Optimal control of quantum dynamics in polyatomic molecules

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Outline

- Molecules
- Why MCTDH?
- What is Optimal control theory (OCT)?
- What have we done?
- What do we want to do?

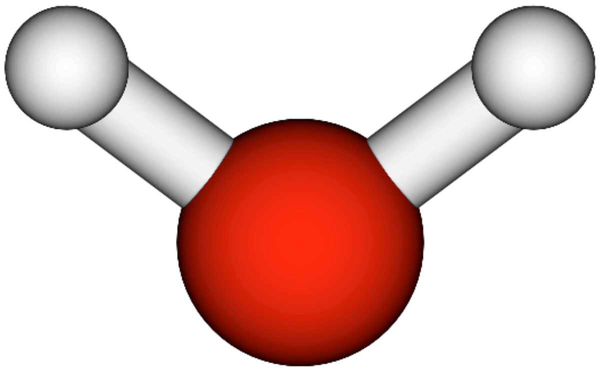
Fundamental Questions?

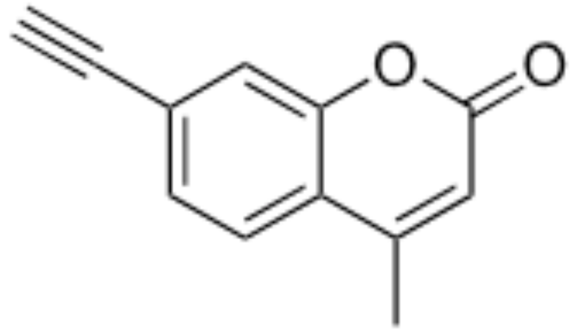
or

Applied Questions?

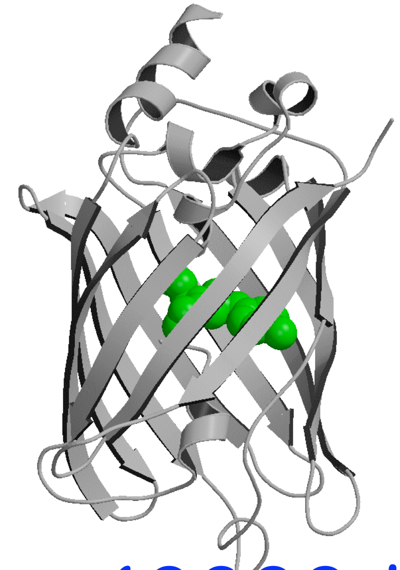
Molecules

Water (H_2O)





22 atoms
60d



~10000d

Calculate a potential energy surface $V(r_1,r_2,\Theta)$

Calculate a dipole moment surface $\mu(r_1,r_2,\Theta)$

Can we determine molecular properties accurately enough?

Ingredients for OCT

Option A) Solve time-independent SE to obtain a basis of eigenstates (and corresponding dipole moment matrix) in which to do your time-dependent OCT calculation

What if your system is too big?

Use simple harmonic/anharmonic models

Only treat "a piece" of the system: Reduced dimensionality

What if your spectrum is not just discrete?

Option B) Perform the time-dependent OCT calculation using the potential and dipole moment surfaces directly

Problem: Multi-dimensional quantum dynamics is hard (exponential scaling)

Why reinvent the wheel?

Use the Multi-Configuration Time Dependent Hartree (MCTDH) approach

http://www.pci.uni-heidelberg.de/cms/mctdh.html

MCTDH

Advantages:
- Can be fast
- Algorithm is small
- Can tackle "real" problems 4-15 degrees of freedom (model problems to much higher dimension)

Disadvantages:
- Hamiltonian must be expanded as a product of one-particle operators (hard for the potential/dipole)
- Is fast only if time-dependent wavepacket can be expanded into a small product basis set

The need for ND quantum dynamics

- New methodologies developed and tested for 1D
- Applications in 1D, 2D, 3D, and 4D*

