Molecular Born-Oppenheimer Theory as a Double Gauge Theory

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A Double Gauge Theory

Born-Oppenheimer theory of polyatomic molecules $(N \geq 3)$ contains two distinct gauge structures.

Each of these is associated with a gauge potential, a curvature form and a family of fiber bundles.

- The Coriolis or rotational gauge structure is associated with overall rotational invariance
- The Mead-Truhlar-Berry gauge structure is associated with adiabatic transport of electronic wave functions, as in Born-Oppenheimer theory

Each of these gauge structures is associated with a vector potential that appears in the kinetic energy in the Hamiltonian.

Coriolis or Rotational Gauge Structure

The Coriolis or rotational gauge structure appears in the dynamics of flexible bodies with no external torques. Applications include:

- Solar systems
- Atoms in the electrostatic model
- Molecules in the Born-Oppenheimer approximation (sort of)
- Self-gravitating, rotating fluid systems

The Coriolis gauge structure involves an $SO(3)$ vector potential $\mathbf{A}_\mu$ and a curvature form

$$\mathbf{B}_{\mu\nu} = \partial_\mu \mathbf{A}_\nu - \partial_\nu \mathbf{A}_\mu - \mathbf{A}_\mu \times \mathbf{A}_\nu .$$

The gauge group is $SO(3)$ which represents overall rotations of the system.

Meaning of Coriolis fields A_μ and $\mathrm{B}_{\mu\nu}$

Coriolis fields $\mathbf{A}_\mu$ and $\mathbf{B}_{\mu\nu}$ are fields on shape space, with coordinates q^μ (more on this in a moment).

The vector potential $\mathbf{A}_\mu$ appears as part of the kinetic energy in the Hamiltonian,

$$\frac{1}{2}(p_\mu - \mathbf{L}\cdot\mathbf{A}_\mu)\, g^{\mu\nu}\, (p_\nu - \mathbf{L}\cdot\mathbf{A}_\nu)$$

where $\mathbf{L}$ is the angular momentum of the system. The curvature $\mathbf{B}_{\mu\nu}$ appears as part of the force (the Coriolis force),

$$g_{\mu\nu}\, \ddot{q}^\nu = \mathbf{L}\cdot\mathbf{B}_{\mu\nu}\, \dot{q}^\nu + \text{other terms}$$

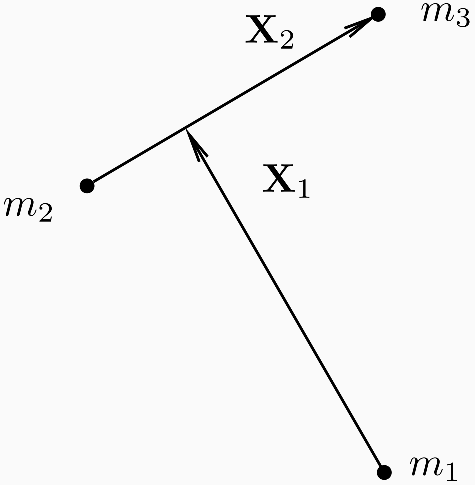
which is like a $e\mathbf{v}\times\mathbf{B}$ magnetic force.

Credits and References for Coriolis gauge theory

- A. Guichardet, Ann. Inst. H. Poincaré **40**, 329(1984).
- A. Tachibana and T. Iwai, Phys. Rev. A **33**, 2262(1986).
- T. Iwai, Ann. Inst. H. Poincaré, **47** 199(1986).
- R. Littlejohn and M. Reinsch, Rev. Mod. Phys. **69**, 213(1997).

Coriolis gauge fields are associated with a geometrical structure on the configuration space of the system that is basic for understanding the Mead-Truhlar-Berry gauge structure in molecules.

Configuration Space in Center-of-Mass Frame



For N particles the center-of-mass configuration requires $N-1$ vectors, $(\mathbf{X}_1, \ldots, \mathbf{X}_{N-1})$, for example, $(\mathbf{X}_1, \mathbf{X}_2)$ in the 3-body problem. If Jacobi vectors are chosen then the kinetic energy is diagonal,

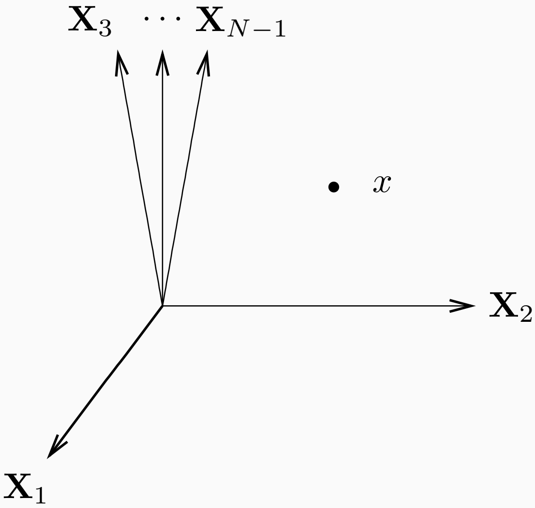
$$K = \sum_{\alpha=1}^{N-1} \frac{\mathbf{P}_\alpha^2}{2m_\alpha}$$

where m_α are reduced masses. We will use

$$x = (\mathbf{X}_1, \ldots, \mathbf{X}_{N-1})$$

for coordinates on configuration space.

Configuration Space is $\mathbb{R}^{3N-3}$



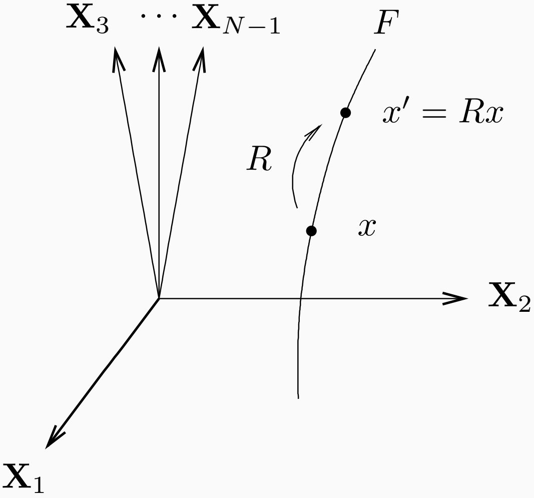
Coordinates on configuration space (CS) are the Jacobi vectors

$$x = (\mathbf{X}_1, \dots, \mathbf{X}_{N-1})$$

or x for short. Also use x for a point of CS. Topologically speaking, CS is the vector space,

$$\mathrm{CS} = \mathbb{R}^{3N-3}.$$

Action of Proper Rotations $\in SO(3)$ on Configuration Space



If $R \in SO(3)$ is a proper rotation, we define

$$Rx = (R\mathbf{X}_1, \ldots, R\mathbf{X}_{N-1}).$$

It is a rigid rotation in the center-of-mass frame. It changes the orientation but not the shape of the configuration.

