A geometric formulation of Ehrenfest molecular dynamics

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Content

- ▶ Introduction: the geometric formalism of Quantum Mechanics
- Geometric Quantum-Classical Molecular Dynamics
- Application I: Ehrenfest Statistical Dynamics and electronic decoherence
- Application II: Definition of hybrid ensembles
- Application III: Control of hybrid systems
- Conclusions and Outlook

Results from many colaborations with J. L. Alonso, P. Bruscolini, J. F. Cariñena, A. Castro, J. C. Cuchí, P. Echenique, J. A. Jover-Galtier and G. Marmo

and

the Bachelor Theses of Carlos Bouthelier (2017) and Cristian-Emanuel Boghiu (2018).

Introduction: GQM

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General formulation of a physical system

 \blacktriangleright A set of states ${\cal S}$ representing the relevant degrees of freedom

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Is it possible to find a common framework for Classical and Quantum Mechanics?

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Dynamics correponds to the integral curve of the Hamiltonian vector field associated to the function h which represents the energy of the system:

 $X_h = \{h, \cdot\}$

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Dynamics can be introduced via Schrödinger equation, associated to the Hamiltonian operator

$$i\hbarrac{\partial}{\partial t}|\psi(t)
angle=H|\psi(t)
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Model is built on the set of physical magnitudes O, which are the real part of a complex C*-algebra.

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- The set of states corresponds to the dual vector space to O, i.e. linear functionals ρ : O → C.

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Measurement corresponds to the action of the operator on the state

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Measurement corresponds to the action of the operator on the state

$$\mathcal{S} \times \mathcal{O} \ni (\rho, K) \mapsto \rho(K) \in \mathbb{R}$$

Dynamics is introduced by Heisenberg equation:

$$i\hbar \frac{\partial}{\partial t} K(t) = HK(t) - K(t)H$$



Summary of GQM



Introduction: GQM

Theoretical and Mathematical Physics, 152(1): 894-903 (2007)

GEOMETRIZATION OF QUANTUM MECHANICS

J. F. Cariñena,* J. Clemente-Gallardo, † and G. Marmo ‡

We show that various descriptions of quantum mechanics can be represented in geometric terms. In particular, starting with the space of observables and using the momentum map associated with the unitary group, we give a unified geometric description of the different pictures of quantum mechanics. This construction is an alternative to the usual GNS construction for pure states.

International Journal of Geometric Methods in Modern Physics Vol. 5, No. 6 (2008) 989–1032 © World Scientific Publishing Company



BASICS OF QUANTUM MECHANICS, GEOMETRIZATION AND SOME APPLICATIONS TO QUANTUM INFORMATION

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Introduction: GQM

Tensorial description of quantum mechanics

J Clemente-Gallardo1 and G Marmo2

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Abstract

Relevant algebraic structures for the description of quantum mechanics in the Heisenberg picture are replaced by tensor fields on the space of states. This replacement introduces a differential geometric point of view which allows for a covariant formulation of quantum mechanics under the full diffeomorphism group.

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Introduction: GQM



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Tensorial dynamics on the space of quantum states

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We choose to consider Hilbert space \mathcal{H} as a real differentiable manifold M_Q . For the sake of simplicity, we will consider that the quantum system is finite-dimensional.

The set

 $|\psi\rangle = \sum z_j |e_j\rangle \Longrightarrow \mathbb{C}^n
i (z^1, \dots, z^n)
ightarrow (\operatorname{Re}(z^1), \operatorname{Im}(z^1), \dots, \operatorname{Re}(z^n), \operatorname{Im}(z^n))$

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The scalar product can be described by a tensor on H:

$$\langle \psi_1 | \psi_2
angle = h(X_{\psi_1}, X_{\psi_2}) \qquad X_{\psi_1} = (\psi, \psi_1); X_{\psi_2} = (\psi, \psi_2)$$

By using the realification introduced

$$X_{\psi_{k}} = (X_{\psi_{k}}^{R}, X_{\psi_{k}}^{I}) \Rightarrow$$

$$h(X_{\psi_{1}}, X_{\psi_{2}}) = (((X_{\psi_{1}}^{R} X_{\psi_{2}}^{R}) + (X_{\psi_{1}}^{I} X_{\psi_{2}}^{I})), (X_{\psi_{1}}^{R} X_{\psi_{2}}^{I}) - (X_{\psi_{1}}^{I} X_{\psi_{2}}^{R}))$$

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By using the realification introduced we obtain two tensors which encode the same information

$$\begin{aligned} X_{\psi_k} &= (X_{\psi_k}^R, X_{\psi_k}^I) \Rightarrow \\ h(X_{\psi_1}, X_{\psi_2}) &= \left(g\left((X_{\psi_1}^R, X_{\psi_1}^I), (X_{\psi_2}^R, X_{\psi_2}^I)\right), \omega\left((X_{\psi_1}^R, X_{\psi_1}^I), (X_{\psi_2}^R, X_{\psi_2}^I)\right)\right) \end{aligned}$$

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$$h\mapsto egin{cases} \mathbf{g}=\sum_k (dq^k\otimes dq^k+dp_k\otimes dp_k)\ \mathbf{\omega}=\sum_k dq^k\wedge dp_k \end{cases}$$

▶ The complex structure of *H* becomes a 1:1 tensor field:

 $J: TM_Q \times T^*M_Q \to C^{\infty}(M_Q); \qquad J(X_{\psi}^R, X_{\psi}^I) = (-X_{\psi}^I, X_{\psi}^R)$



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 $\mathbf{J} = \begin{pmatrix} 0 & -1 & 0 & 0 & \dots & 0 & 0 \\ 1 & 0 & 0 & 0 & \dots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \dots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & \dots & 0 & -1 \\ 0 & 0 & 0 & 0 & \dots & 1 & 0 \end{pmatrix}$

Theorem

Let (\mathcal{H}, h) be a *n*-dimensional Hilbert space. Then (g, ω, J) endow M_Q with a Kähler structure of (real) dimension 2*n*.



