Aspects of
Coherent Control in Open Quantum Systems

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General Structure and Issues:

1. Coherent Control provides a powerful method for controlling molecular processes --- highly successful for isolated molecular processes.

2. Current Major Challenge --- can we use coherent control to manipulate processes that are in contact with an environment? I.e. to understand and ameliorate the effect of decoherence on control. (Such effects occur in warm systems, cold systems, etc.)

3. Outline:
    a. Comments on the general program and its directions.

    b. **Steps towards** quantifying the effect of decoherence: a "conjecture" on specific control within Kraus dynamics.

    c. **Steps towards** obtaining/analyzing the Kraus operators.

    d. **Steps towards** understanding resistance of superposition states to decoherence via overlapping resonances).

Looking to present this material, and to gain insight from other communities.

Pardon "English Greek" --- informal….

Focus generally on issues arising in chemistry/molecular physics—
no engineering of the environment…

Hence --- qualifying a few terms:

Coherent Control is a means of controlling atomic/molecular processes wherein quantum interference between multiple pathways to the final state are manipulated. As usual, interference relies upon the existence of phases (of the matter, i.e. coherence of the density matrix).
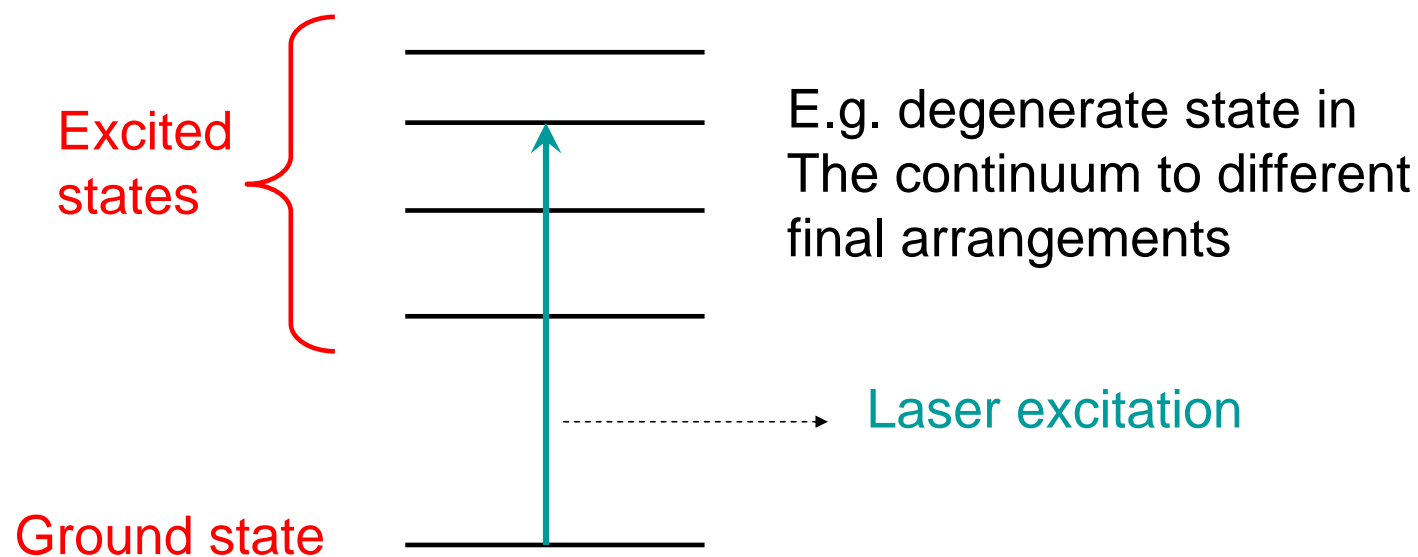
Decoherence of a system results when the system is in contact with a bath, and the bath properties are of no interest (i.e. are traced over). Specifically, by definition, the system is the part that is of interest, the bath is not.

Note --- no size issues are implied here --- we might be considering a three oscillator system, asking about properties of two of them (= the system), tracing over the third (=the bath) --- as in a spin interacting with a nanomechanical resonator

Or, in polyacetylene wire, looking at properties of the electrons (=the system) and tracing over the nuclei (then = bath).

Decoherence subfield (e.g. see "Decoherence and the quantum to classical transition" by M. Schlosshauer, Springer, 2007) =➜ Decoherence as being responsible for our seeing, macroscopically, the classical, rather than quantum, world).
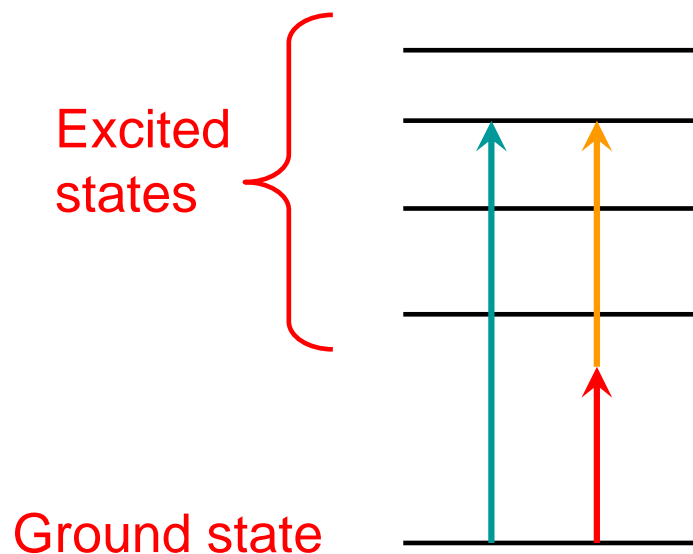
Traditional Photoexcitation in Photochemistry/Photophysics

Excited states

E.g. degenerate state in
The continuum to different
final arrangements

Laser excitation

Ground state

That is, one route to the final state of interest

Coherent Control and "Double Slits" in Photochemistry/Photophysics

Excited states

Ground state

Two (or more) indistinguishable interfering routes to the desired products.
Control laser characteristics ➔
Control Interferences ➔
Control relative cross sections

Hence typical successful coherent control scenarios rely upon multiple pathway interferences such as those below. This is the essence of quantum control, and (hopefully) of less well characterized optimal control schemes.

Bichromatic Control

1 vs 3
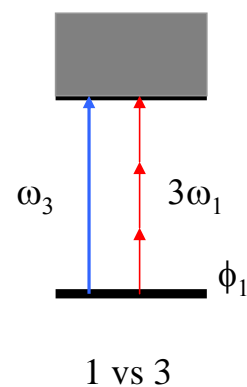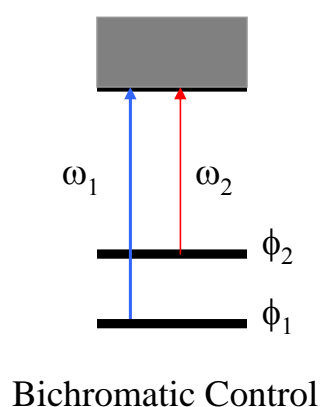
Such schemes rely upon matter phase information and its control. Hence, any loss of phase information --- via decoherence or otherwise – is deleterious.

Clarification:
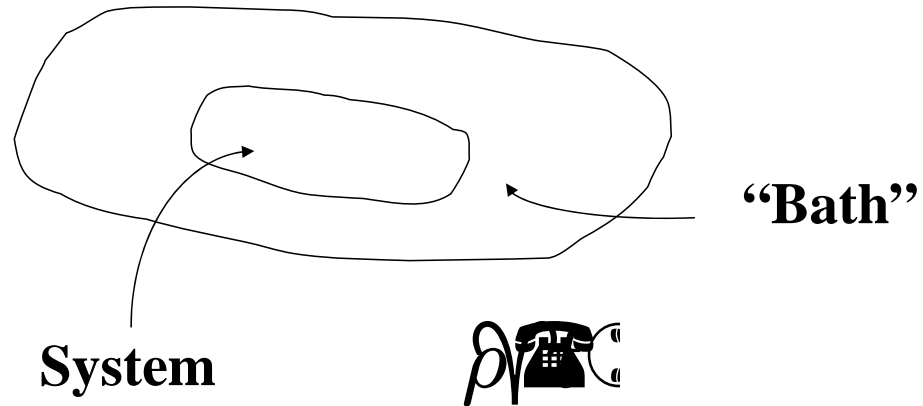
"Bath"

System

Bath = Part being traced over = Not measured

System dynamics: $\rho_S(t) = Tr_B(\rho(t))$

(A) Measure of continuous system decoherence: $Tr(\rho_S^2(t))$

Pure state: $Tr(\rho_S^2(t)) = 1$ Advantage: Basis Indpt.

Mixed state: $Tr(\rho_S^2(t)) < 1$

Termed "purity"; Related, Renyi entropy

E.g. for two levels:

$$Tr[\rho^2] = \rho_{11}^2 + \rho_{22}^2 + 2|\rho_{12}|^2$$

Both two level as well as multilevel examined below

$$Tr\left(\rho^2\right) = \sum_{i,j} \langle i|\rho|j\rangle\langle j|\rho|i\rangle = \sum_{i} |\langle i|\rho|i\rangle|^2 + \sum_{i\neq j} \langle i|\rho|j\rangle\langle j|\rho|i\rangle,$$

Includes two effects, but here interested in short time where population changes are small.

Clarification

Must qualify the statement defining decoherence due to literature.

Current precise definitions (e.g., E. Joos, or Schlosshauer)

DECOHERENCE (OR TRUE DECOHERENCE): Unitary dynamical evolution of the system + bath, without any dynamical change in the system states. E.g.:

$|1\rangle |Phi\rangle \rightarrow |1\rangle |Phi\_1\rangle$ $|i\rangle$ **is system,** $|Phi\_i\rangle$ **is bath**

$|2\rangle |Phi\rangle \rightarrow |2\rangle |Phi\_2\rangle$

So that $(|1\rangle + |2\rangle) |Phi\rangle \rightarrow |1\rangle |Phi\_1\rangle + |2\rangle |Phi\_2\rangle$

And off diagonal density matrix element of system, resulting from trace over bath, has term $|1\rangle\langle2| \langle Phi\_1 | Phi\_2\rangle$.

Hence loss of coherence (decoherence) due to system entangling with different bath components that are dissimilar.

Important Clarification

Hence, in pure decoherence, the system and the bath entangle in unitary dynamics of the pair. Ignoring the bath causes loss of quantum information, and hence decoherence of the system.

$Tr(rho\_s^2)$ is good measure

FAKE DECOHERENCE (E. Joos, Schlosshauer, etc.) or "DEPHASING":

Loss of coherence arising from some averaging mechanism – e.g.

