SEMICLASSICAL MECHANICS IN THE COHERENT CONTROL OF MOLECULAR PROCESSES -

P. BRUMER - UNIV. OF TORONTO

OUTLINE:

INCREASING CLASSICAL

1. How/why QUANTUM CONTROL?
2. LARGER SYSTEMS ⇒ SEMIC.
3. SEMIC. AS TOOL TO EXTRACT
   CONTROL + DEPHASING
4. ALMOST CLASSICAL INSIGHTS
   CLASSICAL WIGNER INT. TERMS
   CLASSICAL DECOHERENCE DYNAMICS

BUT: HIGHLY DIVERSE CROWD

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David Eisenbud ***Green's Conjecture on Free Resolutions and Canonical Curves***

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> ***"Mathematics comes into being through the inspired dreams and passions of individuals; it flourishes in the lively collaborations of small groups; it is stimulated by problems in science and technology."***
> David Eisenbud, Director, MSRI

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IMPORTANT NEW Physics WITHIN WHICH TO DO SEMICLASSICS

Coherent Control - Laser Control of Molecular Processes ⟺ Quantum Interference.

ULTIMATE GOAL:

Affect Molecular Processes At their Most Fundamental - SINGLE MOLECULE - level.

E.g.

$$CH_2Br + I \leftarrow CH_2IBr \xrightarrow{h\nu} CH_2I + Br$$

(CHANNELS $q = 1, 2 ..$)

Traditional APPROACHES - ENSEMBLE METHODS

RELIANCE ON Thermodynamics, Le Chatelier

Modern Approach - I.E. MODERN RESEARCH DIRECTION - LASERS / QUANTUM INTERFERE

To CONTROL, E.G.

$$AB + C \rightarrow A + BC \text{ vs } AC + B$$

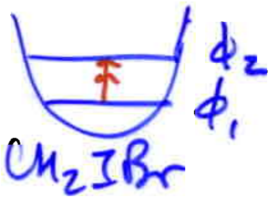
$$ABC \rightarrow AB + C, \text{ vs. } AC + B$$

Refractive Indices, NANODEPOSITION ON SURFACES, QUANTUM COMPUTE, CHIRALITY CONTROL

BY EXAMPLE

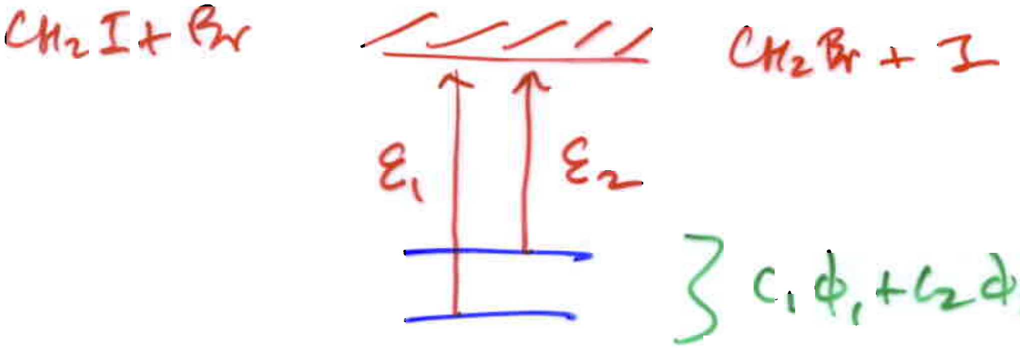
E.G. WE WILL TRY TO UNDERSTAND, THE ORIGINS OF THE following example -

STEP 1



} TWO PHOTON EXCITATION TO FORM $c_1\phi_1 + c_2\phi_2$ (superposition STATE)

STEP 2



} $c_1\phi_1 + c_2\phi_2$

} ONE PHOTON DISSOCIATION (with ω_1, ω_2 photons)

Applied $\varepsilon(t) = \varepsilon_1 \cos(\omega_1 t + \theta_1) + \varepsilon_2 \cos(\omega_2 t + \theta_2)$

NOTE: MOLECULES HAVE PHASES IN WELL DEFINED WAVEFUNCTION & AMPLITUDES

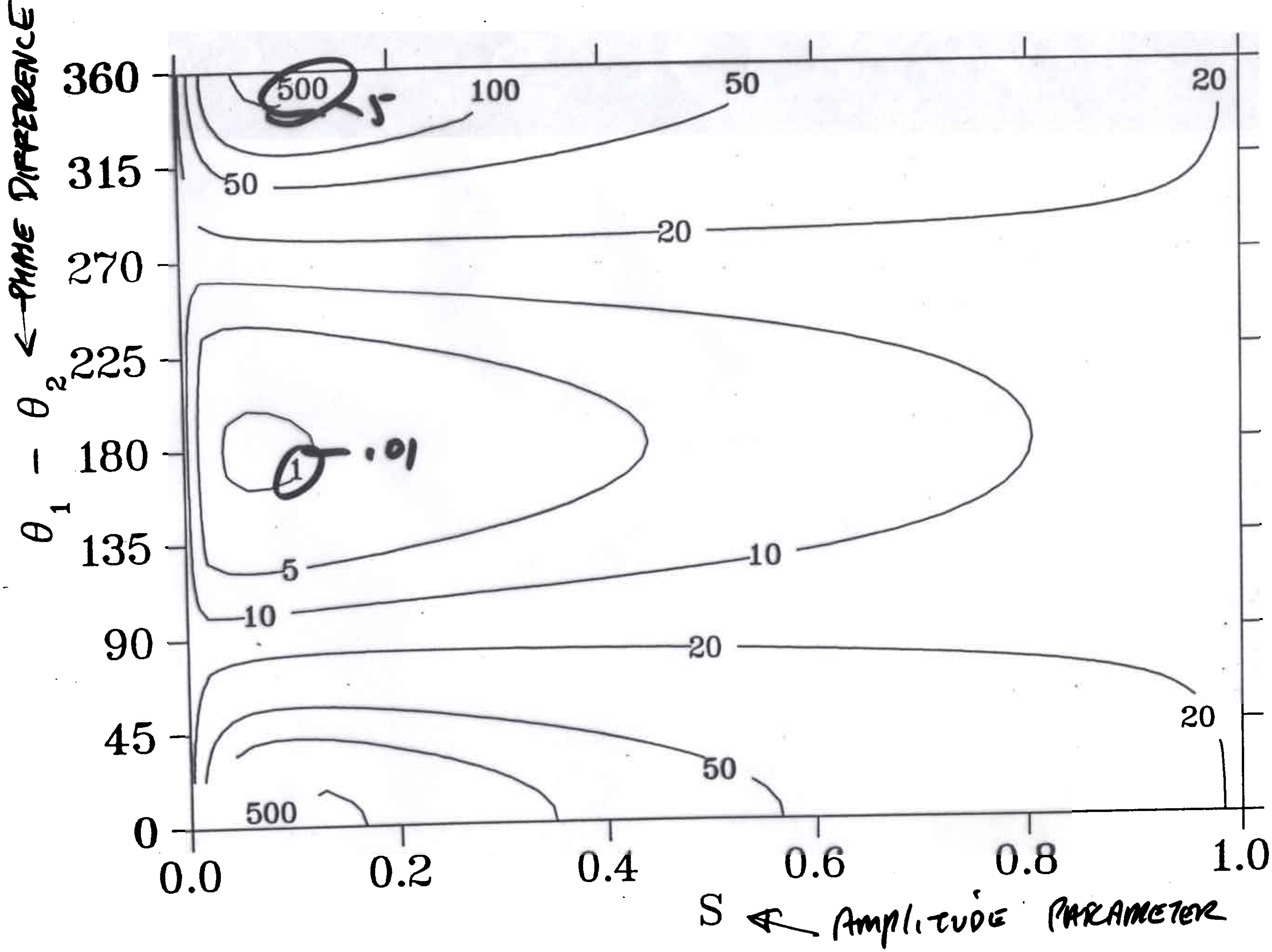
Throughout - "Isolated" Molecules

Electric FIELD IS COHERENT ⟹ WELL DEFINED PHASES

then

I/BR RATIO $[|E_1\rangle + |E_5\rangle$ (x100)]

NON CHAOTIC STATES



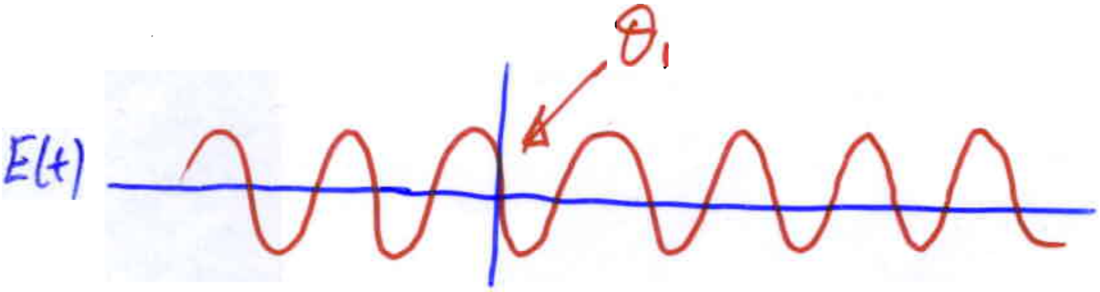
RANGE: .01 MIN

~10 NO CONTROL

5 MAX

Huge Effect

NOTE - $\theta_1 - \theta_2$ IS RELATIVE FIELD PHASE:



$$\mathcal{E}_1(t) = \cos(\omega t + \theta_1) \Rightarrow$$

$$\mathcal{E}_1(0) = \cos(\theta_1)$$

EFFECT OF PHASE SHIFT OF FIELDS $\theta_1 - \theta_2$, IS CLEARLY NONCLASSICAL. RELATED TO COHERENCE OF LIGHT

INDEED NOTE DEFINITION OF COHERENT Light: $\mathcal{E}(t)$ is function of t.

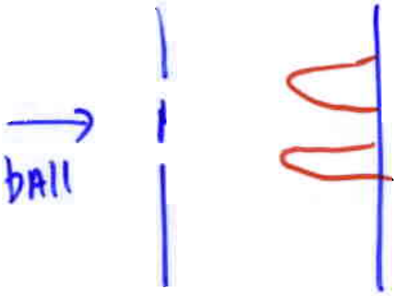
NOT

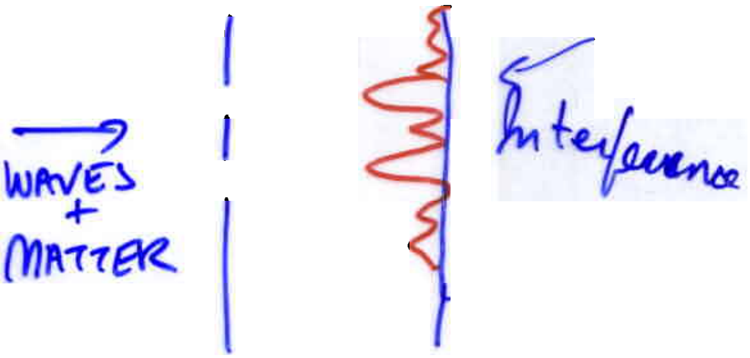
ETC. - This bits + pieces of Coherent light. - Light bulb

How /why? - BOTH QUAL. + QUANT.

QUALITATIVE

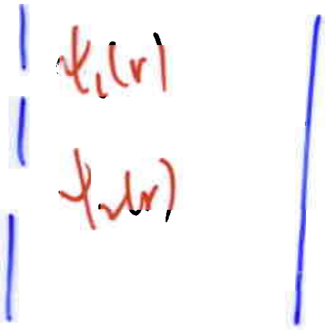
RECALL





NOTE: "TWO ELECTRONS IMPINGE ON SCREEN FROM TWO SOURCES ⇒ VANISH!"

Why?



$$\Psi(r) = \frac{1}{\sqrt{2}}\left(\psi_1(r) + \psi_2(r)\right)$$

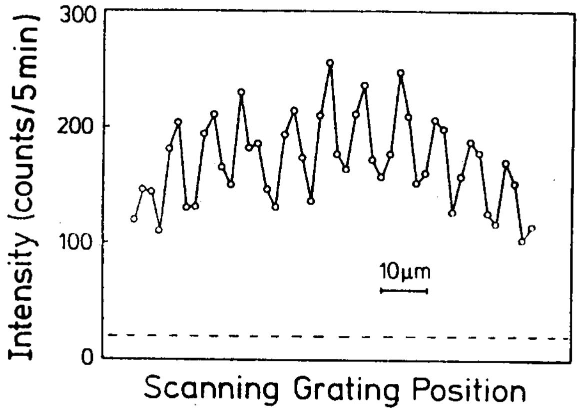
$$|\Psi(r)|^2 = \frac{1}{2}\left[|\psi_1(r)|^2 + |\psi_2(r)|^2 + 2\,\mathrm{Re}\{\psi_1^*(r)\psi_2(r)\}\right]$$

STRUCTURE: (A) ADD AMPLITUDES

(B) $\mathrm{Re}\{\psi_1^*(r)\,\psi_2(r)\}$ can be +/−

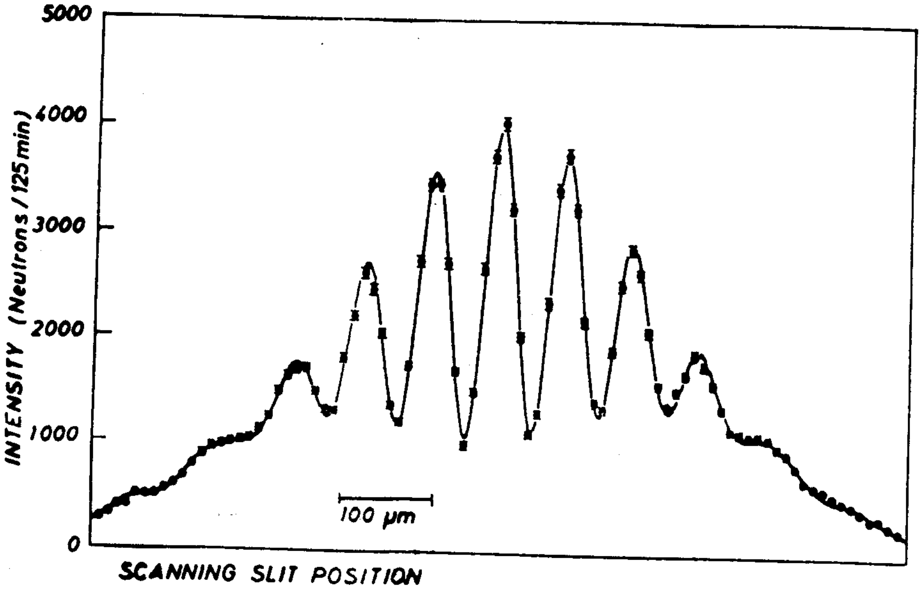
(C) Arises from Coherence of MATTER - I.E. EXISTENCE OF PHASES.