The set of configurations Rx swept out as R runs over $SO(3)$ is the orbit of x under $SO(3)$. If x is noncollinear, it is also the fiber F of the Coriolis or rotational fiber bundle.

We Ignore Collinear Configurations

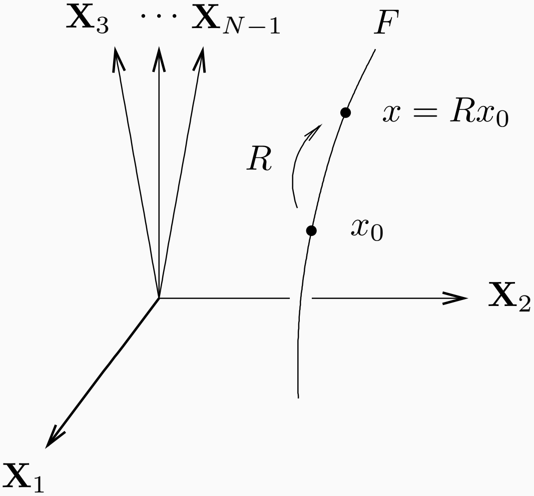
In a polyatomic molecule ($N \geq 3$) the collinear configurations form a subset of measure 0.

The Renner-Teller effect and related phenomena occur in the neighborhood of collinear configurations.

In this talk we exclude the collinear configurations from consideration. Then the orbits of the rotational action are diffeomorphic to $SO(3)$ and are 3-dimensional. These orbits are the fibers of a principal, $SO(3)$ fiber bundle (the Coriolis or rotational fiber bundle).

Collinear configurations can always be considered to be limiting cases of noncollinear configurations.

Orientational Coordinates on Single Fiber

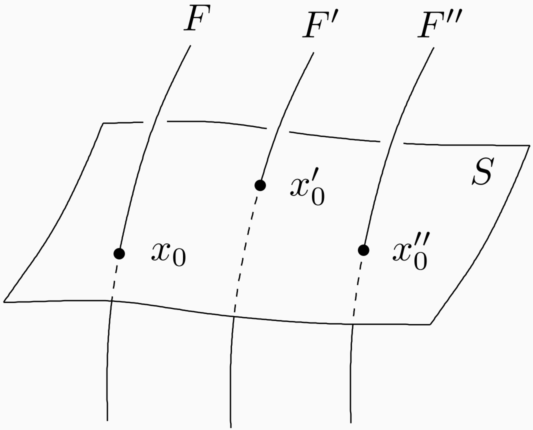


Let F be a noncollinear orbit or fiber of the rotational action. Configurations x_0 and $x = Rx_0$ have the same shape but different orientations.

If x_0 is a reference orientation then the orientation of $x = Rx_0$ is specified by $R \in SO(3)$ or its Euler angles. Thus R or its Euler angles become orientational coordinates on the fiber F.

The choice of the reference orientation x_0 on F is completely arbitrary.

Orientational Coordinates Over a Region Imply a Section



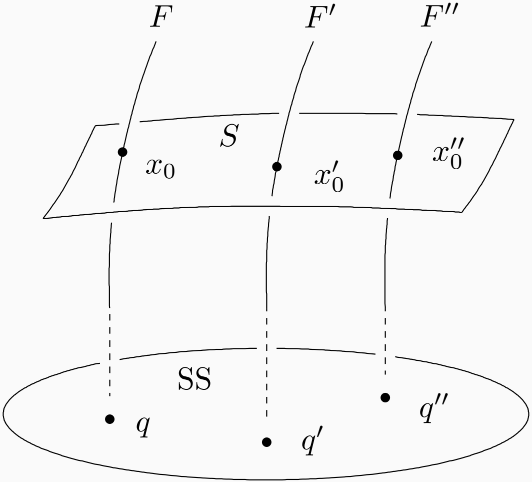
Drop the axes $\mathbf{X}_1$, $\mathbf{X}_2$, etc.

To define orientational coordinates over a region we must assign reference orientations x_0 on a family of fibers F.

We do this in a smooth manner; the reference orientations x_0 sweep out a surface S, a section of the fiber bundle.

$$\begin{aligned} \dim \mathrm{CS} &= 3N-3 \\ \dim F &= 3 \\ \dim S &= 3N-6 \end{aligned}$$

Shape Space



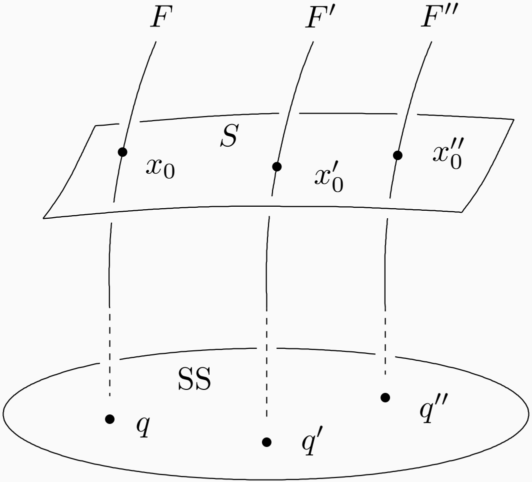
Point of shape space q represents an entire rotational fiber. Shape coordinates q^μ are coordinates of the fibers, while orientational coordinates are coordinates along the fibers.

Shape space has dimension,

$$\dim \mathrm{SS} = 3N - 6$$

Shape coordinates are q^μ, $\mu = 1, \ldots, 3N-6$.

