The density to potential mapping in time-dependent density-functional theory

Robert van Leeuwen

Markus Penz

Michael Ruggenthaler

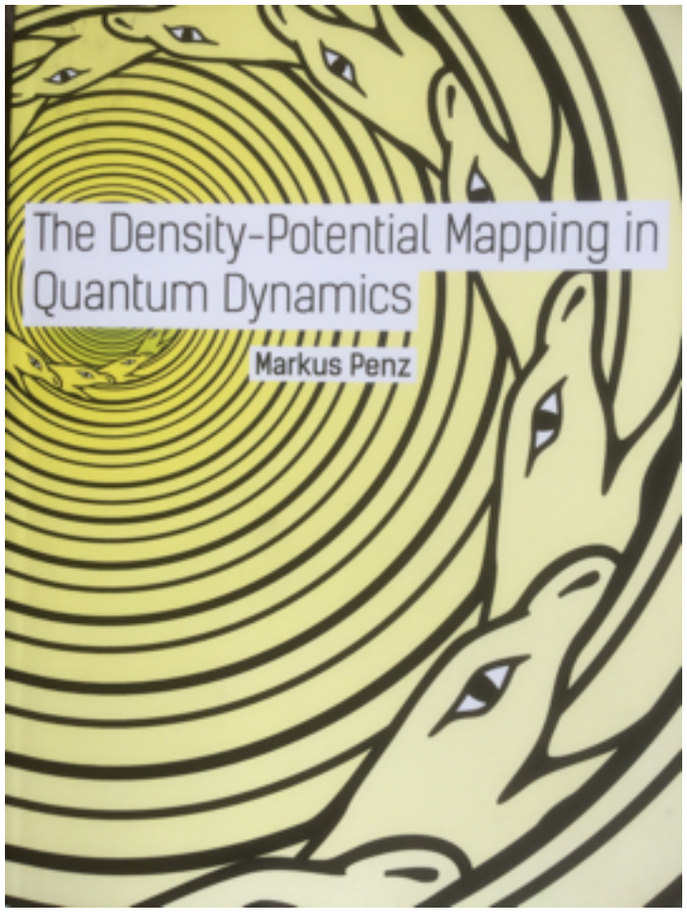
JYVÄSKYLÄN YLIOPISTO

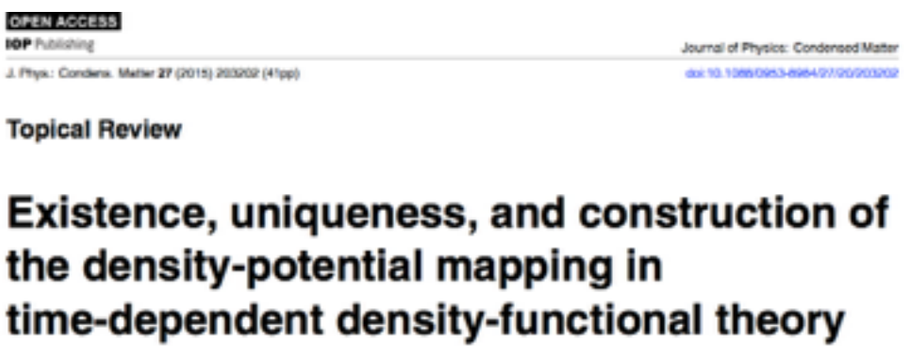
University of Jyväskylä

Benasque 23.9.2016

Overview

- The density-potential or Runge-Gross mapping in quantum dynamics
- New insights in the time-dependent Schrödinger equation
(PhD thesis of Markus Penz)
- Conclusions




