Introduction to Molecular Geometric Phase

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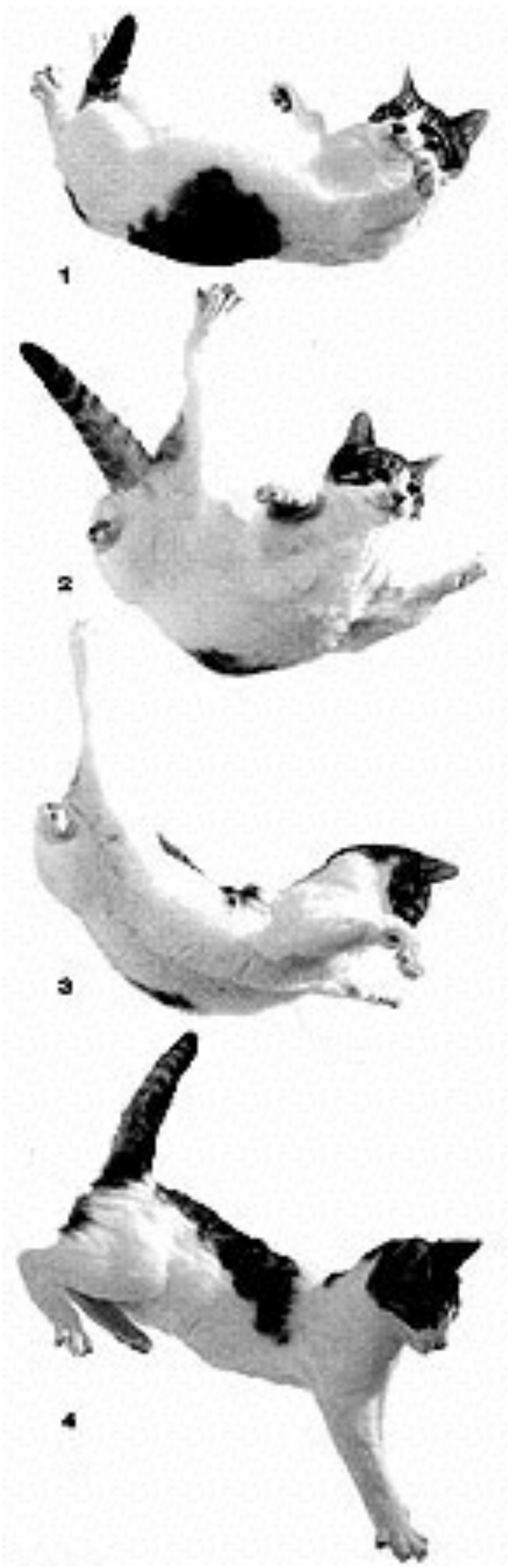
Outline

- I. Geometric phases in action
    - A. Falling cats
    - B. Floppy molecules
- II. Berry phase
    - A. General theory
    - B. Observing the Berry phase
    - C. Generalizations
- III. Molecular geometric phase — Born-Oppenheimer approximation
    - A. Example: $E \otimes e$ Jahn-Teller model
    - B. Experimental observations
- IV. Molecular geometric phase — beyond Born-Oppenheimer approx
    - A. Exact factorization scheme
    - B. Exact molecular geometric phase
    - C. Example: pseudorotation triatomic molecule
    - D. Experimental observation through Ham reduction factors

Geometric phases in action

Example 1: Falling cats



Cats achieve a net rotation by deforming their bodies through a sequence of shapes.

The sequence traces out a closed path in the space of all possible "cat shapes."

Due to the nonholonomic geometry of this path, the final orientation of the cat differs from the initial one by a net rotation angle called an *anholonomy*.

The effect can be described by a gauge theory where the base space is the space of "cat shapes" and the gauge group is SO(3) - the group of rigid rotations in 3D.*

*R. Montgomery, Fields Inst. Commun. 1, 193-218 (1993)

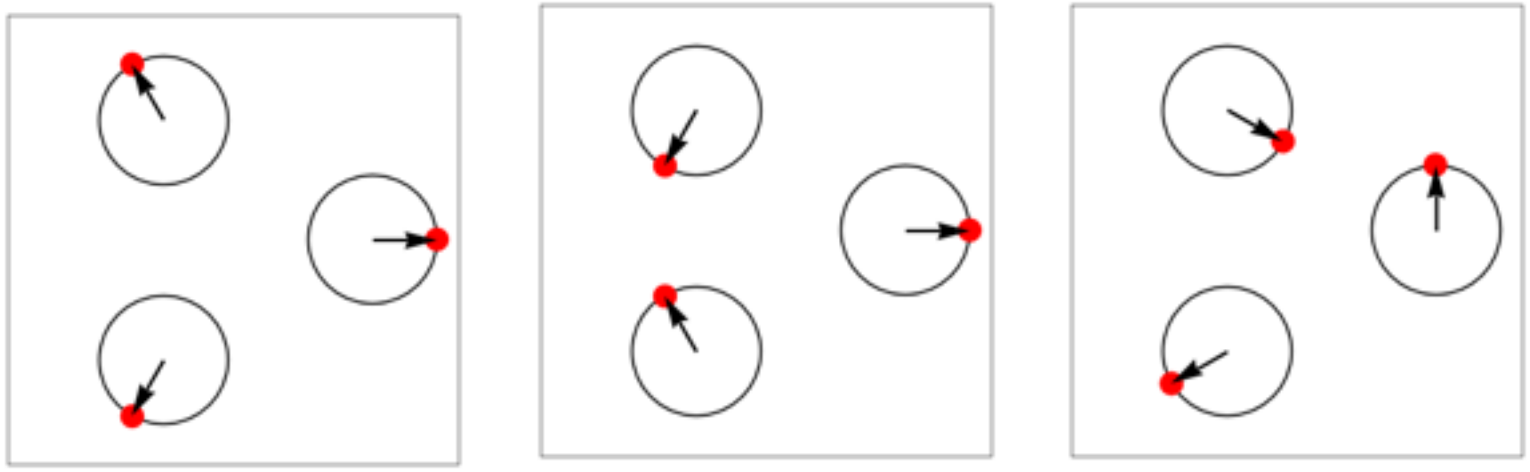
Geometric phases in action

Example 2: Floppy molecules

Like the cat, a molecule can go through a sequence of distortions. This is called a *pseudorotation* when it does not lead to an overall rotation of the molecule.

Instead, the anholonomy occurs for an “internal” degree of freedom, namely the nodal plane of the electronic wavefunction [Longuet-Higgins 1961].

normal mode coordinates (Q_1, Q_x, Q_y)

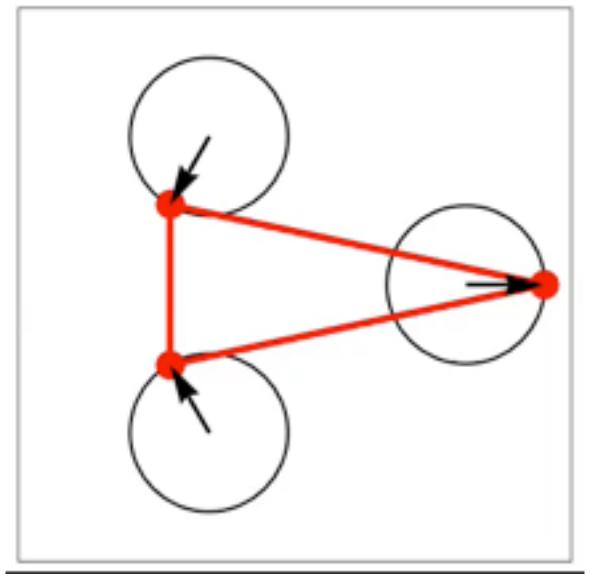


$Q_1 =$ symmetric breathing

$Q_x =$ symmetric bending

$Q_y =$ asymmetric bending

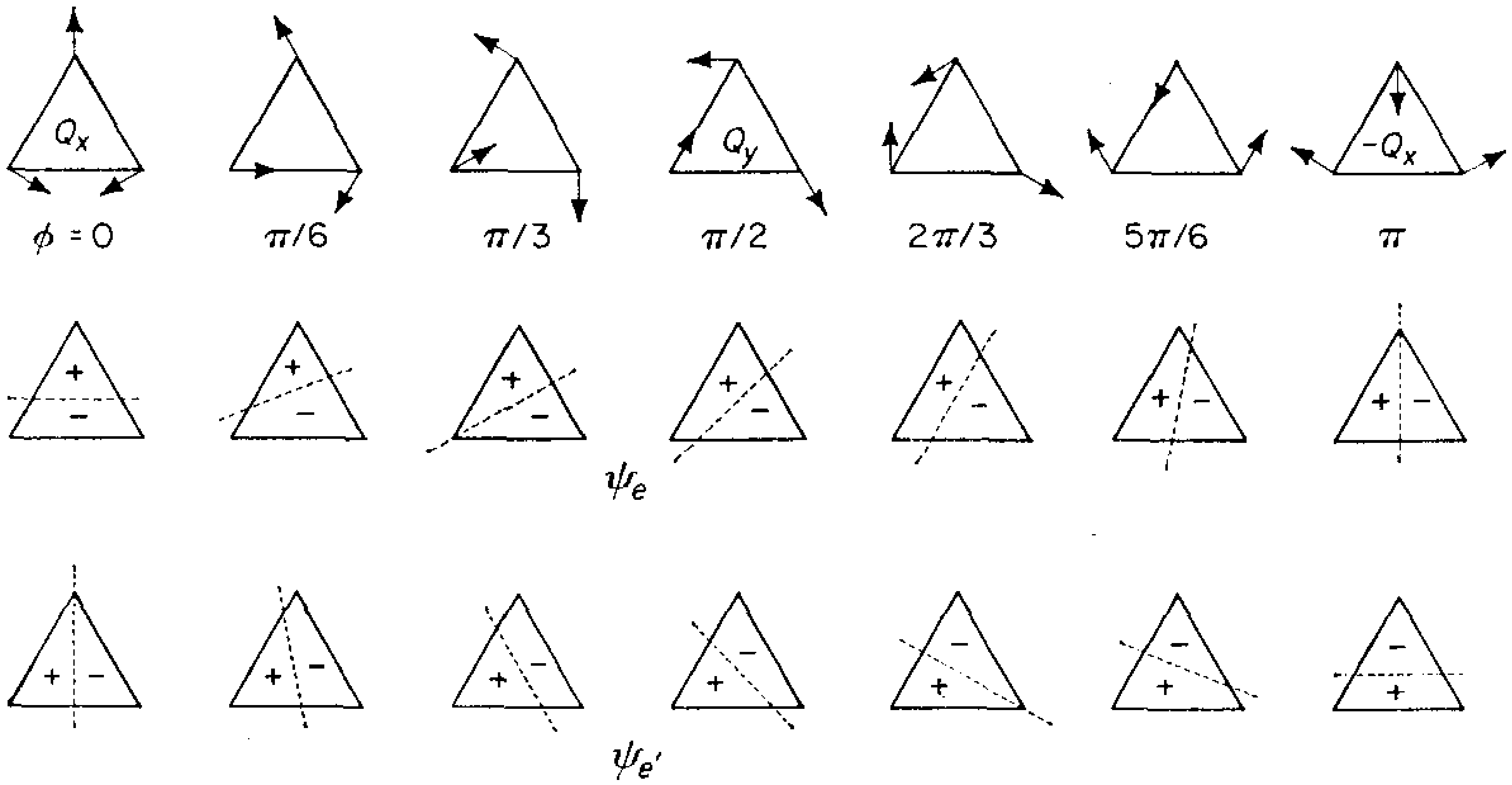
pseudorotation



Geometric phases in action

Example 2: Floppy molecules

$Q_x = Q\cos\eta \qquad Q_y = Q\sin\eta$



Longuet-Higgins, Adv. Spectrosc. 2, 429 (1961)

