Molecular gauge theory - bridging cold gases, condensed matter, and molecular physics

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Workshop “Spin-orbit coupled quantum gases”

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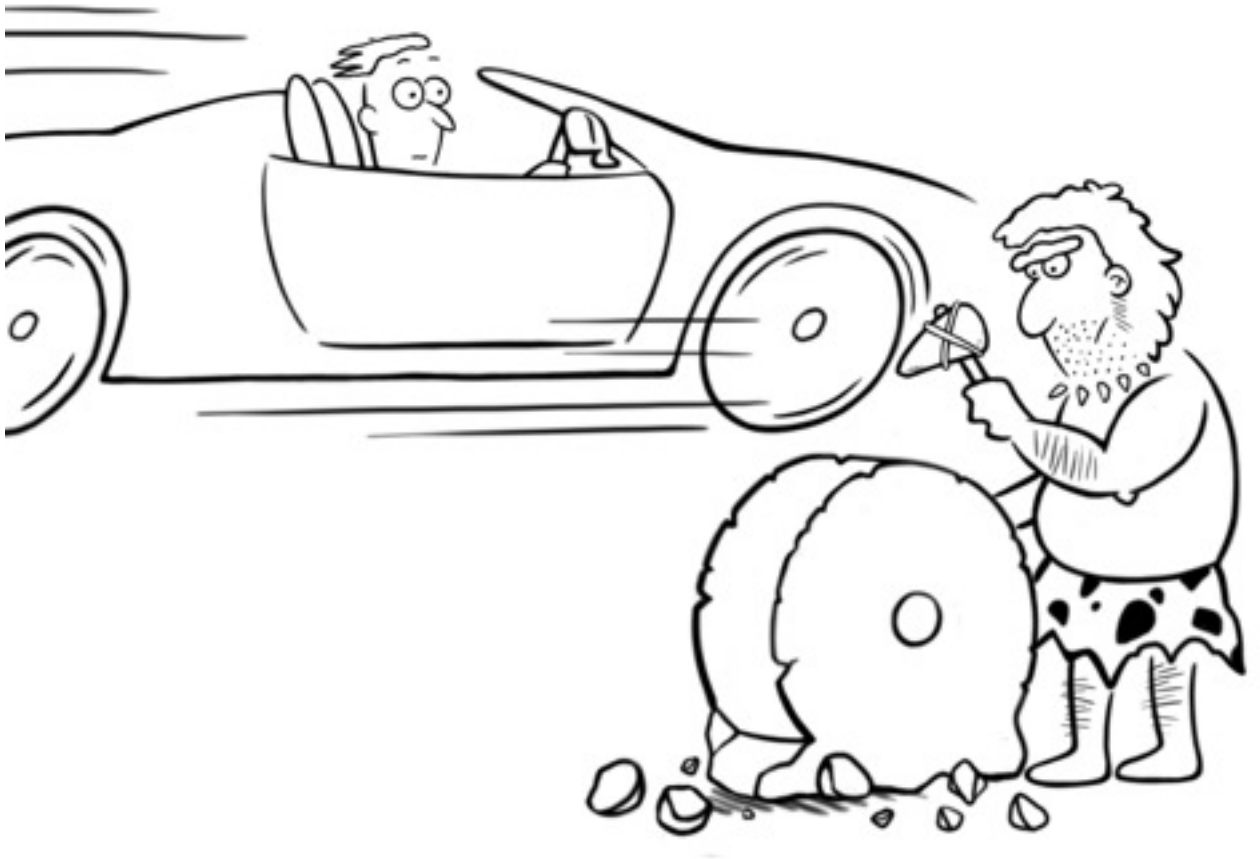
We don’t want to reinvent the wheel



We don’t want to reinvent the wheel

- Öhberg *et al.* (PRL **95** (2005)) suggested the non-Abelian gauge potential

$$\hat{H} = \frac{\hat{p}_x^2}{2m} + \frac{\hat{p}_y^2}{2m} + k\left(\hat{p}_x\hat{\sigma}_x + \hat{p}_y\hat{\sigma}_y\right) + \frac{m\omega^2}{2}\left(\hat{x}^2 + \hat{y}^2\right)$$

- At first it was not realised that this represented a *Rashba* spin-orbit coupling.

- Neither was it understood that this is the $E \times \varepsilon$ - Jahn-Teller Hamiltonian dating back to the 30’th!

- Anderson *et al.* (PRA **78** (2008)) pointed out the coupling to Rashba.

We don't want to reinvent the wheel

- The connection to cond-mat resulted in numerous papers

A new playground to study a plethora of phenomena from cond-mat physics in a controlled manner!

