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Mathematical Methods in Quantum Molecular Dynamics

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Abstract. This report summarizes the 2015 Oberwolfach meeting on mathematical methods in quantum molecular dynamics. Over decades this field has hosted considerable research activity from different disciplines, such as mathematics, chemistry, and physics. The workshop has aimed at bringing together these scientists for mutual benefit.

Mathematics Subject Classification (2010): 82C10.

Introduction by the Organisers

The field of quantum molecular dynamics hosts considerable research activity from different disciplines, such as mathematics, chemistry, and physics. Within these disciplines, powerful mathematical methods have been developed. However, interdisciplinary communication in the field is scarce. Scientists in different disciplines frequently fail to talk to one another and often use different language to mean the same thing. The workshop has aimed at bringing together mathematicians and other scientists in the field for mutual benefit.

In molecular quantum mechanics, one studies systems that have electrons (typically taken to have mass 1) and nuclei that have much larger masses (typically with masses of several thousand or tens of thousands in the same units). In most practical instances, these discrepancies of mass allow one to do an approximate separation of variables when solving the associated Schrödinger equation. This separation of electronic and nuclear motions is usually referred to as a Born–Oppenheimer approximation.

Even when one can use a Born–Oppenheimer approximation, there are serious issues in solving problems of quantum molecular dynamics. One such issue is the "curse of dimension." The time–dependent Schrödinger equation for the nuclei involves $3N$ space dimensions if there are N nuclei whose motion is to be studied. Often this is done numerically, but most numerical approximations have been developed for only a few dimensions, instead of perhaps 12, 15, 18, or more. Several of the speakers in this Workshop (such as Irene Burghardt, Tucker Carrington, Christian Lubich, and Uwe Manthe) directly addressed this problem. Several others (such as Francis Nier, Johannes Keller, Emil Kieri, Giovanni Ciccotti, Sara Bonella, and Anders Szepessy) discussed alternative approximations for addressing the difficulties of computing quantum nuclear motion.

Another issue that has gotten mathematical attention in recent years is the failure of Born–Oppenheimer approximations near level crossings or avoided crossings of electron energy levels that cause relevant nonadiabatic transitions. Several speakers mentioned this problem (such as Jeremy Richardson), and the presentation by Benjamin Goddard was specifically on this topic.

A few speakers in this Workshop (such as Pierre Rouchon, Raymond Kapral, Ben Leihmkuhler, and Stefan Teufel) talked about molecules interacting with a larger environment. This situation occurs, for example, for molecules in a solution, and clearly asks for new mathematical methods.

Several speakers (such as Peter Gill, François Gygi, David Gontier, Mathieu Lewin, Simen Kvaal, and Rupert Klein) discussed electronic states in molecules.

Other speakers addressed related issues or presented alternative approximations and techniques for studying electrons and/or nuclei in molecules. These ranged from topological (Gianluca Panati) and numerical topics (Erwan Faou), to asymptotic analysis and stability theory (Clotilde Fermanian and Anthony Bloch), to quantum computing (Mazyar Mirrahimi) and to alternative approaches to standard quantum mechanics (Bill Poirier).

The 28 talks of the Workshop were held by scientists representing a wide variety of disciplines all with strong interest in molecular quantum mechanics. This diversity of people and backgrounds led to interesting, wide–ranging discussions.

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Workshop: Mathematical Methods in Quantum Molecular Dynamics

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Abstracts

Semiclassical approximations of quantum mechanical equilibrium distributions

Stefan Teufel

(joint work with Wolfgang Gaim)

In his seminal paper from 1932 Eugene Wigner computes what he call the "Quantum correction for thermodynamic equilibrium". In modern language he shows how to obtain an asymptotic expansion in powers of the semiclassical parameter for certain equilibrium expectation values. More precisely, let $h : \mathbb{R}^{2n} \to \mathbb{R}$, $(q,p) \mapsto h(q,p) = \frac{1}{2}p^2 + V(q)$ be the Hamiltonian function and $h^\varepsilon := -\frac{\varepsilon^2}{2}\Delta + V(x)$ the corresponding Schrödinger operator acting on $L^2(\mathbb{R}^n)$, then he gives an explicit expression for the subleading term $c(q,p)$ in

$$\mathrm{Tr}\left(\hat{a}^\varepsilon \, \mathrm{e}^{-\beta \hat{h}^\varepsilon}\right) = \frac{1}{(2\pi\varepsilon)^n} \int_{\mathbb{R}^{2n}} a(q,p) \, \mathrm{e}^{-\beta h(q,p)} \, \left(1 + \varepsilon^2 c(q,p) + \mathcal{O}(\varepsilon^3)\right) \, \mathrm{d}q\mathrm{d}p \, .$$

Here $a : \mathbb{R}^{2n} \to \mathbb{R}$ and $\hat{a}^\varepsilon$ "=" $a(x, \mathrm{i}\varepsilon\nabla_x)$ its Weyl quantization.

We answer a similar question for the case when only some degrees of freedom in a quantum system behave semiclassical, as it happens for example in molecular systems. Such systems are described by Hamiltonians with matrix- or operator-valued symbols:

$$H : \mathbb{R}^{2n} \to \mathcal{L}_{\mathrm{sa}}(\mathcal{H}_{\mathrm{f}}) \, , \quad \hat{H}^\varepsilon = H(x, -\mathrm{i}\varepsilon\nabla_x) \in \mathcal{L}_{\mathrm{sa}}(L^2(\mathbb{R}^n, \mathcal{H}_{\mathrm{f}})) \, .$$

For example, the Hamiltonian describing a molecule has the form

$$\hat{H}^\varepsilon = -\tfrac{\varepsilon^2}{2}\Delta_x \underbrace{-\tfrac{1}{2}\Delta_y + V(x,y)}_{H_{\mathrm{el}}(x)}$$

with $\varepsilon^2 = \frac{1}{M}$ and operator valued symbol

$$H(q,p) = \tfrac{1}{2}|p|^2 + H_{\mathrm{el}}(q) \quad \in \mathcal{L}_{\mathrm{sa}}(L^2(\mathbb{R}^m_y)) \, .$$

Let $e(x)$ be an isolated eigenvalue of $H_{\mathrm{el}}(x)$,

$$H_{\mathrm{el}}(x) \, P_0(x) = e(x) \, P_0(x) \, ,$$

and $P_0(x)$ the corresponding spectral projection. Then the restriction of $\hat{H}^\varepsilon$ to the range of P_0 is

$$P_0 \hat{H}^\varepsilon P_0 = P_0 \left(-\tfrac{\varepsilon^2}{2}\Delta_x + H_{\mathrm{el}}(x)\right) P_0 = P_0 \left(-\tfrac{\varepsilon^2}{2}\Delta_x + e(x)\right) P_0 = P_0 \hat{h}^\varepsilon P_0$$

with $\hat{h}^\varepsilon = h_0(x, -\mathrm{i}\varepsilon\nabla_x)$ for

$$h_0(q,p) = \tfrac{1}{2}|p|^2 + e(q)$$

being again the quantization of a "classical" Hamiltonian function. One would expect and it follows from our results that indeed

$$\mathrm{Tr}\left(\hat{a}^\varepsilon\, f(\hat{H}^\varepsilon)\, P_0\right) = \frac{1}{(2\pi\varepsilon)^n}\int_{\mathbb{R}^{2n}} \mathrm{d}q\mathrm{d}p\; a(q,p)\, f(h_0(q,p))\;\; (1+\mathcal{O}(\varepsilon)) \tag{1}$$

with

$$h_0(q,p) = \tfrac{1}{2}|p|^2 + e(q)\,.$$

Here

$$\mathrm{Ran}P_0 = \{\Psi(x,y)\,|\,\Psi(x,\cdot)\in \mathrm{Ran}P_0(x)\}\,.$$

However, one can ask whether the left hand side of (1) is really the right quantity to compute and, in the sense of Wigner, what the higher order corrections are? The answer to the first questions is basically well understood, also for more general systems where $e(q,p)$ is an isolated eigenvalue of an operator valued symbol $H(q,p)$, i.e. $H(q,p)P_0(q,p) = e(q,p)P_0(q,p)$ (see [2] for an overview). While for $\hat{P}_0^\varepsilon$ one only has

$$\hat{H}^\varepsilon = \hat{P}_0^\varepsilon \hat{H}^\varepsilon \hat{P}_0^\varepsilon + (1-\hat{P}_0^\varepsilon)\hat{H}^\varepsilon(1-\hat{P}_0^\varepsilon) + \mathcal{O}(\varepsilon)\,,$$

under suitable technical conditions there are slightly tilted projections P^ε with symbol

$$P(q,p) = P_0(q) + \mathcal{O}(\varepsilon)$$

such that

$$\hat{H}^\varepsilon = \hat{P}^\varepsilon \hat{H}^\varepsilon \hat{P}^\varepsilon + (1-\hat{P}^\varepsilon)\hat{H}^\varepsilon(1-\hat{P}^\varepsilon) + \mathcal{O}(\varepsilon^\infty)\,.$$

Hence the range of $\hat{P}^\varepsilon$ is an almost invariant subspace for $\hat{H}^\varepsilon$. The following theorem shows that one can compute semiclassical expectations restricted to such almost invariant subspaces completely in terms of a modified classical Hamiltonian system. Let the modified classical Hamiltonian be

$$h^\varepsilon(q,p) = e(q) + \varepsilon\tfrac{\mathrm{i}}{2}\,\mathrm{tr}_{\mathcal{H}_\mathrm{f}}\{P_0|H|P_0\} =: e(q,p) + \varepsilon m(q,p)$$

and the modified symplectic form

$$\sigma_{ij}^\varepsilon := \sigma_{ij}^0 - \mathrm{i}\,\varepsilon\,\mathrm{tr}_{\mathcal{H}_\mathrm{f}}\left(P_0[\partial_i P_0, \partial_j P_0]\right)$$

with corresponding Liouville measure λ^ε.

Theorem 1: (Stiepan, Teufel [3]) Under suitable conditions it holds that

$$\mathrm{Tr}\left(\hat{a}^\varepsilon\, f(\hat{H}^\varepsilon)\, \hat{P}^\varepsilon\right) = \frac{1}{(2\pi\varepsilon)^n}\left(\int_{\mathbb{R}^{2n}} \mathrm{d}\lambda^\varepsilon\; a(q,p)\, f(h^\varepsilon(q,p)) \;+\; \mathcal{O}(\varepsilon^2\|a\|_{L^1})\right)$$

In an upcoming work with Wolfgang Gaim we show that there is also at next order approximation an underlying classical Hamiltonian system.

Theorem 2: (Gaim, Teufel [4]) Under suitable technical conditions it holds that

$$\mathrm{Tr}\left(\hat{a}^\varepsilon\, f(\hat{H}^\varepsilon)\, \hat{P}^\varepsilon\right) = \frac{1}{(2\pi\varepsilon)^n}\left(\int_{\mathbb{R}^{2n}} \mathrm{d}\lambda^\varepsilon\; a(q,p)\, f^\varepsilon(q,p) \;+\; \mathcal{O}(\varepsilon^3\|a\|_{L^1})\right)\,,$$

where

$$f^\varepsilon = f\circ h^\varepsilon + \varepsilon^2\left(f_2^{\mathrm{Wigner}}(e) + f_2^{\mathrm{adi}}(e,P_0)\right)$$

with

$$h^\varepsilon(q,p) = e(q,p) + \varepsilon m_1(q,p) + \varepsilon^2 m_2(q,p)$$

and

$$\mathrm{d}\lambda^\varepsilon = \Big(1 + \varepsilon\, \lambda_1(q,p) + \varepsilon^2 \lambda_2(q,p)\Big)\mathrm{d}q\,\mathrm{d}p$$

the Liouville measure of a symplectic form with second order corrections.

For the corrections to the standard Born-Oppenheimer approximation one finds for example

$$h^\varepsilon(q,p) = \tfrac{1}{2}|p|^2 + e(q) + \varepsilon^2 \left(\langle p, C(q)p\rangle_{\mathbb{C}^n} + \tfrac{1}{2}\mathrm{tr}_{\mathbb{C}^n}\big(D(q)\big)\right)\,,$$

$$\mathrm{d}\lambda^\varepsilon = \Big(1 + 2\,\varepsilon^2\,\mathrm{tr}_{\mathbb{C}^n}\big(C(q)\big)\Big)\mathrm{d}q\,\mathrm{d}p\,,$$

and

$$f_2^{\mathrm{adi}}(q,p) = f''\big(h_0(q,p)\big)\,\langle p, D(q)p\rangle_{\mathbb{C}^n}\,,$$

with

$$C_{ij}(q) = \mathrm{tr}_{\mathcal{H}_\mathrm{f}}\Big(\partial_i P_0(q)\,\big(H_\mathrm{el}(q) - e(q)\big)^{-1}\,\partial_j P_0(q)\Big)$$

and

$$D_{ij}(q) = \mathrm{tr}_{\mathcal{H}_\mathrm{f}}\Big(P_0(q)\,\partial_i P_0(q)\,\partial_j P_0(q)\Big)\,.$$

We find similar higher order approximations in terms of the modified classical system also for the Heisenberg time-evolution of semiclassical observables.

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Variational Multiconfigurational Quantum Dynamics Using Moving Gaussian Basis Sets

Irene Burghardt

(joint work with Sarah Römer, Matthias Ruckenbauer, Pierre Eisenbrandt)

In this contribution, we review the current status and prospects of the Gaussian-based Multiconfiguration Time-Dependent Hartree (G-MCTDH) method [1, 2, 3], with particular emphasis on recently developed two-layer and multi-layer variants [4] as well as multiconfigurational quantum-classical hybrid schemes [5].

The solution of the time-dependent Schrödinger equation using Gaussian wavepackets (GWPs) goes back to Heller [6, 7] and Hagedorn [8] and was later extended to a variational treatment involving superpositions of GWPs by Metiu and collaborators [9]. In the latter case, a non-classical evolution of coupled GWPs results from the application of the Dirac-Frenkel time-dependent variational principle to a parametrized wavefunction [10, 11, 12]. Both "thawed" Gaussians (TGs)

[6, 9], with a flexible width, and "frozen" Gaussians (FGs), with a fixed width [7], are accommodated in this framework. While the approach of Ref. [9] carries over straightforwardly to multi-dimensional GWPs, an unfavorable scaling with dimensionality results due to the nonclassically coupled, "entangled" GWP evolution [13, 14].

For high-dimensional systems it is therefore advantageous to use a multiconfigurational, tensor product wavefunction form, in line with the multiconfiguration time-dependent Hartree (MCTDH) [15, 16] approach. Thus, the Gaussian-based multiconfiguration time-dependent Hartree (G-MCTDH) method [1, 2, 3] involves a variational, non-classical evolution of coupled GWPs propagated in subspaces under the effect of time-dependent mean-field Hamiltonians. This method interpolates between the standard MCTDH scheme and more approximate approaches based upon classically evolving Gaussian basis sets. Further, hybrid representations can be straighforwardly chosen that mix subspaces composed of GWPs vs. standard MCTDH single-particle functions (SPFs). Indeed, the original version of the G-MCTDH method was formulated as a hybrid scheme tailored to unitary system-bath dynamics in many dimensions [1]. A closely related method is the Local Coherent States Approximation (LCSA) by Martinazzo and collaborators [17].

Besides system-bath type situations, an important area of application is *on-the-fly* dynamics in conjunction with ground-state or excited-state electronic structure calculations [14, 18, 19]. Here, the so-called variational multi-configurational Gaussian (vMCG) variant [14, 18] has been employed, where all degrees of freedom are grouped together in high-dimensional GWP particles. This facilitates the correspondence with the configuration space points where electronic structure calculations are carried out, at the expense of unfavorable scaling of the GWP dynamics.

Even though good performance and convergence properties have been achieved to date for the G-MCTDH approach for medium-sized systems, a significantly larger number of GWP functions may be required as compared with the fully flexible basis sets of the MCTDH method, especially if multidimensional FG type GWPs are employed. A remedy is provided by a recently developed two- (and multi-)layer version of the G-MCTDH method which effectively reintroduces flexibility into FG basis sets [4]. Since the first layer(s) consist of MCTDH-like, orthogonal SPFs, this approach can be straightforwardly combined with existing multi-layer MCTDH schemes [20, 21, 22].

In this talk, first applications of the two-layer approach are demonstrated for a model of site-to-site vibrational energy flow in the presence of intrasite vibrational energy redistribution, as well as for nonadiabatically coupled systems. These results are promising and suggest that the multi-layer variant will significantly extend the scope of multiconfigurational GWP-based methods.

Following up on Hagedorn's work on the classical limit of GWP dynamics [23, 24], we further consider a variational, multiconfigurational formulation of quantum-classical dynamics [5], based upon a classical-limit G-MCTDH wavefunction. Using semiclassically scaled GWPs, a multiconfigurational Ehrenfest dynamics is obtained (see also Ref. [25] for a related development). Contrary to standard Ehrenfest dynamics, the multiconfigurational approach accounts for correlations between the quantum and classical subspaces and leads to a consistent quantum-classical description.

Overall, we anticipate that hierarchical hybrid schemes involving fully variational and classical GWP evolution in different subspaces will prove versatile tools in future developments of high-dimensional quantum dynamics.

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A phase-space approach to bosonic quantum mean field dynamics

Francis Nier

(joint work with Zied Ammari)

In a series of articles with Zied Ammari, we developed a phase space approach to bosonic mean field problems, inspired by former works of Berezin, Hepp, Kree and the development around the 1990's of semiclassical or Wigner measures (Shnirelman, Colin de Verdière, Helffer-Martinez-Robert, Gérard-Markowick-Mauser-Poupaud, Lions-Paul...). A rather comprehensive list of references, related to this point of view or other recent works about mean field problems can be found in the articles.

As a starting point, semiclassical Canonical Commutation Relations can be written:

$$[a(g), a^*(f)] = 2h\langle g\,,\, f\rangle_Z = \varepsilon\langle g, f\rangle_Z$$

where $\langle\ ,\ \rangle_Z$ denotes the hermitian scalar product on the one particle Hilbert space Z, h or ε is a small parameter, and $a(g)$ and $a^*(f)$ are the annihilation and creation operators on the bosonic Fock space $\mathcal{H} = \oplus_{n\in\mathbb{N}} Z^{\otimes_{sym} N}$.

The mean field problem is reduced to the asymptotics $\varepsilon = 1/N$ where N is the number of particles, and therefore coincides formally with a semiclassical asymptotics $(h \to 0)$.