(i) similar Hamiltonian evolution to members of an ensemble but different initial conditions (e.g. thermal effects), or

(ii) Collection of identically prepared systems subjected to different Hamiltonians (e.g. work on decoherence of diatom vibrations due to rot'ns)..

Joos: "Here there is no decoherence at all from a microscopic viewpoint".

The challenge to overcome decoherence is considerable. For example, no coherence in two optimal control of chemistry in liquid examples:

Control of "vibrational populations" in methanol in liquid – Analyzed in Spanner and Brumer, Phys. Rev. A 73, 023809 (2006) and Phys. Rev. A 73, 023810 (2006).

Control of isomerization in NK88 –--- analyzed in Hoki and Brumer, Phys Rev Lett. 85, 168305 (2005).

(I know of none other – in open systems -- than have been theoretically analyzed!)

Note. we focus on natural Decoherence; no attempt to engineer system against Decoherence (as in quantum computing).

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   d. **Steps towards understanding resistance of superposition states
   to decoherence via overlapping resonances).**

Number of Theorems on Controllability now exist, but no (?) constructive theorems on Control in open systems. Here discuss decoherence effect.

The Scenario:

Consider, as an example, the following problem (donor-acceptor spectroscopy):
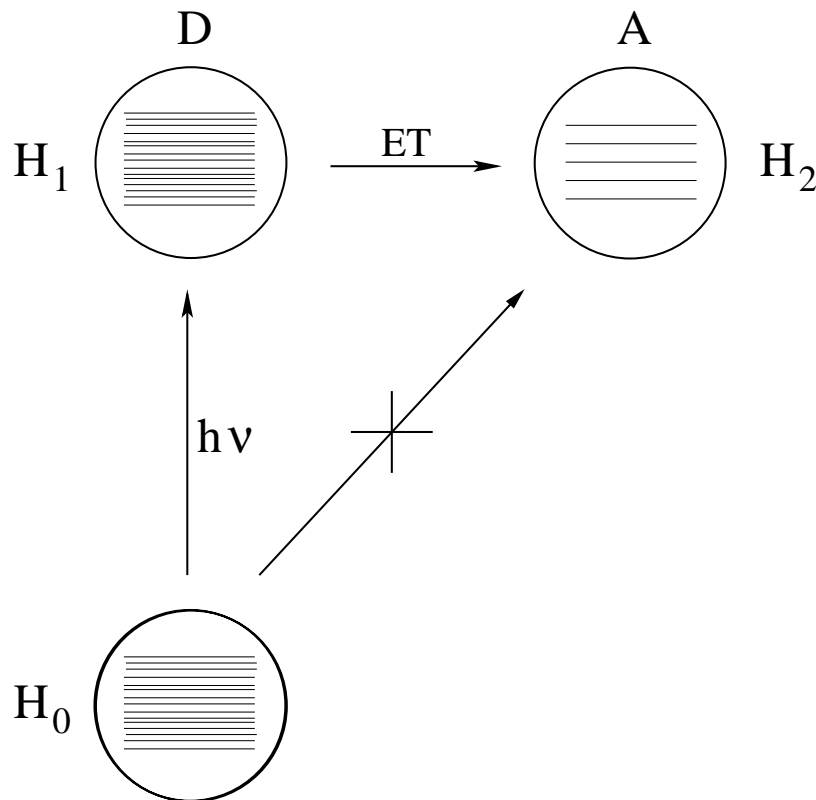
All subspaces are connected dynamically by fields and/or by dynamics. Can I prepare an initial state in H_0 which will not populate H_2, hence "cleaning up" the spectroscopy?

Example of a general problem where H_i is of dimensionality M_i, and we wish to suppress the H_0 to H_2 dynamics. (Other e.g., chemical reactions).

**Closed system answer:
M. Shapiro and P. Brumer,
JCP 103, 483 (1995)**

Conditions on Extent of Control

Closed System: Guaranteed can be done if $M_0 \geq M_2$. Virtually impossible to do if the $M_0 < M_2$.

Open system case: L. Wu, A. Bharioke and P. Brumer, J. Chem. Phys. 129, 041105 (2008)

Basic question --- to what extent does the open system aspect affect the ability to create a state in H_0 that allows for the indicated control? Answer is interesting and prompts more work.

Consider system + bath with density matrix χ

Define system density matrix as (with Trace over bath) $\rho = Tr[\chi]$

Satisfies the general (exact) Master equation

$$\dot{\rho}(t) = -\frac{i}{\hbar}\left[H, \rho(t)\right] + \int_0^t \mathcal{K}_{t,s}\left[\rho(s)\right] ds,$$

What is the form of the solution to this equation?

Conditions on Extent of Control

For the full system (assuming separable initial conditions):

$$\chi(t) = U(t)\chi(0)U^\dagger = U\rho(0) \otimes \rho_B(0)U^\dagger$$

$$\rho_B(0) = \sum_{a,b} p_{ab}|a\rangle\langle b| \qquad \text{Note bath states}$$

Tracing over the bath gives,

$$\rho = \sum_{e,a,b} A^{a,e}\rho(0)B^{a,b,e}$$

$$A^{a,e} = \langle e|U|a\rangle \text{ and } B^{a,b,e} = p_{ab}\langle b|U^\dagger|e\rangle$$

This is general, but the sum is over the bath states. In the case of product initial state Kraus obtained a far more compact form (later)

$$\rho = \sum_{\alpha=1}^{d} E^\alpha\rho(0)E^{\alpha\dagger}$$

Nota Bene: (a) Number d of Kraus Operators $\leq (M_{tot})^2$ With Controls?
(b) E.g., for closed system d=1, Kraus are Unitary evolution ops
(c) Minimum d in open system is 2. (PRL REJECT ☺, Alicki)
(d) The Kraus operators "contain all".

Conditions on Extent of Control

Then consider any fixed Kraus operator set – either determined by the natural system evolution, (or natural evolution plus external controls?).

The practical control problem:
Can we set up an initial state in H_0 so that final population of H_2 is zero ?

I.e. can we set up an initial wavefunction $|\psi_0\rangle$

and associated initial $\rho_{M_0^2} = |\psi_0\rangle\langle\psi_0|$

of dimension $M_0 \times M_0$

that avoids dynamics into H_2. Dynamics of $\rho_{M_0^2}$ into M_2 is

$$\rho_{(2,k_2)(2,k_2)} = \sum_{\alpha=1}^{d} \langle 2, k_2| E^\alpha |\psi_0\rangle \langle\psi_0| E^{\dagger\alpha} |2, k_2\rangle = 0 \qquad (1)$$

[where (j,n$_j$) means H$_j$ subspace and n$_j$ state therein]. Hence no M$_0$ to M$_2$ dynamics means

$$\langle 2, k_2| E^\alpha |\psi_0\rangle = 0 \qquad \text{i.e. both population and coherences are zero.}$$

Conditions on Extent of Control

$$\langle 2, k_2 | E^\alpha | \psi_0 \rangle = 0$$

d M_2 equations in M_0 unknowns hence, if $M_0 \geq d\, M_2$ then control is guaranteed.
Note condition holds for all possible controls imposed on the system. Otherwise control is very difficult, if not necessarily impossible.

Since d=1 is condition for closed system, the open system condition is far more demanding, where "known' that d ranges from d=2 to $(M_0 + M_1 + M_2)^2$

Issues in general

In particular cases, e.g.,

What the research field does not know:
(i.e. motivation for more work):

How many Kraus operators?

How to compute the Kraus ops.

Solutions for only a few simple systems.

What determines d ?
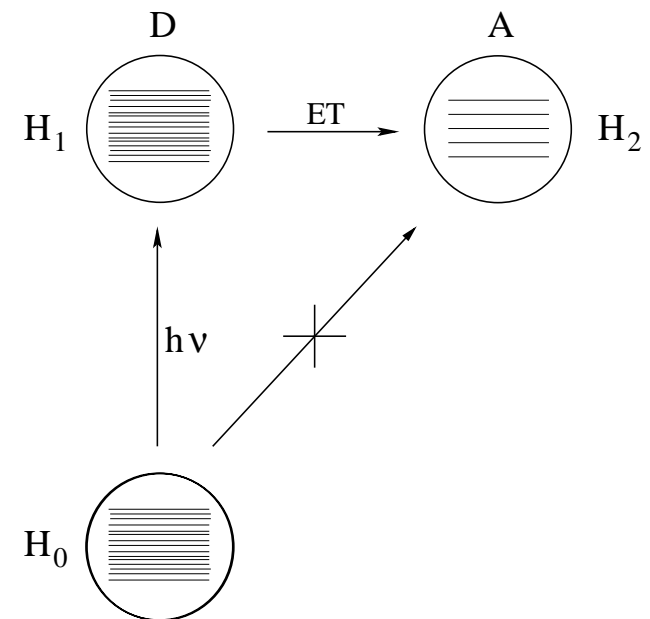
Can search for known state
Aside: can manipulate M_i with lasers

Conditions on Extent of Control

Gives the feeling of the increasing difficulty of meeting a challenge in open quantum systems.

How to approach the Kraus operators in general---

Topic B: Obtaining Kraus Operators --- with Asoka Biswas

So, to learn about the nature of Kraus operators we devised the following method to obtain them **in general**, from the system+bath dynamics. Note, no approximations.

Route:

General Approach, but example of spin ½ interacting with Boson bath:

$$H/\hbar = \omega_0 S_z + \omega a^\dagger a + g_{ph} S_z(a + a^\dagger)$$

$$+ \ g_r(S_+ a + S_- a^\dagger) + g_{nr}(S_+ a^\dagger + S_- a) ,$$

where ω_0 and ω are the fundamental frequencies of the spin and the bath, respectively. The spin operators are $S_\pm = |\pm\rangle\langle\mp|$ and $S_z = (|+\rangle\langle+| - |-\rangle\langle-|)$, where $|\pm\rangle$ are the spin states.

The g_r term in the Hamiltonian represents interaction between the spin and the bosonic bath which would retain under the rotating wave approximation (RWA), whereas the g_{nr} term represents the interaction which would otherwise have been neglected under RWA. The g_{ph} term describes the dephasing of the spin.

We assume that the initial density matrix of the bath at thermal equilibrium at a temperature T is given by $\rho_B(0) = \sum_n p_n |n\rangle\langle n|$, where $p_n = \exp(-n\hbar\omega/k_B T)/Z$ and $Z = \sum_n \exp(-n\hbar\omega/k_B T)$. The evolution of the spin+bath system is described by

Full system-bath evolution via U_1: $\rho_{SB} = U_1[\rho_S(0) \otimes \rho_B(0)]U_1^\dagger$

Insert initial thermal bath rho_B and trace over the bath states |n> :

$$\rho_S(t) = \sum_{m,n} E_{mn}\rho_S(0)E_{mn}^\dagger \; ,$$

where: $\quad E_{mn} = \sqrt{p_n}\langle m|U_1|n\rangle$

As before, not Kraus form since infinite number of terms in rho_s expansion. should be max of 2^2 = 4.