- What about the molecular physics link?

Goal of present talk!

Outlook

1. Molecular structures
    1. Born-Oppenheimer theory
    2. Mead's molecular gauge theory
    3. Conical intersections (CI)

3. Dynamics in the vicinity of a CI
    1. Anomalous evolution
    2. Dual molecular gauge theory (*molecular Hall effect*)

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Born-Oppenheimer theory

- The *Born-Oppenheimer approximation* (1927) captures much of the physics that we are interested in, but not everything!

- At hand, N nuclei and M electrons, interaction via Coulomb

$$\hat{H} = \hat{T}_{nucl} + \hat{T}_{elec} + V_{nn}(R) + V_{ee}(r) + V_{ne}(R, r)$$

- Solve the electronic part

$$\hat{H}_{elec} = \hat{T}_{elec} + V_{ee}(r) + V_{ne}(R, r),$$

$$\hat{H}_{elec}|\phi_i(R)\rangle = V_{PES}^{(i)}(R)|\phi_i(R)\rangle$$

Bohm *et al., The Geometric Phase in Quantum Physics*, (Springer 2006)

Born-Oppenheimer theory

- Express the full state

$$\Psi = \sum_i \psi_i(R)|\phi_i(R)\rangle$$

- Schrödinger equation for the nuclear (vibrational) part (matrix form)

$$\left[-\frac{1}{2M}\nabla_R^2 + V_{nn}(R) + V_{PES}(R) + F(R)\cdot\nabla_R + G(R)\right]\psi(R) = E\psi(R)$$

Here

$$V_{PES}(R) = \mathrm{diag}\left[V_{PES}^{(i)}(R)\right]$$

$$F(R) = -\langle\phi_i(R)|\nabla_R\phi_j(R)\rangle/M$$

$$G(R) = \langle\nabla_R\phi_i|\nabla_R\phi_j\rangle/2M$$

Bohm *et al., The Geometric Phase in Quantum Physics*, (Springer 2006)

Born-Oppenheimer theory

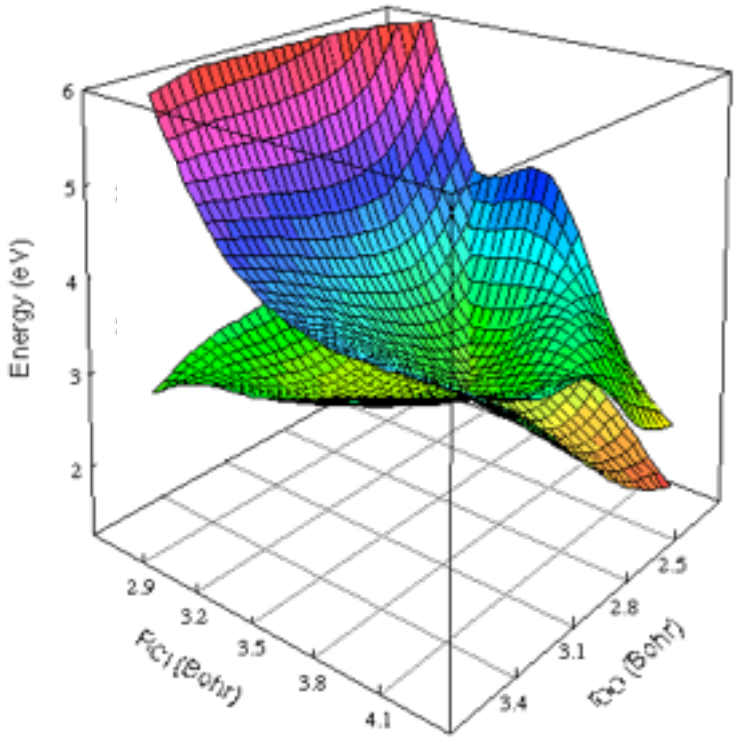
- *Born-Oppenheimer approximation*

$$F(R) = G(R) = 0$$

- Physical motivation: Nuclei much heavier than electrons, *i.e.* smooth functions of R and thereby negligible derivatives.

- *Potential energy surfaces* (PES)

$$V_{PES}^{(i)}(R)$$



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Born-Oppenheimer theory

- Within the *Born-Oppenheimer approximation* the nuclear Hamiltonian is diagonal in the electron basis: no transitions between electronic states.
- Evolution on a multi-dimensional potential surface $V_{PES}^{(i)}(R)$.
- "Adiabatic" approximation; fast variables instantaneous compared to slow ones.
- Adiabatic $\rightarrow$ "rate of change" vs energy gap.
- Molecular symmetries $\rightarrow$ *normal modes* (internal vibrations).