As an example the N-body problem

$$i\partial_t \Psi = \left[-\sum_{i=1}^{N} \Delta_{x_j} + \frac{1}{2N}\sum_{i,j} V(x_i - x_j) \right] \Psi$$

can be written

$$\frac{i}{N}\partial_t \Psi = \left[-\frac{1}{N}\sum_{i=1}^{N} \Delta_{x_j} + \frac{1}{2N^2}\sum_{i,j} V(x_i - x_j) \right] \Psi \,.$$

When $\Psi \in L^2(\mathbb{R}^d;\mathbb{C})^{\otimes_{sym} N} = Z^{\otimes_{sym} N}$ is a N-particle wave functions and $V(x) = V(-x)$, it can be rewritten with $\varepsilon = \frac{1}{N}$:

$$i\varepsilon\partial_t \Psi = H^\varepsilon \Psi \,,$$

where

$$H^\varepsilon = \int_{\mathbb{R}^d} \nabla a^*(x) \nabla a(x) \; dx + \frac{1}{2}\int_{\mathbb{R}^{2d}} V(x-y) a^*(y) a^*(x) a(y) a(x) \; dxdy \,,$$

is the Wick quantization of the energy

$$\mathcal{E}(z) = \int_{\mathbb{R}^d} |\nabla z(x)|^2 \; dx + \frac{1}{2}\int_{\mathbb{R}^{2d}} V(x-y) a^*(y) |z(x)|^2 |z(y)|^2 \; dxdy \,,$$

The mean field dynamics is then given by the Hartree equation

$$i\partial_t z = -\Delta z + (V * |z|^2) z = \partial_{\bar{z}} \mathcal{E} \,,$$

which is exactly the usual semiclassical result when $Z = L^2(\mathbb{R}^d;\mathbb{C})$ is replaced by a finite dimensional Hilbert space.
With this strategy, we obtained in several steps the following results:

A) Existence of Wigner measures in [1]**:** For $f \in Z$ consider the unitary Weyl operator $W_\varepsilon(f) = e^{i\Phi(f)}$ with $\Phi(f) = \frac{a(f)+a^*(f)}{\sqrt{2}}$ and let $\mathbf{N}$ denote the semiclassical number operator $\mathbf{N} = \varepsilon \mathbf{N}_{\varepsilon=1}$ on the Fock space. Let $(\varrho_\varepsilon)_{\varepsilon\in(0,\varepsilon_0)}$ be a family of non negative trace class operators on $\mathcal{H}$ with Tr $[\varrho_\varepsilon] = 1$ (e.g. $\varrho_\varepsilon = |\Psi\rangle\langle\Psi|)$. For a subset $\mathcal{E}' \in (0,\varepsilon_0)$ with $0 \in \overline{\mathcal{E}'}$, we say that the Borel probability measure μ on Z is the Wigner measure of $(\varrho_\varepsilon)_{\varepsilon\in\mathcal{E}'}$, if

$$\lim_{\varepsilon\in\mathcal{E}',\varepsilon\to 0} \mathrm{Tr}\;[\varrho_\varepsilon W_\varepsilon(f)] = \int_Z e^{2i\pi \mathrm{Re}\langle f\,,\,z\rangle} \; d\mu(z) \,.$$

We denote by $\mathcal{M}(\varrho_\varepsilon, \varepsilon\in\mathcal{E})$ the set of Wigner measures obtained for all $\mathcal{E}' \subset \mathcal{E}$ with $0 \in \overline{\mathcal{E}'}$. Under the simple estimate Tr $\left[\varrho_\varepsilon \mathbf{N}^\delta\right] \leq C_\delta$ uniform in ε for some $\delta > 0$ and $C_\delta > 0$, $\mathcal{M}(\varrho_\varepsilon, \varepsilon\in\mathcal{E})$ is not empty.
From the definition, the uniqueness $\mathcal{M}(\varrho_\varepsilon\,, \varepsilon\in\mathcal{E}') = \{\mu\}$ can always be supposed after a subsequence (subfamily) extraction.

B) (PI)-condition [2] **and** [3]**:** After assuming $\mathcal{M}(\varrho_\varepsilon, \varepsilon\in\mathcal{E}) = \{\mu\}$, the (PI)-condition (PI for Polynomial and Identity) is written:

$$\forall k \in \mathbb{N}\,, \quad \lim_{\varepsilon\in\mathcal{E},\varepsilon\to 0} \mathrm{Tr}\;\left[\varrho_\varepsilon \mathbf{N}^k\right] = \int_Z |z|^{2k} \; d\mu(z) \,.$$

It is actually equivalent to the convergence

$$\lim_{\varepsilon\in\mathcal{E},\varepsilon\to 0}\mathrm{Tr}\,\left[\varrho_\varepsilon b^{Wick}\right]=\int_Z b(z)\,d\mu(z)\,.$$

for all $b(z)=\langle z^{\otimes q}\,,\,\tilde{b}z^{\otimes p}\rangle$ with $\tilde{b}$ bounded operator. Contrary to the usual finite dimensional case (for Z), the above conditions may not be satisfied according to what we called in [2] a dimensional defect of compactness ("dimensional" referring to the infinite dimensional phase-space).

Alternatively if the condition (PI) is satisfied, it implies a very strong convergence result about all the reduced density matrices. In the example $Z=L^2(\mathbb{R}^d;\mathbb{C})$ the p-particles reduced density matrix is defined as usual by

$$\gamma_\varepsilon^{(p)}(x,y)=\int_{\mathbb{R}^{d(N-p)}}\overline{\Psi(x,X')}\Psi(y,X')\,dX'\,,$$

and the general definition is

$$\mathrm{Tr}\,\left[\gamma_\varepsilon^{(p)}\tilde{b}\right]=\frac{\mathrm{Tr}\,\left[\varrho_\varepsilon b^{Wick}\right]}{\mathrm{Tr}\,\left[\varrho_\varepsilon(|z|^{2p})^{Wick}\right]}\,.$$

The condition (PI) implies the trace norm convergence

$$\forall p\in\mathbb{N}\,,\quad\lim_{\varepsilon\to 0}\|\gamma_\varepsilon^{(p)}-\gamma_0^{(p)}\|_{\mathcal{L}^1}=0\,,$$

with

$$\gamma_0^{(p)}=\int_Z|z^{\otimes p}\rangle\langle z^{\otimes p}|\,d\mu(z)\,.$$

C) Propagation results in [3] **and** [4] **(see also** [5]**):** Although the written results are more general, let us stick for this short summary to our example with a pair interaction potential, leading to the Hartree equation in the mean field limit. Under different assumptions and with two different techniques we proved in [3] and [4] the following propagation result

$$(\mathcal{M}(\varrho_\varepsilon\,,\varepsilon\in\mathcal{E})=\{\mu_0\})\Leftrightarrow\left(\forall t\in\mathbb{R}\,,\quad\mathcal{M}(e^{-i\frac{t}{\varepsilon}H^\varepsilon}\varrho_\varepsilon e^{i\frac{t}{\varepsilon}H^\varepsilon}\,,\varepsilon\in\mathcal{E})=\{\mu_t\}\right)$$

where $\mu_t=\Phi(t,0)_*\mu_0$ is the push-forward of μ_0 by the nonlinear hamiltonian flow on the phase-space (Z or Z_1 see below) associated with the energy $\mathcal{E}(z))$.

In [3], it was proved for $V\in L^\infty(\mathbb{R}^d)$ under the additional condition that the family $(\varrho_\varepsilon)_{\varepsilon\in\mathcal{E}}$ satisfies the condition (PI). The technical part relied on truncated Dyson expansions, adapted from previous works of J. Fröhlich and collaborators, combined with the a priori information carried by Wigner measures.

In [4], it was proved for a class of singular potentials including the $3D$ attractive or repulsive Coulombic potential $V(x)=\frac{c}{|x|}$, $c\in\mathbb{R}$. Then the nonlinear hamiltonian flow is well defined on $Z_1=H^1(\mathbb{R}^d;\mathbb{C})$. The propagation result was obtained after adapting to our infinite dimensional case, measure transportation techniques developed by Ambrosio, Gigli and Savaré.

An important remark: The folklore often confuses the mean field regime with uncorrelated states. Uncorrelated mean field states are actually coherent states, $\varrho_\varepsilon=|\Psi\rangle\langle\Psi|$, with $\Psi=W(-\sqrt{2}i\varepsilon^{-1}f)$ (then $\mu=\delta_f$), or Hermite (or atomic coherent) states with $\Psi = f^{\otimes N}$, $N\varepsilon \to 1$ (then $\mu = \delta_f^{S^1} = \frac{1}{2\pi}\int_0^{2\pi} \delta_{e^{i\theta} f}\ d\theta)$. In other cases $\gamma_0^{(2)}$ differs from $\gamma_0^{(1)} \otimes \gamma_0^{(1)}$. The propagation of Wigner measures can be used to follow the nonlinear deformations of correlations like $\gamma_0^{(2)}(t) - \gamma_0^{(1)}(t) \otimes \gamma_0^{(1)}(t)$.

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Using Spectrograms for the Semiclassical Propagation of Quantum Expectations

JOHANNES KELLER

(joint work with Caroline Lasser, Tomoki Ohsawa)

Let $\psi_t \in L^2(\mathbb{R}^d, \mathbb{C})$ denote a solution of the time-dependent Schrödinger equation

$$i\varepsilon\partial_t\psi_t = -\tfrac{\varepsilon^2}{2}\Delta\psi_t + V\psi_t, \tag{1}$$

where $0 < \varepsilon \ll 1$ is a small parameter. After conducting the Born-Oppenheimer approximation, (1) appears as the effective equation in atomic units for the vibrational motion of the nuclei in a molecule on a single electronic potential energy surface V. In this application, ε typically equals the square root of the ratio of electronic versus average nuclear mass, and the ε prefactor on the left hand side of (1) is due to a time rescaling.

We want to compute the evolution of quantum expectation values

$$t \mapsto \left\langle \psi_t, \widehat{A}\psi_t \right\rangle_{L^2} \tag{2}$$

for observables $\widehat{A} : L^2(\mathbb{R}^d, \mathbb{C}) \to L^2(\mathbb{R}^d, \mathbb{C})$. If $\widehat{A}$ is obtained from a phase space function (a symbol) $A : \mathbb{R}^{2d} \to \mathbb{R}$ by Weyl quantization, Egorov's theorem implies the semiclassical approximation

$$\left\langle \psi_t, \widehat{A}\psi_t \right\rangle_{L^2} = \int_{\mathbb{R}^{2d}} (A \circ \Phi^t)(z)\mathcal{W}_{\psi_0}(z)dz + O(\varepsilon^2), \tag{3}$$

where $\mathcal{W}_{\psi_0} : \mathbb{R}^{2d} \to \mathbb{R}$ is the Wigner transform of the initial state ψ_0, and Φ^t is the flow of the classical Hamiltonian system

$$\dot{q} = p, \quad \dot{p} = -\nabla V(q). \tag{4}$$

Discretizations of the Egorov theorem (3), like the LSC-IVR method or the Wigner quasi classical method, are well-known in chemistry since decades, see also [KL14]. They all build on a sampling $z_1, \dots, z_N$ from the initial Wigner transform $\mathcal{W}_{\psi_0}$ and subsequent averaging of A over the propagated phase space points $\Phi^t(z_1), \dots, \Phi^t(z_N)$.

The Wigner transform $\mathcal{W}_{\psi_0}$ is typically not a probability density, which creates severe difficulties for the sampling step. A possibility to circumvent this problem is to use the state's Husimi transform

$$\mathcal{H}_{\psi_0} = \mathcal{W}_{\psi_0} * \mathcal{W}_{g_0}, \tag{5}$$

which is a probability density. However, as shown in [KL13], merely replacing $\mathcal{W}_{\psi_0}$ by $\mathcal{H}_{\psi_0}$ in (3) deteriorates the accuracy to $O(\varepsilon)$ errors, unless one includes involved corrections of the dynamics by additional ODEs. In (5), $\mathcal{W}_{g_0}$ denotes the Wigner transform of the harmonic oscillator ground state.

The convolution of two Wigner transforms is always a probability density on phase space. In time-frequency analysis, $\mathcal{W}_{\psi_0} * \mathcal{W}_{\phi}$ with $\phi \in L^2(\mathbb{R}^d, \mathbb{C})$ is called a spectrogram of ψ_0. In [KLO15] we introduce the novel phase space density

$$\mu_{\psi_0} = (1 + \tfrac{d}{2})\mathcal{W}_{\psi_0} * \mathcal{W}_{g_0} - \tfrac{1}{2}\sum_{j=1}^{d} \mathcal{W}_{\psi_0} * \mathcal{W}_{\varphi_{e_j}} \tag{6}$$

consisting of the state's Husimi transform and the spectrograms obtained from the first order multivariate Hermite functions φ_{e_j}, with e_j the jth unit vector in $\mathbb{R}^d$.

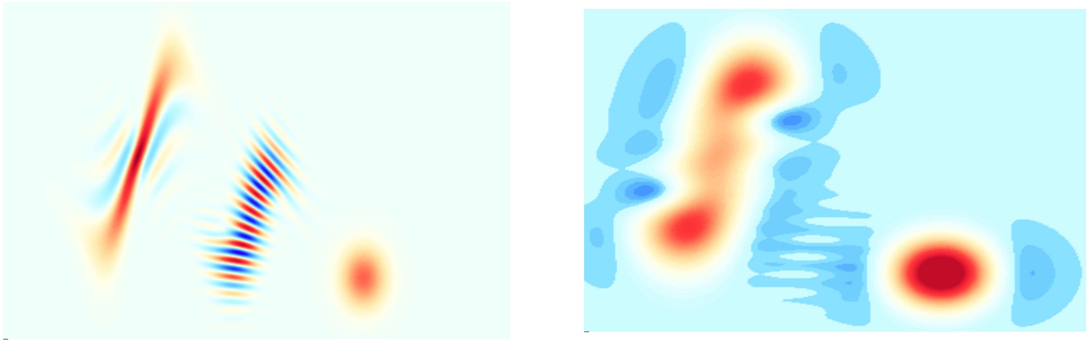

Figure 1. Contour plots of the Wigner function (left) and the density μ_ψ (right) for a one-dimensional superposition of a Gaussian wave packet and a delocalized Lagrangian state. Negative values are indicated by blue color (color in online version only).

In figure 1 one can see an example for the new density μ_ψ in one space dimension. While the nonnegative Husimi transform does not show any of the interferences that arise in the Wigner transform, the new density μ_ψ again attains negative values.

The function μ_{ψ_0} is a linear combination of two smooth probability densities, and hence much better amenable for sampling purposes than the Wigner transform

$\mathcal{W}_{\psi_0}$. As our main result we prove that one can replace the Wigner transform in the Egorov theorem by μ_{ψ_0} without deteriorating the second order accuracy in ε, that is,

$$\left\langle \psi_t, \widehat{A}\psi_t \right\rangle_{L^2} = \int_{\mathbb{R}^{2d}} (A \circ \Phi^t)(z)\mu_{\psi_0}(z)dz + O(\varepsilon^2). \tag{7}$$

In [KLO15] we illustrate the validity and applicability of the semiclassical approximation (7) by means of various numerical experiments.

For instance, we consider the evolution of potential energies for a 32-dimensional Henon-Heiles type system with Gaussian initial data, see figure 2. Since reliable references are not available for this high-dimensional system, we compare the values obtained from discretizations of Egorov's theorem (3), the new spectrogram approximation (7), and the "naive Husimi method" that results from replacing the Wigner transform $\mathcal{W}_{\psi_0}$ in (3) by the Husimi transform $\mathcal{H}_{\psi_0}$. Figure 2 shows that the results of the Wigner and the spectrogram method are almost indistinguishable, while the the outcome of the naive Husimi method differs considerably.

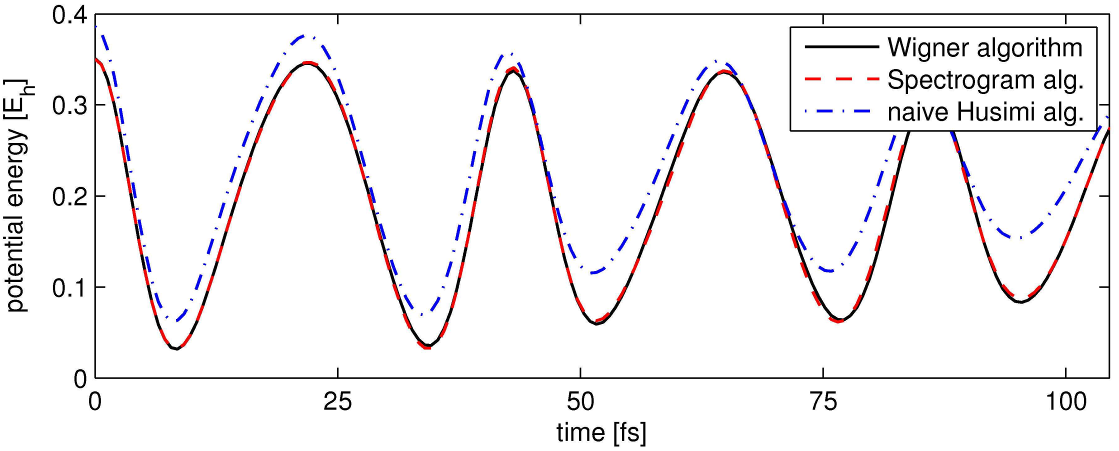

Figure 2. Evolution of potential energies for 32-dimensional Henon-Heiles system with Gaussian initial data and $\varepsilon = 0.0029$.

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Discretised dynamical low-rank approximation in the presence of small singular values

Emil Kieri
(joint work with Christian Lubich, Hanna Walach)

We prove error estimates for a novel time-stepping scheme for low-rank matrix and tensor differential equations. The estimate is robust with respect to small singular values. When a singular value in the approximation approaches zero, standard time-stepping schemes break down. We show that the new method solves this problem.

Low-rank approximations have had much success in the field of quantum dynamics, in particular through the multi-configurational time-dependent Hartree (MCTDH) method [5]. However, also time-stepping schemes for MCTDH have difficulties in the presence of small singular values. MCTDH uses the Tucker format to construct low-rank approximations of tensors. In this work we use a different low-rank tensor format, known as tensor trains or matrix product states.

We consider the low-rank approximation of a large, time-dependent tensor $A(t) \in \mathbb{C}^{n_1 \times \cdots \times n_d}$, given via a tensor differential equation

$$\dot{A}(t) = F(t, A(t)), \qquad A(0) = A_0 \in \mathbb{C}^{n_1 \times \cdots \times n_d}.$$

If we can approximate $A(t)$ by a rank-r tensor train, the amount of data required to represent $A(t)$ would be reduced from $\mathcal{O}(n^d)$ to $\mathcal{O}(dr^2 n)$, with $n = \max n_i$. To keep the notation simple we will in this note only consider the matrix case, i.e., $d = 2$, and aim at approximating $A(t)$ by a rank-r matrix. The results extend to low-rank tensors in the tensor train format with arbitrary d.

Commonly, the singular values of a matrix decay without a distinct gap. This means that the last included and first neglected singular values, σ_r and σ_{r+1}, are of similar size. σ_{r+1} represents neglected information, and if it is not small the low-rank approximation will introduce a large error. We should therefore expect also σ_r to be small. In this work we prove that the splitting scheme is robust in this situation: *If the exact solution is an ε-perturbation of a rank-r matrix, the error can be bounded in terms of ε and the time step, independently of the smallness of σ_r.* For a more precise statement and a proof of this result, see [1].

We approximate $A(t)$ by a matrix of rank r using the SVD-like decomposition

$$A(t) \approx Y(t) = U(t)S(t)V(t)^*,$$

where $U \in \mathbb{C}^{n_1 \times r}$ and $V \in \mathbb{C}^{n_2 \times r}$ have orthonormal columns and $S \in \mathbb{C}^{r \times r}$. We denote the manifold of rank-r matrices by $\mathcal{M}_r$ and its tangent space at Y by $\mathcal{T}_Y\mathcal{M}_r$. We then determine the time-evolution of $Y(t)$ using the Dirac–Frenkel time-dependent variational principle,

$$\dot{Y}(t) = P(Y(t))F(t, Y(t)), \qquad Y(0) = Y_0, \tag{1}$$

where $P(Y)$ is the orthogonal projection onto the tangent space $\mathcal{T}_Y\mathcal{M}_r$. This can also be seen as a Galerkin condition on the tangent space. Subject to a gauge condition, (1) determines a system of differential equations for the matrices U, S and V [2],

$$\begin{aligned}
\dot{U}(t) &= (I - U(t)U(t)^*)F(t, Y(t))V(t)S(t)^{-1}, \\
\dot{S}(t) &= U(t)^*F(t, Y(t))V(t), \\
\dot{V}(t) &= (I - V(t)V(t)^*)F(t, Y(t))^*U(t)S(t)^{-*}.
\end{aligned}$$

We note that this system is stiff if σ_r is small, and does not have a well-defined solution in the limit $\sigma_r \to 0$.

The projection onto the tangent space can be decomposed as

$$P(Y)Z = ZVV^* - UU^*ZVV^* + UU^*Z, \qquad Y = USV^*, \qquad Z \in \mathbb{C}^{n_1 \times n_2}.$$

Recently, a time-stepping scheme based on this splitting was proposed [3]. A similar scheme for the tensor train case has also been constructed [4]. Error bounds in terms of the time step h are available by standard theory for splitting methods, but unfortunately these estimates break down when $\sigma_r \to 0$. Such a break-down is, however, not observed in numerical experiments. The splitting scheme possesses a remarkable exactness property, which gives a first theoretical indication of its robustness: If $A(t) \in \mathcal{M}_r$ for all t and its time-derivative $\dot{A}(t) = F(t)$ is given independently of $A(t)$, then the splitting method is exact for any h and independently of σ_r. Our analysis unifies this property with the standard error estimates.

The error estimate requires F to be Lipschitz continuous. This is a considerable limitation in a quantum dynamics context, since for a discretisation of the Schrödinger equation with spatial step size Δx the Lipschitz constant will be of order Δx^{-2}. This suggests that very small time steps would be needed. Such a time step restriction is however not observed in numerical experiments. The method seems to be robust for partial differential equations, and it would be of interest to extend the theory also to this situation.