OPEN ACCESS

IOP Publishing

Journal of Physics: Condensed Matter

J. Phys.: Condens. Matter **27** (2015) 203202 (41pp)

Topical Review

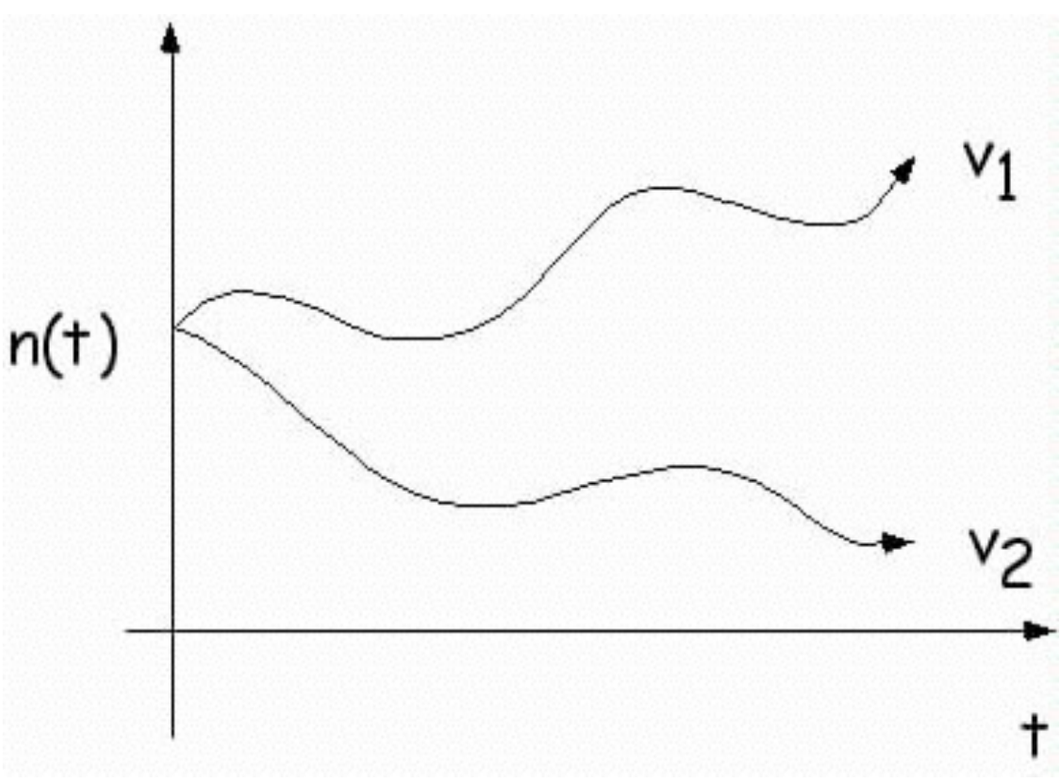
Existence, uniqueness, and construction of the density-potential mapping in time-dependent density-functional theory

Time-dependent DFT

Basic assumptions (we will later see how rigorous this is):

For a given density and initial state there is at most one potential (up to a gauge) that produces this density by solution of the time-dependent Schrödinger equation.

(uniqueness theorem for the Runge-Gross mapping)



Any observable is a functional of the density and the initial state

$$O[n,\Psi_0](t) = \langle \Psi[n](t)|\hat{O}|\Psi[n](t)\rangle$$

From potentials to densities

Hamiltonian

$$\hat{H}(t) = \hat{T} + \hat{V}(t) + \hat{W}$$

Schrödinger equation

$$i\partial_t |\Psi[v](t)\rangle = \hat{H}(t)|\Psi[v](t)\rangle \qquad |\Psi[v](t_0)\rangle = |\Psi_0\rangle$$

Density

$$n[v](\mathbf{r}t) = \langle \Psi[v](t)|\hat{n}(\mathbf{r})|\Psi[v](t)\rangle$$

This maps from a certain domain of potentials to a certain domain of densities

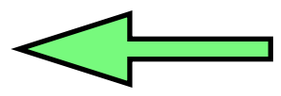
For which class of external potentials and initial states has the initial value problem of the time-dependent Schrödinger equation a solution ?