Bohm *et al., The Geometric Phase in Quantum Physics*, (Springer 2006)

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Mead's molecular gauge theory

On the determination of Born–Oppenheimer nuclear motion wave functions including complications due to conical intersections and identical nuclei

C. Alden Mead and Donald G. Truhlar

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455
(Received 20 September 1978)

We show how the presence of a conical intersection in the adiabatic potential energy hypersurface can be handled by including a new vector potential in the nuclear-motion Schrödinger equation. We show how permutational symmetry of the total wave function with respect to interchange of nuclei can be enforced in the Born–Oppenheimer approximation both in the absence and the presence of conical intersections. The treatment of nuclear-motion wave functions in the presence of conical intersections and the treatment of nuclear-interchange symmetry in general both require careful consideration of the phases of the electronic and nuclear-motion wave functions, and this is discussed in detail.

I. INTRODUCTION

The Born–Oppenheimer adiabatic separation of electronic and nuclear motion provides a widely used frame-

tronic wave function is a continuous, single-valued function of nuclear coordinates and that the nuclear wave function is determined by the usual nuclear Schrödinger

J. Chem. Phys. **70**, 2284 (1979)

Mead's molecular gauge theory

- *Born-Huang approximation*; truncate to a finite set $V_{PES}^{(i)}(R)$ and corresponding eigenstates.

- In the projected space of the slow variable

$$\left[-\frac{1}{2M}\nabla_R^2 + V_{nn}(R) + V_{PES}(R) + F(R)\cdot\nabla_R + G(R)\right]\psi(R) = E\psi(R)$$

- The electronic states $|\phi_i(R)\rangle$ depend parametrically on R, the (slow) operator $-i\nabla_R$ act also on the fast subspace.

- $|\phi_i(R)\rangle$ defined up to a phase factor $\exp(i\theta_i(R))$, changes $F(R)$.

$$\left[-\frac{1}{2M}\left(\nabla_R - A(R)\right)^2 + V_{PES}(R) + \Phi(R)\right]\psi(R) = E\psi(R)$$

Bohm *et al., The Geometric Phase in Quantum Physics*, (Springer 2006)

Mead's molecular gauge theory

- *Mead-Berry connection*

$$A^{ij}(R) = i\langle \phi_i(R) | \nabla_R \phi_j(R) \rangle$$

- *Mead-Berry curvature*

$$F_{ij}^{nm} = \partial_i A_j^{nm}(R) - \partial_j A_i^{nm}(R) - i\left[A_i^{nm}(R), A_j^{nm}(R)\right]$$

- Unitary transformation

$$A(R) \rightarrow U(R)A(R)U^{-1}(R) + iU(R)\nabla_R U^{-1}(R)$$

Proper gauge transformation!

Bohm *et al., The Geometric Phase in Quantum Physics*, (Springer 2006)

Mead's molecular gauge theory

- Natural basis (*diabatic*)

$$\left[-\frac{1}{2M}\nabla_R^2 + V(R)\right]\psi(R) = E\psi(R)$$

$V(R)$ potential matrix, diagonal terms $V_{di}^{(i)}(R)$ *diabatic potential surfaces.*

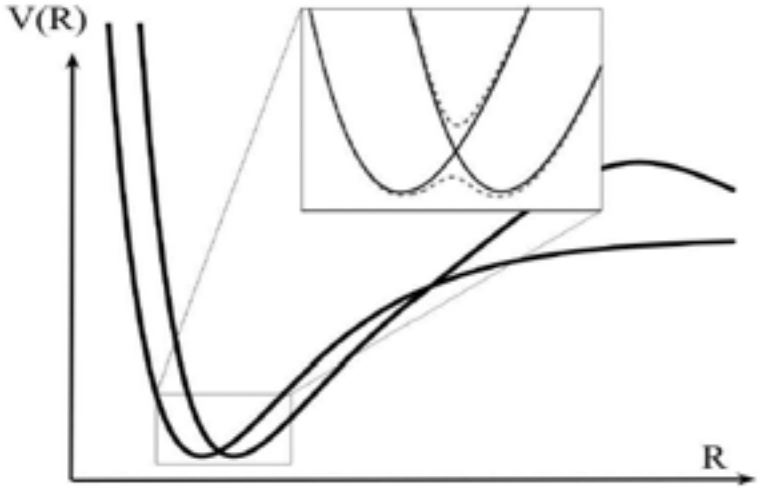
- Diagonalize

$$D(R) = U(R)V(R)U^\dagger(R)$$

$$\nabla_R \to \nabla_R - iU(R)\nabla_R U^\dagger(R)$$

- Eigenstates and eigenvalues of $V(R)$, *adiabatic states and potentials.*

Solid = diabatic,
dashed = adiabatic.