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Convergence of normalized gradient algorithms applied to ground states computations

Erwan Faou

(joint work with Tiphaine Jézéquel)

We consider the convergence of the normalized gradient algorithm used to compute numerically ground states of Schrödinger equations fulfilling symmetry and coercivity conditions as considered in the seminal works of Weinstein [7] and Grillakis, Shatah and Strauss [5, 6].

We consider the focusing cubic non linear Schrödinger equation

$$i\partial_t\psi = -\frac{1}{2}\Delta\psi - |\psi|^2\psi, \tag{NLS}$$

set on $\mathbb{R}$, where $\psi(t,x)$ depends on space variables $x \in \mathbb{R}$. With this equation is associated the energy

$$H(\psi,\bar{\psi}) = \frac{1}{4}\int_{\mathbb{R}} |\nabla\psi|^2 - |\psi|^4, \tag{1}$$

that is preserved by the flow of (NLS) for all times. The equation (NLS) can thus be written

$$i\partial_t\psi = -\frac{1}{2}\Delta\psi - |\psi|^2\psi = 2\frac{\partial H}{\partial\bar{\psi}}(\psi,\bar{\psi}).$$

Let ∇H denote the L^2 derivative of the energy H with respect to *real* functions ψ. The ground state $\eta(x)$ is defined as the unique real symmetric minimizer of the problem

$$\min_{\|\psi\|_{L^2}=1} H(\psi). \tag{2}$$

In the one dimensional cubic case considered in this paper, explicit computations show that

$$\eta(x) := \frac{1}{2}\operatorname{sech}\left(\frac{x}{2}\right).$$

We denote by $-\lambda$ the Lagrange multiplier associated with this minimization problem, such that

$$\nabla H(\eta) = -\frac{1}{2}\Delta\eta - \eta^3 = -\lambda\eta. \tag{3}$$

In general, η is not explicitly known, and one has to rely to numerical simulation. To compute numerically η, the *imaginary time method*, which is a nonlinear version of the normalized gradient algorithm (see [1]). The algorithm consists in defining a sequence $\{\psi_n\}_{n\in\mathbb{N}}$ as follows:

(i) An intermediate function ψ_n^* is defined a a numerical approximation of the solution of the parabolic equation

$$\partial_t\psi = \frac{1}{2}\Delta\psi + |\psi|^2\psi = -\nabla H(\psi) \tag{4}$$

over a time interval $[0,\tau]$, where τ is a given time step. To compute ψ_n^*, we will consider the following time integration methods:

$$\psi_n^* = \psi_n + \tau\widehat{\nabla H}(\psi_n,\psi_n^*).$$

with

$$\widehat{\nabla} H(\psi_n,\psi_n^*) = \frac{1}{2}\Delta\psi_n^* + \begin{cases} |\psi_n|^2\psi_n & \textit{(implicit-explicit)} \\ |\psi_n|^2\psi_n^* & \textit{(linearly implicit)} \\ |\psi_n^*|^2\psi_n^* & \textit{(fully implicit)} \end{cases}$$

(ii) Then we define the normalized function

$$\psi_{n+1} = \frac{\psi_n^*}{\|\psi_n^*\|_{L^2}} \tag{5}$$

Our main result is the following:

Theorem 1.1. *There exists B and τ_0 such that if $\|u_0\|_{H^1} \leq B$ and $\tau \leq \tau_0$, then there exist constant c and C such that*

- *For the* linearly implicit *scheme, we have*

$$\forall n \quad \|\psi_n - \eta\|_{H^1} \leq Ce^{-\rho n\tau}.$$

- *For the* implicit-explicit *and* fully implicit *Êschemes, there exists η_τ such that $\|\eta_\tau - \eta\|_{H^1} \leq C\tau$, and*

$$\forall n \quad \|\psi_n - \eta_\tau\|_{H^1} \leq Ce^{-\rho n\tau}.$$

This result can be extended to the fully-discrete case in space and time by using the analysis of [3] and [2]. The main conclusion is that the linearly implicit schemes has infinite order in time in the numerical computation of the soliton (that is: the exact ground state is also the ground state of the numerical scheme).

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The multi-configurational time-dependent Hartree approach revisited

Uwe Manthe

The multi-configurational time-dependent Hartree (MCTDH) approach facilitates accurate high-dimensional quantum dynamics simulations. In the approach, the wavefunction is expanded in a direct product of self-adapting time-dependent single-particle functions (SPFs). The equations of motion for the expansion coefficients and the SPFs are obtained via the Dirac-Frenkel variational principle. While this derivation yields well-defined differential equations for the motion of occupied SPFs, singularities in the working equations resulting from unoccupied SPFs have to be removed by a regularization procedure. Here an alternative derivation of the MCTDH equations of motion is presented. It employs an analysis of the time-dependence of the single-particle density matrices up to second order. While the analysis of the first order terms yields the known equations of motion for the occupied SPFs, the analysis of the second order terms provides new equations which allow one to identify optimal choices for the unoccupied SPFs. The effect of the optimal choice of the unoccupied SPFs on the structure of the MCTDH equations of motion and their regularization is discussed. Generalized equations applicable in the multi-layer MCTDH framework are presented. Finally, the effects resulting from the initial choice of the unoccupied SPFs are illustrated by a simple numerical example.

Time integration in the multiconfiguration time-dependent Hartree method of molecular quantum dynamics

Christian Lubich

Developed over the last 25 years, the multiconfiguration time-dependent Hartree (MCTDH) method [5, 6] has become a reference method for computing accurate quantum dynamics of small molecules. It combines a low-rank tensor approximation in the Tucker format with the Dirac–Frenkel time-dependent variational principle, which yields a large, highly structured, nonlinear system of differential equations for the core tensor and the single-particle basis functions. This system needs to be solved numerically. It is a known difficulty to deal with the typically ill-conditioned density matrices whose inverses appear in the equations of motion. This leads to severe stepsize restrictions for the known integrators, which are only mitigated by an *ad hoc* regularization of the density matrices.

This talk presents a numerical integrator that avoids this difficulty. A step of the integrator alternates between orthogonal matrix decompositions and solving linear systems of differential equations, which can be efficiently solved by Lanczos approximations. The MCTDH density matrices are nowhere computed, nor are their inverses.

The integrator proposed here can be interpreted as a splitting method that is based on an additive decomposition of the projection onto the tangent space of the low-rank tensor manifold. It extends recently proposed projector-splitting integrators for the dynamical approximation by low-rank matrices [2] and tensors in the tensor train format [3]. In view of numerical and theoretical results for those cases, as given in [1], the MCTDH integrator proposed here is expected to be completely insensitive to the presence of small singular values in matrix unfoldings of the core tensor, or equivalently, insensitive to an ill-conditioning of the density matrices.

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Wigner measures and effective mass theorems

Clotilde Fermanian-Kammerer

(joint work with Victor Chabu, Fabricio Macia)

We consider the equation

$$
\begin{gathered}
i\partial_t\psi^\varepsilon + \tfrac{1}{2}\Delta_x\psi^\varepsilon + \tfrac{1}{\varepsilon^2}V_\Gamma\left(\tfrac{x}{\varepsilon}\right)\psi^\varepsilon + V_{\rm ext}(x)\psi^\varepsilon = 0, \quad (t,x)\in\mathbb{R}\times\mathbb{R}^2, \\
\psi^\varepsilon_{|s=0} = \psi^\varepsilon_0,
\end{gathered} \tag{1}
$$

where (ψ^ε_0) is a bounded family of $L^2(\mathbb{R}^2)$, V_Γ a potential periodic with respect to the lattice $\mathbb{Z}^2$,$V_{\rm ext}$ an external potential that we assume $\mathcal{C}^\infty$ and the parameter ε goes to 0. We are interested in the description of the limit as ε goes to 0 of time averaged of energy densities such as

$$
J^\varepsilon(a) = \frac{1}{2}\int_{-T}^{T}\int_{\mathbb{R}^2} a(x)|\psi^\varepsilon(t,x)|^2 dx\, dt, \quad a\in\mathcal{C}_0^\infty(\mathbb{R}^d).
$$

We consider a special class of initial data that are linked with the following spectral problem : For $\xi\in\mathbb{R}^d$, we consider the operator on the torus $\mathbb{T}^2 = \mathbb{R}^2\backslash\mathbb{Z}^2$,

$$
P(\xi) = \frac{1}{2}\left(\xi + D_y\right)^2 + V(y), \quad y\in\mathbb{T}^2.
$$

The operator $P(\xi)$ is self-adjoint on $L^2(\mathbb{T}^2)$ and has a compact resolvant, hence a nondecreasing sequence of eigenvalues called Bloch energies

$$
\lambda_1(\xi) \leq \lambda_2(\xi) \leq \cdots \leq \lambda_n(\xi) \to +\infty,
$$

and an orthonormal basis of eigenfunctions $(\varphi_j(\xi))_{j\in\mathbb{N}}$, called Bloch waves satisfying for all $\xi \in \mathbb{R}^d$,

$$P(\xi)\varphi_n(\xi,y) = \lambda_n(\xi)\varphi_n(\xi,y), \;\; n \in \mathbb{N}, \;\; y \in \mathbb{T}^2$$

with $\mathbb{Z}^2$-periodic boundary conditions.

We focus on a mode $\lambda_j(\xi)$ that we assume of multiplicity 1. As a consequence, it is an isolated eigenvalue from the rest of the spectrum in the sense that there exists a gap $\delta > 0$ separating $\lambda_j(\xi)$ for the rest of the spectrum. Therefore the functions $\xi \mapsto \lambda_j(\xi)$ and $\xi \mapsto \varphi_j(\xi,\cdot)$ are smooth functions of the variable ξ. We assume that the initial data of our evolution problem (1) is of the form

$$\psi_0^\varepsilon(x) = \left(\varphi_j\,(\varepsilon D, y)\, u_0^\varepsilon(x)\right)_{y=\frac{x}{\varepsilon}}\,, \tag{2}$$

where the family $(u_0^\varepsilon)_{\varepsilon>0}$ is uniformly bounded in $L^2(\mathbb{R}^2)$ and ε-oscillating in the sense that its frequencies of oscillations are not larger than $\frac{1}{\varepsilon}$:

$$\limsup_{\varepsilon\to 0} \int_{|\xi|>R/\varepsilon} \left|\widehat{u_0^\varepsilon}(\xi)\right|^2 d\xi \underset{R\to+\infty}{\longrightarrow} 0. \tag{3}$$

Equivalently, equation (2) writes

$$\psi_0^\varepsilon(x) = (2\pi)^{-d} \int_{\mathbb{R}^d} \mathrm{e}^{i\xi\cdot(x-y)} \varphi\left(\varepsilon\xi, \frac{x}{\varepsilon}\right) u_0^\varepsilon(y) dy d\xi.$$

Under these assumptions, we prove the following result.

Theorem 1.1. *Assume that the initial data of equation (1) satisfies (2), assume that $\lambda_j(\xi)$ is an eigenvalue of constant multiplicity 1 and that the critical points of λ_j are non-degenerated, then there exists a subsequence ε_k which goes to 0 as ε goes to 0 and a function $\gamma(t,x) \in L^\infty(\mathbb{R}, L^1(\mathbb{R}^2))$, $\gamma \geq 0$, such that*

$$\forall a \in \mathcal{C}_0^\infty(\mathbb{R}^2), \;\; J^\varepsilon(a) \underset{\varepsilon\to 0}{\longrightarrow} \int_{\mathbb{R}} \int_{\mathbb{R}^2} \chi(t) a(x) \gamma(t,x) dt\, dx,$$

with $\chi = \frac{1}{2T}\mathbf{1}_{[0,T]}$.

This result relies on a microlocal approach, the use of Wigner measures and in performing a two-microlocal analysis in the spirit of earlier works of two of the authors [3, 4, 5, 6]. We prove in fact a larger result and we are able to give a description of the structure of the limit points of $J^\varepsilon(a)$ in the case where the critical points of λ_j are isolated without any condition on the Hessian of λ_j.The fact that the limit points of $J^\varepsilon(a)$ are described by measures which are absolutely continuous with respect to the Lebesgue measure may fail whenever the non-degeneracy condition on the Hessian of λ_j is not satisfied. In the case where there is only one critical point ξ_0 and where the Hessian is non-degenerated in ξ_0, the density γ is related with an effective mass equation : $\gamma(t,x) = |\Phi(t,x)|^2$ where Φ solves the equation

$$i\partial_t \Phi = \mathrm{Hess}\,\lambda_j(\xi_0) D\cdot D\,\Phi + V(x)\Phi, \;\; \Phi(0) = \Phi_0, \tag{4}$$

where Φ_0 is a weak limit in $L^2(\mathbb{R}^2)$ of the sequence $x \mapsto \mathrm{e}^{\frac{i}{\varepsilon}\xi_0\cdot x}u_0^\varepsilon(x)$. This extends the results of [2, 1] to a larger class of initial data. It also gives another approach which should help to understanding this problems in more general situations such as the case where the set of critical points of λ_j consists in a submanifold.

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The semiclassical limit of time correlation functions by path integrals

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(joint work with Sara Bonella, Michele Monteferrante, Carlo Pierleoni)

The exponential scaling of the computational cost of quantum time evolution with the number of degrees of freedom motivates current attempts to approximate and interpret quantum dynamics via classical trajectories. These can in fact be computed with essentially linear effort and provide a more intuitive representation of the dynamics. In spite of these tempting properties of the trajectories, the accuracy and generality of such attempts requires careful analysis since it is unclear whether they can be successful for condensed phase systems. To illustrate this point, we comment on how and when quantum evolution can be approximated in terms of (generalised) classical dynamics in the calculation of the symmetrised time correlation function [1]

$$G_{AB}(t,\beta) = \frac{1}{Z}\mathrm{Tr}\{\hat{\mathrm{A}}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}\hat{\mathrm{H}}\mathrm{t}_\mathrm{c}^*}\hat{\mathrm{B}}\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\hat{\mathrm{H}}\mathrm{t}_\mathrm{c}}\} \tag{1}$$

in semiclassical conditions. In the expression above, $t_c = t - \frac{i\hbar\beta}{2}$,$\beta = 1/k_BT$ (T is the temperature and k_B Boltzmann's constant), $\hat{H}$ is the Hamiltonian of the system and $Z = \mathrm{Tr}\{\mathrm{e}^{-\beta\hat{\mathrm{H}}}\}$ is the canonical partition function. Eq. (1) is equivalent via a relationship in Fourier space to the standard time correlation $C_{AB}(t,\beta) = \frac{1}{Z}\mathrm{Tr}\{\mathrm{e}^{-\beta\hat{\mathrm{H}}}\hat{\mathrm{A}}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}\hat{\mathrm{H}}\mathrm{t}}\hat{\mathrm{B}}\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\hat{\mathrm{H}}\mathrm{t}}\}$ function, but it also shares some formal properties with classical correlation functions, for example it is by construction a real function, and this suggests that it might be a convenient starting point for describing semiclassical systems (see for example[2-8]). The analysis presented in the following is described in [9] and we refer to that paper for a detailed derivation of the results summarised here.

The starting point of our considerations is the Feynman path integral expression (in a mixed coordinate and momenta representation) of the forward and backward propagators in complex time that appear in eq. (1). To examine the semiclassical limit of that expression, mean and difference paths in the coordinates and momenta are introduced and the exponent of the overall path integrals written as a Taylor series expansion in the difference paths.

First order result

Retaining only terms up to linear order in the Taylor series expansion, the symmetrised function can be written as

$$G^{(1)}_{AB}(t,\beta) = \frac{1}{Z}\int d\bar{r}_0 d\bar{p}_1 e^{-\frac{2\epsilon_\beta}{\hbar}\left[\frac{\bar{p}_1^2}{2m}+V(\bar{r}_0)\right]} A_w(\bar{r}_0,\bar{p}_1) B_w(\bar{r}_N,\bar{p}_N)$$

where O_w stands for the Wigner transform [10] of operator $\hat{O}$ and $(\bar{r}_t,\bar{p}_t)$ are the end points of the classical trajectory evolved from $(\bar{r}_0,\bar{p}_1)$ for a time t. Both the dynamics and the statistical weight in the correlation function above thus reduce to their fully classical counterparts. The Fourier relationship with the standard time correlation function mentioned above can, however, be used to restore some non-classical properties (such as detailed balance) of this quantity, and it is in fact formally identical to the so-called quantum correction procedure that was introduced by Schofield in ref. [1]. However, it is well known that this correction can fail at low temperature even when the system is non-interacting (see [9] for an explanation of this fact) and, more in general, that the temperature and mass range in which it is valid are quite limited.

Second order result

The result of a second order truncation of the series expansion of the exponent, instead, can be expressed as

$$\begin{aligned}
(2)\quad G^{(2)}_{AB}(t,\beta) &= \frac{Z_{cl}(2\epsilon_\beta/\hbar)}{Z}\int d\bar{r}_0 d\bar{r}_N \left\{\prod_{k=1}^{N-1}\int d\bar{r}_k d\bar{p}_k\right\}\frac{d\bar{p}_N}{2\pi\hbar} \\
\times &\left\{\frac{e^{-2\epsilon_\beta/\hbar\left[\frac{\bar{p}_1^2}{2m}+V(\bar{r}_0)\right]}}{Z_{cl}(2\epsilon_\beta/\hbar)}\frac{e^{-\frac{1}{2\sigma^2}\sum_{k=1}^{N}[\bar{r}_k-\bar{r}_{k-1}-\epsilon_t\frac{\bar{p}_k}{m}]^2}}{(\sqrt{2\pi\sigma^2})^N}\frac{e^{-\sum_{k=1}^{N-1}[\frac{\bar{p}_{k+1}-\bar{p}_k+\epsilon_t\nabla V(\bar{r}_k)}{2\hbar\epsilon_\beta|\nabla^2 V(\bar{r}_k)}]^2|}}{(\sqrt{2\pi\sigma^2})^N}\right\} \\
\times &\quad e^{-2\epsilon_\beta/\hbar\sum_{k=2}^{N}\left[\frac{\bar{p}_k^2}{2m}+V(\bar{r}_{k-1})\right]} A_w(\bar{r}_0,\bar{p}_1)B_w(\bar{r}_N,\bar{p}_N)F_\Omega(\{\bar{r}_k\},\{\bar{p}_k\})
\end{aligned}$$

where $(\bar{r}_{k-1},\bar{p}_k)$ $(k = 1,\ldots,N)$ are the positions and momenta along the path, $Z_{cl}(2\epsilon_\beta/\hbar)$ is the classical partition function at inverse temperature $2\epsilon_\beta/\hbar$, and F_Ω is discussed below. The factors in the curly bracket are a probability density and the approximate symmetrised correlation function can then be computed as the expectation of $e^{-2\epsilon_\beta/\hbar\sum_{k=2}^{N}\left[\frac{\bar{p}_k^2}{2m}+V(\bar{r}_{k-1})\right]} A_w(\bar{r}_0,\bar{p}_1)B_w(\bar{r}_N,\bar{p}_N)F_\Omega(\{\bar{r}_k\},\{\bar{p}_k\})$ The variables $(\bar{r}_{k-1},\bar{p}_k)$ can be sampled as follows: The zero time values $\bar{r}_0,\bar{p}_1$ are obtained from the high temperature classical Boltzmann factor

$$e^{-2\epsilon_\beta/\hbar\left[\frac{\bar{p}_1^2}{2m}+V(\bar{r}_0)\right]}/Z_{cl}(2\epsilon_\beta/\hbar)$$

while the other variables are generated recursively from

$$\begin{aligned}\bar{r}_k &= \bar{r}_{k-1}+\epsilon_t\frac{\bar{p}_k}{m} \qquad k\in[1,N]\\ \bar{p}_{k+1} &= \bar{p}_k-\epsilon_t\nabla V(\bar{r}_k) \qquad k\in[1,N-1]\end{aligned}$$

where ξ_k and η_{k+1} are Gaussian white noises. This scheme illustrates how quantum mechanical delocalisation sets in in this semiclassical representation of the correlation function. Within this approximation in fact, both the new coordinates and momenta are sampled at each complex time step from Gaussian distributions centred around classically evolved phase space points. The dispersion around the classical path is determined by the variances $\sigma^2 = \frac{\hbar\epsilon_\beta}{m}$ and $\hbar\epsilon_\beta\nabla^2V(\bar{r}_k)$. The classical limit is restored for $\hbar\to 0$ and/or $\beta\to 0$ when these variances tend to zero. For finite values of Planck's constant or of the inverse temperature, the non classical nature of the time evolution of the system appears at each time step in the form of Gaussian random displacements from the "driving" classical propagation. While this interpretation is intriguing, the actual interest of the driving classical trajectory depends crucially on the system. If the potential is everywhere convex, the function F_Ω in the integrand is well defined (it reduces essentially to the determinant of Hessian of the potential computed along the path) and the estimate of the average as a mean over paths generated as outlined above is viable. In the more general case of potentials with regions of negative curvature, on the other hand, this function does not have an explicit form, and there is no reason to expect that it will be localised around the complex paths generated via the sampling scheme of eq. (2). Furthermore, it can be shown that small variations in its argument result in "explosively" different values for F_Ω. Attempts to interpret or estimate the average above via a scheme based on localised paths are therefore doomed to failure for two reasons: first, the integrand is not peaked around the sampling function, second it is a numerically unstable function. These characteristics are a direct manifestation of delocalisation, an intrinsic property of quantum mechanics that it is very difficult, if not impossible, to represent within this semiclassical scheme.