General theory of the Berry phase

in adiabatically-driven closed quantum systems

Suppose we are given a Hamiltonian $H(\mathbf{R})$ depending parametrically on a set of variables $\mathbf{R} = (R_1, R_2, \ldots, R_n)$. Consider a closed path $\mathbf{R}(t)$.

$$i\frac{d}{dt}|\psi(t)\rangle = H(\mathbf{R})|\psi(t)\rangle \qquad |\psi(0)\rangle = |n(\mathbf{R}(0))\rangle$$

$$H(\mathbf{R})|n(\mathbf{R})\rangle = E_n(\mathbf{R})|n(\mathbf{R})\rangle$$

Adiabatic theorem implies

$$|\psi(t)\rangle = \underline{e^{-i\int_0^t E_n(\mathbf{R}(s))ds}}\,\underline{e^{i\gamma_n(t)}}|n(\mathbf{R}(t))\rangle + \text{small corrections}$$

dynamical phase factor $= e^{-i\int_0^t E_n(\mathbf{R}(s))ds}$

Berry phase factor $= e^{i\gamma_n(t)}$

M. V. Berry, Proc. R. Soc. Lond. A, 392, 45 (1984)

General theory of the Berry phase

in adiabatically-driven closed quantum systems

$$|\psi(t)\rangle = \underline{e^{-i\int_0^t E_n(\mathbf{R}(s))ds}}\,\underline{e^{i\gamma_n(t)}}\,|n(\mathbf{R}(t))\rangle + \text{small corrections}$$

dynamical phase factor $= e^{-i\int_0^t E_n(\mathbf{R}(s))ds}$

Berry phase factor $= e^{i\gamma_n(t)}$

$$\frac{d\gamma_n(t)}{dt} = i\langle n(\mathbf{R})|\nabla_{\mathbf{R}} n(\mathbf{R})\rangle \cdot \frac{d\mathbf{R}}{dt}$$

$$\boxed{\gamma_n(C) = i\oint_C \langle n(\mathbf{R})|\nabla_{\mathbf{R}} n(\mathbf{R})\rangle \cdot d\mathbf{R}}$$

if $n(\mathbf{R})$ is single-valued on the closed path C

M. V. Berry, Proc. R. Soc. Lond. A, 392, 45 (1984)

General theory of the Berry phase

generalized Stokes's theorem

$$\gamma_n(C) = -\oint_C \mathbf{A}_n \cdot d\mathbf{R}$$

$C =$ closed path

$$= -\iint_S \mathbf{B}_n(\mathbf{R}) \cdot d\mathbf{S}$$

$S =$ surface bounded by C

effective vector potential

$$\mathbf{A}_n(\mathbf{R}) = \mathrm{Im}\langle n(\mathbf{R})|\nabla n(\mathbf{R})\rangle$$

("Berry connection")

effective magnetic field

$$\mathbf{B}_n(\mathbf{R}) = \nabla \times \mathbf{A}_n(\mathbf{R})$$

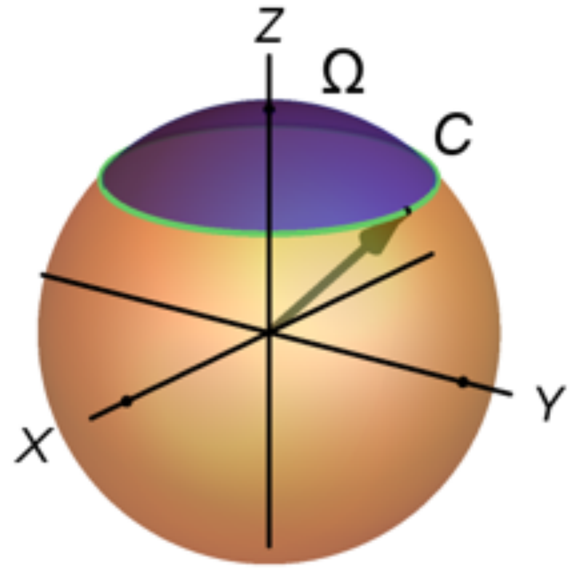
$$= \mathrm{Im} \sum_{m\neq n} \frac{\langle n|\nabla H|m\rangle \times \langle m|\nabla H|n\rangle}{(E_m - E_n)^2}$$

Example: two-level system

$\gamma_n(C) =$ flux of $\mathbf{B}_n(\mathbf{R})$

$$H(\mathbf{R}) = \frac{1}{2}\begin{pmatrix} Z & X - iY \\ X + iY & -Z \end{pmatrix}$$

$$\mathbf{B}_\pm(\mathbf{R}) = \pm\frac{1}{2}\frac{\mathbf{R}}{|\mathbf{R}|^3}$$



$$\boxed{\gamma_\pm(C) = \mp\Omega(C)/2}$$

$\Omega(C) =$ solid angle subtended by C

M. V. Berry, Proc. R. Soc. Lond. A, 392, 45 (1984)

Properties of the Berry phase

$$\gamma_n(C) = i \oint_C \langle n(\mathbf{R}) | \nabla_{\mathbf{R}} n(\mathbf{R}) \rangle \cdot d\mathbf{R}$$

- Path dependent: depends on the *history* of the dynamics
- Gauge invariant. $\gamma(C)$ is invariant to the gauge transformation
  $$|n(\mathbf{R})\rangle \to e^{i\lambda(\mathbf{R})}|n(\mathbf{R})\rangle \quad \Rightarrow \quad i\langle n(\mathbf{R})|\nabla n(\mathbf{R})\rangle \to i\langle n(\mathbf{R})|\nabla n(\mathbf{R})\rangle - \nabla\lambda(\mathbf{R})$$
- $\gamma(C)$ can be interpreted as the flux of an effective (induced) magnetic field
- Mathematically, it is the holonomy of $U(1)$ fiber bundle over parameter space; the adiabatic theorem defines the parallel-transport Berry connection [Simon PRL 51, 2167 1983].

Observing the Berry phase

Berry phases can be observed in several ways.

They are observable as shifts in the interference fringes in experiments involving superpositions of multiple pathways.

$$|\Psi\rangle = c_1 e^{-i\gamma_1}|1\rangle + c_2 e^{-i\gamma_2}|2\rangle$$

$$\langle\Psi|\hat{\mathcal{O}}|\Psi\rangle = |c_1|^2\langle 1|\hat{\mathcal{O}}|1\rangle + |c_2|^2\langle 2|\hat{\mathcal{O}}|2\rangle + 2\mathrm{Re}[c_1 c_2^* e^{i(\gamma_1-\gamma_2)}\langle 1|\hat{\mathcal{O}}|2\rangle]$$

They modify the energy spectrum as observed in vibrational spectroscopy [von Busch, *et al.*, PRL 81, 4585 (1998)].

Generalizations of the Berry phase

- Open-path geometric phase
  [Samuel Bandari PRL 60, 2339 (1988); Mukunda Simon Ann. Phys. 228, 269 (1993)]

- Non-adiabatic geometric phase
  Aharonov-Anandon phase [PRL 58, 1593 (1987)]

- Non-Abelian geometric phase $U(1) \to U(N)$
  [Wilczek Zee PRL 52, 2111 (1984)]

- Geometric phase of Bloch functions in the Brillouin zone
  [Thouless *et al* PRL 49, 405 (1982); Zak PRL 62, 2747 (1989); King-Smith Vanderbilt PRB 47, 1651 (1993)]

- Molecular geometric phase
  [Longuet-Higgins et al. Proc. R. Soc. London, Ser. A 244, 1 (1958); Gidopoulos Gross Phil. Trans. Roy. Soc. A 372, 20130059 (2014); Min Abedi Kim Gross PRL 113, 263004 (2014); RR Tandetzky Gross PRA 93, 042108 (2016)]

Molecular geometric phase

$$\Psi(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}) \approx \Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}})\chi(\underline{\underline{\mathbf{R}}})$$ Born-Oppenheimer approximation

$$\left(\sum_i^{\text{elec}} \frac{\mathbf{p}_i^2}{2m_e} + \hat{V}_{ee} + \hat{V}_{nn} - \sum_i^{\text{elec}} \sum_n^{\text{nucl}} \frac{Z_n e^2}{|\mathbf{r}_i - \mathbf{R}_n|}\right) \Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}}) = \mathcal{E}(\underline{\underline{\mathbf{R}}}) \Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}})$$

electronic and nuclear coordinates

$\underline{\underline{\mathbf{r}}} = (\mathbf{r}_1, \mathbf{r}_2, \ldots)$ $\quad \underline{\underline{\mathbf{R}}} = (\mathbf{R}_1, \mathbf{R}_2, \ldots)$