General procedure– to relate/obtain Kraus from via exact eigenstates |gamma> and eigenvalues E_{gamma} of H:

Expand propagator in E_{mn}: $\quad E_{mn} = \sum_\gamma e^{-iE_\gamma t/\hbar}\langle m|\gamma\rangle\langle\gamma|n\rangle\sqrt{p_n}\; .$

Note spin operator $\quad \langle m|\gamma\rangle\langle\gamma|n\rangle$

Expand the |gamma> in terms of zeroth order states: $|\pm, n\rangle$

Define overlap: $C^{\gamma}_{\pm,n} = \langle \pm, n | \gamma \rangle$

Expand operators E_{mn} in complete set of spin operators:

$$E_{mn} = I_{mn}\mathbf{1} + Z_{mn}S_z + X_{mn}S_x + Y_{mn}S_y$$

$$I_{mn} = \frac{1}{2}\sum_{\gamma} e^{-iE_{\gamma}t/\hbar}\sqrt{p_n}(C^{\gamma}_{+m}C^{\gamma*}_{+n} + C^{\gamma}_{-m}C^{\gamma*}_{-n})$$

$$Z_{mn} = \frac{1}{2}\sum_{\gamma} e^{-iE_{\gamma}t/\hbar}\sqrt{p_n}(C^{\gamma}_{+m}C^{\gamma*}_{+n} - C^{\gamma}_{-m}C^{\gamma*}_{-n})$$

$$X_{mn} = \frac{1}{2}\sum_{\gamma} e^{-iE_{\gamma}t/\hbar}\sqrt{p_n}(C^{\gamma}_{+m}C^{\gamma*}_{-n} + C^{\gamma}_{-m}C^{\gamma*}_{+n})$$

$$Y_{mn} = \frac{i}{2}\sum_{\gamma} e^{-iE_{\gamma}t/\hbar}\sqrt{p_n}(C^{\gamma}_{+m}C^{\gamma*}_{-n} - C^{\gamma}_{-m}C^{\gamma*}_{+n}).$$

Then,
$$\rho_S(t) = \sum_{k,l=x,y,z,1} \theta_{kl} S_k \rho_S(0) S_l \, ,$$

With
$$\theta_{kl} = \sum_{m,n} K_{mn} L^*_{mn}, \quad K, L = X, Y, Z, I$$

Still not Kraus since have off diagonal contributions to the ops

But if you diagonalize the (Hermitian) theta matrix with U

$$U^\dagger \theta U = \mathrm{diag}(\, d_{11} \quad d_{22} \quad d_{33} \quad d_{44} \,)$$

then

$$\rho_S(t) = \sum_{i=1}^{4} O_i \rho_S(0) O_i^\dagger$$

$$O_i = \sqrt{d_{ii}}(U_{ix} S_x + U_{iy} S_y + U_{iz} S_z + U_{i1} \mathbf{1}) \, .$$

Can also show sum rule.

Kraus Operator sum form with four operators.

NOT UNIQUE!

Applied to various specific cases to gain some insight into qubit case, qudit case, etc.

Summary of this results---

Provides one **GENERAL** approach to obtaining Kraus operators.

Applied without controls but can consider case with controls.

Useful to think about qualitative content of the Kraus operators.

Useful to examine and analyze approximations – such as Markovian approximations, approximations to the |gamma>

But ---open question -- -how to determine SMALLEST set of O_i ?

Topic C; Identifying Aspects of Superposition States Stable to Decoherence --- The Role of Overlapping Resonances (with Moshe Shapiro and Asoka Biswas)

Consider a system interacting with a bath with Hamiltonian:

H = H_s + H_b + H_{sb}

e.g. focus on example of spin ½ interacting with general bosonic bath:

$$H/\hbar = \omega a^\dagger a + \frac{\omega_0}{2} S_z + g_r(S_+ a + S_- a^\dagger) + g_{nr}(S_+ a^\dagger + S_- a) + g_{ph} S_z (a + a^\dagger) ,$$

$$S_\pm = |\pm\rangle\langle\mp|, \; S_z = |+\rangle\langle+| \; - \; |-\rangle\langle-|$$

would be neglected in the RWA. The g_{ph} term corresponds to dephasing of the spin due to the operator S_z, which induces a relative phase between the spin states $|+\rangle$ and $|-\rangle$. The g_r and g_{nr} terms mediate energy exchange between the spin and the bath. Our focus below is in the region of strong coupling, where g_{nr} and g_r are both greater than ω_0.

Note: Strong Coupling Regime!

The class of Hamiltonians [Eq. (1)] possesses a plane defined by $g_r = g_{nr}$ in the three dimensional g_{nr}, g_r, g_{ph} parameter space upon which the system displays a decoherence free subspace (DFS). That is, in these special cases the Hamiltonian Eq. (1) leads to a DFS due

Question: What attributes of the system (i.e. coupling parameters) lead to the possibility of increased stability of a superposition of spin states:

$$|\psi\rangle = c_+|+\rangle + c_-|-\rangle,$$

Again, consider initial product of zeroth order states of uncoupled spin and bath density matrix (thermal bath contributing 20 states) .

Introduce zeroth order states (eigenstates of H_s and H_b) and exact eigenstates |gamma>. Then latter can be expanded in terms of the former with coefficients:

$$\langle k, m | \gamma \rangle$$

where k is + or − (spin state) and m is a bath state.

Indeed, the form of Tr(rho^2) of the system depends on products of such coefficients, such as

$$\langle k, m | \gamma \rangle \langle \gamma' | l, m \rangle \langle \gamma | +, n \rangle \langle -, n | \gamma' \rangle$$

If two zeroth order states $\langle k, m | \gamma \rangle$ (i.e. different k or m) have nonzero overlap with a |gamma> then they are said to be overlapping resonances (spacing between zeroth order states is smaller than width of zeroth order states).

Complicated expressions show dependence of system purity on the overlapping resonances.

These resonances are property of the Hamiltonian and its parameters.

Consider the stability, under interaction with the bath, of the superposition:

$$|\psi\rangle = c_+|+\rangle + c_-|-\rangle$$

Of particular interest is the measure of the overlapping resonances associated with the | +> and | -> spins. E.g. the following measure:

$$A_{+-} = \sum_{m \neq n} A_+^{m,n} A_-^{m,n} \ , \ A_\pm^{m,n} = \left[\sum_\gamma |\langle \pm, m|\gamma\rangle\langle\gamma|\pm, n\rangle|\right].$$

For a pair of the bosonic states $|m\rangle$ and $|n\rangle$, $A_+^{m,n}$ determines the overlap (summed over all eigenstates $|\gamma\rangle$) between the bare states $|+, m\rangle$ and $|+, n\rangle$, when the spin state is $|+\rangle$. If, for the same combination of $|m\rangle$ and $|n\rangle$, there exists non-zero overlap $A_-^{m,n}$ between the bare state $|-, m\rangle$ and $|-, n\rangle$, then we can interpret A_{+-} as a measure of the overlap between the states $|+\rangle$ and $|-\rangle$, that arises through the overlap between the states $|\pm, m\rangle$ and $|\pm, n\rangle$.

Demonstration: Determine maximum achievable purity S_{max} for different Hamiltonian parameters for different parameter sets. Correlates with A_{+-}.
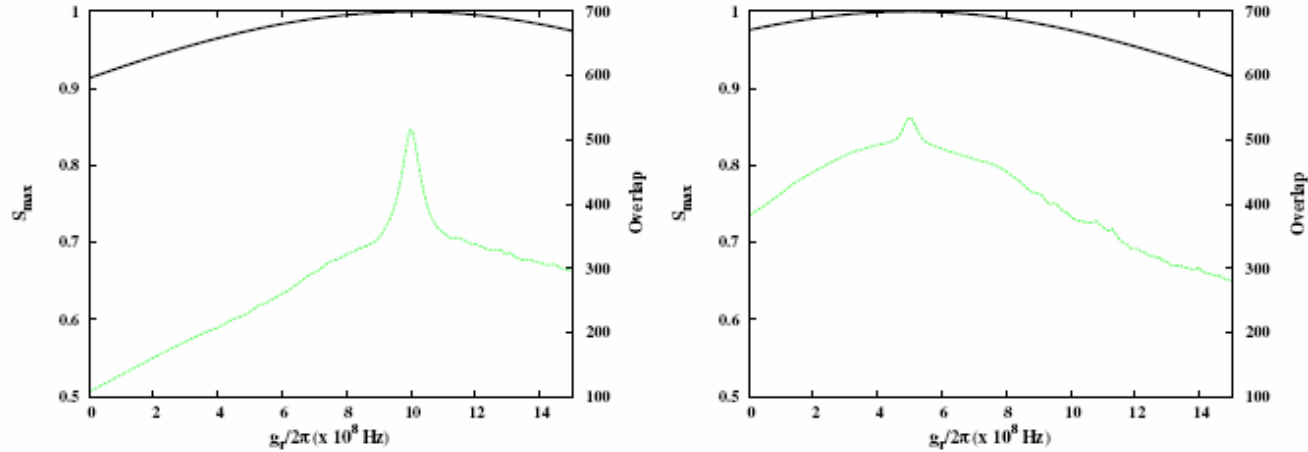
FIG. 1: (Color online) The dependence of the maximum achievable purity S_{max} of the system (solid line) and the overlapping resonance A_{+-} (green dashed line; right y-axis) on the coupling strength $g_r/(2\pi)$. We choose (a) $g_{ph} = 2\pi \times 500$ MHz, $g_{nr} = 2\pi$ GHz and (b) $g_{ph} = 2\pi$ GHz, $g_{nr} = 2\pi \times 500$ MHz. The other parameters are $\omega = 2\pi$ GHz, $\omega_0 = 2\pi \times 100$ MHz, and the temperature $T = 25$ mK. The purity is calculated at a time $t = 0.1$ ns.

