c_l(t) = \frac{-V_{ln}}{E_l - E_n} \left[ f(t) e^{\frac{i(E_l - E_n)t}{\hbar}} - \int_0^t dt' e^{\frac{i(E_l - E_n)t'}{\hbar}} \frac{d}{dt'} f(t') \right]$$

Thus, in adiabatic case, 

$$c_m(t) = \frac{-V_{mn}}{E_m - E_n} f(t) e^{\frac{i(E_m - E_n)t}{\hbar}}$$, for \(m \neq n\),

while 

$$c_n(t) = 1 - \frac{-i}{\hbar} V_{nn} \int_0^t dt' f(t').$$
Amplitude to jump to state \( m \neq n \), approximated here in first order,

\[
\langle \Psi(T) | \psi_f^m \rangle = \left\langle \left[ (1 - \frac{-i}{\hbar} V_{nn} \int_0^t dt' f(t')) \psi_n - \sum_{l \neq n} \frac{V_{ln}}{E_l - E_n} \psi_l + \ldots \right] e^{\frac{-i E_n T}{\hbar}} | \psi_m + \sum_{k \neq m} \frac{V_{km}}{E_m - E_k} \psi_k + \ldots \right\rangle
\]

Now obtain the \( n \rightarrow m \) transition amplitude in 1st order:

take \( [1] e^{\frac{-i E_n T}{\hbar}} \) (left) and \( \frac{V_{km}}{E_m - E_k} \psi_k \) (right):

This contributes \( e^{\frac{i E_n T}{\hbar}} \frac{V_{nm}}{E_m - E_n} \).

Now, take \( -e^{\frac{-i E_n T}{\hbar}} \sum_{l \neq n} \frac{V_{ln}}{E_l - E_n} \psi_l \) (left) and \( \psi_m \) (right): \( e^{\frac{-i E_n T}{\hbar}} \frac{V_{nm}}{E_m - E_n} \psi_n \):

This contributes \( -e^{\frac{i E_n T}{\hbar}} \frac{V_{nm}}{E_m - E_n} \).

net result: 0

No transitions in first order. This is the Kato theorem.

Now we remove restriction to small \( V \)
Divide \((0,T)\) in \(N\) time slices

\[
\text{In every slice,} \quad \Delta V \approx \frac{V}{N}
\]

Since first-order is 0, total goes like

\[
N \frac{V^2}{N^2} \to 0 \quad \text{for} \quad N \to \infty
\]

**Adiabatic theorem:**

\[H[R] \quad \text{discrete spectrum with no degeneracy}\]

\[\Rightarrow \quad \text{for slow enough changes}\]

\[H[R]a_{n}[R] = E_{n}[R]a_{n}[R]\]

\[c_{m} = 0 \quad \text{for} \quad m \neq n \quad \text{in adiabatic limit.}\]

The adiabatic theorem grants that the system remains in state \(n\), but does not specify what happens to the phase.
Density operator

If a system is known to be in quantum state $\psi_i$, the expectation value of any operator $A$ is $\langle \psi_i | A | \psi_i \rangle$.

If a system is in an impure or mixed state and is known to be in quantum state $\psi_i$ with probability $p_i$, the expectation value of any operator $A$ is

$$\langle A \rangle = \sum_i p_i \langle \psi_i | A | \psi_i \rangle.$$

Example

Electron gun fires 1 pA of 1 Ev electrons

Detector

Electron gun fires 2 pA of 10 Ev electrons

$$\langle E \rangle = \frac{1}{3} \times 1eV + \frac{2}{3} \times 10eV$$
One introduces the density operator
\[ \hat{\rho} = \sum_n p_n |n\rangle \langle n| \]
when the system in a mixed state has probability \( p_n \) of being in state \( |n\rangle \).

\[ \langle A \rangle = \sum_i p_i \langle \psi_i | A | \psi_i \rangle = \sum_i \langle \psi_i | \hat{\rho} A | \psi_i \rangle = Tr(\hat{\rho} A) \]

Density matrix is the matrix of \( \hat{\rho} \) in any basis.

Pure state: the density operator is \( \hat{\rho} = |n\rangle \langle n| \).

In many cases the probabilities are of thermal origin (Boltzman)

In equilibrium, \( p_n = \frac{\exp(-\beta E_n)}{Z} \) on the basis of H eigenvectors.
Let T=0 (absolute 0) and $\hat{\rho} = |0\rangle\langle 0|$.

(system is in instantaneous ground state at time 0).

If evolution is adiabatic $\hat{\rho}$ all the time (Kato theorem).

Now assume that the system evolves slowly, but at a finite speed.
One must envisage an adiabatic perturbation theory to evaluate the corrections to the exactly adiabatic limit. Corrections are particularly important to evaluate matrix elements that vanish in the ground state.

Quasi-adiabatic density matrix (Niu-Thouless)

$\hat{\rho}_i = |0,t\rangle\langle 0,t| \text{ instantaneous adiabatic density operator:}$

Slow t dependence $\Rightarrow \rho = \rho_i + \Delta \rho$

with $\Delta \rho$ small by adiabatic theorem
Slow $t$ dependence $\Rightarrow \rho = \rho_i + \Delta \rho$

with $\Delta \rho$ small by adiabatic theorem:

$\Rightarrow \Delta \rho_{mn}$ with $m$ and $n$ excited on instantaneous eigenstate basis is twice small = negligible if $m \neq 0, n \neq 0$.

First-order correction $\Delta \rho \approx \sum_{n>0} \left( \Delta \rho_{on} \langle 0, t | n, t \rangle + \Delta \rho_{n0} | n, t \rangle \langle 0, t | \right)$

$|0\rangle$ changes slowly.