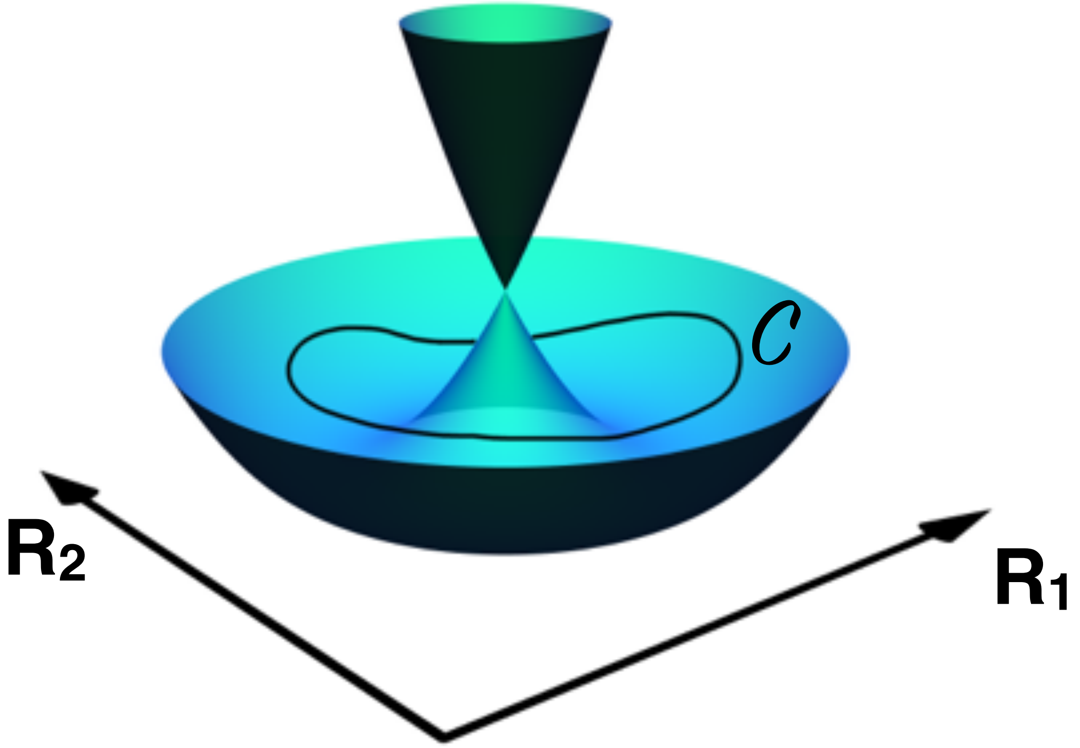
a real-valued electronic function $\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}})$ changes sign when transported along $\mathcal{C}$

$$\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}}) \to -\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}})$$

$\Rightarrow$ Berry phase equals π
(here called Longuet-Higgins phase*)

$\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}})$ and $\chi(\underline{\underline{\mathbf{R}}})$ are multivalued

conical intersection of
Born-Oppenheimer
potential energy surfaces



*Longuet-Higgins, Opik, Pryce & Sack, Proc. R. Soc. London, Ser. A 244, 1 (1958)

Molecular geometric phase

Φ_R and χ can be made single-valued by multiplying by a Dirac phase factor*

$$\Phi_{\underline{\underline{\mathbf{R}}}} \rightarrow \tilde{\Phi}_{\underline{\underline{\mathbf{R}}}} = e^{\frac{i}{\hbar}\int \underline{\underline{\mathbf{A}}}\cdot d\underline{\underline{\mathbf{R}}}}\, \Phi_{\underline{\underline{\mathbf{R}}}}$$

$$\chi \rightarrow \tilde{\chi} = e^{-\frac{i}{\hbar}\int \underline{\underline{\mathbf{A}}}\cdot d\underline{\underline{\mathbf{R}}}}\, \chi$$

with

$$\underline{\underline{\mathbf{A}}} = (\mathbf{A}_1, \mathbf{A}_2, \ldots)$$

$$\mathbf{A}_n = \mathrm{Im}\langle \tilde{\Phi}_{\underline{\underline{\mathbf{R}}}} | \nabla_{\mathbf{R}_n} \tilde{\Phi}_{\underline{\underline{\mathbf{R}}}} \rangle$$

$$\left[\sum_n \frac{(\mathbf{P}_n + \mathbf{A}_n)^2}{2M_n} + \mathcal{E}(\underline{\underline{\mathbf{R}}}) \right] \tilde{\chi}(\underline{\underline{\mathbf{R}}}) = E\tilde{\chi}(\underline{\underline{\mathbf{R}}})$$

$$\begin{aligned} \gamma(C) &= -\oint_C \mathrm{Im}\langle \tilde{\Phi}_{\underline{\underline{\mathbf{R}}}} | \nabla_{\underline{\underline{\mathbf{R}}}} \tilde{\Phi}_{\underline{\underline{\mathbf{R}}}} \rangle \cdot d\underline{\underline{\mathbf{R}}} \\ &= -\oint_C \underline{\underline{\mathbf{A}}} \cdot d\underline{\underline{\mathbf{R}}} \\ &= 0 \text{ or } \pi \end{aligned}$$

Born-Oppenheimer
molecular geometric phase

*Mead & Truhlar, J. Chem. Phys., 70, 2284 (1979)

Example: $E \otimes e$ Jahn-Teller model

Two degenerate electronic states $|u\rangle$ and $|g\rangle$ coupled to two degenerate vibrational normal modes Q_2 and Q_3

Born-Oppenheimer Hamiltonian

$$\hat{H}^{\mathrm{BO}} = \frac{K}{2}(Q_2^2 + Q_3^2) + g \begin{pmatrix} Q_2 & -Q_3 \\ -Q_3 & -Q_2 \end{pmatrix}$$

polar coor.'s

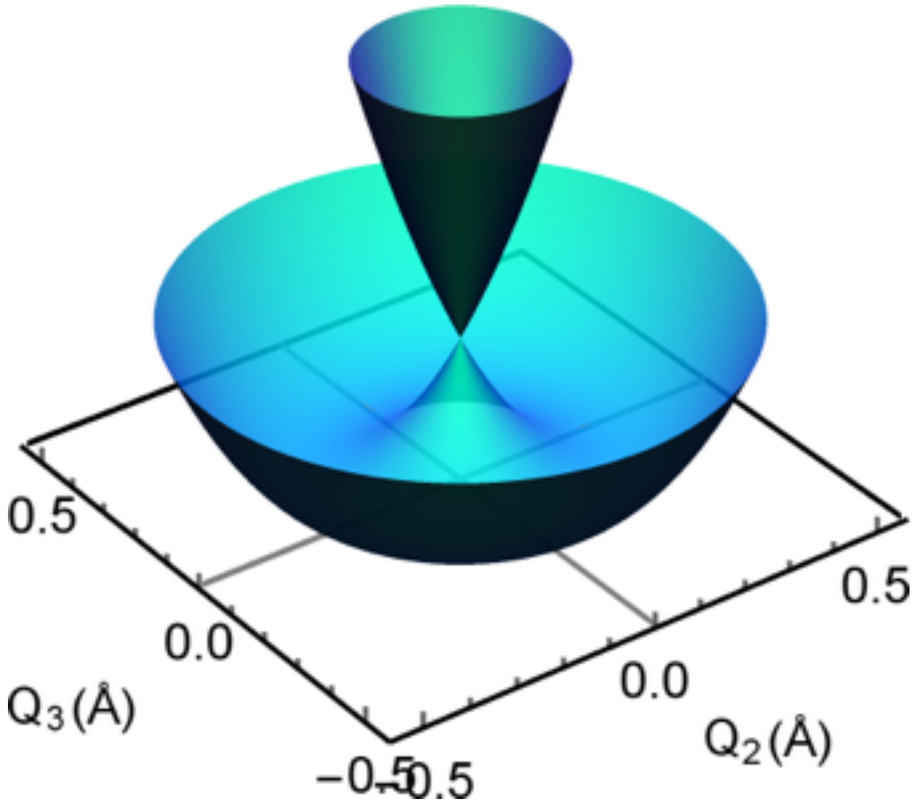
$$Q = \sqrt{Q_2^2 + Q_3^2}$$

$$\eta = \tan^{-1}(Q_3/Q_2)$$

Born-Oppenheimer potential energy surfaces

$$E_\pm = \frac{K}{2}Q^2 \pm gQ$$

$$= \frac{K}{2}\left(Q \pm \frac{g}{K}\right)^2 - \frac{g^2}{2K}$$



Example: $E \otimes e$ Jahn-Teller model

Real-valued Born-Oppenheimer eigenstates

$$\Phi_- = \begin{pmatrix} \sin\frac{\eta}{2} \\ \cos\frac{\eta}{2} \end{pmatrix} \quad \Phi_+ = \begin{pmatrix} \cos\frac{\eta}{2} \\ -\sin\frac{\eta}{2} \end{pmatrix}$$

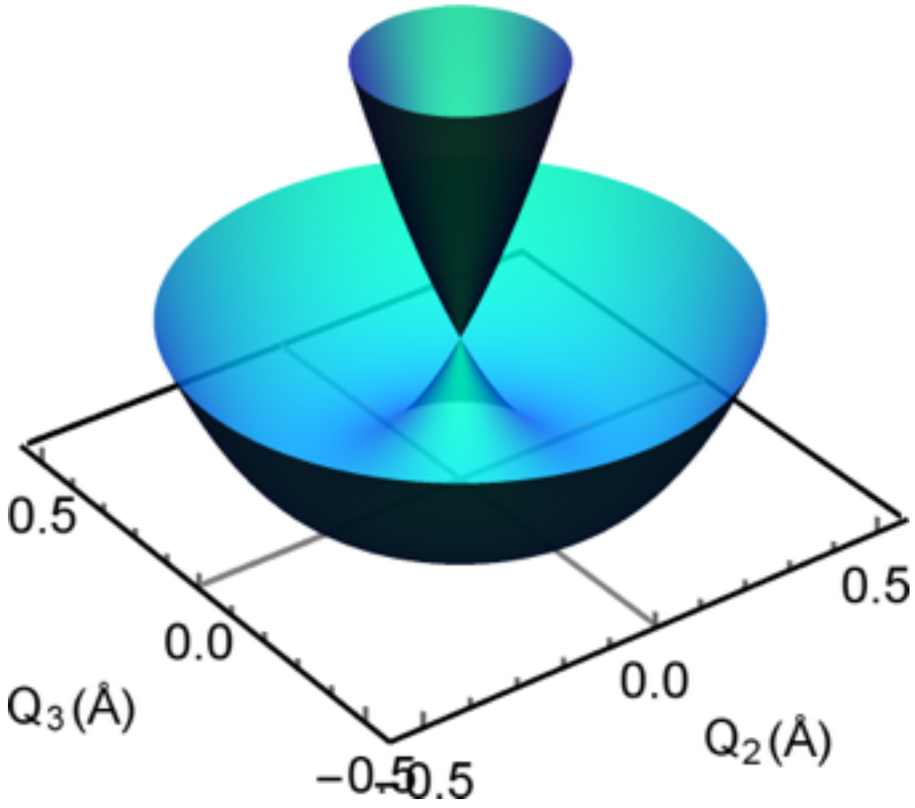
(change sign when $\eta \to \eta + 2\pi$)