E.G.



Atoms (1991)

Figure 1–8 *Interference of Atoms.* The interference pattern obtained by Mlynek and Carnal, demonstrating atom interference. SOURCE: Reproduced with permission from O. Carnal and J. Mlynek, "Young's double-slit experiment with atoms: A simple atom interferometer," *Phys. Rev. Lett.*, vol. 66, p. 2689 (1991), published by The American Physical Society.



NEUTRONS (1991)

Figure 1–5 *Interference of Neutrons.* The interference pattern obtained by Gähler and Zeilinger, demonstrating neutron interference. SOURCE: Reproduced with permission from R. Gähler and A. Zeilinger, "Wave-optical experiments with very cold neutrons," *Amer. J. Phys.*, vol. 59, p. 316 (1991).

C_{60}! FROM THERMAL OVEN!

Nairz, Brezger, Arndt + Zeilinger,

Phys. Rev. Lett. 87, 160401, 2001

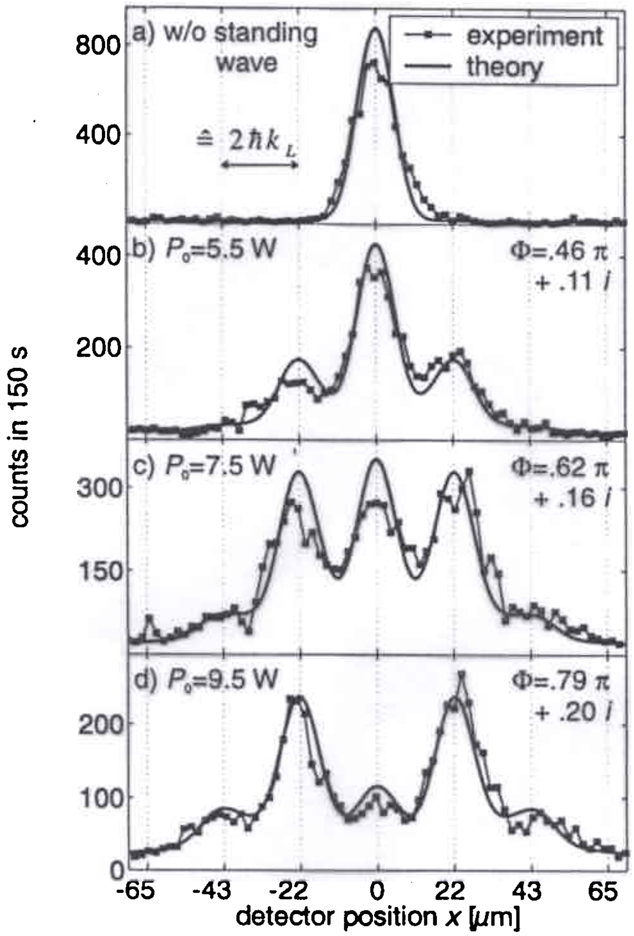
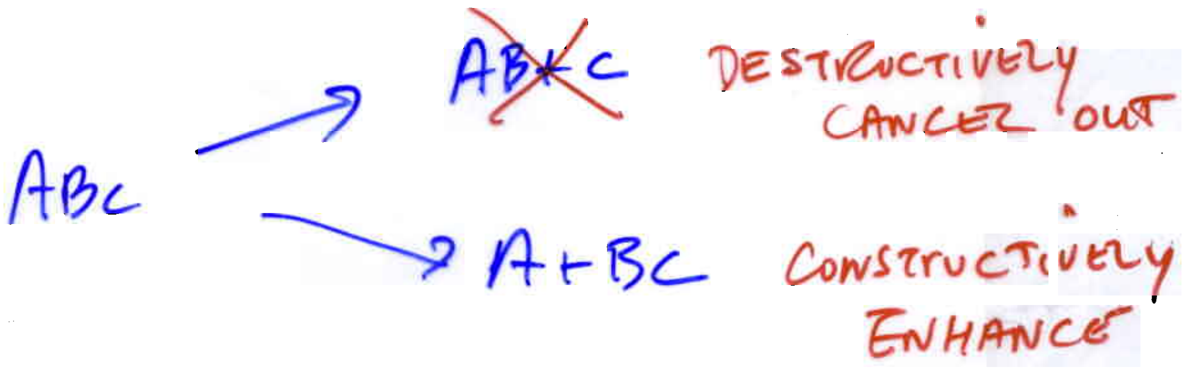


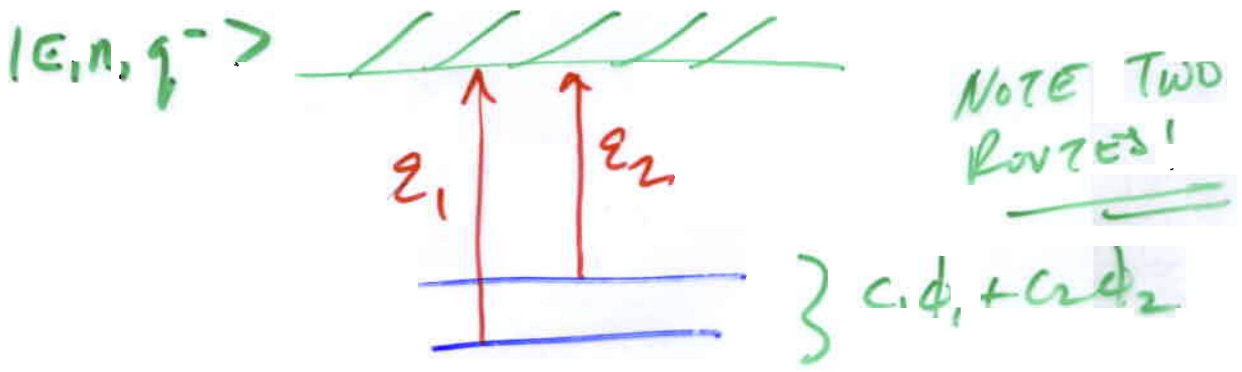
FIG. 2. Interference patterns for C_{60} for different laser powers. Φ is the phase shift parameter as defined in Eq. (3). Twice its imaginary part gives the mean absorbed photon number [Eq. (5)]. The diffraction efficiency into each of the first diffraction orders in case (d) can be estimated to be about 25%.

QUALITATIVE SOURCE OF DOUBLE SLIT INTERFERENCE - TWO INDEPENDENT PATHWAYS TO SAME FINAL STATE WHICH ARE ~~BE~~ EXPERIMENTALLY INDISTINGUISHABLE.

⇒ CAN WE USE THIS IDEA ~~TO~~ + WAVE-LIKE PROPERTY OF MATTER TO, E.G.



YES! COHERENT CONTROL. E.G.



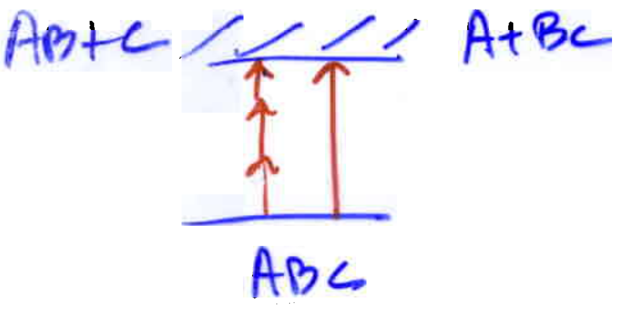
this scenario: Bichromatic Control.

CONTROL? VARY LASER/SYSTEM PARAMETERS ⇒ VARY INTERFERENCE ⇒ VARY PRODUCT.

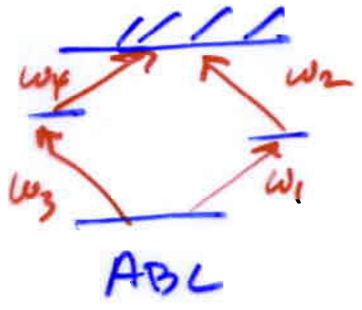
ALTERNATIVE: VARY LASER/SYSTEM PARAMETERS ⇒ VARY DYNAMICAL ENCODING ⇒ VARY PRODUCT.

HENCE: CONTROL VIA INTERFERING ROUTES

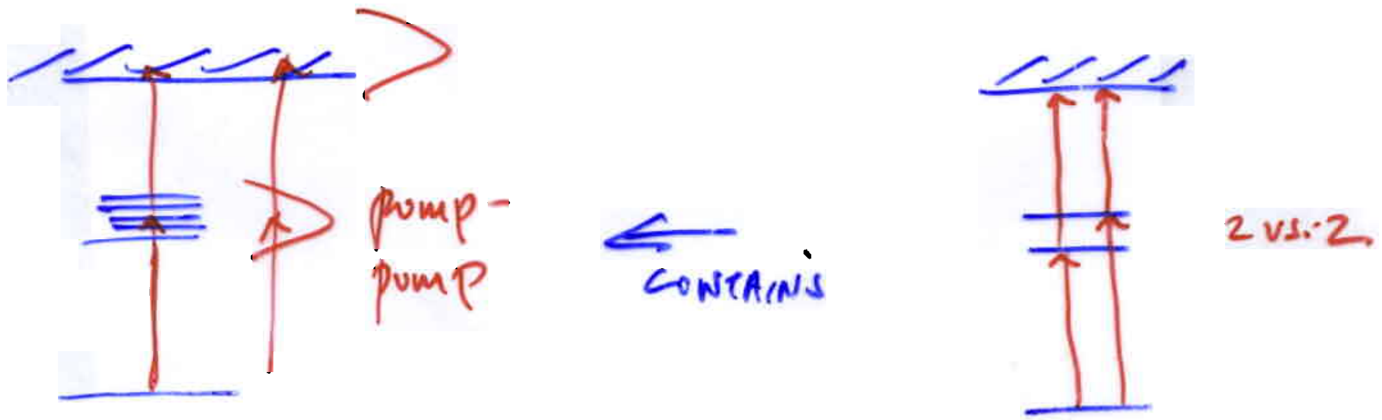
WITH THE RULE IN HAND [IE MULTIPLE INPT. CONTROLLABLE PATHWAYS] – "EASY" – E.G.



1 vs 3



2 vs. 2



⑥

[redacted]

QUANTITATIVE ASIDE: ["NO ONE" USES IT.]

Interfering pathways must be EXPERIMENTALLY INDISTINGUISHABLE.

Distinguishability of two states ψ_1, ψ_2 : $U_{P_K}(\psi_1,\psi_2)$

Interference "power" of ψ_1, ψ_2 $I_{P_\ell'}(\psi_1,\psi_2)$

$$I_{P_\ell'}(\psi_1,\psi_2) \geq U_{P_K}(\psi_1,\psi_2)$$

[quant-ph 9904003]

where $\{P_\ell'\}$ and $\{P_K\}$ are C.S.C.O. AND

$$U_{P_K}(\psi_1,\psi_2) = \sum_K \left[\frac{\langle\psi_1|P_K|\psi_1\rangle\langle\psi_2|P_K|\psi_2\rangle}{\langle\psi_1|\psi_1\rangle\langle\psi_2|\psi_2\rangle}\right]^{\frac{1}{2}}$$

$$I_{P_\ell'}(\psi_1,\psi_2) = \sum_\ell \frac{|\langle\psi_1|P_\ell'|\psi_2\rangle|}{\sqrt{\langle\psi_1|\psi_1\rangle\langle\psi_2|\psi_2\rangle}}$$

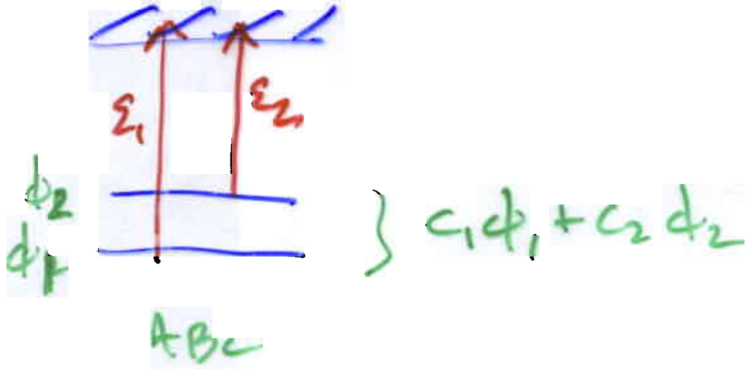
NOTE:

(1) CONTROL IS ACHIEVED BY VARYING QUANTUM INTERFERENCE.

(2) CONTROL IS ACHIEVED AT FIXED ENERGY (ALL SCHEMES) HENCE NOT "BEATING OUT IVR RATES", ETC. [Recall time evolution $\Rightarrow \Delta E$ to]

③ ANY LOSS OF COHERENCE (IN LASER OR IN MOLECULE) ⇒ LOSS OF EXTENT OF CONTROL

E.G. – QUANTITATIVELY –

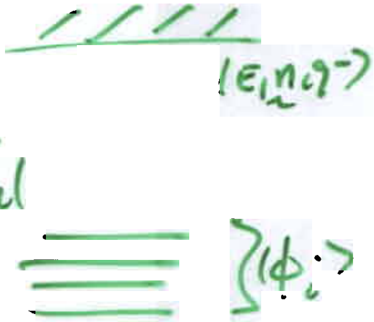


for WEAK fields – USE PERTURBATION THEORY.

$$(q=2)\quad AC(n) + B \leftarrow ABC \rightarrow AB(n) + C \quad (q=1)$$

$$H = H_M + V(t)$$

$$V(t) = -\mu \cdot \epsilon(t)$$



$$H_M|\phi_i> = E_i|\phi_i>$$

product q.n.

product channel

$$H_M|E,\underset{\sim}{n},q^-> = E\,|E,\underset{\sim}{n},q^->$$

where boundary condition

$$\int e^{-iEt}|E,\underset{\sim}{n},q^-> C_{E,n,q}\,dE \xrightarrow{t\to\infty} \int e^{-iEt}|E,\underset{\sim}{n},q^0> C_{E,n,q}\,dE$$

$|E,\underset{\sim}{n},q^0>$ = product state; e.g. AB(n) + C etc.

Important Insight: If you want to make product in channel $q=1$, e.g., then populate, somehow, the $|E,n,q=1^->$ states.

Issue - do so to the exclusion of the $q \neq 1$ states.

c.c. (INTERFERENCE) DOES JUST THAT.