Note DFS point

Obtained from computations like
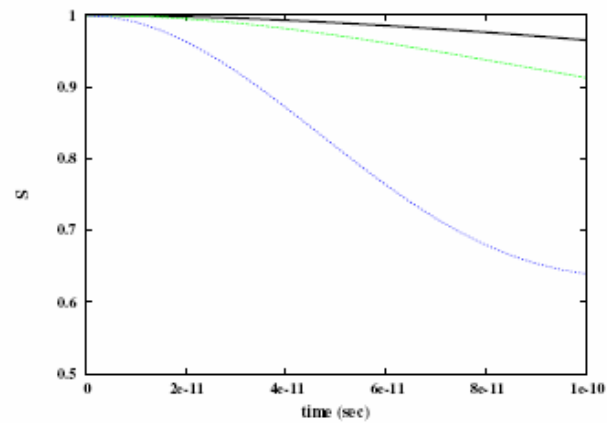
FIG. 2: (Color online) Variation of purity with time for the initial states $(-0.539998|+\rangle + 0.841665|-\rangle)$ (solid line), $(|+\rangle + |-\rangle)/\sqrt{2}$ (green dashed line), and $|+\rangle$ (blue dotted line). We choose the interaction strengths $g_r = 2\pi \times 400$ MHz, $g_{nr} = 2\pi$ GHz, and $g_{ph} = 2\pi \times 500$ MHz. The other parameters are as in Fig. 1.

Similarly, can correlates S_{diff}= S_{max} − S_{min} with A_{+-}.
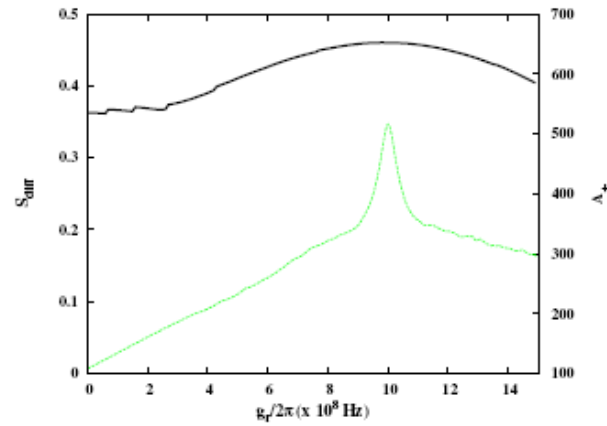
FIG. 3: Variation of S_{diff} (solid line) and the overlap A_{+-} (green dashed line; right y-axis) with g_r

for $g_{nr} = 2\pi$ GHz and $g_{ph} = 2\pi \times 500$ MHz. The remaining parameters are as in Fig. 1.

Range of S_{diff} dependent on Hamiltonian, but correlation persists. E.g. Cooper pair box with nanomechanical resonator:

Consider, for example, an interesting case of the Hamiltonian in Eq. (1), the interaction of a Cooper pair box with a nanomechanical resonator[11]. This system is given by:

$$H_{CPB} = 4E_C \delta n S_z - (E_J/2)S_x + \hbar \omega a^\dagger a + \hbar g S_z (a + a^\dagger) , \tag{10}$$

where E_C and E_J are the charging energy and the Josephson energy of the CPB, ω is the fundamental frequency of the nanomechanical resonator, and δn lies between $-1/2$ and $1/2$. At the degeneracy point $\delta n = 0$ this Hamiltonian can be written in the form of that of Eq. (1) under a similarity transformation, where we identify $\omega_0 = E_J$, $g_{ph} = 0$, and $g_r = g_{nr} = g$. The similarity transformation is given by the operator e^{iS_y}, with S_y being the y-projection of the spin operator.

and again S_{diff} correlation with A_{+-}.
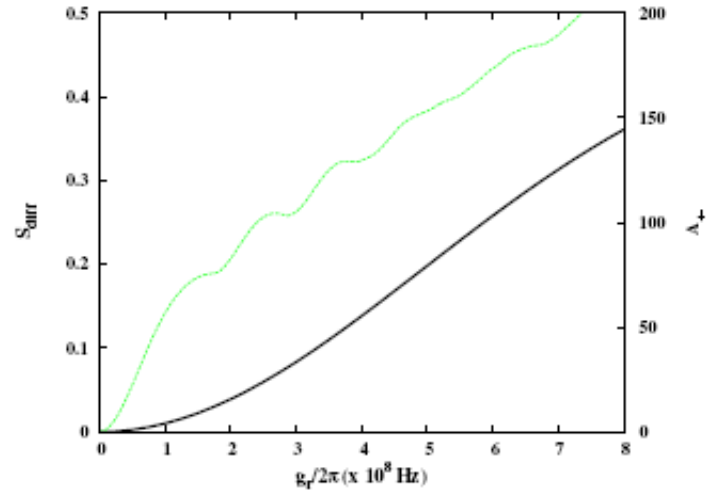
FIG. 4: Variation of S_{diff} (solid line) and the overlap A_{+-} (green dashed line; right y-axis) with $g_r = g_{nr}$ for $g_{ph} = 0$. The other parameters are as in Figs. 1.

Summary:

Three "starts" in open system control;

1. Quantification of the difficulty of preparing superpositions that bypass a subspace in an open quantum system,

2. A route to begin understanding the Kraus operator sum representation.

3. An appreciation for the role of overlapping resonances in determining the maximum possible stable superposition state in the strong coupling regime.

All provide challenging questions to pursue.

Thanks to

Kraus Operator Generation:
   Dr. Asoka Biswas (U of Toronto)

Theorem on Control in Open Systems:
   Lianao Wu (University of Toronto) and
         Arjun Bharioke (Uof T → Cambridge)

Decoherence and Overlapping Resonances:
   Dr. Asoka Biswas (U of Toronto), and
         Moshe Shapiro (Weizmann → ←UBC)

NOTE CQIQC-III CONFERENCE IN AUGUST (Award of the First Bell Prize)

Sample Realistic Challenges:

B. Control of laser induced current in molecular wire via coherent control

Main physical motivation: create controlled currents on femtosecond time Scale.

Approach: symmetry-breaking laser induced currents

By using femtosecond pulses of this character:
Induction of currents in a femtosecond
timescale, a new standard…

Ultrafast molecular switches, simply not
achievable by conventional means…
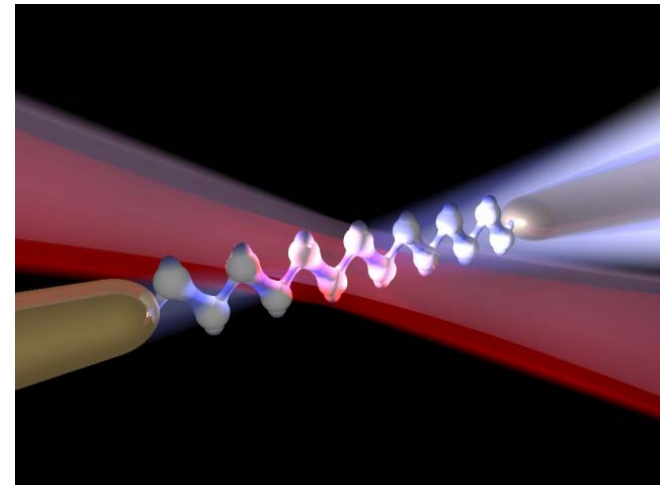
A Michael Spanner creation

$$E(t) = \epsilon_\omega \cos(\omega t)$$

e-

**photoexcited
electrons**

$$j(t) = 0$$

No net current

$E(t)$

**left/right
symmetry**

no bias voltage

metal

trans-polyacetylene oligomer

metal
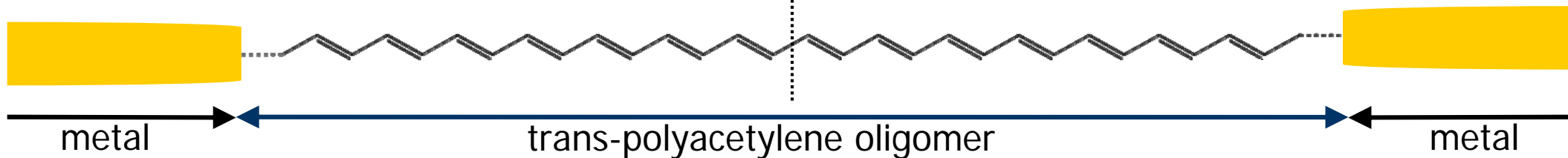
The General Problem of Interest

However, may be able to induce current by

$$E(t) = \epsilon_\omega \cos(\omega t + \phi_\omega) + \epsilon_{2\omega} \cos(2\omega t + \phi_{2\omega})$$

e-

Laser-induced symmetry breaking

$E(t)$

left/right symmetry

$j(t) \neq 0$

no bias voltage

metal

trans-polyacetylene oligomer

metal
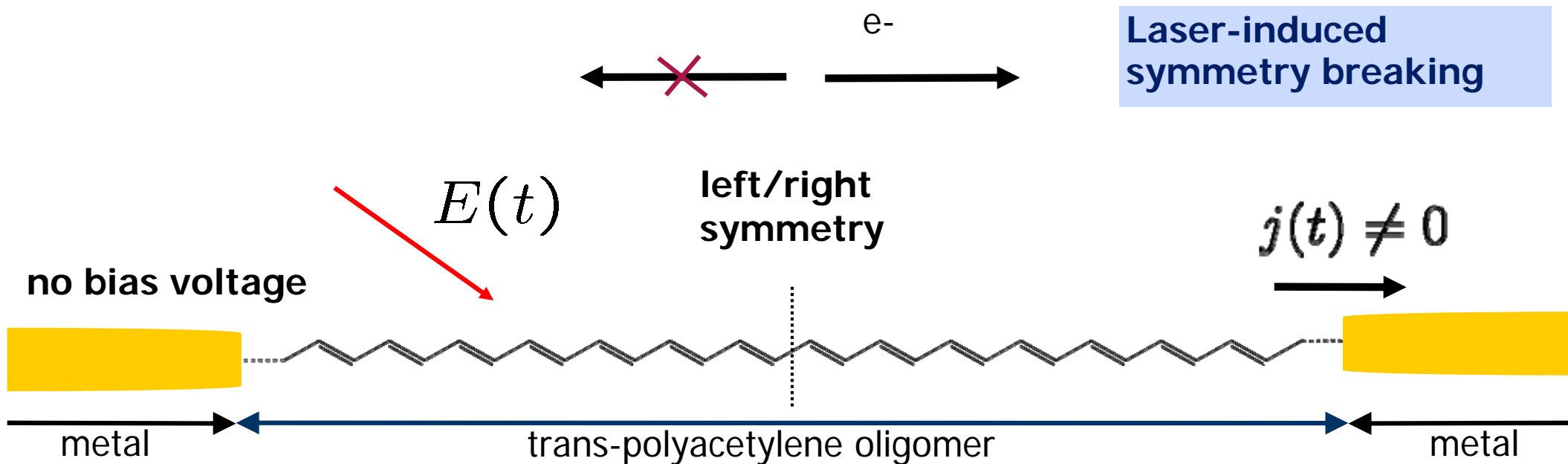
This is a type of rectification:

AC source → DC response!

$$\langle j \rangle \sim \overline{E(t)^3} \sim \epsilon_\omega^2 \epsilon_{2\omega} \cos(2\phi_\omega - \phi_{2\omega} + \alpha)$$

$$E(t) = \epsilon_\omega \cos(\omega t + \phi_\omega) + \epsilon_{2\omega} \cos(2\omega t + \phi_{2\omega})$$

$$\langle j \rangle \sim \epsilon_\omega^2 \epsilon_\omega \cos(2\phi_\omega - \phi_{2\omega} + \alpha)$$

$|E, \text{odd}\rangle$

$|E, \text{even}\rangle$

$\hbar\omega$

$2\hbar\omega$

$\hbar\omega$

$2\hbar\omega$ 1-photon absorption

$\hbar\omega$

$\hbar\omega$ 2nd order '2-photon' absorption

$|\text{even}\rangle$
couples states with
opposite parity

$|\text{even}\rangle$
couples states with
the same parity

Final State:

$|\text{odd}\rangle$ = $|\text{odd}\rangle$ + $|\text{even}\rangle$
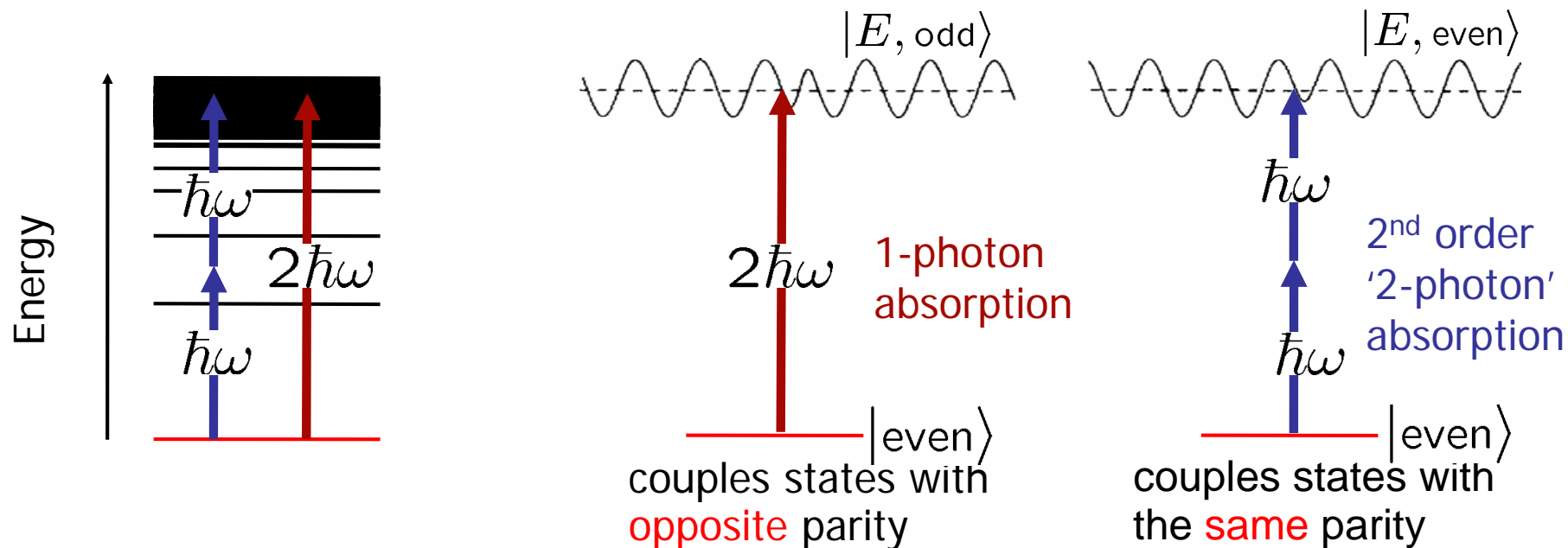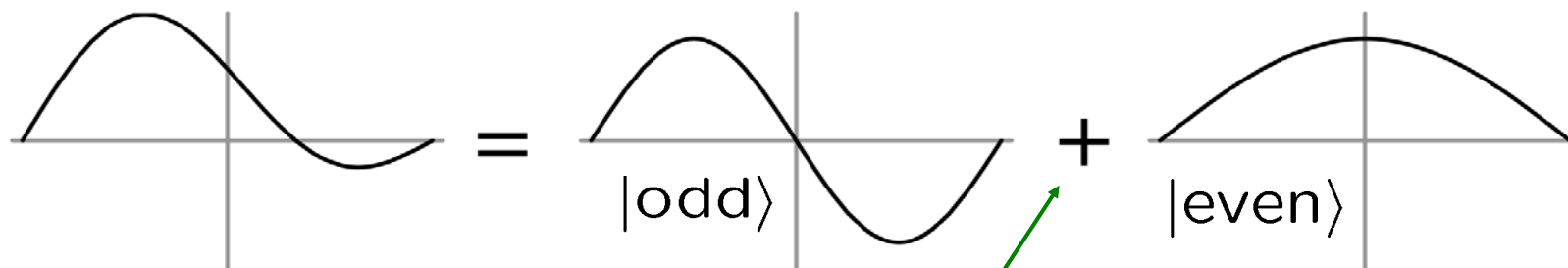
Not a parity eigenstate:
Broken symmetry

Laser controllable

I.e, :

After the $\omega + 2\omega$ field, the excitation left on the system:

$$|\Psi(t)\rangle = c_1 e^{-iEt/\hbar}|E, \text{odd}\rangle + c_2 e^{-iEt/\hbar}|E, \text{even}\rangle$$

    from the 1-photon absorption   from the 2-photon absorption

Net photoinduced momentum:

$$\langle p \rangle = |c_1|^2 \langle E, \text{odd}|p|E, \text{odd}\rangle + |c_2|^2 \langle E, \text{even}|p|E, \text{even}\rangle + 2\text{Re}\{c_1 c_2^* \langle E, \text{even}|p|E, \text{odd}\rangle\}$$

    Direct terms   Interference contribution

Only the interference contribution survives:

$$\langle p \rangle = 2\text{Re}\{c_1 c_2^* \langle E, \text{even}|p|E, \text{odd}\rangle\} \sim A\cos(\phi_{2\omega} - 2\phi_\omega + \alpha)$$

Laser control: Changing the relative phase of the lasers changes the magnitude and sign of the current.

E.g. done exptly in quantum wells by Corkum's group, PRL 74, 3596 (1995)

Well analyzed theoretically and explored experimentally. But now D&D effects severe.

Theoretically:

Note the general phenomenon can be accounted for from:

1) The coherent control perspective of interfering optical pathways
G. Kurizki, M. Shapiro and P. Brumer Phys. Rev. B **39**, 3435 (1989);
M. Shapiro and P. Brumer, Principles of the Quantum Control of Molecular Processes (Wiley, 2003)

1 vs. 2
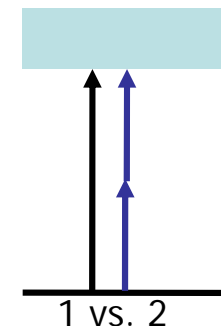
2) Nonlinear response theory arguments
I. Franco and P. Brumer Phys. Rev. Lett. **97**, 040402 (2006);
Goychuk and P. Hänggi, Europhys. Lett. **43**, 503 (1998)

$$\langle \mu(t) \rangle = \chi^{(1)} E(t) + \chi^{(2)} E^2(t) + \chi^{(3)} E^3(t) + \cdots$$

3) Space-time symmetry analyses of the equations of motion
I. Franco and P. Brumer J. Phys. B 41, 074003 (2008)
S. Flach, O. Yevtushenko. and Y. Zolotaryuk, Phys. Rev. Lett. **84**, 2358 (2000)

$\rho_{C/W}(\mathbf{x}, \mathbf{p}, t_0) \longrightarrow \rho_{C/W}(\mathbf{x}, \mathbf{p}, t)$

$\mathcal{T}_\alpha \rho_{C/W}(\mathbf{x}, \mathbf{p}, t_0) \longrightarrow \rho_{C/W}^{(\alpha)}(\mathbf{x}, \mathbf{p}, t) = \mathcal{T}_\alpha \rho_{C/W}(\mathbf{x}, \mathbf{p}, t)$

This scenario exploits the coherence properties of appropriately constructed superposition states

$$|\Psi(t)\rangle = c_1 \mathrm{e}^{-iEt/\hbar}|E, \mathrm{odd}\rangle + c_2 \mathrm{e}^{-iEt/\hbar}|E, \mathrm{even}\rangle$$

$$\langle p \rangle = 2\mathrm{Re}\{c_1 c_2^*\langle E, \mathrm{even}|p|E, \mathrm{odd}\rangle\} \sim A\cos(\phi_{2\omega} - 2\phi_\omega + \alpha)$$

Loss of coherence ························➤ **Loss of control**

Typical sources of decoherence and dephasing:

Coupling with an external environment
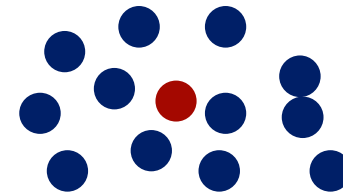
Coupling with internal but irrelevant degrees of freedom --- here electrons (the system) with the nuclei (the bath)

electrons ⟷ nuclei

conjugated polymers

| electrons | ⟷ | nuclei |

| Electronic excitations | ⟷ | Lattice distortions |
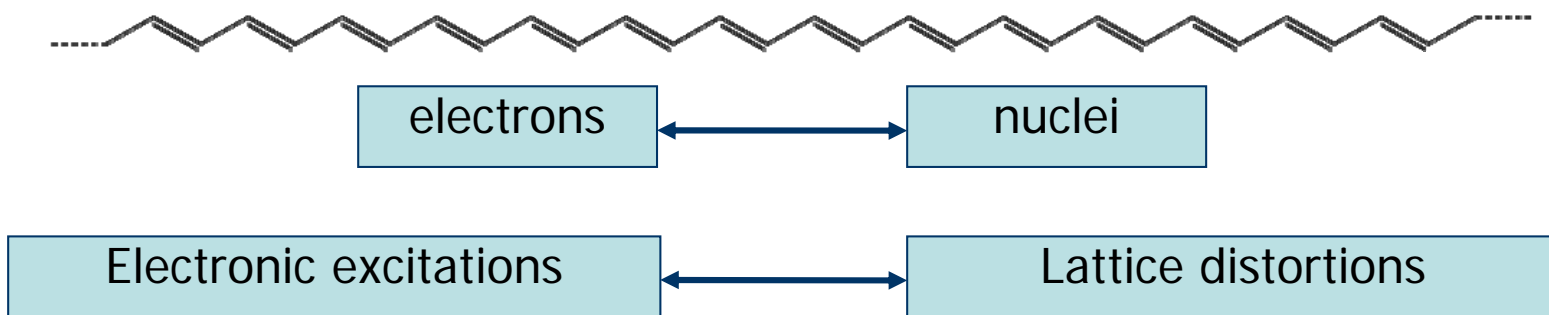
This coupling introduces:

Rich photophysics | Polarons | Breathers | Kinks or Solitons |

Ultrafast electronic dephasing   ~10 fs

Internal relaxation mechanisms

jeopardizes the control

Challenge: How to effectively exert laser control of the electronic dynamics in the presence of ultrafast decoherence due to vibronic couplings?