- Reduced dimensionality models for N-D

- Study of HCN $\rightarrow$ HNC

- S. Shah and S.A. Rice, JCP 113, 6536 (2000)
- investigated as a function of # of DOF (1,2,3)
- control achieved for any # DOF

BUT

- the optimal control field generated using a simpler dynamical description is not a good guide to the one associated with a more complex dynamical description

Wang et al., JCP **125**, 014402 (2006)

Marry OCT with MCTDH

Schröder, Carreon-Macedo, AB, PCCP, 10, 850 (2008)
Schröder and AB, JCP, 131, 034101 (2009)

Optimal Control Theory

Maximize objective functional

$$J = \left\langle \psi(T) \middle| \hat{O} \middle| \psi(T) \right\rangle$$

$$J = \left| \left\langle \Phi \middle| \psi(T) \right\rangle \right|^2$$

Objective functional

Population transfer

Formulating the problem

Population transfer

A given initial state → Laser field $\mathcal{E}(t)$ → A desired final state

$\psi_i(t=0)$ $\qquad$ ϕ_f

Need to find this!!

Caveat

Would like the laser field to be "realistic"

Experimentally realizable
(at least in some place, at some time)

We need to consider constraints

Optimal Control Theory

$$J = \left| \langle \Phi(T) \mid \psi(T) \rangle \right|^2 \; -\alpha \int \frac{\varepsilon^2(t)}{s(t)} dt$$

Objective functional

Population transfer

Constraints on the laser field

α = penalty parameter (constant)

$$= \mathrm{J}_1 - \mathrm{J}_2$$

Solve iteratively: Rabitz or Krotov algorithms

PROBLEM: Must solve the TDSE many times!

Generalized filtering of fields in OCT

How do you put constraints on the field?

How do you retain monotonic convergence?

OCT with constraints

Write the control functional:

$$J(\varepsilon,\psi,\Phi,\gamma) = \left|\langle \Phi | \psi(T)\rangle\right|^2 - \alpha\int_0^T \frac{\left[\varepsilon(t)-\varepsilon_{ref}(t)\right]^2}{s(t)}dt - \left\|\left(\gamma\middle|Q\middle|\varepsilon\right)\right\|$$

$$-\mathrm{Re}\left\{\langle \psi(T)|\Phi\rangle \int_0^T \left\langle \Phi(t)\middle| i\left((H_0-\mu\varepsilon(t))-\frac{\partial}{\partial t}\right)\middle|\psi(t)\right\rangle\right\}$$

$$= J_1 - J_2 - J_3 - J_4$$

J_1 = target state population

J_2 = “punishes” the field strength

J_4 = TDSE must be fulfilled

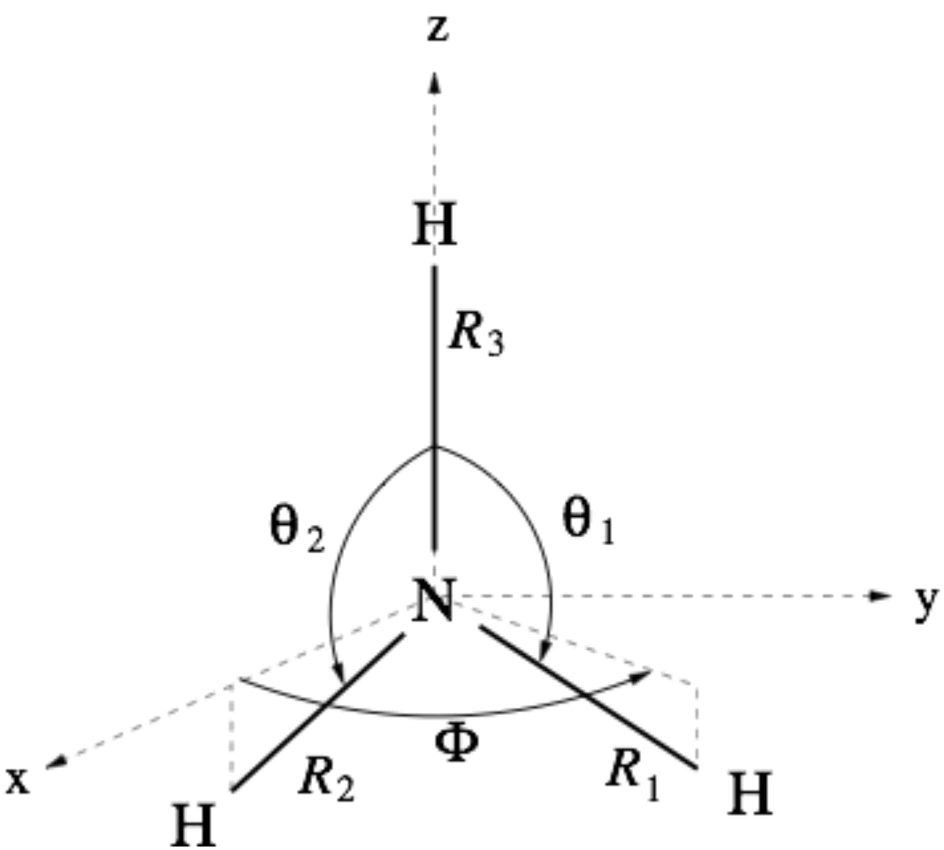
J_3 = punishes for contributions after operation w/ Q

