

A geometric formulation of Ehrenfest molecular dynamics

XXVII International Fall
Workshop on Geometry and
Physics,
Sevilla, 3-7 September 2018

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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 collaborations 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



Introduction: the problem of GQM

General formulation of a physical system

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- ▶ A way of representing the measurement process, i.e., an application $\mathcal{S} \times \mathcal{O} \rightarrow \mathbb{R}$ assigning a real number to the measurement of every magnitude on every state.

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

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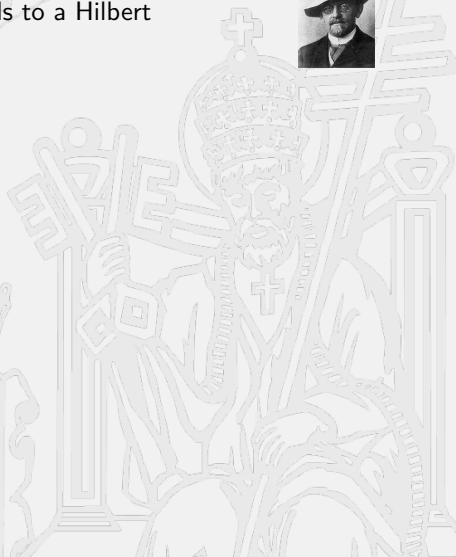
- ▶ Dynamics corresponds to the integral curve of the Hamiltonian vector field associated to the function h which represents the energy of the system:

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



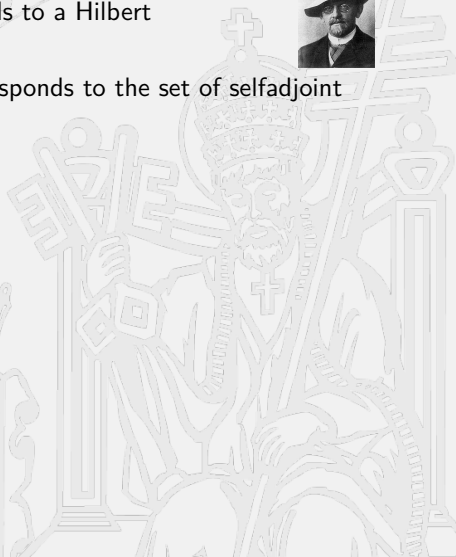
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- ▶ Dynamics can be introduced via Schrödinger equation, associated to the Hamiltonian operator

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = H |\psi(t)\rangle$$



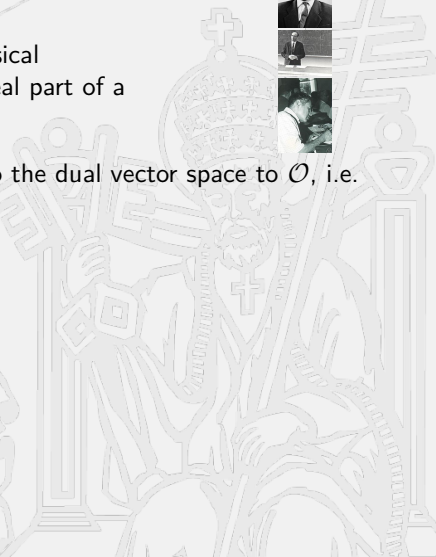
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$$i\hbar \frac{\partial}{\partial t} K(t) = HK(t) - K(t)H$$



Summary of QM



Geometric Quantum Mechanics

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.

Geometric Quantum Mechanics

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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Received 8 May 2008
Accepted 12 June 2008

Geometric Quantum Mechanics

IOP PUBLISHING

PHYSICA SCRIPTA

Phys. Scr. **T153** (2013) 014012 (4pp)

doi:10.1088/0031-8949/2013/T153/014012

Tensorial description of quantum mechanics

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Received 10 September 2012

Accepted for publication 18 September 2012

Published 28 March 2013

Online at stacks.iop.org/PhysScr/T153/014012

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.

PACS numbers: 03.65.Ca, 03.65.Aa

Geometric Quantum Mechanics

IL NUOVO CIMENTO
DOI 10.1393/ncc/i2013-11522-6

VOL. 36 C, N. 3

Maggio-Giugno 2013

COLLOQUIA: MSQS 2012

The Ehrenfest picture and the geometry of Quantum Mechanics

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ricevuto il 15 Febbraio 2013

Geometric Quantum Mechanics

IOP Publishing

Journal of Physics A: Mathematical and Theoretical

J. Phys. A: Math. Theor. **50** (2017) 365301 (34pp)<https://doi.org/10.1088/1751-8121/aa8182>

Tensorial dynamics on the space of quantum states

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and G Marmo^{3,4}

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Received 22 December 2016, revised 14 June 2017

Accepted for publication 24 July 2017

Published 9 August 2017



Physical states I: Hilbert space

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

$$|\psi\rangle = \sum_j z_j |e_j\rangle \implies \mathbb{C}^n \ni (z^1, \dots, z^n) \rightarrow (\operatorname{Re}(z^1), \operatorname{Im}(z^1), \dots, \operatorname{Re}(z^n), \operatorname{Im}(z^n))$$

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- ▶ The scalar product can be described by a tensor on \mathcal{H} :

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

By using the realification introduced

$$X_{\psi_k} = (X_{\psi_k}^R, X_{\psi_k}^I) \implies$$

$$h(X_{\psi_1}, X_{\psi_2}) = (((X_{\psi_1}^R X_{\psi_2}^R) + (X_{\psi_1}^I X_{\psi_2}^I)), (X_{\psi_1}^R X_{\psi_2}^I) - (X_{\psi_1}^I X_{\psi_2}^R))$$

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

$$X_{\psi_k} = (X_{\psi_k}^R, X_{\psi_k}^I) \implies h(X_{\psi_1}, X_{\psi_2}) = (g((X_{\psi_1}^R, X_{\psi_1}^I), (X_{\psi_2}^R, X_{\psi_2}^I)), \omega((X_{\psi_1}^R, X_{\psi_1}^I), (X_{\psi_2}^R, X_{\psi_2}^I)))$$

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

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

- The complex structure of \mathcal{H} becomes a 1:1 tensor field:

$$J : TM_Q \times T^*M_Q \rightarrow C^\infty(M_Q); \quad J(X_\psi^R, X_\psi^I) = (-X_\psi^I, X_\psi^R)$$

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

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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 $2n$.

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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



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Questions:

- ▶ How can we define the projective space corresponding to \mathcal{H} ?