Complex amp + phase

So $V(t) = -\mu \cdot \mathcal{E}(t) = -\mu \int d\omega\, \mathcal{E}(\omega) \cos(\omega t + \phi_\omega)$

STANDARD DIRAC APPROACH

$$|\psi(t)\rangle = |\chi(t)\rangle + \sum_{n,q} \int dE\, B(E,n,q|t)\, |E,n,q^-\rangle\, e^{-iEt/\hbar}$$

Solve for $B(E,n,q|\infty)$ to get Probability:

$$P(E;q) = \sum_n |B(E,n,q|\infty)|^2$$

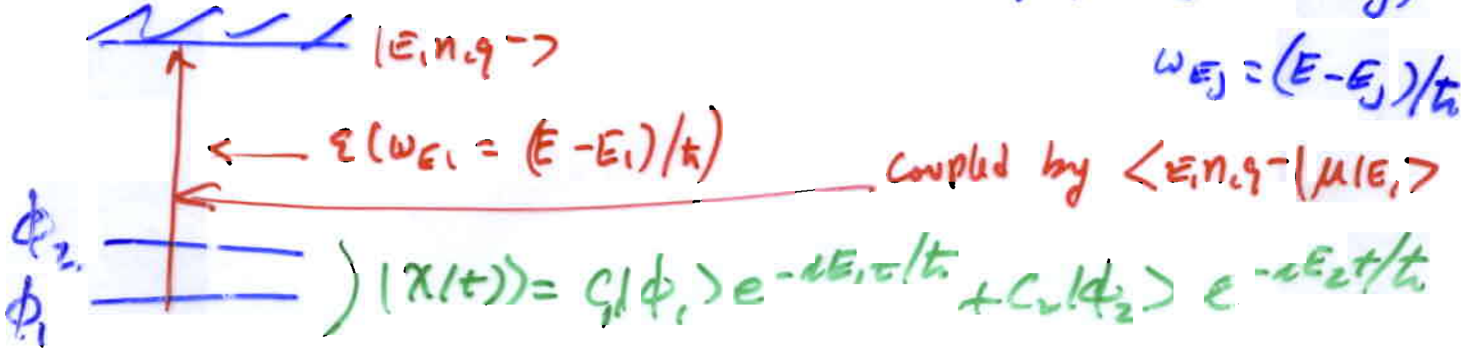
By perturbation theory + rotating wave approx:

$$B(E,n,q|t) = \frac{i}{2\hbar} \int d\omega\, \mathcal{E}(\omega) \int dt' \, \langle E,n,q^-|\mu|\chi(t)\rangle\, e^{it'(E/\hbar - \omega)}$$

For case of $|\chi(t)\rangle = c_1|\phi_1\rangle e^{-iE_1t/\hbar} + c_2|\phi_2\rangle e^{-iE_2t/\hbar}$

$$B(E,n,q|\infty) = \left(\frac{\pi i}{\hbar}\right) \sum_{j=1}^{2} c_j \langle E,n,q^-|\mu|E_j\rangle\, \mathcal{E}(\omega_{E_j})$$

$\omega_{E_j} = (E-E_j)/\hbar$



WEAK FIELDS

$$P(E,q) = \sum_n |B(E,n,q|\infty)|^2$$

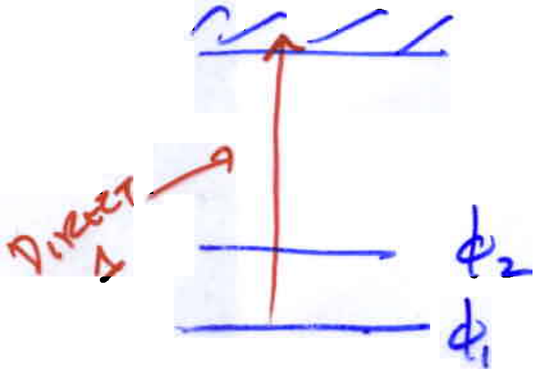
$$=$$

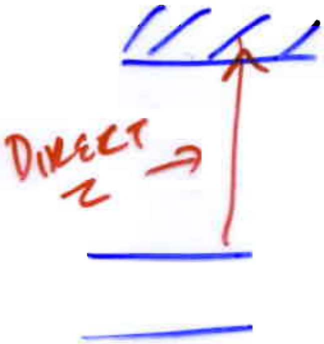
$$|c_1|^2 \, |\epsilon_1(\omega_{E_1})|^2 \sum_n |\langle E,n,q^-|\mu|E_1\rangle|^2 +$$

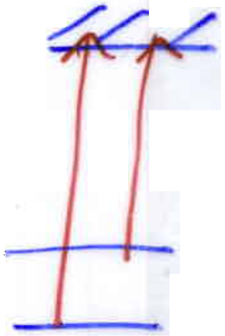
$$|c_2|^2 \, |\epsilon_2(\omega_{E_2})|^2 \sum_n |\langle E,n,q^-|\mu|E_2\rangle|^2 +$$

$$2 \, \mathrm{Re} \left\{ c_1 \epsilon_1(\omega_{E_1}) \cancel{a_2} c_2^* \epsilon_2^*(\omega_{E_2}) \sum_n \langle E_1|\mu|E,n,q^-\rangle \langle E,n,q^-|\mu|E_2\rangle \right\}$$

NOTE FORM: DIRECT (1) + DIRECT (2) + INTERFERE







+ Interfere
(TWO SIMULTANEOUS ROUTES)

AS IN DOUBLE SLIT.

CRUCIAL PRACTICALLY: NOTE INTERFERENCE Depends on AMPLITUDES + PHASES OF $\epsilon(\omega_{E_1})$, $\epsilon(\omega_{E_2})$, c_1, c_2. DEPENDS ON q.

HENCE SELECTIVE CONTROL OF PARTICULAR CHEMICAL PRODUCT IS POSSIBLE.

E.G. TO PRODUCE CH_2IBr plots from before, define

$$\epsilon(\omega_{Ej})\, c_j = f_j\, e^{i\theta_j}$$

$$\mu_{ij}^{(q)} = |\mu_{i,j}^{(q)}|\, e^{i\alpha_{ij}^{(q)}} \qquad x = f_2/f_1$$

Ampl. parameter ($s = |f_2|^2 / [|f_1|^2 + |f_2|^2]$

phase parameter ($\theta_1 - \theta_2$ ← NOTE GENERALIZATION of just LASER PHASE.

AND –

COMPUTE $\langle \phi_i | \mu | E, n, q^- \rangle$ [DIFFICULT!]

AFTER BUILDING POTENTIAL SURFACES [Challenge]

ENORMOUS CONTROL OVER MULTI Arrangement Problem. NOTE Again: CONTROL IS AT FIXED E.

ENCODING OF LASER INFORMATION IN MOLECULE - CW CASE.

Above: $\mathcal{E}(t) = \mathcal{E}_1 \cos(\omega_1 t + \theta_1) + \mathcal{E}_2 \cos(\omega_2 t + \theta_2)$

MOLECULAR WAVEFUNCTION BECAME, UPON EXCITATION:

$$t \to \infty \quad |\psi(t)\rangle = |\chi(t)\rangle + \left(\frac{\pi i}{\hbar}\right) \sum_{n,q} \Big[\sum_j c_j \langle E, n, q^- | \mu | E_j \rangle \, \mathcal{E}(\omega_{E_j}) \Big] |E, n, q^-\rangle \, e^{-iEt/\hbar}$$

MULTIPLE ROUTES

Complex, amplitude + phase

i.e. LASER has transferred Amplitude + phase information to Molecule.

this ENCODING of QUANTUM information INFLUENCES THE MOLECULAR DYNAMICS + OUTCOME.

STATUS ?

1. THEORY / REALISTIC COMPUTATION'S (ISOLATED SYSTEMS)

A. VAST RANGE OF SCENARIO'S PROPOSED FOR UNIMOLECULAR PROCESSES.

B. A NUMBER OF APPLICATIONS PROPOSED FOR MATERIAL PROP'S [REFRACTIVE INDEX, CONTROL OF CURRENTS, NANODEPOSITION]

C. PRELIMINARY THEORY DONE FOR BIMOLECULAR CONTROL

$(A + B \rightarrow C + D)$

D. PUSHING TOWARDS
  1. LARGE MOLECULES (SEMICLASSICAL)
  2. UNIQUE PHYSICS (BELOW)

REFERENCES -

E.G.

Rice + Zhao - Optical Control of Molecular Dynamics (Wiley, 2000)

Shapiro + Brumer -
Adv. Atomic, Molecular + Optical Physics 42, (2000)

Elementary: Scientific American 1995

Shapiro + Brumer - "Principles of the QUANTUM CONTROL of MOLECULAR PROCESSES" (Wiley, 2003)

WILEY

Principles of the Quantum Control of Molecular Processes

MOSHE SHAPIRO
PAUL BRUMER

BUT CHEMISTRY OFTEN DEALS WITH

1. LARGE MOLECULES
2. COMPLEX DYNAMICS
3. DECOHERING, RELAXATION PROCESSES. (preventing q. control)

GAIN INSIGHT VIA SEMICLASSICAL DYNAMICS -

COMMENT ON FOCUS -

ALSO HAVE EXAMINED FUNDAMENTALS [E.G. MASLOV INDICES, STATIONARY PHASE APPROACHES, QUANTUM/CLASSICAL CORR. IN HILBERT SPACE]

BUT HERE - NUMERICAL ISSUES FAR FROM TRIVIAL

ABOVE: THE FOREST

BELOW: THE TREES

PHYSICS QUESTION: CAN WE CONTROL MOLECULAR PROCESSES IN THE presence of decoherence?

SEMICLASSICAL issue: IS THE METHOD(S) USEFUL/EFFECTIVE in giving insight + numbers?

1. LArge system - IVR methods
2. Dynamics of DECOHERENCE
   a. WHEN QUANTUM/SEMIC?
   b. WHEN CLASSICAL.

If time:

CLASSICAL Wigner BASED Approach

THE PROBLEM OF DECOHERENCE.

SYSTEM ≡ part of interest to us

BATH ≡ REMAINDER

Problem

QUANTUM DYNAMICS OF SYSTEM CAN BE "DESTROYED" BY BATH.

INDEED: SUFFICIENT SPECIFIC TYPES OF DECOHERENCE HAS CLASSICAL MECHANICS EMERGE FROM QUANTUM

System Dynamics not Unitary

[e.g. GONG + BRUMER, Phys. Rev E, 60, 1643 (1999)]

OUR PROBLEM:

DECOHERENCE ⟹ LOSS OF QUANTUM

⟹ LOSS OF COHERENT CONTROL

$$H_s = \frac{1}{2}\left(p_x^2 + p_y^2 + \alpha x^2 y^2\right) + \frac{\beta}{2}\left(x^4 + y^4\right)$$

$\beta = 0.01$ $\alpha = 1.0$

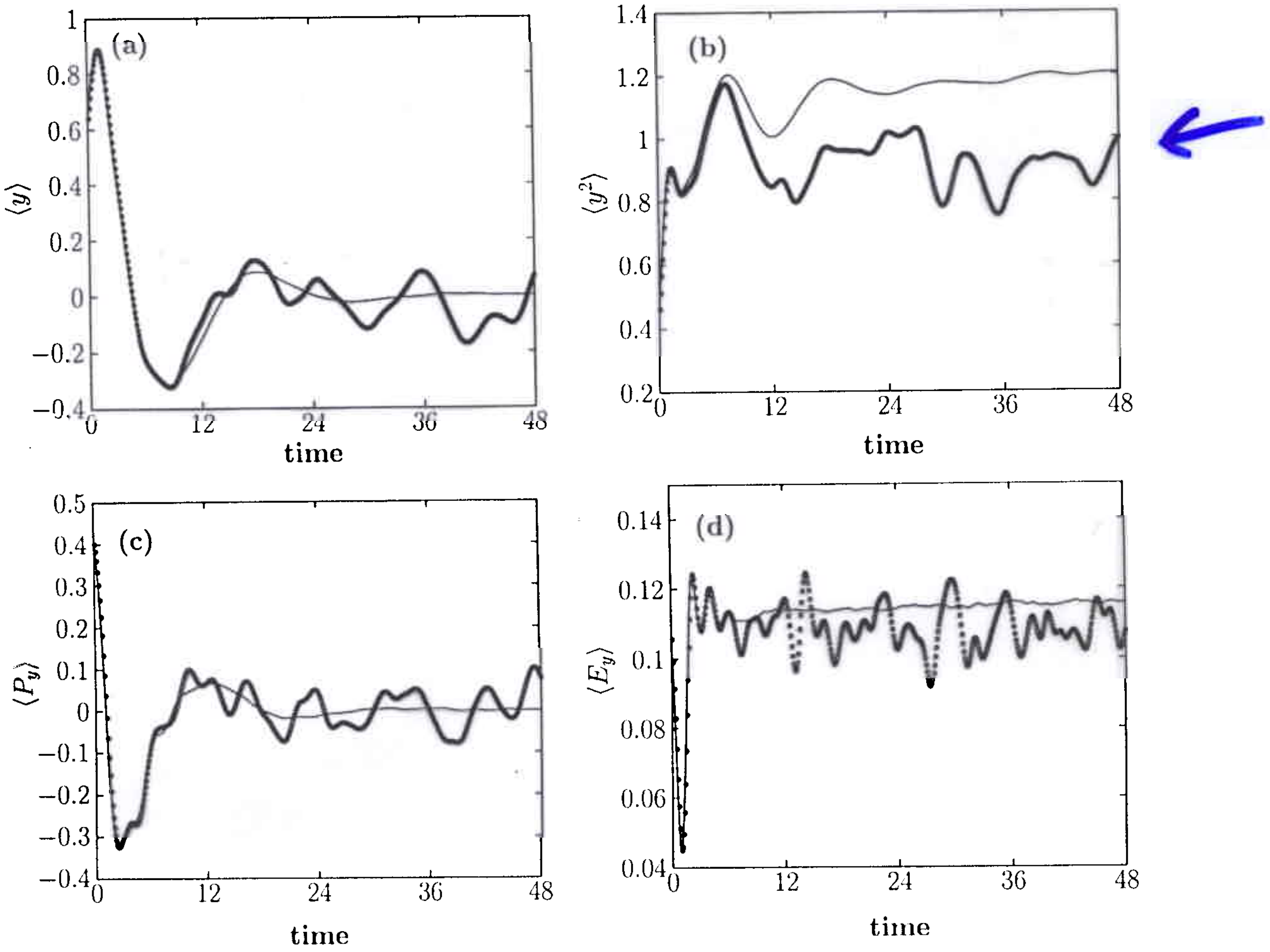
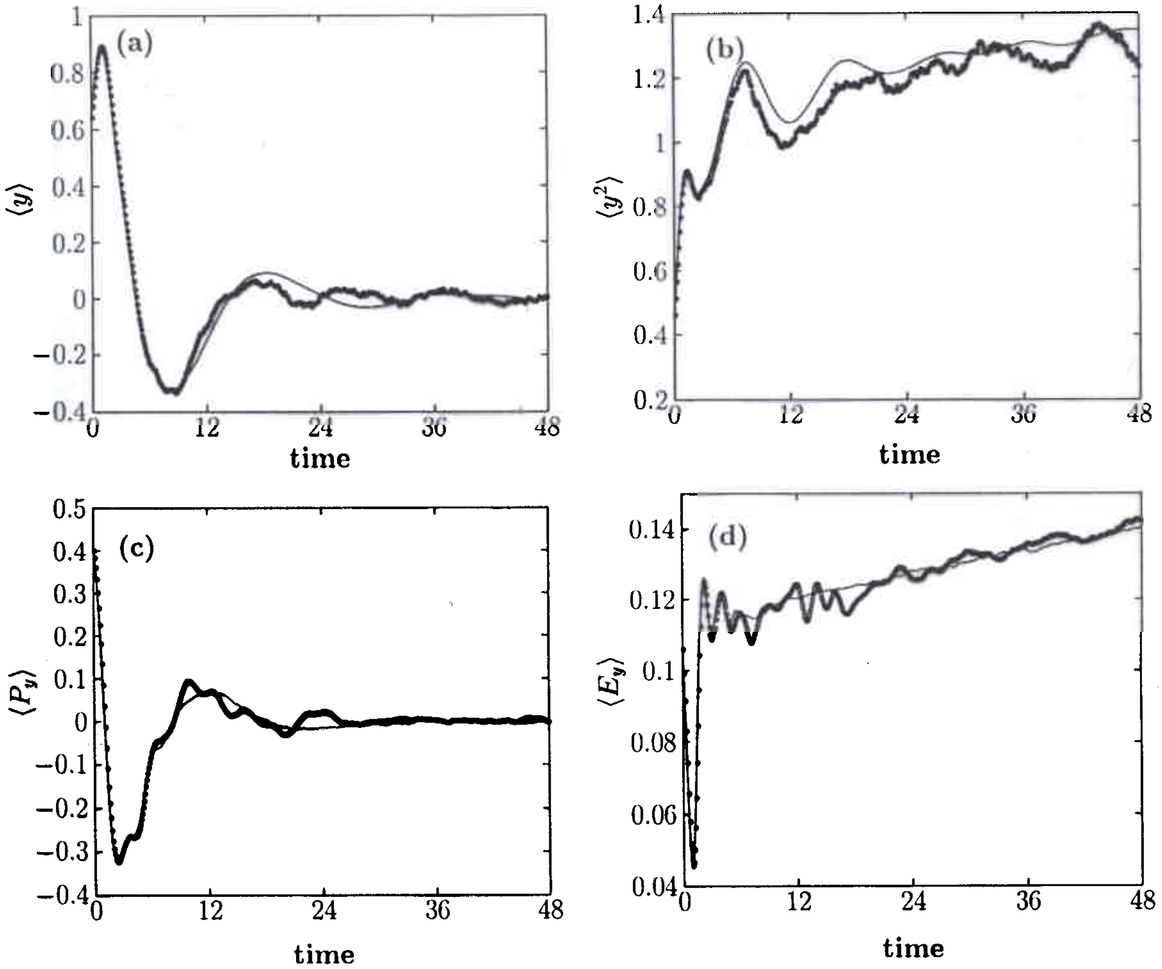