Local force equation

Equations of motion for the density and current operators (RG 1984)

$$\partial_t n(\mathbf{r}t) = -\nabla \cdot j(\mathbf{r}t)$$

$$\partial_t j(\mathbf{r}t) = -i\langle \Psi(t)| \left[\hat{j}(\mathbf{r}), \hat{H}(t)\right] |\Psi(t)\rangle$$



local force

Combination of both then gives

$$-\nabla \cdot (n([v],\mathbf{r}t)\nabla v(\mathbf{r}t)) = q([v],\mathbf{r}t) - \partial_t^2 n([v],\mathbf{r}t)$$

where

$$q([v],\mathbf{r}t) = -i\nabla \cdot \langle \Psi(t)| \left[\hat{j}(\mathbf{r}), \hat{T} + \hat{W}\right] |\Psi(t)\rangle$$

Let us now replace n([v],rt) by a given density n(rt) subject to the conditions

$$n(rt_0) = \langle \Psi_0 | \hat{n}(\mathbf{r}) | \Psi_0 \rangle \qquad \partial_t n(rt_0) = -\langle \Psi_0 | \nabla \cdot \hat{j}(\mathbf{r}) | \Psi_0 \rangle$$

This is a nonlinear equation for v(rt)

$$-\nabla \cdot (n(\mathbf{r}t)\nabla v(\mathbf{r}t)) = q([v], \mathbf{r}t) - \partial_t^2 n(\mathbf{r}t)$$

If we propagate the TDSE with the solution v(rt) also have

$$-\nabla \cdot (n([v], \mathbf{r}t)\nabla v(\mathbf{r}t)) = q([v], \mathbf{r}t) - \partial_t^2 n([v], \mathbf{r}t)$$

Subtracting both equations we have

$$\partial_t^2 \rho(\mathbf{r}, t) - \nabla \cdot (\rho(\mathbf{r}t)\nabla v(\mathbf{r}t)) = 0 \qquad \rho(\mathbf{r}t) = n([v], \mathbf{r}t) - n(\mathbf{r}t)$$

with initial conditions

$$\rho(\mathbf{r}t_0) = 0 \qquad \partial_t \rho(\mathbf{r}t_0) = 0$$

The unique solution satisfying the initial conditions is $\rho(\mathbf{r}t) = 0$

$$n(\mathbf{r}t) = n([v], \mathbf{r}t)$$

If we now choose

$$n(\mathbf{r}t) = n_{W'}([u, \Phi_0], \mathbf{r}t)$$

to be the density obtained from the TDSE in a system with different interactions W' , external potential u(rt) and a different initial state Φ_0

then the existence of a solution to

$$-\nabla \cdot (n(\mathbf{r}t)\nabla v(\mathbf{r}t)) = q([v], \mathbf{r}t) - \partial_t^2 n(\mathbf{r}t)$$

implies

1) v-representability of n(rt) in our system

2) uniqueness for W=W' and $\Phi_0 = \Psi_0$ implies the Runge-Gross theorem

From time-propagation we have

$$\mathcal{P} : v_0 \mapsto q[v_0]$$

We then solve

$$-\nabla \cdot (n(\mathbf{r}t)\nabla v_1(\mathbf{r}t)) = q([v_0], \mathbf{r}t) - \partial_t^2 n(\mathbf{r}t)$$