Shape Space and Shape Coordinates



Shape space is the quotient space,

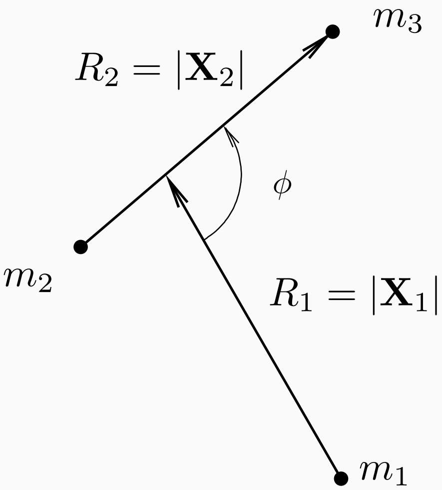
$$\text{SS} = \frac{\text{CS}}{SO(3)}$$

Shape coordinates are rotationally invariant functions of the Jacobi vectors,

$$\begin{aligned} q^\mu &= q^\mu(\mathbf{X}_1, \dots, \mathbf{X}_{N-1}) \\ &= q^\mu(x) = q^\mu(Rx), \qquad \forall R \in SO(3) \end{aligned}$$

The q^μ are functions of $\mathbf{X}_\alpha \cdot \mathbf{X}_\beta$ and $\mathbf{X}_\alpha \cdot (\mathbf{X}_\beta \times \mathbf{X}_\gamma)$.

Bond-Angle Coordinates

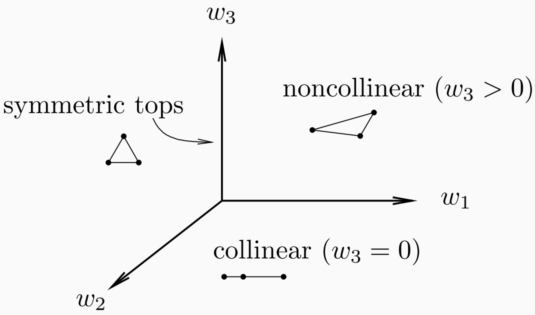


Example of shape coordinates are bond-angle coordinates,

$$q^\mu = (R_1, R_2, \phi) \tag{1}$$

in 3-body problem.

Hopf Coordinates in 3-body Problem



Hopf coordinates $q^\mu = (w_1, w_2, w_3)$,

$$\begin{aligned} w_1 &= m_1 R_1^2 - m_2 R_2^2 \\ w_2 &= 2\sqrt{m_1 m_2}\, \mathbf{X}_1 \cdot \mathbf{X}_2 \\ w_3 &= 2\sqrt{m_1 m_2}\, |\mathbf{X}_1 \times \mathbf{X}_2| \end{aligned}$$

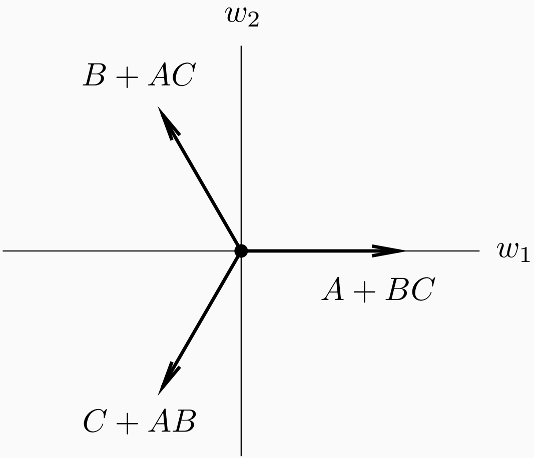
Shape space is region $w_3 \geq 0$.

$$\mathrm{SS} = (1/2) \text{ of } \mathbb{R}^3$$

Bounding plane $w_3 = 0$ consists of collinear shapes.

Region $w_3 > 0$ consists of noncollinear shapes

Collinear Configurations: w_1-w_2 Plane

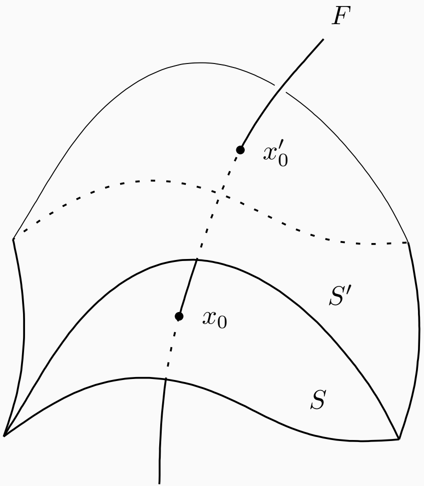


3 Radial half-lines: 2-body collisions

Also entrance and exit channels in scattering

Origin $w_1 = w_2 = 0$: 3-body collision. Monopole source of Coriolis curvature tensor $\mathbf{B}_{\mu\nu}$

Change of Section



Change of reference orientations = Change of Section $S \to S'$

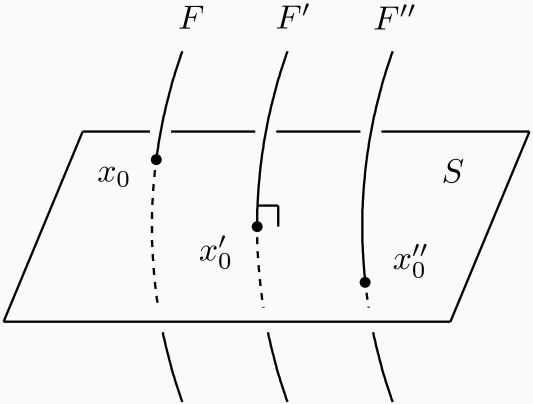
Specified by field of rotation matrices $T(q) \in SO(3)$ over shape space

Sections are highly arbitrary

Change of Section = gauge transformation

$$A_\mu \to T^{-1} A_\mu T + T^{-1} \partial_\mu T \qquad (2)$$

Requirements of a Section



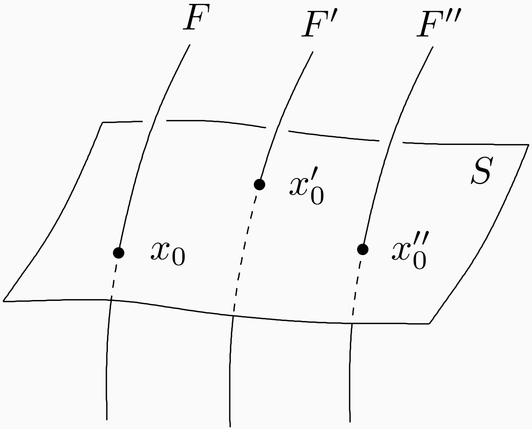
Section need only be transverse to fibers (means, not tangent)

It may be orthogonal to fibers at single point but cannot be orthogonal everywhere.