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Conical intersections

Studies of the Jahn–Teller effect
II. The dynamical problem

By H. C. Longuet-Higgins,* U. Öpik,† M. H. L. Pryce, F.R.S.‡
and R. A. Sack§

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†Department of Applied Mathematics, University College of Wales, Aberystwyth
‡Department of Physics, University of Bristol

(*Received* 14 *August* 1957)

This paper examines the vibronic energy levels of a symmetrical non-linear molecule in a spatially doubly degenerate electronic state which is split in first order by a doubly degenerate vibrational mode. The vibronic levels are classified by a quantum number, which in certain cases is formally related to the combined angular momentum of electronic and vibrational motion, and numerical values are obtained for the energies of these levels as functions of this quantum number and a dimensionless parameter measuring the magnitude of the electronic-vibrational coupling.

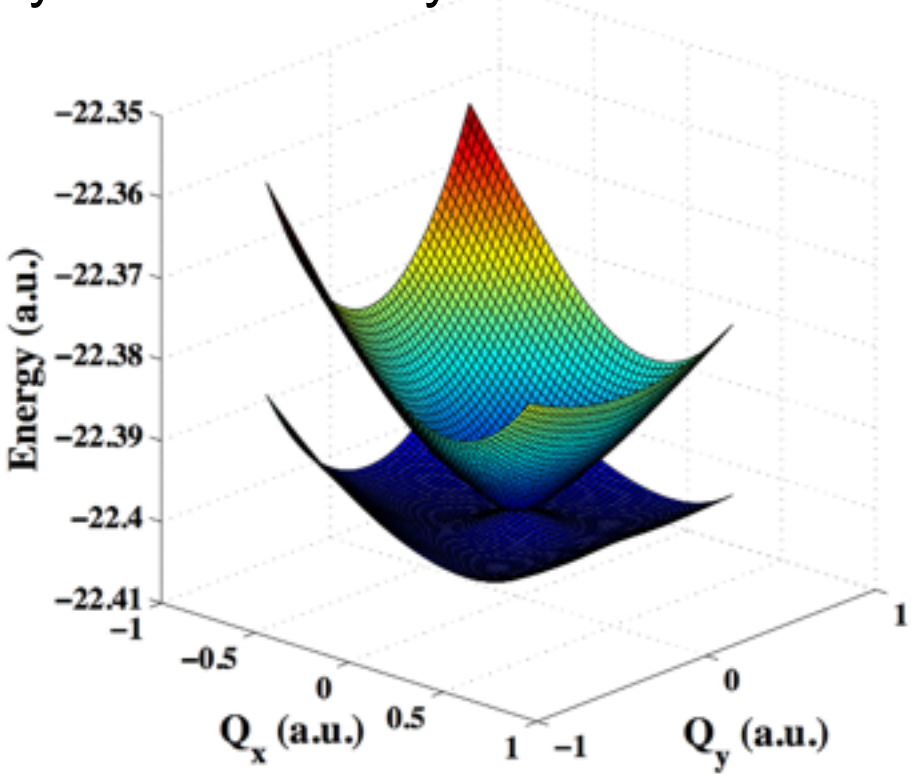
It is shown that the selection rules for transitions from these vibronic levels to those of a non-degenerate electronic state allow changes in vibrational energy of any integral number of quanta, as though the Jahn–Teller effect were equivalent to a distortion which makes allowed vibrational transitions which would otherwise be forbidden.

Numerical values are given for the oscillator strengths of vibronic absorption or emission

Proc. R. Soc. London Ser. A **244**, 1 (1958)

Conical intersections

- Breakdown of BOA ($A(R),\ \Phi(R) \to 0$) whenever gap closes.
- Given configuration $\{R\}$, the molecule may possess some point symmetry $\rightarrow$ degeneracy. May exist without symmetries!
- *Conical intersection* (CI), linear potentials.
- *Glancing intersections* (Renner-Teller), quadratic potentials.
- "Seam of CI's" in higher dimensions.