Outline III : The Practical Issue

1. **Laser-induced symmetry breaking and the 1 vs. 2 coherent control scenario**

1 vs. 2
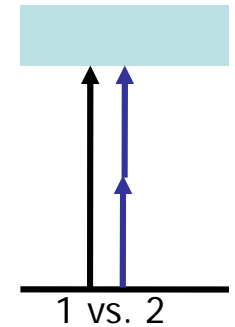
2. **Applications to molecular wires: challenges and motivations**

$E(t)$

$j(t)$
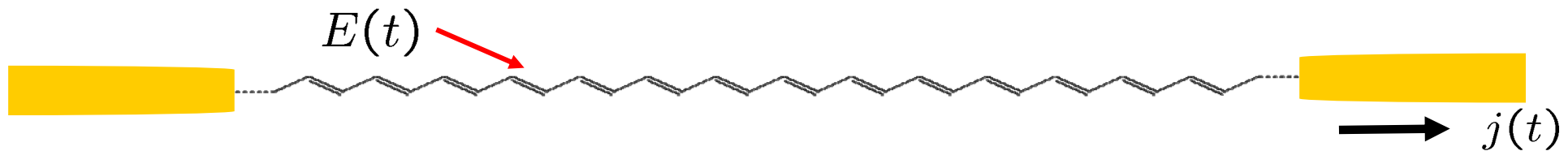
3. **The model**

$$H(t) = H_{\text{L}} + H_{\text{S-L}} + H_{\text{S}}(t) + H_{\text{S-R}} + H_{\text{R}}.$$

4. **Mixed quantum-classical photoinduced dynamics**

Classical nuclei   ⟷   Quantum electrons

5. **Results :**

   Sketch only; **extensive details in: JCP X 2**

Sketch of computation:

1. **Nuclei move classically in the average of electronic potential energies (Ehrenfest Approx).**

2. **Electrons evolve quantum mechanically and respond instantaneously to changing nuclear positions.**

3. **Electron density matrix elements are expanded in time evolving electron orbitals.**

4. **Leads to which molecules are attached are quantitatively incorporated as sinks for electrons over the lead Fermi level (which is computed as a function of time). This the hard part.**

5. **Gives set of N(N+2) coupled first order ODE, where N is number of Carbons in the chain. (typically N= 20)**

6. **Average the dynamics over the initial nuclear configuration---e.g. 40,000 initial conditions (since decoherence must converge), or 1000 for Stark case**

7. **Variety of pulses, with "weak" being 10^9 W/cm^2 for 2 omega "strong" being 2 X 10^10 W/cm^2**

Vibrational effects in laser rectification

Flexible (real) wire ←——→ Rigid wire

Lattice is allowed to vibrate

Results are obtained by averaging over the ensemble of trajectories

Lattice is **not** allowed to vibrate

System begins and stays at the optimal geometry

1. **Characteristic dephasing timescale**

1. **Currents through multiphoton absorption processes**

1. **Currents through the dynamic Stark effect**
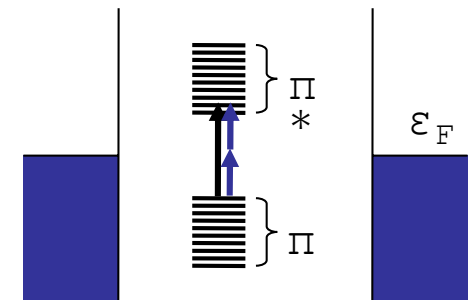
Dephasing time-scale in isolated chains

$$|\Psi(t)\rangle = \frac{1}{2}(|G\rangle + |E\rangle)$$

~10 fs!

Control wise, basically the worst case scenario

Tune the laser frequencies at or near resonance

The resulting multiphoton absorption processes

create laser-induced rectification

transfer population to transporting states
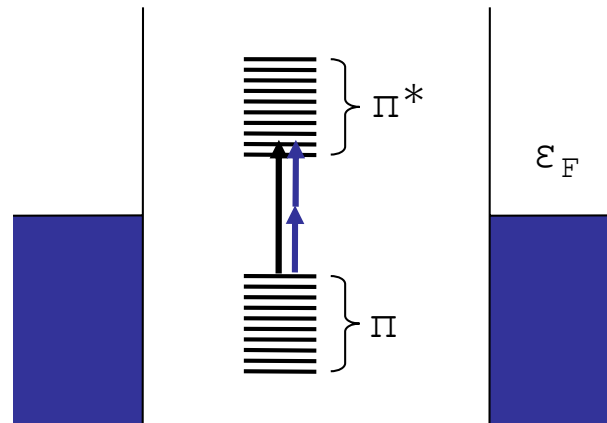
Currents through multiphoton absorption: **total charge extracted**

20 site wire

$$\eta = \frac{q_L - q_R}{q_L + q_R}$$

This regime is fragile to electronic dephasing processes induced by the vibronic couplings

$$\phi_{2\omega} - 2\phi_\omega = 0$$

weak, 300 fs pulse   strong, 300 fs pulse
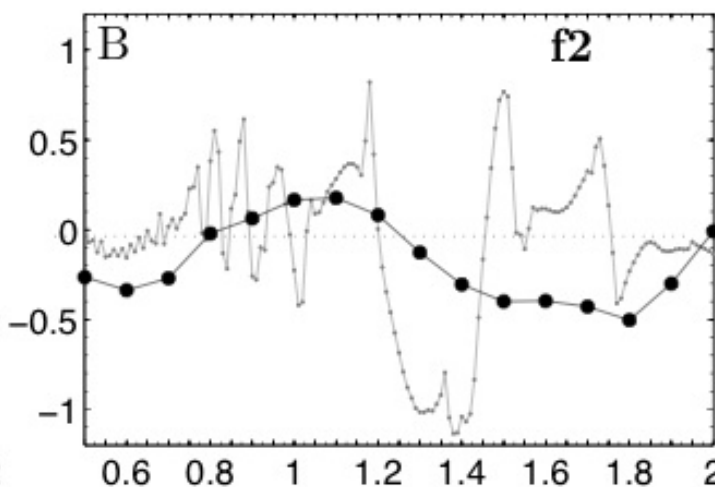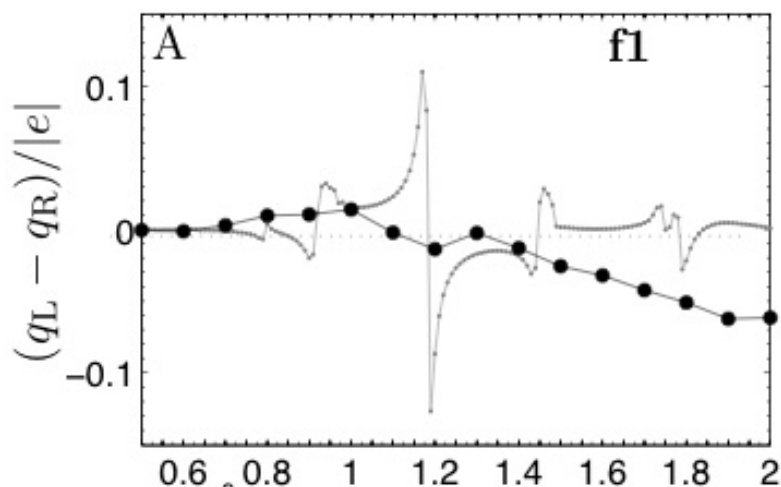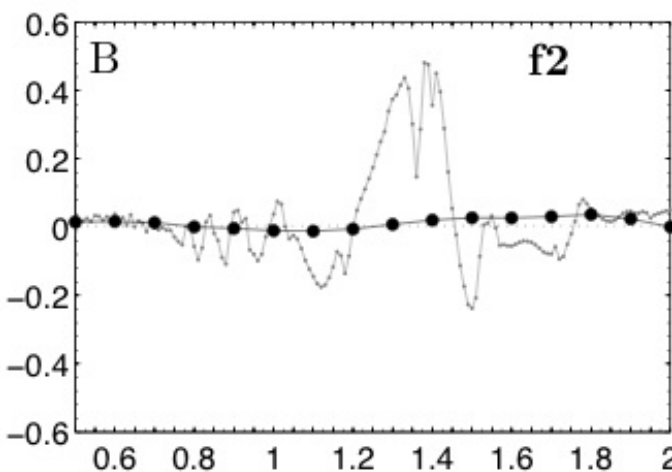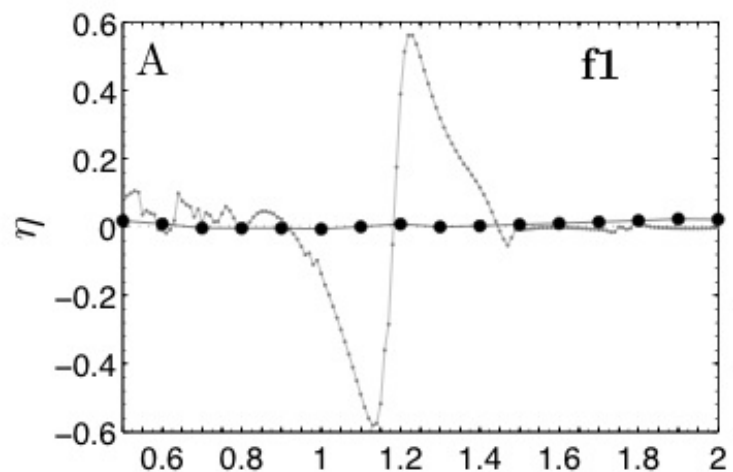
- flexible wire
— rigid wire
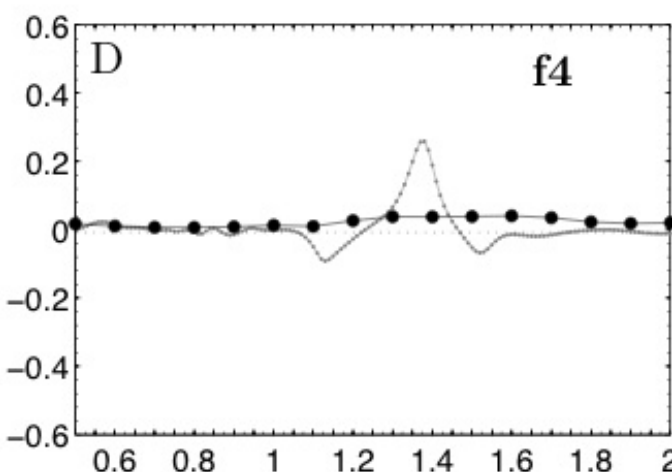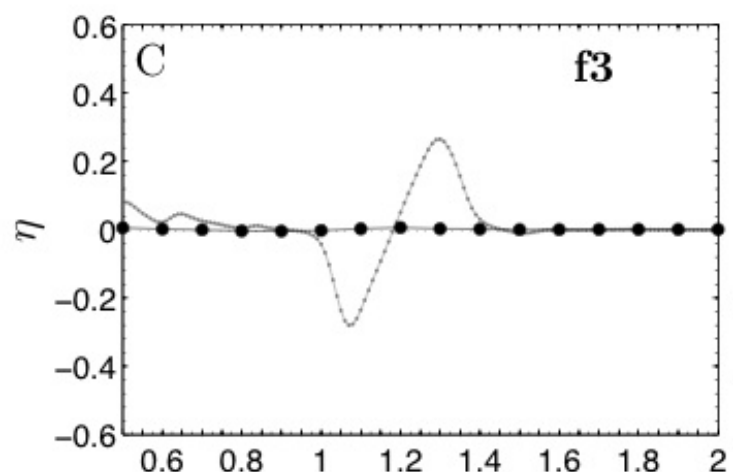
weak, 10 fs pulse   strong, 10 fs pulse