We shall find that the off-diagonal density matrix is

$\Delta \rho_{0n} = i\hbar \frac{\langle \hat{0} | n \rangle}{E_0 - E_n}$

which is almost self-evident on dimensional grounds.
Proof

Slow \ t \ dependence \ \Rightarrow \ \rho = \rho_i + \Delta \rho, \ with
\rho_i = |0,t\rangle\langle 0,t| \ instantaneous \ density \ matrix \ at \ T=0

Heisenberg EOM: \ \ \ i \frac{d}{dt}(\rho_i + \Delta \rho) = [\rho_i + \Delta \rho, H]

\Delta \rho \ small \ by \ adiabatic \ theorem \ \Rightarrow \ \ i \frac{d}{dt}\Delta \rho \ twice \ small=negligible

\Rightarrow \ get \ \Delta \rho \ from \ equation \ of \ motion \ \ -i \frac{d}{dt}(\rho_i) = [H, \rho_i + \Delta \rho] .

\Rightarrow \ -i \frac{d}{dt}(0,t\rangle\langle 0,t|) = [H, \Delta \rho]

Let's take matrix element \ \langle 0,t|\cdots|n,t\rangle

\langle 0,t| -i \frac{d}{dt}(\rho_i) |n,t\rangle = -\langle 0| i \frac{d}{dt}(0,t\rangle\langle 0,t|) |n\rangle = \langle 0,t|[H, \Delta \rho]|n,t\rangle
Let's take matrix element $\langle 0,t|\cdots|n,t \rangle$

$$\langle 0,t|-i \frac{d}{dt}(\rho_i)|n,t \rangle = -\langle 0|i \frac{d}{dt}(|0,t\rangle\langle 0,t|)|n \rangle = \langle 0,t|[H,\Delta\rho]|n,t \rangle$$

$$\Rightarrow i\langle 0|\frac{d}{dt}(|0,t\rangle\langle 0,t|)|n \rangle = \langle 0|[H,\Delta\rho]|n \rangle = \langle 0|H\Delta\rho - \Delta\rho H|n \rangle = (E_0 - E_n)\Delta\rho_{0n}$$

$$\Rightarrow \Delta\rho_{0n} = -i \frac{\langle 0|\frac{d}{dt}(|0,t\rangle\langle 0,t|)|n \rangle}{(E_0 - E_n)}$$

numerator= $\langle 0|\frac{d}{dt}(|0,t\rangle\langle 0,t|)|n \rangle$ needed

$\frac{d}{dt}$ acts on bra and ket. Trick: let $\frac{d}{dt}$ act on everything on the right, then subtract

$$\langle 0\big|\frac{d}{dt}(|0,t\rangle\langle 0,t|)|n \rangle = \langle 0|\frac{d}{dt}(|0,t\rangle\langle 0,t|\big|n,t \rangle)|n \rangle - \langle 0,t\big|0,t\rangle\langle 0,t\big|\frac{d}{dt}|n(t) \rangle$$

but $\langle 0,t\big|n,t \rangle = 0$, $\langle 0,t\big|0,t \rangle = 1 \Rightarrow$
We arrive at \[ \langle 0 | \frac{d}{dt} | 0, t \rangle \langle 0, t | n \rangle = -\langle 0, t | \frac{d}{dt} | n(t) \rangle, \]
but since \( \langle 0, t | n, t \rangle = 0, \)
one can simplify:

\[
\text{numerator} = \langle \dot{0}, t | n, t \rangle
\]

\[ \Rightarrow \Delta \rho_{0n} = -i \frac{\langle \dot{0} | n \rangle}{E_0 - E_n} \]

The correction to the expectation value of any operator \( \hat{A} \)

\[ \Delta \langle A \rangle = \Delta Tr \rho A \approx \sum_n \rho_{0n}(t) A_{n0} = -i \sum_n A_{n0} \frac{\langle \dot{0} | n \rangle}{E_0 - E_n}. \]

This is particularly relevant to problems in which \( A_{00} = 0. \)
The many-sided Quantum phases

Gauge Transformations

Without the gauge invariance, any theory is untenable. In classical theory, the Hamiltonian of a charged particle is

\[ H = \frac{(\vec{p} - \frac{e}{c} \vec{A})^2}{2m} + eV(x) \]

where \( p \) is the canonical momentum and \( A \) the vector potential. Both are unobservable. The SE reads:

\[ \left\{ \frac{(p - \frac{e}{c} A)^2}{2m} + eV(x) \right\} \Psi = i\hbar \frac{\partial \Psi}{\partial t} \]
One could have started with new potentials giving the same fields:

$$A' = A + \nabla \chi(x, t) \quad V' = V - \frac{1}{c} \frac{\partial \chi}{\partial t}$$

This gives a new Schroedinger equation and a new wave function:

$$\left( p - \frac{e}{c} [A + \nabla \chi] \right)^2 \left\{ \frac{1}{2m} + e[V(x) - \frac{1}{c} \frac{\partial \chi}{\partial t}] \right\} \Psi' = i\hbar \frac{\partial \Psi'}{\partial t}$$

which is solved by

$$\Psi'(x,t) = \Psi(x,t) \exp\left[ \frac{ie \chi(x,t)}{\hbar} \right]$$; no change in the physics.