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Hermitian structure can also be encoded in the tensor fields:

$$h \mapsto \begin{cases} G = \sum_{k} \left(\frac{\partial}{\partial q^{k}} \otimes \frac{\partial}{\partial q^{k}} + \frac{\partial}{\partial p_{k}} \otimes \frac{\partial}{\partial p_{k}} \right) \\ \Omega = \sum_{k} \frac{\partial}{\partial q^{k}} \wedge \frac{\partial}{\partial p_{k}} \end{cases}$$
Physical States II: the projective space

Introduction: GQM



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Questions:

▶ How can we define the projective space corresponding to *H*?



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- Can we characterize the tensor fields introduced above?



Physical States II: the projective space

Questions:

▶ How can we define the projective space corresponding to *H*?

Can we characterize the tensor fields introduced above?



True physical states correspond to the equivalence class:

$$\begin{split} |\psi_1\rangle, |\psi_2\rangle &\in \mathcal{H}_0 = \mathcal{H} - \{\vec{0}\} \\ |\psi_1\rangle \sim |\psi_2\rangle \Leftrightarrow |\psi_2\rangle = \lambda |\psi_1\rangle; \quad \lambda \in \mathbb{C} \\ \text{The set of these equivalence classes} \\ \text{define the projective space } \mathcal{PH}, \text{ which} \\ \text{is diffeomorphic to the space of} \\ \text{projectors on one-dimensional} \\ \text{subspaces of the Hilbert space } \mathcal{H}: \end{split}$$

 $[\psi] \simeq \frac{|\psi\rangle\langle\psi|}{|\psi|}$







Consider two vector fields on M_Q :

$$\underline{\Delta = \sum_{k} \left(q^{k} \frac{\partial}{\partial q^{k}} + p_{k} \frac{\partial}{\partial p_{k}} \right)}_{\text{dilations}} \qquad \left[\Gamma = J(\Delta) = \sum_{k} \left(q^{k} \frac{\partial}{\partial p_{k}} - q^{k} \frac{\partial}{\partial p_{k}} \right) \right]$$

00000000

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 Δ y Γ define an integrable distribution on M_Q , and hence a foliation \mathcal{P} . This foliation is the geometric analogue of \mathcal{PH} .



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We thus have a projection

$$\pi: M_Q \to \mathcal{P}.$$

But tensors G and Ω can not be projected directly

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But tensors G and Ω can not be projected directly

$$\mathcal{L}_{\Delta}G = -2G$$
 $\mathcal{L}_{\Delta}\Omega = -2\Omega.$

Solution:

 $G_{\mathcal{P}} = \langle \psi | \psi
angle G - \Delta \otimes \Delta - \Gamma \otimes \Gamma$ $\Omega_{\mathcal{P}} = \langle \psi | \psi
angle \Omega - (\Delta \otimes \Gamma - \Gamma \otimes \Delta)$

Physical magnitudes I: functions

Let us consider the sesquilinear forms defined on M_Q :

$$f_{\mathcal{A}}(\psi(ec{q},ec{p})) = rac{1}{2} \langle \psi(ec{q},ec{p}) | \mathcal{A}\psi(ec{q},ec{p})
angle, \mathcal{A} \in \operatorname{End}(\mathcal{H})$$

We shall denote as $\mathcal{F}_2(M_Q)$ the set of those functions.

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Physical magnitudes II: algebraic structures

Let us consider $\operatorname{End}(\mathcal{H})$ and $\mathcal{F}_2(M_Q)$

Physical magnitudes II: algebraic structures

On $\operatorname{End}(\mathcal{H})$ we have three algebraic structrues

The associative product:

 $A, B \mapsto A.B$

its symmetrical part

 $A, B \mapsto A \circ B = (AB + BA)$

and the skew-symmetrical one:

 $A, B \mapsto [A, B] = -i(AB - BA)$

Physical magnitudes II: algebraic structures

Tensors G and Ω define on $\mathcal{F}_2(M_Q)$ the following structures:

 G recovers the anti-commutator of the operators

 $G(df_A, df_B) = f_{A \circ B}$

Poisson tensors recovers the commutator:

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and the skew-symmetrical one:

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Physical magnitudes II: algebraic structures

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Associative product

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Physical magnitudes III: Projective space

Question: If we consider the system defined on the projective space P, how can we represent the observables?

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Expectation values

$$e_{\mathcal{A}}(ec{q},ec{p}) = rac{\langle \psi(ec{q},ec{p}) | \mathcal{A}\psi(ec{q},ec{p})
angle}{\langle \psi(ec{q},ec{p}) | \psi(ec{q},ec{p})
angle}$$

Physical magnitudes III: Projective space

Question: If we consider the system defined on the projective space P, how can we represent the observables?

Expectation values

$$e_{\mathcal{A}}(ec{q},ec{p}) = rac{\langle \psi(ec{q},ec{p}) | \mathcal{A}\psi(ec{q},ec{p})
angle}{\langle \psi(ec{q},ec{p}) | \psi(ec{q},ec{p})
angle}$$

Dispersions:

$$\Delta A = \frac{\langle \psi(q,p) | A^2 \psi(\vec{q},\vec{p}) \rangle}{\langle \psi(\vec{q},\vec{p}) | \psi(\vec{q},\vec{p}) \rangle} - \left(\frac{\langle \psi(\vec{q},\vec{p}) | A\psi(\vec{q},\vec{p}) \rangle}{\langle \psi(\vec{q},\vec{p}) | \psi(\vec{q},\vec{p}) \rangle} \right)^2 = e_{A^2}(\psi) - e_A(\psi)^2 = G_{\mathcal{P}}(de_A, de_A)$$

Physical magnitudes: Spectral information

Let us denote as $\mathcal{E}(M_Q)$ the set of expection value functions.