It may be chosen to be a hyperplane $(\dim = 3N - 6)$ but can be curved, too.

Eckart section is a hyperplane orthogonal to fiber at equilibrium configuration.

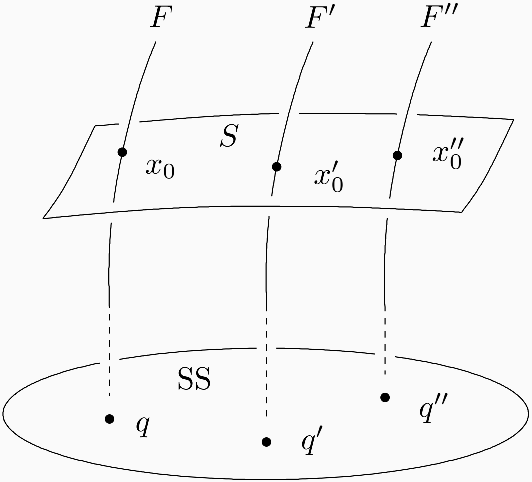
What Is a Section Good For?



A section of the rotational fiber bundle is necessary for:

- Define orientational coordinates
- Define a body frame
- Electronic structure calculations take place on a section
- Internal wave functions live on section

Section vs. Shape Space



Isn't the section just a copy of shape space???

NO: Topology: Global sections do not exist

Triviality vs nontriviality of rotational fiber bundle

Shape space is a distinct space from configuration space, not a subspace of configuration space.

Molecular and Electronic Hamiltonians; Models and Rotations

$$H_{\mathrm{mol}} = \sum_{\alpha=1}^{N-1} \frac{\mathbf{P}_\alpha^2}{2m_\alpha} + H_e(x; \mathbf{r}, \mathbf{p}, \mathbf{S})$$

where

$$x = (\mathbf{X}_1, \ldots, \mathbf{X}_{N-1}) \qquad \text{remind}$$

Use Electrostatic Model: H_e depends only on dot products:

$$\boxed{H_e(x; \mathbf{r}, \mathbf{p}) = H_e(Rx; R\mathbf{r}, R\mathbf{p})}$$

for all $R \in SO(3)$

Full molecular H_{mol} vs. electronic Hamiltonian H_e

Models for electronic Hamiltonian $H_e(x)$:

- Electrostatic, $H_e = H_e(x; \mathbf{r}, \mathbf{p})$, indep of spin
- Fine Structure, $N_e = \mathrm{even}$
- Fine Structure, $N_e = \mathrm{odd}$
- Point symmetries

Angular Momentum and Rotation Operators

Orbital angular momenta:

$$\begin{aligned} \mathbf{L}_n &= \sum_{\alpha=1}^{N-1} \mathbf{X}_\alpha \times \mathbf{P}_\alpha, \\ \mathbf{L}_e &= \sum_{\beta=1}^{N_e} \mathbf{r}_\beta \times \mathbf{p}_\beta, \end{aligned}$$

Rotation operators:

$$\begin{aligned} U_n(\hat{\mathbf{n}}, \theta) &= \exp\left(-\frac{i}{\hbar}\theta\hat{\mathbf{n}} \cdot \mathbf{L}_n\right) \\ U_e(\hat{\mathbf{n}}, \theta) &= \exp\left(-\frac{i}{\hbar}\theta\hat{\mathbf{n}} \cdot \mathbf{L}_e\right) \end{aligned}$$

- Nuclear orbital angular momentum $\mathbf{L}_n$
- Electron orbital angular momentum $\mathbf{L}_e$

Parameterize rotations in axis-angle form,

$$R(\hat{\mathbf{n}}, \theta) \in SO(3),$$

$\hat{\mathbf{n}} \in \text{unit sphere}, \ 0 \leq \theta \leq \pi.$

Parameterize rotation operators,

$$\begin{aligned} U_n(R) &= U_n(\hat{\mathbf{n}}, \theta), \\ U_e(R) &= U_e(\hat{\mathbf{n}}, \theta). \end{aligned}$$

Electronic Hamiltonian Along Rotation Fibers

Electronic rotation operators act on electronic positions and momenta,

$$\begin{array}{rcl} U_e(R)\,\mathbf{r}_\beta\,U_e(R)^\dagger & = & R^{-1}\mathbf{r}_\beta, \\ U_e(R)\,\mathbf{p}_\beta\,U_e(R)^\dagger & = & R^{-1}\mathbf{p}_\beta, \end{array}$$

therefore if we conjugate electronic Hamiltonian,

$$U_e(R)\,H_e(x;\mathbf{r},\mathbf{p})\,U_e(R)^\dagger = H_e\big(x;R^{-1}\mathbf{r},R^{-1}\mathbf{p}\big) = H_e(Rx;\mathbf{r},\mathbf{p}).$$

Simplify notation, $H_e(x;\mathbf{r},\mathbf{p}) \to H_e(x)$, then

$$\boxed{U_e(R)\,H_e(x)\,U_e(R)^\dagger = H_e\big(Rx\big).}$$

Electronic Eigenvalues and Eigenstates

Electronic Hamiltonian $H_e(x)$ has eigenvalues and eigenstates that depend on x:

- Energy eigenvalues: $\epsilon_k(x)$, $k =$ sequencing number;
- Energy eigenstates: $|x;k\rangle$

That is

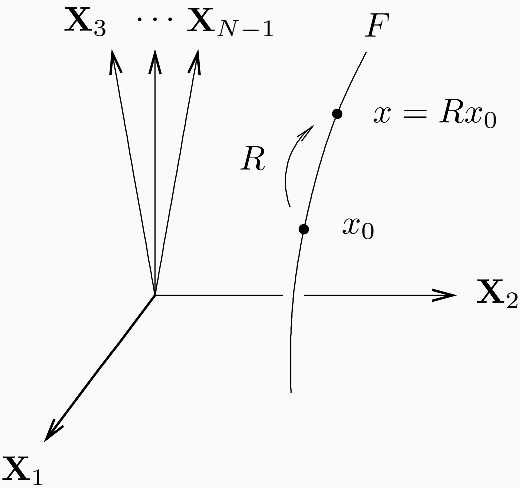
$$H_e(x)\,|x;k\rangle = \epsilon_k(x)\,|x;k\rangle$$

Cases:

- If nondegenerate $|x;k\rangle$ only determined to within a phase, and $k = k_0$
- If degenerate $|x;k\rangle$ only determined to within a choice of frame in degenerate eigenspace, and $k = k_0, k_0+1, \ldots, k_0+n-1$

Usually $k_0 =$ ground state. Problem of phase and frame conventions (same thing).