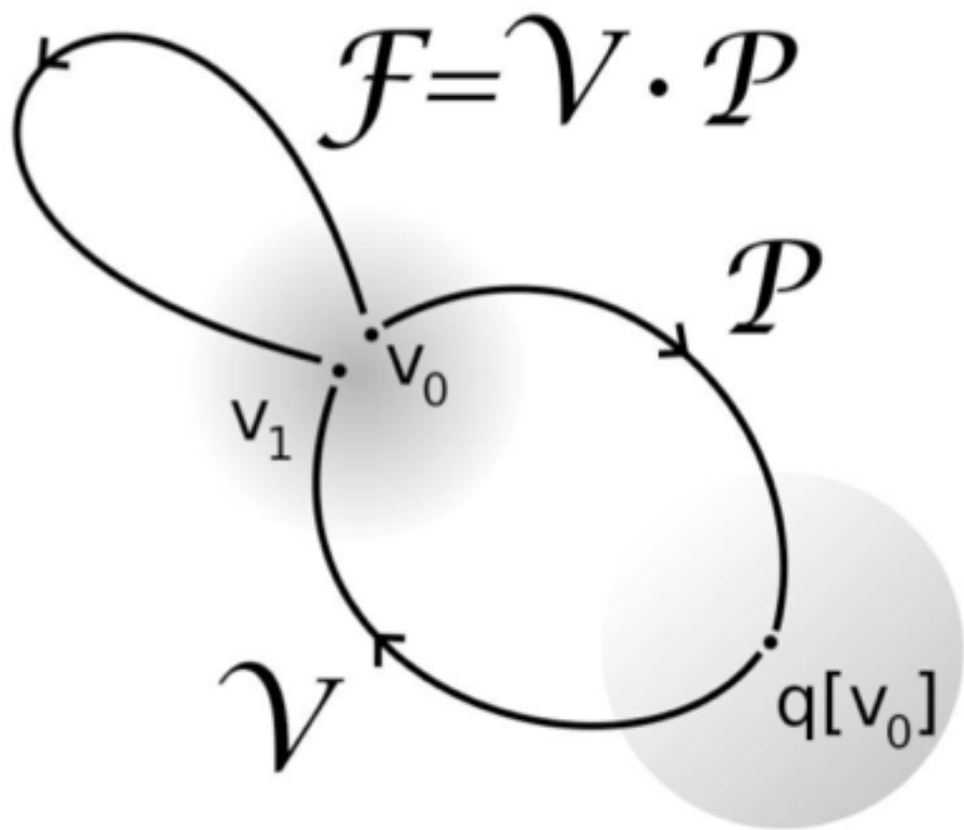
for $v_1(rt)$. This yields a mapping

$$\mathcal{V} : q[v_0] \mapsto v_1$$

The combined mapping

$$\mathcal{F}[v_0] = (\mathcal{V} \circ \mathcal{P})[v_0] = v_1$$

maps potentials to potentials



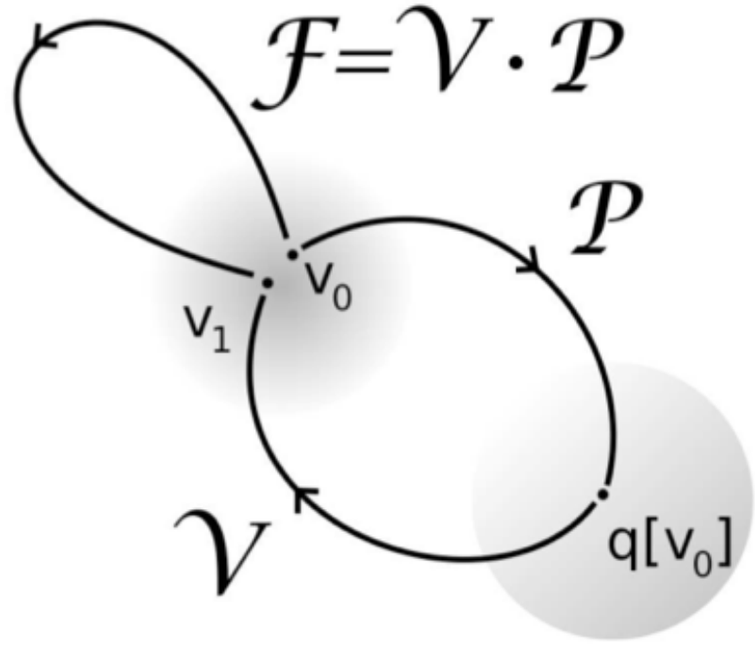
M.Ruggenthaler, RvL,
Europhysics Lett. 95, 13001 (2011)

Whenever we have

$$\mathcal{F}[v] = v$$

then we are solving

$$-\nabla \cdot (n(\mathbf{r}t)\nabla v(\mathbf{r}t)) = q([v], \mathbf{r}t) - \partial_t^2 n(\mathbf{r}t)$$



The question whether a solution to this equation exists and is unique is thus equivalent to the question whether a unique fixed point of the mapping F exists.