Theorem

Let A be a Hermitian operator on \mathcal{H} , $\lambda \in \mathbb{R}$ an eigenvalue and $|\psi_*\rangle \in \mathcal{H}$ one corresponding eigenvector. Then:

• e_A has a critical point at ψ_*

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$$e_A(\psi_*) = \lambda$$



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- \blacktriangleright e_{A} has a critical point at ψ_*
- $e_A(\psi_*) = \lambda$

Therefore $\mathcal{E}(M_Q)$ allows us:

- to represent the expectation value of physical observables
- to recover the spectral information

Summary

QM: $\mathcal{S} = (\mathcal{H}, h) \text{ or } \mathcal{S} = \mathcal{PH}$ $\mathcal{O} = \operatorname{Herm}(\mathcal{H})$ CM: $\mathcal{S} = (\mathcal{M}, \Omega)$ $\mathcal{O} = \mathcal{F}(\mathcal{M})$	GQM $\bullet S = (M_Q, G, \Omega)$ or $S = (\mathcal{P}, G_{\mathcal{P}}, \Omega_{\mathcal{P}})$ $\bullet \mathcal{O} = \mathcal{F}_2(M_Q) \text{ or }$
$(\psi A\psi)$	$\mathcal{E}(M_Q)$ $\blacktriangleright f_A(\psi) \text{ or } e_A(\psi)$

Introduction: GQM

How can we define the dynamics

Introduction: GQM

Question: How can we define the dynamics?



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How can we define the dynamics

Introduction: GQM

Question: How can we define the dynamics?

- We consider the function $f_H \in \mathcal{F}_2(M_Q)$ or $e_H \in \mathcal{E}(M_Q)$
- and the corresponding Hamiltonian vector fields (from Ω or Ω_P) por Ω:

$$X_{f_H} = \hbar^{-1} \{ f_H, \cdot \}; \qquad X_{e_H} = \hbar^{-1} \{ f_H, \cdot \}_{\mathcal{P}}$$

Finally, we claim that the solutions of the physical dynamics correspond to the integral curves of the Hamiltonian vector fields X_{f_H} or X_{e_H}



Aplication: Molecular dynamics

System: When modeling a molecule, it is impossible to treat all degrees of freedom as a quantum system. As the dynamical time scales are very different, we assume that the core can be represented as a point in a classical manifold (M_C) while the valence electrons are represented as rays on a Hilbert space \mathcal{H} .

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Quantum-classical molecular dynamics

Quantum-classical molecular dynamics as an approximation to full quantum dynamics

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This paper presents a mathematical derivation of a model for quantum-classical molecular dynamics (QCMD) as a *partial* classical limit of the full Schrödinger equation. This limit is achieved in two steps: separation of the full wave function and short wave asymptotics for its "classical" part. *Both* steps can be rigorously justified under the *same* smallness assumptions. This throws some light on the time-dependent self-consistent-field method and on mixed quantum-semiclassical models, which also depend on the separation step. On the other hand, the theory leads to a characterization of the critical situations in which the QCMD model is in danger of largely deviating from the solution of full Schrödinger equation. These critical situations are exemplified in an illustrative numerical simulation: the collinear collision of a classical particle with a harmonic quantum oscillator. © 1996 American Institute of Physics. [S0021-9606(96)00727-1]

Quantum-classical molecular dynamics

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ON THE SINGULAR LIMIT OF THE QUANTUM-CLASSICAL MOLECULAR DYNAMICS MODEL*

FOLKMAR A. BORNEMANN[†] AND CHRISTOF SCHÜTTE[‡]

Abstract. In molecular dynamics applications there is a growing interest in so-called mized quantum-classical models. These models describe most atoms of the molecular system by means of classical mechanics but describe an important, small portion of the system by means of quantum mechanics. A particularly extensively used model, the quantum-classical molecular dynamics (QCMD) model, consists of a singularly perturbed Schrödinger equation nonlinearly coupled to a classical Newtonian equation of motion.

This paper studies the singular limit of the QCMD model for finite dimensional Hilbert spaces. The main result states that this limit is given by the time-dependent Born–Oppenheimer model of quantum theory–provided the Hamiltonian under consideration has a smooth spectral decomposition. This result is strongly related to the *quantum adiabatic theorem*. The proof uses the method of *weak convergence* by directly discussing the density matrix instead of the wave functions. This technique avoids the discussion of highly oscillatory phases.

On the other hand, the limit of the QCMD model is of a different nature if the spectral decomposition of the Hamiltonian happens not to be smooth. We will present a generic example for which the limit set is not a unique trajectory of a limit dynamical system but rather a *funnel* consisting of infinitely many trajectories.

Key words. QCMD model, Born-Oppenheimer model, quantum adiabatic theorem, weak convergence, density matrix, funnel, Takens-chaos

AMS subject classifications. 34E15,81Q15,81V55

Quantum-classical molecular dynamics

The basic steps to link the full quantum description of the complete system with the hybrid quantum-classical description are the following:

First of all, we assume that the wave function of the total system is separable, i.e., Ψ(r, R) ∈ L²(ℝ⁶) can be written as:

 $\Psi = \chi_{\mathsf{N}}(\mathsf{R}) \otimes \psi_{\mathsf{e}}(\mathsf{r}); \qquad \chi(\mathsf{R}), \psi_{\mathsf{e}}(\mathsf{r}) \in \mathcal{L}^{2}(\mathbb{R}^{3}),$

These two wave functions are chosen to satisfy a couple of self-consistent equations associated to the original Schrödinger equation.

$$i\hbar\dot{\chi} = -\frac{\hbar}{2m}\Delta_R\chi + \langle\psi|V\psi\rangle; \ \chi(R,0) = \chi_0(R)$$
$$i\hbar\dot{\psi} = -\frac{\hbar}{2m}\Delta_r\psi + \langle\chi|V\chi\rangle; \ \psi(r,0) = \psi_0(r)$$
The nuclear wave function can be approximated by an approximate delta function (roughly speaking, this implies that the probability density is a gaussian function with variance ε)

Then, it can be proved that:

Theorem

The error of considering the evolution $\Psi(t)$ as a separable state is of order ϵ/L , where L is the natural length of the system.