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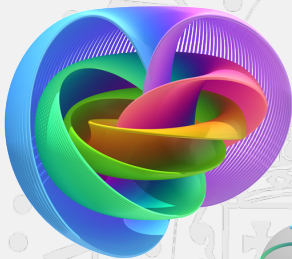
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True physical states correspond to the equivalence class:

$$|\psi_1\rangle, |\psi_2\rangle \in \mathcal{H}_0 = \mathcal{H} - \{\vec{0}\}$$

$$|\psi_1\rangle \sim |\psi_2\rangle \Leftrightarrow |\psi_2\rangle = \lambda|\psi_1\rangle; \quad \lambda \in \mathbb{C}$$

The set of these equivalence classes define the **projective space** $\mathcal{P}\mathcal{H}$, which is diffeomorphic to the space of projectors on one-dimensional subspaces of the Hilbert space \mathcal{H} :

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

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Solution:

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

Physical magnitudes I: functions

Let us consider the sesquilinear forms defined on M_Q :

$$f_A(\psi(\vec{q}, \vec{p})) = \frac{1}{2} \langle \psi(\vec{q}, \vec{p}) | A \psi(\vec{q}, \vec{p}) \rangle, A \in \text{End}(\mathcal{H})$$

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

Physical magnitudes I: functions

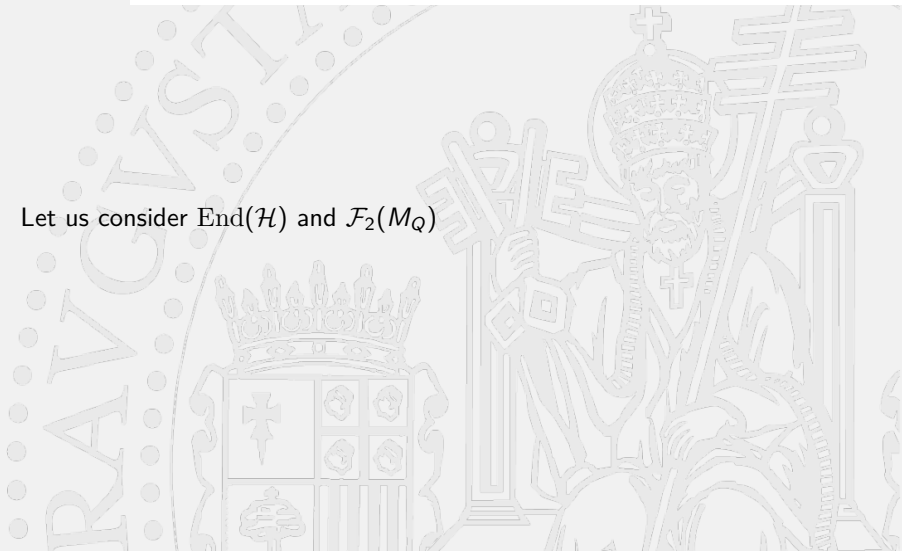
Let us consider the sesquilinear forms defined on M_Q :

$$f_A(\psi(\vec{q}, \vec{p})) = \frac{1}{2} \langle \psi(\vec{q}, \vec{p}) | A \psi(\vec{q}, \vec{p}) \rangle, A \in \text{End}(\mathcal{H})$$

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

Physical magnitudes II: algebraic structures

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



Physical magnitudes II: algebraic structures

On $\text{End}(\mathcal{H})$ we have three algebraic structures

- ▶ 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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$$f_{AB} = \frac{1}{2}G(df_A, df_B) + \frac{i}{2}\Omega(df_A, df_B)$$

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Physical magnitudes III: Projective space

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- Expectation values

$$e_A(\vec{q}, \vec{p}) = \frac{\langle \psi(\vec{q}, \vec{p}) | A \psi(\vec{q}, \vec{p}) \rangle}{\langle \psi(\vec{q}, \vec{p}) | \psi(\vec{q}, \vec{p}) \rangle}$$

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- Dispersions:

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

Physical magnitudes: Spectral information

Let us denote as $\mathcal{E}(M_Q)$ the set of expectation 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_*
- ▶ $e_A(\psi_*) = \lambda$

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

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

Summary

QM:

- ▶ $\mathcal{S} = (\mathcal{H}, h)$ or
 $\mathcal{S} = \mathcal{PH}$
- ▶ $\mathcal{O} = \text{Herm}(\mathcal{H})$
- ▶ $\langle \psi | A \psi \rangle$

CM:

- ▶ $\mathcal{S} = (M, \Omega)$
- ▶ $\mathcal{O} = \mathcal{F}(M)$
- ▶ $f(\vec{q}, \vec{p})$

QGM

- ▶ $\mathcal{S} = (M_Q, G, \Omega)$
or
 $\mathcal{S} = (\mathcal{P}, G_{\mathcal{P}}, \Omega_{\mathcal{P}})$
- ▶ $\mathcal{O} = \mathcal{F}_2(M_Q)$ or
 $\mathcal{E}(M_Q)$
- ▶ $f_A(\psi)$ or $e_A(\psi)$

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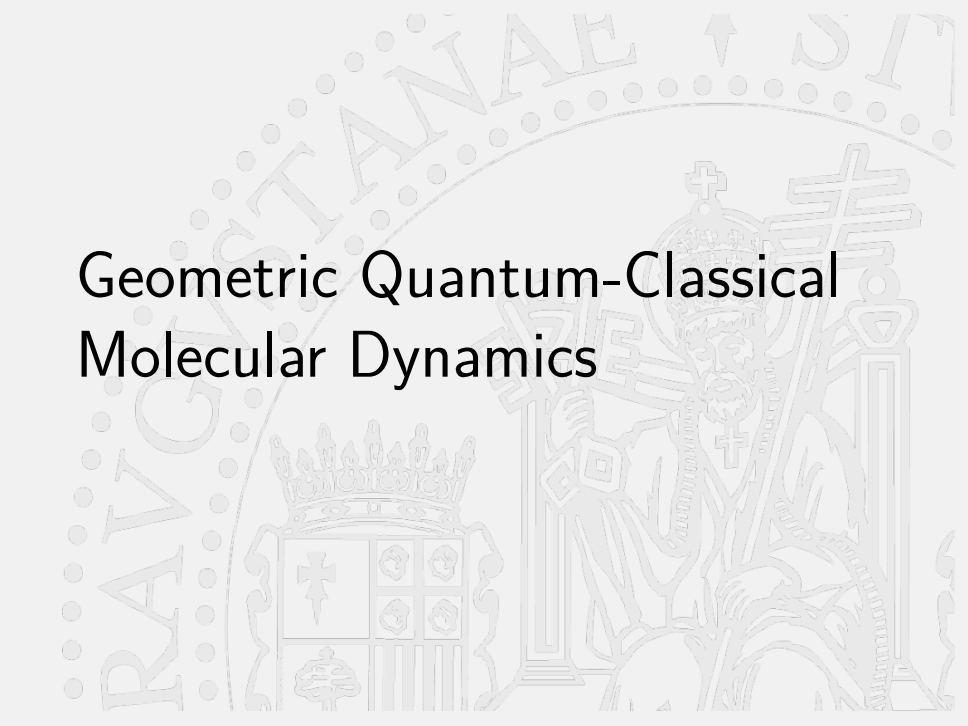
Question: How can we define the dynamics?

