A geometric formulation of Ehrenfest molecular dynamics

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Introduction: GQM
Introduction: the problem of GQM

General formulation of a physical system

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- A set of observables $O$ containing the possible representations of physical magnitudes in our model
- A way of representing the measurement process, i.e., an application $S \times O \rightarrow \mathbb{R}$ assigning a real number to the measurement of every magnitude on every state.

Is it possible to find a common framework for Classical and Quantum Mechanics?
Introduction: the problem of GQM

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- Besides, if we intend to define a dynamical system, we have to add a differential (difference) equation whose solutions represent the trajectories of the physical system.
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Is it possible to find a common framework for Classical and Quantum Mechanics?
Classical nonrelativistic Hamiltonian system

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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:

$$X_h = \{ h, \cdot \}$$
Nonrelativistic Hamiltonian quantum system (Schrödinger formalism)

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$$S \times \mathcal{O} \ni (\psi, K) \mapsto \frac{\langle \psi | K \psi \rangle}{\langle \psi | \psi \rangle} \in \mathbb{R}$$

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

$$i\hbar \frac{\partial}{\partial t} \lvert \psi(t) \rangle = H \lvert \psi(t) \rangle$$
Nonrelativistic Hamiltonian quantum system (Heisenberg formalism):

- Model is built on the set of physical magnitudes $\mathcal{O}$, which are the real part of a complex $\mathcal{C}^*$-algebra.

- The set of states corresponds to the dual vector space to $\mathcal{O}$, i.e. linear functionals $\rho: \mathcal{O} \to \mathbb{C}$.

- Measurement corresponds to the action of the operator on the state $S \times \mathcal{O} \ni (\rho, K) \mapsto \rho(K) \in \mathbb{R}$.

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Introduction: GQM

Summary of GQM
Geometric Quantum Mechanics

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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.
Introduction: GQM

Geometric Quantum Mechanics
Tensorial description of quantum mechanics

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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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The Ehrenfest picture and the geometry of Quantum Mechanics

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Introduction: GQM

Geometric Quantum Mechanics

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

$$|\psi\rangle = \sum_j z_j |e_j\rangle \mapsto \mathbb{C}^n \ni (z^1, \ldots, z^n) \rightarrow (\text{Re}(z^1), \text{Im}(z^1), \ldots, \text{Re}(z^n), \text{Im}(z^n))$$
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$$|\psi\rangle = \sum_j z_j |e_j\rangle \Longrightarrow \mathbb{C}^n \ni (z^1, \ldots, z^n) \rightarrow (q^1, p_1, \ldots, q^n, p_n) \in \mathbb{R}^{2n} \sim M_Q$$
Physical states I: Hilbert space

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- The set

$$|\psi\rangle = \sum_j z_j |e_j\rangle \implies \mathbb{C}^n \ni (z^1, \ldots, z^n) \rightarrow (q^1, p_1, \ldots, q^n, p_n) \in \mathbb{R}^{2n} \sim M_Q$$

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

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

By using the realification introduced

$$X_{\psi_k} = (X^R_{\psi_k}, X^I_{\psi_k}) \Rightarrow$$

$$h(X_{\psi_1}, X_{\psi_2}) = \left( \left( X^R_{\psi_1} X^R_{\psi_2} \right) + \left( X^I_{\psi_1} X^I_{\psi_2} \right), \left( X^R_{\psi_1} X^I_{\psi_2} \right) - \left( X^I_{\psi_1} X^R_{\psi_2} \right) \right)$$
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$$\langle \psi_1 | \psi_2 \rangle = h(X_{\psi_1}, X_{\psi_2}) \quad X_{\psi_1} = (\psi, \psi_1); X_{\psi_2} = (\psi, \psi_2)$$