To conclude, the path integral expression of the symmetrised correlation function is a useful tool to examine how and when quantum evolution can be approximated via (generalised) classical trajectories. In particular, the second order result presented in the previous section shows how, in the semiclassical limit, the most relevant contributions to the path integral localise or, pathologically, de-localise around guiding or poorly guiding classical trajectories for general systems. While we employed the path integral formalism to illustrate how a picture based on classical dynamics is usually not enough to compute quantum properties, the difficulty to account for delocalisation appears also in other approximations of quantum mechanics (e.g. Wigner-Liouville, semiclassical IVR) pointing to the inherent difficulty of using a trajectory based picture to represent this phenomenon.

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Quantum Dynamics with (almost) classical trajectories?

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(joint work with Giovanni Ciccotti, Michele Monteferrante, Carlo Pierleoni, Julien Beutier, Rodolphe Vuilleumier)

Several simulation methods for computing approximate quantum time dependent properties of high dimensional systems employ the so called linearisation approximation. In this framework, time correlation functions are obtained via mixed schemes in which a set of initial conditions are sampled from the exact quantum thermal density via Monte Carlo and then evolved classically via standard molecular dynamics. The advantage of these methods is that the additional numerical effort compared to classical simulations is concentrated entirely in the sampling of the initial conditions. The two key questions in this context are: (1) how to reduce as much as possible the cost of initial condition sampling without loss of accuracy; (2) how to improve on the linearised dynamics when a fully classical propagation fails to capture important properties of the system such as quantum coherence. In this presentation these questions will be addressed: a numerically efficient algorithm for (1) will be mentioned, and an attempt to address (2) will be briefly described together with some open questions related to it.

Both questions above can be addressed, with different degree of success, starting from the linearised expression of the symmetrised time correlation function (STCF)[1, 2, 3, 4, 5, 6]. This quantity is defined as

$$(1) \qquad G_{AB}(t,\beta) = \frac{1}{Z}\mathrm{Tr}\{\hat{\mathrm{A}}\mathrm{e}^{\frac{\mathrm{i}}{\hbar}\hat{\mathrm{H}}\mathrm{t}_\mathrm{c}^*}\hat{\mathrm{B}}\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\hat{\mathrm{H}}\mathrm{t}_\mathrm{c}}\}$$

where $t_c = t - \frac{i\hbar\beta}{2}$,$\beta = 1/k_BT$ (T is the temperature and k_B Boltzmann's constant), $\hat{H}$ is the Hamiltonian of the system and $Z = \mathrm{Tr}\{\mathrm{e}^{-\beta\hat{\mathrm{H}}}\}$ is the canonical partition function. The Fourier transform of $G_{AB}(t,\beta)$ is related to those of the standard and Kubo quantum time correlation functions, so all these quantities carry equivalent information. The linearised expression of the STCF can be obtained via a path integral representation of the forward and backward propagators in complex time t_c, combined with an approximation of the real time path integral propagation valid to second order in $\hbar$ (see ref. [7] for details). The approximate form of the correlation function can then be expressed as an expectation value of the form

$$(2) \qquad \frac{< e^{-\frac{i}{\hbar}p_0\Delta}A(r_0)B_w(r_t,p_t) >}{< e^{-\frac{i}{\hbar}p\Delta} >}$$

In the expression above, the expectation value is taken with respect to an explicit probability density determined by the path integral expression of the quantum thermal density reorganised to contain an explicit dependence on the momentum p_0 (see ref.[7]), Δ and r_0 are two of the path variables, and $B_w(r_t,p_t)$ is the Wigner transform [8] of the operator $\hat{B}$ evaluated at the end point of a classical trajectory with initial conditions r_0, p_0. The numerical difficulty with eq.(2) lies in the presence of the phase factor $e^{-\frac{i}{\hbar}p_0\Delta}$ in the function to be averaged. This is, for general system, a highly oscillatory function whose rapid changes of sign make numerical converge of the average extremely difficult. As shown in [9], this phase factor can however be controlled via a cumulant expansion which leads to the definition of a new estimator for the linearised STCF given by

$$(3) \qquad < A(r_0)B_w(r_t,p_t) >_{\mathcal{P}}$$

which does not contain any phases. The price to pay for this rewriting is that, as a consequence of the use of cumulants, the probability $\mathcal{P}$ contains terms that can only be estimated numerically and are thus known with some uncertainty. Due to this, standard Monte Carlo methods cannot be applied to sampling $\mathcal{P}$. In ref. [9], we showed that this sampling can, however, be accomplished by combining the Penalty [10] and Kennedy [11] methods for Monte Carlo of noisy probability densities. These two methods combine standard techniques to generate trial moves with non-standard acceptance probabilities, which have been modified so as to compensate for the effect of the noise and ensure that detailed balance is satisfied. A detailed description of the algorithm can be found in [9]. The solution of this phase problem makes it possible to apply the linearised approximation of the STCF to multidimensional realistic models of condensed phase systems. For example, in ref [12] the scheme was used to reliably compute the quantum structure factor for a system of 64 Neon atoms described by a standard pair potential in the semiclassical regime.

In spite of this and other useful applications [13, 14], the linearised approximation to the quantum dynamics fails when quantum effects play a more significant role in the system's dynamics. A possible solution to solve (or mitigate) this problem originates from the observation that linearisation is valid for short times. The idea is then to use the time composition property of the exact quantum propagators in complex time to break the overall propagation in a sequence of shorter time intervals and to use a linearised approximation to represent each short time propagator [15]. The expression of the STCF at longer times is then obtained by concatenating these short time propagators. The underlying dynamics in complex time can be written as a sequence of exact samplings of quantum thermal densities at high temperature and classical real time propagations. Unfortunately, while numerical evidence on model systems suggests that this scheme does indeed enable to extend the accuracy of the approximation to longer times [15], this method suffers from several drawbacks that make it not only numerically expensive, but also in need of more detailed theoretical analysis. From the numerical point of view, the problem is that with each linearised short time propagator, a phase factor appears in the estimator of the STCF. Unlike what happens in the fully linearised case, the new phase factors cannot be effectively controlled via cumulants. This implies a dramatic increase in the cost of the calculation with the number of segments. From a theoretical point of view, there are two main open questions. Firstly, the precise nature of the limit of the approximate expression when the number of segments goes to infinity is unclear and, in particular, so far it has not been possible to prove that the exact quantum result is recovered. Secondly, the linearisation approximation on the individual short time segments is difficult to justify formally for deeply quantum systems. These difficulties notwithstanding, the method just mentioned is, to the best of our knowledge, one of the few - if not the only - attempt to systematically improve the accuracy of linearised schemed and may provide an interesting point of departure for future developments.

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Dynamically protected cat-qubits: a new paradigm for universal quantum computation

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(joint work with Z. Leghtas, V. Albert, S. Touzard, R.J. Schoelkopf, L. Jiang, M.H. Devoret)

We present a new hardware-efficient paradigm for universal quantum computation which is based on encoding, protecting and manipulating quantum information in a quantum harmonic oscillator. This proposal exploits multi photon driven dissipative processes to encode quantum information in logical bases composed of Schrödinger cat states. More precisely, we consider two schemes. In a first scheme, a two-photon driven dissipative process is used to stabilize a logical qubit basis of two-component Schrödinger cat states. While such a scheme ensures a protection of the logical qubit against the photon dephasing errors, the prominent error channel of single-photon loss induces bit-flip type errors that cannot be corrected. Therefore, we consider a second scheme based on a four-photon driven dissipative process which leads to the choice of four-component Schrödinger cat states as the logical qubit. Such a logical qubit can be protected against single-photon loss by continuous photon number parity measurements. Next, applying some specific Hamiltonians, we provide a set of universal quantum gates on the encoded qubits of each of the two schemes. In particular, we illustrate how these operations can be rendered fault-tolerant with respect to various decoherence channels of participating quantum systems. Finally, we also propose experimental schemes based on quantum superconducting circuits and inspired by methods used in Josephson parametric amplification, which should allow to achieve these driven dissipative processes along with the Hamiltonians ensuring the universal operations in an efficient manner. This work has been published in New Journal of Physics [1] and have led to preliminary experiments [2].

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Semiclassical Green's functions and an instanton formulation of electron transfer in the nonadiabatic limit

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(joint work with Rainer Bauer and Michael Thoss)

Electron transfers are a key step in many important molecular processes, including redox reactions in electrochemistry and charge separation in photosynthesis and solar cells [1]. The electron resides initially on a donor molecule and is transferred to an acceptor, accompanied by a reorganization of the polar environment. This reaction can be characterized as a transition between two nuclear potential-energy surfaces, describing the reactant and product environments. We are thus interested in studying a curve-crossing problem, which as it involves discrete electronic states, is inherently quantum mechanical.

We consider a general multidimensional system with two electronic states,

$$\hat{H} = \hat{H}_0 \, |0\rangle\langle 0| + \hat{H}_1 \, |1\rangle\langle 1| + \Delta\big(|0\rangle\langle 1| + |1\rangle\langle 0| \big), \tag{1}$$

where $\hat{H}_n = |\hat{\mathsf{p}}|^2/2m + V_n(\hat{\mathsf{x}})$ is the nuclear Hamiltonian for the electronic state $|n\rangle$. For this system, we wish to derive a practical computational method to provide good approximations to the golden-rule reaction probability [2, 3],

$$P(E) = 4\hbar^2\Delta^2 \iint \langle \mathsf{x}' | \operatorname{Im} \hat{G}_0(E) | \mathsf{x}'' \rangle \, \langle \mathsf{x}'' | \operatorname{Im} \hat{G}_1(E) | \mathsf{x}' \rangle \, \mathrm{d}\mathsf{x}' \mathrm{d}\mathsf{x}'', \tag{2}$$

where the Green's functions are given in the position representation by

$$\langle \mathsf{x}' | \hat{G}_n(E) | \mathsf{x}'' \rangle = -\frac{\mathrm{i}}{\hbar} \int_0^\infty \langle \mathsf{x}' | \mathrm{e}^{-\mathrm{i}\hat{H}_n t/\hbar} | \mathsf{x}'' \rangle \, \mathrm{e}^{\mathrm{i}Et/\hbar} \, \mathrm{d}t. \tag{3}$$

This golden-rule definition is valid only for weak electronic coupling, Δ.

The thermal reaction rate is in turn given by the Boltzmann average

$$k = \frac{1}{2\pi\hbar Z_0} \int P(E) \, \mathrm{e}^{-\beta E} \, \mathrm{d}E, \tag{4}$$

where the reactant partition function is $Z_0 = \mathrm{Tr}[\mathrm{e}^{-\beta \hat{H}_0}]$.

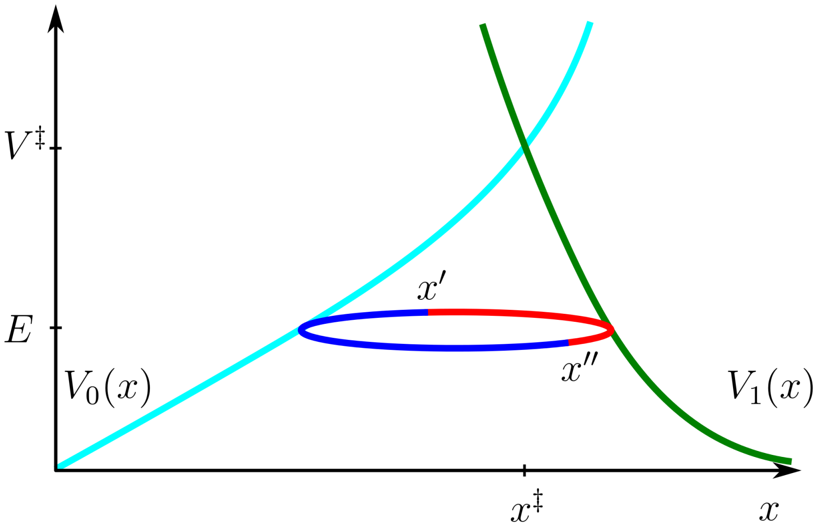

FIGURE 1. Schematic showing the two imaginary-time bounce trajectories with energy E in a one-dimensional, two-state system. The left trajectory is on $|0\rangle$ and the right on $|1\rangle$. The steepest-descent integration of positions will be taken about the crossing point $x' = x'' = x^\ddagger$ at which $V_0(x^\ddagger) = V_1(x^\ddagger) = V^\ddagger$.

Following Gutzwiller [4], we begin by replacing the propagator using van-Vleck's semiclassical approximation,

$$\langle \mathsf{x}'|\mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar}|\mathsf{x}''\rangle \propto \sum_{\text{cl. traj}} \mathrm{e}^{\mathrm{i}S_n/\hbar}, \tag{5}$$

where we take a sum over all classical trajectories travelling from x'' to x' in time t with phases determined by the classical action, S_n. Because our electron transfer problem includes nuclear tunnelling, the end-points x' and x'' of interest are in the classically-forbidden region where $E < V_n(\mathsf{x})$. The stationary-phase points in Eq. (3) correspond to imaginary-time trajectories (known as instantons) with energy E. Deforming the integration contour so as to pass through these points and evaluating it using steepest descent leads to the following semiclassical approximation to the Green's functions:

$$\langle \mathsf{x}'|\hat{G}_n(E)|\mathsf{x}''\rangle \propto \sum_{\text{cl. traj}} \mathrm{e}^{-\bar{W}_n/\hbar - \mathrm{i}\nu\pi/2}, \tag{6}$$

where $\bar{W}_n = \int \sqrt{2m[V_n(\mathsf{x}) - E]}\,|\mathrm{d}\mathsf{x}|$ is a line integral along the trajectory. The Maslov-Morse index, ν, counts the number of times the trajectory bounces at a turning point, where $E = V_n(\mathsf{x})$, and determines the phase. The dominant imaginary part, which appears in Eq. (2), thus comes from trajectories which bounce exactly once.

This semiclassical approximation to the Green's functions can be employed in Eq. (2) to give the reaction probability and hence in Eq. (4) for the golden-rule rate. Performing the integrals over positions and energy using the method of steepest descents, defines two dominant classical trajectories which join together smoothly into a periodic orbit of length $\beta\hbar$, as shown in Fig. 1. We thereby obtain a semiclassical formula for the golden-rule rate of a multidimensional system, exponentially dependent on the total Euclidean action around the periodic orbit. This formula is similar to one derived by Cao and Voth [5] based on a less rigorous foundation. In the high-temperature limit, the instanton pathway collapses to a point and the rate formula recovers the classical golden-rule transition-state theory result [3].

The method is applicable to study electron-transfer rates in polar environments of interest in chemistry. The instanton trajectory can be located in such complex multidimensional systems using a discretization scheme [6]. In this approach, the pathway is described using a ring polymer and the action integral obtained using the trapezium rule. The ring-polymer geometry is optimized to give a stationary value of the action functional and thus the pathway of the required trajectory. In this form, the golden-rule instanton method can be seen to be strongly related to Wolynes' quantum instanton approach [7].

The semiclassical Green's functions are also a powerful tool for deriving other chemical reaction rate theories. In a similar way, it is possible to rederive the usual adiabatic instanton theory [6], which includes the Born-Oppenheimer approximation, and we are researching applications to more general nonadiabatic reactions.

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Using Smolyak interpolants to solve the vibrational Schroedinger equation

TUCKER CARRINGTON

(joint work with Gustavo Avila)

At the workshop, I presented new ideas for computing the vibrational spectrum of a polyatomic molecule. The goal is to calculate many energy levels of a Hamiltonian, $H = K + V$, for which the potential energy surface (PES) is general and the kinetic energy operator (KEO) is exact. In particular, the methods I discussed do not require representing the PES as a sum of products or a sum of terms depending on a subset of the coordinates. We have published several papers about using basis pruning schemes, Smolyak quadratures, and efficient evaluation of matrix-vector products to compute vibrational spectra. In this talk, I focused on collocation, which obviates the need for quadrature. To devise a good quadrature method or a good collocation method one must confront two problems. First, the size of the basis needed to solve the Schroedinger equation scales exponentially. Second, the size of the quadrature or collocation grid needed to compute matrix elements or interpolate the wavefunctions also scales exponentially. A method that can be used with a general potential must be able to cope with both these manifestations of the curse of dimensionality.

Why collocation? If one uses a variational (Galerkin) method then to avoid a generalized eigenvalue problem it is common to choose basis functions and quadratures so that the overlap (Gram) matrix is an identity. This is important because there are no efficient iterative (i.e. Krylov-based) eigensolvers for generalised eigenvalue problems. The need to make the identity matrix an identity (and the desire to have exact KEO matrix elements) often forces one to choose non-optimal basis functions and quadrature points. In addition, it is only possible to find good nested sets of quadrature points if the 1-D basis functions are classical orthogonal polynomials. If instead, one uses collocation there are no integrals (and no quadratures) and no need to have exact KEO matrix elements and one is free to choose any basis functions. Nonetheless, established collocation methods have the key disadvantage that they require solving a generalized eigenvalue problem. Using Smolyak interpolants enables one to obviate, even in many dimensions, the need to solve a generalized eigenvalue problem.

Two new developments were presented at the workshop. First, I showed that a Smolyak collocation method can also be used with curvilinear internal coordinates. This is important because coupling will often be less important in curvilinear (than normal) coordinates and it is therefore possible to choose better basis functions and reduce the number of required points. Curvilinear coordinates are better suited for describing large amplitude motion and high-lying states. In curvilinear coordinates, the KEO is more complicated. It is easier to use collocation than variational (Galerkin) methods when the KEO is complicated because collocation obviates the need to determine a basis representation of the KEO. Second, I reported new ideas for writing an interpolated wavefunction as a sum of product basis functions and showed that they facilitate the evaluation of matrix-vector products for the KEO. The KEO matrix-vector products are computed using a sequential summation approach. Rather than evaluating a matrix-vector product for a term in the kinetic energy operator (KEO) by implicitly constructing a grid representation of the operator and applying it to a vector labelled by points, we instead apply the operator to basis functions and then evaluate at collocation points. Obviating the need to do matrix-vector vector products with vectors labelled by points reduces the CPU cost by orders of magnitude. Transforming the grid vector to a basis vector is not simple because the basis is not a direct product basis (it is pruned) and the grid is not a direct product grid (it is a Smolyak grid). Evaluating KEO matrix-vector products in this manner, the collocation method is as efficient as a Smolyak quadrature method but it allows one to use better basis functions.

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A new algorithm to compute the $\mathbb{Z}_2$ invariant of time-reversal symmetric topological insulators

Gianluca Panati
(joint work with D. Fiorenza, D. Monaco)

In my talk, I consider a gapped periodic quantum system with time-reversal symmetry of fermionic type, *i. e.* the time-reversal operator squares to $-\mathbb{1}$. With my collaborators, we investigated the existence of periodic and time-reversal invariant Bloch frames in dimensions 2 and 3. In 2*d*, the obstruction to the existence of such a frame is shown to be encoded in a **$\mathbb{Z}_2$-valued topological invariant**, which can be computed by a simple algorithm. We prove that the latter agrees with the Fu-Kane index. In 3*d*, instead, four $\mathbb{Z}_2$ invariants emerge from the construction, again related to the Fu-Kane-Mele indices. When no topological obstruction is present, we provide a **constructive algorithm** yielding explicitly a periodic and time-reversal invariant Bloch frame. The result is formulated in an abstract setting, so that it applies both to discrete models and to continuous ones.