The phase of $\Psi'(x,t)$ can be changed arbitrarily and independently at any point of space-time: it's just a gauge.
Let the origin O' of frame K' move with speed $\bar{w}$ with respect to K: for a particle at $\bar{r}'$ its position in rest frame K is $\bar{r}=\bar{r}'+\bar{w}t$; in K,
\[\bar{p}=\bar{p}'+m\bar{w}\quad E=\frac{1}{2}m(\bar{w}+\bar{v})^2 = \frac{1}{2}m\bar{w}^2 + \frac{1}{2}m\bar{v}'^2 + m\bar{w}\bar{v}' = E'+\frac{1}{2}m\bar{w}^2 + m\bar{w}\bar{v}'\]

Plane wave in K \[\psi(\bar{r})=\exp\left[\frac{i}{\hbar}(\bar{p}\bar{r}-Et)\right]\]
Plane wave in K' \[\psi'(\bar{r}')=\exp\left[\frac{i}{\hbar}(\bar{p}'\bar{r}'-E't)\right]\]

Plane wave in K
\[\psi(\bar{r})=\exp\left[\frac{i}{\hbar}(\bar{p}'+m\bar{w})(\bar{r}'+\bar{w}t)-(E'+\frac{1}{2}m\bar{w}^2 + m\bar{w}\bar{v}')t\right]\]

\[=\psi'(\bar{r}')\exp\left[\frac{i}{\hbar}m\bar{w} \frac{\bar{r}'+\bar{r}'}{2}\right].\text{ Setting } r'=r-wt\]

\[=\psi'(\bar{r}')\exp\left[\frac{i}{\hbar}(m\bar{w}\bar{r} - \frac{m\omega^2 t}{2})\right]\]
\[
\left\{ \frac{p^2}{2m} + eV(x) \right\} \Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t};
\]
in a moving frame
\[
x' = x - vt, y' = y, z' = z.
\]

\[
\psi(\vec{r}) = \psi'(\vec{r}') \exp\left[ \frac{i}{\hbar} (m \vec{\omega} \vec{r} - \frac{m\omega^2 t}{2}) \right]
\]
holds for all Fourier components.

\[
\Psi'(x', y', z', t) = \Psi(x, y, z, t)e^{-i\phi(x, y, z, t)}
\]
\[
\phi(x, y, z, t) = \frac{m \omega \vec{r}}{\hbar} - \frac{m \omega^2 t}{2\hbar}
\]
**Macroscopic quantum phenomena: Josephson effect**

Ginzburg-Landau theory: $\psi = \text{order parameter with charge } \tilde{e} = 2e$

$$\Rightarrow \text{current } J_s = \frac{\hbar \tilde{e}}{2mi} [\psi^* \nabla \psi - \chi \nabla \psi^*] - \frac{\tilde{e}^2}{m^* c} |\psi|^2 \tilde{A}$$

In elementary quantum problems if there is no bias, $\psi(z)$ can be taken real and there is no current. In ordinary circumstances, there is dissipation and no phase coherence over macroscopic distances.
But superconductivity is a macroscopic quantum phenomenon. A phase difference is generated by a voltage $V$.

A bias creates a phase difference $\theta_2 - \theta_1$ proportional to time analogous to the $e^{-iEt}$ factor of elementary QM, according to

$$2eV=\hbar \frac{\partial \theta}{\partial t}, \quad I=I_c \sin(\theta(t)) \quad I_c = \text{critical current}$$

DC josephson effect

(Shapiro 1963)

Matching $\psi(z)$ in barrier $\psi(z) = \psi_1 e^{-\beta z} + \psi_2 e^{\beta(z-b)}$, $b =$ barrier width $\psi_1$ and $\psi_2$ approximately constant

$$\Rightarrow J_s = \psi_1^* \psi_2 - \psi_1 \psi_2^* = \sin(\theta_2 - \theta_1).$$

$$\Rightarrow$$ The phase difference across the barrier implies a current with no bias. If $V \neq 0$ the current oscillates rapidly and averages to 0.
Typical I-V characteristic of a superconducting tunnel junction, a common kind of Josephson junction. The scale of the vertical axis is 50 µA and that of the horizontal one is 1 mV. The bar at $U = i$ represents the DC Josephson effect, while the current at large values of $|U|$ is due to the finite value of the superconductor bandgap and not reproduced by the above equations.
AC josephson effect

A bias which creates a energy difference $\theta_2 - \theta_1$ proportional to time analogous to to the $e^{-iEt}$ factor of elementary QM,

$E \rightarrow \theta_2 - \theta_1 = \tilde{e}Vt$

$\Rightarrow J_s = \psi_1^* \psi_2 - \psi_1 \psi_2^* \approx \sin(\theta_2 - \theta_1)$

$\Rightarrow I = I_0 \sin \left[ \frac{2eV}{\hbar} (t - t_0) \right],

AC response to DC bias!

$I = I_0 \sin \left[ \frac{2eV}{\hbar} (t - t_0) \right], \quad I_0 = \text{constant}$
Topologic phases

Start from north pole towards Rome bringing a pendulum oscillating parallel to the Rome meridian, reach the equator, then turn left along the equator without changing the plane of oscillator, reach the Parallel of Moscou and follow it back to the North pole; now the oscillator swings towards Moscou. The angle between the planes of oscillation is topological and reflects the sphericity of the Earth.
Topologic phases

Pancharatnam phase

The Indian physicist S. Pancharatnam in 1956 introduced the concept of a topological phase.

Let \( H(\xi) \) be an Hamiltonian which depends from some parameters, represented by \( \xi \); let \( |\psi(\xi)\rangle \) be the ground state.

Compute the phase difference \( \Delta \phi_{ij} \) between \( |\psi(\xi_i)\rangle \) and \( |\psi(\xi_j)\rangle \):

\[
\Delta \phi_{ij} = \mathcal{F}(\xi_i) - \mathcal{F}(\xi_j)
\]

We may define

\[
\langle \psi(\xi_i) | \psi(\xi_j) \rangle = e^{i\Delta \phi_{ij}} \langle \psi(\xi_i) | \psi(\xi_j) \rangle.
\]

However, this is gauge dependent and cannot have any physical meaning. Now consider 3 points \( \xi \) and compute the total phase \( \gamma \) in a closed circuit \( \xi_1 \rightarrow \xi_2 \rightarrow \xi_3 \rightarrow \xi_1 \); remarkably,

\[
\gamma = \Delta \phi_{12} + \Delta \phi_{23} + \Delta \phi_{31}
\]

is gauge independent!