Single-valued Born-Oppenheimer eigenstates

$$\tilde{\Phi}_- = e^{-i\eta/2} \begin{pmatrix} \sin\frac{\eta}{2} \\ \cos\frac{\eta}{2} \end{pmatrix} \quad \tilde{\Phi}_+ = e^{-i\eta/2} \begin{pmatrix} \cos\frac{\eta}{2} \\ -\sin\frac{\eta}{2} \end{pmatrix}$$

Born-Oppenheimer molecular geometric phase

$$\begin{aligned} \gamma(C) &= -\int_0^{2\pi} \mathrm{Im}\langle \tilde{\Phi}_- | \partial_\eta \tilde{\Phi}_- \rangle d\eta \\ &= \int_0^{2\pi} \frac{d\eta}{2} \\ &\boxed{= \pi} \end{aligned}$$



Observations of the molecular geometric phase

$$\Phi_- = \begin{pmatrix} \sin\frac{\eta}{2} \\ \cos\frac{\eta}{2} \end{pmatrix}$$

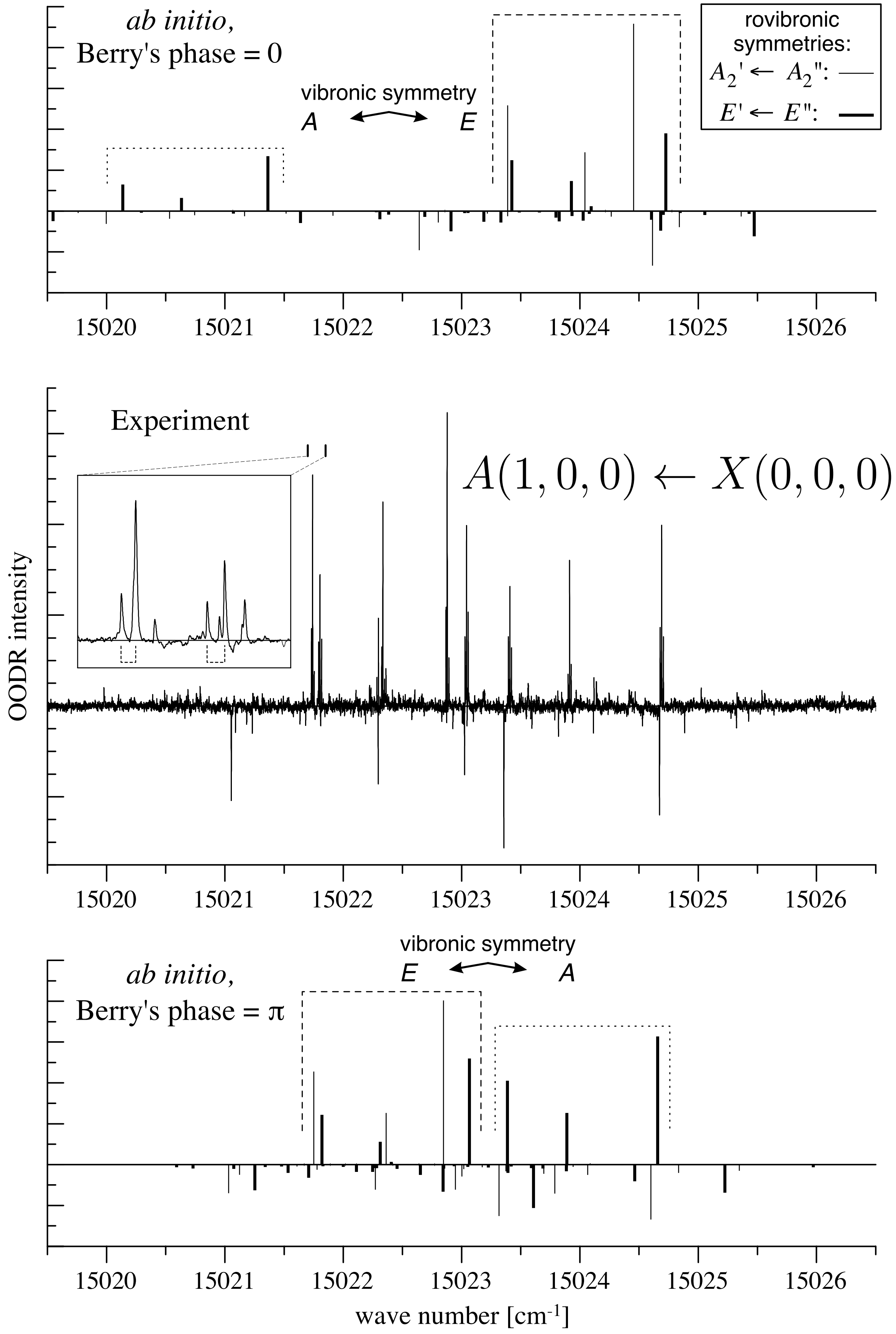
$$\Phi_-(\eta + 2\pi) = -\Phi_-(\eta)$$

$$\Rightarrow \chi(Q, \eta + 2\pi) = -\chi(Q, \eta)$$

(antiperiodic boundary conditions)

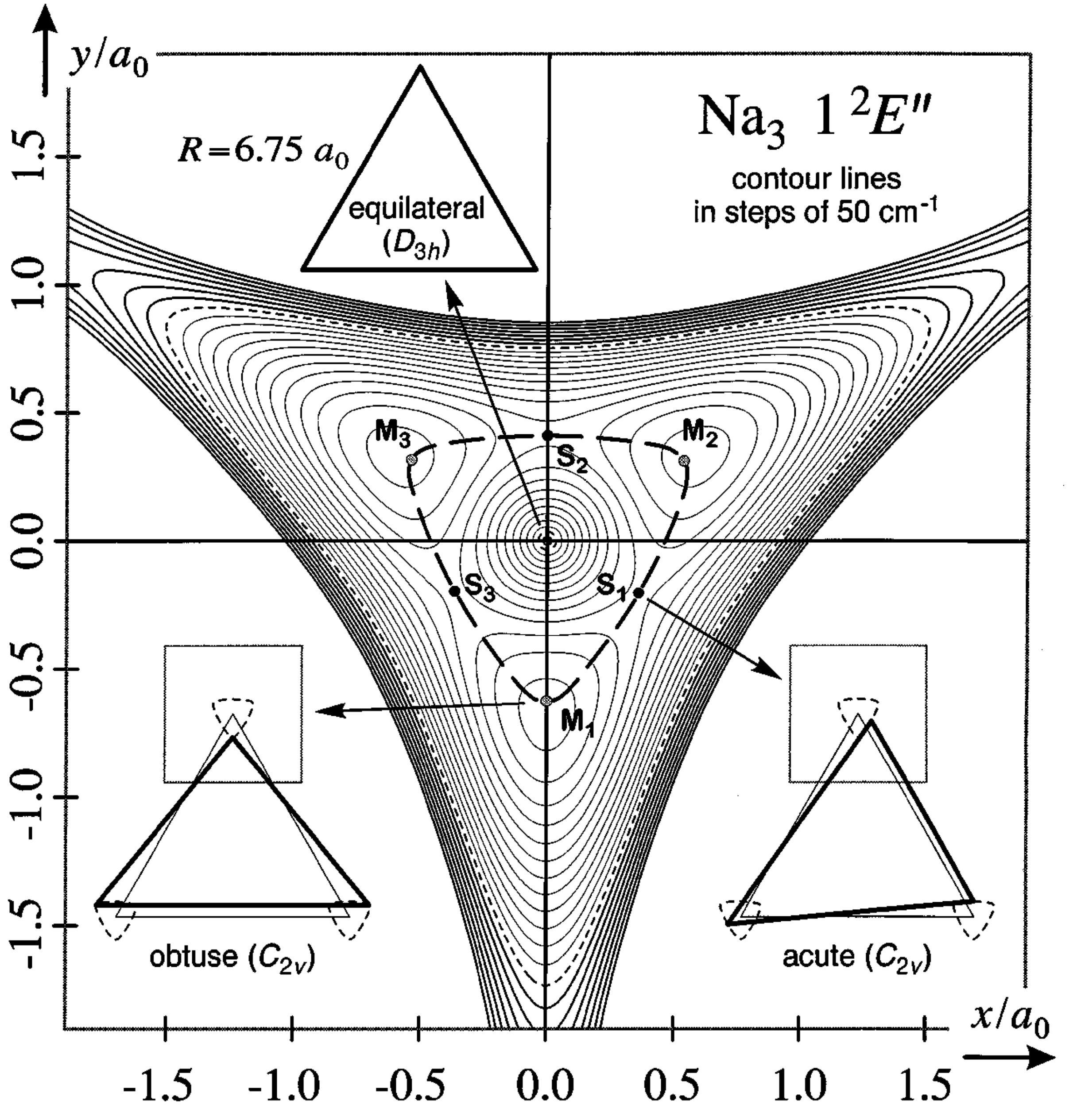
$$\chi(Q, \eta) = f(Q)e^{im\eta}, \quad m = \pm\frac{1}{2}, \pm\frac{3}{2}, \ldots$$