Schröder and AB, NJP, 11, 105031 (2009)

A toolbox to examine a variety of OCT problems

Problem: Need molecular properties

Ammonia: Coordinate system



- Inversion covered by Φ
- Asymmetric bending covered by θ_i
- Reduced 3D model possible by “freezing” bond lengths
- Accurate potential energy and dipole surfaces

Gatti et al. JCP **114**, 8275 (2001)

Yurchenko et al. JCP **123**, 134308 (2005)

Multi-target OCT

$$K_{fi} = \sum_{k=1}^{N} \left| \langle \psi_{ik}(T) | \phi_{fk} \rangle \right|^2 - \alpha \int_0^T |\varepsilon(t)|^2 dt$$

$$-2\,\mathrm{Re}\left\{ \langle \psi_{ik}(T) | \phi_{fk} \rangle \int_0^T \langle \psi_{fk}(t) | i[H_0 - \mu \cdot \varepsilon(t)] + \partial/\partial t | \psi_{ik}(t) \rangle dt \right\}$$

Determine the pulse for the CNOT gate

$$\mathrm{CNOT}\,|00\rangle \rightarrow |00\rangle$$

$$\mathrm{CNOT}\,|01\rangle \rightarrow |01\rangle$$

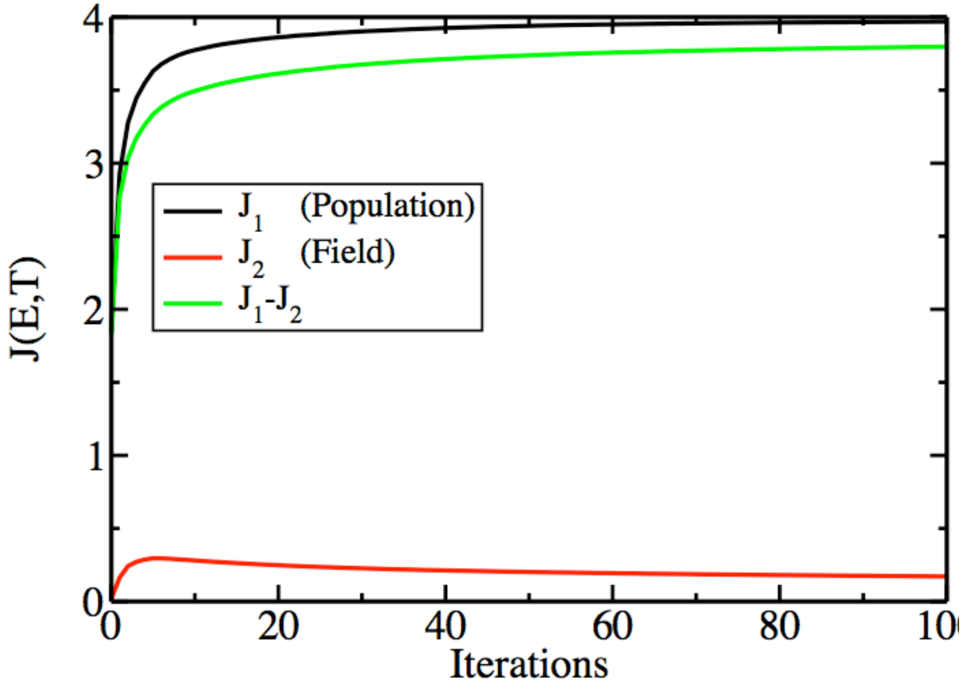
$$\mathrm{CNOT}\,|10\rangle \rightarrow |11\rangle$$