- ▶ 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 $\Omega_{\mathcal{P}}$) por Ω :

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

- ▶ 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}

Geometric Quantum-Classical Molecular Dynamics



Geometric Quantum-Classical Molecular Dynamics

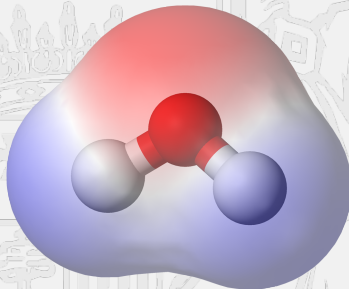
Application: Molecular dynamics

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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Images: wikipedia



Quantum-classical molecular dynamics

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

Folkmar A. Bornemann, Peter Nettesheim, and Christof Schütte^{a)}
Konrad-Zuse-Zentrum Berlin, Heilbronner Str. 10, D-10711 Berlin, Germany

(Received 7 February 1996; accepted 8 April 1996)

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

SIAM J. APPL. MATH.
Vol. 59, No. 4, pp. 1208–1224

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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 *mixed 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., $\Psi(r, R) \in \mathcal{L}^2(\mathbb{R}^6)$ can be written as:

$$\Psi = \chi_N(R) \otimes \psi_e(r); \quad \chi(R), \psi_e(r) \in \mathcal{L}^2(\mathbb{R}^3),$$

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

$$i\hbar\dot{\chi} = -\frac{\hbar}{2m}\Delta_R\chi + \langle\psi|V\psi\rangle; \quad \chi(R, 0) = \chi_0(R)$$

$$i\hbar\dot{\psi} = -\frac{\hbar}{2m}\Delta_r\psi + \langle\chi|V\chi\rangle; \quad \psi(r, 0) = \psi_0(r)$$

- ▶ 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

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

The corresponding equations for the amplitude and the phase read:

$$\frac{\partial S}{\partial t} + \frac{1}{2M}(\nabla_R S)^2 + \langle \psi | V \psi \rangle = 0$$

$$\frac{\partial A^2}{\partial t} + \text{div}_R \left(A^2 \frac{\nabla_R S}{M} \right) = 0$$

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

$$P = \nabla_R S.$$

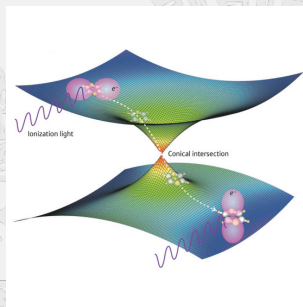
Combining WKB expansion and the approximate-delta assumption, it is possible to prove, rigorously, that error considering the wave function constructed as the tensor product of these (Ehrenfest) equations as the solution of the original complete Schrödinger equation is of order $((\epsilon/L)^2 + \sqrt{m/M})$.

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

$$\dot{R}^k = \frac{P^k}{M_k}$$

$$\dot{P}_k = -\text{grad}_{\vec{R}} \langle \psi | H_e(\vec{R}) | \psi \rangle$$

$$i\hbar \frac{d|\psi(t)\rangle}{dt} = H_e(\vec{R})|\psi(t)\rangle$$

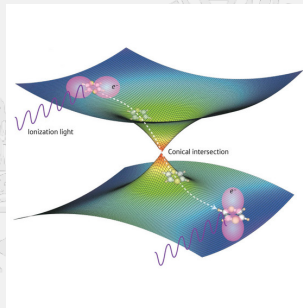


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Question: Is it possible to identify a Hamiltonian structure for these equations?

Statistics and Nosé formalism for Ehrenfest dynamics

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P Echenique^{1,2,3,5} and F Falceto^{1,2}

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Received 7 April 2011, in final form 26 July 2011

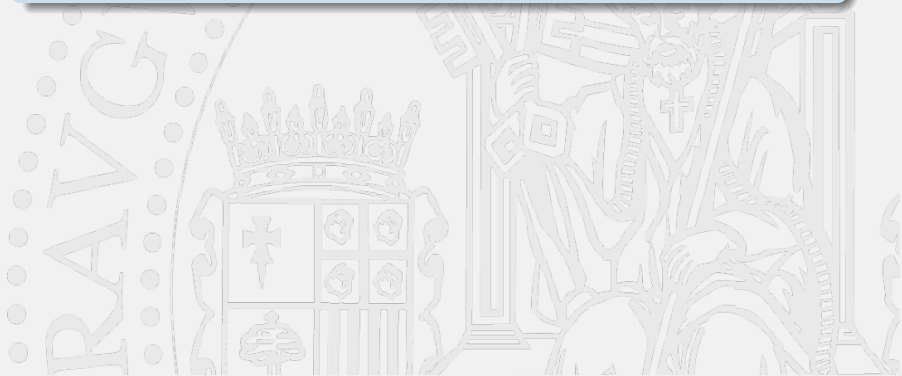
Published 7 September 2011

Online at stacks.iop.org/JPhysA/44/395004

Abstract

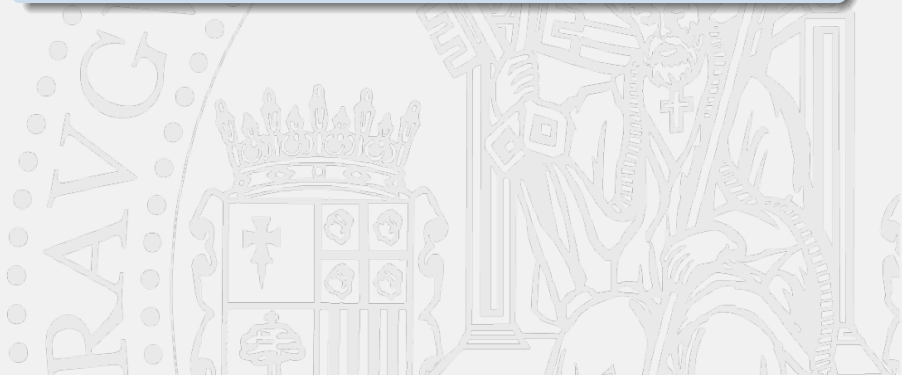
Quantum dynamics (i.e. the Schrödinger equation) and classical dynamics (i.e. Hamilton equations) can both be formulated in equal geometric terms: a Poisson bracket defined on a manifold. In this paper, we first show that the hybrid quantum-classical dynamics prescribed by the Ehrenfest equations can 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.