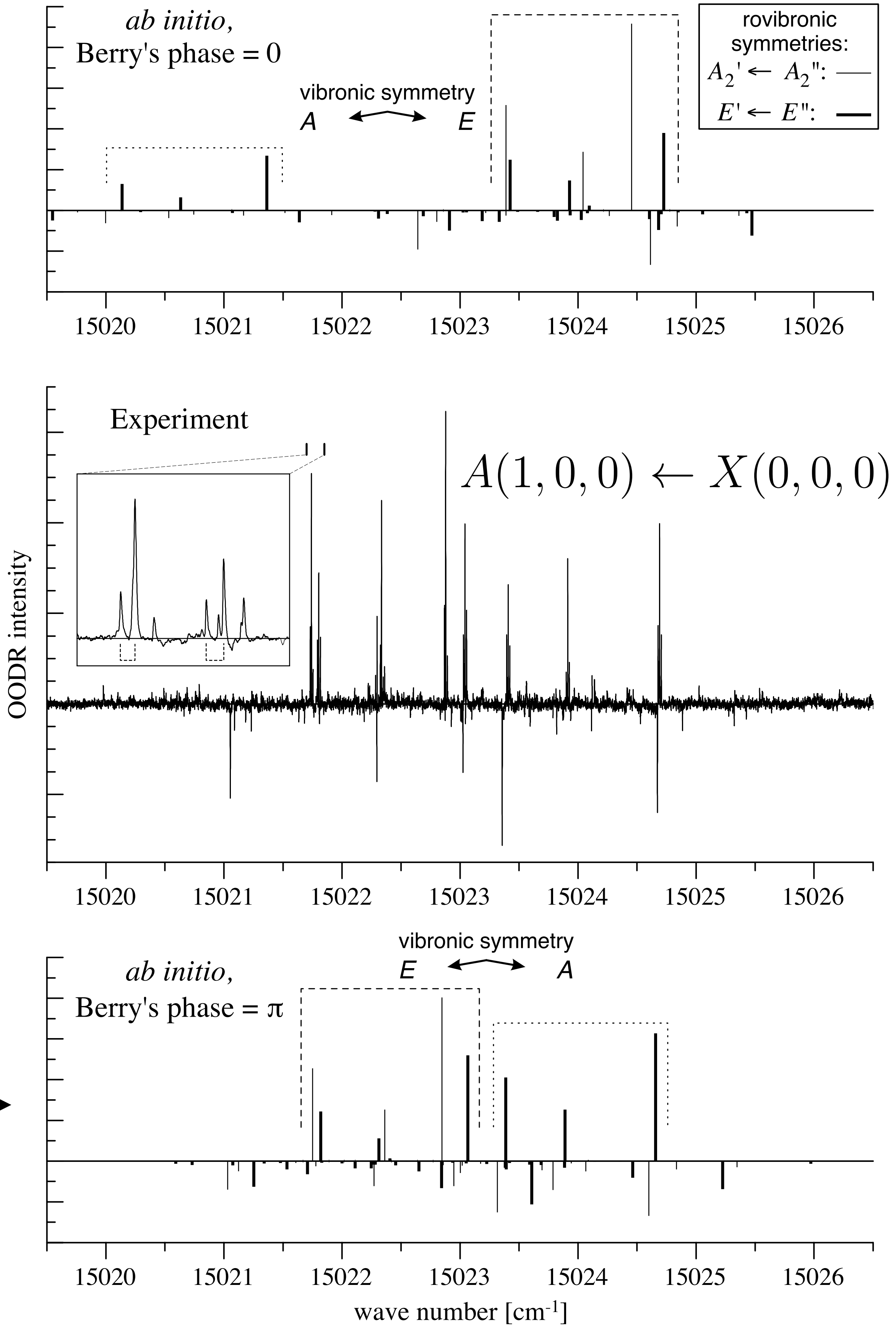
Two-fold ground state degeneracy is connected to the molecular Berry phase



von Busch, *et al.*, PRL 81, 4585 (1998)

Observations of the molecular geometric phase





<u>Vibrational spectroscopy for Na_3</u>:
D_{3h} symmetry has E and A irreducible representations

von Busch, *et al.*, PRL 81, 4585 (1998)

Does the interpretation of experiment depend on the Born-Oppenheimer approximation?

In our calculations, the molecular geometric phase of π appeared to depend on the existence of a conical intersection, yet the point of conical intersection is precisely where the Born-Oppenheimer approximation breaks down.

The geometric phase of a subsystem, as originally defined, depended on an adiabatic separation of fast and slow degrees of freedom, e.g. $\underline{\underline{\mathbf{r}}}$ and $\underline{\underline{\underline{\mathbf{R}}}}$, with the latter being interpreted as *parameters* that drive the quantum state of the former.*

One may therefore wonder whether the experimental observations really observe a molecular geometric phase of π.

*M. V. Berry, Proc. R. Soc. Lond. A, 392, 45 (1984)

Exact factorization scheme

$\Psi(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}) \approx \Phi^{BO}_{0\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}})\chi^{BO}_0(\underline{\underline{\mathbf{R}}})$ Born-Oppenheimer approximation

$\Psi(\underline{\underline{\mathbf{r}}}, \underline{\underline{\mathbf{R}}}) = \Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}})\chi(\underline{\underline{\mathbf{R}}})$ Exact factorization

$\chi(\underline{\underline{\mathbf{R}}}) =$ marginal nuclear wavefunction

$\rightarrow$ nuclear probability $|\chi(\underline{\underline{\mathbf{R}}})|^2$

and current density $\mathbf{J}_\mu = \operatorname{Im} \chi^*(\underline{\underline{\mathbf{R}}})\nabla_\mu \chi(\underline{\underline{\mathbf{R}}}) + |\chi(\underline{\underline{\mathbf{R}}})|^2 \mathbf{A}_\mu$

$\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}}) =$ conditional electronic wavefunction

partial normalization condition $\rightarrow \int \Phi^*_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}})\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}})d\underline{\underline{\mathbf{r}}} = 1$

Hunter, Int. J. Quant. Chem. 9, 237 (1975); Abedi, Maitra & Gross, Phys. Rev. Lett. 105, 123002 (2010);
Gidopoulos & Gross, Phil. Trans. R. Soc. A, 372, 20130059 (2014)

Coupled exact factorization equations

$$\hat{H}_{elec}\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}}) = \mathcal{E}(\underline{\underline{\mathbf{R}}})\Phi_{\underline{\underline{\mathbf{R}}}}(\underline{\underline{\mathbf{r}}})$$

$$\left[\sum_n \frac{1}{2M_n}(-i\nabla_n + \mathbf{A}_n)^2 + \mathcal{E}(\underline{\underline{\mathbf{R}}})\right]\chi(\underline{\underline{\mathbf{R}}}) = E\chi(\underline{\underline{\mathbf{R}}})$$

$$\hat{H}_{elec} = \hat{T}_e + \hat{V}_{en} + \hat{V}_{ee} + \hat{V}_{nn} + \sum_n \frac{1}{2M_n}\left[(-i\nabla_n - \mathbf{A}_n)^2 + (-i\nabla_n\chi/\chi + \mathbf{A}_n)(-i\nabla_n - \mathbf{A}_n)\right]$$

Exact potential energy surface: $\mathcal{E}(\underline{\underline{\mathbf{R}}}, t) = \langle\Phi_{\underline{\underline{\mathbf{R}}}}|\hat{H}^{BO}|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle + \mathcal{E}_{\text{geo}}(\underline{\underline{\mathbf{R}}}, t)$

$$\mathcal{E}_{\text{geo}}(\underline{\underline{\mathbf{R}}}, t) = \sum_n \frac{\langle\nabla_n\Phi_{\underline{\underline{\mathbf{R}}}}|(1 - |\Phi_{\underline{\underline{\mathbf{R}}}}\rangle\langle\Phi_{\underline{\underline{\mathbf{R}}}}|)|\nabla_n\Phi_{\underline{\underline{\mathbf{R}}}}\rangle}{2M_n}$$

Exact *induced* vector potential: $\mathbf{A}_n = \mathrm{Im}\langle\Phi_{\underline{\underline{\mathbf{R}}}}|\nabla_n\Phi_{\underline{\underline{\mathbf{R}}}}\rangle$ (Berry connection)

Hunter, Int. J. Quant. Chem. 9, 237 (1975); Abedi, Maitra & Gross, Phys. Rev. Lett. 105, 123002 (2010);
Gidopoulos & Gross, Phil. Trans. R. Soc. A, 372, 20130059 (2014)

Exact molecular geometric phase

Nonadiabatic effects are usually included through the Born-Huang expansion

$$\Psi(\underline{\mathbf{r}}, \underline{\underline{\mathbf{R}}}) = \sum_n \Phi^{BO}_{n\underline{\underline{\mathbf{R}}}}(\underline{\mathbf{r}})\chi^{BO}_n(\underline{\underline{\mathbf{R}}})$$

…but that does not give us a way to calculate corrections to the phase

To define an exact molecular geometric phase, replace $\Phi^{BO}_{\underline{\underline{\mathbf{R}}}} \to \Phi_{\underline{\underline{\mathbf{R}}}}$ in in the Berry connection $\mathbf{A}_n = \mathrm{Im}\langle \Phi_{\underline{\underline{\mathbf{R}}}} | \nabla_n \Phi_{\underline{\underline{\mathbf{R}}}} \rangle$

exact molecular geometric phase†

$$\gamma(C) = -\oint_C \underline{\underline{\mathbf{A}}} \cdot d\underline{\underline{\mathbf{R}}} \qquad \underline{\underline{\mathbf{A}}} = (\mathbf{A}_1, \mathbf{A}_2, \ldots)$$

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†Gidopoulos & Gross, Phil. Trans. Roy. Soc. A 372, 20130059 (2014); Min, Abedi, Kim & Gross, Phys. Rev. Lett. 113, 263004 (2014); RR, Tandetzky & Gross, PRA 93, 042108 (2016)

Exact molecular geometric phase

Gidopoulos & Gross and Min *et al.* posed the following question:

Is the molecular Berry phase an artifact of the Born-Oppenheimer approximation?