Figure 5.1: Time dependence of four statistical moments ($\langle y\rangle$, $\langle y^2\rangle$, $\langle P_y\rangle$ and $\langle E_y\rangle$) for the system in the absence of decoherence. Dark dots denote quantum results, thin solid lines are classical results. From Fig. 1, Ref. [163]

NO DECOHERENCE

(HAMILTONIAN SYSTEM)



← N.B

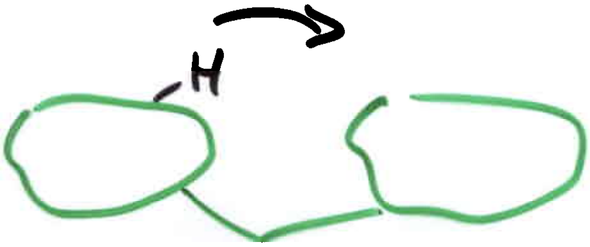
Figure 5.2: As in the previous figure, but in the presence of decoherence. From Fig. 2, Ref. [163]

WITH DECOHERENCE

CLARIFICATION OF "THE BATH":

(1) INTRINSIC DECOHERENCE ≡
WITHIN SINGLE MOLECULE.

E.g.



H = system

BATH = REMAINDER OF MOLECULE.

FORMALLY $\hat{\rho}(t) = |\psi(t)\rangle\langle\psi(t)|$

$$\hat{\rho}_s = \mathrm{Tr}_B[\hat{\rho}(t)]$$ {Renyi Entropy}

<u>EXAMPLE</u>: PROTON TRANSFER IN (HPO=)
2-(2'-HYDROXYPHENYL)-OXAZOLE

N.B. – THIS IS SOURCE OF DECOHERENCE
IN MANY MANY-BODY SYSTEMS –
i.e. focus on Subsystem.

(2) EXTRINSIC DECOHERENCE:

SYSTEM = MOLECULE UNDERGOING DYNAMICS

BATH = COLLISIONS UNDESIRED DISSOCIATION, ETC.

EXAMPLE: CONTROL OF CHIRALITY IN DIMETHYL ALLENE.

CONTROL OF MOLECULES IN SOL'N.

BATISTA + BRUMER - PRL 89, 14301 (2002)

~~FIGURES~~

INTRINSIC DECOHERENCE IN HPO

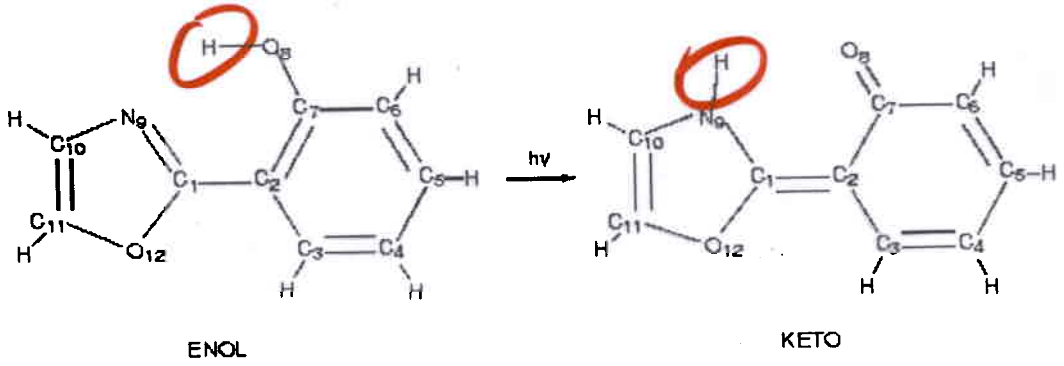


FIG. 1. Molecular structural diagram describing the excited state intramolecular proton transfer reaction in 2-(2'-hydroxyphenyl)-oxazole.

Proton Transfer
One big qubit!

NONCONTROLLED SYSTEM:

PROTON TRANSFER RATE ~
15% PRODUCT ~~[illegible]~~ AT ~~380~~ 100 fs.

QUESTION: CAN WE CONTROL THIS REACTION DESPITE DEPHASING / DECOHERENCE OF H by 50 DEGREES OF FREEDOM?

WHAT TOOLS DO WE HAVE?

QUANTUM PROPAGATION – IMPOSSIBLE.

SEMICLASSICAL APPROACHES?

A. VAN VLECK Type Propagators

Kay's help

$$K_t(x',x) = \langle x' | e^{-iHt/\hbar} | x \rangle$$

Choose form $K_t(x',x) = A_t(x',x)\, e^{iS_t(x',x)/\hbar}$

Insert in S. Eqn

As usual generate $\left\{ \begin{array}{l} \text{H–J Eqn for } S \\ \text{continuity for } A \end{array} \right.$

Gives

$$K_t(x,x') = \sum_{\substack{\text{All traj} \\ x \to x' \text{ in } t}} \frac{1}{(2\pi i \hbar)^{1/2}} \frac{e^{iS_t(x',x) - i\pi\nu/2}}{|\partial x'/\partial p|^{1/2}}$$

Problems (Numerical): Maslov indices, caustics

⇒ Two point boundary value problem!

B. INITIAL VALUE REPRESENTATION(S)

MILLER (1970), MILLER (LAST DECADE)

KAY, HELLER, US, HERMAN + KLUK

JUST SUMMARIZE SINCE NEXT IS MILLER "TBA" (THE $\left\{\begin{matrix}\text{BETTER}\\ \text{BEST}\end{matrix}\right\}$ APPROACH?)

Review: W.H. Miller, J. Phys. Chem A 105, 2942

Consider: $K_{n_2,n_1}(t) = \langle \psi_{n_2} | e^{-iHt/\hbar} | \psi_{n_1} \rangle$

$$= \int dx_2 \, dx_1 \; \psi^*_{n_2}(x_2) \, \psi_{n_1}(x_1) \; \langle x_2 | e^{-iHt/\hbar} | x_1 \rangle$$

Insert Van-Vleck Propagator

$$\approx \sum_{\substack{\text{all}\\ \text{Traj}}} \int dx_1 \, dx_2 \; \psi^*_{n_2}(x_2) \, \psi_{n_1}(x_1) \left[(2\pi i \hbar)^F \left| \frac{\partial x_2}{\partial p_1} \right| \right]^{-1/2}$$

$$\uparrow$$

$$e^{iS_t(x_2,x_1)/\hbar}$$

But x_1 at initial time, x_2 at final time

Change variables: $\sum_{\text{all traj}} \int dx_2 = \int dp_1 \left| \frac{\partial x_2}{\partial p_1} \right|$

gives

$$K_{n_2,n_1}(t) = \int dx_1 dp_1 \left[\left| \frac{\partial x_t(x_1,p_1)}{\partial p_1} \right| \Big/ (2\pi i\hbar)^F \right]^{1/2}$$

$$e^{iS_t(x_1,p_1)/\hbar} \, \psi^*_{n_2}(x_t)\, \psi_{n_1}(x_1)$$

$$S_t(x_1,p_1) = \int_0^t \underline{p}(t')\, \underset{\sim}{\dot{x}}(t') - H(\underline{p}(t'), \underset{\sim}{x}(t'))\, dt'$$

OR

$$e^{-iHt/\hbar} = \int dx_0 dp_0 \left[\frac{\partial x_t(x_0,p_0)}{\partial p_0} \right]^{1/2} (2\pi i\hbar)^{-F/2} e^{iS_t/\hbar} \, |x_t\rangle\langle x$$

ALSO Coherent STATES version (Herman - Kluk)

N.B. - NO CAUSTICS

NO TWO point boundary value Problem

BUT: High dimensional integral with highly oscillatory integrand.

The physics

MUCH EFFORT ON HANDLING These integrals Numerically for wide variety of problems

UTILITY? E.g. CHAOTIC SMALL SYSTEM

QUANTUM

10^5 traj.

SPECTRAL DENSITY $\propto$ $\mathrm{Re}\int dt\, e^{iEt}\, C(t)$

$C(t) = \langle \Phi_0 | e^{-iHt} | \Phi_0 \rangle$

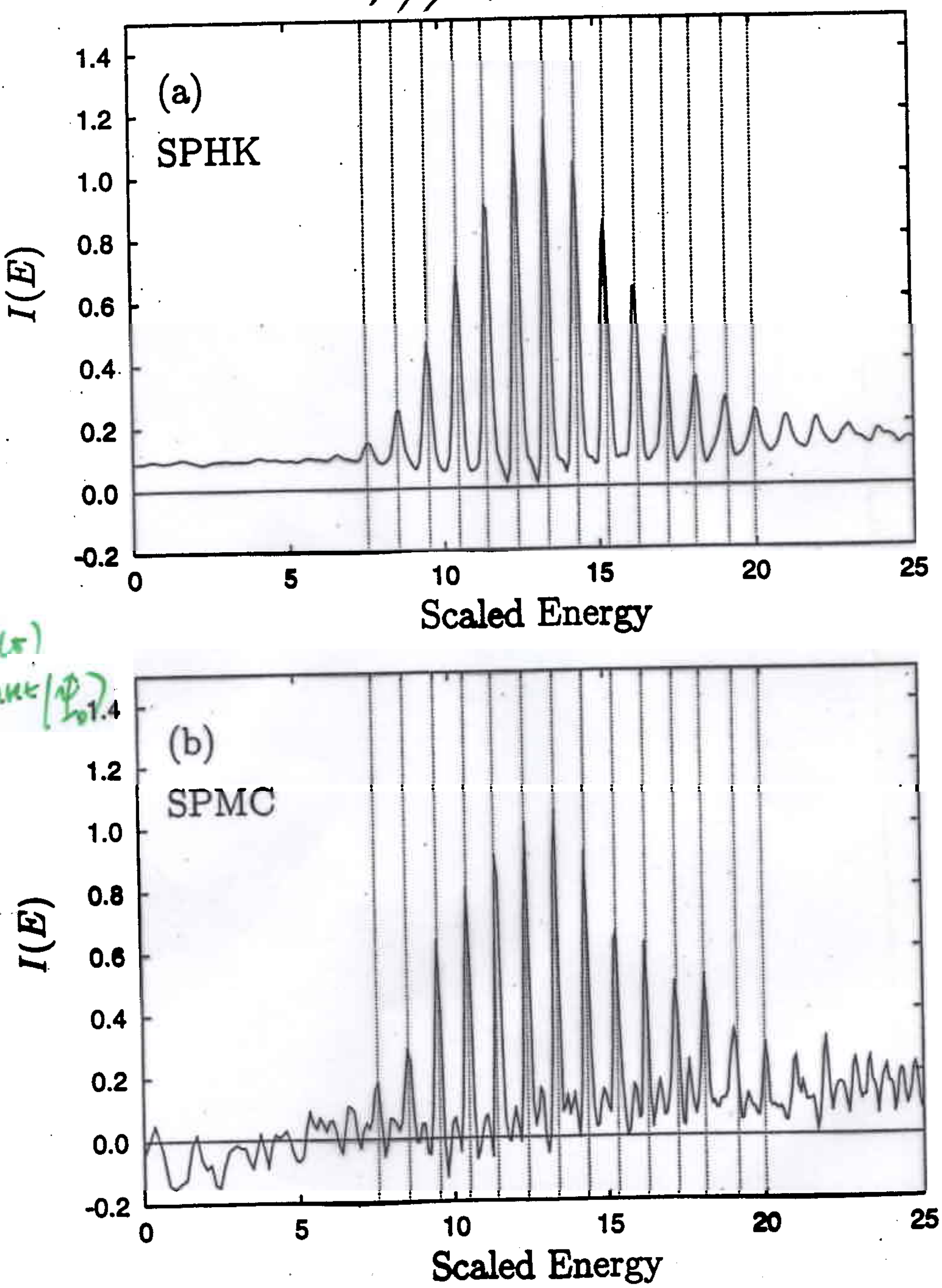
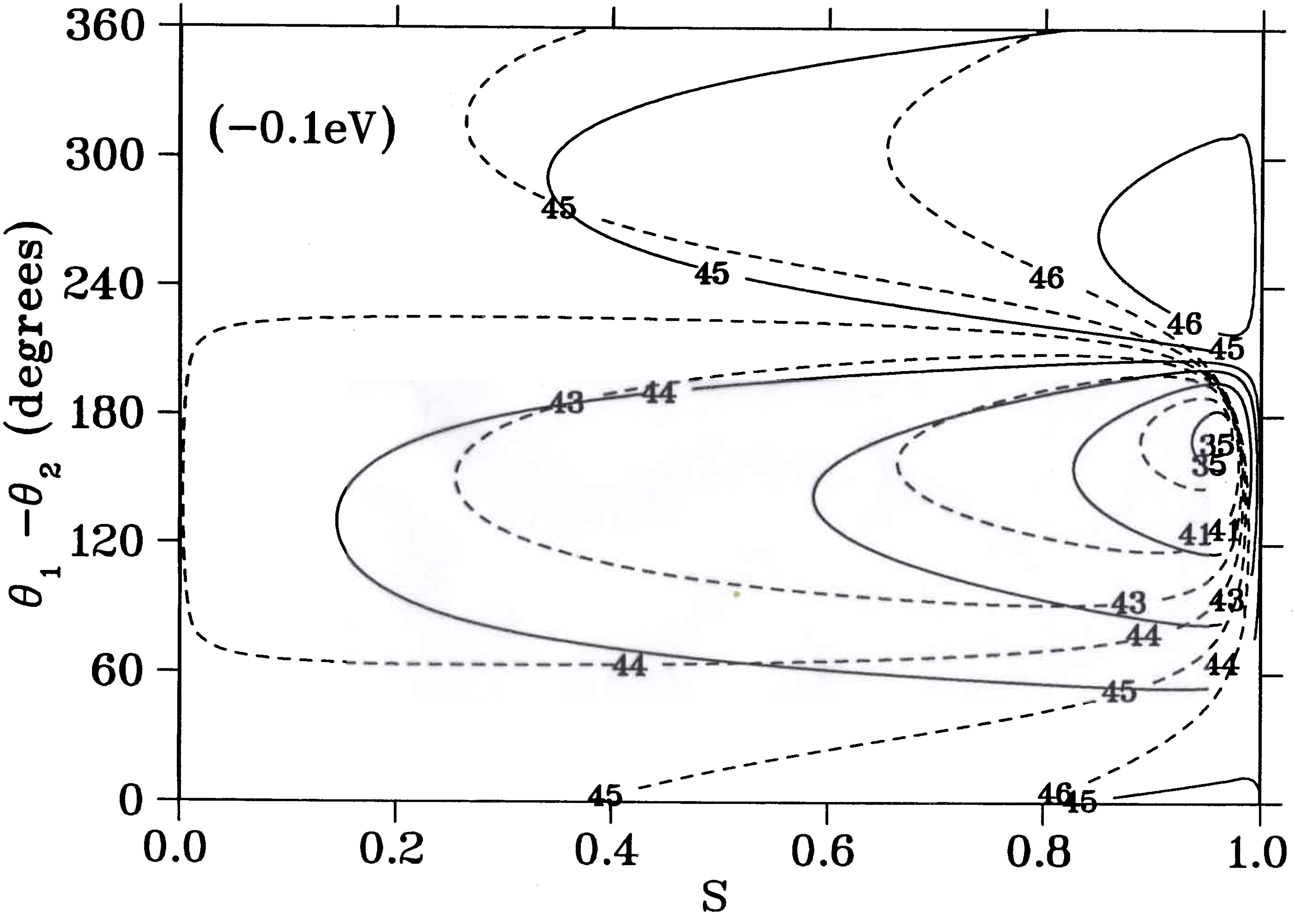