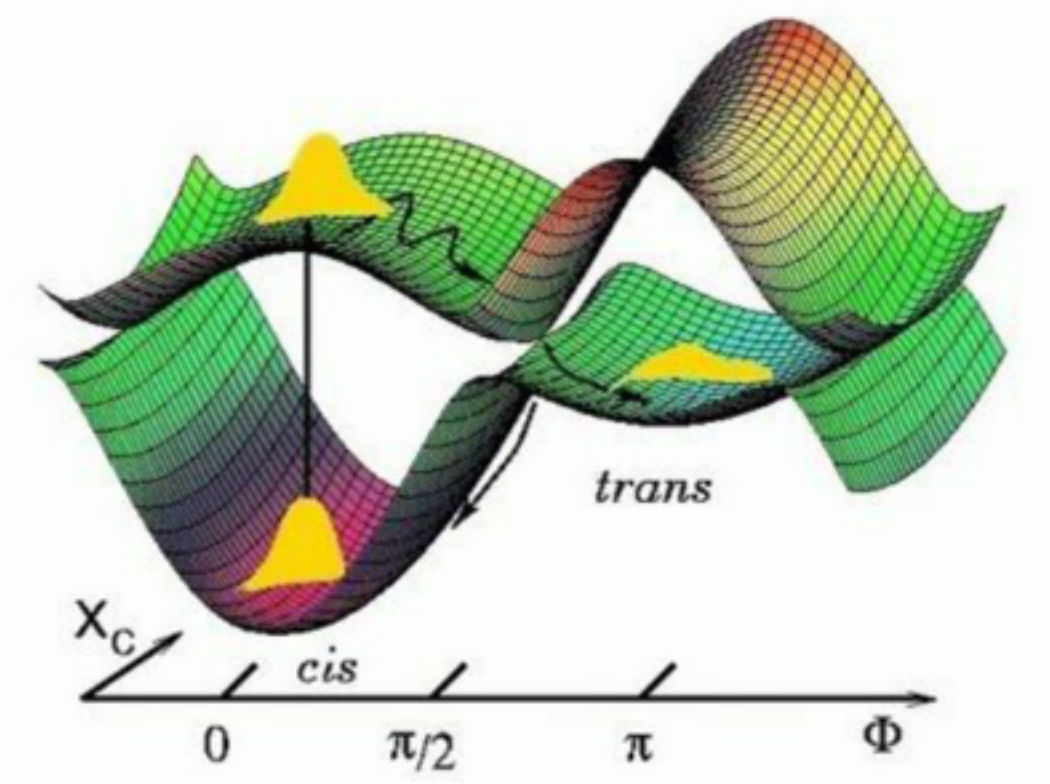
M. Bear. *Beyond Born-Oppenheimer (Wiley, 2006)*

Conical intersections

- Breakdown of BOA may drive chemical reactions.

- DNA exposed to UV radiation. CI's provides a relaxation channel. Excess energy in heating of the gas.

  Without CI's the DNA would dissociate/break apart!



Conical intersections

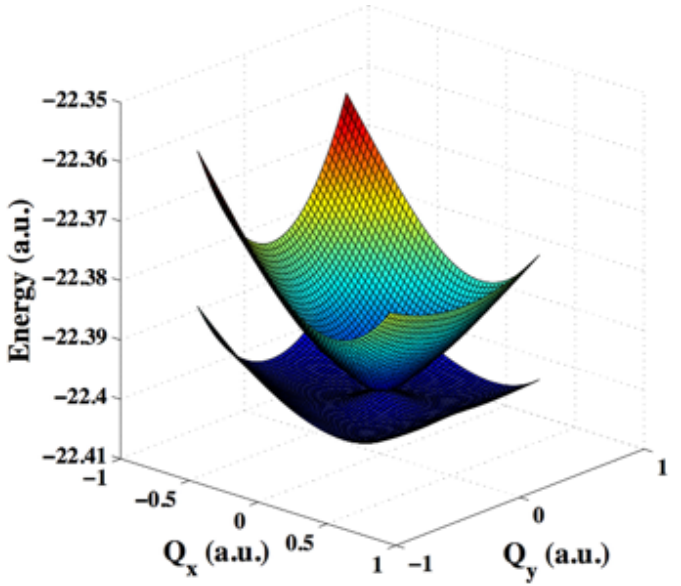
- Linearize the CI

$$\hat{H}_{E\times\varepsilon} = \frac{\hat{p}_x^2}{2m} + \frac{\hat{p}_y^2}{2m} + \frac{m\omega^2}{2}\left(\hat{x}^2 + \hat{y}^2\right) + k\left(\hat{x}\hat{\sigma}_x + \hat{y}\hat{\sigma}_y\right)$$

- In gauge formalism. Magnetic flux penetrating the CI.

- Encircling the CI $\rightarrow \pi$ phase shift.
  Molecular Ahronov-Bohm effect.