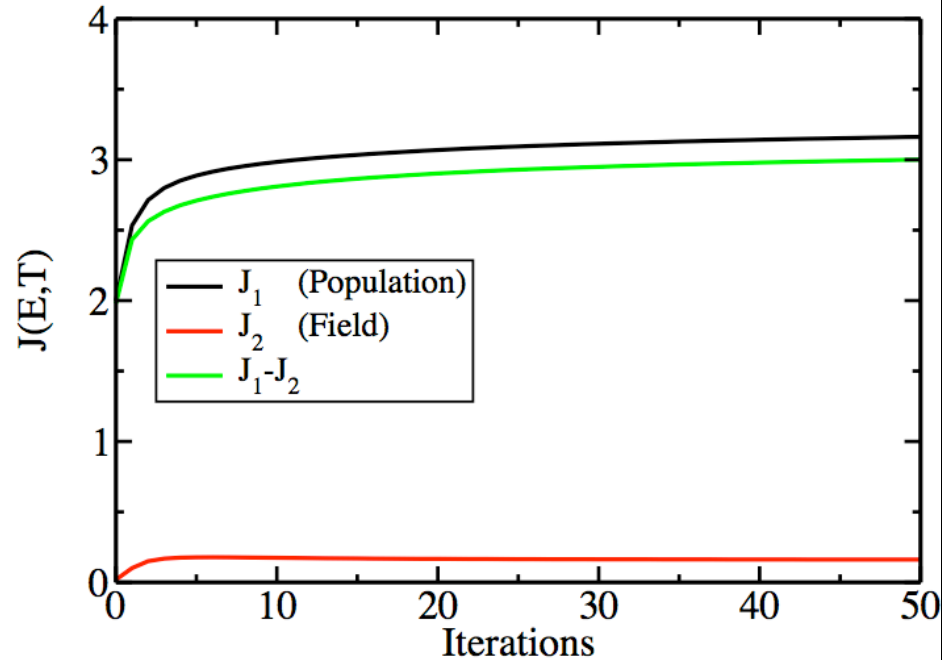
$$\mathrm{CNOT}\,|11\rangle \rightarrow |10\rangle$$