Fig. 3. Quartic oscillator. The vertical lines are some of the dominant quantum eigenvalues [28], although the additional peaks (above the noise) also reproduce the quantum result.

$$H = \frac{p_x^2}{2} + \frac{p_y^2}{2} + \frac{1}{2}x^2y^2 + \frac{\beta}{4}(x^4+y^4)$$

$\lambda = 0.93$

$CH_2Br + I \leftarrow$ "CH_2IBr" $\rightarrow CH_2I + Br$ E.g. Photodissociation



Batista + Brumer, JCP 114, 10321 (2001)

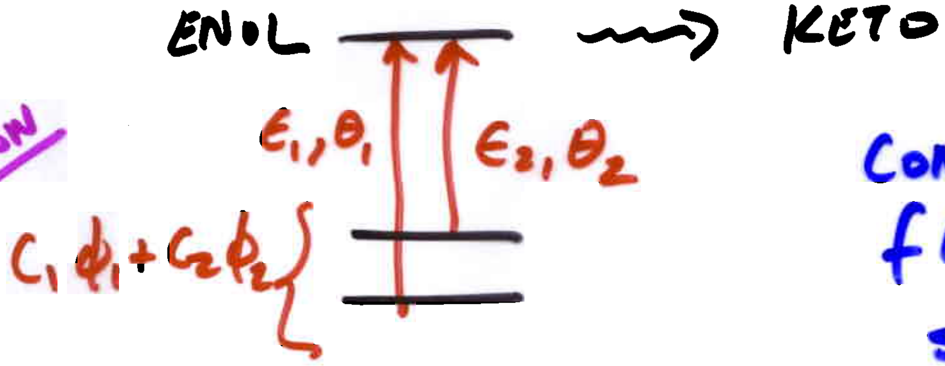
BACK TO HPO - IS THERE CONTROL?

APPROACH:

(1) SEMICLASSICAL MECHANICS ON FULLY VIBRATING SYSTEM À LA GUAILLAR, BATISTA & MILLER, JCP 113, 9510 (2000) [REALISTIC POTENTIAL SURFACE].

(2) CONTROL VIA BICHROMATIC CONTROL SCENARIO, AS ONE POSSIBLE APPROACH.

pulsed version



CONTROL IS $f(\theta_1 - \theta_2, s)$

$$s = \frac{|\epsilon_2/\epsilon_1|^2}{1 + |\epsilon_2/\epsilon_1|^2}$$

ϕ_1 = ground vib'l STATE

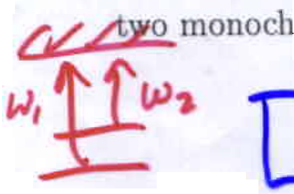
ϕ_2 = EXCITATION of $C_1C_2C_7$ ANGLE (in-plane bend)

E.g. in the HPo case -

coupled degrees of freedom and 16 out-of-the-plane vibrational modes that are approximately decoupled from the reaction coordinate. The potential was computed [?] at the CIS level using Gaussian 94. The system is prepared in an initial coherent superposition state on the ground electronic state:

$$\boxed{\mid \Psi_0\rangle = c_1 \mid 1\rangle + c_2 \mid 2\rangle,} \tag{1}$$

where $\mid i\rangle$ is a nuclear eigenstate of energy E_i. This superposition state is photoexcited by two monochromatic laser pulses with a total electric field $\boldsymbol{\epsilon}(t)$



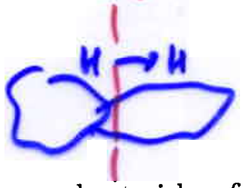
$$\boxed{\boldsymbol{\epsilon}(t) = F_1(t-t_1)\,\boldsymbol{\epsilon}_1\, e^{-i(\omega_1 t+\theta_1)} + F_2(t-t_2)\boldsymbol{\epsilon}_2\, e^{-i(\omega_2 t+\theta_2)} + \text{c.c},} \tag{2}$$

Applied laser field

where $\boldsymbol{\epsilon}_j = \epsilon_j\hat{\boldsymbol{\epsilon}},\ j = 1, 2$ are time independent real vectors, and c.c. denotes the complex conjugate of the preceding terms. The functions F_j in Eq. (2), describe the pulse shapes, and θ_j are the phases of the two pulses. Hence, in this pulsed laser variant of cw bichromatic coherent control [?], the superposition of $|1\rangle$ and $\mid 2\rangle$ are photoexcited by the laser field with frequencies ω_1 and ω_2. The state created by the two photoexcitation routes interfere with one another, and these quantum mechanical interferences affect the time dependent reactant population $P(t)$ of the proton. Here $P(t)$ is defined as

R=0 n 1

$$\boxed{P(t) \equiv \langle\Psi_t \mid R \mid \Psi_t\rangle,} \tag{3}$$



where R is a function of the proton coordinate that is zero on the product side of a dividing surface in configuration space and unity on the reactant side. Assuming that the field is sufficiently weak to allow the use of first order perturbation theory, we obtain the time evolved wave function $\mid \Psi_t\rangle$ as

$|\Psi_t\rangle$

$$\boxed{\mid \Psi_t\rangle = -\frac{i}{\hbar}\sum_{j=1}^{2} c_j \int_{-\infty}^{t} dt' \left[\sum_{k=1}^{2} \epsilon_k e^{-i[(E_j+\hbar\omega_k)t'/\hbar+\theta_k]} F_k(t'-t_k)\right] e^{-i\hat{H}(t-t')/\hbar}\hat{\boldsymbol{\epsilon}}\cdot\boldsymbol{\mu} \mid j\rangle,} \tag{4}$$

where $\hat{H}$ is the Hamiltonian on the excited electronic surface, $\boldsymbol{\mu}$ is the electric dipole operator and where only the near resonant terms have been retained (the rotating wave approximation). Substituting Eq. (4) into Eq. (3), we obtain the time dependent reactant population in the weak field limit

Interference from sup'n

NOTE STRUCTURE

gives

$$\begin{aligned} P(t) = \hbar^{-2} \int_{-\infty}^{t} dt' \int_{-\infty}^{t} dt'' \boxed{\sum_{j,j'=1}^{2} c_j c_{j'}^*} \langle j' \mid \hat{\boldsymbol{\epsilon}} \cdot \boldsymbol{\mu} e^{i\hat{H}(t-t'')/\hbar} R e^{-i\hat{H}(t-t')/\hbar} \hat{\boldsymbol{\epsilon}} \cdot \boldsymbol{\mu} \mid j \rangle \\ \times\ e^{i(E_{j'}t''-E_j t')/\hbar}\, \epsilon_1^2\, [\underline{F_1(t'-t_1)\, F_1(t''-t_1)\, e^{i\omega_1(t''-t')}} + \\ \underline{F_2(t'-t_2)\, F_2(t''-t_2)\, x^2\, e^{i\omega_2(t''-t')}} + \underline{F_2(t'-t_2)\, F_1(t''-t_1)} \\ \times\ x\, e^{i[(\omega_1 t''-\omega_2 t')+\Theta]} + F_1(t'-t_1)\, F_2(t''-t_2)\, x\, e^{i[(\omega_2 t''-\omega_1 t')-\Theta]}], \end{aligned} \tag{5}$$

as a function of the laser controllable parameters $x = \epsilon_2/\epsilon_1$, and $\Theta = \theta_1 - \theta_2$. Note that Eq. (5) contains terms in $|c_j|^2$ corresponding to direct contributions, as well as terms in $c_j c_j'$ that correspond to interference terms. Hence, by altering the c_j we can control the interference term, and hence the dynamics.

Equation (5) requires the exact quantum propagation of the system, a computational task that becomes daunting, if not intractable , for systems with more than six degrees of freedom (e.g., a molecule with four atoms). We therefore replace the time evolution operators by the coherent state expression in the initial value representation (IVR) [?]. That is,

HERMAN-KLUK

$$\boxed{e^{-i\hat{H}t/\hbar} = (2\pi\hbar)^{-N} \int d\mathbf{p}_0 \int d\mathbf{q}_0\, e^{iS_t(\mathbf{p}_0,\mathbf{q}_0)/\hbar}\, C_t(\mathbf{p}_0,\mathbf{q}_0) \mid g_{\mathbf{q}_t,\mathbf{p}_t}\rangle\langle g_{\mathbf{q}_0,\mathbf{p}_0} \mid,} \tag{6}$$

where $\mid g_{\mathbf{q},\mathbf{p}}\rangle$ is a coherent state. The integration variables $(\mathbf{p}_0, \mathbf{q}_0)$ in Eq. (6) are the initial conditions for classical trajectories and $\mathbf{q}_t \equiv \mathbf{q}_t(\mathbf{p}_0, \mathbf{q}_0)$ and $\mathbf{p}_t \equiv \mathbf{p}_t(\mathbf{p}_0, \mathbf{q}_0)$ are the time-evolved nuclear coordinates and momenta. The classical action $S_t(\mathbf{p}_0, \mathbf{q}_0)$ along this trajectory is obtained by integrating the equation:

WITH

$$\boxed{\dot{S}_t = \mathbf{p}_t \cdot \dot{\mathbf{q}}_t - H(\mathbf{p}_t, \mathbf{q}_t),} \tag{7}$$

along with Hamilton's equations of motion for $\mathbf{p}_t$ and $\mathbf{q}_t$. Here, $H(\mathbf{q}, \mathbf{p})$ is the full-dimensional model Hamiltonian [?] that explicitly describes the motion of all degrees of freedom in the system. The pre-exponential factor $C_t(\mathbf{p_0}, \mathbf{q_0})$, introduced in Eq. (6), involves the monodromy matrix elements that are propagated in accord with reference [?].