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

$$X_{\psi_k} = (X_{\psi_k}^R, X_{\psi_k}^I) \Rightarrow h(X_{\psi_1}, X_{\psi_2}) = (g ((X_{\psi_1}^R, X_{\psi_1}^I), (X_{\psi_2}^R, X_{\psi_2}^I)), \omega ((X_{\psi_1}^R, X_{\psi_1}^I), (X_{\psi_2}^R, X_{\psi_2}^I)))$$
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By using the realification introduced we obtain two tensors which encode the same information

$$h \mapsto \begin{cases} g = \sum_k (dq^k \otimes dq^k + dp_k \otimes dp_k) \\ \omega = \sum_k dq^k \wedge dp_k \end{cases}$$
The complex structure of $\mathcal{H}$ becomes a 1:1 tensor field:

\[ J : TM_Q \times T^* M_Q \rightarrow C^\infty(M_Q); \quad J(X^R_\psi, X^I_\psi) = (-X^I_\psi, X^R_\psi) \]

\[
J = \begin{pmatrix}
0 & -1 & 0 & 0 & \ldots & 0 & 0 \\
1 & 0 & 0 & 0 & \ldots & 0 & 0 \\
& & \ddots & & & & \\
& & & & & & \\
0 & 0 & 0 & 0 & \ldots & 0 & -1 \\
0 & 0 & 0 & 0 & \ldots & 1 & 0 \\
\end{pmatrix}
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\end{pmatrix}$$

**Theorem**

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

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

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

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:

$|\psi_1\rangle, |\psi_2\rangle \in H_0 = H - \{\vec{0}\}

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

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

$|\psi\rangle \cong |\psi\rangle \langle \psi| \langle \psi|$
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$[\psi] \simeq \frac{|\psi\rangle\langle\psi|}{\langle\psi|\psi\rangle}.$
Question: How can we construct this object from $M_Q$?
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Consider two vector fields on $M_Q$:
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Consider two vector fields on $M_Q$:

$$\Delta = \sum_k (q_k \frac{\partial}{\partial q_k} + p_k \frac{\partial}{\partial p_k})$$

Dilations $\Gamma = J(\Delta) = \sum_k (q_k \frac{\partial}{\partial p_k} - q_k \frac{\partial}{\partial p_k})$

Global phase change

Lemma $\Delta y \Gamma$ define an integrable distribution on $M_Q$, and hence a foliation $P$.

This foliation is the geometric analogue of $PH$.

We thus have a projection $\pi: M_Q \rightarrow P$.

But tensors $G$ and $\Omega$ can not be projected directly:

$$L_\Delta G = -2G$$

$$L_\Delta \Omega = -2\Omega$$

Solution:

$$G_P = \langle \psi | \psi \rangle G - \Delta \otimes \Delta - \Gamma \otimes \Gamma \Omega_P = \langle \psi | \psi \rangle \Omega - (\Delta \otimes \Gamma - \Gamma \otimes \Delta)$$
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**dilations**

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**global phase change**

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global phase change

Lemma

$\Delta$ and $\Gamma$ define an integrable distribution on $M_Q$, and hence a foliation $\mathcal{P}$. This foliation is the geometric analogue of $\mathcal{P}H$. 

Solution:

$$
G_{\mathcal{P}} = \langle \psi | \psi \rangle
$$

$$
G_{\Delta} \otimes \Delta - \Gamma \otimes \Gamma \Omega_{\mathcal{P}} = \langle \psi | \psi \rangle \Omega_{\mathcal{P}} - (\Delta \otimes \Gamma - \Gamma \otimes \Delta)
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\mathcal{L}_\Delta G = -2G \quad \mathcal{L}_\Delta \Omega = -2\Omega.
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**Solution:**

\[
G_\mathcal{P} = \langle \psi | \psi \rangle G - \Delta \otimes \Delta - \Gamma \otimes \Gamma \quad \Omega_\mathcal{P} = \langle \psi | \psi \rangle \Omega - (\Delta \otimes \Gamma - \Gamma \otimes \Delta)
\]
Let us consider the sesquilinear forms defined on $M_Q$:

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

We shall denote as $\mathcal{F}_2(M_Q)$ the set of those functions.
Let us consider the sesquilinear forms defined on $M_Q$:

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

We shall denote as $\mathcal{F}_2(M_Q)$ the set of those functions.
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:
  
  \[ A, B \mapsto AB \]

- 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 $\Omega$ 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 recover the commutator:
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On $\text{End}(\mathcal{H})$ we have three algebraic structures:

- The associative product:
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Introduction: GQM

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

- **Associative product**
  \[ f_{AB} = \frac{1}{2} G(df_A, df_B) + \frac{i}{2} \Omega(df_A, df_B) \]

- $G$ recovers the anti-commutator of the operators
  \[ G(df_A, df_B) = f_{A \circ B} := \{ f_A, f_B \} + \]

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

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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

$$e_A(\vec{q}, \vec{p}) = \frac{\langle \psi(\vec{q}, \vec{p}) | A \psi(\vec{q}, \vec{p}) \rangle}{\langle \psi(\vec{q}, \vec{p}) | \psi(\vec{q}, \vec{p}) \rangle}$$
Question: If we consider the system defined on the projective space $P$, how can we represent the observables?

- **Expectation values**

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

- **Dispersions:**

$$\Delta A = \frac{\langle \psi(q, p) | A^2 \psi(q, p) \rangle}{\langle \psi(q, p) | \psi(q, p) \rangle} - \left( \frac{\langle \psi(\bar{q}, \bar{p}) | A \psi(\bar{q}, \bar{p}) \rangle}{\langle \psi(\bar{q}, \bar{p}) | \psi(\bar{q}, \bar{p}) \rangle} \right)^2 = e_A^2(\psi) - e_A(\psi)^2 = G_P(de_A, de_A)$$
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 $\psi_*$
- $e_A(\psi_*) = \lambda$
Let us denote as $\mathcal{E}(MQ)$ 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 $\psi_*$
- $e_A(\psi_*) = \lambda$

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

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

Summary

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

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

GQM
- $S = (M_Q, G, \Omega)$ or $S = (\mathcal{P}, G_P, \Omega_P)$
- $\mathcal{O} = \mathcal{F}_2(M_Q)$ or $\mathcal{E}(M_Q)$
- $f_A(\psi)$ or $e_A(\psi)$
Introduction: GQM

How can we define the dynamics

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- We consider the function $f_H \in \mathcal{F}_2(M_Q)$ or $e_H \in \mathcal{E}(M_Q)$
How can we define the dynamics

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 $\Omega$ or $\Omega_P$) por $\Omega$:

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

- 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
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 \(\mathcal{H}\).
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 \(\mathcal{H}\).
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.

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

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

- 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 $\epsilon$).

Then, it can be proved that:

**Theorem**

*The error of considering the evolution $\Psi(t)$ as a separable state is of order $\epsilon/L$, where $L$ is the natural length of the system.*
By using WKB method, the nuclear wave function can be written as

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

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 \((\frac{\epsilon}{L})^2 + \sqrt{m/M})\).
Dynamics: Ehrenfest equations \((\vec{R}, \vec{P}) \in M_C \text{ and } |\psi\rangle \in \mathcal{H},\) 
\(H_e(\vec{R}) \in \text{Herm}(\mathcal{H}))\)

\[
\begin{align*}
\dot{\vec{R}}^k &= \frac{P^k}{M_k} \\
\dot{P}_k &= -\text{grad}_\vec{R}\langle \psi | H_e(\vec{R}) \psi \rangle \\
i\hbar \frac{d|\psi(t)\rangle}{dt} &= H_e(\vec{R})|\psi(t)\rangle
\end{align*}
\]
Dynamics: Ehrenfest equations ( $(\vec{R}, \vec{P}) \in M_C$ and $|\psi\rangle \in \mathcal{H}$, $H_e(\vec{R}) \in \text{Herm}(\mathcal{H})$)

$$\dot{R}^k = \frac{P^k}{M_k}$$
$$\dot{P}_k = -\text{grad}_\vec{R} \langle \psi | H_e(\vec{R}) \psi \rangle$$
$$i\hbar \frac{d |\psi(t)\rangle}{dt} = H_e(\vec{R}) |\psi(t)\rangle$$

