Quantum Control with Quantum Light

Controlling Non-Adiabaticity in Molecules

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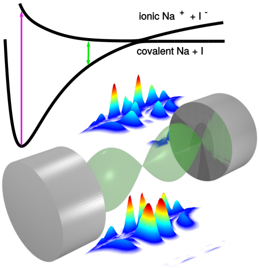
July 10, 2019

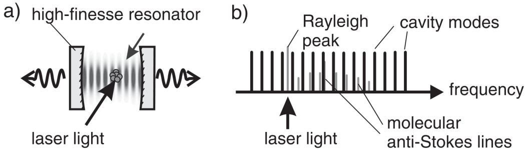
Overview



Introduction

Molecules In Cavities

- Confined light modes
- Strong coupling
- Modification of potential energy surfaces
- Applications in photo chemistry
- Quantum Optimal Control?



Morigi et al. PRL **99**, 073001 (2007)
Schlawin et al. NJP, **19**, 013009 (2017)
Brumer, Shapiro, "Quantum Control of Molecular Processes" (2012)

Quantizing the Photon Mode

From Control with Classical Light to Control with Quantum Light

Classical light:

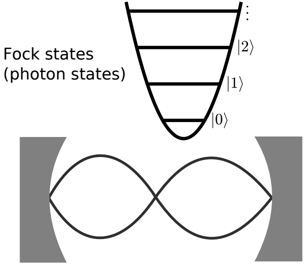
- Single mode
- Dipole interaction
- $V_c = -\mu(R) E_0 \cos(\omega_L t + \phi)$

Quantum light:

- Single cavity mode
- Dipole interaction
- Fock states

$$H_c = \hbar\omega_c \left(a^\dagger a + \frac{1}{2} \right)$$

$$V_c = \varepsilon_c \mu(R) \left(a^\dagger + a \right) \left(\sigma^\dagger + \sigma \right)$$

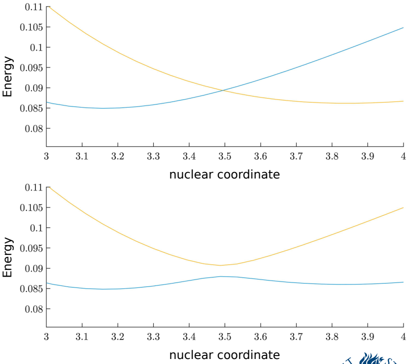


Kowalewski et al., PNAS, **114**, 3278 (2017)

To Diagonalize or not to Diagonalize?

Dressed States vs. Bare States

- **Bare molecular states:**
- Fock states
- Only position dependent couplings $g(R)$
- PES less intuitive?
- **Photon displacement coords:**
- Arbitrary photon states
- Beyond RWA $(a^{\dagger}\sigma^{\dagger} + a\sigma)$
- **Dressed states:**
- Avoided crossings
- Derivative couplings

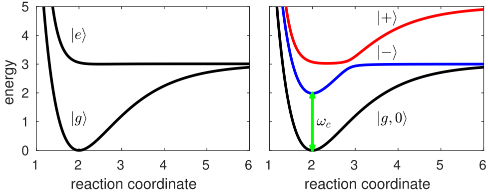


Dressed States Non-adiabatic dynamics

Theoretical Chemist's Picture

- Nonadiabatic couplings in the curve crossing region: $f = \langle \phi_k | \partial_q \phi_l \rangle$
- Adiabatic curves, avoided crossings:
  $\rightarrow$ Localized couplings, intuitive picture from QC
- Detuning, gradient difference, derivative of tr. dipole

$$\hat{H}_{kl} = \hat{T} + \delta_{kl} \hat{V}_{kl} + \sum_i \frac{1}{m_i} \left(f_{kl}^{(i)} \frac{\partial}{\partial q_i} + \frac{1}{2} h_{kl}^{(i)} \right)$$



M. Kowalewski et al., J. Chem. Phys., **144**, 054309 (2016)

J. Galego et al., Phys. Rev. X, **5**, 041022 (2015)

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From Fock States to Displacement Coordinates

Putting the photon mode and vibrational coordinates on the same footing

Field anhilation operator:

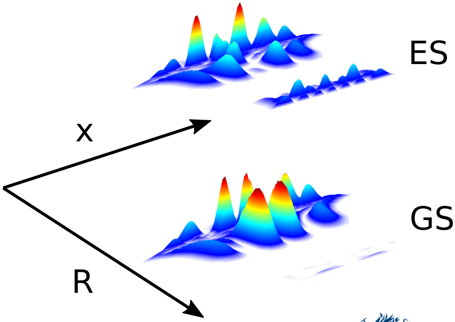
$$a = \sqrt{\frac{\omega_c}{2\hbar}}\left(\hat{\mathbf{x}} + \frac{i}{\omega_c}\hat{\mathbf{p}}\right)$$

In displacement coordinates:

$$H_c = \frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}\mathbf{x}^2} + \frac{1}{2}\omega_c^2\hat{\mathbf{x}}^2$$

$$V_c = g\sqrt{2\hbar\omega_c}\hat{\mathbf{x}}\left(\hat{\sigma}^\dagger + \hat{\sigma}\right)$$

x: dimensionless coordinate.



Kowalewski et al. JPCL, **7**, 2050 (2016)
Flick et al., JCTC, **13**, 1616 (2017)

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Coherent Control with Laser Pulses

Classical Coherent Control vs. Coherent Control with Quantum Light

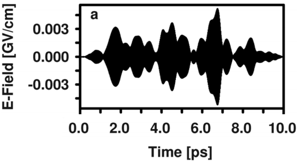
$$E(t) = \sum_n E_n cos(\omega_n t + \phi_n)$$

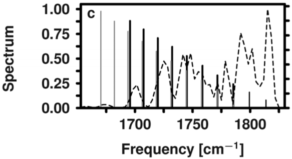
Pulse shaping, classical light:

- Frequency domain
- Amplitude
- Phase
- (Polarization)

Quantum light:

- Super pos. Fock states
- Different photon numbers
- Amplitude, phase
- Non-classical states





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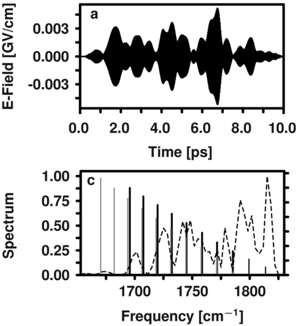
→ Idea: start with single mode

$$E(t) = \sum_n E_n cos(\omega_n t + \phi_n)$$



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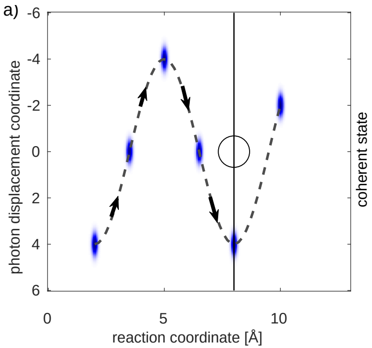
Coherent states:



- Two electronic states
- Nuclear coordinate
- Photon coordinate
- Linear coupling
- $V_c = g\sqrt{2\hbar\omega_c}\hat{x}\left(\hat{\sigma}^\dagger + \hat{\sigma}\right)$

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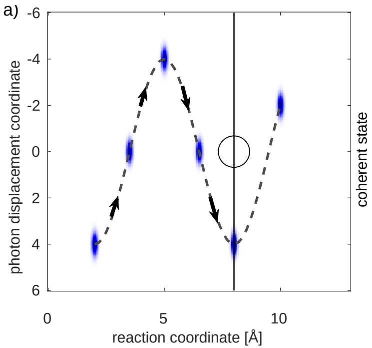
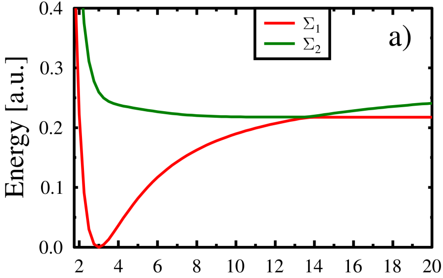
Quantum Light and Molecules

Combining the photon mode with vibrational degrees of freedom

Coherent states:



Control avoided crossing:



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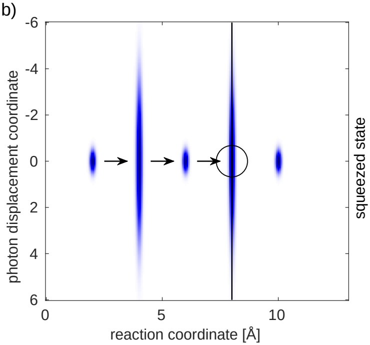
Squeezed vaccum state:



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- Nuclear coordinate
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Quantum Light and Molecules

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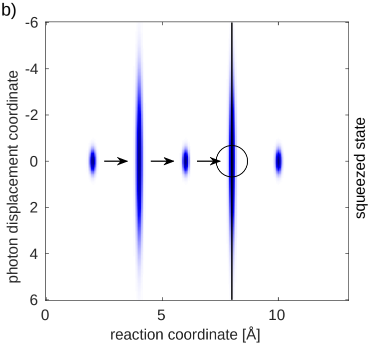
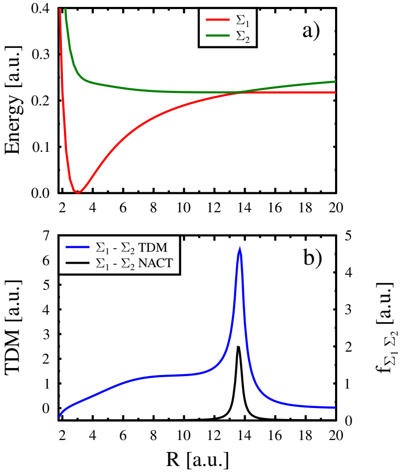


- Two electronic states
- Nuclear coordinate
- Photon coordinate
- Linear coupling
- $V_c = g\sqrt{2\hbar\omega_c}\hat{x}\left(\hat{\sigma}^\dagger + \hat{\sigma}\right)$

$\rightarrow$ control coupling via shape of photon wave packet

Test Case: Lithium Fluoride

Controlling population transfer at the avoided crossing



- Pump-Pulse launches dynamics in Σ_2
- Cavity mode resonant at avoided crossing
- Different initial states of photon mode
- Fock, squeezed vacuum, squeezed coherent

A. Csehi et al. arXiv:1904.12693 (2019)

J. F. Triana, et al. JPCA **122**, 2266 (2018)

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- Photon coordiante displacement coordinates x
- Nuclear coordinate R
- Intrinsic avoided crossing
- MCDTH for WP dynamics

$$\begin{aligned} H_{kl} = \delta_{kl} &\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial R^2} + \hat{V}_k(R) - \frac{\hbar^2}{2}\frac{\partial^2}{\partial x^2} + \frac{1}{2}\omega_c^2\hat{x}^2\right) \\ &+ (1-\delta_{kl})\, g(R)\sqrt{2\hbar\omega_c}\hat{x} \\ &+ (1-\delta_{kl})\,\frac{1}{2m}\left(2f_{kl}(R)\frac{\partial}{\partial R} + \frac{\partial}{\partial R}f_{kl}(R)\right) \end{aligned}$$

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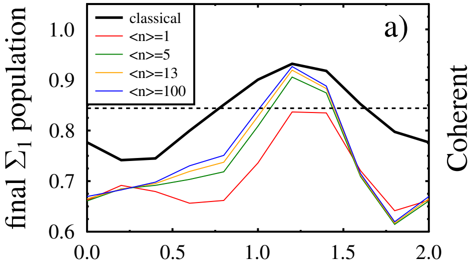
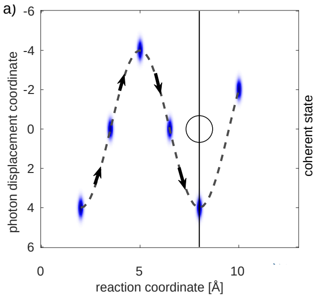
Coherent States

The classical analogy?

Control parameter: initial displacement phase ($\equiv$ carrier phase)
fixed initial displacement parameter.



Coherent state phase

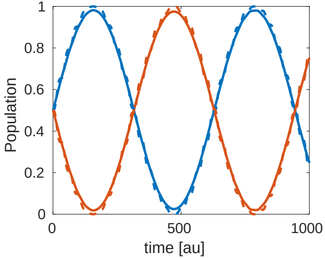


What's the Closest Correspondence to a Classical State?

