Mathematical Quantum Control
Molecular Dynamics

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Motivations and open questions

- **Planar molecule** Approximate controllability of a planar molecule has been established in [1]. The Schrödinger equation

$$i\frac{\partial}{\partial t}\psi(\theta,t)=\Big(-\frac{\partial^2}{\partial\theta^2}+u_1(t)cos\theta+u_2(t)sin\theta\Big)\psi(\theta,t),\quad \psi(t)\in L^2(S^1).$$

- **Linear molecule** Approximate controllability of a linear molecule has been established in [2]. The Schrödinger equation

$$i\frac{\partial}{\partial t}\psi(\theta,\phi,t)=-\Delta\psi(\theta,\phi,t)+(u_1(t)sin\theta cos\phi+u_2(t)sin\theta sin\phi+u_3(t)cos\theta)\psi(\theta,\phi,t),\quad \psi(t)\in L^2(S^2),$$

- **Symmetric molecule** Is a natural generalization of a linear molecule, one more degree of freedom. We characterized its controllability in terms of its dipole moment. This is done by applying Lie-Galerkin technique, analyzing the controllability of finite-dimensional subspaces and taking the limit under good resonance assumptions. This problem was an open question, for example, in [3].

- **Asymmetric molecule** Its controllability properties are not known yet, the main difficulty being the non explicit structure of the spectrum. Anyway, one degenerate quantum number vanishes, due to the asymmetry, and this could seriously help the controllability of the system.

- **Infinite-dimensional chiral molecules** Its controllability properties have been recently studied for small finite-dimensional subsystems ([4]), but a rigorous mathematical approach should be adopted for its corresponding Schrödinger PDE.

[1], U. Boscain, M. Caponigro, T. Chambrion, M. Sigalotti, *A weak spectral condition for the controllability of the bilinear Schrödinger equation with application to the control of a rotating planar molecule*, Comm. in Math. Phys. (2012) [2], U. Boscain, M. Caponigro, M. Sigalotti, *Multi-input Schrödinger equation: Controllability, tracking, and application to the quantum angular momentum*, J. of Diff. Eq. (2014) [3], C. P. Koch, M. Lemeshko, D. Sugny, *Quantum control of molecular rotation*, Review of Modern Phys. (2018) [4], T.F. Giesen, and C.P. Koch, and M. Leibscher, *Principles of enantio-selective excitation in three-wave mixing spectroscopy of chiral molecules*, J. Chem. Phys. 2019.
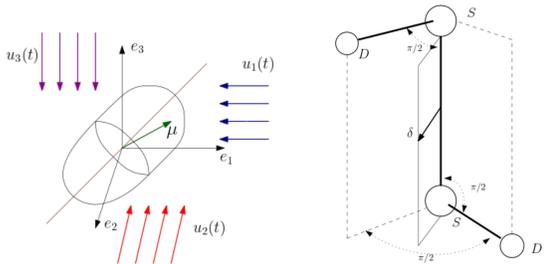
Symmetric-top

We consider a permanent dipole moment $\mu=(\mu_a,\mu_b,\mu_c)^t$ inside the molecule. e_1,e_2,e_3 is the fixed frame, $I_1=I_2\neq I_3$ are the moments of inertia of the molecule.

- **Schrödinger equation** The rotational dynamics of a molecule controlled by three orthogonally polarized electric fields in the directions e_1,e_2,e_3

$$i\frac{\partial}{\partial t}\psi(R,t)=H\psi(R,t)+\sum_{l=1}^{3}u_l(t)B_l(R,\mu)\psi(R,t),$$

$$\psi(t)\in L^2(SO(3)),\ H=\frac{1}{2}\Big(\frac{P_1^2}{I_1}+\frac{P_2^2}{I_2}+\frac{P_3^2}{I_3}\Big),\ B_l(R,\mu)=-\langle R\mu,e_l\rangle, R\in SO(3).$$

The *eigenstates* of H are given by the Wigner functions $D^j_{k,m}=|j,k,m\rangle$. Three quantum numbers needed to figure out the motion: $j\in\mathbb{N}$, $k,m=-j,...,j$. The *energy levels* are given by:

$$H|j,k,m\rangle=\Big[\frac{j(j+1)}{2I_2}+\Big(\frac{1}{2I_3}-\frac{1}{2I_2}\Big)k^2\Big]|j,k,m\rangle=:j_k|j,k,m\rangle.$$