The main existence and uniqueness question of TDDFT is in this way reformulated as a fixed point question

A proof strategy is to construct a contractive mapping in appropriate norms

Numerical application of fixed-point iteration

$$-\nabla(n\nabla v_{k+1}) = q[v_k] - \partial_t^2 n$$

$$= \partial_t^2(n[v_k] - n) - \nabla(n[v_k]\nabla v_k))$$

Elimination of “q” numerically advantageous

Numerical details discussed in

S.Nielsen, M.Ruggenthaler, RvL, Europhys. Lett. 101, 33001 (2013),
arXiv 1412.3794 (2014)…and poster by Sören

A proof for the existence and convergence to a fixed point must consider the two basic mappings:

1) Propagation with the TDSE with a potential obtained from solving the local force equation
2) Solution of the local force equation

Here we consider the first mapping in more detail.

Time-dependent Schrödinger equation

Simple example, particle in a box

$$i\partial_t \Psi(x,t) = -\frac{1}{2}\frac{d^2}{dx^2}\Psi(x,t) = \hat{H}\Psi(x,t) \qquad \hat{H} = -\frac{1}{2}\frac{d^2}{dx^2}$$

$$\Psi(0,t) = \Psi(L,t) = 0$$

Formal solution of the initial value problem

$$\Psi(x,t) = e^{-i\hat{H}t}\,\Psi(x,0) = \sum_{n=0}^{\infty} \frac{(-it\hat{H})^n}{n!}\Psi(x,0)$$

$$= \sum_{n=0}^{\infty} \left(\frac{it}{2}\right)^n \frac{1}{n!}\frac{d^{2n}}{dx^{2n}}\Psi(x,0)$$

Requires the initial state to be infinitely spatially differentiable, but this is not sufficient to guarantee a proper solution

Time-dependent Schrödinger equation

Simple example, particle in a box

$$i\partial_t \Psi(x,t) = -\frac{1}{2}\frac{d^2}{dx^2}\Psi(x,t) = \hat{H}\Psi(x,t) \qquad \hat{H} = -\frac{1}{2}\frac{d^2}{dx^2}$$

$$\Psi(0,t) = \Psi(L,t) = 0$$

Formal solution of the initial value problem

$$\Psi(x,t) = e^{-i\hat{H}t}\,\Psi(x,0) = \sum_{n=0}^{\infty} \frac{(-it\hat{H})^n}{n!}\Psi(x,0)$$

$$= \sum_{n=0}^{\infty} \left(\frac{it}{2}\right)^n \frac{1}{n!}\frac{d^{2n}}{dx^{2n}}\Psi(x,0)$$

Requires the initial state to be infinitely spatially differentiable, but this is not sufficient

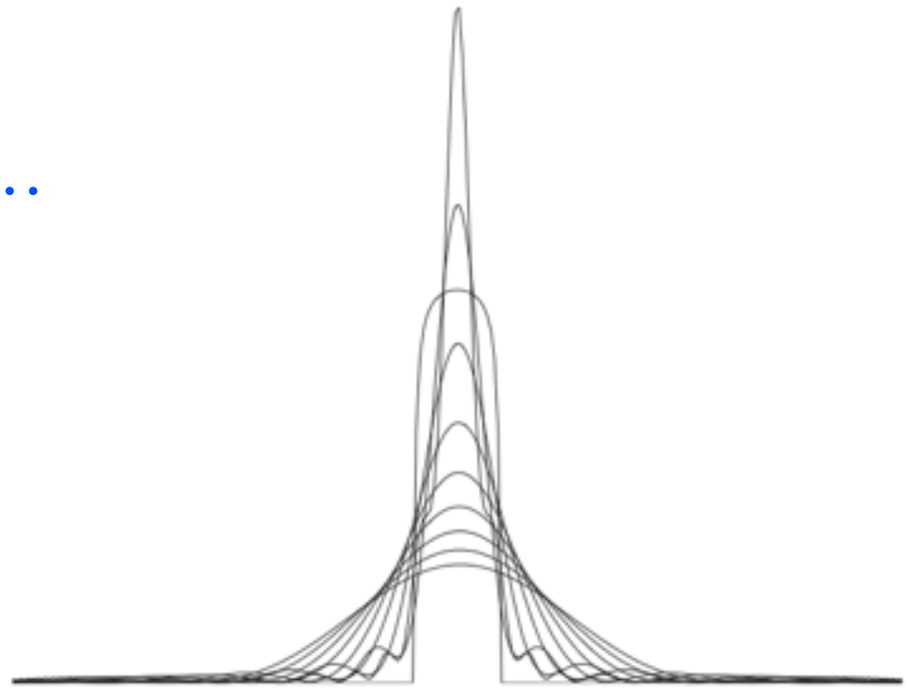
Take the following infinitely smooth initial state