Substituting Eq. (6) into Eq. (5) gives the semiclassical IVR for $P(t)$

~150 dimensional integral

$$\begin{aligned}
P(t) = \hbar^{-2}\, (2\pi\hbar)^{-2N} \textstyle\int d\mathbf{p}_0 \int d\mathbf{q}_0 \int d\mathbf{p}'_0 \int d\mathbf{q}'_{\mathbf{0}} \int_{-\infty}^{t} dt' \int_{-\infty}^{t} dt'' \sum_{j,j'} c_j c_{j'}^{*} \\
\times\ e^{i(S_{t-t'}(\mathbf{p}_0,\mathbf{q}_0) - S_{t-t''}(\mathbf{p}'_0,\mathbf{q}'_0))/\hbar} C_{t-t'}(\mathbf{p}_0, \mathbf{q}_0) C^{*}_{t-t''}(\mathbf{p}'_0, \mathbf{q}'_0) \\
\times\ \langle j' \mid \mathbf{p}'_0, \mathbf{q}'_0 \rangle \langle \mathbf{p}'_{\mathbf{t-t''}}, \mathbf{q}'_{t-t''} \mid R \mid \mathbf{p}_{t-t'}, \mathbf{q}_{t-t'} \rangle \langle \mathbf{p}_0, \mathbf{q}_0 \mid j \rangle \\
\times\ e^{i(E_{j'} t'' - E_j t')/\hbar}\, \epsilon_1^2\, [F_1(t' - t_1)\, F_1(t'' - t_1)\, e^{i\omega_1 (t'' - t')} + \\
\times\ F_2(t' - t_2)\, F_2(t'' - t_2)\, x^2\, e^{i\omega_2 (t'' - t')} + F_2(t' - t_2)\, F_1(t'' - t_1) \\
\times\ x\, e^{i[(\omega_1 t'' - \omega_2 t') + \Theta]} + F_1(t' - t_1)\, F_2(t'' - t_2)\, x\, e^{i[(\omega_2 t'' - \omega_1 t') - \Theta]}],
\end{aligned} \tag{8}$$

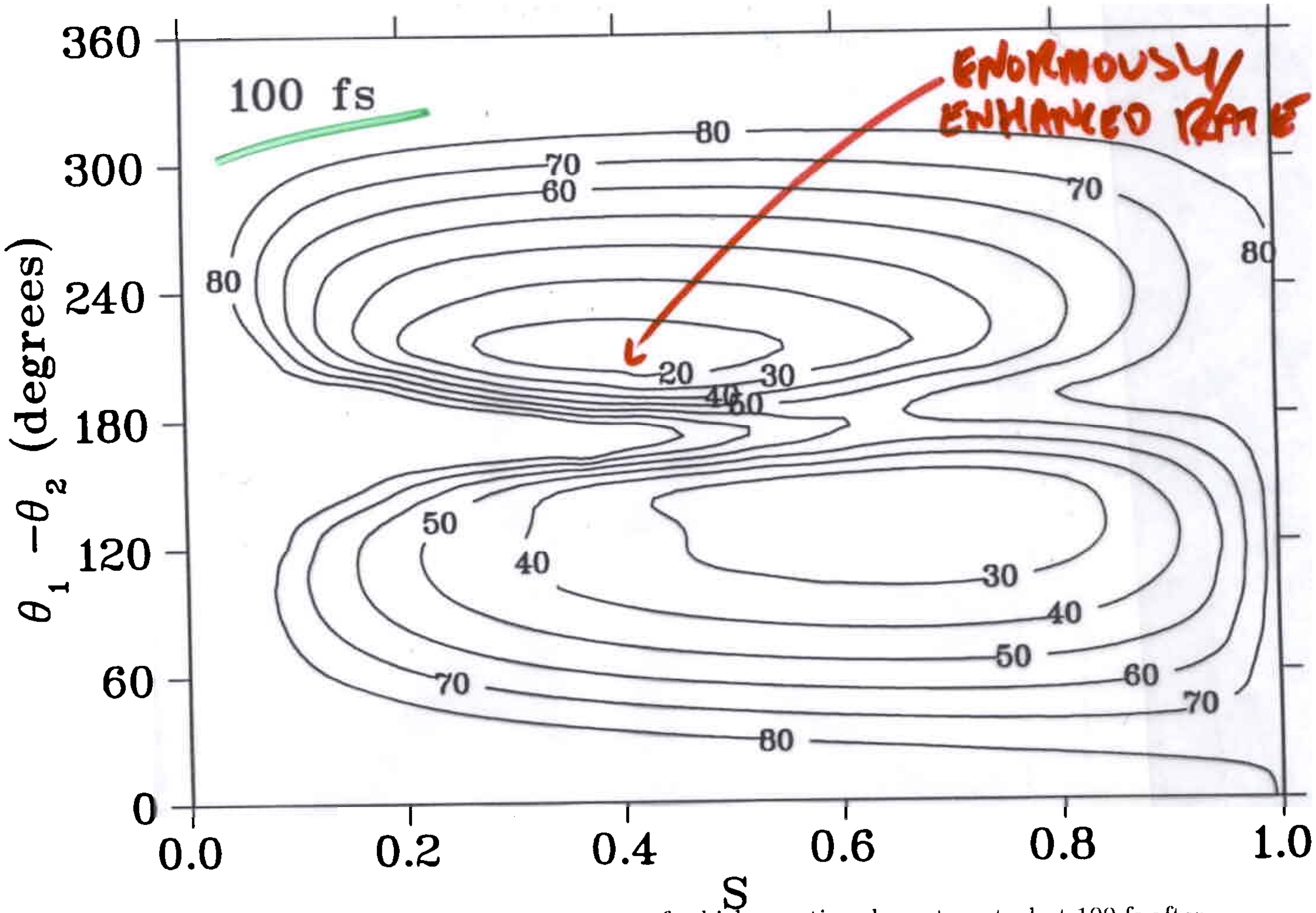
As an example, we consider the case where the initial superposition state [Eq. (1)] involves state $|1\rangle$ as the ground vibrational state of the internal oxazole-hydroxyphenyl in-the-plane bending mode —i.e., bending motion of the $C_1C_2C_7$ angle (Fig. 1), and state $|2\rangle$ as the first excited state associated with this vibrational mode. In addition, $c_j = c_k = 1/\sqrt{2}$, and the temporal profiles of the laser pulses are Gaussian; $F_1(t - t_1) = F_2(t - t_2) = (\beta/\pi)^{1/4} \exp(-\beta\, t^2/2)$, where $\beta = 2\ln(2)/25\ \text{fs}^{-1}$ and $t_1 = t_2 = 0$. Hence, the FWHM of the pulse is chosen to be 25 fs and ω_1 and ω_2 are taken as 324.7 nm and 327.8 nm, respectively.

Substituting these conditions into the SC-IVR approximation of $P(t)$ gives a "direct" SC-IVR approach for computations of bichromatic coherent-control at *finite* times after photoexcitation of the system (i.e., an approach that computes $P(t)$, as a function of the

USE HOST of M.C. Tricks.

89, 143201 (2002)

BATISTA + BRUMER, PRL, (~~submitted~~)



ENORMOUSLY ENHANCED RATE

FIG. 2. Contour plot of the percentage reactant for bichromatic coherent-control at 100 fs after photoexcitation of the system.

(Huge Computation)

NOTE:

NATURAL RATES

CONTROL RANGE

Pulse Parameters: (Gaussian)

$\tau = 25$ fs ; $\lambda_1 = 324.7$ nm , $\lambda_2 = 327.8$ nm

Powers: perturbation theory

CONTROL [illegible] PERSISTS -

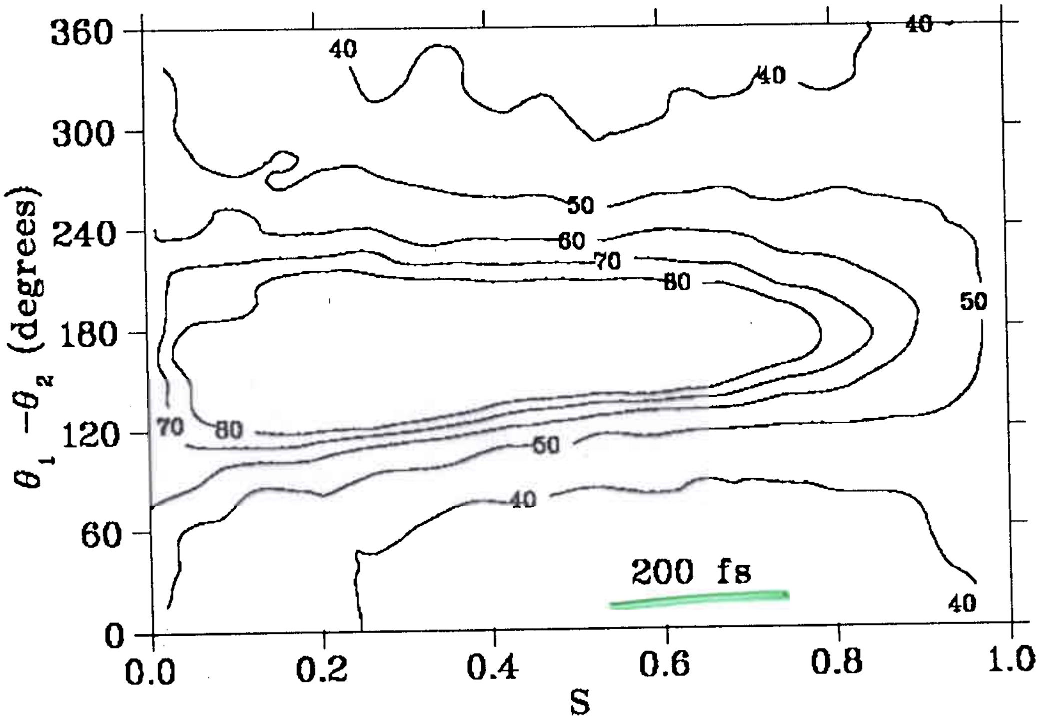


FIG. 3. Contour plot of the percentage reactant for bichromatic coherent-control at 200 fs after photoexcitation of the system.

BUT IS THERE DECOHERENCE??

MEASURE OF STATE PURITY -

$\mathrm{Tr}(\rho_s^2)$

IF PURE $\mathrm{Tr}(\rho_s^2) = \mathrm{Tr}(\rho_s) = 1$

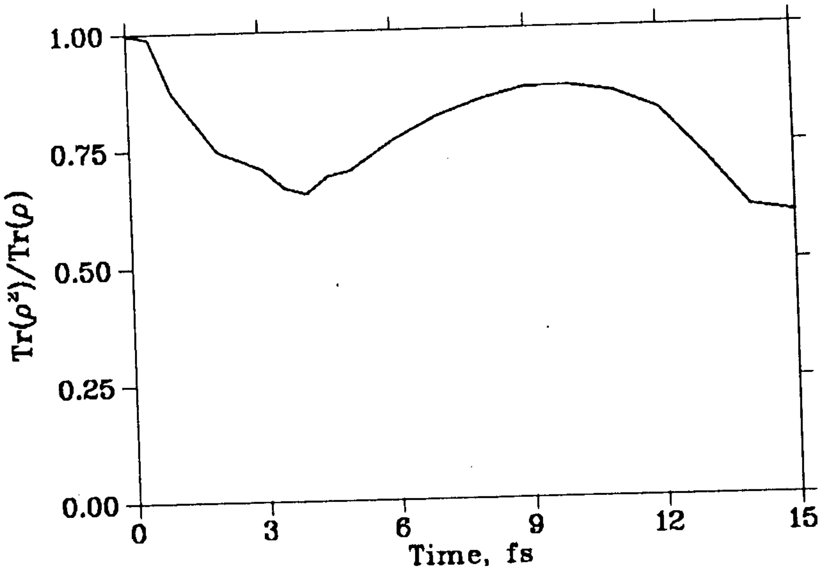
If DECOHERING

$$\mathrm{Tr}(\rho_s^2) < 1$$

NOTE

USUALLY MODEL CALC

HERE FULL DYNAMICAL (SEMICLASS)
COMPUTATION



(.38)

200 fs

FIG. 4. Trace of ρ^2 as a function of time during the first 15 fs of dynamics after photoexcitation of the system.

HENCE SIGNIFICANT RAPID DECOHERENCE (INTRINSIC) + CONTROL O.K.

⇒ BODES VERY WELL FOR CONTROLLED DYNAMICS IN LARGE MOLECULES.

BUT LOOK AT THIS!

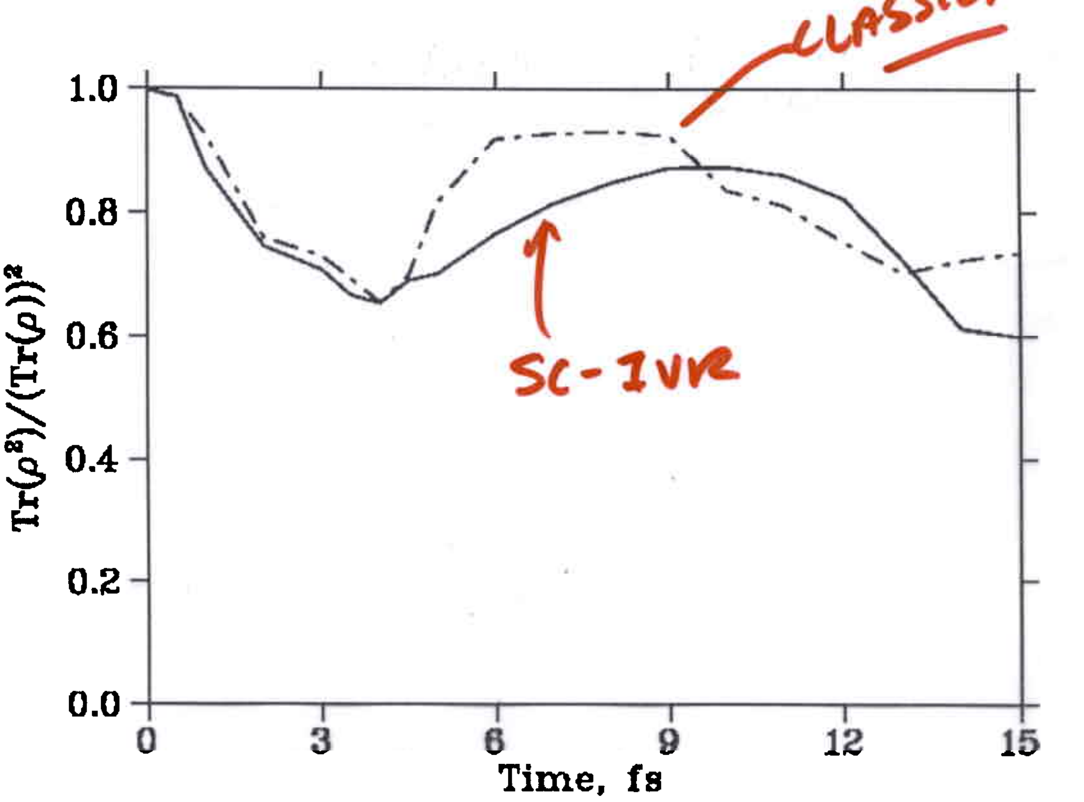


FIG. 5: Trace of ρ^2 as a function of time during the first 15 fs of dynamics after photoexcitation of the system. Solid line: HK SC-IVR; Broken line: Classical Wigner model.

IS THERE CLASSICAL ANALOG TO DECOHERENCE? CAN WE USE IT? WHEN VALID (i.e. Q/C CORRESPONDENCE OF DECOHERENCE DYNAMICS!)

But Decoherence (phase loss) is quantum??

QUANTUM & QUASICLASSICAL DECOHERENCE

QUANTUM MECHANICS:

Density $\hat{\rho}(t)$; Phase-Space Rep'n : $\rho^{w}(p,q;t)$

Dynamics: $\frac{\partial \rho^{w}}{\partial t} = \{H, \rho^{w}\}_{M}$

$$\{H, \rho^{w}\}_{M} = \frac{2}{\hbar} \sin\left[\frac{\hbar}{2}\left(\frac{\partial^{(H)}}{\partial q}\frac{\partial^{(\rho)}}{\partial p} - \frac{\partial^{(H)}}{\partial p}\frac{\partial^{(\rho)}}{\partial q}\right)\right]$$

$$\times \; H_{w}\, \rho^{w}$$

One of several complete phase space repn's of quantum dynamics.