- **Genuine symmetric-top** Is a symmetric-top which verifies $\mu=(0,0,\mu_c)^t$, that is, dipole component only on the symmetry axis. Due to Noether's Theorem, we found

Theorem *The quantum number k is invariant in the controlled motion of the genuine symmetric-top. That is,*

$$L^2(SO(3))=\oplus_{k\in\mathbb{N}}\mathcal{L}_k,\quad \mathcal{L}_k:=\overline{span}\{|j,k,m\rangle\ |\ j\in\mathbb{N},m=-j,...,j\},$$

is a decomposition in orthogonal invariant subspaces (and reachable sets).

- **Accidentally symmetric-top** Is a symmetric-top which verifies $\mu_a\neq 0$ or $\mu_b\neq 0$.

Driving all the transitions between the symmetric states, by exciting the polarizations at three different type of *frequencies*, we obtained
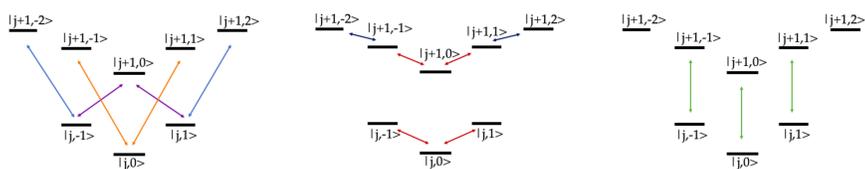

Fig.: The first frequency is $|(j+1)_{(k+1)}-j_k|$, the second is $|j_{(k+1)}-j_k|$, both driven by μ_a or μ_b. The third is $|(j+1)_k-j_k|$ driven by μ_c.

Theorem *If $I_3/(I_2-I_3)\notin\mathbb{Q}$ and $\mu_c\neq 0$, the Schrödinger equation of the accidentally symmetric-top is approximately controllable.*

Idea of the proof
1) Controllability of the system projected onto

$$\mathcal{H}_j\oplus\mathcal{H}_{j+1},\quad \mathcal{H}_l:=\overline{span}\{|j,k,m\rangle\ |\ k,m=-l,...,l\},$$

using spectral gaps excitation of the projected interaction Hamiltonians: $\mathcal{E}_\sigma(iB_l)$.
2) Since the spectral gaps are off-diagonally non resonant, we can conclude the approximate controllability in $\oplus_{j\in\mathbb{N}}\mathcal{H}_j=L^2(SO(3))$.

- **The orthogonal accidentally symmetric-top** Its dipole is orthogonal to the symmetry axis, that is, $\mu_c=0$. Here we used a rotated version of the Wang states

$$S^j_{k,m,\gamma}(\theta):=2^{-1/2}(e^{ik\theta}|j,k,m\rangle+(-1)^\gamma e^{-ik\theta}|j,-k,m\rangle),\quad j\in\mathbb{N}, k=1,...,j, m=-j,...,j, \gamma=0,1,$$

$\theta\in[0,2\pi)$, to find the following symmetry
**Theorem** *If $\mu_c=0$, the parity of $j+\gamma+k$ is conserved. That is,*

$$L^2(SO(3))=L^2_e(SO(3))\oplus L^2_o(SO(3)),\quad L^2_{e(o)}(SO(3)):=\overline{span}\{S^j_{k,m,\gamma}\ |\ j+\gamma+k\ is\ even\ (odd)\},$$

is a decomposition in orthogonal invariant subspaces (and reachable sets).