By using WKB method, the nuclear wave function can be written as

$$\chi(R,t) = A(R,t)e^{\frac{i}{\hbar}S(R,t)} + \mathfrak{o}\left(\sqrt{\frac{m}{M}}\right)$$

The corresponding equations for the amplitude and the phase read:

$$\frac{\partial S}{\partial t} + \frac{1}{2M} (\nabla_R S)^2 + \langle \psi | V \psi \rangle = 0$$
$$\frac{\partial A^2}{\partial t} + \operatorname{div}_R \left(A^2 \frac{\nabla_R S}{M} \right) = 0$$

First equation can be read as a Hamilton-Jacobi equation for the momentum

$$P = \nabla_R S.$$

Combining WKB expansion and the approximate-delta assumption, it is possible to prove, rigorously, that error considering the wave function constructed as the tensor product of these (Ehrenfest) equations as the solution of the original complete Schrödinger equation is of order $((\epsilon/L)^2 + \sqrt{m/M})$.

Dynamics: Ehrenfest equations ($(\vec{R}, \vec{P}) \in M_C$ and $|\psi\rangle \in \mathcal{H}$, $H_e(\vec{R}) \in \text{Herm}(\mathcal{H})$)

$$egin{aligned} \dot{R}^k &= rac{P^k}{M_k} \ \dot{P}_k &= - ext{grad}_{ec{R}} \langle \psi | H_e(ec{R}) \psi
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Question: Is it possible to identify a Hamiltonian structure for these equations?

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Statistics and Nosé formalism for Ehrenfest dynamics

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Abstract

Quantum dynamics (i.e. the Schrödinger equation) and classical dynamics (i.e. Hamilton equations) can both be formulated in equal geometric terms: a Poisson bracket defined on a manifold. In this paper, we first show that the hybrid quantum-classical dynamics prescribed by the Ehrenfest equations can also be formulated within this general framework, what has been used in the literature to construct propagation schemes for Ehrenfest dynamics. Then, the existence of a well-defined Poisson bracket allows us to arrive to a Liouville. equation for a statistical ensemble of Ehrenfest systems. The study of a generic toy model shows that the evolution produced by Ehrenfest dynamics is ergodic and therefore the only constants of motion are functions of the Hamiltonian. The emergence of the canonical ensemble characterized by the Boltzmann distribution follows after an appropriate application of the principle of equal a priori probabilities to this case. Once we know the canonical distribution of an Ehrenfest system, it is straightforward to extend the formalism of Nosé (invented to do constant temperature molecular dynamics by a non-stochastic method) to our Ehrenfest formalism. This work also provides the basis for extending stochastic methods to Ehrenfest dynamics.





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- The space of states is $S = M_C \times M_Q$



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- And a Hamiltonian function written as $f_H(\vec{R}, \vec{P}, \vec{q}, \vec{p}) = \sum_k \frac{P_k^2}{2M_k} + \frac{\langle \psi | H_e(R)\psi \rangle}{\langle \psi | \psi \rangle}$



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Ehrenfest equations define a Hamiltonian system on $(M_C \times M_Q, \omega)$.



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Ehrenfest equations define a Hamiltonian system on $(M_C \times M_Q, \omega)$.

Corolary

Being Hamiltonian and symplectic, we can use the symplectic volume to define a measure on $M_C \times M_Q$ which is invariant under the dynamics:

 $\mu = \omega^{\dim(M_C \times M_Q)}$

Example: Classical integrable system (action-angle variables) coupled to a two-level quantum system (very simplified model of an atom adsorbed in a metal)



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$$f_{H}(J, heta,q,p) = J_{ heta} + rac{\langle \psi(q,p) | (\sigma_x + \epsilon J \cos heta \sigma_z) | \psi(q,p)
angle}{\langle \psi(q,p) | \psi(q,p)
angle}$$



Blue curve ($\epsilon = 0.15$) almost linear behavior and red curve ($\epsilon = 1.55$), clearly non-linear.

Statistical mechanical system

Let us consider the symplectic measure $d\mu_{QC}=\omega^n$ and the family of measures of the form

$$d\hat{\mu} = F_{QC}(\xi,\psi)d\mu_{QC},$$

where $F_{QC}(\xi, \psi)$ satisfies

 $\int_{M} d\mu_{QC}(\xi,\psi) F_{QC}(\xi,\psi) = 1, \qquad F_{QC}(\xi,\psi) \ge 0, \ \forall \xi \in M_{C}, \psi \in M_{Q}$

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Theorem

If $F_{QC}(\xi, \psi)$ is a constant of the motion, $d\hat{\mu}$ is an invariant measure for Ehrenfest dynamics

Ehrenfest Statistical Models

Definition of the statistical model

A physical observable A will now be represented by a function f_A on the manifold M. To define statistical averages of observables depending on classical and quantum degrees of freedom (i.e., functions as $f_A(\xi, \psi)$) we will consider a probability density F_{QC} defined on M, which allows us to write

$$\langle A \rangle = \int_M d\mu_{QC}(\xi,\psi) F_{QC}(\xi,\psi) f_A(\xi,\psi),$$



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Example

If we consider the Hamiltonian function of the hybrid system above, we obtain

$$\langle H \rangle = \int_{M} d\mu_{QC}(\xi, \psi) F_{QC}(\xi, \psi) f_{H}(\xi, \psi),$$

If $F_{QC}(\xi, \psi)$ is not a constant of the motion for Ehrenfest dynamics, the measure is not invariant. We can define thus the master equation for our system as the Hamiltonian flow of f_H on $C^{\infty}(M_C \times M_Q)$:

 $\frac{dF_{QC}}{dt} = \{F_{QC}, f_H\}$

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From the solution, we can define the time-dependence of the corresponding average values associated to the time-dependent probability distribution $F_{GQ}(\xi, \psi; t)d\mu(\xi, \psi)$:

 $\langle A \rangle(t) = \int_{M} d\mu_{QC}(\xi,\psi) F_{QC}(\xi,\psi;t) f_{A}(\xi,\psi),$