Characterizing the hybrid system



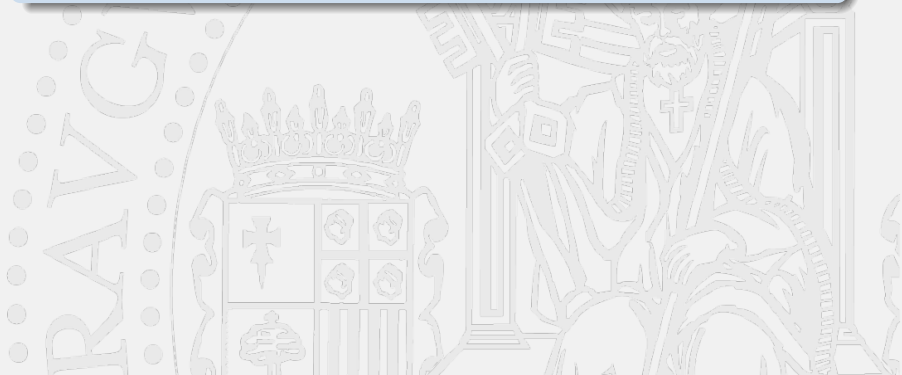
Characterizing the hybrid system

- ▶ The quantum subsystem is assumed to be finite dimensional
- ▶ The space of states is $\mathcal{S} = M_C \times M_Q$



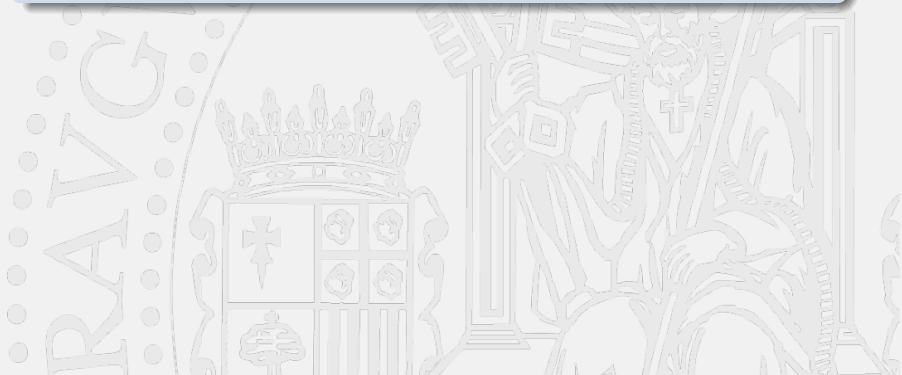
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Corolary

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:

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

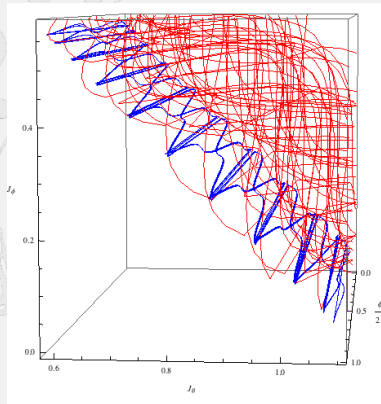
Example: Classical integrable system (action-angle variables) coupled to a two-level quantum system (very simplified model of an atom adsorbed in a metal)

$$f_H(J, \theta, q, p) = J_\theta + \frac{\langle \psi(q, p) | (\sigma_x + \epsilon J \cos \theta \sigma_z) | \psi(q, p) \rangle}{\langle \psi(q, p) | \psi(q, p) \rangle}$$

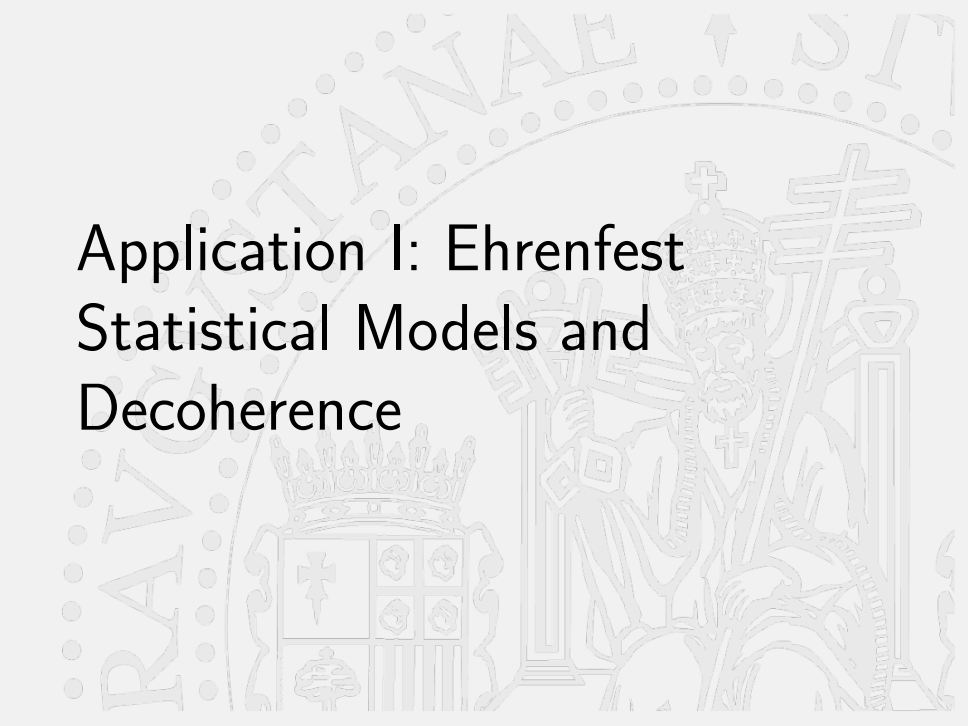


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Blue curve ($\epsilon = 0.15$) almost linear behavior and red curve ($\epsilon = 1.55$), clearly non-linear.