Frame Conventions Along a Rotational Fiber



Choose frame conventions $|x_0; k\rangle$ at reference x_0. Define at $x = Rx_0$:

$$\begin{aligned} H_e(x_0)\,|x_0; k\rangle &= \epsilon_k(x_0)\,|x_0; k\rangle \\ |x; k\rangle &= U_e(R)\,|x_0; k\rangle \end{aligned}$$

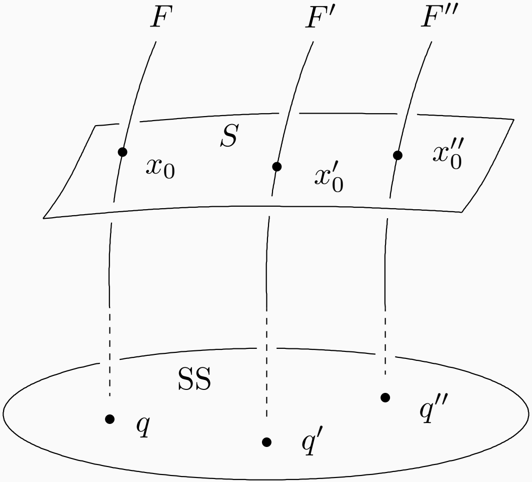
Then $|x; k\rangle$ actually are energy eigenstates at x:

$$H_e(x)\,|x; k\rangle = \epsilon_k(x_0)\,|x; k\rangle$$

but notice, with eigenvalue at x_0. Thus

$$\epsilon_k(x) = \epsilon_k(Rx_0) = \epsilon_k(x_0).$$

Energy Eigenvalues are Functions on Shape Space



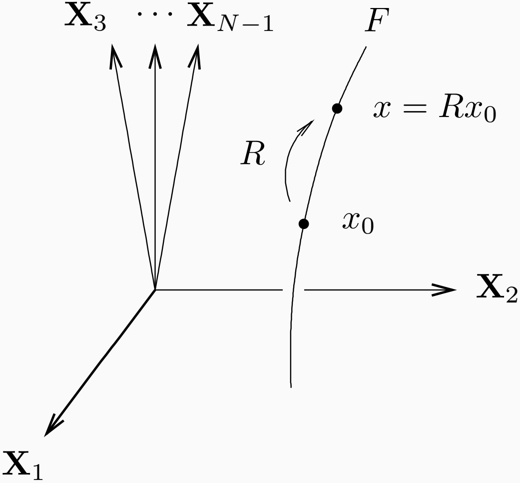
Since

$$\epsilon_k(x) = \epsilon_k(Rx_0) = \epsilon_k(x_0).$$

energy eigenvalues $\epsilon_k(x)$ are constant along rotational fibers. They are functions on shape space:

$$\epsilon_k = \epsilon_k(q)$$

Energy Eigenfunctions Depend on Orientation



We have defined

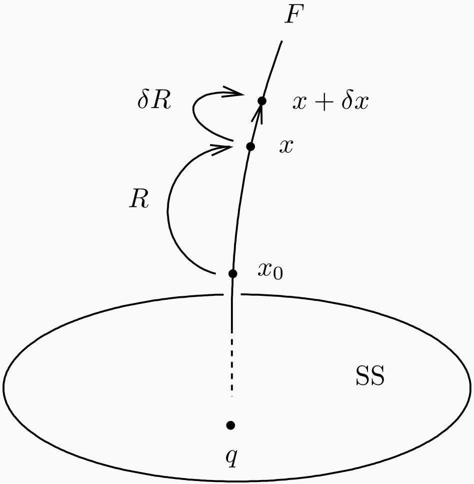
$$|x; k\rangle = |Rx_0; k\rangle = U_e(R)\,|x_0; k\rangle$$

This implies

$$\boxed{|Rx; k\rangle = U_e(R)\,|x; k\rangle}$$

(any x, not just x_0).

Now Let $R \to \delta R =$ infinitesimal



If $\theta \ll 1$,

$$\begin{aligned} R(\hat{\mathbf{n}}, \theta) &= I + \theta \hat{\mathbf{n}} \times \\ U_e(R) &= 1 - \frac{i}{\hbar} \theta \hat{\mathbf{n}} \cdot \mathbf{L}_e \end{aligned}$$

so

$$\begin{aligned} \sum_{\alpha=1}^{N-1} \hat{\mathbf{n}} \cdot \left(\mathbf{X}_\alpha \times \frac{\partial}{\partial \mathbf{X}_\alpha} \right) |x; k\rangle \\ = -\frac{i}{\hbar} (\hat{\mathbf{n}} \cdot \mathbf{L}_e) |x; k\rangle \end{aligned}$$

or

$$\boxed{(\mathbf{L}_n + \mathbf{L}_e)|x; k\rangle = 0}$$

Three Hilbert Spaces

Ignore spin.

Electronic Hilbert space:

$$\phi(\mathbf{r}), \qquad \mathbf{r} = (\mathbf{r}_1, \dots, \mathbf{r}_{N_e}),$$

Nuclear Hilbert space:

$$\psi(x), \qquad x = (\mathbf{X}_1, \dots, \mathbf{X}_{N-1}),$$

Molecular Hilbert space:

$$\Psi(x, \mathbf{r})$$

And hybrid things:

$$|x; k\rangle \longleftrightarrow \phi_k(x; \mathbf{r}).$$

And so we understand $(\mathbf{L}_n + \mathbf{L}_e)\,|x; k\rangle = 0$.