In the recent past, the solid state physics community has developed an increasing interest in phenomena having topological and geometric origin. The first occurrence of systems displaying different quantum phases which can be labelled by topological indices can be traced back at least to the seminal paper by Thouless, Kohmoto, Nightingale and den Nijs [TKNN], in the context of the Integer Quantum Hall Effect. The first topological invariants to make their appearance in the condensed matter literature were thus *Chern numbers*: two distinct insulating quantum phases, which cannot be deformed one into the other by means of continuous (adiabatic) transformations without closing the gap between energy bands, are indexed by different *integers* (see [Gr] and references therein). These topological invariants are related to an observable quantity, namely to the transverse (Hall) conductivity of the system under consideration [TKNN, Gr]; the fact that the topological invariant is an integer explains why the observable is quantized. Beyond the realm of Quantum Hall systems, similar non-trivial topological phases appear whenever time-reversal symmetry is broken, even in absence of external magnetic fields, as early foreseen by Haldane [Hal]. Since this pioneering observation, the field of *Chern insulators* flourished [SPFKS, Ch, FC].

More recently, a new class of materials has been first theorized and then experimentally realized, where instead interesting topological quantum phases arise while preserving time-reversal symmetry: these materials are the so-called *time-reversal symmetric* (TRS) *topological insulators* (see [An, HK] for recent reviews). The peculiarity of these materials is that different quantum phases are labelled by *integers modulo 2*; from a phenomenological point of view, these indices are connected to the presence of spin edge currents responsible for the Quantum Spin Hall Effect [KM_1, KM_2]. It is crucial for the display of these currents that time-reversal symmetry is of *fermionic* (or *odd*) type, that is, the time-reversal operator Θ is such that $\Theta^2 = -\mathbb{1}$.

In a milestone paper [KM_1], Kane and Mele consider a tight-binding model governing the dynamics of an electron in a 2-dimensional honeycomb lattice subject to nearest- and next-to-nearest-neighbour hoppings, similarly to what happens in the Haldane model [Hal], with the addition of further terms, including time-reversal invariant spin-orbit interaction. This prototype model is used to propose a $\mathbb{Z}_2$ index to label the topological phases of $2d$ TRS topological insulators, and to predict the presence of observable currents in Quantum Spin Hall systems. An alternative formulation for this $\mathbb{Z}_2$ index is then provided by Fu and Kane in [FK], where the authors also argue that such index measures the obstruction to the existence of a continuous periodic Bloch frame which is moreover compatible with time-reversal symmetry. Similar indices appear also in 3-dimensional systems [FKM].

Since the proposals by Fu, Kane and Mele, there has been an intense activity in the community aimed at the explicit construction of smooth symmetric Bloch frames, in order to connect the possible topological obstructions to the $\mathbb{Z}_2$ indices [SV_3], and to study the localization of Wannier functions in TRS topological insulators [SV_1, SV_2]. However, while the geometric origin of the integer-valued topological invariants is well-established (as was mentioned above, they represent Chern numbers of the *Bloch bundle*, in the terminology of [Pa]), the situation is less clear for the $\mathbb{Z}_2$-valued indices of TRS topological insulators. Many interpretations of the $\mathbb{Z}_2$ indices have been given, using homotopic or K-theoretic classifications [AZ, MB, Ki, RSFL], C^*-algebraic approaches [Pr_1, Pr_2, Sch], the bulk-edge correspondence [ASV, GP], monodromy arguments [Pr_3], or gauge-theoretic methods [FW]. However, we believe that a clear and simple topological explanation of how they arise from the symmetries of the system is still missing in the literature.

In a recent paper [FMP_2], we provide a geometric characterization of these $\mathbb{Z}_2$ indices as topological obstructions to the existence of continuous periodic and time-reversal symmetric Bloch frames, thus substantiating the claim in [FK] on mathematical grounds. We consider a gapped periodic quantum system in presence of fermionic time-reversal symmetry, and we investigate whether there exists a global continuous Bloch frame which is both periodic and time-reversal symmetric. While in $1d$ this always exists, a topological obstruction may arise in $2d$. We show that such obstruction is encoded in a $\mathbb{Z}_2$ index δ, which is moreover a *topological invariant* of the system, with respect to those continuous deformations which preserve the symmetries. We prove that $\delta \in \mathbb{Z}_2$ agrees with the Fu-Kane index $\Delta \in \mathbb{Z}_2$ [FK], thus providing a proof that the latter is a topological invariant. Lastly, we investigate the same problem in $3d$, yielding to the definition of four $\mathbb{Z}_2$-valued topological obstructions, which are compared with the indices proposed by Fu, Kane and Mele in [FKM]. In all cases where there is no topological obstruction (*i. e.* the $\mathbb{Z}_2$ topological invariants vanish), we also provide an *explicit algorithm* to construct a global smooth Bloch frame which is periodic and time-reversal symmetric.

The main advantage of our method is that, being geometric in nature, it is based only on the *fundamental symmetries* of the Hamiltonian modeling the system, namely invariance by lattice translations (*i. e.* periodicity) and fermionic time-reversal symmetry. No further assumptions on the Hamiltonian and its gaps are needed in our approach, thus making it *model-independent*; in particular, it applies both to continuous and to tight-binding models, and both to the 2-dimensional and 3-dimensional setting. To the best of our knowledge, our method appears to be the first obstruction-theoretic characterization of the $\mathbb{Z}_2$ invariants in the pioneering field of 3-*dimensional* TRS topological insultators.

Another strong point in our approach is that the construction is algorithmic in nature, and gives also a way to *compute* the $\mathbb{Z}_2$ invariants in a given system. This makes our proposal well-suited for numerical implementation, which may be particularly appealing to the computational physics community [SV_1, SV_3].

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Improved quantum chemistry via electrons on D-dimensional spheres

Peter M.W. Gill
(joint work with Anneke Knol, Caleb Ball, Davids Agboola, Pierre-François Loos)

The primary goal of many quantum chemists is to know the electronic energy of a given system of nuclei and electrons. Under certain assumptions, this energy is given by an eigenvalue of the associated Schrödinger equation but, in all but the simplest of cases, the equation is impossible to solve exactly. For this reason, it is common to use self-consistent field (or mean field) methods to obtain a good approximation and then to append a small correction to the eigenvalue which is designed to fix most of the error in that approximation.

Following Wigner (1934) and Löwdin (1959), the correction is often called the "electron correlation" energy E_{c} and, in density functional theory, it is assumed that it can be written as a functional $F[\rho]$ of the electron density $\rho(\mathbf{r})$. Although the existence of F has been proven [1], its form is unknown and it is often supposed that, for electrons moving in $\mathbb{R}^D$, it may be approximated by the so-called Local Density Approximation (LDA)

$$E_{\mathrm{c}} = \int_{\mathbb{R}^D} \rho(\mathbf{r})\, \epsilon_{\mathrm{c}}^D(r_{\mathrm{s}}(\mathbf{r}))\, \mathrm{d}\mathbf{r} \tag{1}$$

where r_{s} is the Seitz radius and $\epsilon_{\mathrm{c}}^D(r_{\mathrm{s}})$ is the correlation energy per electron of the D-dimensional infinite uniform electron gas (UEG) with Seitz radius r_{s}. The function $\epsilon_{\mathrm{c}}^D(r_{\mathrm{s}})$ is not known exactly but has been calculated accurately over a wide range of r_{s} values using quantum Monte Carlo (QMC) calculations [2] and various types of perturbation theory.

Recently, we showed that (1) gives incorrect correlation energies when applied to *finite* UEGs, such as those that form when n electrons are confined to a D-sphere, i.e. the surface of a $(D+1)$-dimensional ball [3]. This revealed that the correlation energy of a UEG is not uniquely determined by its Seitz radius and that, therefore, at least one other defining parameter is required. We have argued that, because the Seitz radius measures the one-electron density at each point in space, it is natural to introduce a parameter η that measures (in some way) the two-electron density at each point and then to propose

$$E_{\mathrm{c}} = \int_{\mathbb{R}^D} \rho(\mathbf{r})\, \epsilon_{\mathrm{c}}^D(r_{\mathrm{s}}(\mathbf{r}), \eta(\mathbf{r}))\, \mathrm{d}\mathbf{r} \tag{2}$$

to generalize (1) so that it is exact for both infinite and finite gases.

There are many reasonable definitions for η but we have begun by investigating

$$\eta(\mathbf{r}) = C_D r_{\mathrm{s}}(\mathbf{r})^{D+2} \frac{\nabla^2 \rho_2(\mathbf{r},\mathbf{r})}{\rho(\mathbf{r})} \tag{3}$$

where ρ_2 is the spinless reduced two-electron density matrix. The quantity (3) is a dimensionless measure of the curvature of the electron-electron hole at $\mathbf{r}$.

To develop an understanding of the two-variable function $\epsilon_{\mathrm{c}}^D(r_{\mathrm{s}}, \eta)$, we have begun a systematic analytic and numerical investigation of the correlation energies of electrons on D-spheres with a range of r_{s} and η values. In the course of this investigation, we have discovered several families of closed-form solutions to the Schrödinger equation for two electrons on a D-sphere [5, 6, 7] and we have developed a variety of algorithmic techniques [8, 9, 10, 11, 12] for obtaining accurate numerical solutions for three or more electrons.

The study is complete for $D = 1$ [4] (i.e. rings) but is still underway for $D = 2$ and $D = 3$. Once the correlation energies have been obtained, they can be fit to judiciously chosen functional forms and the resulting Generalized Local Density

Approximation (GLDA) represented by (2) tested on non-uniform D-dimensional electronic systems.

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State and parameter estimations for open quantum systems

Pierre Rouchon

The first quantum feedback experiment has been realized in the cavity quantum electro-dynamics group of Serge Haroche and Jean-Michel Raimond in 2011. The mathematical models underlying these feedback-loops are hidden state Markov chains. In these experiments, the hidden quantum state is the density operator of a quantum harmonic oscillator. It is estimated in real-time from the measurement outcomes via a discrete-time adaptation of Belavkin quantum filters. These filters rely essentially on quantum probability attached to the collapse of the wave packet resulting from the measurement process, decoherence seen as unread fictitious measurements done by the environment, and classical probabilities to take into-account measurement imperfections.

We expose the mathematical structure of such quantum filters. We show with elementary arguments that their formulations are based on completely positive linear maps, indexed by the measurement outcomes, and non-necessarily trace preserving. In the continuous-time (diffusive) case, such formulations are equivalent to usual stochastic master equations driven by Wiener processes and governing the density operator dynamics. They provide also numerically efficient formulations of particle quantum filters for Bayesian estimations of classical parameters. To illustrate the practical interest of these formulations we show how to precisely estimate the detection efficiency from experimental data collected for a superconducting qubit whose fluorescence field is measured using a heterodyne detector.

Quantum mechanics without wavefunctions

Bill Poirier

(joint work with Gérard Parlant, Jeremy Schiff, and Hung-Ming Tsai)

This presentation explores an alternate "Many Interacting Worlds" [1, 2, 3, 4, 5, 6, 7, 8], quantum framework in which the wavefunction $\Psi(t, \mathbf{x})$ plays no role. Instead, quantum states are represented as ensembles of real-valued trajectories, $\mathbf{x}(t, \mathbf{C})$, where $\mathbf{C}$ labels a trajectory. Quantum effects arise from the mutual interaction of different trajectories or "worlds," manifesting as partial derivatives with respect to $\mathbf{C}$. The quantum trajectory ensemble $\mathbf{x}(t, \mathbf{C})$ satisfies an action principle, leading to a dynamical PDE (via a generalized Euler-Lagrange procedure), as well as to conservation laws (via Noether's theorem). The action is *extremized* as in classical Lagrangian mechanics—rather than exponentiated and summed over, as in the path-integral formulation. All quantities are real-valued, and $\mathbf{x}(t, \mathbf{C})$ foliates spacetime (for a single particle). The "worlds" are therefore interacting but non-branching—exactly opposite behavior from "Everett Many Worlds" [9].

The original, nonrelativistic version of the trajectory-based theory was found to be mathematically equivalent to the time-dependent Schrödinger equation [1, 2, 3, 10, 11], although it can be derived completely independently [1, 2, 3]. On the other hand, a more recent, relativistic generalization (for single, spin-zero, massive particles) [5] is *not* equivalent to the Klein-Gordon (KG) equation—and in fact, avoids certain well-known issues of the latter, such as negative probability density. It therefore makes new physical predictions that could in principle be validated or refuted by experiment. Likewise, a discretized version of the nonrelativistic theory that was recently proposed [6, 7, 8] could also lead to new physical predictions.

Consider a trajectory $x(t)$ for a single spatial coordinate x and time coordinate t, presumed to be the solution of some as-yet-unspecified dynamical law (ODE). We wish to determine $x(t)$, as well as the dynamical law itself, solely by applying the two bedrock physical principles of action extremization and energy conservation. The former implies that $x(t)$ obeys an Euler-Lagrange equation obtained from a Lagrangian L, which we take to be of the form

$$L[x, \dot{x}] = T[\dot{x}] - V[x]. \tag{1}$$

For the moment, $T[\dot{x}]$ and $V[x]$ are arbitrary. By Noether's theorem, the lack of implicit dependence of L on t implies a conserved quantity along $x(t)$. If we take this to be the energy $E[x, \dot{x}] = T[\dot{x}] + V[x]$, this results in a *constraint on the allowed forms for* $T[\dot{x}]$ *and* $V[x]$, thereby determining the dynamical law.

Specifically, one finds that $T[\dot{x}]$ *must* take the form of a constant times $\dot{x}^2$ ($V[x]$ is arbitrary). Identifying that constant as one half the mass ($m/2$) leads to Newton's ODE. Thus is the familiar classical dynamical law derived, presuming only a Lagrangian of the generic Eq. (1) form, in addition to the two physical principles. Moreover, it can be shown [2] that a more generalized $L[x, \dot{x}]$ form—i.e., not restricted to Eq. (1)—gives rise to the generalized (non-Euclidean x) dynamical law of standard classical Lagrangian mechanics. Thus, *only* the standard forms of classical physics emerge as permissible dynamical laws, when the Lagrangian is first order in the time derivatives of x (with one caveat [2]).

Conversely, any nonclassical dynamical laws must arise from Lagrangians involving higher-order derivatives. Towards this end, a kinematic "quantum correction" is presumed, leading to the following modified expressions:

$$\begin{aligned} L[x, \dot{x}, \ddot{x}, \ldots] &= T[\dot{x}] - V[x] - Q[\dot{x}, \ddot{x}, \dddot{x}, \ldots] \\ E[x, \dot{x}, \ddot{x}, \ldots] &= T[\dot{x}] + V[x] + Q[\dot{x}, \ddot{x}, \dddot{x}, \ldots] \end{aligned}$$

The existence of a nontrivial $Q[\dot{x}, \ddot{x}, \dddot{x}, \ldots]$ (i.e., not $Q = \text{const}$) that satisfies both physical principles is not guaranteed *a priori*. A systematic, order-by-order search reveals the following to be the simplest, lowest-order, meromorphic solution:

$$Q[\dot{x}, \ddot{x}, \dddot{x}] = B \left(\frac{\dddot{x}}{\dot{x}^3} - \frac{5}{2} \frac{\ddot{x}^2}{\dot{x}^4} \right) \tag{2}$$

Other dynamical laws also exist, at third order, and every higher odd order.

The identification $B = \frac{\hbar^2}{4m}$ in Eq. (2) leads to trajectories that are equivalent to those of Bohmian mechanics [12] in the special case of 1D time-independent stationary scattering. The Q of Eq. (2) is therefore the "quantum potential," although it is derived here without reference to a wavefunction—nor indeed, to any quantum mechanical postulates whatever. Note that in this context, a single quantum trajectory represents a single quantum state in one-to-one fashion.

For time-dependent 1D applications, a single trajectory no longer suffices to represent a single quantum state; rather, a one-parameter ensemble of trajectories, $x(C, t)$, must be used. For the time-independent special case described above, these trajectories must all be time-delayed copies of one another (i.e., effectively a single trajectory, as discussed), so that, e.g., $x(C, t) = x(C - \alpha t)$. Because all terms in Eq. (2) are invariant under the rescaling $t \to -\alpha t$, the time derivatives may be replaced with "spatial" (C) derivatives—suggesting a more general form of Q, suitable also for the time-dependent case. Equivalently, energy and action considerations of the type discussed above also lead to this same, C-derivative Q form. The resulting Euler-Lagrange dynamical PDE for $x(C, t)$ is

$$m\ddot{x} + \frac{\partial V(x)}{\partial x} + \frac{\hbar^2}{4m} \left(\frac{x''''}{x'^4} - 8 \frac{x''' x''}{x'^5} + 10 \frac{x''^3}{x'^6} \right) = 0 \;, \tag{3}$$

where primes denote partial derivatives with respect to C, keeping t fixed.

The trajectories emerging from Eq. (3) are equivalent to those of Bohmian mechanics – and the trajectory theory equivalent to 1D time-dependent Schrödinger theory – provided that: (a) probability is presumed to be conserved along trajectories; (b) the parameter C is presumed to "uniformize" the probability density – i.e.

$f(C) = \text{const}$, where $|\Psi(x)|^2 dx = \rho(x) dx = f(C) dC$. (Arbitrary reparametrizations of C may also be considered, but will not be here). For many-D applications, x is replaced with the vector $\mathbf{x} = x^i$, and C with $\mathbf{C} = C^i$. Equation (3) becomes

$$m\,\ddot{x}^i + \frac{\partial V(\mathbf{x})}{\partial x^i} - \frac{\hbar^2}{4m}\frac{\partial}{\partial C^m}\left(K^k_{\ i} K^m_{\ j}\frac{\partial^2 K^l_{\ j}}{\partial C^k \partial C^l}\right) = 0\ , \tag{4}$$

where $K = J^{-1}$ is the inverse Jacobi matrix, i.e. $K^i_{\ j} = \partial C^i / \partial x^j$. Einstein notation is used, albeit with mismatched indices, as Euclidean $\mathbf{x}$ space is presumed.

The quantum force term in Eq. (4) can be easily rewritten in terms of metric tensors, leading to a straightforward single-free-particle relativistic generalization:

$$\begin{aligned}
\frac{\partial^2 x^\alpha}{\partial \mathcal{T}^2} &= \exp\left[-\frac{2Q}{mc^2}\right]\frac{f^\alpha}{m} - \left(\frac{1}{mc^2}\right)\frac{\partial Q}{\partial \mathcal{T}}\frac{\partial x^\alpha}{\partial \mathcal{T}}\,, \qquad (5)\\
\text{where}\quad Q &= -\frac{\hbar^2}{2m}\gamma^{-1/4}\,\partial_i\left[\gamma^{1/2}\,\gamma^{ij}\,\partial_j \gamma^{-1/4}\right]\,,\\
f^\alpha &= -\eta^{\alpha\beta}\frac{\partial C^i}{\partial x^\beta}\,\partial_i Q = -\frac{\partial x^\alpha}{\partial C^i}\,\gamma^{ij}\,\partial_j Q\,,
\end{aligned}$$

η is the usual (flat) Minkowski spacetime metric, γ is the spatial part of the (block-diagonal) metric tensor g in the curvilinear $(c\mathcal{T}, \mathbf{C})$ coordinates, and $\mathcal{T}$ is the global "ensemble proper time" coordinate. Equation (5) reduces seamlessly to both classical relativistic mechanics and nonrelativistic quantum mechanics in the appropriate limits. It also introduces a generalized "global simultaneity" into relativity theory, as well as a purely quantum "time compression" effect [5].

Broad ranging ramifications of the trajectory-based approach continue to be realized, including new conservation laws, numerical algorithms, mixed quantum classical methods, experimental predictions, interpretations of "wavefunction collapse" and measurement, etc.