Application I: Ehrenfest Statistical Models and Decoherence

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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

$$\int_M d\mu_{QC}(\xi, \psi) F_{QC}(\xi, \psi) = 1, \quad F_{QC}(\xi, \psi) \geq 0, \quad \forall \xi \in M_C, \psi \in M_Q$$

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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

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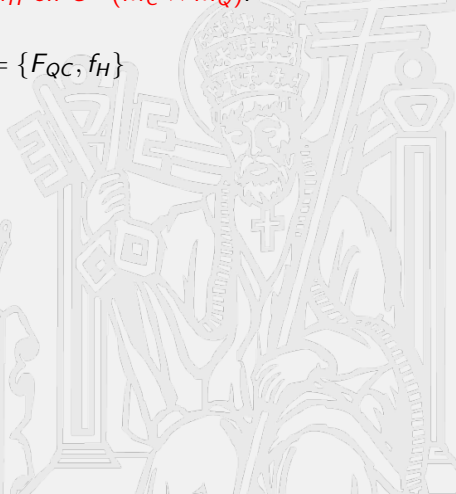
Example

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

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

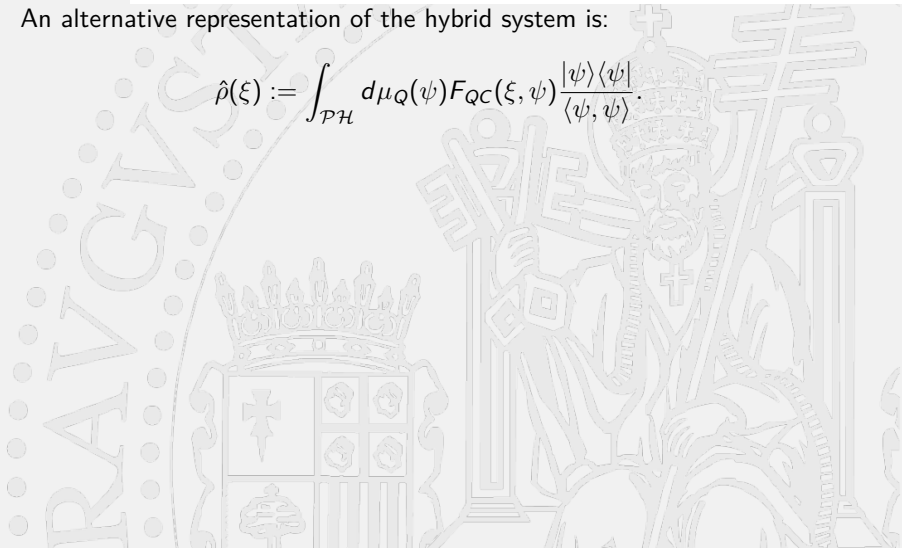
$$\langle A \rangle(t) = \int_M d\mu_{QC}(\xi, \psi) F_{QC}(\xi, \psi; t) f_A(\xi, \psi),$$

Application I: Ehrenfest Statistical Models and Decoherence

An alternative framework

An alternative representation of the hybrid system is:

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



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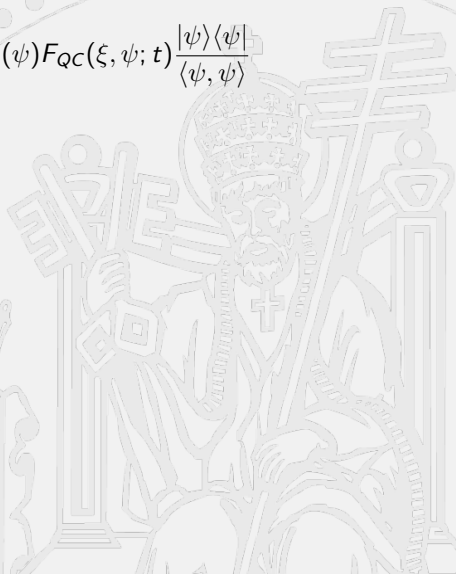
Proposition

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

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

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

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



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We can also build the density matrix of the marginal quantum distribution of the hybrid system:

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The density matrix representing the quantum subsystem of our hybrid system is obtained by averaging the effect of the classical subsystem

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

Proposition

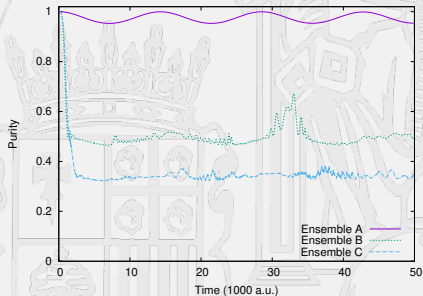
The dynamics associated to the statistical description defines a non-unitary evolution which is able to exhibit decoherence effects on the quantum subsystem. This is useful for applications, since the non-statistical description is not able to capture decoherence.



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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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(Received 1 May 2012; accepted 5 July 2012; published online 2 August 2012)

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>]

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Ehrenfest Statistical Dynamics in Chemistry: Study of Decoherence Effects

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J. Chem. Theory Comput., Article ASAP

DOI: [10.1021/acs.jctc.8b00951](https://doi.org/10.1021/acs.jctc.8b00951)

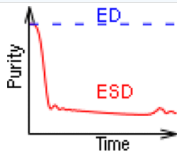
Publication Date (Web): June 26, 2018

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Cite this: *J. Chem. Theory Comput.* XXXX, XXX, XXX-XXX

Abstract



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Abstract

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Application II: Definition of hybrid ensembles



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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:

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

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

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

Application II: Definition of hybrid ensembles

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 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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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

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

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

Definition

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

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

Application II: Definition of hybrid ensembles

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 mutual exclusiveness of the set of events.

Application II: Definition of hybrid ensembles

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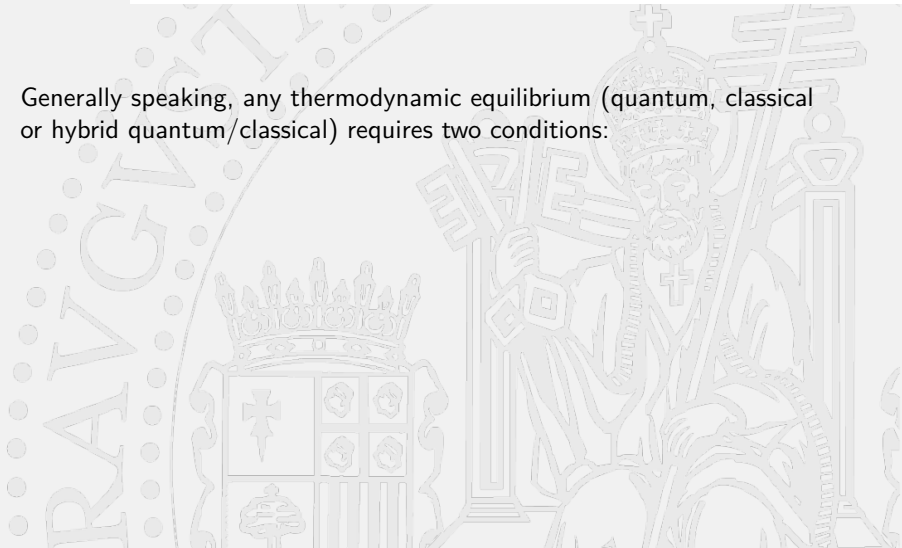
where the entropy density $S(\xi)$ is defined as

$$S(\xi) = \text{Tr} (\hat{\rho}(\xi) \log \hat{\rho}(\xi)).$$

Application II: Definition of hybrid ensembles

Hybrid ensembles: definition

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



Hybrid ensembles: definition

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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**.

Hybrid ensembles: definition

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

- ▶ 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.