Classical Mechanics:

Density $\rho^{c}(p,q;t)$

Dynamics : $\frac{\partial \rho^{c}}{\partial t} = \{H, \rho^{c}\}$ ← Poisson Bracket

Note Beautiful classical / quantum analog

E.G. Can define eigenfunctions, eigenvalues, etc.
of Time Evolution Op [Liouville op] etc.
Hilbert Space, etc. — e.g. Koopmans
Prigogine

(Our) Prior applications:

QUANTUM CLASSICAL Correspondence:

Jaffe + Brumer, J. Chem. Phys. 82, 2330, '85

Complete Q/C Regular + Chaotic

Wilkie + Brumer, Phys. Rev. A 55, 27, '97

Wilkie + Brumer, Phys. Rev. A 55, 43, '97

CLASSICAL Analog of Superposition State:

Jaffe, Kanfer + Brumer, PRL 54, 8 (1985)

Is there classical Analogue to decoherence?

I.e. (1) Start with QUANTAL initial state

(2) Subject to Classical Mechanics

(3) Measure classical decoherence via classical measures.

(4) Learn from + compare to quantum evolution

QQ3

Goals:

(1) A correspondence theory of decoherence [not the role of decoh. in correspondence!]

(2) New insights into dependence on coupling and $\hbar$

(3) "Simpler" derivations of useful results

(4) Conditions when quantum entropy production ≠ classical entropy production

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NOTA BENE: Focus is on time evolution of measures of decoherence
"decoherence dynamics"

Result:
- Can formulate classical decoherence
- Amazingly transparent classical-quantum difference
- Dependence on system-environment coupling is strong

Macroscopic system with no classical decoherence

Consider, for simplicity, one-D system coupled to harmonic bath:

(1) $$H = H^s(P,Q) + \sum_j p_j^2/2m_j + m_j\omega_j^2 q_j^2/2 + V^{sb}$$

Coupling: $$V^{sb} = \sum_{j=1}^{N} c_j f(Q)\, q_j$$

↑ gen'l possible

system coord.

N.B.: $f(Q)$ can be linear or nonlinear

common

(2) Define reduced system density, both class. + quant.

$$\tilde{\rho}_c(Q,P,t) = \int \rho^c(Q,P,\{q_j,p_j\},t)\, \Pi_j\, dq_j\, dp_j$$

$$\tilde{\rho}_W(Q,P,t) = \int \rho^W(Q,P,\{q_j,p_j\},t)\, \Pi_j\, dq_j\, dp_j$$

(3) Measures of decoherence (sample)

(a) linear entropy: $S = 1 - \mathrm{Tr}(\tilde{\rho}^2)$

Quantal: $$S_q = 1 - 2\pi\hbar \int \tilde{\rho}_W^2(Q,P,t)\, dQ\, dP$$

Classical: $$S_c = 1 - 2\pi\hbar \int \tilde{\rho}_c^2(Q,P,t)\, dQ\, dP$$

(b) Off-diagonal Matrix Element

$\langle Q_1 | \tilde{\rho}(t) | Q_2 \rangle$

DEF'N: QUANTUM: $\int dP \, \tilde{\rho}_W(\bar{Q}, P, t) \, e^{i \Delta Q P / \hbar}$

CLASSICAL ! : $\int dP \, \tilde{\rho}_c(\bar{Q}, P, t) \, e^{i \Delta Q P / \hbar}$

$\Delta Q = Q_1 - Q_2 \quad ; \quad \bar{Q} = (Q_1 + Q_2)/2$

Possible Treatments

(A) Exact Dynamics (ongoing)

(B) Perturbative for short time ⟨ Importance for decoherence control

(C) Strong decoherence, for all time

↑ quantum computing

Perturbation theory

$$S_c(t) = S_c(0) + t/\tau_{c,1} + t^2/\tau_{c,2}^2 + \dots$$

$$S_q(t) = S_q(0) + t/\tau_{q,1} + t^2/\tau_{q,2}^2 + \dots$$

⑥

⑥ $= 2\int d\theta dp \rho_s^0 \left[\left(\frac{\partial H_s}{\partial \theta}\right)^2 \frac{\partial^2 \rho_s^0}{\partial p^2} - \frac{\partial H_s}{\partial \theta} \frac{\partial}{\partial p}\left(\frac{\partial H_s}{\partial p} \frac{\partial \rho_s^0}{\partial \theta}\right) \right]$

$= 2\int d\theta dp \rho_s^0 \frac{\partial^2 \rho_s^0}{\partial p^2}\left(\frac{\partial H_s}{\partial \theta}\right)^2 + 2\int d\theta dp \frac{\partial H_s}{\partial p} \frac{\partial \rho_s^0}{\partial \theta} \frac{\partial \rho_s^0}{\partial p} \frac{\partial H_s}{\partial \theta}$

$= -2\int d\theta dp \left(\frac{\partial \rho_s}{\partial p}\right)^2 \left(\frac{\partial H_s}{\partial \theta}\right)^2 + 2\int d\theta dp \frac{\partial H_s}{\partial p} \frac{\partial H_s}{\partial \theta} \frac{\partial \rho_s^0}{\partial \theta} \frac{\partial \rho_s^0}{\partial p}$

$= -$ ① $-$ ③$/2$ Thus: ① + $\frac{③}{2}$ + ⑥ = 0

~~Thanks~~ Much above a bit...

Dr. Jianglin Gong!

⑦ $= 2\int d\theta dp \rho_s^0 \frac{\partial H_s}{\partial \theta} \frac{\partial^2 \rho_s^2}{\partial p^2} \frac{\partial f(\theta)}{\partial \theta} \sum_j C_j \langle g(q_j) \rangle_b$

⑨ $= -2\int d\theta dp \rho_s^0 \frac{\partial H_s}{\partial p} \frac{\partial}{\partial \theta}\left(\sum_j C_j \langle g(q_j) \rangle_b \frac{\partial f(\theta)}{\partial \theta} \frac{\partial \rho_s^0}{\partial p} \right)$

$= 2\int d\theta dp \sum_j C_j \langle g(q_j) \rangle_b \frac{\partial f(\theta)}{\partial \theta} \frac{\partial \rho_s^0}{\partial p} \frac{\partial H_s}{\partial p} \frac{\partial \rho_s^0}{\partial \theta}$

⑩ $= 2\int d\theta dp \rho_s^0 \sum_j C_j \langle g(q_j) \rangle_b \frac{\partial}{\partial p}\left(\frac{\partial H_s}{\partial \theta} \frac{\partial \rho_s^0}{\partial p} - \frac{\partial H_s}{\partial p} \frac{\partial \rho_s^0}{\partial \theta} \right) \frac{\partial f(\theta)}{\partial \theta}$

$= -2\int d\theta dp \sum_j \langle g(q_j) \rangle_b \frac{\partial \rho_s^0}{\partial p} \left(\frac{\partial H_s}{\partial \theta} \frac{\partial \rho_s^0}{\partial p} - \frac{\partial H_s}{\partial p} \frac{\partial \rho_s^0}{\partial \theta} \right) \frac{\partial f(\theta)}{\partial \theta}$

⑤ $= 4\int d\theta dp \sum_j C_j \frac{\partial f(\theta)}{\partial \theta} \frac{\partial \rho_s^0}{\partial \theta} \frac{\partial \rho_s^0}{\partial p} \langle g(q_j) \rangle_b \left(\frac{\partial H_s}{\partial \theta} \frac{\partial \rho_s^0}{\partial p} - \frac{\partial H_s}{\partial p} \frac{\partial \rho_s^0}{\partial \theta} \right)$

Thus ⑦ + ⑨ + ⑩ + ⑤ = 0

⑧ $= -2\int d\theta dp \rho_s^0 \frac{\partial H_s}{\partial p} \frac{\partial}{\partial \theta}\left(\frac{\partial H_s}{\partial \theta} \frac{\partial \rho_s^0}{\partial p} - \frac{\partial H_s}{\partial p} \frac{\partial \rho_s^0}{\partial \theta} \right)$

$= 2\int d\theta dp \frac{\partial H_s}{\partial p} \left(\frac{\partial H_s}{\partial \theta} \frac{\partial \rho_s^0}{\partial p} - \frac{\partial H_s}{\partial p} \frac{\partial \rho_s^0}{\partial \theta} \right) \frac{\partial \rho_s^0}{\partial \theta}$

$= -2\int d\theta dp \left(\frac{\partial H_s}{\partial p}\right)^2 \frac{\partial \rho_s^0}{\partial \theta} \frac{\partial \rho_s^0}{\partial \theta} + 2\int d\theta dp \frac{\partial H_s}{\partial p} \frac{\partial H_s}{\partial \theta} \frac{\partial \rho_s^0}{\partial p} \frac{\partial \rho_s^0}{\partial \theta}$

$= -$② $- \frac{③}{2}$ Thus: ⑧ + ② + $\frac{③}{2}$ = 0

Finally we have: ① + ② + ③ + ⑤ + ⑦ + ⑧ + ⑥ + ⑨ + ⑩ = 0

$\Rightarrow \frac{1}{\tau_{c,12}^2} \propto$ ④ + ⑪

$$1/\tau_{q,1} = 1/\tau_{c,1} = 0$$

$$1/\tau_{q,2}^2 = \frac{c_b}{\hbar}\int dQ_1 dQ_2 \,|\langle Q_1|\tilde{\rho}(0)|Q_2\rangle|^2 \Delta Q^2 \left[\frac{\Delta f(\bar{Q})}{\Delta Q}\right]^2$$

$$1/\tau_{c,2}^2 = \frac{c_b}{\hbar}\int dQ_1 dQ_2 \,|\tilde{\rho}_c(Q_1,Q_2,0)|^2 \Delta Q^2 \left[\frac{df(\bar{Q})}{d\bar{Q}}\right]^2$$

where $\Delta f(\bar{Q}) = f(\bar{Q}+\Delta Q/2) - f(\bar{Q}-\Delta Q/2)$

$= f(Q_1) - f(Q_2)$

Recall : $|\langle Q_1|\tilde{\rho}(0)|Q_2\rangle|^2 = \tilde{\rho}_c(Q_1,Q_2,0)$ [time zero]

Hence:

the sole difference between quantum + classical (perturbative - short time) is

$$\frac{\Delta f(\bar{Q})}{\Delta Q} \text{ vs. } \frac{df(\bar{Q})}{d\bar{Q}} \quad \text{over } \tilde{\rho}_c(Q_1,Q_2,0) \text{ region}$$

Reminder

Reminder $f(Q)$ is system dep'nce of coupling

i.e. $$\frac{f(\bar{Q}+\frac{\Delta Q}{2}) - f(\bar{Q}-\frac{\Delta Q}{2})}{\Delta Q} \text{ vs. } \frac{df(\bar{Q})}{d\bar{Q}}$$

$\Rightarrow$ Note result applies to any coupling $f(Q)$

Qualitative Consequences:

E.g. Zurek / Caldeira-Leggett

(1) If $f(Q) = aQ + bQ^2$ then $1/\tau_{c,2}^2 = 1/\tau_{q,2}^2$

i.e. classical is exact for linear + quadratic system-bath coupling! "of course" but ...

(2) For any $f(Q)$; whenever $\langle Q_1|\bar{\rho}(0)|Q_2\rangle$ decays fast enough with ΔQ so that $\Delta f/\Delta Q \simeq df/dQ$ then class $\equiv$ quant.

(3) For any ~~not~~ nonlinear/nonquadratic $f(Q)$: $\Delta f/\Delta Q \neq df/dQ$ then class $\not\equiv$ quant.

Correspondence depends crucially on s-b coupling!

E.g. Initial distribution:

$Q_a = \bar{Q}_{ab} - \Delta Q_{ab}/2$ $\qquad$ $Q_b = \bar{Q}_{ab} + \Delta Q_{ab}/2$

← Coherent superposition of 2 localized sharp gaussian

$$\rho \sim \delta(\Delta Q - \Delta Q_{ab})\,\delta(\bar{Q} - \bar{Q}_{ab})$$

$\Longrightarrow$

$$1/\tau_{q,2}^2 \propto \frac{C_b}{\hbar}\,\Delta Q_{ab}^2 \left[\frac{\Delta f(\bar{Q}_{ab})}{\Delta Q_{ab}}\right]^2 \propto \left[\frac{\Delta f(\bar{Q}_{ab})}{\Delta Q_{ab}}\right]^2$$

$$1/\tau_{c,2}^2 \propto \frac{C_b}{\hbar}\,\Delta Q_{ab}^2 \left[\frac{df(\bar{Q}_{ab})}{d\bar{Q}_{ab}}\right]^2 \propto \left[\frac{df(\bar{Q}_{ab})}{d\bar{Q}_{ab}}\right]^2$$

then, e.g.

(1) $f(Q) = Q^3$

$$1/\tau_{q,2}^2 \propto \left[f(\bar{Q}_{ab} + \Delta Q_{ab}/2) - f(\bar{Q}_{ab} - \tfrac{\Delta Q_{ab}}{2})/\Delta Q_{ab}\right]^2 \neq 0$$

$$1/\tau_{c,2}^2 \propto (3\bar{Q}_{ab}^2)^2 = 0 \quad \text{for } \bar{Q}_{ab} = 0$$

$\Rightarrow$ Quantum decoherence with no classical entropy production!

(2) $f(Q) = \sin(2\pi Q/\Delta Q_{ab} + \pi/4)$

$1/\tau_{q,2}^2 \sim 0$ since $f(Q_a) = f(Q_b)$

$1/\tau_{c,2}^2 \neq 0$

$\Rightarrow$ classical entropy production but no (quantum) decoherence!

Behavior with increasing ΔQ_{ab}: "Saturation"?

Easily seen quantum mechanically:

$$1/\tau_{q,2}^2 \propto \Delta Q^2 \left[\frac{\Delta f(\bar{Q})}{\Delta Q}\right]^2 = f(Q_1) - f(Q_2)$$

If $f(Q)$ bounded $\Rightarrow$ $1/\tau_{q,2} \rightarrow$ constant
as $|Q_1 - Q_2| \rightarrow$ large
i.e. saturates

Not true classically.

$\Rightarrow$ classical dynamics decoheres widely separated states more effectively than does quantum mechanics ("amusement")

What about longer times?

Look at strong decoherence case; $\underline{\underline{H_s \sim 0}}$

Can obtain both

$$\rho_c(Q_1, Q_2, t) \quad \text{vs.} \quad \langle Q_1 | \rho(t) | Q_2 \rangle$$

$$S_q(t) \quad \text{vs.} \quad S_c(t)$$

Can Carry out "Arithmetic" - find

QUANTUM:

$$\langle Q_1|\tilde{\rho}(t)|Q_2\rangle = \langle Q_1|\tilde{\rho}(0)|Q_2\rangle e^{i\phi_q(t)} \exp\left[-\Delta Q^2 \left[\frac{\Delta f(Q)}{\Delta Q^2}\right]^2 B_2(t)\right]$$

$$\updownarrow$$

Note even phase info!