In a 2D Shin-Metiu model, they found that the molecular geometric phase, which was π in the Born-Oppenheimer approximation, vanished in a numerically exact calculation.
[Min Abedi Kim Gross, PRL 113, 263004 (2014)]

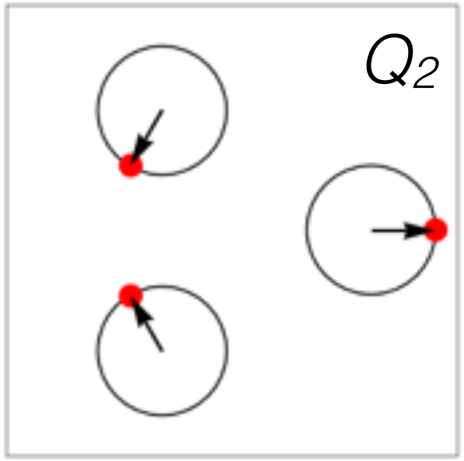
Is it always zero? — No, in dynamical Jahn-Teller systems where the Born-Oppenheimer molecular geometric phase has been observed, the *exact* molecular geometric phase is nonzero.
[RR Tandetsky Gross, PRA 93, 042108 (2016)]

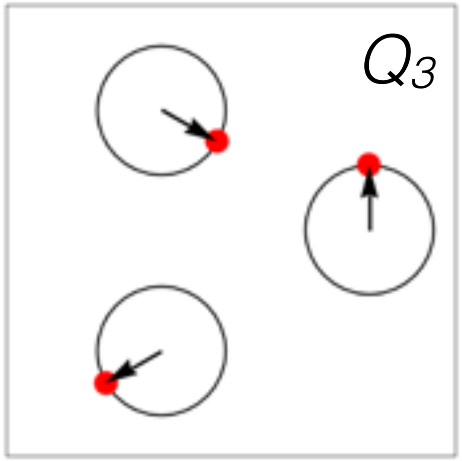
Gidopoulos & Gross, Phil. Trans. Roy. Soc. A 372, 20130059 (2014); Min, Abedi, Kim & Gross, Phys. Rev. Lett. 113, 263004 (2014)

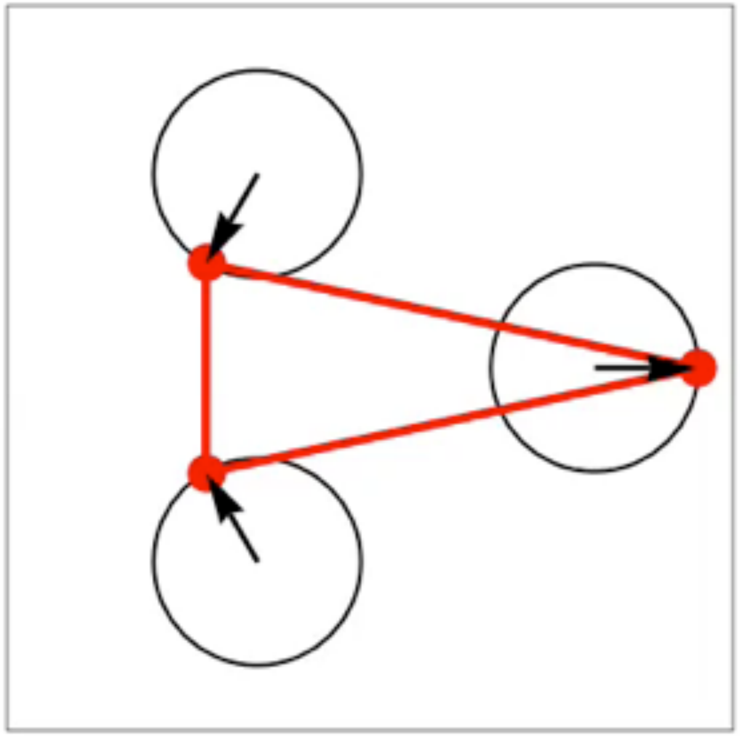
Model pseudorotating triatomic molecule

Electrons: tight-binding approximation assuming one *s*-like electron per atom

Nuclei: normal mode coordinates (Q_1, Q_2, Q_3)





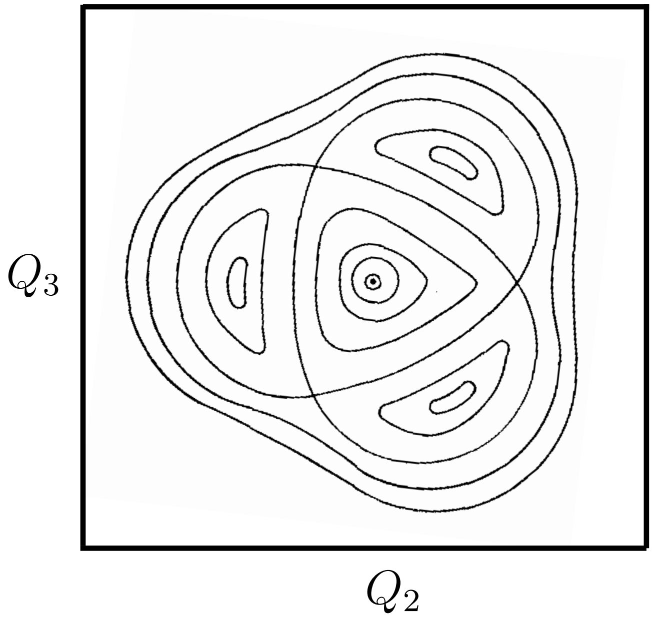


$(Q_2, Q_3) \rightarrow (Q, \eta)$

$$\hat{H} = -\sum_{n\sigma}\left(t_{n,n+1}(R)c^{\dagger}_{n\sigma}c_{n+1\sigma} + H.c.\right) + \hat{T}_n + \hat{V}_{nn} + \hat{V}_{ee}$$

$$\hat{T}_n = -\frac{\hbar^2}{6M}\left(\frac{1}{Q}\frac{d}{dQ}Q\frac{d}{dQ} + \frac{1}{Q^2}\frac{d^2}{d\eta^2}\right), \qquad \hat{V}_{nn} = \frac{K}{2}Q^2$$

$$t_{n,n+1}(R) = t_0 + \frac{g}{\sqrt{3}}(|\mathbf{R}_{n+1} - \mathbf{R}_n| - \sqrt{3}R_0)$$



Allen, Abanov & RR, Phys. Rev. A 71, 043203 (2005); RR, Tandetzky, Gross, PRA 93, 042108 (2016)

Electronic states and coupling

Single-particle orbitals

$$\phi_0 = \frac{1}{\sqrt{3}}(1,1,1)$$

$$\phi_+ = \frac{1}{\sqrt{3}}(e^{i2\pi/3}, e^{-i2\pi/3}, 1)$$

$$\phi_- = \frac{1}{\sqrt{3}}(e^{-i2\pi/3}, e^{i2\pi/3}, 1)$$

$$\hat{T}_{\mathrm{e}} + \hat{V}_{\mathrm{en}} = -\sum_{n\sigma}\left(t_{n,n+1}(R)c^\dagger_{n\sigma}c_{n+1\sigma} + H.c.\right)$$

$$\hat{T}_{\mathrm{n}} + \hat{V}_{\mathrm{nn}} = -\frac{\hbar^2\nabla^2}{2M} + \frac{K}{2}Q^2$$

3-electron Hilbert space, $S = 1/2,\ S_z = 1/2$

$\langle\hat{T}_{\mathrm{e}}\rangle$	state
$-3t_0$	$\lvert a\rangle = \lvert\uparrow\,\updownarrows\,0\rangle$
	$\lvert b\rangle = \lvert 0\,\updownarrows\,\uparrow\rangle$
$+\,3t_0$	$\lvert c\rangle = \lvert\updownarrows\,0\,\uparrow\rangle$
	$\lvert d\rangle = \lvert\uparrow\ 0\,\updownarrows\rangle$
0	$\lvert e\rangle = \lvert 0\,\uparrow\,\updownarrows\rangle$
	$\lvert f\rangle = \lvert\updownarrows\,\uparrow\,0\rangle$
0	$\lvert g\rangle = -\frac{i}{\sqrt{6}}\Big(2\lvert\uparrow\downarrow\uparrow\rangle - \lvert\uparrow\uparrow\downarrow\rangle - \lvert\downarrow\uparrow\uparrow\rangle\Big)$
	$\lvert h\rangle = -\frac{1}{\sqrt{2}}\Big(0\lvert\uparrow\downarrow\uparrow\rangle + \lvert\uparrow\uparrow\downarrow\rangle - \lvert\downarrow\uparrow\uparrow\rangle\Big)$

Quasi-isotropic regime

$$t_0 \gg \hbar\sqrt{\frac{K}{M}} \gg -\frac{g^2}{2K}$$

$\hbar\sqrt{\frac{K}{M}}$ = vibrational frequency

$-\frac{g^2}{2K}$ = static Jahn-Teller stabilization energy

Symmetries of the model

Schrodinger equation solved by exact diagonalization in an electron-nuclear product basis $|a\rangle \otimes |nm\rangle$

$$\langle Q\eta|nm\rangle = \rho_{nm}(Q)e^{im\eta} \quad \rho_{nm}(Q) \sim \text{Laguerre polynomials}$$