Indeed, the phase of any \( \psi \) can be changed at will by a gauge transformation, but such arbitrary changes cancel out in computing \( \gamma \). This clearly holds for any closed circuit with any number of \( \xi \).

Therefore \( \gamma \) is entitled to have physical meaning.

There may be observables that are not given by Hermitean operators.
For instance, consider a Linear Combination of Atomic Orbitals (LCAO) model for a molecule or cluster (or a Hubbard Model, neglecting overlaps)

Peierls prescription: to introduce $\vec{A}$

$$t_h \rightarrow t_h \exp\left[ \frac{2\pi i}{\phi_0} \int_a^b \vec{A} \cdot d\vec{\ell} \right], \quad \phi_0 = \frac{hc}{e} \approx 4 \times 10^{-7} \text{ Gauss cm}^2 = \text{fluxon}$$

In the case of $H_2$ this can be gauged away, but with three or more atoms the physical meaning is that a magnetic flux $\varphi$ is concatenated with the molecule; changing $\varphi$ by a fluxon has no physical meaning, however.

By complex hoppings, one can introduce a concatenated magnetic flux
3-site cluster with flux

$$\tau_{23} = \tau_{13} = 1, \quad \tau_{12} = e^{i\gamma}, \quad \phi_0 = \frac{hc}{e}$$

$$\gamma = 2\pi \frac{\phi}{\phi_0} = \frac{e\phi}{c\hbar}$$

$$\implies E_{gs} = E_{gs}(\phi)$$

**Ground state Energy $E_{gs}(\phi)$ has period=2 $\pi$**
Adiabatic theorem and Berry phase

Let \( H = H[R(t)] \) depend on a set of several parameters which vary in time.

Consider the evolution of n-th eigenvector \( \psi_n \) starting from \( t=0 \). Expanding on an instantaneous eigenvector basis,

\[
\psi_n(t) = c_n(t) a_n[R(t)] + \sum_{m \neq n} c_m a_m[R(t)],
\]

with \( c_n(0) = 1 \). However if the evolution is adiabatic, we know that we can drop \( \sum_{m \neq n} c_m a_m[R(t)] \).

Therefore, \( c_n(t) \) is enough.

\[
|c_n(t)|^2 = 1 \quad \Leftrightarrow \quad c_n(t) = e^{i\theta_n(t) + i\gamma_n(t)},
\]

where along with

\[
\hbar \theta_n(t) = -\int_0^t dt' E_n[R(t')] = \text{trivially expected dynamical phase},
\]

there is also the topological Berry phase \( \gamma \).
To find $\gamma(t)$, let us impose that $\frac{i\hbar}{\partial t}\psi_n = H\psi_n$. 

$\{a_n\}$=instantaneous eigenvector basis.

Using the ansatz $\psi_n(t) = a_n[R(t)]e^{i\theta_n(t)+i\gamma(t)}$,

where $\hbar\theta_n(t) = -\int_0^t dt' E_n[R(t')]$,

since $\frac{\partial}{\partial t}a_n(R[t]) = \frac{d\tilde{R}}{dt} \cdot \tilde{\nabla}_R a_n$, $\tilde{\nabla}_R$ in parameter space, one finds

$$\frac{\partial}{\partial t}\psi_n(t) = \frac{\partial}{\partial t}\{a_n[R(t)]e^{i\theta_n(t)+i\gamma(t)}\} = \left(\frac{-i}{\hbar} E_n + i\dot{\gamma} + \hat{R}\cdot\nabla_R\right)a_n e^{i\gamma(t)-\frac{i}{\hbar}\int_0^t dt' E_n[R(t')]}

\Rightarrow$ The r.h.s. of the Schroedinger equation reads:

$$H\psi_n(t) = E_n(t)a_n[R(t)]e^{i\theta_n(t)+i\gamma(t)}.$$ 

$E_n(t) =$ instantaneous eigenvalue

Therefore, the Schroedinger equation reads:

$$\left(E_n - \hbar\ddot{\gamma} + i\hbar\dot{R}\cdot\nabla_R\right)a_n e^{i\gamma(t)+i\Theta_n} = E_n a_n e^{i\gamma(t)+i\Theta_n}$$ 

that is,

$$\left(-\hbar\ddot{\gamma} + i\hbar\dot{R}\cdot\nabla_R\right)a_n e^{i\gamma(t)+i\Theta_n} = 0$$
\[ \text{Result: } \left(-\hbar \dot{\gamma}_n + i\hbar \dot{R} \cdot \nabla_R \right) a_n e^{i\gamma_n(t) + i\Theta_n} = 0 \]

\[
\dot{\gamma}_n = i\dot{R} \cdot \left\langle a_n[R(t)] | \nabla_R | a_n[R(t)] \right\rangle
\]

The matrix element looks similar to minus a momentum average, but the gradient is in parameter space. The overall phase change is a line integral

\[
\Delta \gamma_n = i \int_0^T dt \left\langle a_n \right| \nabla_R | a_n \right\rangle \dot{R} = i \int_0^T \left\langle a_n \right| \nabla_R | a_n \right\rangle . d\dot{R}
\]

This has no meaning, it's a gauge, but...

\[
\gamma_n(C) = i \oint_C \left\langle a_n \right| \nabla_R | a_n \right\rangle \cdot dR \text{ is a topological phase}
\]

and vanishes in simply connected parameter spaces (no holes) but in multiply connected spaces yields a quantum number!
Vibronic coupling and the ‘unexpected’ Berry phase