An alternative framework

An alternative representation of the hybrid system is:

$$\hat{\rho}(\xi) := \int_{\mathcal{PH}} d\mu_Q(\psi) F_{QC}(\xi, \psi) \frac{|\psi\rangle \langle \psi|}{\langle \psi, \psi \rangle}$$

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By construction, $\hat{
ho}(\xi)$ is self-adjoint, positive definite, and normalized as

$$\int_{M_C} d\mu(\xi) \mathrm{Tr} \hat{\rho}(\xi) = 1$$



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Proposition

By construction, $\hat{\rho}(\xi)$ allows us to obtain the average value of any observables of the form $\hat{A}(\xi)$ as

$$\int_{M_{\mathcal{C}}} d\mu(\xi) \operatorname{Tr}(\hat{\rho}(\xi) \hat{A}(\xi)) = 1$$

The solution of the dynamical equation allows us to write the expression of the dynamics for the matrix $\hat{\rho}(\xi)$:

 $\hat{
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This construction is formally analogous to the usual partial trace method for the contraction of a quantum system.

Proposition

The dynamics associated to the statistical description defines a non-unitary evolution which is able to exhibit decoherence effects on the quantum subsystem. This is useful for applications, since the non-statistical description is not able to capture decoherence.



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We considered a simple example of an ensemble of Na^+ ions, simulated with the code Octopus, each with the same initial quantum state but with different classical initial conditions, we obtain a change in the purity of the quantum subsystem depending on the number of particles considered in the ensemble and their initial (classical) conditions:



Ehrenfest dynamics is purity non-preserving: A necessary ingredient for decoherence

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We discuss the evolution of purity in mixed quantum/classical approaches to electronic nonadiabatic dynamics in the context of the Ehrenfest model. As it is impossible to exactly determine initial conditions for a realistic system, we choose to work in the statistical Ehrenfest formalism that we introduced in Alonso *et al.* [J. Phys. A: Math. Theor. **44**, 396004 (2011)]. From it, we develop a new framework to determine exactly the change in the purity of the quantum subsystem along with the evolution of a statistical Ehrenfest system. In a simple case, we verify how and to which extent Ehrenfest statistical dynamics makes a system with more than one classical trajectory, and an initial quantum pure state become a quantum mixed one. We prove this numerically showing how the evolution of purity depends on time, on the dimension of the quantum state space *D*, and on the number of classical trajectories *N* of the initial distribution. The results in this work open new perspectives for studying decoherence with Ehrenfest dynamics. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4737861]



Composing molecular systems

Let us consider first the composition of hybrid systems. Given two hybrid systems, defined in phase spaces $M_C^1 \times M_Q^1$ and $M_C^2 \times M_Q^2$, we shall define a composed hybrid system in $M_C \times M_Q$ where

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the classical subsystem is the Cartesian product of the classical subsystems:

 $M_C = M_C^1 \times M_C^2;$

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$$M_C = M_C^1 \times M_C^2;$$

the set of quantum states of the product system corresponds to the projective space of the tensor product space

$$M_Q = M_Q^1 \otimes M_Q^2.$$

Non-interacting particles: internal energy

If we consider a system composed of N_m independent subsystems, the Hamiltonian operator \hat{H} is defined as a family of operators parametrized N_m

by the classical variables $\xi \in M_C$ acting on the Hilbert space $\mathcal{H} \otimes \cdots \otimes \mathcal{H}$ (\mathcal{H} being a *d*-dimensional complex vector space that represents the quantum degrees of freedom of each component and $n = d^{N_m}$ the dimension of the total Hilbert space), with the expression:
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$$\hat{H}(\xi) = \sum_{k=1}^{N_m} \hat{H}_k(\vec{\xi}_k) = \sum_{k=1}^{N_m} \widehat{\mathbb{1}}_{\mathcal{H}} \otimes \cdots \otimes \widehat{\mathbb{1}}_{\mathcal{H}} \otimes \hat{h}(\vec{\xi}_k) \otimes \widehat{\mathbb{1}}_{\mathcal{H}} \otimes \cdots \otimes \widehat{\mathbb{1}}_{\mathcal{H}},$$

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where $\hat{h}(\vec{\xi}_k)$ denotes the Hamiltonian of each component in the system, which depends on the classical degrees of freedom of the corresponding classical space, and $\hat{\mathbb{I}}_{\mathcal{H}}$ is the identity operator on \mathcal{H} .

In general, we can write that, if we consider the classical variables as $\xi = (R, P)$, and a coupling of the quantum degrees of freedom to the "position" variables

$$\hat{h}(R_k, P_k) = \left(\frac{P_k^2}{2M_k} + V(R)\right)\mathbb{I} + \hat{h}(R_k).$$

In general, we can write that, if we consider the classical variables as $\xi = (R, P)$, and a coupling of the quantum degrees of freedom to the "position" variables

$$\hat{h}(R_k, P_k) = \left(\frac{P_k^2}{2M_k} + V(R)\right)\mathbb{I} + \hat{h}(R_k).$$

Definition

The internal energy of the hybrid system is defined as the expression

$$U = \langle f_H \rangle = \int_{M_C} d\mu_C(\xi) \operatorname{Tr}(\hat{\rho}(\xi) \hat{H}(\xi))$$



The entropy of a hybrid system

When defining the entropy of any statistical system it is very important to take into account the proper definition of its probabilistic nature. When considering the entropy of a system the set of microstates considered must be chosen in such a way that each one of them defines a mutually exclusive event with respect to any other state. This is what von Neumann entropy does for purely quantum systems, where the spectral decomposition of the density matrix implements the mutually exclusiveness of the set of events.

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In the case of a hybrid system, two points of the phase space $(\xi_1, \psi_1), (\xi_2, \psi_2) \in M_C \times M_Q$ represent mutually exclusive events if and only if $\xi_1 \neq \xi_2$ or $\langle \psi_1 | \psi_2 \rangle = 0$. For each value of ξ , we can compute the value of the von Neumann entropy $S(\xi)$ associated with $\rho(\xi)$. This is thus a function of the classical manifold M_Q and as such can be considered to be a *classical-density* for the total entropy.