Application II: Definition of hybrid ensembles

Hybrid ensembles: Microcanonical

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

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

Application II: Definition of hybrid ensembles

Hybrid ensembles: Microcanonical

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

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 .

Application II: Definition of hybrid ensembles

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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and

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

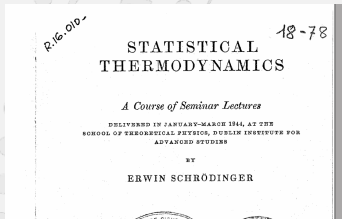
Additivity of the thermodynamic functions

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.

Application II: Definition of hybrid ensembles

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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 quantum-mechanical 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 or No. 2 or No. 3, etc. I 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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MATHEMATICAL FOUNDATIONS
OF
QUANTUM STATISTICS

By

A. Y. KHINCHIN

TRANSLATION FROM THE FIRST (1951) RUSSIAN EDITION

EDITED BY IRWIN SHAPIRO

Lincoln Laboratory, M. I. T.

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JOURNAL OF MATHEMATICAL PHYSICS

VOLUME 39, NUMBER 12

DECEMBER 1998

The quantum canonical ensemble

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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^n endowed with a Kählerian structure given by the Fubini-Study metric and an associated symplectic form. We can then interpret the Schrödinger equation as generating a Hamiltonian dynamics on Γ . Based upon the geometric structure of the quantum 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. © 1998 American Institute of Physics. [S0022-2488(98)00212-6]

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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 momenta of a system of oscillators, the classical Gibbs measure appears naturally as an invariant measure. We show that the Gibbs measure associated to the Schrödinger equation viewed as an infinite dimensional dynamical system induces the classical ensemble on expectations. This type of analysis can be extended to systems with non quadratic Hamiltonian and at low temperature the so called effective potential replaces the classical potential in the Gibbs distribution. The quantum states typical in this regime for the ensembles considered are the coherent states in the case of oscillators and a simple generalization of them otherwise. We briefly discuss the connection with the usual canonical density matrix.

Additivity of the thermodynamic functions

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Journal of Statistical Mechanics: Theory and Experiment
An IOP and SISSA journal

A generalized quantum microcanonical ensemble

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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](https://doi.org/10.1088/1742-5468/2006/06/P06015)

Abstract. We discuss a generalized quantum microcanonical ensemble. It describes isolated systems that are not necessarily in an eigenstate of the Hamilton operator. Statistical averages are obtained by combining a time average and a maximum entropy argument to resolve the lack of knowledge about initial conditions. As a result, statistical averages of linear observables coincide with values obtained in the canonical ensemble. Non-canonical averages can be obtained by taking into account conserved quantities which are non-linear functions of the microstate.

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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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(Received 2 March 2009; published 30 November 2009)

This work describes the statistics for the occupation numbers of quantum levels in a large isolated quantum system, where all possible superpositions of eigenstates are allowed provided all these superpositions have the same fixed energy. Such a condition is not equivalent to the conventional microcanonical condition because the latter limits the participating eigenstates to a very narrow energy window. 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 occupation numbers of quantum states exhibit in the present case weak algebraic dependence on energy. In the macroscopic limit, this dependence is routinely accompanied by the condensation into the lowest-energy quantum state. This work contains initial numerical tests of the above statistics for finite systems and also reports the following numerical finding: when the basis states of large but finite random matrix Hamiltonians are expanded in terms of eigenstates, the participation of eigenstates in such an expansion obeys the newly obtained statistics. The above statistics might be observable in small quantum systems, but for the macroscopic systems, it rather re-enforces doubts about self-sufficiency of nonrelativistic quantum mechanics for justifying the Boltzmann-Gibbs equilibrium.

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THE JOURNAL OF CHEMICAL PHYSICS 133, 034509 (2010)

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

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(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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Quantum fluctuation relations for ensembles of wave functions

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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:10.1088/1367-2630/15/11/115008

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 measurement postulate, these new fluctuation relations do not involve any quantum collapse, but involve instead a notion of work as the change in expectation of the Hamiltonian.

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.

PHYSICAL REVIEW E **91**, 022137 (2015)

Nonextensive thermodynamic functions in the Schrödinger-Gibbs ensemble

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(Received 24 July 2014; published 25 February 2015)

Schrödinger suggested that thermodynamical functions cannot be based on the gratuitous allegation that quantum-mechanical levels (typically the orthogonal eigenstates of the Hamiltonian operator) are the only allowed states for a quantum system [E. Schrödinger, *Statistical Thermodynamics* (Courier Dover, Mineola, 1967)]. Different authors have interpreted this statement by introducing density distributions on the space of quantum pure states with weights obtained as functions of the expectation value of the Hamiltonian of the system. In this work we focus on one of the best known of these distributions and prove that, when considered in composite quantum systems, it defines partition functions that do not factorize as products of partition functions of the noninteracting subsystems, even in the thermodynamical regime. This implies that it is not possible to define extensive thermodynamical magnitudes such as the free energy, the internal energy, or the thermodynamic entropy by using these models. Therefore, we conclude that this distribution inspired by Schrödinger's idea cannot be used to construct an appropriate quantum equilibrium thermodynamics.

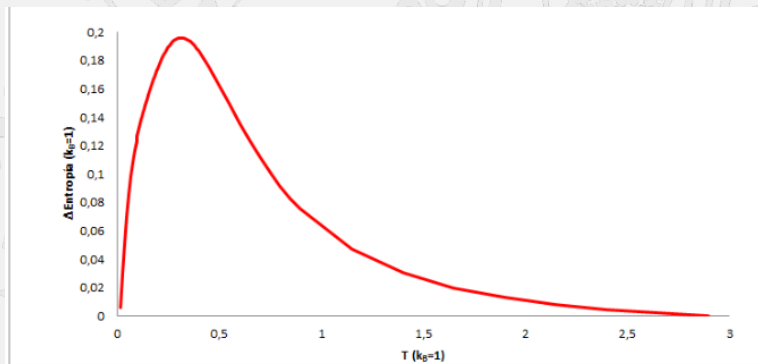
DOI: 10.1103/PhysRevE.91.022137

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

Application II: Definition of hybrid ensembles

Results for few particles

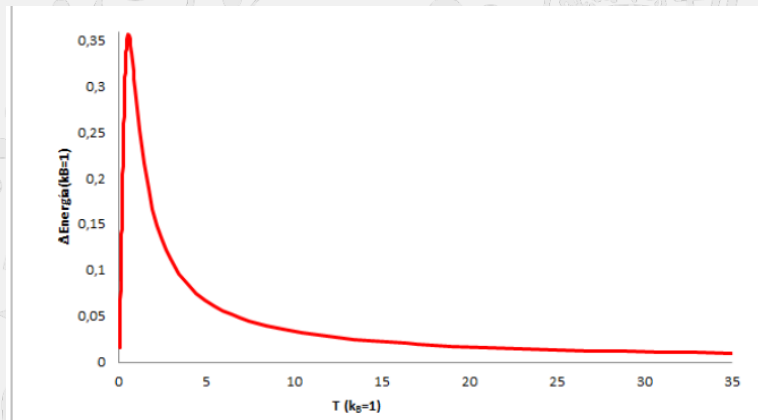
A very simple model with $M_C = \mathbb{R}^2$, $M_Q = \mathbb{C}\mathbb{P}^1$ and $V = 0$ (quantum coupling to the position degrees of freedom in the form $\sqrt{1 + \epsilon \cos \theta} \hat{H}$), where \hat{H} corresponds to a two-level system.