Recall: Total H

\[ H_{\text{tot}}(r, R) = T_e(r) + T_N(R) + V(r, R) \]

that is, \( H_{\text{tot}}(r, R) = T_N(R) + H_e(r, R) \)

Born-Oppenheimer approximation: the recipe

Neglect \( T_N(R) = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial R^2} \).

adiabatic hamiltonian for electrons. Solve \( H_e(r, R)\psi_n(r, R) = E_n(R)\psi_n(r, R) \)

Then, use \( E_0(R) \) as a potential and \( T_N = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial R^2} \)

Within BO: one expects \( -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial R^2} \chi(R) + E_0\chi(R) = W\chi(R) \Rightarrow \text{nuclear motion.} \)

How good is this approximation?
Nuclear wave Functions do not (strictly) exist

There is a wave function that depends on electrons and nuclei and cannot be factored.
Nuclei and electrons are entangled.

Even in the H atom problem there exists no nuclear wave function!

On the other hand we do need physically motivated approximations.
Nuclear wave Functions one step Beyond Born-Oppenheimer Approximation

The Adiabatic Approximation is a cheap way to go somewhat beyond. Adiabatic= assuming evolution confined to lowest \((n=0)\) energy surface computed solving for electrons at fixed \(R\), seek \(\chi(R)\) variationally

\[
\text{ansatz : } \Psi_{\text{trial}}(r, R) = \chi(R)\psi_0(r, R)
\]

\(\psi_0(r, R) = \) electron \(\psi_0\) calculated with nuclei at \(R\).

\(r = \) set of electron coordinates
\(R = \) set of nuclear coordinates
\(\chi(R) = \) nuclear wavefunction
ansatz: $\Psi_{\text{trial}}(r, R) = \chi(R)\psi_0(r, R)$

$r =$ set of electron coordinates

$R =$ set of nuclear coordinates

$\chi(R) =$ nuclear wavefunction

Variational approach to $\chi$ based on Energy functional

$$F[\chi] = \langle H_{\text{tot}} \rangle = \langle \chi(R)\psi_0(r, R) | T_N + H_e | \chi(R)\psi_0(r, R) \rangle$$

Does $F$ yield:

$$-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial R^2} \chi(R) + E_0 \chi(R) = W \chi(R)$$

where $E_0(R) = \langle \psi_0(r, R) | H_e | \psi_0(r, R) \rangle$? This would be the BO

Minimize

$$-\frac{\hbar^2}{2M} \int drdR \chi^* \psi_0^* \frac{\partial^2}{\partial R^2} \chi \psi_0 + \int dR E_0(R) \chi(R)^* \chi(R) - W \int dR \chi(R)^* \chi(R)$$

$\langle T_N \rangle$

$\langle H_e \rangle$

$W =$ Lagrange multiplier (normalization)
ansatz: \( \Psi_{trial}(r, R) = \Psi_0(r, R) = \chi(R)\psi_0(r, R) \)

we need the derivative:

\[
\frac{\partial^2}{\partial R^2} (\chi \psi_0) = \psi_0 \frac{\partial^2}{\partial R^2} \chi + \chi \frac{\partial^2}{\partial R^2} \psi_0 + 2 \frac{\partial}{\partial R} \psi_0 \frac{\partial}{\partial R} \chi.
\]

Minimize:

\[
-\frac{\hbar^2}{2M} \left[ \int dR \chi^* \frac{\partial^2}{\partial R^2} \chi + 2 \int dr dR \chi^* \psi_0 \frac{\partial}{\partial R} \psi_0 \frac{\partial}{\partial R} \chi_0 + \int dR \chi^* \chi \int dr \psi_0^* \frac{\partial^2}{\partial R^2} \psi_0 \right] + \int dR \chi(R)^* E_0(R) \chi(R) - W \int dR \chi(R)^* \chi(R)
\]

Vary \( \chi^* \) and find best \( \chi \)

\[
-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial R^2} \chi + E_0(R) \chi(R) + \Lambda(R) \chi(R) = W \chi(R)
\]

\[
\Lambda(R) = -\frac{\hbar^2}{M} \left( \int dr \psi_0^* \frac{\partial \psi_0}{\partial R} \right) \frac{\partial}{\partial R} - \frac{\hbar^2}{2M} \left( \int dr \psi_0^* \frac{\partial^2 \psi_0}{\partial R^2} \right)
\]

The electron wave function depends parametrically on nuclear coordinates.
\[-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial R^2} \chi + E_0(R) \chi(R) + \Lambda(R) \chi(R) = W \chi(R)\]

\[
\Lambda(R) = -\frac{\hbar^2}{M} \left( \int dr \psi_0^* \frac{\partial \psi_0}{\partial R} \right) \frac{\partial}{\partial R} - \frac{\hbar^2}{2M} \left( \int dr \psi_0^* \frac{\partial^2 \psi_0}{\partial R^2} \right)
\]

This is an unexpected, gauge-dependent nonadiabatic term!

Nonadiabatic \( \Lambda(R) \) often ignored since for real functions

\[
\left( \int dr \psi_0^* \frac{\partial \psi_0}{\partial R} \right) = \frac{1}{2} \frac{\partial}{\partial R} \int dr \psi_0^2 = 0
\]

However, this is not always the case! Not even with \( B = 0 \).

(see below – a Berry phase can arise).

Moreover, the excuse for neglecting the other term is:

\[-\frac{\hbar^2}{2M} \left( \int dr \psi_0^* \frac{\partial^2 \psi_0}{\partial R^2} \right) = O\left( \frac{m}{M} \right) \text{ nonadiabatic term} \]

Not reassuring. Typically vibrations are 0.1 eV or less, electronic jumps require 1 eV or more. But close electronic levels (e.g. Renner-Teller) can be mixed by vibrations!
Recall the Jahn-Teller theorem:

any nonlinear molecule with a spatially degenerate electronic ground state will undergo a geometrical distortion that removes that degeneracy.