The vibronic couplings make the rectification inefficient

Hence 1vs2 "standard" rectification mechanism:
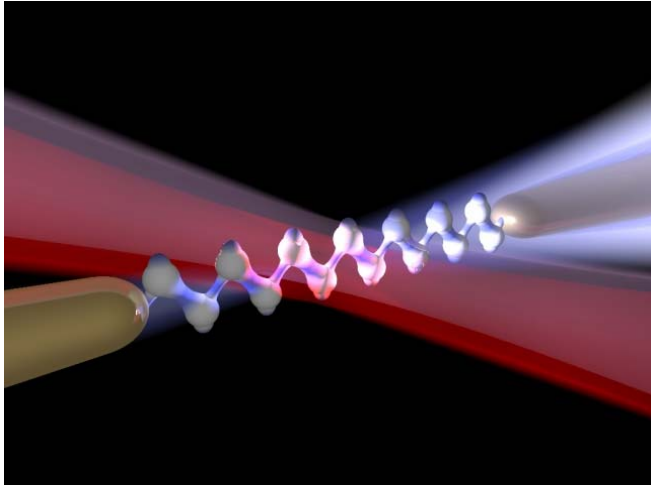
Laser frequencies tuned at or near resonance

Regime is fragile to vibronic couplings

Efficiencies less than 4% --- lots electrons absorbed few contribute to current. Even classical control (if that is limit) is hence weak

Employing faster or stronger pulses is not helpful

In order to induce sizable currents considerable energy from the laser field needs to be dumped into the nanojunction, compromising its structural integrity.

Hence aim for new alternate route ---

Before pulses were on resonance --- consider off-resonant

The field frequencies are tuned **far off-resonance** so that Stark shifts, and not photon absorption, dominate the dynamics.
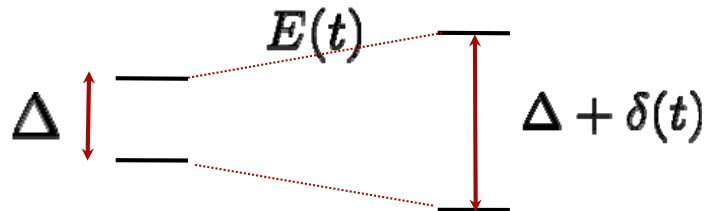
The Stark effect:
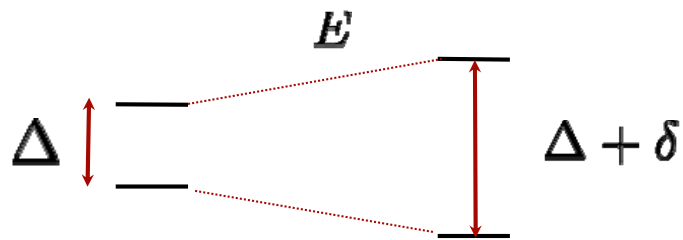
turning on an electric field shifts the energy levels

$$\delta \sim \alpha E + \beta E^2 + \cdots$$

The dynamic Stark effect:

$$\delta(t) \sim \alpha E(t) + \beta E(t)^2 + \cdots$$

the energy levels oscillate in time with the external field

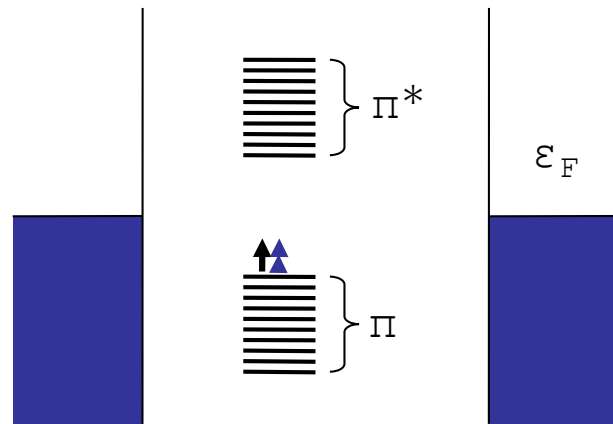**For spatially symmetric systems:** $\delta(t) \sim \beta E(t)^2 + \cdots$

100-site chain
Field intensity $\sim 10^9$ W/cm^2

$$E(t) = \epsilon_\omega \cos(\omega t + \phi_\omega) + \epsilon_{2\omega} \cos(2\omega t + \phi_{2\omega})$$

Field frequency $\hbar\omega$ = 0.13 eV $\ll$ energy gap $\sim$ 1.3 eV

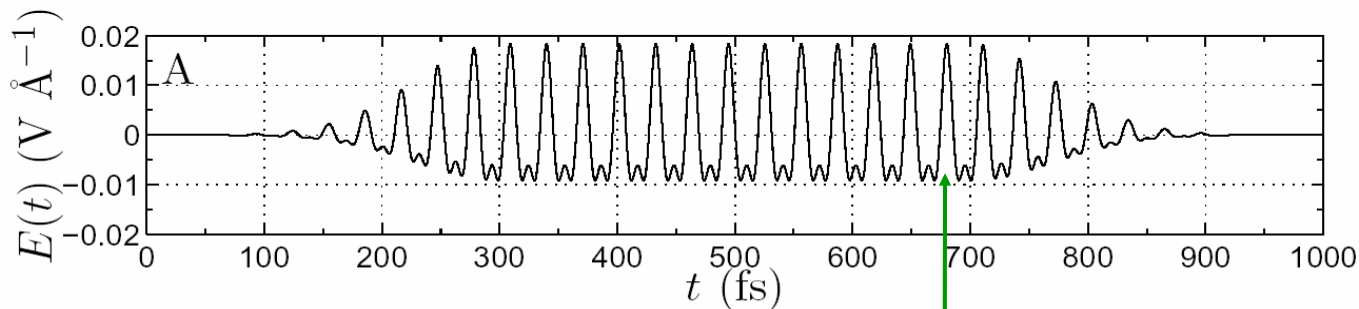**Far from resonance**

π^*

ε_F

π

Currents through the dynamic Stark effect

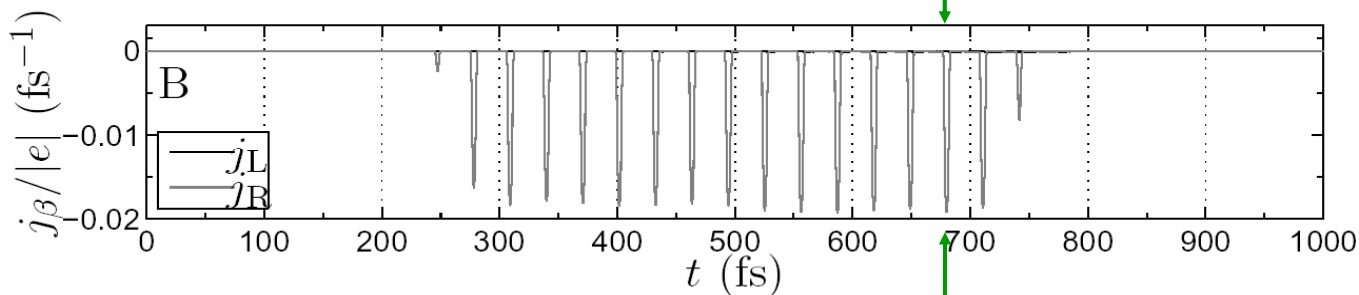Stark shifts ~ E(t) ^{2} (symmetric systems)

The laser closes the energy gap causing crossings between the valence and conduction band in individual trajectories

Case 1: $2\phi_\omega - \phi_{2\omega} = 0$ $E(t) = \epsilon_\omega \cos(\omega t + \phi_\omega) + \epsilon_{2\omega} \cos(2\omega t + \phi_{2\omega})$
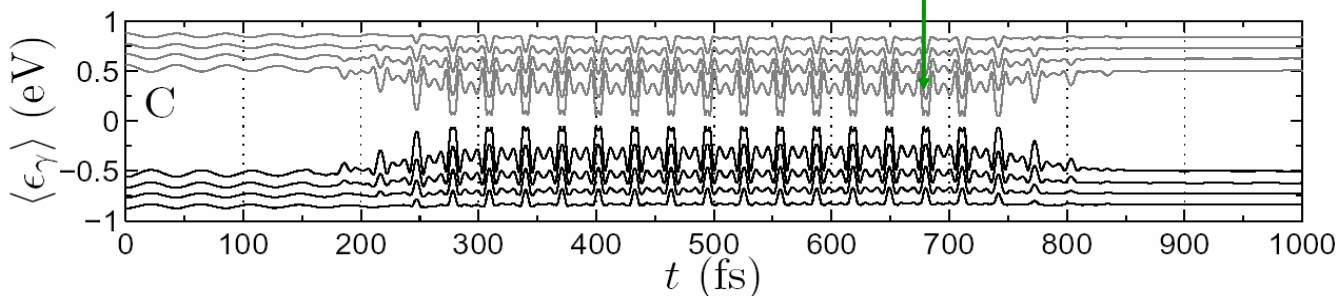
Field