Born-Oppenheimer Representation

Expand molecular wave function

$$\Psi(x,\mathbf{r}) = \sum_k \psi_k(x)\,\phi_k(x;\mathbf{r})$$

We say, $\psi_k(x)$ is the "Born-Oppenheimer representation" of $\Psi(x,\mathbf{r})$. Likewise with operators. Let A be an operator on molecular Hilbert space,

$$\Psi'(x,\mathbf{r}) = (A\Psi)(x,\mathbf{r})$$

Then A corresponds to a matrix A_{kl} of operators on the nuclear Hilbert space,

$$\psi'_k(x) = \sum_l (A_{kl}\,\psi_l)(x)$$

that is,

$$\boxed{\Psi(x,\mathbf{r}) \longleftrightarrow \psi_k(x)} \qquad \text{and} \qquad \boxed{A \longleftrightarrow A_{kl}}$$

Examples of Operators in BO Representation

If A is a function of the nuclear coordinates,

$$A = f(x) \longleftrightarrow A_{kl} = f(x)\,\delta_{kl}$$

In particular, this applies when $A = \mathbf{X}_\alpha$.

If A is a nuclear momentum $\mathbf{P}_\alpha = -i\hbar\nabla_\alpha = -i\hbar\,\partial/\partial\mathbf{X}_\alpha$,

$$\boxed{\mathbf{P}_\alpha \longleftrightarrow \mathbf{P}_\alpha\,\delta_{kl} - i\hbar\,\mathbf{F}_{\alpha,kl}}$$

where

$$\boxed{\mathbf{F}_{\alpha,kl} = \langle x;k|\nabla_\alpha|x;l\rangle}$$

is the Mead-Truhlar-Berry connection aka derivative couplings.

Purely Electronic Operators in BO Representation

Case $A =$ purely electronic operator, e.g., $A = \mathbf{L}_e$:

$$\mathbf{L}_e \longleftrightarrow \langle x; k|\mathbf{L}_e|x; l\rangle$$

Becomes a matrix of multiplicative operators in the BO representation.

Another example, the electronic Hamiltonian:

$$H_e(x) \longleftrightarrow \langle x; k|H_e(x)|x; l\rangle = \epsilon_k(x)\,\delta_{kl}$$

Becomes the (diagonal) potential energy in the BO representation.

Molecular Hamiltonian and the Born-Oppenheimer Approximation

Molecular Hamiltonian,

$$H_{\mathrm{mol}} = \sum_{\alpha=1}^{N-1} \frac{\mathbf{P}_\alpha^2}{2m_\alpha} + H_e(x)$$

becomes

$$H_{\mathrm{mol},kl} = \sum_{\alpha=1}^{N-1} \left[\frac{1}{2m_\alpha} \sum_m (\mathbf{P}_\alpha \, \delta_{km} - i\hbar \, \mathbf{F}_{\alpha,km}) \cdot (\mathbf{P}_\alpha \, \delta_{ml} - i\hbar \, \mathbf{F}_{\alpha,ml}) \right] + \epsilon_k(x) \, \delta_{kl}$$

Derivative couplings $\mathbf{F}_{\alpha,kl}$ are small, they vanish on the diagonal $F_{\alpha,kk} = 0$, and they couple the energy levels together. If we neglect them the energy levels decouple,

$$H_{\mathrm{mol},kk} = \sum_{\alpha=1}^{N-1} \frac{\mathbf{P}_\alpha^2}{2m_\alpha} + \epsilon_k(x),$$

which is usually called the Born-Oppenheimer approximation. It looks like a Hamiltonian on the nuclear Hilbert space.

About the Born-Oppenheimer Hamiltonian

The Hamiltonian in the Born-Oppenheimer approximation,

$$H_{\mathrm{mol},kk} = \sum_{\alpha=1}^{N-1} \frac{\mathbf{P}_\alpha^2}{2m_\alpha} + \epsilon_k(x),$$

has many defects:

- It is not valid where energy levels $\epsilon_k(x)$ come close together
- Otherwise it is valid on simply connected regions but not others

It possesses rotational invariance, since

$$\epsilon_k(x) = \epsilon_k(Rx), \qquad \forall R \in SO(3)$$

therefore it commutes with

$$\mathbf{L}_n = \sum_{\alpha=1}^{N-1} \mathbf{X}_\alpha \times \mathbf{P}_\alpha$$

Angular Momentum in BO Approximation

BO Hamiltonian commutes with $\mathbf{L}_n$, the nuclear orbital angular momentum. Eigenstates can be labeled by (L, M) quantum numbers, referring to $\mathbf{L}_n$.

But $\mathbf{L}_n$ is not a good quantum number of the exact, molecular Hamiltonian. The latter commutes with the total orbital angular momentum,

$$\mathbf{L} = \mathbf{L}_n + \mathbf{L}_e$$

that is, including the electronic angular momentum, where

$$\mathbf{L}_e = \sum_{\beta=1}^{N_e} \mathbf{r}_\beta \times \mathbf{p}_\beta .$$

Has the Born-Oppenheimer approximation replaced one exact conservation law with a different one? How do we interpret this physically?

Molecular Representation vs. BO Representation of Angular Momentum

Convert $\mathbf{L} = \mathbf{L}_n + \mathbf{L}_e$ from molecular representation to BO representation,

$$\begin{aligned}
(\mathbf{L}_n + \mathbf{L}_e)\Psi(x,\mathbf{r}) &= (\mathbf{L}_n + \mathbf{L}_e)\sum_k \psi_k(x)\,\phi_k(x;\mathbf{r}) \\
&= \sum_k [(\mathbf{L}_n + \mathbf{L}_e)\psi_k](x)\,\phi_k(x,\mathbf{r}) + \sum_k \psi_k(x)[(\mathbf{L}_n + \mathbf{L}_e)\phi_k](x,\mathbf{r}) \\
&= \sum_k (\mathbf{L}_n\psi_k)(x)\,\phi_k(x,\mathbf{r})
\end{aligned}$$

because of our phase conventions. In other words,

$$\boxed{\mathbf{L}_n + \mathbf{L}_e \longleftrightarrow \mathbf{L}_n\,\delta_{kl}}$$

What appears to be the nuclear orbital angular momentum in the BO representation is actually the total orbital angular momentum (including the electrons). This is exact.