True within the Born-Oppenheimer approximation.

Born-Oppenheimer Approximation:

Neglect of nuclear momenta

The energy surfaces have $N_{JT}$ several equivalent minima corresponding to different distortions; e.g. a cube can be squeezed in several equivalent ways.
At strong vibronic coupling, the energy surfaces have $N_{JT}$ deep and distant minima and the nuclear degrees of freedom can hardly tunnel between them. Then, the kinetic energy of the nuclei does not play a role, and one can observe a static JT effect with broken symmetry.

At weak coupling the system oscillates between several minima and, one speaks about dynamic JT effect; the overall symmetry remains unbroken.

The time scale of the experiment is the criterion for weak and strong. In fast experiments with hard X rays the symmetry is broken.
Nuclear wave Functions Beyond Born-Oppenheimer

Jahn-Teller theorem: degenerate wave functions lead to distortions and distortions have the symmetry of degenerate normal modes.

Several interacting Jahn-Teller minima arise

Full problem: $H_{\text{tot}}(r, R) = T_N(R) + H_e(r, R) = T_N(R) + T_e(r) + V(r, R)$

$T_N(R) = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial R^2}$, \quad $H_{\text{tot}}(r, R)\Psi_{\text{tot}}(r, R) = W\Psi_{\text{tot}}(r, R)$

In this more complex case we do not attempt a variational approach but we must allow the mixing of the different equivalent minima.
Full problem: $H_{tot}(r, R) = T_N(R) + H_e(r, R) = T_N(R) + T_e(r) + V(r, R)$

$$T_N(R) = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial R^2}, \quad H_{tot}(r, R)\Psi_{tot}(r, R) = W\Psi_{tot}(r, R)$$

In this more complex case we do not attempt a variational approach but we must allow the mixing of the different equivalent minima.

We must generalize to several minima the above approach

$$\Psi_{trial}^{tot}(r, R) = \chi(R)\psi_0(r, R)$$

where $\psi_0(r, R)$ = electron $\psi_0$ calculated with nuclei at R.

The nuclear motion is the unknown. Scheme:

compute the electronic $\Psi^e_n(r, R_{0n})$ with fixed $R_{0n}$

corresponding to all the minima, with $R_{0n}$ symmetrically distorted geometries. Different minima yield orthogonal $\Psi^e_n(r, R_{0n})$, otherwise we orthogonalize.
\[ H_{tot}(r, R) = T_N(R) + T_e(r) + V(r, R) \]

New Ansatz: summing over the minima, treated on equal footing

\[ \Psi_{tot}^{trial}(r, R) \approx \sum_{k}^{n} \chi_k(R) \Psi_k^e(r), \]

\( \Psi_k^e(r) \) = electronic wave function for minimum k, assumed known

\( \chi_k(R) \) are the unknown.

The electron-nuclei interaction \( V(r, R) \) mixes the nuclear \( \chi_n(R) \).

Substitute \( \Psi_{tot}^{trial}(r, R) \) into

\[ H_{tot}(r, R)\Psi_{tot}^{tot}(r, R) = W\Psi_{tot}^{tot}(r, R) \]

take the electronic scalar product with the electronic wave function

\( \Psi_m^e(r, R_0) \) for minimum at \( r, R_0 \) and get

\[ \int dr \Psi_m^e(r) \left[ H_{tot}(r, R) - W \right] \sum_{k}^{n} \chi_k(R) \Psi_k^e(r, R_0) = 0. \]

More explicitly,

\[ \int dr \Psi_m^e(r, R_0) \left[ -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial R^2} + T_e(r) + V(r, R) - W \right] \sum_{k} \chi_k(R) \Psi_k^e(r, R_0) = 0. \]
\[
\int dr \Psi_m^*(r, R_0) \left[ -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial R^2} + T_e(r) + V(r, R) - W \right] \sum_k \chi_k(R) \Psi_k^e(r, R_0) = 0
\]

Use shorthand notation \( H_e(r, R) \):

\[
\int dr \Psi_m^*(r) \left( -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial R^2} + H_e(r, R) - W \right) \sum_k \chi_k(R) \Psi_k^e(r) = 0
\]

\( dr \) integrates over electrons, and we are assuming orthogonality of electronic wave functions.

First term: upon integration over \( r \) only \( k=m \) remains and we get the simplified first term:

\[
\int dr \Psi_m^*(r) \left( -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial R^2} \right) \sum_k \chi_k(R) \Psi_k^e(r) = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial R^2} \chi_m(R). \text{ Hence,}
\]

\[
-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial R^2} \chi_m(R) + \int dr \Psi_m^*(r) \left( H_e(r, R) - W \right) \sum_k \chi_k(R) \Psi_k^e(r) = 0
\]
Set: \[ V_{mk}(R) = \int dr \Psi^e_m(r) H_e(r, R) \Psi^e_k(r) \]

matrix elements of the electronic Hamiltonian between electronic wave functions belonging to different minima.

\[ \Rightarrow - \frac{\hbar^2}{2M} \frac{\partial^2 \chi_m(R)}{\partial R^2} + \sum_k \left( V_{mk} - W \delta_{mk} \right) \chi_k(R) = 0 \]

coupled equations for the nuclear wave functions, that mix those of different minima via the electronic \( V_{mk}(R) \).