$$\Psi(x,0) = \begin{cases} \exp\left(\frac{1}{(x-a)^2-b^2}\right) & |x-a| < b \\ 0 & |x-a| \geq b \end{cases}$$

If we believe the series then we find the paradoxical result that the initial wave packet does not leave its support and does not spread

$$\Psi(x,t) = 0 \quad \forall\ t \geq 0, |x-a| \geq b$$

..but in fact the wave packet does spread…
what went wrong?



It is useful to have a more general viewpoint, consider

$$e^{\hat{A}} = \sum_{n=0}^{\infty} \frac{1}{n!} \hat{A}^n$$

When is this expression meaningful? We make some estimates

$$\|e^{\hat{A}}\Psi\| = \|\sum_{n=0}^{\infty} \frac{1}{n!} \hat{A}^n \Psi\| \leq \sum_{n=0}^{\infty} \frac{1}{n!} \|\hat{A}^n \Psi\|$$

This is a meaningful expression when the operator is bounded, i.e.

$$\|\hat{A}\Psi\| \leq M\|\Psi\|$$

since then

$$\|e^{\hat{A}}\Psi\|\| \leq \sum_{n=0}^{\infty} \frac{M^n}{n!} \|\Psi\| = e^M \|\Psi\|$$

The trouble with our example was that the Hamilton operator was not bounded.

The terms $\|\hat{H}^n\Psi\|$ grow to fast with n to make the series converge.

However, operators on a finite dimensional Hilbert space are always bounded.

This is what one does typically when discretising for numerical applications….

But then, what goes wrong in the continuum limit?

Let's see

Let's discretise the equation on a finite grid

$$\frac{d^2\Psi}{dx^2}(x_j,t) \approx \frac{1}{(\Delta x)^2}(\Psi(x_{j+1},t) - 2\Psi(x_j,t) + \Psi(x_{j-1},t))$$

$$\Psi(x_0,t) \;=\; \Psi(x_{N+1},t) \;=\; 0$$

The Hamiltonian becomes a finite matrix

$$H = -\frac{1}{2(\Delta x)^2}\begin{pmatrix} -2 & 1 & 0 & \dots & \dots & \dots & 0 \\ 1 & -2 & 1 & 0 & \dots & \dots & 0 \\ 0 & 1 & -2 & 1 & 0 & \dots & 0 \\ \vdots & & & \ddots & & & \vdots \\ 0 & \dots & 0 & 1 & -2 & 1 & 0 \\ 0 & \dots & \dots & 0 & 1 & -2 & 1 \\ 0 & \dots & \dots & \dots & 0 & 1 & -2 \end{pmatrix}$$

acting on the N-dimensional vector

$$(\Psi(x_1,t),\dots,\Psi(x_N,t))$$

Now we have to solve ordinary differential equations of the form

$$i\partial_t \Psi(x_j,t) = \sum_{k=1}^{N} H_{jk}\Psi(x_k,t)$$

with a well-defined solution

$$\Psi(x_j,t) = \sum_{k=1}^{N} \left(e^{-itH}\right)_{jk} \Psi(x_k,0) = \sum_{k=1}^{N}\sum_{m=0}^{\infty} \frac{(-it)^m}{m!} \left(H^m\right)_{jk} \Psi(x_k,0)$$