As any other point in M_C is mutually exclusive with respect to ξ , in order to define consistently the entropy of the hybrid system, we must consider:

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The entropy of the hybrid system is obtained as the corresponding sum over all possible classical events, i.e., the integral

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$$S = -k_B \int_{M_C} d\mu_C(\xi) S(\xi),$$

where the entropy density $S(\xi)$ is defined as

 $S(\xi) = \operatorname{Tr} \left(\hat{\rho}(\xi) \log \hat{\rho}(\xi) \right).$



Hybrid ensembles: definition

Generally speaking, any thermodynamic equilibrium (quantum, classical or hybrid quantum/classical) requires two conditions:

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- a state of equilibrium (we see examples later),
- and associated thermodynamic functions (such as entropy and internal energy) that are extensive.

We can safely consider a composition of non-interacting subsystems, which is an approximation valid for real hybrid systems which are, either uncoupled or which have only short-range interactions. In such a case, the effect of the interaction on the total behavior is negligible and the approximation of independent systems is reasonable.

Hybrid ensembles: Microcanonical

Consider the total phase space of the hybrid system $M = M_C \times M_Q$ and the energy function

$$f_H = \sum_k \frac{P_k^2}{2M_k} + V(R) + e_H(R, P, \psi)$$

Hybrid ensembles: Microcanonical

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The state of equilibrium of the hybrid microcanonical ensemble corresponds to a distribution on M where all points with a fixed energy E are equally probable, i.e.

$$F_{QC}^{MC}(\xi,\psi) = \frac{\delta(E - f_H(\xi,\psi))}{V_E}$$

where $V_E = \int_M d\mu_{QC} \,\delta(E - f_H(\xi, \psi))$ represents the total volume of the level set of the energy with value *E*.

Hybrid ensembles: Canonical

The canonical ensemble can be constructed from the micro-canonical one exactly as in the classical case. The probability density corresponding to the state of equilibrium is written thus as:

$$F_{QC}^{C}(\xi,\psi)=Z_{HCE}^{-1}e^{-\beta f_{H}(\xi,\psi)},$$

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where

$$Z_{HCE} = \int_{M} d\mu_{QC}(\xi, \psi) e^{-\beta f_{H}(\xi, \psi)}$$

 $f_{H} = \sum_{k} \frac{P_{k}^{2}}{2M_{k}} + V(R) + e_{H}(R, P, \psi).$

and

Additivity of the thermodynamic functions

With these definitions, it is now time to characterize the additive behavior of the functions when considering a composed system. It is important to notice that the pure quantum limit of the HCE, exhibits a strange behavior in this regard.

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The Appendix added to the Second Edition contains the general proof, that a consistent procedure, based on very simple assumptions, always gives the same results. The thermodynamical functions depend on the quantum-mechanical level-scheme, not on the gratuitous allegation that these levels are the only allowed states.

We shall always regard the state of the assembly as determined by the indication that system No. 1 is in state, say, l_{1} , No. 2 in state $l_{2}, ..., No. N$ in state l_{N} . We shall adhere to this, though the attitude is altogether wrong. For, a quantummechanical system is not in this or that state to be described by a complete set of commuting variables chosen once and for all. To adopt this view is to think along severely 'classical' lines. With the set of states chosen, the individual system can, at best, be relied upon as having a certain probability amplitude, and so a certain probability, of being, on inspection, found in state No. 1 on No. 2 or No. 3, etc. 1 said: at best a probability amplitude. Not even that much of determination of the single system need there be. Indeed, there is no clear-cut argument for attributing to the single system a 'pure state' at all.

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JOURNAL OF MATHEMATICAL PHYSICS

VOLUME 39, NUMBER 12

DECEMBER 1998

The quantum canonical ensemble

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Lane P. Hughston^{b)}

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(Received 22 June 1998; accepted for publication 19 August 1998)

The phase space Γ of quantum mechanics can be viewed as the complex projective space CP^{μ} endowed with a Kählerian structure given by the Fubini-Study metric and an associated symplectic form. We can then interpret the Schrödinger equation hequatum phase space we introduce the corresponding natural microcanonical and canonical ensembles. The resulting density matrix for the canonical Γ ensemble differs from the density matrix of the conventional approach. As an illustration, the results are applied to the case of a spin one-half particle in a heat bath with an applied magnetic field. \odot 1998 American Institute of Physics. [S0022-2488(90)0021-6]

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> Canadian Mathematical Society Conference Proceedings Volume 28, 2000

Invariant measures under Schrödinger evolution and quantum statistical mechanics

G. Jona-Lasinio

ABSTRACT. If one considers the evolution of quantum expectations of coordinates and nonsents of a system of collitars, the classical Glibbs measure asports naturally as an invariant measure. We show that the Glibbs measure associated to the Schrödinger equation viewed as an infinite dismissional dynamical system induces the classical ensemble on expectations. This type of analysis can be excluded to systems with non quadratic Hamiltonian and a low temperature the so called effective potential replaces the classical potention of the meaning classical effective potential replaces the classical potention ensemble considered as are the classical potention ensemble considered as are the classical of coefficients and a simple generalization of them otherwise. We briefly discuss the connection with the sparal aconside density matrix.



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ournal of Statistical Mechanics: Theory and Experiment

A generalized quantum microcanonical ensemble

Jan Naudts and Erik Van der Straeten¹

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Received 16 May 2006 Accepted 4 June 2006 Published 23 June 2006

Online at stacks.iop.org/JSTAT/2006/P06015 doi:10.1088/1742-5468/2006/06/P06015

Abstract. We discus a generalized quantum microanomical ensemble. It describes isolated systems that are not necessarily in an eigenstate of the Hamilton operator. Statistical averages are obtained by combining a time avorage and a maximum entropy argument to resolve the lack of knowledges about initial conditions. As a result, statistical averages of linear observables conducid with values obtained in the consonical ensemble. Non-consciola averages can be obtained by taking into account conserved quantities which are non-linear functions of the microatac.