\[ \Rightarrow \text{effective nuclear dynamics accounting for the effect of electrons.} \]
The Nuclear wavefunctions are obtained from matrix Schroedinger equation; the matrix is the Jahn-Teller Hamiltonian

\[ H_{JT} = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial R^2} + \begin{pmatrix} V_{11} & \cdots & V_{1n} \\ \vdots & \ddots & \vdots \\ V_{n1} & \cdots & V_{nn} \end{pmatrix}, \quad V_{mk}(R) = \int dr \Psi_m^{e*}(r) H_e(r, R) \Psi_k^e(r). \]

Finally, \( \Psi^{tot}(r, R) \approx \sum_{k}^{n} \chi_k(R) \Psi_k^e(r). \)
Our unknown is a column vector: for 2 minima we get

\[ -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial R^2} \begin{pmatrix} \chi_1(R) \\ \chi_2(R) \end{pmatrix} + \begin{pmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{pmatrix} \begin{pmatrix} \chi_1(R) \\ \chi_2(R) \end{pmatrix} \]

\( \chi_1(R), \chi_2(R) = \) nuclear wave functions for minima 1,2, taking the mixing into account.

Finally,

\[ \Psi_{tot}^\ell (r, R) \approx \sum_{k=1}^{2} \chi_k(R) \Psi_{e}^k(r). \]
Example of $E \times \varepsilon$ problem: Na$_3$ molecule

$(\psi_x, \psi_y)$ known electronic wave functions $\in E$

By Jahn-Teller theorem: symmetric geometry is unstable,
Electronic degeneracy challenged by degenerate vibrational mode.

$(q_x, q_y)$ normal modes $\in E$ producing potentials $(V(x), V(y))$ acting on electrons and driving the nuclei to a two-state situation, reminiscent of a spin.
The nuclear $\chi_1(R), \chi_2(R)$ of the 2 minima are linear combinations of the normal modes of the same symmetry of the undistorted system, thus we analyze the effects of normal modes.

\[ \frac{\partial^2}{\partial R^2} \] must be written in terms of normal coordinates, thus excluding translations and rotations. For $n=2$,

\[ H_{JT} = -\frac{\hbar^2}{2M} \frac{\partial^2 \chi_m(R)}{\partial R^2} + \sum_k V_{mk} \chi_k(R) \text{ becomes} \]

\[ H_{JT} = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial q_x^2} - \frac{\hbar^2}{2M} \frac{\partial^2}{\partial q_y^2} + q_x \begin{pmatrix} V(x)_{xx} & V(x)_{xy} \\ V(x)_{yx} & V(x)_{yy} \end{pmatrix} + q_y \begin{pmatrix} V(y)_{xx} & V(y)_{xy} \\ V(y)_{yx} & V(y)_{yy} \end{pmatrix} + Kq^2 \]

2x2 matrices represent operators acting on nuclear wave functions $(\chi_x, \chi_y)$.
\[
H_{JT} = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial q_x^2} - \frac{\hbar^2}{2M} \frac{\partial^2}{\partial q_y^2} + q_x \begin{pmatrix} V(x)_{xx} & V(x)_{xy} \\ V(x)_{yx} & V(x)_{yy} \end{pmatrix} + q_y \begin{pmatrix} V(y)_{xx} & V(y)_{xy} \\ V(y)_{yx} & V(y)_{yy} \end{pmatrix} + Kq^2
\]

2x2 matrices represent operators acting on nuclear wave functions

\[
H_{JT} = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial q_x^2} - \frac{\hbar^2}{2M} \frac{\partial^2}{\partial q_y^2} + q_x \begin{pmatrix} 0 & \lambda \\ \lambda & 0 \end{pmatrix} + q_y \begin{pmatrix} \lambda & 0 \\ 0 & -\lambda \end{pmatrix} + Kq^2
\]

that is, \( H_{JT} = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial q_x^2} - \frac{\hbar^2}{2M} \frac{\partial^2}{\partial q_y^2} + \lambda[q_x \sigma_x + q_y \sigma_y] + K(q_x^2 + q_y^2) \)

Group theory predicts the form of the vibronic interaction, using the direct product of representations, but here I skip the argument (see Topics and Methods page196) leading to:

Nuclear kinetic energy
\[ H_{JT} = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial q_x^2} - \frac{\hbar^2}{2M} \frac{\partial^2}{\partial q_y^2} + q_x \begin{pmatrix} 0 & \lambda \\ \lambda & 0 \end{pmatrix} + q_y \begin{pmatrix} \lambda & 0 \\ 0 & -\lambda \end{pmatrix} + Kq^2 \]

that is, \[ H_{JT} = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial q_x^2} - \frac{\hbar^2}{2M} \frac{\partial^2}{\partial q_y^2} + \lambda[q_x \sigma_x + q_y \sigma_z] + K(q_x^2 + q_y^2) \]

**Incidentally: Second-quantized version:**

\[ H_{JT} = \left(a_x^\dagger a_x + \frac{1}{2}\right)\hbar \omega + \left(a_y^\dagger a_y + \frac{1}{2}\right)\hbar \omega + \lambda \left[(a_x^\dagger + a_x)\sigma_x + (a_y^\dagger + a_y)\sigma_y \right] \]

(two levels and two-bosons problem) and is among those exactly solved by the recursion method of Excitation Amplitudes. Here we shall consider the static limit.

\[ H_{JT} = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial q_x^2} - \frac{\hbar^2}{2M} \frac{\partial^2}{\partial q_y^2} + \lambda[q_x \sigma_x + q_y \sigma_z] + K(q_x^2 + q_y^2) \text{ for } M \to \infty \]
Although the model can be solved, we shall work out the Born-Oppenheimer limit \( M \to \infty \): molecule with static distortion, to obtain the JT Hamiltonian acting on nuclear coordinates and the nuclear wave functions. One can study their angular dependence setting \( q_x = q \cos \theta \), \( q_y = q \sin \theta \),

\[
H_{JT} = \lambda q_x \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + \lambda q_y \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + Kq^2 = \lambda q \begin{pmatrix} 0 & \cos \theta \\ \cos \theta & 0 \end{pmatrix} + \lambda q \begin{pmatrix} \sin \theta & 0 \\ 0 & -\sin \theta \end{pmatrix} + Kq^2.
\]