To make the solution more explicit we calculate the eigenfunctions

$$\sum_{k=1}^{N} H_{jk}\varphi^{(l)}(x_k) = \epsilon^{(l)}\varphi^{(l)}(x_j)$$

$$\Delta x \sum_{j=1}^{N} \varphi^{(k)}(x_j)\varphi^{(l)}(x_j) = \delta_{kl}$$

with the explicit form

$$\varphi^{(l)}(x_j) = \sqrt{\frac{2}{L}} \sin\left(\frac{l\pi x_j}{L}\right)$$

$$\epsilon^{(l)} \qquad = \frac{2}{(\Delta x)^2} \sin^2\left(\frac{l\pi \Delta x}{2L}\right)$$

The initial state can be expanded in these eigenfunctions

$$\Psi(x_j, 0) = \sum_{l=1}^{N} c_l \, \varphi^{(l)}(x_j)$$

$$c_l = \Delta x \sum_{j=1}^{N} \varphi^{(l)}(x_j) \Psi(x_j, 0)$$

and therefore

$$\Psi(x_j,t) = \sum_{k,l=1}^{N} c_l \sum_{m=0}^{\infty} \frac{(-it)^m}{m!} \left(H^m\right)_{jk} \varphi^{(l)}(x_k)$$

$$= \sum_{l=1}^{N} c_l \sum_{m=0}^{\infty} \frac{(-it)^m}{m!} (\epsilon^{(l)})^m \varphi^{(l)}(x_j) = \sum_{l=1}^{N} c_l \, e^{-it\epsilon^{(l)}} \varphi^{(l)}(x_j)$$

The explicit solution of our discretised problem is therefore

$$\Psi(x_j,t) = \Delta x \sum_{k,l=1}^{N} e^{-it\epsilon^{(l)}} \varphi^{(l)}(x_j)\varphi^{(l)}(x_k)\Psi(x_k,0)$$

$$\left(e^{-itH}\right)_{jk} = \Delta x \sum_{l=1}^{N} e^{-it\epsilon^{(l)}} \varphi^{(l)}(x_j)\varphi^{(l)}(x_k)$$

Let us now take the continuum limit $\Delta x \to 0$, then we find

$$\Psi(x,t) = \sum_{l=0}^{\infty} e^{-it\epsilon^{(l)}} \varphi^{(l)}(x) \int_0^L dx' \varphi^{(l)}(x') \Psi(x',0)$$

where

$$\varphi^{(l)}(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{l\pi x}{L}\right)$$

$$\epsilon^{(l)} = \frac{(l\pi)^2}{2L^2}$$

This can be formally written as

$$\Psi(x,t) = \int_0^L dx' \, U(x,x',t) \Psi(x',0)$$

$$U(x,x',t) = \sum_{l=1}^{\infty} e^{-it\epsilon^{(l)}} \varphi^{(l)}(x) \varphi^{(l)}(x')$$

The correct way to define the evolution operator is by its spectral representation

$$e^{-i\hat{H}t} \equiv \sum_j e^{-iE_j t} |\Psi_j\rangle\langle\Psi_j|$$

For our single particle problem this becomes more explicitly

$$\Psi(x,t) = \sum_{l=0}^{\infty} e^{-it\epsilon^{(l)}} \varphi^{(l)}(x) \int_0^L dx' \varphi^{(l)}(x') \Psi(x',0)$$

This expression is well-defined even for initial states that are not differentiable…

We seem to have bumped into a generalised solution of the time-dependent Schrödinger equation…..

Analyticity in space and time

Our initial series expansion, however does seem to make sense for some initial states, for example a finite linear combination of eigenfunctions

$$\Psi(x,0) = \sum_{k=1}^{N} \alpha_k \, \varphi^{(k)}(x)$$

We obtain a correct solution to the TDSE

$$\Psi(x,t) = \sum_{n=0}^{\infty} \sum_{k=1}^{N} \alpha_k \left(\frac{it}{2}\right)^n \frac{1}{n!} \frac{d^{2n}}{dx^{2n}} \varphi^{(k)}(x)$$

$$= \sum_{n=0}^{\infty} \sum_{k=1}^{N} \alpha_k \left(-it\epsilon^{(k)}\right)^n \frac{1}{n!} \varphi^{(k)}(x) = \sum_{k=1}^{N} \alpha_k e^{-it\epsilon^{(k)}} \varphi^{(k)}(x)$$