Number of quanta in bend

Number of quanta in inversion

3D vs 6D Ammonia: CNOT Gate Control functional



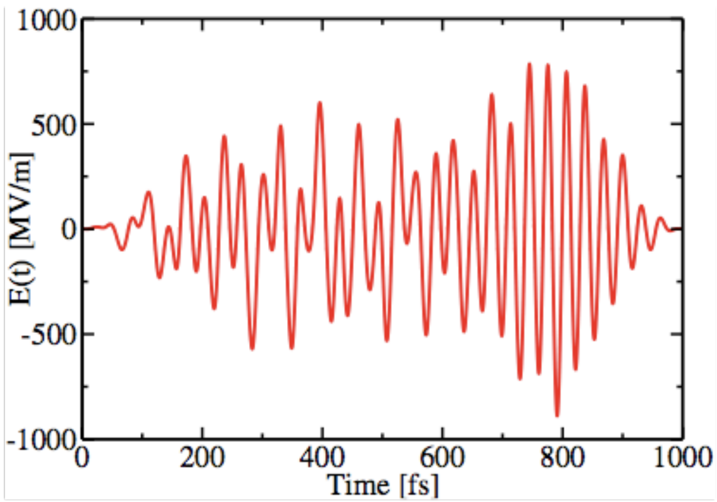


- Average yield 99.2%

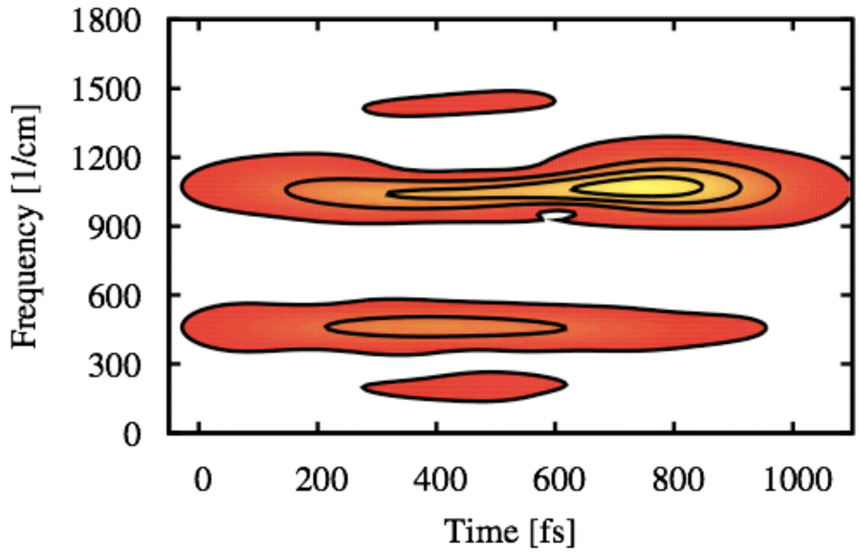
- Average yield 79%

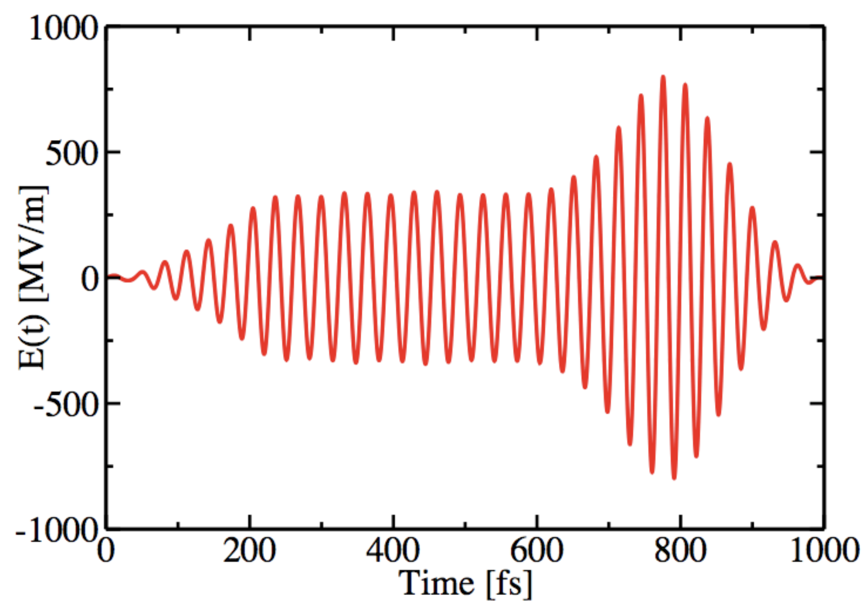
Schröder and AB, JCP, 131, 034101 (2009)