\( \theta \) specifies the mixture of \( x \) and \( y \) normal modes of lowest energy that is the angle of deformation, due to the vibronic coupling

\(<K> q^2 \) is an additive constant, with no dynamics, and formally \( H_{JT} \) is the Hamiltonian for a spin in a magnetic field \( B = (q_x, 0, q_y) \).
Born-Oppenheimer limit $M \to \infty$

$$H_{JT} = \lambda q \begin{pmatrix} 0 & \cos \theta \\ \cos \theta & 0 \end{pmatrix} + \lambda q \begin{pmatrix} \sin \theta & 0 \\ 0 & -\sin \theta \end{pmatrix} + Kq^2$$

2x2 matrices represent operators acting on nuclear wave functions $(\chi_x, \chi_y)$, 

$\theta$ represents frozen ($M \to \infty$) nuclear displacements.

$$H_{JT} = \lambda q \begin{pmatrix} \sin \theta & \cos \theta \\ \cos \theta & -\sin \theta \end{pmatrix} + Kq^2 := \lambda q M + Kq^2 \quad M = \begin{pmatrix} \sin \theta & \cos \theta \\ \cos \theta & -\sin \theta \end{pmatrix}$$

$$\det(M) = -(\sin \theta)^2 - (\cos \theta)^2 = -1$$

$$\text{Tr}(M) = 0$$

*M has eigenvalues $\pm 1$, independent of $\theta$. There is no preferred angle of deformation!*

$$M = +1 \quad E_{JT} = \lambda q + Kq^2 \quad \text{independent of } \theta$$

$$M = -1 \quad E_{JT} = -\lambda q + Kq^2 \quad \text{independent of } \theta$$
Here the potential energy surfaces $E(q)$ are obtained by rotating two intersecting parabolas around the energy axis.

Minimum away from $q=0$. Energy eigenvalues independent of angle, but nuclear wave function depends on angle in a special way.
Photoelectron spectroscopy and electronic structure of clusters of the group V elements. II. Tetramers: Strong Jahn–Teller coupling in the tetrahedral $^2E$ ground states of $P_4^+$, $As_4^+$, and $Sb_4^+$

Lai-Sheng Wang, B. Niu, Y. T. Lee, and D. A. Shirley
Department of Chemistry, University of California and Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

E. Ghelichkhani and E. R. Grant
Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

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FIG. 4. The normal modes of vibrations for tetrahedral $M_4$ molecules. The $x$, $y$, and $z$ axes lie along the three twofold axes.

Modes of E symmetry of tetrahedral molecules giving the wizard heat

Wizard heat $\rightarrow$ singularity

Multiply connected parameter space $\rightarrow$ Berry phase

FIG. 5. Diagram showing the adiabatic potential energy surfaces of the linear $E \otimes e$ Jahn–Teller Hamiltonian. $E(\rho, \phi)$ is plotted according to Eq. (2), for $k = 5.75$, a value deduced from spectral simulations to be that most appropriate for $P_4^+$. The floor of the potential lies at an energy of 16.5, in units of the zeroth-order harmonic frequency, below the conical intersection.
\[ H_{JT} = \lambda q \begin{pmatrix} \sin \theta & \cos \theta \\ \cos \theta & -\sin \theta \end{pmatrix} \]

\[ H_{JT} \begin{pmatrix} a(q_x, q_y) \\ b(q_x, q_y) \end{pmatrix} = E(q_x, q_y) \begin{pmatrix} a(q_x, q_y) \\ b(q_x, q_y) \end{pmatrix} \]

**Eigenvalue -1**

\[ \chi_-(\theta) = \begin{pmatrix} \cos\left(\frac{\theta}{2} + \frac{\pi}{4}\right) \\ \cos\left(\frac{\theta}{2} + \frac{\pi}{4}\right) \\ -\sin\left(\frac{\theta}{2} + \frac{\pi}{4}\right) \end{pmatrix} \]

**Eigenvalue +1**

\[ \chi_+(\theta) = \begin{pmatrix} \sin\left(\frac{\theta}{2} + \frac{\pi}{4}\right) \\ \sin\left(\frac{\theta}{2} + \frac{\pi}{4}\right) \\ \cos\left(\frac{\theta}{2} + \frac{\pi}{4}\right) \end{pmatrix} \]

This changes sign under \( \theta \rightarrow \theta + 2\pi \), which is normal for spin rotation, but wrong here.

Nuclear wave functions **must** be single-valued functions of normal coordinates!
We did an honest calculation. Why do we get a wrong result?

We can fix it, but must insert phase factors:

\[
\chi_-(\theta) = e^{\frac{i\theta}{2}} \begin{pmatrix}
\cos\left(\frac{\theta + \frac{\pi}{4}}{2}\right) \\
-\sin\left(\frac{\theta + \frac{\pi}{4}}{2}\right)
\end{pmatrix} \quad \chi_+(\theta) = e^{-\frac{i\theta}{2}} \begin{pmatrix}
\sin\left(\frac{\theta + \frac{\pi}{4}}{2}\right) \\
\cos\left(\frac{\theta + \frac{\pi}{4}}{2}\right)
\end{pmatrix}
\]

This compensates for the changed sign under \( \theta \rightarrow \theta + 2\pi \).

Nuclear wave functions are single-valued but complex.

**Berry phase!**