Three-fold rotational symmetry

$$\hat{C}_3 = \hat{C}_{3e}\hat{C}_{3\eta}$$

$$\hat{C}_{3e}:\ 1 \rightarrow 2 \rightarrow 3 \rightarrow 1$$

$$\hat{C}_{3\eta}\chi(Q,\eta) = \chi(Q,\eta + 2\pi/3)$$

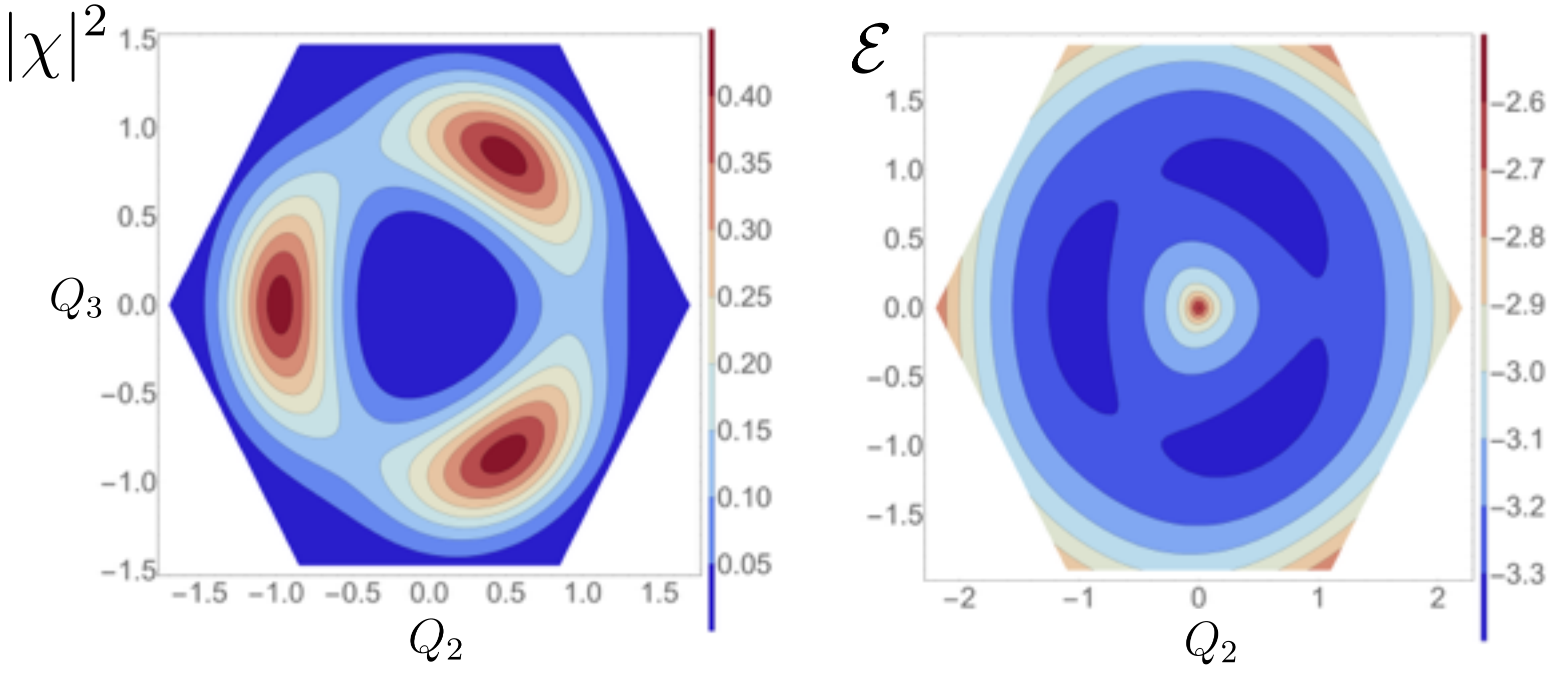
Irreducible representations

E and A

Ground state is two-fold degenerate with E symmetry

RR, Tandetzky & Gross, PRA 93, 042108 (2016)

Nuclear density and $\mathcal{E}(Q_2, Q_3)$



complex state $|\Psi_+\rangle$ $\quad$ $\hat{C}_3|\Psi_+\rangle = e^{i2\pi/3}|\Psi_+\rangle$

$$M = 100\frac{\hbar^2}{eV\mathring{A}^2} \quad g = 0.75\frac{eV}{\mathring{A}} \quad K = 1.00\frac{eV}{\mathring{A}^2}$$

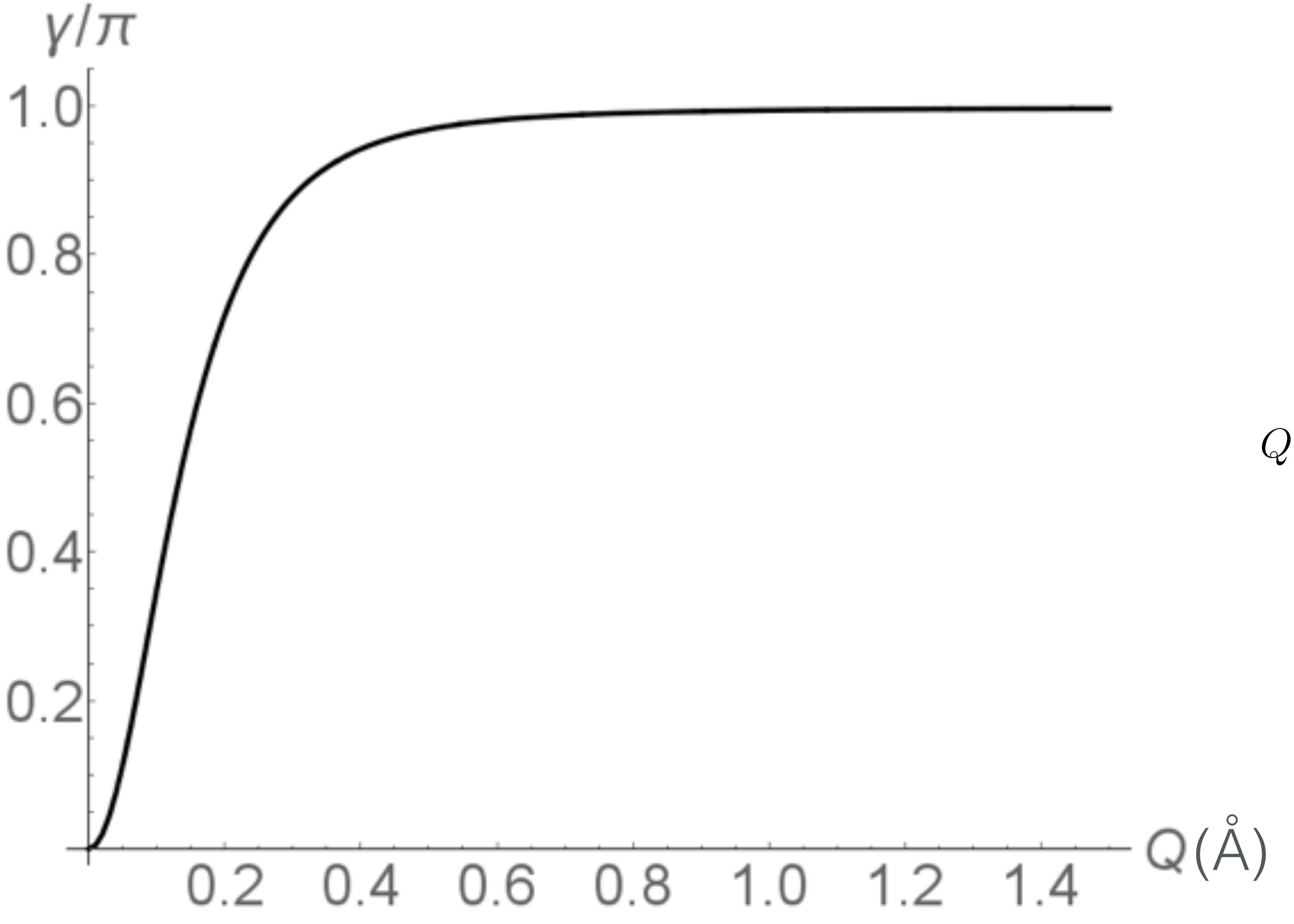
Geometric phase and Berry curvature

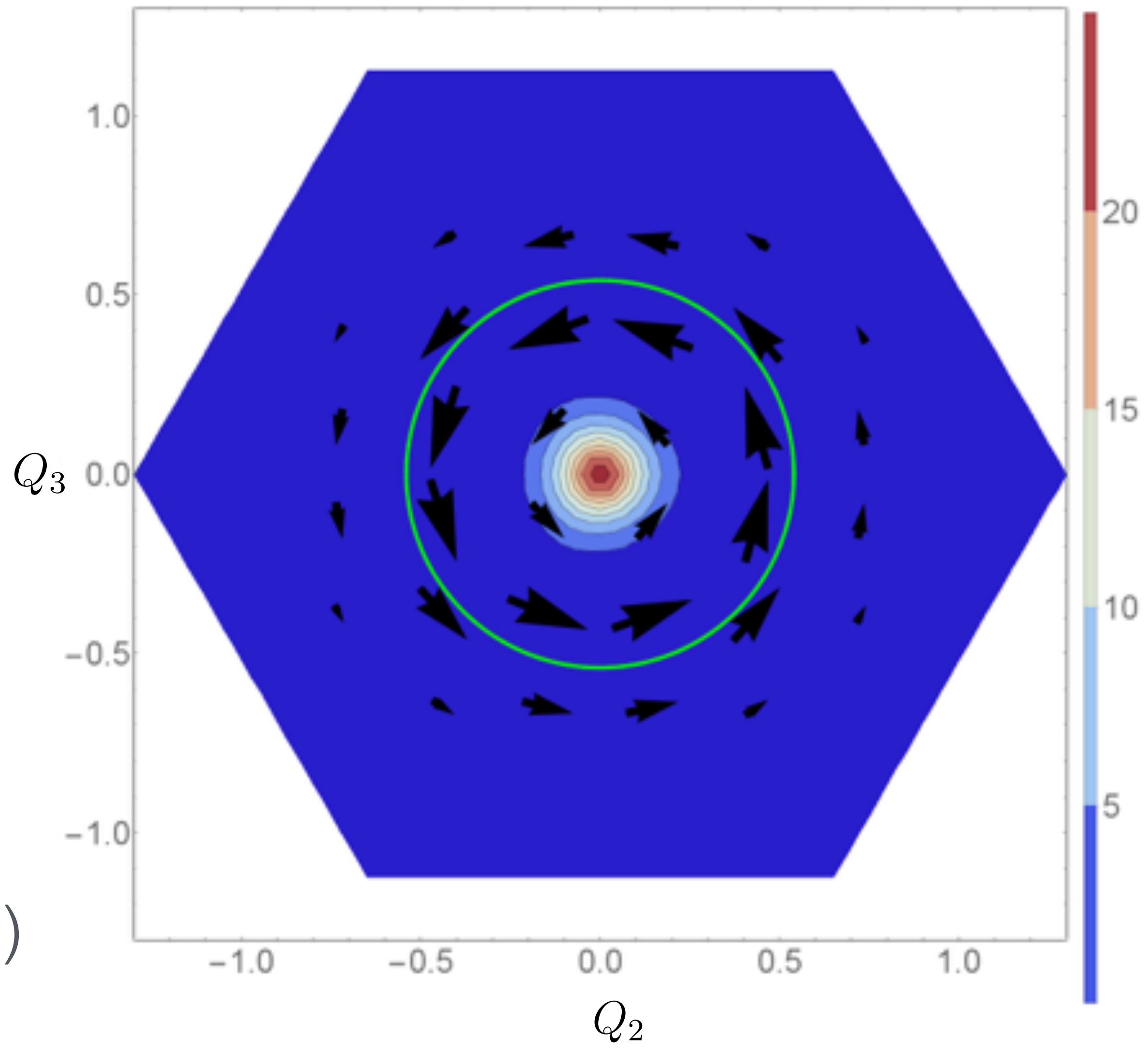
$$\begin{aligned}\gamma(C) &= -\iint_S \mathbf{B}\cdot d\mathbf{S}\\ &= -\iint_S B_\perp dQ_2 dQ_3\end{aligned}$$