3D Ammonia: CNOT Gate
Laser field

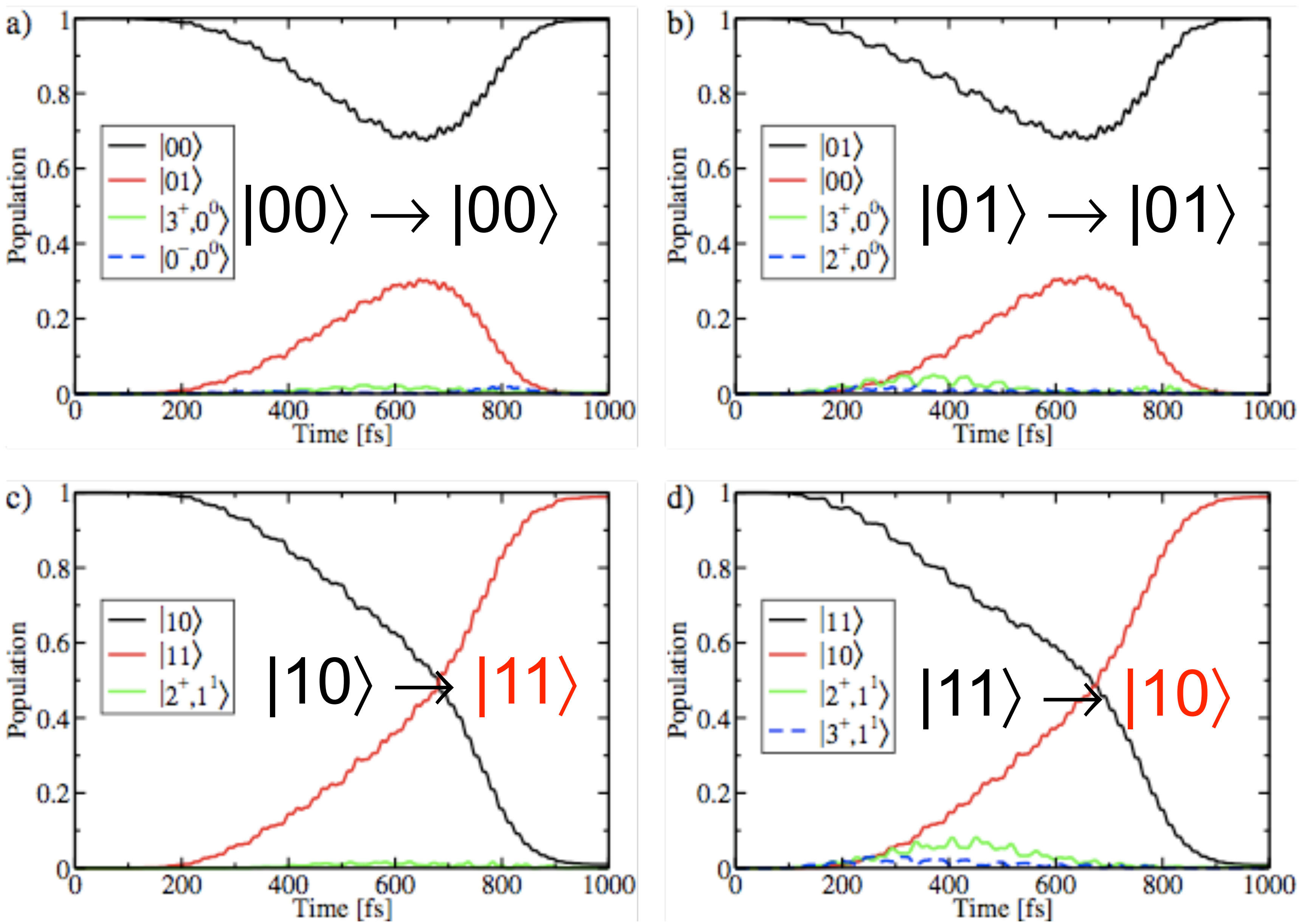


Wow! This control field looks exciting! What does it mean?