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PHYSICAL REVIEW E 80, 051130 (2009)

Typical state of an isolated quantum system with fixed energy and unrestricted participation of eigenstates

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This work describes the statistics for the occupation numbers of quantum levels in a large isolated quantum system, where all possible superpositions or eigennatists are allowed provided all these superpositions have the same fixed energy. Such a confidion is not equivalent to the conventional microconsonical condition because the latter limits the participating eigenstates to a work partice. The statistics is obtained analytically for both the entire system and its small subsystem. In a significant departure from the Boltzmann-Gibbs statistics, the average compation numbers of quantum states estimation is the over-entropy quantum states. This work contains infail numerical tests of the about the software statistics of the average dense on energy. In the macroscopic limit, this dependence is routiled y accompation by the condensation into the loweretenergy quantum states. This work estimation is the loweretenergy quantum states. This wave statistics, the participation of eigenstates in such an expansion obcycly the nerdy obstancia statistics. The average valuation is applied to the statistic of the integration of the macroscopic systems, its rather to reduce statistics and the average valuation is applied to the statistic of the integration of eigenstates and the statistic of the integration of eigenstates and the statistic of the integration of eigenstates and the statistic of the integration of eigenstates in the obstate mace lists of the integration of eigenstates in the obstate of the integration of eigenstates in the obstate of the condensatistic integration of eigenstates in the eigenstate integration of eigenstates and the eigenstates in the obstate of the integration of eigenstates in the entry eigenstates in the eigenstates in the eigenstates in the entry eige

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THE JOURNAL OF CHEMICAL PHYSICS 133, 034509 (2010)

Emergence of equilibrium thermodynamic properties in quantum pure states. I. Theory

Barbara Fresch^{a)} and Giorgio J. Moro^{b)}

Department of Chemical Science, University of Padova, Via Marzolo 1, Padova 35131, Italy

(Received 16 March 2010; accepted 2 June 2010; published online 20 July 2010)

Investigation on foundational aspects of quantum statistical mechanics recently entered a renaissance period due to novel intuitions from quantum information theory and to increasing attention on the dynamical aspects of single quantum systems. In the present contribution a simple but effective theoretical framework is introduced to clarify the connections between a purely mechanical description and the thermodynamic characterization of the equilibrium state of an isolated quantum system. A salient feature of our approach is the very transparent distinction between the statistical aspects and the dynamical aspects in the description of isolated quantum systems. Like in the classical statistical mechanics, the equilibrium distribution of any property is identified on the basis of the time evolution of the considered system. As a consequence equilibrium properties of quantum system appear to depend on the details of the initial state due to the abundance of constants of the motion in the Schrödinger dynamics. On the other hand the study of the probability distributions of some functions, such as the entropy or the equilibrium state of a subsystem, in statistical ensembles of pure states reveals the crucial role of typicality as the bridge between macroscopic thermodynamics and microscopic quantum dynamics. We shall consider two particular ensembles: the random pure state ensemble and the fixed expectation energy ensemble. The relation between the introduced ensembles, the properties of a given isolated system, and the standard quantum statistical description are discussed throughout the presentation. Finally we point out the conditions which should be satisfied by an ensemble in order to get meaningful thermodynamical characterization of an isolated quantum system. © 2010 American Institute of Physics. [doi:10.1063/1.3455998]

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New Journal of Physics

Quantum fluctuation relations for ensembles of wave functions

Michele Campisi

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New Journal of Physics **15** (2013) 115008 (12pp) Received 24 June 2013 Published 13 November 2013 Online at http://www.njp.org/ doi:10.1088/1367-26301/511/115008

Abstract. New quantum fluctuation relations are presented. In contrast with the standard approach, where the initial state of the driven system is described by the (micro) canonical density matrix, here we assume that it is described by a (micro) canonical distribution of wave functions, as originally proposed by Schrödinger. While the standard fluctuation relations are based on von Neumann measurements, bat introve instead a notion of work as the change in expectation of the Hamiltonian.

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PHYSICAL REVIEW E 91, 022137 (2015)

Nonextensive thermodynamic functions in the Schrödinger-Gibbs ensemble

J. L. Alsone,^{12,3} A. Castos,¹³ J. C. Clemento-Gallando,^{13,4} J. C. Cuchi,¹ P. Echeningue,^{13,45} J. G. Estere,¹² and F. Factero),¹² ¹³Dyparamento de Fisica Articia, Universidad de Zampeez, Martino Esquillor vin, 50018 Zampeez, Spain ¹⁴Indiato de Biocompatedore Sin Diversidad de Zampeez, Martino Esquillor vin, 50018 Zampeez, Spain ¹⁴Unada Activida (JP, 874), Universidad de Zampeez, Martino Esquillor vin, 50018 Zampeez, Spain ¹⁴Indiato da Nociola (JP, 874), Universidad de Zampeez, Martino Esquillor vin, 50018 Zampeez, Spain ¹⁴Indiato da NaUD, Dintersidad de Zampeez, Martino Esquillor vin, 50018 Zampeez, Spain ¹⁴Daparamento El Espivera la Activity Constructiona Superior d'Espiryent Activity, Science Jackie, Science Ja

Schedunger suggested hut thermodynamical functions cannot be based on the granitons altergation that quantum-mechanical levels typically the technogonal eigenstates of the Hamiltonian operative are the only allowed states for a quantum system [E. Schrödinger, *Statistical Thermodynamics* (Conferi Dover, Maneola, 1997)]. Different antices have interpreted this statement by invitationing density distributions on the space of quantum myce states with weights obtained as functions of the expectation value of the Hamiltonian of the system. In this work because on our of the existence of the activations and prove that, which considered in of the somitmeric distribution of the system. This invites the solution of the system is the thermodynamical regime. This implies that it is not possible to define extensive lemendynamical magnitudes such as the fere encourge, this interple encourse, for the temolynamical entropy by using these models. Therefore, we conclude that this distribution inspired by Schrödinger's idea cannot be used to construct an appropriate quantum qualibland the theorethynamical regime.