Berry curvature

$$B_\perp = 2\mathrm{Im}\left\langle \frac{d\Phi_{\underline{\underline{\mathbf{R}}}}}{dQ_2}\middle|\frac{d\Phi_{\underline{\underline{\mathbf{R}}}}}{dQ_3}\right\rangle$$

of current-carrying state $|\Psi_+\rangle$

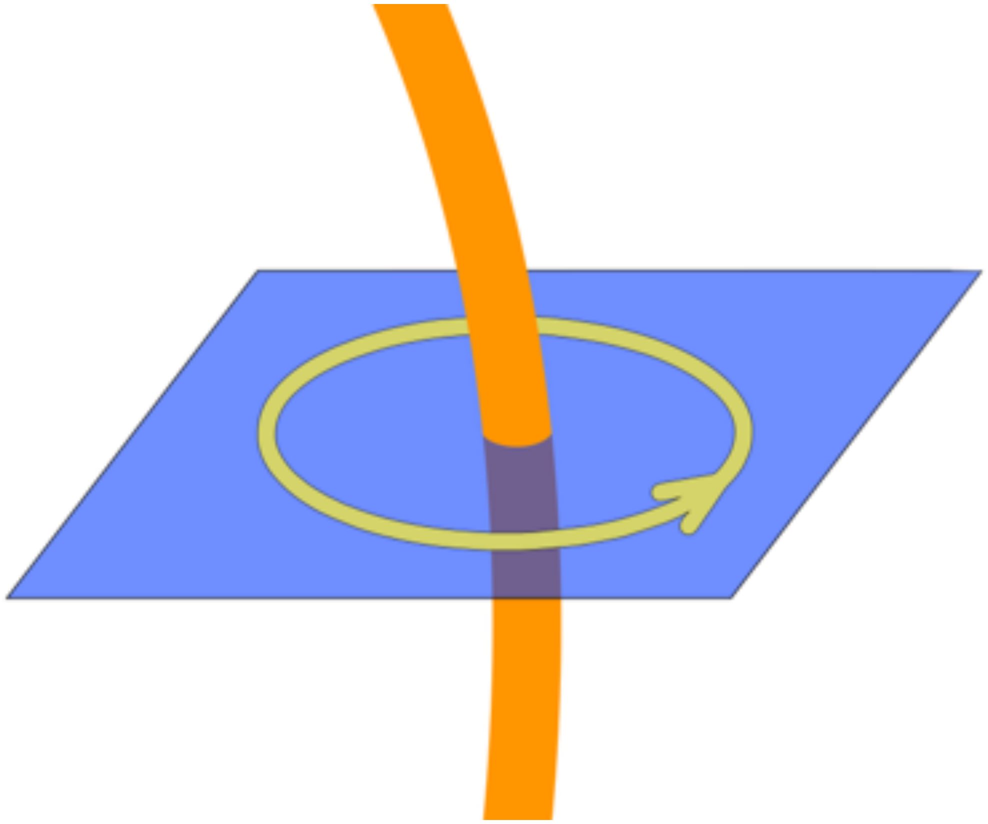




RR, Tandetzky & Gross, PRA 93, 042108 (2016)

Topological invariant vs geometric phase

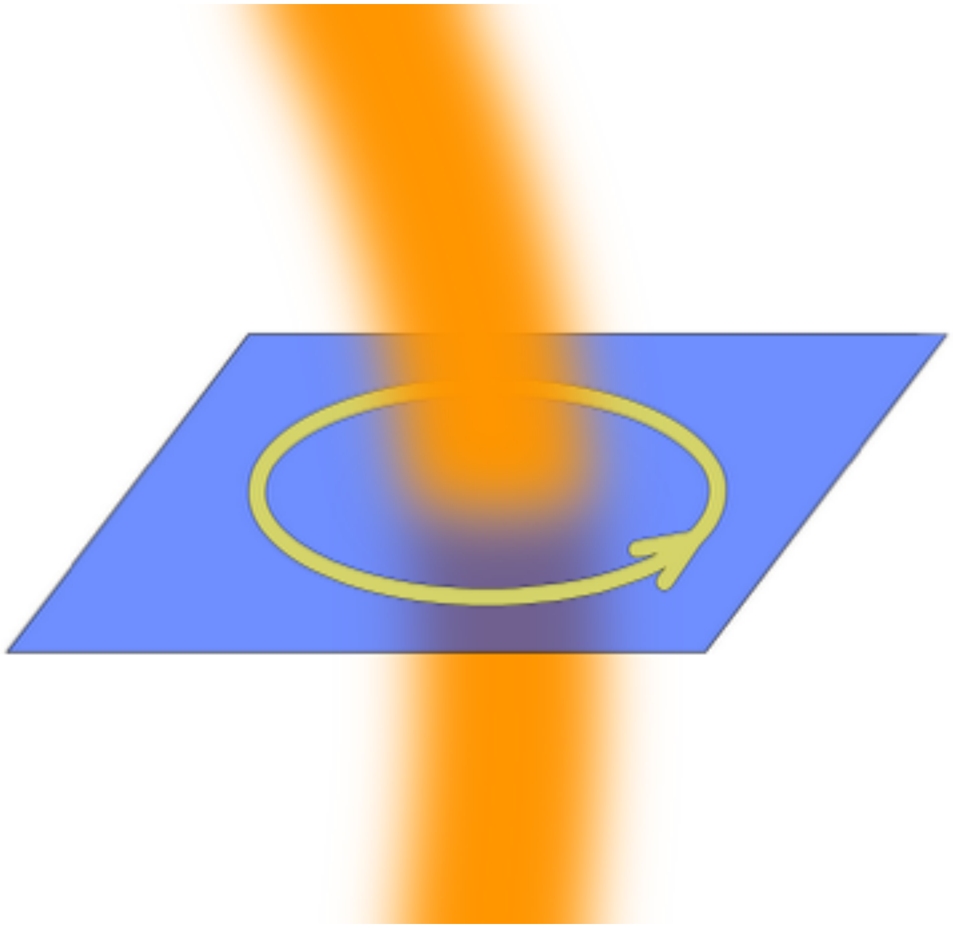
Infinitesimal Aharonov-Bohm flux tube
in Born-Oppenheimer approximation



Conical intersections of real
Hamiltonians have codimension 2

⇒ line or “seam” in 3D

Smeared-out flux tube
in exact factorization



Characteristic width

$$\frac{\hbar K^{1/2}}{g M^{1/2}}$$

Distinguishing the Born-Oppenheimer and exact molecular geometric phases

Since $\gamma(C)$ is a path-dependent quantity and we cannot force the nuclei to follow a specific path $\underline{\underline{\mathbf{R}}}(t)$, we do not know how to measure $\gamma(C)$ directly.

Actually, the expectation value of any electronic observable is a $|\chi(\underline{\underline{\mathbf{R}}})|^2$-weighted average:

$$\langle\Psi|\hat{\mathcal{O}}_{\text{elec}}|\Psi\rangle = \int |\chi(\underline{\underline{\mathbf{R}}})|^2 \langle\Phi_{\underline{\underline{\mathbf{R}}}}|\hat{\mathcal{O}}_{\text{elec}}|\Phi_{\underline{\underline{\mathbf{R}}}}\rangle \, d\underline{\underline{\mathbf{R}}}$$

However, we can infer the difference between $\gamma(C)$ and $\gamma^{BO}(C)$ through the response of the system to <u>external perturbations</u>, such as magnetic fields and strain, or to <u>additional interactions</u>, such as spin-orbit, hyperfine and nuclear quadrupole interactions.*

*F. S. Ham, Int. J. Quant. Chem. 5, 191 (1971)

Ham effect

Jahn-Teller models describe the coupling of electronic and vibrational states of given symmetry.

The symmetry of the electrons in the absence of electronic-vibrational coupling is determined by the nuclear geometry, e.g. the molecular geometry or the local crystal field of a transition metal in a bulk crystal.

Symmetry determines how a perturbation $\hat{V}$ couples to the system.

When the electronic-vibrational coupling is turned back on, the purely electronic eigenstates, say $|u\rangle$ and $|g\rangle$, transform into electronic-vibrational (vibronic) states $|\Psi_u\rangle$ and $|\Psi_g\rangle$.

Therefore, the *form* of the perturbation $\hat{V}$ remains the same but the parameters are renormalized — this is called the Ham effect.

*F. S. Ham, Phys. Rev. 166, 307 (1968)

Ham reduction factors

For example, a triatomic molecule with D_{3h} symmetry can be described by an $E \otimes e$ Jahn-Teller model.

$E \otimes e$ means that the electronic states belong to a twofold degenerate irreducible representation E of the D_{3h} point group and that the vibrational modes belong to the same E representation (lower case is used to distinguish vibrational states from electronic states).

For the E electronic states, a generic perturbation is

$$\hat{V} = V_0 \hat{I} + \vec{V} \cdot \hat{\vec{\sigma}}$$

For vibronic states, this becomes

$$\hat{V} = V_0 \hat{I} + q V_1 \hat{\sigma}_1 + p V_2 \hat{\sigma}_2 + q V_3 \hat{\sigma}_3$$

with reduction factors $p = \dfrac{\langle \Psi_u | \hat{\sigma}_2 | \Psi_g \rangle}{\langle u | \hat{\sigma}_2 | g \rangle}$ and $q = \dfrac{\langle \Psi_u | \hat{\sigma}_1 | \Psi_g \rangle}{\langle u | \hat{\sigma}_1 | g \rangle} = \dfrac{\langle \Psi_u | \hat{\sigma}_3 | \Psi_u \rangle}{\langle u | \hat{\sigma}_3 | u \rangle}$

Ham reduction factors

Ham reduction factors p and q can be expressed in terms of $\gamma(C)$

$$p = 2\pi \int_0^\infty dQQ|\chi(Q)|^2 \left[1 - \frac{\gamma(Q)}{\pi}\right]$$

p varies between 0 and 1, and approaches 0 in the limit $M \to \infty$

Deviations between $\gamma(Q)$ and $\gamma^{BO}(Q)$ lead to $p \neq 0$

Quenching of the perturbation is incomplete due to nonadiabatic effects

RR, Proetto & Gross, PRA 96, 062503 (2017)

Recap

- Geometric phases arise from the nontrivial twisting of an angular variable (internal or external) as parameters are varied along a path

- Molecular geometric phase is a special case of Berry phase where the parameters are nuclear coordinates $\underline{\underline{\mathbf{R}}}(t) = \{\mathbf{R}_1, \mathbf{R}_2, \ldots\}$

- Exact factorization scheme leads to the definition of an exact molecular geometric phase that takes into account the full quantum mechanical motion of the nuclei

- Nonadiabatic effects change the topological Longuet-Higgins phase into a geometric quantity that deviates from exactly 0 and π

- Deviations from the Born-Oppenheimer result can be inferred from Ham reduction factors, describing the quenching of external perturbations by electronic-vibrational coupling