  1. Half integer angular momentum.
  2. Ground state *E* symmetry, not *A*.



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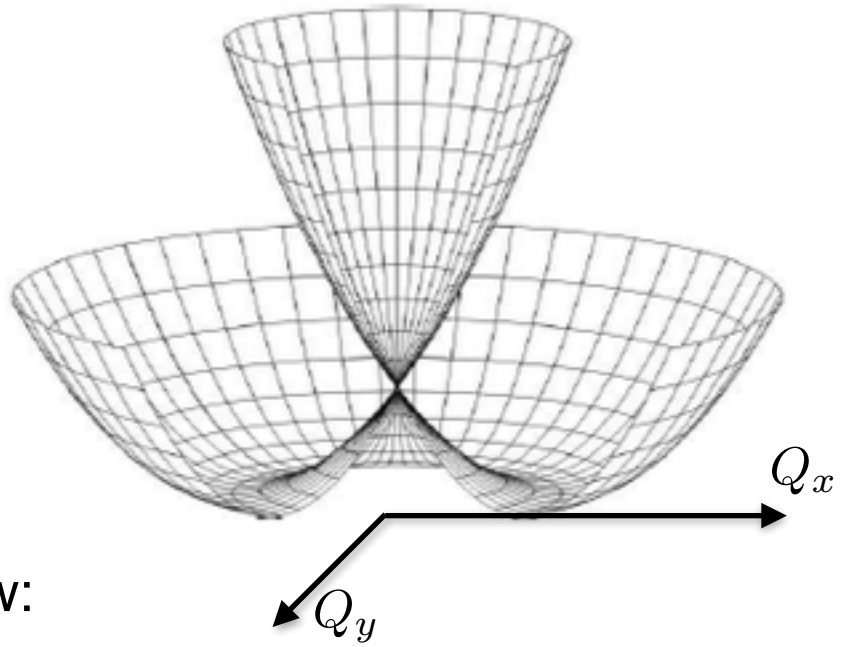
Anomalous molecular evolution

- Mead's gauge theory predates Berry.
- Longuet-Higgins knew about the sign change around the CI.
- The cond-mat community explored in detail *Dirac cones* 'independently' of AMO.
- They even more recently started exploring "glancing intersections" (Renner-Teller) without open the molecular literature.
- Let's turn the coin:

Where do known phenomena from other fields manifest themselves in molecular physics?

Anomalous molecular evolution

- Adiabatic PES of $E \times \varepsilon$



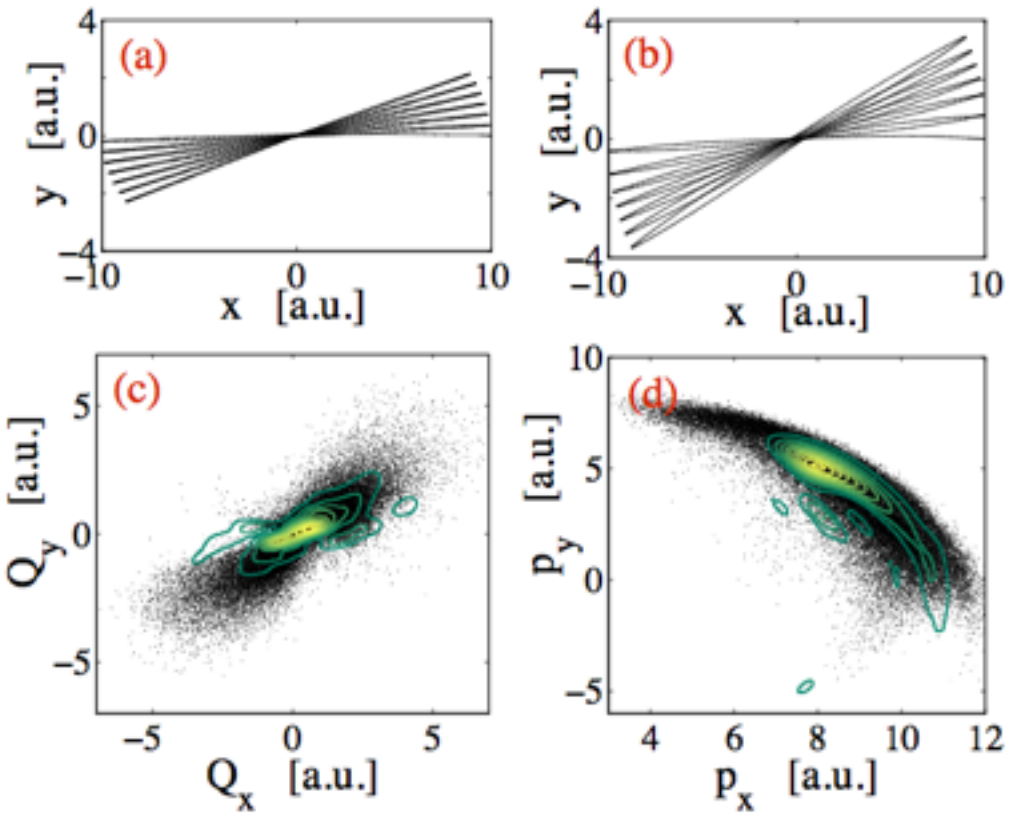
- What do we know:

1. Breakdown of BOA at the CI.
2. Polar symmetry involving both $\hat{L}_z$ and $\hat{\sigma}_z$.
3. Synthetic magnetic field through the CI.
4. Field (thereby also Lorentz force) zero away from the CI.

Anomalous molecular evolution

- Gaussian initial state at lower surface,

  How will it evolve?



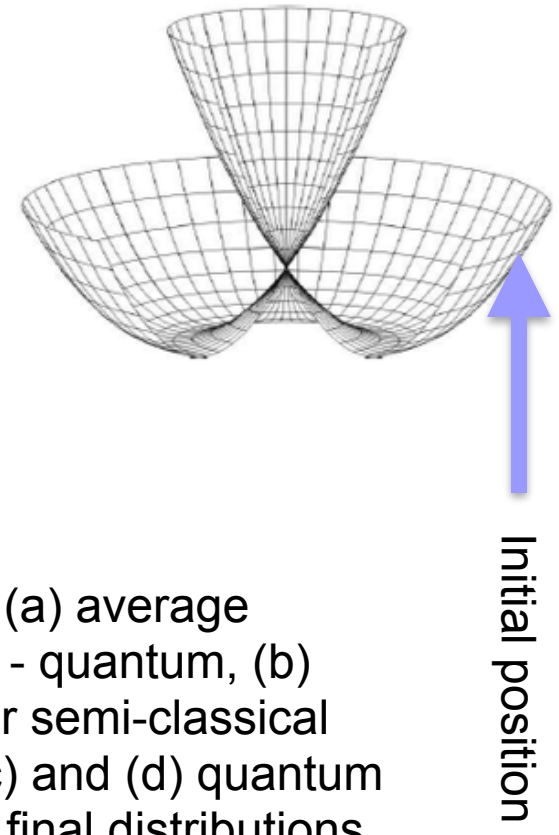


Figure. (a) average position - quantum, (b) same for semi-classical TWA. (c) and (d) quantum vs TWA final distributions.

J. Larson E. N. Ghasemi, Å. Larson, EPL **101**, 43001 (2013).

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Dual molecular gauge theory - molecular Hall effect

- First let's try Mead's gauge theory

$$\hat{H}_{E\times\varepsilon} = \omega\left(\frac{\hat{P}_x^2}{2}+\frac{\hat{P}_y^2}{2}+\frac{\hat{Q}_x^2}{2}+\frac{\hat{Q}_y^2}{2}\right)+k\left(\hat{Q}_x\hat{\sigma}_x+\hat{Q}_y\hat{\sigma}_y\right)$$

$$\hat{A}_x = \frac{\hat{Q}_y}{\hat{Q}_x^2+\hat{Q}_y^2}, \qquad \hat{A}_y = -\frac{\hat{Q}_x}{\hat{Q}_x^2+\hat{Q}_y^2}$$

$$\hat{F}_{jk} = \partial_j\hat{A}_k - \partial_k\hat{A}_j - i\left[\hat{A}_j,\hat{A}_k\right]$$

No synthetic Lorentz force outside the CI, solely a potential force

$$F = -\nabla V_{PES}(Q_x,Q_y)$$

J. Larson E. N. Ghasemi, Å. Larson, EPL **101**, 43001 (2013).

Dual molecular gauge theory - molecular Hall effect

- Semi-classical Heisenberg equations

$$
\begin{aligned}
\dot{Q}_x &= \omega P_x, \\
\dot{P}_x &= -\omega Q_x - k s_x, \\
\dot{Q}_y &= \omega P_y, \\
\dot{P}_y &= -\omega Q_y - k s_y, \\
\dot{s}_x &= k Q_y s_z, \\
\dot{s}_y &= -k Q_x s_z, \\
\dot{s}_z &= k \left(Q_x s_y - Q_y s_x \right)
\end{aligned}
$$

Transverse position $\ddot{Q}_y = -\omega^2 Q_y - \omega k s_y$. Linearize for small times

$$Q_y \sim k^2 t^3$$

Must derive from coupling of P_y to s_y- spin-orbit coupling.