Current

Ensemble averages

Orbital energies

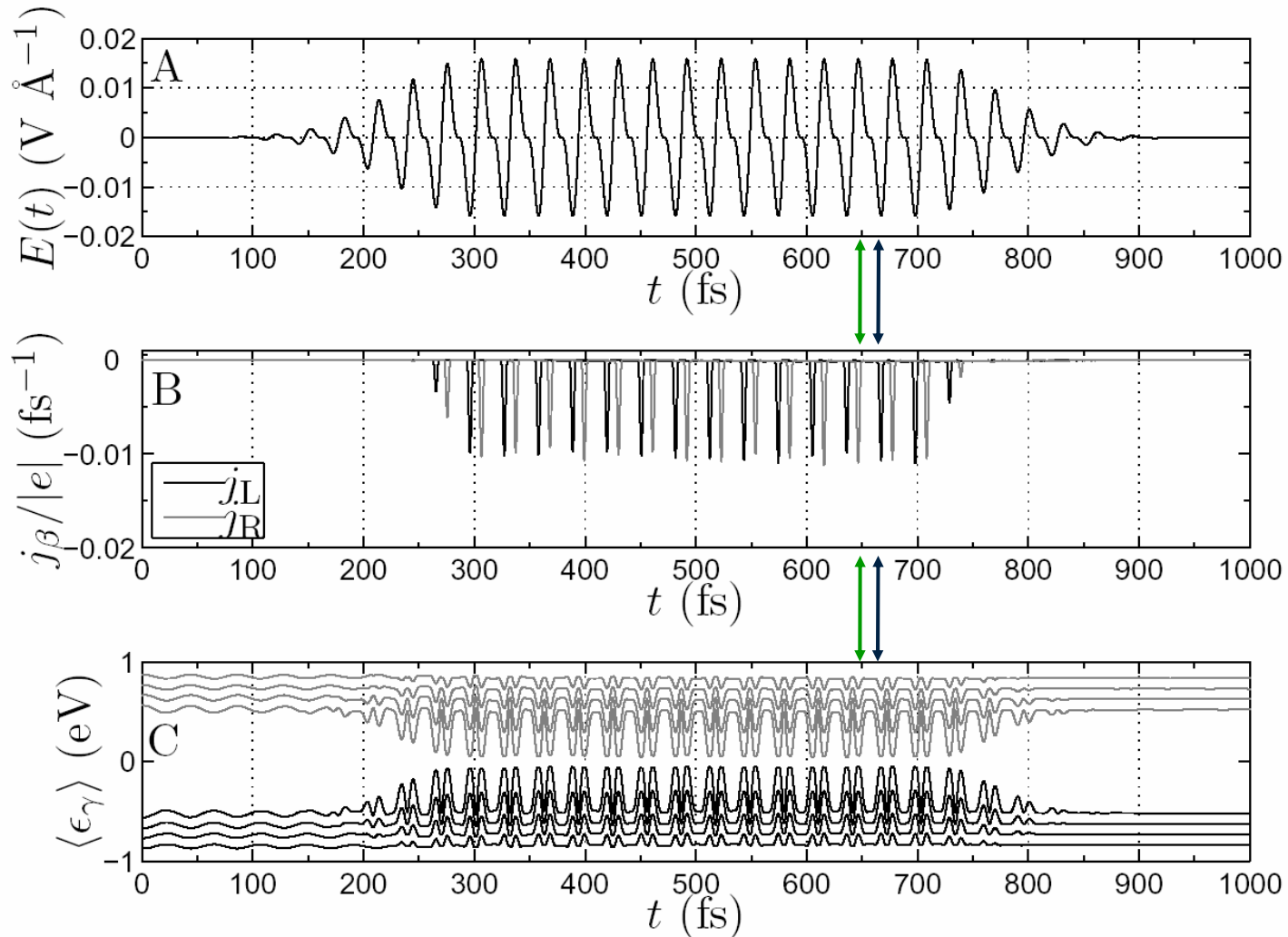Almost all excited electrons are deposited in the right contact only

Currents through the dynamic Stark effect

$$E(t) = \epsilon_\omega \cos(\omega t + \phi_\omega) + \epsilon_{2\omega} \cos(2\omega t + \phi_{2\omega})$$
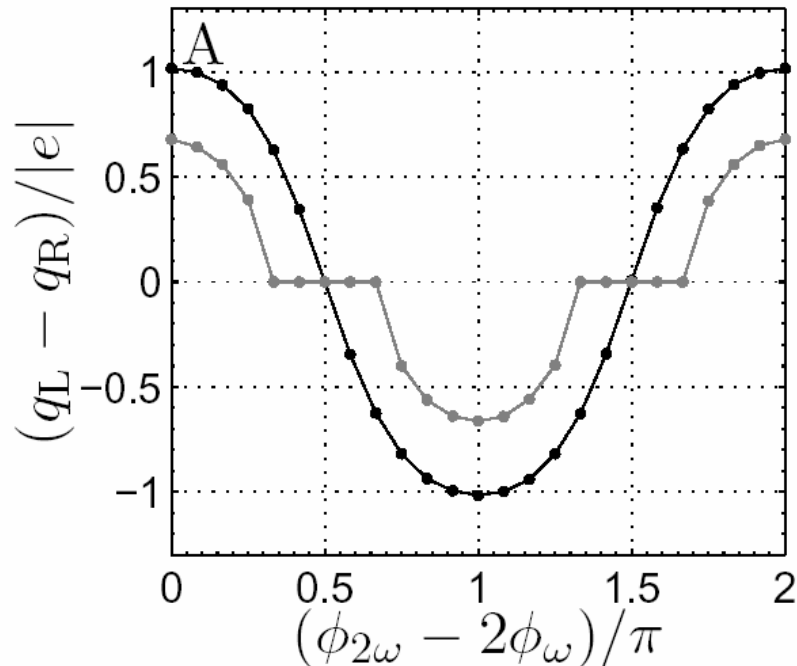
Case 2: $2\phi_\omega - \phi_{2\omega} = \pi/2$

The field changes sign between consecutive interband couplings and no net current is produced
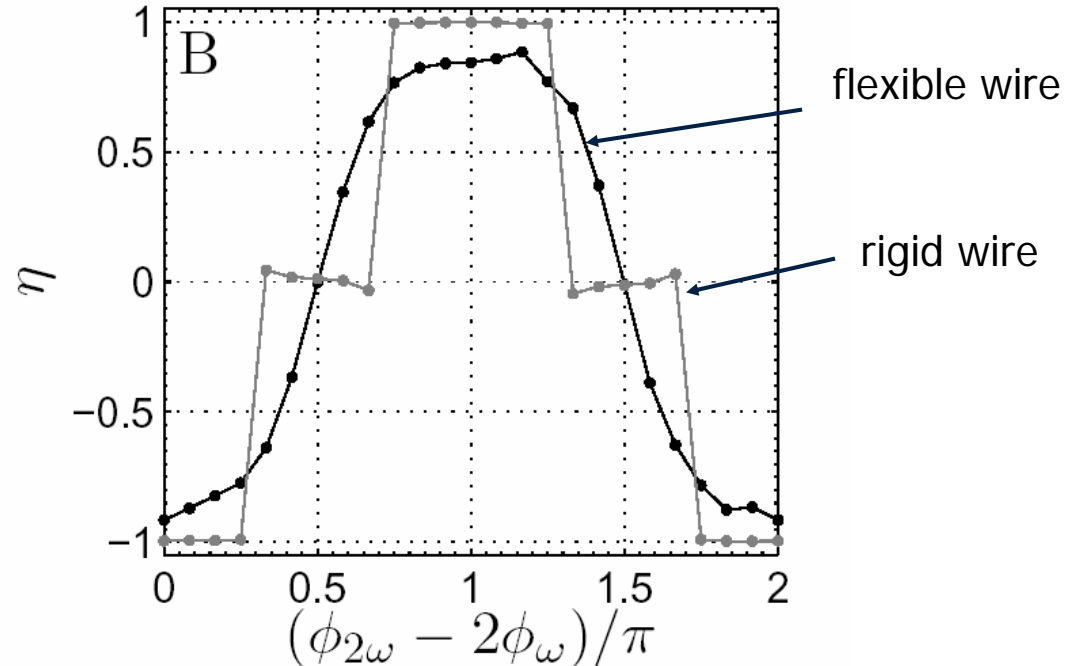
Almost complete laser control in the presence of strong decoherence

Net rectification   Efficiency

The mechanism is robust to electron-vibrational couplings and is able to induce large currents with efficiencies as high as 90%!

Note that for certain range of phases the currents are phonon-assisted

I. Franco, M. Shapiro, P. Brumer, Phys. Rev. Lett. **99**, 126802 (2007)

I. Franco, M. Shapiro, P. Brumer, J. Chem. Phys. 128, 244905 and 244906 (2008)

So --- in summary --- in these examples—

1. Wire --- decoherence hampers effect. Must bypass

2. Semiconductor QD --- decoherence can be avoided using fast dynamics

3. General theorem implies increasing difficulty (but still possible) of control in sample open systems thoerem.

Strategies:

Avoid it --- using appropriate control scenarios

        advantages: avoids problem
        disadvantages: must be possible

Beat it (timewise) ---use fast pulse techniques

        advantages: provides direct approach to avoiding problem
        disadvantages: broad energy spectrum brings in unwanted

Control it --- if possible

Engineer it --- design scheme to avoid decoherence (e.g. q. computing)

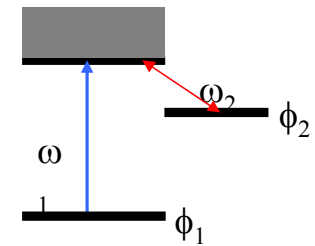   advantages: may well eliminate decoherence
        disadvantages: not dealing with problem

Here discuss examples of first two. Third is another talk ☺

Clearly, decoherence presents a formidable problem.

Possible directions:

1. Continued efforts of processes where decoherence can be bypassed.

2. Utilization of methods that are decoherence insensitive---e.g.

ω_2
ϕ_2
ω_1
ϕ_1

Incoherent Interference
Control

3. Efforts to control decoherence itself … in progress

Thanks to

Control in Molecular Wires:
Ignacio Franco (U of Toronto → Northwestern), and
Moshe Shapiro (Weizmann → ←UBC)

Control in Semiconductor Quantum Dots
David Gerbasi (U of T → Canadian Coast Guard Academy)
and Greg Scholes (U of Toronto),

Theorem on Control in Open Systems
Lianao Wu (University of Toronto) and
Arjun Bharioke (Uof T → Cambridge)