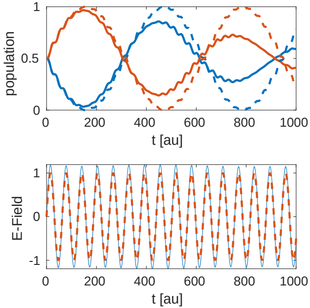
Fock state or coherent state?

Let's have look at a two level atom coupled to a cavity:

Fock state



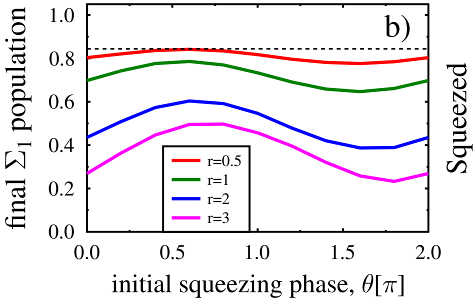
Coherent state

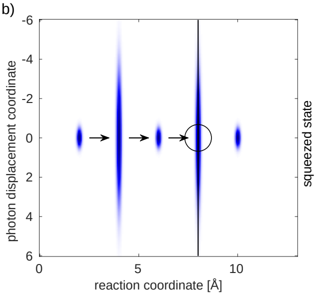


Squeezed Vacuum States

Quantum Light – No classical analogy

Control parameter: initial squeezing phase
fixed squeezing parameter.





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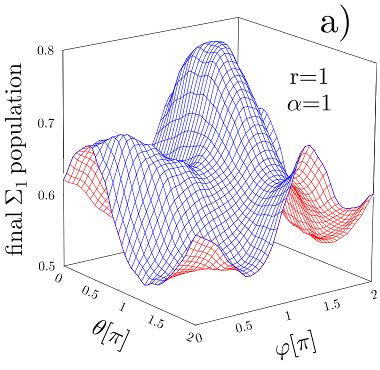
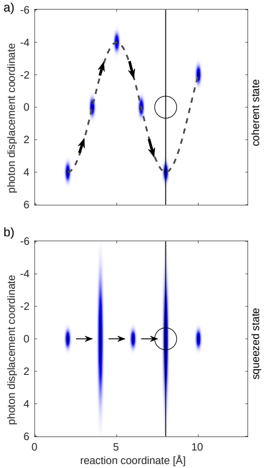
Squeezed Coherent States

Control landscapes



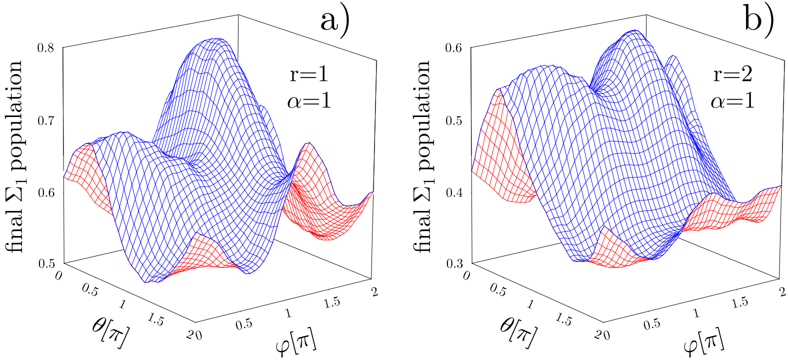


Squeezing phase: Θ

Coherent state phase: φ

Squeezed Coherent States

Control landscapes



Squeezing phase: Θ

Coherent state phase: φ

Summary and Outlook

Summary:

- Quantized field modes and molecular quantum dynamics
- Non-classical states of light steer population
- Single cavity mode
- Only suppresstion of population has been observed
- Control beyond phase/amplitude control of laser pulses

Outlook:

- Multiple modes (laser pulse analogy)
- Molecular ensembles
- Investigate different control scenarios
- Creation of initial states?

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Acknowledgment

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Stockholm 2021?

Conference Announcement

- Nordita: Coherent Control with Modified Vacuum Fields
- Summer school
- Conference & Workshop
- Planned for ≈August 2021
- We need to get funding first!

→ If you are interested send an email to
markus.kowalewski@fysik.su.se
Subject "Cavities in Stockholm 2021"