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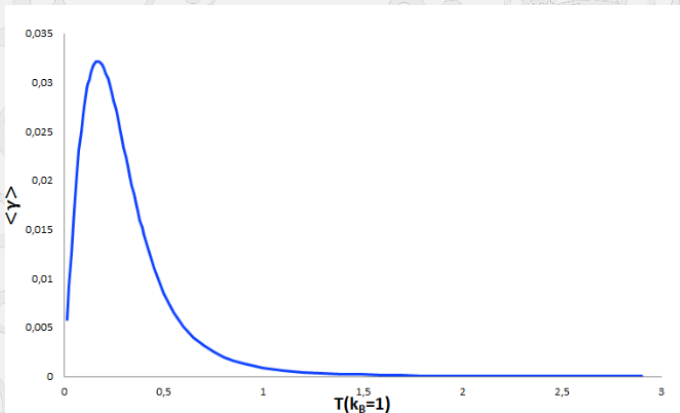
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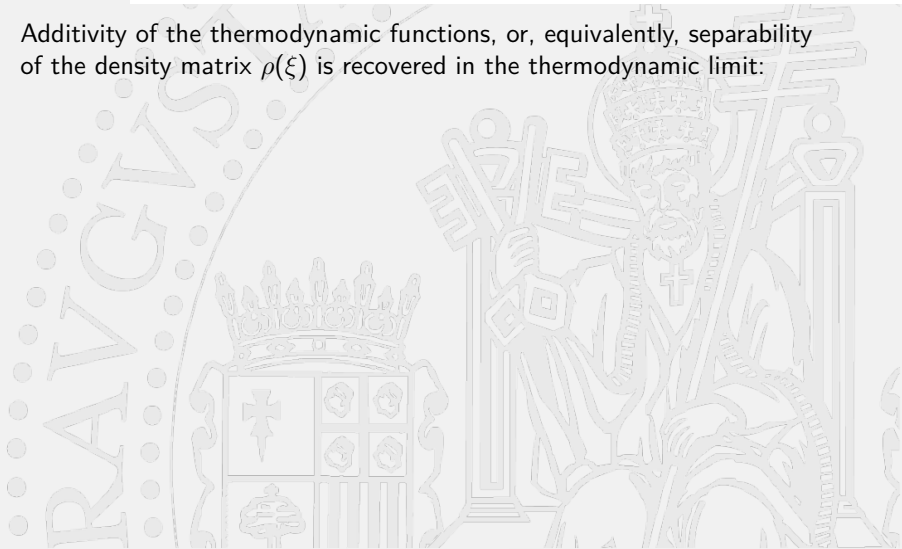
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Thermodynamic limit

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

$$A^\infty = \lim_{N_m \rightarrow \infty} A^{N_m}; \quad (1)$$

and the limit process satisfies that

$$\lim_{N_m \rightarrow \infty} V^{N_m} / N_m \text{ is constant.} \quad (2)$$

Application II: Definition of hybrid ensembles

Thermodynamic limit

Theorem

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

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

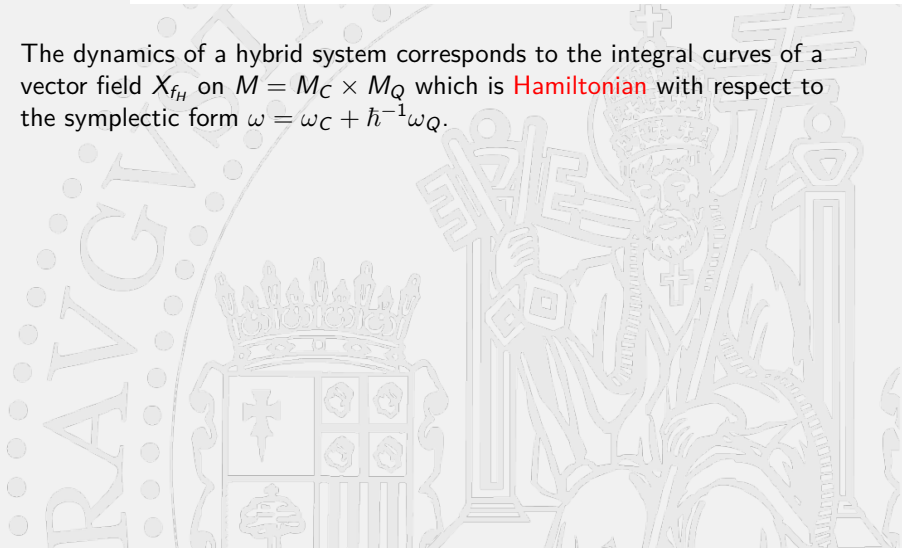
Such an operator is trivially separable at any temperature and leads to additive entropy and energy functions, also at any temperature.

Application III: Control of hybrid ensembles



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

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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.

PRL **109**, 100501 (2012)

PHYSICAL REVIEW LETTERS

week ending
7 SEPTEMBER 2012

Quantum Splines

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(Received 20 June 2012; published 4 September 2012)

A quantum spline is a smooth curve parametrized by time in the space of unitary transformations, whose associated orbit on the space of pure states traverses a designated set of quantum states at designated times, such that the trace norm of the time rate of change of the associated Hamiltonian is minimized. The solution to the quantum spline problem is obtained, and is applied in an example that illustrates quantum control of coherent states. An efficient numerical scheme for computing quantum splines is discussed and implemented in the examples.