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Quantum dynamics in open quantum-classical systems

Raymond Kapral

Open quantum systems interact with their environments and these environmental interactions can lead to decoherence and dissipation. Often, the dynamics of the environment may be treated classically to a good approximation so that the system may be classified as an open quantum-classical system. The talk described such open quantum-classical systems whose dynamics is given by the quantum-classical Liouville equation,

$$\frac{\partial}{\partial t}\hat{\rho}_W(X,t) = -\frac{i}{\hbar}[\hat{H}_W, \hat{\rho}_W(t)] + \frac{1}{2}\Big(\{\hat{H}_W, \hat{\rho}_W(t)\} - \{\hat{\rho}_W(t), \hat{H}_W\}\Big).$$

Here $\hat{\rho}_W(X,t)$ is the density matrix with $X=(R,P)$ the phase space variables of the environment, and the square and curly brackets denote the commutator and Poisson brackets, respectively. This equation may derived by first taking a partial Wigner transform over the environmental degrees of freedom, then passing to the quantum-classical limit through either an expansion in the ratio of the mass of the (light) quantum subsystem particles to the mass of the (heavy) environmental particles, or though an analysis based on linearized path integrals. For reviews with references see Refs. [1, 2]

In the quantum-classical Liouville equation written above, no specific representation for the quantum subsystem was specified. In the talk a representation in terms of the eigenstates of the subsystem Hamiltonian was considered. Rather than dealing directly with this representation of the equation, the eigenstates and quantum operators were then transformed into the mapping basis in order to obtain a phase space description of the quantum degrees of freedom. The mapping representation associates a basis of singly occupied harmonic oscillators states with each subsystem quantum state. For example the subsystem quantum state $|\lambda\rangle$ is mapped to the state $|0,\cdots,1_\lambda,\cdots,0\rangle$ where the 1 appears in the λ position. Operators may then be written in terms of annihilation and creation operators on these mapping states. The resulting quantum-classical Liouville equation may be written as [3, 4, 5]

$$\begin{aligned}\frac{\partial}{\partial t}\rho_m(\mathcal{X},t) &= \{H_m, \rho_m(t)\}_{\mathcal{X}} \\ &\quad -\frac{\hbar}{8}\frac{\partial h_{\lambda\lambda'}}{\partial R}\Big(\frac{\partial}{\partial r_{\lambda'}}\frac{\partial}{\partial r_\lambda} + \frac{\partial}{\partial p_{\lambda'}}\frac{\partial}{\partial p_\lambda}\Big)\cdot\frac{\partial}{\partial P}\rho_m(t),\end{aligned}$$

where $x=(r,p)$ are the phase space variables that arise from a further Wigner transform over the mapping variables. We use the notation $\{A_m, B_m(t)\}_{\mathcal{X}}$ for a Poisson bracket in the full mapping-bath phase space of the entire system,

$\chi = (x, X)$. The first Poisson bracket term on the right side of the equation specifies a Hamiltonian dynamics that can be solved in terms of an ensemble if independent trajectories. Often, but not always, the dynamics described by this term provides an accurate description of nonadiabatic dynamics. It may happen that the dynamics described by the first term alone takes the system out of the physical mapping space. If the second term is also taken into account then no such independent-trajectory description is possible. The dynamics described by the full quantum-classical Liouville equation where both terms are taken into account is confined to the physical space. [5]

Another solution to the quantum-classical Liouville equation may be obtained by again starting from its representation in the mapping basis. Now however one writes the formal solution in terms of forward and backward quantum-classical propagators, analogous to the formal solution for the full quantum mechanical problem. Given this starting point, writing the solution as a concatenation of short-time segments and inserting complete sets of coherent states, an approximate solution may be constructed [6, 7] The equations of motion that govern phase space variables that enter this forward-backward solution have a Hamiltonian form,

$$\frac{d\chi_\mu}{dt} = \frac{\partial H_e(\chi, \pi)}{\partial \pi_\mu}, \qquad \frac{d\pi_\mu}{dt} = -\frac{\partial H_e(\chi, \pi)}{\partial \chi_\mu},$$

where

$$\begin{aligned} H_e(\chi, \pi) &= P^2/2M + V_{\mathrm{fb}}(R) \\ &\quad + \frac{1}{2\hbar} h_{\lambda\lambda'}(R)(q_\lambda q_{\lambda'} + p_\lambda p_{\lambda'} + q'_\lambda q'_{\lambda'} + p'_\lambda p'_{\lambda'}), \end{aligned}$$

with $\chi = (R, q, q')$, and $\pi = (P, p, p')$ where the lower case unprimed and primed variables arise from forward and backward quantum dynamics, respectively. The matrix elements of the Hamiltonian (minus the kinetic energy of the environmental degrees of freedom) are $h_{\lambda\lambda'}(R)$ and $V_{\mathrm{fb}}(R)$ is the potential energy of the environment minus the trace of $\hat{h}$. Because of the Hamiltonian structure of these equations the dynamics is easily simulated. To obtain this solution, it was assumed that the coherent state overlap matrix elements that connect the small time intervals in the solution are Dirac delta functions. This approximation may be relaxed systematically obtain a numerically exact solution, albeit at a considerably increased computational cost. The simple forward-backward solution is often very accurate and its validity can be checked by the systematic relaxation of the orthogonality approximation.

The quantum-classical Liouville equation is equivalent to full quantum dynamics for the entire system for an arbitrary quantum subsystem bilinearly coupled to a harmonic bath. For nonlinear coupling an and nonlinear baths it is an approximation to full quantum dynamics. Since it is exact for an important class of systems the accuracy of simulation methods may easily be assessed and connections to other theories established.

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Accurate Thermodynamics with a Noisy Gradient

Ben Leimkuhler

Thermostats are distributional controls commonly used to sample the canonical distribution in molecular dynamics simulation where the underlying model is a conservative system or gradient flow. In many applications, however, the forces are corrupted by perturbations due to incomplete averaging in another scale regime. For example, this situation arises in many types of mixed quantum-classical dynamics (Ehrenfest dynamics, TDDFT, QM-MM). It is also an important characteristic of dynamics-based Bayesian inference procedures being used by Google and others in the data science community.

The usual solutions proposed in the literature include (i) the use of standard stochastic gradient dynamics (Brownian or Langevin dynamics), ignoring the perturbation, with the assumption that errors "average out," and (ii) quantification of the error relative to an underlying gradient model coupled with a correction procedure. The first of these approaches is demonstrably wrong–the effect of the force error is typically an additional random perturbation and failure to take it into consideration will introduce substantial errors in the equilibrium state, whereas the second is not practical in many cases as it is computationally difficult to directly extract the unknown underlying force field in the presence of noise.

It is possible to design a robust thermostat-based procedure addressing the noisy gradient sampling problem when the noise is Gaussian of unknown variance[1] this is a reasonable assumption in many cases due to the central limit theorem. Our methods come in several flavors, for example Adaptive Langevin which can be viewed as a sort of Langevin dynamics in which the dissipation coefficient is automatically determined by local kinetic energy control; it is effectively a hybrid of Nose-Hoover dynamics and Langevin dynamics (but different than Nose-Hoover-Langevin). Although our analysis assumes a fixed variance, the methods can be generalized to the case where the variance evolves adiabatically as a function of position. We have have already deployed adaptive thermostats for QM/MM simulation in [2].

Our work on numerical analysis for Langevin dynamics [3, 4, 5] has uncovered numerical methods that have exceptional properties with respect to the invariant measure, specifically they are exact for harmonic systems, highly accurate for weakly perturbed harmonic models, and for general anharmonic systems exhibit high order of accuracy (superconvergence) for configurational averages in the high friction regime. In [6] we have demonstrated that a certain integration scheme for the Adaptive Langevin method inherits these accuracy properties; dramatic improvements in sampling accuracy are therefore unlocked for multiscale simulation. Several model examples have been considered which illustrate the properties and efficiencies attainable.

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Computational error estimates for molecular dynamics

Anders Szepessy

(joint work with Christian Bayer, Håkon Hoel, Ashraful Kadir, Petr Plecháč, Mattias Sandberg)

We have three types of errors in molecular dynamics simulations: time discretization error, sampling error and modeling error. The time discretization error comes from approximating the differential equation for molecular dynamics positions X_t, at time t, with a numerical method, based on replacing time derivatives with difference quotients and time steps Δt. The sampling error is due to truncating the infinite τ and using a finite value of τ in determining a molecular dynamics observable $\int_0^\tau g(X_t)dt/\tau$. The modeling error originates from eliminating the electrons in the Schrödinger nuclei-electron system and replacing the nuclei dynamics with their classical paths; this approximation error was first analyzed by Born and Oppenheimer in their seminal paper 1927.

The time discretization and truncation error components are in some sense simpler to handle by comparing simulations with different choices of Δt and τ, although it can, of course, be difficult to know that the behavior does not change with even smaller Δt and larger τ. The modeling error is more difficult to check since a direct approach requires the solution of the Schrödinger equation. Consequently the modeling error requires mathematical error analysis.

Egorov's theorem is one of the main tools to estimate approximation error of molecular dynamics observables as compared to quantum observables in the micro canonical ensemble. Shnirelman and others have shown how observables for the time-independent Schrödinger equation is approximated by ergodic dynamics. Our work [1] focuses on the following mathematical modifications, which are important in a computational setting.

- In general, ergodicity is hard to verify theoretically and computationally. We use an alternative assumption, which can be tested computationally based on finite time convergence rate, also leading to an error estimate of molecular dynamics observables.
- The standard proofs use L^2-estimates of remainders in Weyl quantization compositions which lead to maximum norm bounds on derivatives of the observable up to the order of the number of particles. We show how to avoid this many derivatives, using instead a maximum norm estimate of a regularized observable.

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The Lieb-Oxford inequality and the Jellium model

MATHIEU LEWIN

(joint work with Elliott H. Lieb)

One of the central problems in density functional theory is the estimation of the indirect part $E_{\rm Ind}$ of the Coulomb energy in the ground state. Ideally, this estimate should be local, that is, it must be given by an integral of some function of $\rho(x)$ and its derivatives.

The indirect part of the Coulomb energy of an N-particle (symmetric) probability distribution P_N on $\mathbb{R}^{3N}$ is defined by

$$E_{\rm Ind} = \int_{\mathbb{R}^{3N}} \left(\sum_{1\le j<k\le N} \frac{1}{|x_j - x_k|} \right) {\rm d}P_N - D(\rho,\rho) \tag{1}$$

where $\rho(x) = N\int_{\mathbb{R}^{3(N-1)}} {\rm d}P_N(x, x_2, ..., x_N)$ is the corresponding density and

$$D(\rho,\rho) = \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|}\,{\rm d}x\,{\rm d}y \tag{2}$$

is its (direct) Coulomb energy. A well known bound on E_{Ind} is the Lieb-Oxford inequality [9]

$$E_{\mathrm{Ind}} \geq -1.68 \int_{\mathbb{R}^3} \rho(x)^{4/3}\,\mathrm{d}x \tag{3}$$

which was based on an earlier inequality in [7] with the constant 8.52 instead of 1.68, and which was later improved by Chan and Handy to 1.64 in [5].

The Lieb-Oxford inequality has been used to construct some exchange-correlation functionals, like the famous Perdew-Burke-Erzenhof functional [11]. Due to its impact on the models used by practinioners, it is important to find the best constant in the Lieb-Oxford inequality (3). The latter is not yet known. It was conjectured in [10, 12] that the best constant is attained when ρ is the characteristic function of a large set of volume $V \to \infty$, and that the lowest value of $E_{\mathrm{Ind}}/\int \rho^{4/3}$ that can be reached with N-particle probability distributions over $\mathbb{R}^{3N}$ yielding such a density ρ is -1.4442. This value comes from the Jellium problem, as will be discussed below.

In [6], we gave two new inequalities which are better than the original Lieb-Oxford inequality for a slowly varying ρ and, in particular, when ρ is constant on a large set. Our inequality is

$$E_{\mathrm{Ind}} \geq -\left(\frac{3}{5}\left(\frac{9\pi}{2}\right)^{\frac{1}{3}} + \alpha\right)\int_{\mathbb{R}^3} \rho^{\frac{4}{3}} - \begin{cases} \dfrac{0.001206}{\alpha^3}\displaystyle\int_{\mathbb{R}^3} |\nabla\rho| \\ \dfrac{0.1236}{\alpha^2}\displaystyle\int_{\mathbb{R}^3} |\nabla\rho^{\frac{1}{3}}|^2 \end{cases} \tag{4}$$

for all $\alpha > 0$. After optimizing over α in (4), an equivalent formulation is

$$E_{\mathrm{Ind}} \geq -\frac{3}{5}\left(\frac{9\pi}{2}\right)^{\frac{1}{3}}\int_{\mathbb{R}^3} \rho^{\frac{4}{3}} - \begin{cases} 0.3270\left(\displaystyle\int_{\mathbb{R}^3} |\nabla\rho|\right)^{\frac{1}{4}}\left(\displaystyle\int_{\mathbb{R}^3} \rho^{\frac{4}{3}}\right)^{\frac{3}{4}} \\ 0.9416\left(\displaystyle\int_{\mathbb{R}^3} |\nabla\rho^{\frac{1}{3}}|^2\right)^{\frac{1}{3}}\left(\displaystyle\int_{\mathbb{R}^3} \rho^{\frac{4}{3}}\right)^{\frac{2}{3}}. \end{cases} \tag{5}$$

The constants have been slightly optimized as compared to [6]. The inequality on the second line uses a non-optimal estimate for Hardy-Littlewood maximal functions, and this is why it is much worse than the first line, which is based on simpler arguments. Our constant $3/5(9\pi/2)^{1/3} \simeq 1.4508$ is very close to the supposedly optimal 1.4442 for a slowly varying ρ. Our result extends a previous work of Benguria, Bley and Loss [1] who got a similar inequality, but involving the nonlocal term $(\sqrt{\rho}, |\nabla|\sqrt{\rho})$ instead of our gradient corrections. The constant $3/5(9\pi/2)^{1/3}$ also already appeared in a previous work [8] of Lieb and Narnhofer dealing with Jellium.

Our bounds (5) were numerically studied in [4, 3]. In particular, in [4] it was found that the new bound is not better than the usual Lieb-Oxford bound (3) for spherically symmetric atoms with $Z \leq 88$. Dividing our constant 0.3270 by a factor two would make it better for all $Z \geq 2$. It is therefore an important challenge to improve our bounds.

Let us now discuss a relation between the Jellium problem and the indirect energy, which is often mentioned in the literature. The Jellium problem consists in optimizing the positions of classical Coulomb particles in a neutralizing uniform background. A famous conjecture of Wigner [13, 2] is that the particles are, in the minimizing position, placed on a Body-Centered Cubic (BCC) lattice. The indirect energy problem has no background but there is a way to interpret the term $D(\rho,\rho)$ as coming from a fictitious uniform background, provided that the density ρ of P_N is constant.

Let $\mathcal{L}$ be the BCC lattice with unit cell Q of volume 1 and with $0\in\mathcal{L}$. We pick a big ball B_R of radius R (or any other fixed set that is dilated of a factor R) and place $N=\#\mathcal{L}\cap B_R$ particles on the sites $z_1,...,z_N$ of $\mathcal{L}$ that are in this ball. Next we average the corresponding probability density $(N!)^{-1}\sum_{\sigma\in\mathfrak{S}_N}\prod_{j=1}^N\delta_{z_j}(x_{\sigma(j)})$ over the translations of the unit cell. We thereby obtain a probability density P_N which has the constant density $\rho\equiv 1$ over the union $\Omega=\cup_{j=1}^N Q+z_j$ of the cells that intersect the ball B_R. The Coulomb energy of this probability density does not change, by translation-invariance, and the indirect energy of P_N is thus

$$E_{\rm ind}(N)=\frac{1}{2}\sum_{x\neq y\in\mathcal{L}\cap B_R}\frac{1}{|x-y|}-\frac{1}{2}\int_\Omega\int_\Omega\frac{{\rm d}x\,{\rm d}y}{|x-y|}.$$

Now if we think of having particles at the centers of the cells and a uniform background in the domain Ω, the Jellium energy is

$$E_{\rm Jell}(N)=\frac{1}{2}\sum_{x\neq y\in\mathcal{L}\cap B_R}\frac{1}{|x-y|}-\sum_{x\in\mathcal{L}\cap B_R}\int_\Omega\frac{{\rm d}y}{|x-y|}+\frac{1}{2}\int_\Omega\int_\Omega\frac{{\rm d}x\,{\rm d}y}{|x-y|}. \tag{6}$$

A calculation shows that $E_{\rm Jell}(N)/N\to\zeta_{\mathcal{L}}(1)\simeq-1.4442$ as $N\to\infty$, where $\zeta_{\mathcal{L}}(s)=\sum_{z\in\mathcal{L}\setminus\{0\}}|z|^{-s}$ is the Epstein Zeta function, analytically continued to $s=1$, see [2]. In the literature, the second term in (6) above is sometimes claimed to be the same quantity as the third term in (6), up to a factor of 2, in the limit $N\to\infty$. In this manner, one is led to think that one has constructed a probability density P_N with an indirect energy that is exactly the same as the Jellium energy, namely -1.4442 in the limit $N\to\infty$. Unfortunately, *this expectation is not fulfilled*, as we have shown in [6]. Indeed, a careful calculation gives

$$\lim_{N\to\infty}\frac{E_{\rm Ind}(N)-E_{\rm Jell}(N)}{N}=\int_{\mathbb{R}^3}\left(\frac{1}{|x|}-\int_Q\frac{1}{|x-y|}{\rm d}y\right){\rm d}x =\frac{2\pi}{3}\int_Q|x|^2\,{\rm d}x\simeq 0.4935. \tag{7}$$

Our result relies on the long range of the Coulomb potential. For any other potential that decays slightly faster than $1/|x|$ at infinity, the Jellium and indirect energies coincide in the limit. After this computation, it is not clear anymore that the best Lieb-Oxford inequality is ≥ 1.4442. Given the importance of the uniform electron gas model in density functional theory, we hope that our work will stimulate further investigations of the indirect energy problem at constant density.

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Coupled Hill's Equations and the Lorentz Oscillator Model

Anthony M. Bloch
(joint work with Fred C. Adams, Rohit Gupta, Hamed Razavi)

We study the stability of a class of coupled Hill's equations with application to the Lorentz Oscillator Model. In particular we show that there is a transformation from the Lorentz Oscillator model to the coupled Hill's equation which removes the dissipation terms and illustrates the stability of both systems. We analyze the stability using Floquet theory and discuss the structure of the transfer matrix. The Lorentz Oscillator models bound electron motion. We are interested in this model in dielectric materials where electric and magnetic response is of interest. The work here is inspired by the research in [3]. We include both numerical analysis of the stability regions and analysis of the Floquet multipliers.

The general n-dimensional coupled Hills equations (CHE) have the form

$$\ddot{\boldsymbol{x}} + B(t)\boldsymbol{x} = 0 \tag{1}$$

where $\boldsymbol{x}$ is $n \times 1$ and $B(t)$ is an $n \times n$ periodic real matrix.

We are interested in a particular two-dimensional model which is related to the Lorentz Oscillator model:

$$\ddot{x} + p(t)x = -q(t)z \tag{2}$$
$$\ddot{z} + p(t)z = q(t)x\,, \tag{3}$$

where $p(t)$ is even and periodic and $q(t)$ is odd and periodic, both smooth with common period T.