State selection for asymmetric chiral molecules

A chiral molecule can be seen as a direct sum system $\mathcal{H}\oplus\mathcal{H}$, where $\mathcal{H}$ is the Hilbert space of a symmetric or asymmetric-top. The two dipole moments are μ^+ and μ^-, one component with changed sign. For example, $\mu^+=(\mu_a,\mu_b,\mu_c)^t$, $\mu^-=(\mu_a,\mu_b,-\mu_c)$.
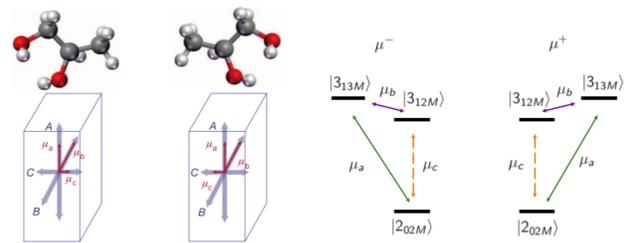
- **A sufficient condition for state selection in $j,j+1$-subspaces** Denote by $|j_0 m\rangle$, $m=-j,...,j$, $|(j+1)_1 m\rangle$, $|(j+1)_2 m\rangle$, $m=-j-1,...,j+1$ the asymmetric states of a chiral system.

Consider one right-circularly polarized electric field, excited at frequencies $|(j+1)_2-j_0|$ and $|(j+1)_2-(j+1)_1|$, and one e_3-polarized electric field at frequency $|(j+1)_1-j_0|$.

Theorem *If the three spectral gaps are all different and the Rabi frequencies of one right-circularly polarized electric field are all different, then this chiral system is state selective starting from the ground state.*

We remark that here we are dealing with *finite-dimensional* controllability.

- **A numerical simulation** The previous Theorem has been tested and exploited in a numerical simulation by prof. Koch's group of Theoretical Physics in the University of Kassel, Germany, to obtain *state selection* using *quantum optimal control*.
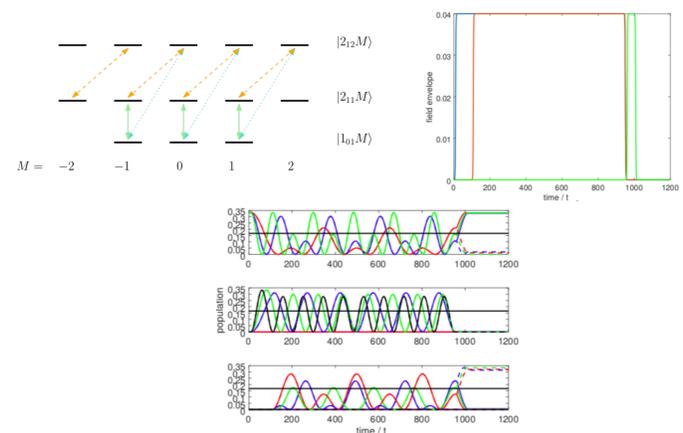

Fig.: Control strategy, shape of the pulses, population's transfer in the three states of the two molecules (different colours for different m-states, dotted or not for the two molecules.)

What is chiral controllability?

Multi-input bilinear Schrödinger equation of the form

$$i\frac{d}{dt}\psi(t)=(H+\sum_{j=1}^{m}u_j(t)B_j)\psi(t),\quad \psi(t)\in\mathcal{H},$$

where H and the B_i's are self-adjoint operators on the (possibly infinite dimensional) Hilbert space $\mathcal{H}$.

- Take piecewise constant controls $(u_1,...,u_m)$ and consider the propagator $\Gamma^u_t:=e^{-it(H+\sum_{j=1}^m u_j B_j)}$. The system is **approximately controllable** if for every $\psi_0,\psi_1\in\mathcal{H}$, $\|\psi_0\|=\|\psi_1\|=1$ and $\epsilon>0$ there exist a time T and a piecewise constant controls u such that

$$\|\psi_1-\Gamma^u_T(\psi_0)\|_\mathcal{H}<\epsilon.$$

- If $\dim\mathcal{H}<\infty$, the condition above is equivalent to say that $Lie(-iH,-iB_1,...,-iB_m)=\mathfrak{su}(\mathcal{H})$. The system is **chiral controllable** if

$$Lie(-i(H\oplus H),-i(B_1\oplus B_1),...,-i(B_m\oplus -B_m))=\mathfrak{su}(\mathcal{H})\oplus\mathfrak{su}(\mathcal{H}).$$

The system is **state selective** starting from $|a\rangle^+\oplus|a\rangle^-\in\mathcal{H}\oplus\mathcal{H}$, if

$$Reach(|a\rangle^+\oplus|a\rangle^-)\ni|b\rangle^+\oplus|c\rangle^-,$$

with $|b\rangle\neq|c\rangle$.