DOI: [10.1103/PhysRevLett.109.100501](https://doi.org/10.1103/PhysRevLett.109.100501)

PACS numbers: 03.67.Ac, 02.30.Xx, 02.60.Ed, 42.50.Dv

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International Journal of Geometric Methods in Modern Physics
Vol. 15, No. 9 (2018) 1850147 (22 pages)
© World Scientific Publishing Company
DOI: [10.1142/S0219887818501473](https://doi.org/10.1142/S0219887818501473)



A general framework for quantum splines

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Received 20 December 2017
Accepted 20 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

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

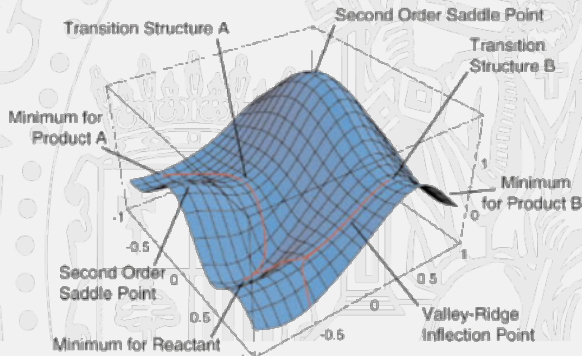
in such a way that the hybrid system driven by the vector field X_{f_H} ($f_H = \sum_i \frac{P_i^2}{2M_i} + V(R_i) + e_{H(t)}$) passes arbitrarily close to the given points at the given times, and minimizes the power injected in the system that can be computed as

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

Application III: Control of hybrid ensembles

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 correspond to local minima of the **Potential Energy Surface (PES)** of the system, parametrized by the classical degrees of freedom of the molecule.



Application III: Control of hybrid ensembles

A toy model of hybrid splines

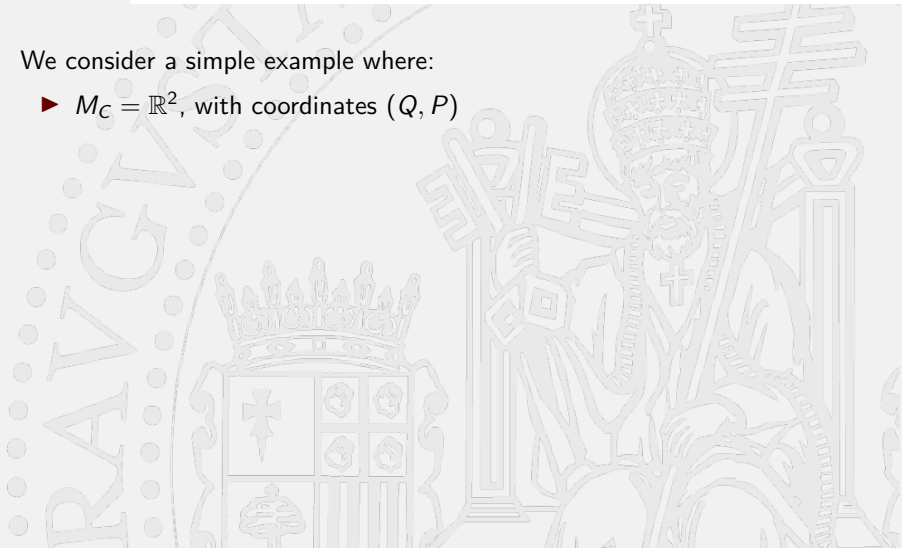
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- ▶ The distance to the target points is defined as the sum of the canonical riemannian distances (classical and quantum).

Preliminary results

Two limiting cases:

Limit of pure classical points

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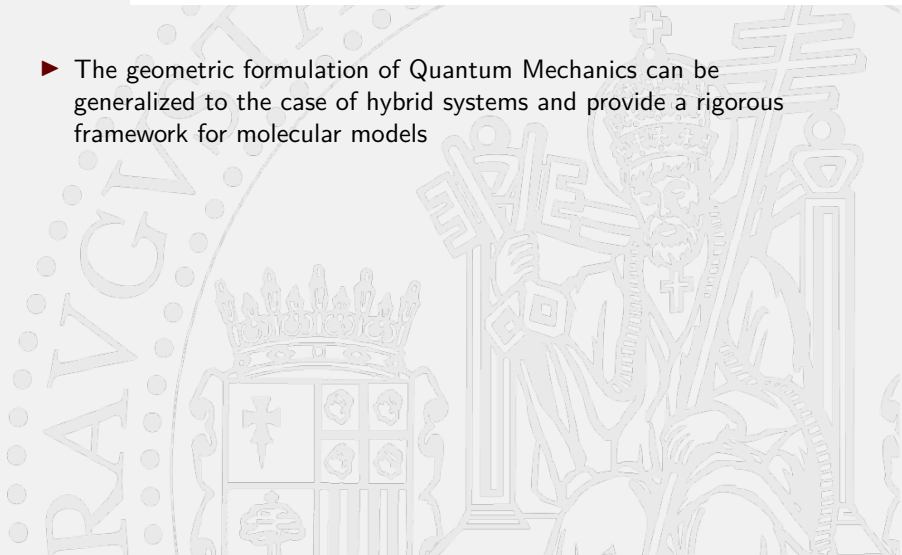
Limit of pure quantum points

Conclusions and Outlook



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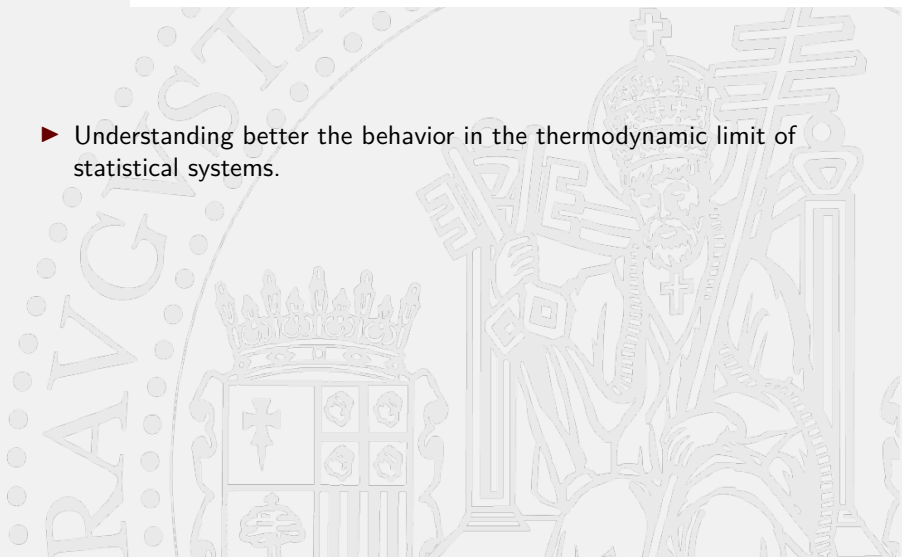
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- ▶ The additivity of thermodynamical functions is a difficult issue that fails for small number of particles, although it is well behaved in the thermodynamic limit. This is relevant when considering computer simulations.
- ▶ The nonlinear molecular dynamics, when considered within (classical) control theory, offers a wide and interesting range of relevant applications and problems.

Outlook

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- ▶ Suggestions? ...

Thanks for your attention :-)