The Lorentz Oscillator Model (LOM) mentioned above is described by the coupled differential equations

$$\ddot{x} + \gamma_x\dot{x} + \omega_x^2 x = \frac{qE_0}{m}\cos(\omega t) - \frac{qB_0}{m}\cos(\omega t)\dot{z}\,, \tag{4}$$
$$\ddot{z} + \gamma_z\dot{z} + \omega_z^2 z = \frac{qB_0}{m}\cos(\omega t)\dot{x}\,. \tag{5}$$

This model described bound electron motion subject to external electric and magnetic fieldsand amplitudes E_o and B_0 respectively. Scaling appropriately we can rewrite as:

$$\ddot{x} + \gamma_x\dot{x} + \Omega_x^2 x = \epsilon\cos t - \beta(\cos t)\dot{z}\,, \tag{6}$$
$$\ddot{z} + \gamma_z\dot{z} + \Omega_z^2 z = \beta(\cos t)\dot{x}\,. \tag{7}$$

Definition: The LOM is said to be *symmetric* if

$$\gamma_x = \gamma_z = \gamma, \quad \Omega_x^2 = \Omega_z^2 = \Omega^2. \tag{8}$$

We can use a transformation to write the symmetric homogeneous LOM as a CHE. Define the complex function

$$y = x + iz = W\exp\left[-\frac{1}{2}\gamma t + \frac{i}{2}\beta\sin t\right]\,. \tag{9}$$

Then we define $W = \chi + i\zeta$ and let

$$a \equiv \Omega^2 - \frac{\gamma^2}{4} + \frac{\beta^2}{8} \qquad \text{and} \qquad b \equiv \frac{\beta^2}{8}\,. \tag{10}$$

The differential equations then become

$$\ddot{\chi} + [a + b\cos 2t]\,\chi = \frac{1}{2}\beta\,(\gamma\cos t - \sin t)\,\zeta \tag{11}$$
$$\ddot{\zeta} + [a + b\cos 2t]\,\zeta = -\frac{1}{2}\beta\,(\gamma\cos t - \sin t)\,\chi\,. \tag{12}$$

We now consider the use of Floquet theory to analyze the general coupled Hills equations

$$\ddot{x} + p(t)x = -q(t)z \tag{13}$$
$$\ddot{z} + p(t)z = q(t)x\,, \tag{14}$$

where $p(t), q(t)$ are smooth periodic functions with a common period T. This system can be written in the form

$$\frac{d\mathbf{v}}{dt} = A(t)\mathbf{v}\,. \tag{15}$$

This system is linear periodic, hence we can apply Floquet theory ([4]) to study the stability of the solutions. Let T be the common period of $p(t)$ and $q(t)$, i.e. $p(t+T) = p(t)$ and $q(t+T) = q(t)$.

We can prove the following result:

Theorem: The transfer matrix has the following block form

$$\mathbb{M} = \begin{bmatrix} \mathbb{A} & -\mathbb{B} \\ \mathbb{B} & \mathbb{A} \end{bmatrix}, \tag{16}$$

where $\mathbb{A}$ and $\mathbb{B}$ are 2×2 matrices. The constituent matrices $\mathbb{A}$ and $\mathbb{B}$ have the general forms

$$\mathbb{A} = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \qquad \text{and} \qquad \mathbb{B} = \begin{bmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{bmatrix}. \tag{17}$$

Further the largest Floquet multiplier is determined generically by a formula of the form

$$\lambda = a_{11} \pm \left[a_{11}^2 - 1\right]^{1/2}. \tag{18}$$

Thus the stability of symmetric coupled Hills system can be studied by only looking at one element of the transfer matrix, a_{11}.

We can study the stability regions for a special case of the Hills equations which was found from the rotation of the LOM:

$$\begin{aligned} \ddot{x} + [a + b\cos 2t]\, x &= -c\sin(t)z \\ \ddot{z} + [a + b\cos 2t]\, z &= c\sin(t)z\,. \end{aligned} \tag{19}$$

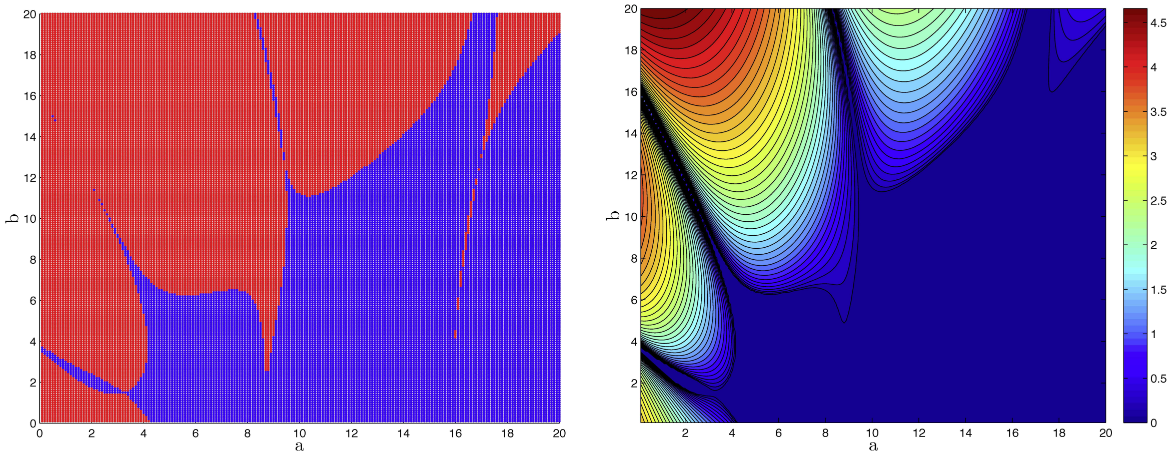

Figure 1. (a,b) Stability diagrams in the (a, b) plane for the coupled equations (19) for the parameter $c = 5$.

We provide a picture (linear and logarithmic) of the stability regions in a, b parameter space for a sample value of c. Level sets of largest Floquet multiplier are given. See Figure 1. We note how this generalizes the regions one finds in the Mathieu equation for example. Details and analysis are given in a forthcoming paper. We also intend to extend to the setting where the equations are subject to noise, building on the work in [1] and [2] and related publications.

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Algorithms for DFT Ab Initio Molecular Dynamics

Francois Gygi

First-Principles molecular dynamics (FPMD) simulations performed within the Born-Oppenheimer approximation are a popular approach for the description of condensed matter at finite temperature. This approach is most often used within the framework of Density Functional Theory [1] and requires the solution of the Kohn-Sham equations[2]. The accuracy of a DFT calculation depends critically on the choice of functional used to describe the exchange and correlation energy[3]. Recently, a new class of density functionals (called "hybrid" density functionals) was introduced in order to improve the accuracy of the exchange and correlation energy. Hybrid functionals include in their definition a fraction of the Hartree-Fock exchange energy

$$E_{\mathrm{x}}^{\mathrm{HF}} = -\frac{1}{2} \sum_{i,j=1}^{N} \int \frac{\phi_i^*(r)\phi_j^*(r)\phi_j(r')\phi_i(r')}{|r-r'|} dr dr'. \tag{1}$$

where $\phi_i(r)$ are Kohn-Sham orbitals, and N denotes the number of occupied orbitals. The inclusion of this term results in a large increase of the computational cost of simulations involving hybrid functionals. Although this cost can be mitigated by expanding the Kohn-Sham orbitals on atom-centered, localized basis functions (e.g. gaussians), we are interested in using the plane wave (or Fourier) basis for condensed systems because of their good translational invariance properties, and the absence of basis set superposition errors (BSSE) in that basis. The computational cost of the Hartree-Fock exchange energy is $O(N^3 \log N)$ when using plane waves and exploiting the efficiency of the fast Fourier transform (FFT) algorithm. This high cost has severely hindered the use of hybrid DFT calculations for large systems (i.e. systems including several hundred atoms). It has been noted by several authors that localized orbitals could be used to reduce this cost since an exchange integral for a pair of orbitals (ϕ_i, ϕ_j) can be neglected if the orbitals are localized in distinct domains in real space. According to the "near-sightedness" principle proposed by Kohn[4], it is in general possible to obtain a representation of the Kohn-Sham occupied subspace in terms of localized orbitals. One approach used to generate such localized orbitals is the calculation of Maximally Localized Wannier Functions (MLWFs)[5, 6], which were shown to be exponentially localized in systems exhibiting a finite gap between the eigenvalues of occupied and empty orbitals[7]. Following this approach, Wu *et al* have demonstrated efficient calculations of the Hartree-Fock exchange energy in liquid water[8].

We have developed an alternative approach[9] to the localization of orbitals, based on the CS decomposition[10]. In this approach, which we refer to as recursive subspace bisection (RSB), projectors $P^{(k)}, k = x, y, z$ are associated with bisecting planes that divide the simulation domain into subdomains Ω_k of equal size in the x, y, and z directions, e.g.

$$P^{(x)} f(x,y,z) = \begin{cases} f(x,y,z) & x < a/2 \\ 0 & x > a/2 \end{cases} \tag{2}$$

where a is the size of the simulation domain in the direction x. The matrices $A^{(k)}$ representing these projectors in the subspace of occupied orbitals are defined by

$$a_{ij}^{(k)} = \langle \phi_i, P^{(k)} \phi_j \rangle \tag{3}$$

Performing an approximate simultaneous diagonalization[11] of the matrices $A^{(k)}$ in the subspace of occupied orbitals provides singular values $c_i^{(k)}$ and $s_i^{(k)} = \sqrt{1 - c_i^2}$ that characterize the localization of the approximate computed eigenvectors in the subdomains Ω_k. For example, if $c_i^{(x)} \simeq 1$, the ith eigenvector is mostly localized in the region $x < a/2$. If however $c_i^{(x)} \simeq 0$, it is mostly localized in the region $x > a/2$. Given a threshold value $\epsilon > 0$, orbitals can then be truncated to one of these two subdomains if $(c_i^{(x)})^2 > 1 - \epsilon$ or if $(c_i^{(x)})^2 < \epsilon$, respectively. If the singular values have intermediate values, i.e. $\epsilon < (c_i^{(k)})^2 < 1 - \epsilon$, the eigenvector is not localized, and therefore it is not truncated. Using this truncation criterion based on a predefined threshold value ϵ, it is guaranteed that the truncation procedure does not introduce an error larger than $\sqrt{\epsilon}$ in 2-norm. We used this truncation procedure to accelerate the computation of the Hartree-Fock exchange energy in plane wave calculations. In that approach, exchange integrals for a pair (i, j) in (1) are not computed if the orbitals ϕ_i and ϕ_j can be truncated to separate domains for a given value of the threshold ϵ. A large acceleration of the computation results, as was shown in applications to various systems including liquid water, a chloride ion solvated in water, and a vacancy in a silicon crystal [12]. When using this truncation method, the 2-norm error threshold ϵ can be continuously reduced to zero, leading to smaller errors and a correspondingly smaller gain in computational speed. The error in the exchange energy can also be shown to be positive, since each neglected exchange integral is negative (this is apparent when representing the convolution integrals in (1) as Fourier sums). This property guarantees that convergence to the exact exchange energy is monotonic, which facilitates the error analysis in hybrid DFT simulations.

Further developments of the recursive subspace bisection method are under way to accelerate the computation of other quantities related to the correlation energy.

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Nanadiabatic transitions through avoided crossings

BENJAMIN GODDARD

(joint work with Volker Betz, Stefan Teufel)

For most molecular dynamics applications, the Born-Oppenheimer (infinite nuclear mass) approximation is used; it is assumed that the electronic energy levels are well-separated. However, in many chemical systems this is not valid. Typical examples are ultra-fast chemical reactions, such as the photodissociation of sodium iodide and the reception of light in the retina. We have considered the fundamental case of two electronic energy levels with one nuclear degree of freedom x, with Schrödinger equation

$$\mathrm{i}\epsilon\partial_t \begin{pmatrix}\psi_1(x,t)\\ \psi_2(x,t)\end{pmatrix} = \left(-\frac{\epsilon^2}{2}\partial_x^2 \boldsymbol{I} + \begin{pmatrix}X(x) & Z(x)\\ Z(x) & -X(x)\end{pmatrix} + d(x)\boldsymbol{I}\right)\begin{pmatrix}\psi_1(x,t)\\ \psi_2(x,t)\end{pmatrix},$$

where $\boldsymbol{I}$ is the 2×2 unit matrix, ϵ^2 is the nuclear-electron mass ratio, and $\psi = (\psi_1, \psi_2)^T \in L^2(\mathrm{d}x, \mathbb{C}^2)$.

An interesting physical case is where the two Born-Oppenheimer energy levels become close but do not cross – an avoided crossing. It is natural to change to the adiabatic representation in which the potential matrix becomes diagonal, and the two levels decouple up to errors of order ϵ. Interest lies in starting a wavepacket on the upper level and investigating the (exponentially small) part transmitted, via the avoided crossing, to the lower level, far away from the crossing (in the scattering limit). This exponential smallness, coupled with the highly oscillatory nature of the wavepackets, makes numerical simulations very computationally expensive.

By considering generalizations of the adiabatic representation [1], we derived a closed form approximation to the transmitted wavepacket, which is in excellent agreement (around 1–2% relative error) with high-precision numerics for a wide range of potentials and wavepackets. In contrast to most previous mathematical results, it is highly suited to numerical implementation, requiring only multiplication in momentum space. When the slope of the potential near the crossing, given by $\lambda = \frac{\mathrm{d}d}{\mathrm{d}x}|_{x=0}$, is small the formula is

$$\widehat{\psi_-}^{\epsilon}(k,t) = \mathrm{e}^{\frac{-\mathrm{i}}{\epsilon} t \hat{H}^-} \chi_{\{k^2>4\delta\}} \frac{\eta+k}{2|\eta|} \mathrm{e}^{\frac{\mathrm{i}\tau_\delta}{2\delta\epsilon}|k-\eta|} \widehat{\phi}^{\epsilon}(\eta),$$

where $\hat{H}^-$ is the Born-Oppenheimer propagator on the lower level, $\widehat{\cdot}^{\epsilon}$ denotes a scaled Fourier transform, χ is the characteristic function (corresponding to energy conservation), $\eta = \mathrm{sgn}(k)\sqrt{k^2 - 4\delta}$ is the classical incoming momentum for outgoing momentum k, ϕ is the wavepacket on the upper level at $t = 0$, and τ, δ, and γ are constants easily derivable from X and Z. When λ is not small, the formula is analogous but more complicated [2, 3]. Some typical results are given in Figure 1.

The next avenues of this research involve application of the results to real-world chemical systems, such as the photodissociation of NaI, and the extension to higher dimensions. In particular we are interested in tackling the dynamics near a true crossing, say in 2D, in the case that the centre of the wavepacket travels along a path well away from the crossing, resulting in a type of avoided crossing with a non-zero gap.

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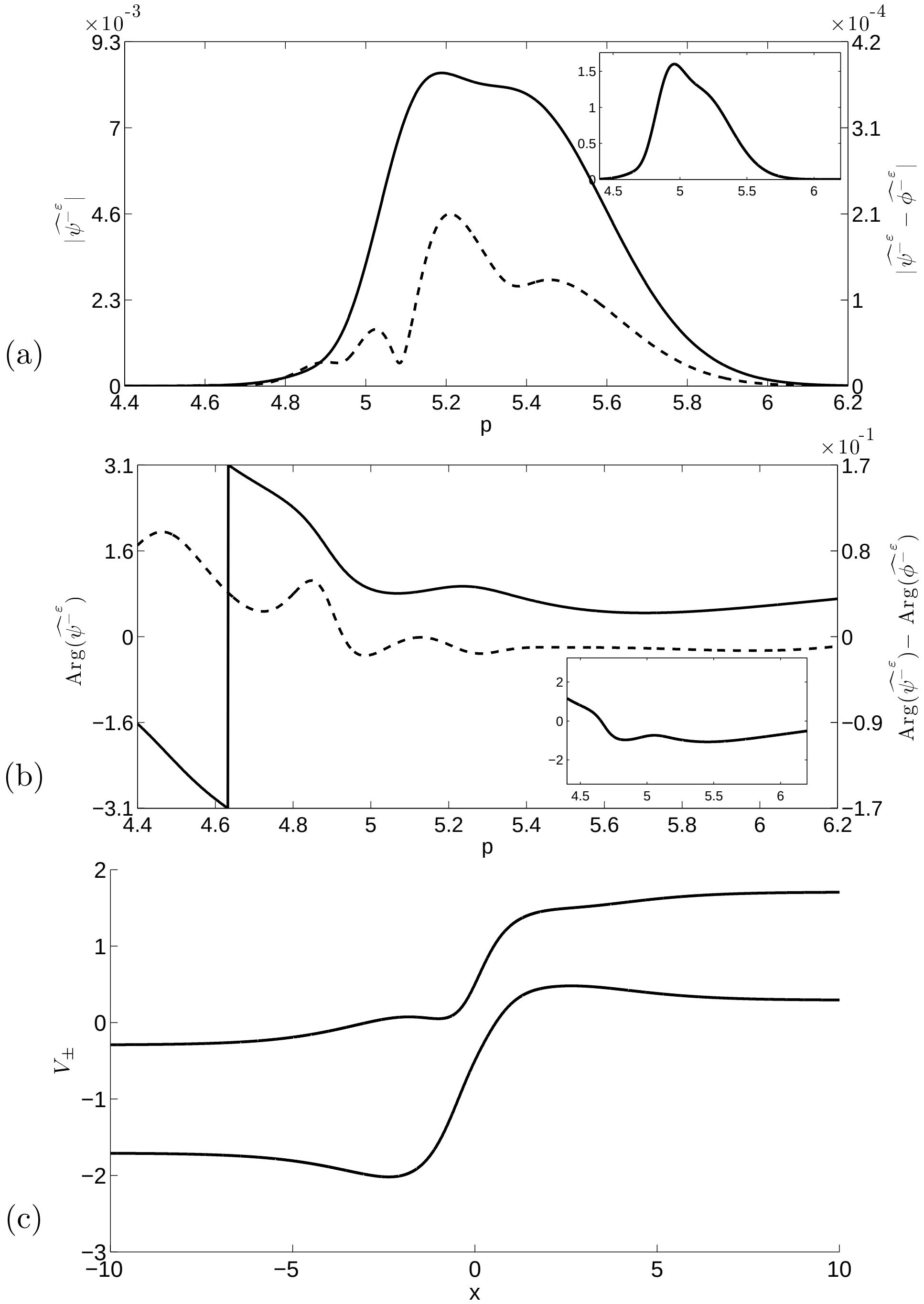

Figure 1. (a) The wavepacket on the upper level at the crossing point (subplot), along with the transmitted wavepacket (solid, left axis) and relative error (dashed, right axis). (b) Phase of the wavepackets, and error in the phase; axes as in (a). (c) The potential energy surfaces, the avoided crossing is at $x = 0$. The relative error is around 1.8% with a transmission probability of around 10^{-5}.

A mathematical analysis of the GW^0 method

David Gontier
(joint work with Eric Cancès, Gabriel Stoltz)

The aim of this talk was to present a mathematical framework to understand the properties of the GW^0 method, which has been proven very successful to predict electronic-excited energies [1]. This method relies on the study of the one-body Green's function for electronic systems. Numerically, the Green's function (which is an operator-valued distribution) is difficult to evaluate from its standard definition, due to the curse of dimensionality. The state-of-the-art method to computeit consists in solving Hedin's equations [2].

In this talk, I first exposed the properties of the one-body Green's function. This function is very irregular in the time or frequency domain, so that its analysis is tedious on these axes. It is possible however to consider its analytical continuation, provided some *stability condition* is satisfied. This continuation is regular, and contains the same information as the original function.

I then focused on the GW^0 equations. These equations are obtained from Hedin's equations by neglecting some terms. The GW^0 equations involve many operator-valued distributions, among which the dynamically screened Coulomb operator W, the self-energy Σ and the Green's function G. The mathematical definition of these operators were clarified during the talk. The GW^0 equations are traditionally set on the time-axis, but it is possible to recast them into formally equivalent equations on an imaginary axis, where the operator-valued functions under consideration are smooth.

In the last part of my talk, I investigated the resulting GW^0 equations. They are non-linear equations which are solved self-consistently in practice. Our main result is that, in some perturbative regime, where the Coulomb interaction is weakened, the GW^0 equations are well-posed, in the sense that they admit a unique solution close to a reference Green's function. Moreover, we proved that the self-consistent procedure converges exponentially fast towards this unique solution.

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The bivariational principle for the time-dependent Schrödinger equation and coupled-cluster theory

Simen Kvaal

Solving the Schrödinger equation via variational techniques. Deriving accurate approximations of solutions to the time-dependent Schrödinger equation is an important task in the study of many physical phenomena, e.g., ionization of atoms and molecules in intense laser fields and chemical reactions. The Dirac–Frenkel/McLachlan variational principle is a cornerstone of the development of such approximations [1, 2]. Virtually all common schemes are derived from it. In brief, letting $\mathcal{H}$ be the Hilbert space of wavefunctions and H the system Hamiltonian, one considers the "action functional" $\mathcal{A} : \mathcal{H} \times [0,T] \to \mathbb{R}$, defined by

$$\mathcal{A}[\psi(\cdot)] = \int_0^T \langle \psi(t) | (i\partial_t - H) | \psi(t) \rangle \; dt, \tag{1}$$

a functional dependent on the whole history $\psi(\cdot)$ of the system. For simplicity, we assume that H is bounded, in addition to being self-adjoint.