Other Molecular Models

If fine structure effects are included in $H_e(x)$ and the number of electrons is even, then

$$\mathbf{J} = \mathbf{L}_n + \mathbf{L}_e + \mathbf{S} \longleftrightarrow \mathbf{L}_n \, \delta_{kl}$$

while if the number of electrons is odd, then

$$\mathbf{J} = \mathbf{L}_n + \mathbf{L}_e + \mathbf{S} \longleftrightarrow (\mathbf{L}_n + \mathbf{K})\delta_{kl}$$

where $\mathbf{K}$ is the spin operator of a pseudo particle of spin–$1/2$ moving on the BO surface, associated with the Kramers doublet. All these results are exact.

I cannot find any acknowledgement of these facts in the chemical literature, or anyone who knows about them. Yet they are fundamental to the physical interpretation of the BO solutions.

What About the BO Approximation?

Return to exact molecular Hamiltonian in BO representation,

$$H_{\mathrm{mol},kl} = \sum_{\alpha=1}^{N-1} \left[\frac{1}{2m_\alpha} \sum_m (\mathbf{P}_\alpha\, \delta_{km} - i\hbar\, \mathbf{F}_{\alpha,km}) \cdot (\mathbf{P}_\alpha\, \delta_{ml} - i\hbar\, \mathbf{F}_{\alpha,ml}) \right] + \epsilon_k(x)\, \delta_{kl}$$

Instead of throwing away off-diagonal terms, better to transform them away.

$$\begin{aligned} \psi' &= e^S\, \psi, \\ H' &= e^S\, H\, e^{-S} = H + [S,H] + \frac{1}{2}[S,[S,H]] + \ldots, \end{aligned}$$

$S =$ anti-Hermitian, $e^S =$ unitary. That is,

$$\begin{aligned} \psi'_k &= \sum_l (e^S)_{kl}\, \psi_l, \\ H'_{kl} &= \sum_{mn} (e^S)_{km}\, H_{mn}\, (e^{-S})_{nl}, \end{aligned}$$

and choose S to eliminate off-diagonal terms.

New View of Born-Oppenheimer Approximation

Then "Born-Oppenheimer approximation" is replaced by sequence of unitary transformations that are exact in the sense of formal power series.

This applies to large amplitude motions, not just in neighborhood of equilibrium.

Series is in $\kappa^2 = (m/M)^{1/2}$. Use Weyl symbol calculus and Moyal product rule to expand commutators (a semiclassical method). Credits:

- S. Weigert and R. Littlejohn, Phys. Rev. A**47**, 3506(1993).
- G. Panati, H. Spohn and S. Teufel, Phys. Rev. Lett. **88**, 250405(2002).
- S. Teufel, *Adiabatic Perturbation Theory* (Springer-Verlag, Berlin, 2003).

Consequence of Moyal-Born-Oppenheimer Expansion

In the "Born-Oppenheimer Approximation" operators such as the nominal nuclear positions $\mathbf{X}_\alpha$ are actually dressed variables

$$e^S\,\mathbf{X}_\alpha\,e^{-S} \qquad \text{not} \qquad \mathbf{X}_\alpha$$

and $|\psi(x)|^2$ is not the probability density for nuclear positions (not exactly).

The transformation gives rise to an extra term at second order,

$$H_{2,kk} = \sum_{l\neq k}\sum_{\alpha\beta}\frac{1}{m_\alpha m_\beta}\frac{(\mathbf{P}_\alpha\cdot\mathbf{F}_{\alpha,kl})\cdot(\mathbf{P}_\beta\cdot\mathbf{F}_{\beta,lk})}{\epsilon_k(x)-\epsilon_l(x)}$$

Small but same order as terms routinely retained.

Credits for Extra Term

- J. Moody, A. Shapere and F. Wilczek, ”Adiabatic Effective Lagrangians” in *Geometric Phases in Physics*, p. 160 (World Scientific, Singapore, 1989).
- S. Weigert and R. Littlejohn, Phys. Rev. A**47**, 3506(1993).
- A. S. Goldhaber, Phys. Rev. A **71**, 062102(2005).

Angular Momentum in the Moyal-Born-Oppenheimer Expansion

If we dress the angular momentum, we get

$$\mathbf{L}_n \to e^S\, \mathbf{L}_n\, e^{-S} = \mathbf{L}_n + [S, \mathbf{L}_n] + \frac{1}{2}[S, [S, \mathbf{L}_n]] + \dots \tag{3}$$

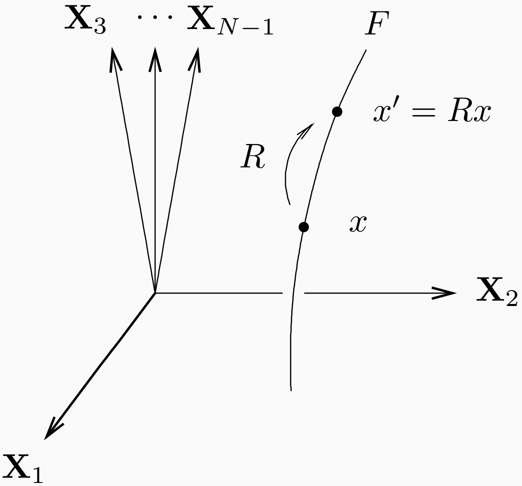
But the generator S is rotationally invariant, so $[S, \mathbf{L}_n] = 0$. Thus, the dressed value of $\mathbf{L}_n$ is the same as $\mathbf{L}_n$, and

$$\boxed{\mathbf{L}_n + \mathbf{L}_e \longleftrightarrow \mathbf{L}_n\, \delta_{kl}}$$

is valid to all orders of the Moyal-Born-Oppenheimer perturbation theory.

The Hamiltonian may not be exact in Born-Oppenheimer theory, but the angular momentum is, and it includes the electronic angular momentum.