J. Larson E. N. Ghasemi, Å. Larson, EPL **101**, 43001 (2013).

Dual molecular gauge theory - molecular Hall effect

- Rewrite

$$\hat{H}_{E\times\varepsilon} = \omega \left[\frac{\left(\hat{Q}_x - \hat{A}_x\right)^2}{2} + \frac{\left(\hat{Q}_y - \hat{A}_y\right)^2}{2} + \frac{\hat{P}_x^2}{2} + \frac{\hat{P}_x^2}{2} \right] + \hat{\Phi}$$

with the 'dual' gauge potentials

$$\hat{A}_{x,y} = -\frac{k}{\omega}\hat{\sigma}_{x,y}$$

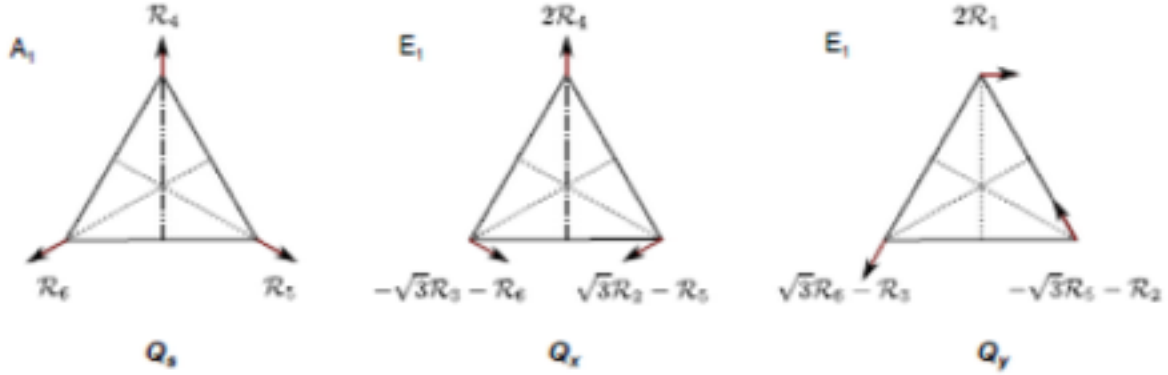
Rashba spin-orbit coupling in dual space.

Intrinsic spin-Hall effect!!

J. Larson E. N. Ghasemi, Å. Larson, EPL **101**, 43001 (2013).

Dual molecular gauge theory - molecular Hall effect

- Do we see the effect in real molecular systems?
  - We need a conical intersection.
  - The PES's should be stable, ideally CI between the lowest bound PES's.
  - Too strong spin-orbit coupling, distort the localized wave packet too rapidly.
- Li_3 a good candidate.
- 9 degrees-of-freedom, but three normal vibrational modes.



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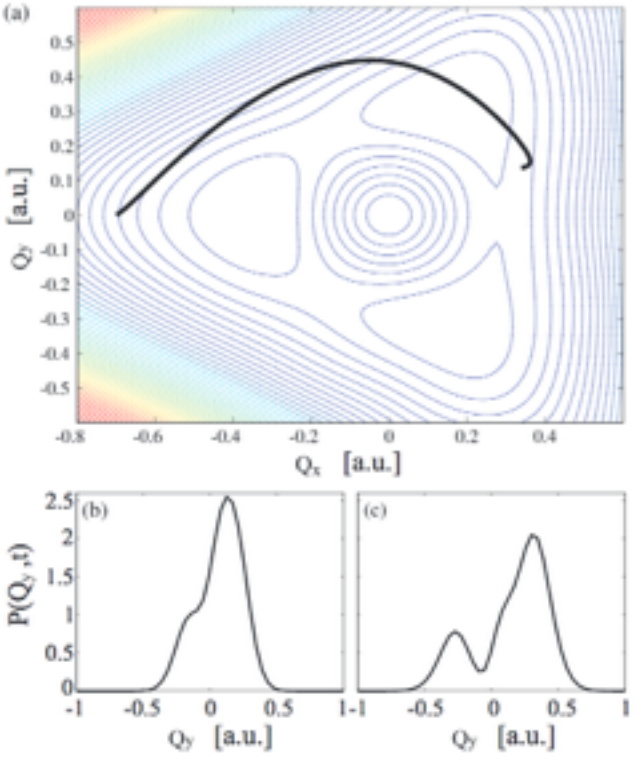
Dual molecular gauge theory - molecular Hall effect

- Third dimension, seam of CI's. Focus on projection on 'bending' and 'asymmetric stretching' modes. Minima along the third symmetric mode.
- Clear Hall effect.
- Wave-packet distorted after a few classical oscillations.
- Should be visible within 'pump-probe' experiments.



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Thanks!