DOI: 10.1103/PhysRevE.91.022137

PACS number(s): 05.30.Ch, 05.70.-a, 03.65.Aa

Results for few particles

A very simple model with $M_C = \mathbb{R}^2$, $M_Q = \mathbb{CP}^1$ and V = 0 (quantum coupling to the position degrees of freedom in the form $\sqrt{1 + \epsilon \cos \theta} \hat{H}$), where \hat{H} corresponds to a two-level system.



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Thermodynamic limit

Additivity of the thermodynamic functions, or, equivalently, separability of the density matrix $\rho(\xi)$ is recovered in the thermodynamic limit:

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Definition

Consider a family of models, each defined on a phase space of the form $M_C^{N_m} \times M_Q^{N_m}$, and an observable A^{N_m} . Consider also the volume V^{N_m} associated to the (classical) degrees of freedom of the positions of the classical subsystems, which we assume that do not interact. Then, we will claim that A^{∞} is the thermodynamic limit of the magnitude A if

$$A^{\infty} = \lim_{N_m \to \infty} A^{N_m}; \tag{1}$$

(2)

and the limit process satisfies that

$$\lim_{N_m\to\infty}V^{N_m}/N_m \text{ is constant.}$$

Thermodynamic limit

Theorem

The thermodynamic limit of the HCE ensemble is represented by the operator

$$\hat{\rho}(\xi) = e^{-\beta \frac{\operatorname{Tr}(\hat{H}(\xi))}{\dim(M_Q)}} \mathbb{I}_{\dim M_Q} = \bigotimes_k e^{-\beta \frac{\operatorname{Tr}(\hat{H}(\xi_k))}{\dim(M_Q^k)}} \mathbb{I}_{\dim M_Q^k}.$$

Such an operator is trivially separable at any temperature and leads to additive entropy and energy functions, also at any temperature.



Application III: Control of hybrid ensembles

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Control of hybrid systems: the concept

The dynamics of a hybrid system corresponds to the integral curves of a vector field X_{f_H} on $M = M_C \times M_Q$ which is Hamiltonian with respect to the symplectic form $\omega = \omega_C + \hbar^{-1}\omega_Q$.

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Controls on the dynamics as elements in the Hamiltonian f_H give rise to control vector fields X_{C_i} which are also Hamiltonian and a controlled dynamical system which can be written as

$$X = X_{f_{\mathcal{H}}} + \sum_{i} u_i(t) X_{C_i}.$$

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Notions as local accessibility/controlability can be formulated, as it is usually done on classical systems, by using Rashevsky-Chow theorem. This has important applications in the control of chemical reactions and processes where the quantum aspect of electron dynamics becomes relevant, such as photo-induced processes.
Control of hybrid systems: hybrid splines

We can consider the generalization of the definition of cubic splines for classical or quantum manifolds.



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A general framework for quantum splines

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> Received 20 December 2017 Accepted 26 April 2018 Published 6 June 2018



Control of hybrid systems: hybrid splines

We can consider the generalization of the definition of cubic splines for classical or quantum manifolds.

Problem

Given a set of k points in the hybrid phase space $M = M_C \times M_Q$ and a set of times $\{t_j\}_{j=1,\dots,k}$, find the control functions $\{u_\alpha\}_\alpha$ which define the electronic Hamiltonian rate change

$$\frac{dH(t)}{dt}=u(t);$$

in such a way that the hybrid system driven by the vector field X_{f_H} $(f_H = \sum_i \frac{P_i^2}{2M_i} + V(R_i) + e_{H(t)})$ passes arbitrarily close to the given points at the given times, and minimizes the power injected in the system that can be computed as

$$\int dt \left\langle \frac{dH}{dt}, \frac{dH}{dt} \right\rangle.$$

Control of hybrid systems: hybrid splines

Why? This is an approach which may serve to define controls for chemical reactions, where the states of the different chemical species correpond to local minima of the **Potential Energy Surface (PES)** of the system, parametrized by the classical degrees of freedom of the moleculae.



A toy model of hybrid splines

We consider a simple example where:

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- $M_C = \mathbb{R}^2$, with coordinates (Q, P)
- M_Q = CP¹. We will use the representation as orthogonal projectors on one-dimensional subspaces of C² (i.e., pure density matrices ρ)

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$$f_{H} = \frac{P^{2}}{2} + \frac{Q^{2}}{2} + Q * \operatorname{Tr}(\rho H)$$

and H is the quantum-Hamiltonian whose time-dependence must be determined

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 The distance to the target points is defined as the sum of the canonical riemannian distances (classical and quantum).

Preliminary results

Two limiting cases:

Limit of pure classical points



Preliminary results

Two limiting cases:

Limit of pure quantum points

Conclusions

The geometric formulation of Quantum Mechanics can be generalized to the case of hybrid systems and provide a rigorous framework for molecular models

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- Because of the Hamiltonian nature of the dynamics, we are able to formulate a Statistical Dynamical model for Ehrenfest equations, which allows us to recover electronic decoherence.
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Conclusions

- The geometric formulation of Quantum Mechanics can be generalized to the case of hybrid systems and provide a rigorous framework for molecular models
- Because of the Hamiltonian nature of the dynamics, we are able to formulate a Statistical Dynamical model for Ehrenfest equations, which allows us to recover electronic decoherence.
- The additivity of thermodynamical functions is a difficult issue that fails for small number of particles, although it is well behaved in the thermodynamic limit. This is relevant when considering computer simulations.
- The nonlinear molecular dynamics, when considered within (classical) control theory, offers a wide and interesting range of relevant applications and problems.

Outlook

Understanding better the behavior in the thermodynamic limit of statistical systems.

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- Use of machine-learning techniques to optimize parameters in the models. Application to the design and synthesis of organic dyes for DSSC solar cells.

Suggestions? ...

Thanks for your attention :-)