Mead-Truhlar-Berry Connection Along Rotation Fibers



MTB Gauge Potential:

$$\mathbf{F}_{\alpha,kl}(x) = \langle x; k|\nabla_\alpha|x; l\rangle$$

Transformation property of basis states along rotational fibers:

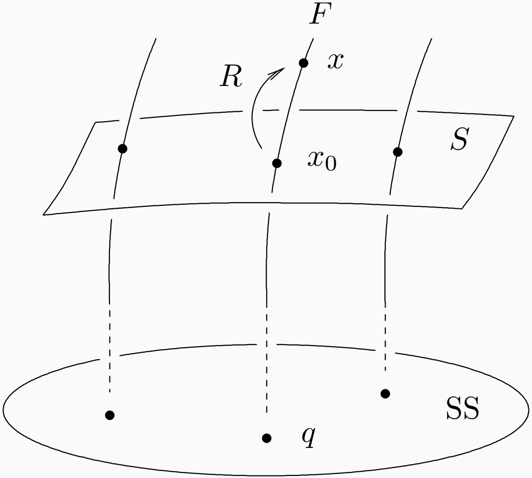
$$|Rx; k\rangle = U_e(R)\,|x; k\rangle$$

implies transformation of MTB gauge potential

$$\mathbf{F}_{\alpha,kl}(Rx) = R\mathbf{F}_{\alpha,kl}(x)$$

If $\mathbf{F}_\alpha$ is known on section, it is known everywhere.

Shape and Orientational Coordinates



A coordinate transformation:

$$x = (\mathbf{X}_1, \ldots, \mathbf{X}_{N-1}) \to (q^\mu, \theta^i)$$

where θ^i, $i = 1, 2, 3$ are Euler angles.

Define the section:

$$\mathbf{X}_{b\alpha} = \mathbf{X}_{b\alpha}(q)$$

where b means "body frame", so

$$\mathbf{X}_\alpha(q, \theta) = R(\theta)\mathbf{X}_{b\alpha}(q).$$

Transforming the Hamiltonian

Hamiltonian in Born-Oppenheimer approximation (single surface):

$$H = \sum_{\alpha=1}^{N-1} \frac{\mathbf{P}_\alpha^2}{2m_\alpha} + V(x),$$

(with defects) where $V(x) = \epsilon_k(x)$. After transformation:

$$\begin{aligned} H &= \frac{1}{2}\mathbf{L} \cdot M^{-1}(q) \cdot \mathbf{L} \\ &+ \frac{1}{2}(p_\mu - \mathbf{L} \cdot \mathbf{A}_\mu)\, g^{\mu\nu}\, (p_\nu - \mathbf{L} \cdot \mathbf{A}_\nu) \\ &+ \hbar^2 V_2(q) + V(q) \end{aligned}$$

(vertical, horizontal, potential terms).

Horizontal and Vertical Kinetic Energies

Vertical kinetic energy:

$$\frac{1}{2}\mathbf{L} \cdot M^{-1}(q) \cdot \mathbf{L}$$

where $M(q) =$ moment of inertia tensor (in body frame) and $\mathbf{L} =$ angular momentum (in body frame). Horizontal kinetic energy:

$$\frac{1}{2}(p_\mu - \mathbf{L} \cdot \mathbf{A}_\mu)\, g^{\mu\nu}\, (p_\nu - \mathbf{L} \cdot \mathbf{A}_\nu)$$

where $p_\mu = -i\hbar\, \partial/\partial q^\mu$ and $\mathbf{A}_\mu =$ Coriolis gauge potential:

$$\mathbf{A}_\mu(q) = M^{-1}(q) \sum_\alpha m_\alpha\, \mathbf{X}_{b\alpha}(q) \times \frac{\partial \mathbf{X}_{b\alpha}}{\partial q^\mu}$$

and where $g^{\mu\nu}$ is metric on shape space.

Including the MTB Vector Potential

But if we do it right the Hamiltonian is

$$H_{kl} = \sum_{\alpha=1}^{N-1} \left[\frac{1}{2m_\alpha} \sum_m (\mathbf{P}_\alpha \, \delta_{km} - i\hbar \, \mathbf{F}_{\alpha,km}) \cdot (\mathbf{P}_\alpha \, \delta_{ml} - i\hbar \, \mathbf{F}_{\alpha,ml}) \right] + V_{kl}(x)$$

for coupled states (diabatic basis). Shape and orientational coordinates for this?

Will need horizontal and vertical components of MTB connection (a differential form).

$$\begin{aligned} \mathbf{F}^v &= \sum_\alpha \mathbf{X}_\alpha \times \mathbf{F}_\alpha, \\ F^h_\mu &= \sum_\alpha \mathbf{X}_{\alpha;\mu} \cdot \mathbf{F}_\alpha. \end{aligned}$$

where

$$\mathbf{X}_{\alpha;\mu} = \frac{\partial \mathbf{X}_\alpha}{\partial q^\mu} - \mathbf{A}_\mu \times \mathbf{X}_\alpha$$

(a covariant derivative). Symbol F really means a matrix F_{kl}.

The Vertical Kinetic Energy

What happens to the internal Hamiltonian? Vertical KE first.

$$\frac{1}{2}\mathbf{L}\cdot M^{-1}(q)\cdot\mathbf{L}\rightarrow\frac{1}{2}(\mathbf{L}-i\hbar\mathbf{F}^{v})\cdot M^{-1}(q)\cdot(\mathbf{L}-i\hbar\mathbf{F}^{v})$$

angular momentum gets correction term,

$$i\hbar\,\mathbf{F}^{v}_{kl}=i\hbar\sum_{\alpha}\mathbf{X}_{\alpha}\times\langle x;k|\nabla_{\alpha}|x;l\rangle=-\langle x;k|\mathbf{L}_{n}|x;l\rangle=+\langle x;k|\mathbf{L}_{e}|x;l\rangle$$

So the correction term is the electronic angular momentum; and note that $\mathbf{L}-\mathbf{L}_e$ is the nuclear orbital angular momentum, so we get

$$\frac{1}{2}(\mathbf{L}-\mathbf{L}_{e})\cdot M^{-1}(q)\cdot(\mathbf{L}-\mathbf{L}_{e})$$

Next, Horizontal Kinetic Energy

This is

$$\frac{1}{2}(p_\mu - \mathbf{L}\cdot\mathbf{A}_\mu)\, g^{\mu\nu}\,(p_\nu - \mathbf{L}\cdot\mathbf{A}_\nu)$$

which becomes

$$\frac{1}{2}(p_\mu - \mathbf{L}\cdot\mathbf{A}_\mu - i\hbar\, F^h_\mu)\, g^{\mu\nu}\,(p_\nu - \mathbf{L}\cdot\mathbf{A}_\nu - i\hbar\, F^h_\mu)$$

Shape derivative $p_\mu = -i\hbar\,\partial/\partial q^\mu$ gets corrected to gauge-invariant covariant derivative by extra term F^h_μ.

The End

THE END