Question: Is it possible to identify a Hamiltonian structure for these equations?
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.
Characterizing the hybrid system

The quantum subsystem is assumed to be finite dimensional. The space of states is $S = M_C \times M_Q$. The set of physical magnitudes is $O = C_\infty(M_C \times M_Q)$. We define a symplectic structure as $\omega = \omega_C + \hbar \omega_Q$. And a Hamiltonian function written as $f_H(\vec{R}, \vec{P}, \vec{q}, \vec{p}) = \sum_k P_k^2 M_k + \langle \psi | H e(R) | \psi \rangle \langle \psi | \psi \rangle$.

Theorem

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

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: $\mu = \omega \dim(M_C \times M_Q)$.
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- And a Hamiltonian function written as
  \[
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**Corollary**

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
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

$$\int_{M} d\mu_{QC}(\xi, \psi)F_{QC}(\xi, \psi) = 1, \quad F_{QC}(\xi, \psi) \geq 0, \quad \forall \xi \in M_C, \psi \in M_Q.$$
Application I: Ehrenfest Statistical Models and Decoherence

Statistical mechanical system

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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*
**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

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

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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 $F_{GQ}(\xi, \psi; t)d\mu(\xi, \psi)$:

$$\langle A \rangle(t) = \int_M d\mu_{QC}(\xi, \psi) F_{QC}(\xi, \psi; t)f_A(\xi, \psi),$$
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, \( \hat{\rho}(\xi) \) is self-adjoint, positive definite, and normalized as

\[ \int_{\mathcal{M}_c} d\mu(\xi) \text{Tr} \hat{\rho}(\xi) = 1 \]
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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

$$\int_{\mathcal{M}_C} d\mu(\xi) \text{Tr}(\hat{\rho}(\xi)\hat{A}(\xi)) = 1.$$
The solution of the dynamical equation allows us to write the expression of the dynamics for the matrix $\hat{\rho}(\xi)$:

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

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

**Definition**

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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\hat{\rho}(t) := \int_{M_C} d\mu_C(\xi) \hat{\rho}(\xi; t)
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This construction is formally analogous to the usual partial trace method for the contraction of a quantum system.
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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.
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.

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]
Ehrenfest Statistical Dynamics in Chemistry: Study of Decoherence Effects


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Abstract

Purity

ED

Time

ESD
Application II: Definition of hybrid ensembles
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
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

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

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

- the classical subsystem is the Cartesian product of the classical subsystems:
  \[ M_C = M^1_C \times M^2_C; \]
- the set of quantum states of the product system corresponds to the projective space of the tensor product space
  \[ M_Q = M^1_Q \otimes M^2_Q. \]
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 $H \otimes \cdots \otimes H$ ($H$ 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:
Application II: Definition of hybrid ensembles

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$$\hat{H}(\xi) = \sum_{k=1}^{N_m} \hat{H}_k(\vec{\xi}_k) = \sum_{k=1}^{N_m} \hat{I}_\mathcal{H} \otimes \cdots \otimes \hat{I}_\mathcal{H} \otimes \hat{h}(\vec{\xi}_k) \otimes \hat{I}_\mathcal{H} \otimes \cdots \otimes \hat{I}_\mathcal{H},$$
Application II: Definition of hybrid ensembles

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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 $\hat{I}_H$ 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

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\]

**Definition**

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

\[
U = \langle f_H \rangle = \int_{M_C} d\mu_C(\xi) \text{Tr}(\hat{\rho}(\xi)\hat{H}(\xi))
\]
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.
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 mutually exclusiveness of the set of events.