CLASSICAL:

$$\tilde{\rho}_c(Q_1,Q_2,t) = \tilde{\rho}_c(Q_1,Q_2,0)\, e^{i\phi_c(t)} \exp\left[-\Delta Q^2 \left[\frac{df(\bar{Q})}{d\bar{Q}}\right]^2 B_2(t)\right]$$

$$\phi_c(t) = \Delta Q\, f(\bar{Q}) \frac{df(\bar{Q})}{d\bar{Q}} B_1(t)/\hbar$$

$$\updownarrow$$

$$\phi_q(t) = \Delta Q\, f(\bar{Q}) \left[\frac{\Delta f(\bar{Q})}{\Delta Q}\right] B_1(t)/\hbar$$

Again just $\frac{df(\bar{Q})}{d\bar{Q}}$ vs. $\frac{\Delta f(\bar{Q})}{\Delta Q}$

AND AGAIN

For Entropy -

QQ12

Linear Entropy

~~QUANTUM~~: CLASSICAL

$$S_q(t) = 1 - \int dQ_1 dQ_2 \, |\bar{\rho}_c(Q_1, Q_2, 0)|^2 \times$$

$$\exp\left\{ -2(\Delta Q)^2 \left[\frac{df(\bar{Q})}{d\bar{Q}}\right]^2 B_2(t) \right\}$$

~~CLASSICAL~~: QUANTUM:

$$S_c(t) = 1 - \int dQ_1 dQ_2 \, |\langle Q_1 | \bar{\rho}(0) | Q_2 \rangle|^2 \times$$

$$\exp\left\{ -2(\Delta Q)^2 \left[\frac{\Delta f(\bar{Q})}{\Delta Q}\right] B_2(t) \right\}$$

Hence, if you set up an initial superposition state, the subsequent decoherence dynamics is:

SHORT TIME

(1) CLASSICAL if coupling $\propto aQ + bQ^2$

(2) CLASSICAL for ANY coupling if $\Delta f / \Delta Q \sim df/dQ$ over $|\langle Q_1 | \tilde{\rho}(0) | Q_2 \rangle|^2$

(3) NONCLASSICAL if NOT (1) or (2)

ALL TIME: STRONG DECOH

AS ABOVE

CAN WE USE to compute/etc. ?

SAMPLE INTRINSIC DECOH CASE:

$$H = \frac{p_1^2}{2} + \frac{p_2^2}{2} + \frac{0.01}{4}(\theta_1^4 + \theta_2^4) + 0.2\sin(10.0\,\theta_1)\,\theta_2^2$$

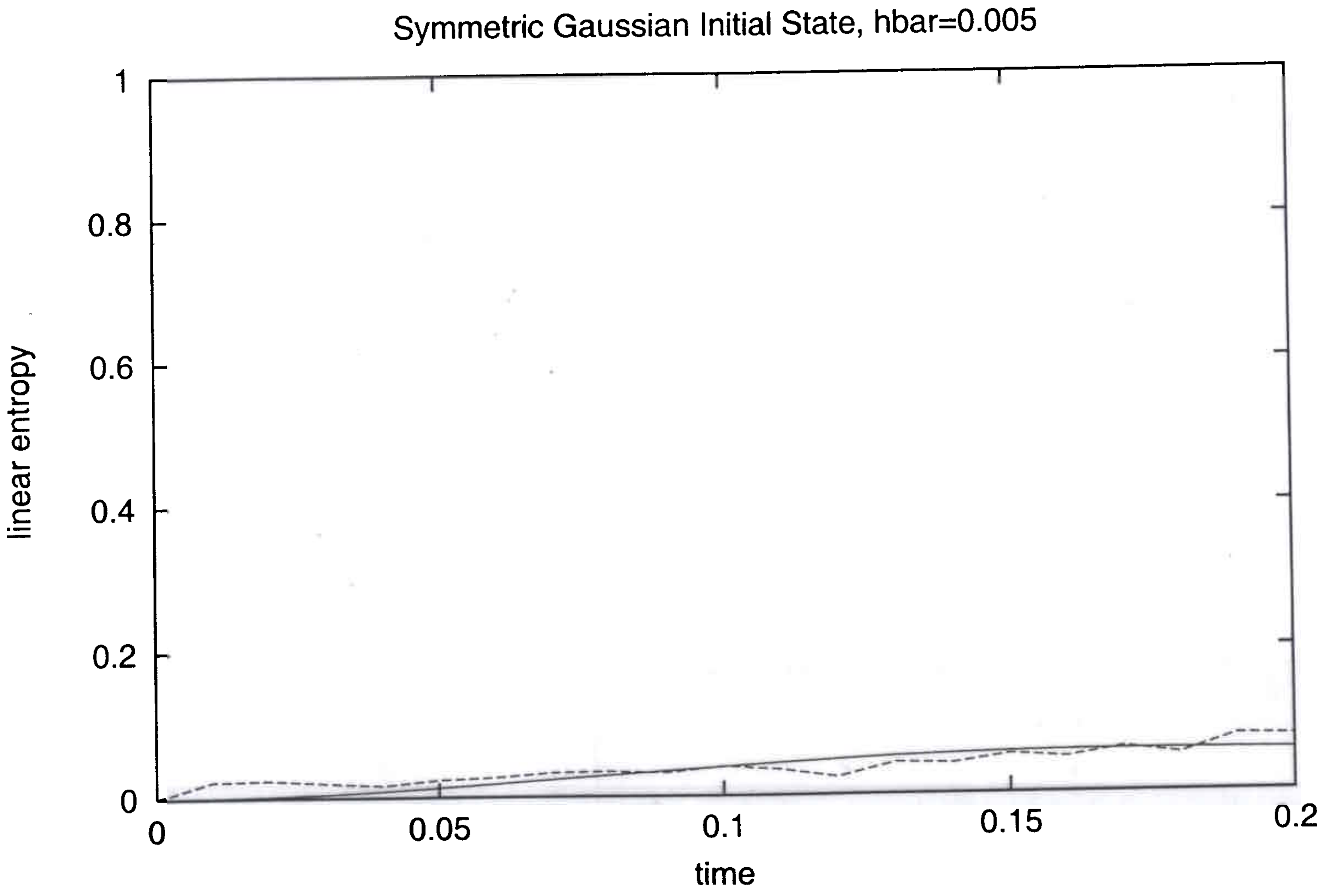
$$S = 1 - \mathrm{Tr}\,\hat{\rho}_1^2$$

$$\hbar = 0.005$$

$$\theta_1^0 = 0, \quad \theta_2^0 = 0.6$$

$$\sqrt{\Delta^2\theta_1^0} = \sqrt{\frac{\hbar}{2}} = \sqrt{\Delta^2 p_1^0}$$

NEAR "CLASSICAL LIMIT IN $\hbar$" -SMALL STATE


Symmetric Gaussian Initial State, hbar=0.005

$$H = \frac{p_1^2}{2} + \frac{p_2^2}{2} + \frac{0.01}{4}(\theta_1^4 + \theta_2^4) + 0.2\,\mathrm{Sin}(10.0\,\theta_1)\,\theta_2^2$$

$$S = 1 - T_r \hat{\rho}_1^2$$

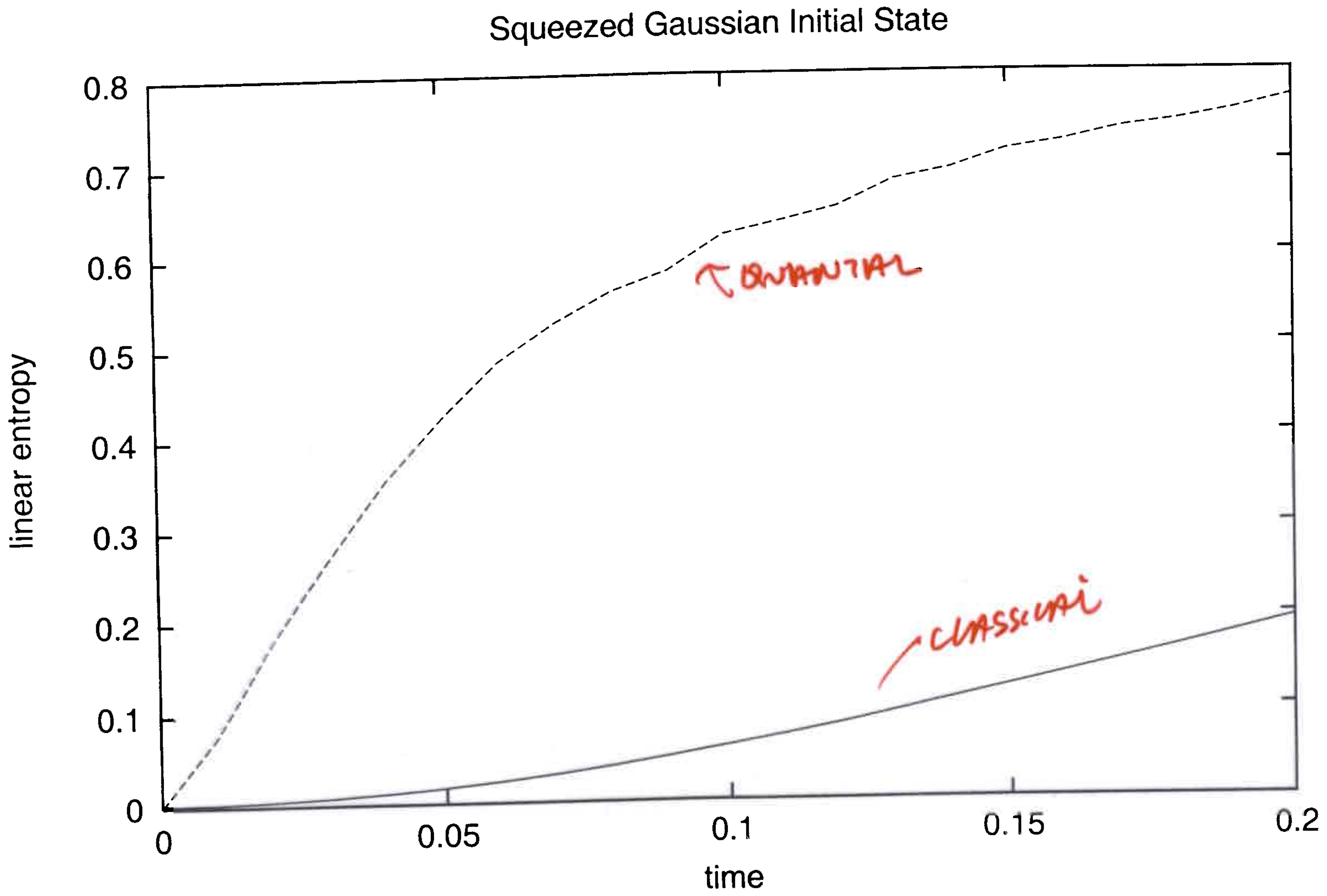
$$\hbar = 0005$$

$$\theta_1^0 = 0 \qquad \theta_2^0 = 0.6$$

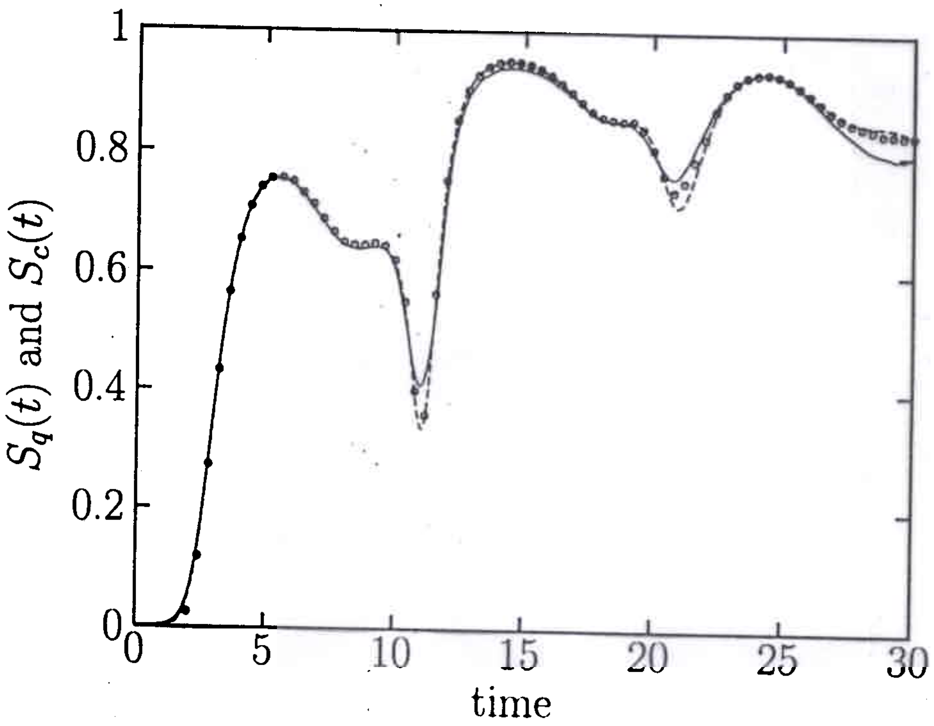
$$\sqrt{\Delta^2\theta_1^0} = \sqrt{\frac{\hbar}{2}} * 25$$

$$\Delta Q_1^0 \sim 1.0$$

"NEAR CLASSICAL LIMIT in ħ" - LARGE STATE



⇒ decoherence does not suffice to ensure classical limit in decoh measures!


1
0.8
0.6
0.4
0.2
0
$S_q(t)$ and $S_c(t)$
0
5
10
15
20
25
30
time

Consequences

- Rethink generality of results from linear coupling [e.g. Zurek model,

  Chaos role:

  Pattanayak + Brumer, PRL 79, 4131 (1997)

  Pattanayak, PRL 83, 4526 (1999)

- Motivate More on Nonlinear Coupling
- Utility of classical to calculate Decoherence rates?
- Understand ∃ classical analog To decoherence + hence expose what is quantum about decoherence dynamics
- On To entanglement loss

  ENTANGLEMENT ⟺ DECOHERENCE

SUMMARY

1. QUANTUM INTERFERENCE - COHERENT CONTROL. OFFERS POWERFUL TOOL TO CONTROL (All SORTS of) MOLECULAR PROCESSES.

2. Application TO REAL SYSTEMS REQUIRES SEMICLASSICAL TOOLS.

3. STATUS: they WORK - BUT **VERY** COMPUTATIONALLY INTENSIVE
   SOME DIFF. TOOLS USEFUL?

4. DECOHERENCE OFTEN STILL ALLOWS CONTROL

5. DECOHERENCE DYNAMICS DESCRIBABLE CLASSICALLY? YES UNDER CONDITIONS $\hbar$ "less relevant"

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$ ONR , PRO $

B. McQuarrie (U of T) - Classical Wigner