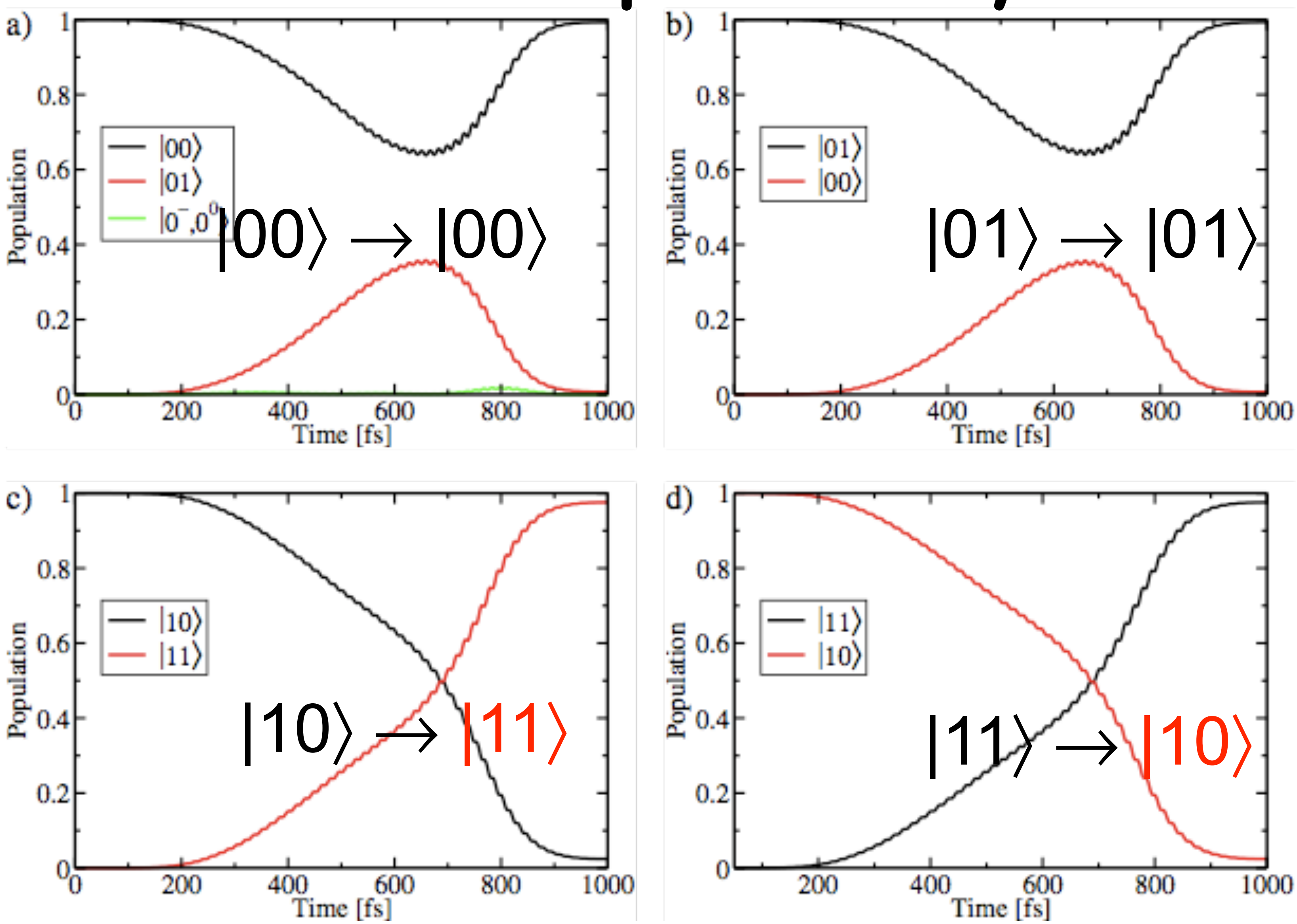




3D Ammonia: Population Dynamics



3D Ammonia: Population Dynamics



Average 98.5% population transfer

On-going/Future Work in OCT

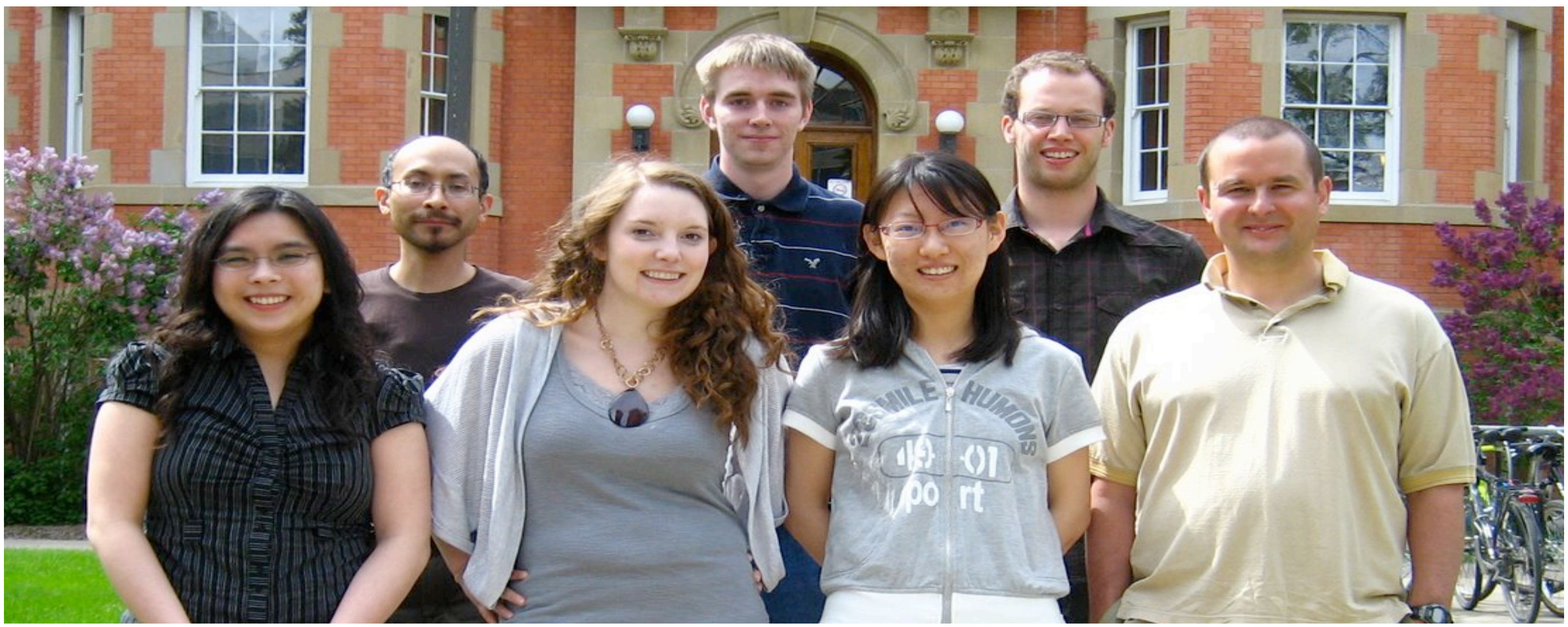
1. Applications:
   - Molecular quantum computing in N-D
   - Control of IVR/Isomerization
   - Working on PESs and dipole moments (NN fitting)
2. Use of optimized fields for (N-1)-dimensional systems to guide searching for N-d systems
   $\rightarrow$ multi-dimensional quantum dynamics
3. Genetic algorithms in the frequency domain (connection w/ experiment)

$$\epsilon(\nu_j) = \epsilon_0 \sqrt{A(\nu_j)} \exp\left[-2\ln 2\left(\frac{\nu_j - \nu_0}{\Delta\nu}\right)^2\right] \exp\left[i\phi(\nu_j)\right]$$

Acknowledgements

M. Schröder

H-D. Meyer (MCTDH)



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