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 \(\xi\), 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 \( \xi \), in order to define consistently the entropy of the hybrid system, we must consider:

**Definition**

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

\[
S = -k_B \int_{M_C} \mu_C(\xi) S(\xi),
\]

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

\[
S(\xi) = \text{Tr}(\hat{\rho}(\xi) \log \hat{\rho}(\xi)).
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Hybrid ensembles: definition

Generally speaking, any thermodynamic equilibrium (quantum, classical or hybrid quantum/classical) requires two conditions:
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- and associated thermodynamic functions (such as entropy and internal energy) that are extensive.
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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.
Consider the total phase space of the hybrid system $M = M_C \times M_Q$ and the energy function

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

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.,

$$\mathcal{F}_MC_Q(\xi, \psi) = \delta(E - f_H(\xi, \psi))$$

$V_E$ represents the total volume of the level set of the energy with value $E$. 
Consider the total phase space of the hybrid system \( M = M_C \times M_Q \) and the energy function

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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.

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

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:

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

where
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:

\[
F_{QC}^C(\xi, \psi) = Z_{HCE}^{-1} e^{-\beta f_H(\xi, \psi)},
\]

where

\[
Z_{HCE} = \int_M d\mu_{QC}(\xi, \psi) e^{-\beta f_H(\xi, \psi)}.
\]

and

\[
f_H = \sum_k \frac{P_k^2}{2M_k} + V(R) + e_H(R, P, \psi).
\]
Application II: Definition of hybrid ensembles

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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The quantum canonical ensemble

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The phase space $\Gamma$ of quantum mechanics can be viewed as the complex projective space $\mathbb{CP}^n$ 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 $\Gamma$. 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 $\Gamma$-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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Quantum fluctuation relations for ensembles of wave functions

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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.
Results for few particles

A very simple model with $M_C = \mathbb{R}^2$, $M_Q = \mathbb{C}P^1$ 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.
Application II: Definition of hybrid ensembles

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Application II: Definition of hybrid ensembles

Thermodynamic limit

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

**Definition**

Consider a family of models, each defined on a phase space of the form \( M^N_m \times M^N_m \), 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 \( A^\infty \) is the thermodynamic limit of the magnitude \( A \) if

\[
A^\infty = \lim_{N_m \to \infty} A^N_m;
\]  

(1)

and the limit process satisfies that

\[
\lim_{N_m \to \infty} \frac{V^N_m}{N_m} \text{ is constant.}
\]  

(2)
Theorem

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

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

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
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 $\omega = \omega_C + \hbar^{-1}\omega_Q$. 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 $X = X_{f_H} + \sum_i u_i(t) X_{C_i}$.

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.
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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Application III: Control of hybrid ensembles

Control of hybrid systems: hybrid splines

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Problem

Given a set of \( k \) points in the hybrid phase space \( M = M_C \times M_Q \) and a set of times \( \{t_j\}_{j=1,\ldots,k} \), 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 correspond to local minima of the Potential Energy Surface (PES) of the system, parametrized by the classical degrees of freedom of the molecules.
Application III: Control of hybrid ensembles

A toy model of hybrid splines

We consider a simple example where:

$$M_C = \mathbb{R}^2$$, with coordinates $$(Q, P)$$

$$M_Q = CP_1$$. We will use the representation as orthogonal projectors on one-dimensional subspaces of $$\mathbb{C}^2$$ (i.e., pure density matrices $$\rho$$)

We consider as energy function $$f_{H} = P^2 + Q^2 + Q^* \text{Tr}(\rho_H)$$ and $$H$$ is the quantum-Hamiltonian whose time-dependence must be determined.

The distance to the target points is defined as the sum of the canonical riemannian distances (classical and quantum).
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Application III: Control of hybrid ensembles

Preliminary results

Two limiting cases:

Limit of pure classical points
Application III: Control of hybrid ensembles

Preliminary results

Two limiting cases:

Limit of pure quantum points
Conclusions and Outlook
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- 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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Conclusions and Outlook

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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.
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.
Outlook

- Understanding better the behavior in the thermodynamic limit of statistical systems.
- Study in detail the notion of controllability of hybrid systems and the applications of the notion of hybrid splines in Chemistry.
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Thanks for your attention :-)