The Euler–Lagrange equations for stationarity of $\mathcal{A}$ under arbitrary variations in $\psi(\cdot)$ are the time-dependent Schrödinger equation and its complex conjugate, i.e.,

$$i\partial_t \left| \psi(t) \right\rangle = H \left| \psi(t) \right\rangle , \quad -i\partial_t \left\langle \psi(t) \right| = \left\langle \psi(t) \right| H. \tag{2}$$

Importantly, in order to arrive at Eq. (2), one uses the assumption that H is self-adjoint.

Approximate schemes are typically derived by devising a complex approximation manifold $\mathcal{M} \subset \mathcal{H}$ and restricting the action integral to paths $t \mapsto \varphi(t) \in \mathcal{M}$.

Equation (1) is a time-dependent analogue of the common Rayleigh–Ritz variational procedure for computation of the smallest eigenvalue of the self-adjoint operator H. Assuming that H is below bounded and has a smallest eigenvalue E_0 (the ground-state energy), this eigenvalue can be computed via

$$E_0 = \inf \left\{ \langle \psi | H | \psi \rangle / \|\psi\|^2 \;\mid\; \psi \in \mathcal{H},\ \psi \neq 0 \right\}. \tag{3}$$

Approximate ground-state energies can be computed via restriction of the minimization to the manifold $\mathcal{M}$, i.e.

$$E_0 \leq E_0[\mathcal{M}] = \inf \left\{ \langle \psi | H | \psi \rangle / \|\psi\|^2 \;\mid\; \psi \in \mathcal{M},\ \psi \neq 0 \right\}. \tag{4}$$

For systems of many degrees of freedom, such as molecular systems in the Born–Oppenheimer approximation, the cost of systematically refinable "variational methods" for the time-independent or time-dependent Schrödinger equation scale exponentially with the number N of particles, the so-called "curse of dimensionality". The most widely used method today is the multiconfigurational time-dependent Hartree method (MCTDH) and variants (e.g., MCTDHF for Fermions) [3, 4, 5]. (By "systematically refonable" we mean that $\mathcal{M}$ carries a discretization parameter h, such that, as $h \to 0$, we recover $\mathcal{H}$ i a certain sense.)

The bivariational principle. In 1983, a generalization of the above variational principles was suggested, independently, by P.-O. Löwdin [6] and J. Arponen [7]. If one lifts the assumption that H is self-adjoint, the left- and right eigenvectors of H are no longer simply related via complex conjugation. Therefore, it makes sense to consider the functional $\mathcal{E} : \mathcal{H}' \times \mathcal{H} \to \mathbb{C}$ given by

$$\mathcal{E}(\tilde{\psi}, \psi) = \frac{\langle\tilde{\psi}|H|\psi\rangle}{\langle\tilde{\psi}|\psi\rangle}. \tag{5}$$

It is straightforward to verify, that $(\tilde{\psi}, \psi)$ is a critical point of $\mathcal{E}$ if and only if $\langle\tilde{\psi}|\psi\rangle \neq 0$ and

$$H\,|\psi\rangle = E\,|\psi\rangle\,, \quad \langle\tilde{\psi}|\,H = E\,\langle\tilde{\psi}|\,, \tag{6}$$

with $E = \mathcal{E}(\tilde{\psi}, \psi)$ being the critical value. Thus, $\langle\tilde{\psi}|$ is a left eigenvector of H and $|\psi\rangle$ is a right eigenvector of H belonging to the eigenvalue E.

The corresponding generalization of the Dirac–Frenkel/McLachlan action functional is

$$\mathcal{S}(\tilde{\psi}(\cdot), \psi(\cdot)) = \int_0^T \langle\tilde{\psi}(t)|\,(i\partial_t - H)\,|\psi(t)\rangle\; dt, \tag{7}$$

which Euler–Lagrange equations are

$$i\partial_t\,|\psi(t)\rangle = H\,|\psi(t)\rangle\,, \quad -i\partial_t\,\langle\tilde{\psi}(t)| = \langle\tilde{\psi(t)}|\,H. \tag{8}$$

Approximations can be made by introducing a submanifold $\mathcal{N} \subset \mathcal{H}' \times \mathcal{H}$, restricting the time-independent and time-dependent functional to $\mathcal{N}$ and evaluating the corresponding critical point and Euler–Lagrange equations. This approach is referred to as *the (time-dependent or time-independent) bivariational principles* (BIVPs). Of course, H is indeed self-adjoint. However, by not *using* the assumption, we introduce $\langle\tilde{\psi}|$ as an additional variable, obtaining a more flexible parameterization.

Indeed, Arponen introduced the BIVPs in the context of the coupled-cluster (CC) method [8, 9], nowadays a very popular method for the solution of the Schrödinger equation. In quantum chemistry, The CC method is anomalous in the sense that it is *not* obtained using the Rayleigh–Ritz or Dirac–Frenkel/McLachlan variational principles. Moreover, the CC method has the virtue that it *breaks the curse of dimensionality*, scaling only polynomially with the number N of particles in the system. From the perspective of this work, Arponen's main point was that it may be more natural to view CC as derived from the bivariational principle instead of the common similarity transformation and projection approach, see Ref. [8].

The bivariational approach of Löwdin and Arponen is considered unconventional. One of the challenges is that the mathematical foundation of the BIVPs has not yet been worked out. For example, since $\mathcal{E}$ is not below bounded, can we be sure that a critical value of $\mathcal{E}$ (restricted to the manifold $\mathcal{N}$) is in fact an approximation to an eigenvalue? Can we be sure that approximate dynamics from the time-dependent BIVP will in fact exist?

Contents of talk. In the talk, the BIVPs are presented and discussed in some detail, and Arponen's unconventional approach to CC is outlined. Some ideas and preliminary results concerning the rigorous mathematical analysis of the BIVPs are also discussed. As proof of concept, the orbital-adaptive time-dependent CC method (OATDCC) is described [10]. The OATDCC method is a hierarchy of approximations to the popular MCTDHF method, based on the time-dependent BIVP and including the usual CC method as a special case. OATDCC includes the *orbitals* as additional bivariational variables. OATDCC breaks the curse of dimensionality in the context of the time-dependent Schrödinger equation, while still being systematically refinable towards the exact solution. A numerical experiment is shown, indicating that OATDCC compares favorably with MCTDHF.

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Dynamics of individual Wannier-Mott-type excitons

Rupert Klein

The motivation for this work in progress lies in artificial photosynthesis, more specifically in the desire to turn photonic energy into chemically bound energy with the help of some device preferably made from anorganic materials. A central element of one possible design of such a device is a semiconductor (nano-) structure that captures the energy of photons of visible light by absorption into localized electronic excitations called "excitons" here. The energy stored in these excitons can be harvested for chemical energy conversion only at the surface of the semiconductor material where it is in contact, e.g., with an electrolyte. State of the art models for the "diffusion" and "decay" of excitons within the bulk of the material consist of custom-designed random walk models whose parameters are fitted to experimental data, [1, 2].

In a joint activity with C. Draxl (Humboldt University, Berlin), Carlos Garcia-Cervera (UC Santa Barbara), Eric Cancès (CERMICS, Paris) we aim at developing a first-principles, quantum mechanical description of the time dependent evolution of localized excitons in semi-conductor materials. Focusing on anorganic semiconductors in which the Coulomb interaction of electrons is strongly "screened" owing to large dielectricity, it is reasonable to assume the excitations to feature characteristic spacial scales large compared to the crystal lattice spacing. Thus we aim to describe them by multiple scales asymptotic techniques.

In the presentation I have discussed two aspects of this project. The first is the derivation of an effective evolution equation for what is called an "electron-hole (e-h) pair". Starting from a bosonic Schrödinger equation for the two quasi-particles

$$\imath\,\partial_t\psi = (\mathrm{H}_e + \mathrm{H}_h + \varepsilon\,\mathrm{H}_{eh})\,\psi \qquad (\varepsilon \ll 1) \tag{1}$$

that is used in practice to compute the excitation spectrum of the considered material, we have considered the time dependent version of the equation and developed an effective evolution equation for an excitation envelope.

In (1), $\mathrm{H}_e, \mathrm{H}_h$ denote the individual particle Hamiltonians for electron and hole, respectively, that feature the particles' kinetic energy and lattice periodic potentials, i.e.,

$$\mathrm{H}_x = -\frac{1}{2}\nabla_x^2 + V_x \qquad (x \in \{e, h\})\,. \tag{2}$$

Note that we have neglected that electron and hole generally have different effective masses in such a description. Next, H_{eh} in (1) is the electon-hole interaction term which, in the considered simplified setting, is a multiplicative, screened Coulomb interaction of the form

$$\mathrm{H}_{eh}(\boldsymbol{r}_e, \boldsymbol{r}_h) = \frac{1}{\epsilon(\boldsymbol{r}_e, \boldsymbol{r}_h)|\boldsymbol{r}_e - \boldsymbol{r}_h|} \tag{3}$$

where $\epsilon(\boldsymbol{r}_e, \boldsymbol{r}_h)$ is the material's dielectricity.

The small parameter $\varepsilon \ll 1$ in (1) indicates that the dielectric screening of the Coulomb interaction is strong in that the effective dielectricity is $\varepsilon/\epsilon(\boldsymbol{r}_e, \boldsymbol{r}_h)$, where $\epsilon(\boldsymbol{r}_e, \boldsymbol{r}_h) = O(1)$ as $\varepsilon \to 0$ by the chosen non-dimensionalization. Note the notational compromise between the material scientists' custom of labelling dielectricity by "epsilon" (here ϵ), while mathematicians usually reserve "epsilon" for their small singular perturbation parameter (here ε).

A more or less straightforward multiple scales expansion allows us to formally derive an effective evolution equation for the envelope $A(\varepsilon^2 t, \varepsilon\boldsymbol{r}_e, \varepsilon\boldsymbol{r}_h)$ of an electron-hole wavepacket described by a WKB-type ansatz,

$$\Psi = \exp\left(\frac{\imath}{\varepsilon^2}\left(S^{(0)} + \varepsilon S^{(1)}\right)\right)\left[A\,\varphi_0^e\varphi_0^h + \varepsilon\psi^{(1)} + \varepsilon^2\psi^{(2)}\right] + \text{h.o.t.} \tag{4}$$

where we have introduced amplitude and phase functions depending on appropriate slow space and time coordinates,

$$\begin{aligned} A &\quad\to\quad A(\varepsilon^2\, t, \varepsilon\, \boldsymbol{r}_e, \varepsilon\, \boldsymbol{r}_h)\,, \\ S^{(i)} &\quad\to\quad S^{(i)}(\varepsilon^2\, t)\,, \end{aligned} \tag{5}$$

where $\varphi_0^e(\boldsymbol{r}_e), \varphi_0^h(\boldsymbol{r}_h)$ are the lattice-periodic ground state eigenfunctions of the single-particle Hamiltonians in (2), and where the higher-order terms have a general multiscale dependence according to

$$\psi^{(i)} \to \psi^{(i)}(\varepsilon^2\, t, \boldsymbol{r}_e, \boldsymbol{r}_h, \varepsilon\, \boldsymbol{r}_e, \varepsilon\, \boldsymbol{r}_h)\,. \tag{6}$$

In the sequel we abbreviate

$$\varepsilon^2 t \equiv \tau\,, \qquad \varepsilon\, \boldsymbol{r}_x \equiv \boldsymbol{\xi}_x \qquad (x \in \{e, h\})\,. \tag{7}$$

Expansion of the electron-hole Schrödinger equation in (1) to second order in ε and applying the sublinear growth condition to the second-order solution one obtains an evolution equation for the (complex) amplitude, A,

$$\imath A_t = \mathcal{H} A \tag{8}$$

where the effective Hamiltonian is given by

$$\mathcal{H} = -\frac{1}{2}\,(\mathrm{Id} - \mathrm{U}^e) : (\nabla_{\boldsymbol{\xi}_e} \circ \nabla_{\boldsymbol{\xi}_e}) - \frac{1}{2}\left(\mathrm{Id} - \mathrm{U}^h\right) : (\nabla_{\boldsymbol{\xi}_h} \circ \nabla_{\boldsymbol{\xi}_h}) - W \tag{9}$$

with anisotropic contributions to the effective mass tensors, $(\mathrm{Id} - \mathrm{U}^x)$, given by

$$\mathrm{U}^x = \frac{1}{2}\, \langle \varphi_0^x |\, \boldsymbol{r}_x \circ \boldsymbol{r}_x \,| \varphi_0^x \rangle - \frac{1}{2}\, \langle \varphi_0^x |\, \boldsymbol{r}_x \,| \varphi_0^x \rangle \circ \langle \varphi_0^x |\, \boldsymbol{r}_x \,| \varphi_0^x \rangle \tag{10}$$

and an effective potential

$$W = W^e + W^h + W^{eh} \tag{11}$$

that involves self-interactions of the electron and hole and an electron-hole interaction term,

$$W^x = \sum_{i \neq 0} \frac{\langle \varphi_0^x \varphi_0^y |\, V_{eh} \,| \varphi_i^x \varphi_0^y \rangle^2}{E_i^x - E_0^x} \tag{12}$$

$$W^{eh} = \sum_{\substack{j \neq 0 \\ \hat{E}k \neq 0}} \frac{\langle \varphi_j^e \varphi_k^h |\, V_{eh} \,| \varphi_0^e \varphi_0^h \rangle^2}{(E_j^e - E_0^e) + (E_k^h - E_0^h)}\,. \tag{13}$$

Here the φ_j^e and φ_k^h are the lattice-periodic eigenfunctions of the single-particle Hamiltonians from (2) for eigenvalues E_j^e and E_k^h, respectively. The conclusion from this exercise is that it seems entirely feasible to construct a theory for exciton dynamics from first principles using multiple scales techniques, provided one can justify the two-particle Schrödinger equation from (1) in the first place.

Some thoughts on this latter issue I discussed in the second part of the lecture. The two-particle problem from (1) arises as part of Bethe-Salpeter theory described, e.g., by Strinati, [3]. In this theory one is interested in two-particle Green's functions of the form

$$G(t, \boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \boldsymbol{r}_4) = \langle N, 0|\, \Psi^\dagger(t, \boldsymbol{r}_1)\, \Psi(t, \boldsymbol{r}_2)\, \Psi^\dagger(0, \boldsymbol{r}_3)\, \Psi(0, \boldsymbol{r}_4)\, |N, 0\rangle \ . \tag{14}$$

Here $|N, t\rangle$ denotes a N–particle state evaluated at time t, typically the ground state of the system under consideration, and $\Psi(t, \boldsymbol{r})$ and $\Psi^\dagger(t, \boldsymbol{r})$ are the particle annihilation and creation field operators of second quantization in the Heisenberg view, respectively. Now, what is the physical interpretation of (14) and does it inform us about "particles (electrons) and holes"?

Consider first the action of the (singular) field operators on a smooth wave function for time zero. Let $|N, 0\rangle$ be represented by a fermionic, i.e., antisymmetric wave function $\phi_N(\boldsymbol{r}_1, ..., \boldsymbol{r}_N)$. Then detailed elaboration of the definitions of the field operators found, e.g., in [4] yields

$$\Big(\Psi(0, \boldsymbol{r})\, |N, 0\rangle\Big)\, (\boldsymbol{r}_2, ..., \boldsymbol{r}_N) = \sqrt{N}\, \phi_N(\boldsymbol{r}, \boldsymbol{r}_2, ..., \boldsymbol{r}_N) \tag{15}$$

and

$$\Big(\Psi^\dagger(0, \boldsymbol{r})\, |N, 0\rangle\Big)\, (\boldsymbol{r}_0, ..., \boldsymbol{r}_N) = \sqrt{N+1}\, \mathcal{AS}\, [\delta_{\boldsymbol{r}}, \phi_N]\, (\boldsymbol{r}_0, ..., \boldsymbol{r}_N) \tag{16}$$

where

$$\begin{aligned} &\mathcal{AS}\, [\varphi, \phi_N]\, (\boldsymbol{r}_0, ..., \boldsymbol{r}_N) = \\ &\frac{1}{N+1} \left[\varphi(\boldsymbol{r}_0)\phi_N(\boldsymbol{r}_1, ..., \boldsymbol{r}_N) - \sum_{j_2}^{N} \varphi(\boldsymbol{r}_j)\phi_N(\boldsymbol{r}_1, ... \underbrace{, \boldsymbol{r}_0,}_{j} ...\boldsymbol{r}_N) \right] \end{aligned} \tag{17}$$

and $\delta_{\boldsymbol{r}}(\boldsymbol{r}_0) = \delta(\boldsymbol{r}_0 - \boldsymbol{r})$. We note that, even if ϕ_N is a normalized wave function, the results of applying the field operators are generally not. Thus, the field operators $\Psi(\boldsymbol{r})\,, \Psi^\dagger(\boldsymbol{r})$ to not create proper N–1– and N+1–particle states, respectively.

Nevertheless, in the physics literature these operators are generally interpreted to "annihilate a particle from $\boldsymbol{r}$" or "to create a hole at $\boldsymbol{r}$" for $\Psi(\boldsymbol{r})$ and to "create a particle at $\boldsymbol{r}$" for $\Psi^\dagger(\boldsymbol{r})$. The formulae in (15), (16) reveal that the "mechanics" of the field operators is as follows: $\Psi(\boldsymbol{r})$ simply fixes the first coordinate of the wave function ϕ_N at $\boldsymbol{r}$ while leaving the functional dependencies on $(\boldsymbol{r}_2, ..., \boldsymbol{r}_N)$ untouched. It thus creates an antisymmetric N–1–particle function, though not a normalized one. Similarly, $\Psi^\dagger(\boldsymbol{r})$ generates an antisymmetrized multiplication of ϕ_N with a delta-distribution at $\boldsymbol{r}$ for an additional particle coordinate $\boldsymbol{r}_0$. The result is an antisymmetric N+1–particle *distribution* that is again not normalized and even not square integrable. The physical interpretations mentioned above are therefore to be taken with a grain of salt.

Next we recall that in the Heisenberg view, the field operators at time $t > 0$ are defined by

$$\Psi(t, \boldsymbol{r}) = U_{N-1}^{-t}\, \Psi(\boldsymbol{r})\, U_N^t \tag{18}$$

where U_N^t is the N–particle time evolution operator. With this relation in place and recalling that $\Psi^\dagger(\boldsymbol{r})$ and U_N^{-t} are the transposes of $\Psi(\boldsymbol{r})$ and U_N^t, respectively, and vice versa we rewrite (14) as

$$G(t,\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3,\boldsymbol{r}_4) = \left\langle \Psi^\dagger(\boldsymbol{r}_2)\,\Psi(\boldsymbol{r}_1)\;N,t \,\middle|\, U_N^t \Psi^\dagger(\boldsymbol{r}_3)\,\Psi(\boldsymbol{r}_4)\;N,0 \right\rangle . \tag{19}$$

If we buy into the physical interpretations of the field operators given above, then the interpretation of this two-particle Green's function is clear: Suppose at time 0 we "create a hole at $\boldsymbol{r}_4$ and then a particle at $\boldsymbol{r}_3$" and let the resulting N–particle function evolve to time t under the N–particle Hamiltonian. Then we project the resulting (non-normalized) state onto the (non-normalized) state that obtains by first evolving $|N,0\rangle$ to time t and then creating a hole in $\boldsymbol{r}_1$ and a particle in $\boldsymbol{r}_2$.

Difficulties with the normalization set aside for the moment, the resulting quantity provides a rough answer to the question: "What is the probability amplitude that the particle–hole perturbation created at time 0 on top of $|N,0\rangle$ evolves into a state that corresponds to some other particle–hole perturbation created at time t on top of $|N,t\rangle$?" Put differently we may also say: "How likely is it that the perturbed state created at time 0 evolves into a fresh perturbation at time t on top of the state $|N,t\rangle$ that evolved *unperturbed* from $|N,0\rangle$?" This is equivalent to asking how likely it is that the perturbed electronic system has not responded to the perturbation except for a shift of the perturbation locations. It seems that the central question of how the many-body system would react and rearrange as a consequence of the initial perturbation cannot be answered by studying this quantity since we project onto a state that.

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