This solution is analytic in space and time

$$\Psi(x,t) = \sum_{k,l=0}^{\infty} c_{kl} \, (t-t_0)^k (x-x_0)^l$$

However, analyticity is not enough. Take the following initial wave packet on the real line

$$\Psi(x,0) = \frac{1}{1+x^2} = \frac{i}{2}\left(\frac{1}{x+i} - \frac{1}{x-i}\right)$$

Then our series expansion gives

$$\Psi(x,t) = \sum_{n=0}^{\infty} \left(-\frac{it}{2}\right)^n \frac{(2n)!}{n!} \frac{i}{2} \left(\frac{1}{(x+i)^{2n+1}} - \frac{1}{(x-i)^{2n+1}}\right)$$

This series does not converge at any space-time point and the solution is not analytic in time

A necessary condition for convergence is that the initial state is at least an entire function (analytic in the whole complex plane)

(Sophie Kowalewskaya, Journal für Reine und Angewandte Mathematik 80, 1 (1875))

Mild solutions

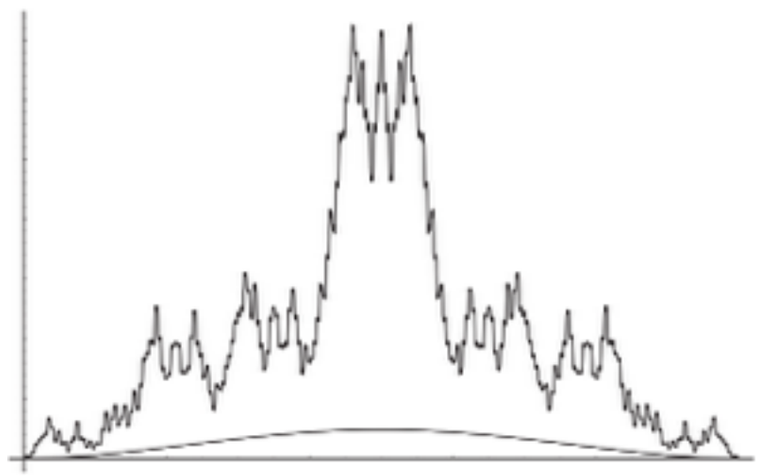
Let us go back to the spectrum representation and take as initial state

$$\Psi(x,0) = \begin{cases} 1/\sqrt{L} & x \in]0, L[\\ 0 & x = 0 \text{ or } x = L \end{cases} \qquad \langle \varphi^{(l)} | \Psi(0) \rangle = \frac{\sqrt{2}}{l\pi}(1 - (-1)^l)$$

Then the time evolution is given by the series

$$\Psi(x,t) = \frac{4}{\pi\sqrt{L}} \sum_{k=0}^{\infty} \frac{e^{-i\pi^2(2k+1)^2 t/(2L^2)}}{2k+1} \sin\left[\frac{(2k+1)\pi x}{L}\right]$$

This function is nowhere spatially differentiable at almost all times (Weierstrass function)



This is a so-called "mild" solution to the TDSE which solves the integral form of the time-dependent Schrödinger equation

$$\Psi(x,t) = \Psi(x,0) - i\hat{H}\int_0^t ds\,\Psi(x,s) \quad = \Psi(x,0) + \frac{i}{2}\frac{d^2}{dx^2}\int_0^t ds\,\Psi(x,s)$$

The main reason for the non-differentiability is the fact that the initial state was outside the domain of the Hamiltonian, i.e. we can make a series of smooth functions satisfying the boundary conditions such that

$$\varphi_n \to \Psi_0 \qquad\qquad \|\hat{H}\varphi_n\| \to \infty$$

We can take an initial state that is in the domain of the Hamiltonian but then it could still happen that a higher time-derivative of the wave function is outside this domain and leads to complications

(Fournais et al. Phys.Rev.A93,062510 (2016))

As a simple example we take $\Psi_0(x) = x(L-x)$

The time-dependent wave function is nice and differentiable

$$\Psi(x,t) = C\sum_{k=0}^{\infty} \frac{e^{-i\pi^2(2k+1)^2 t/(2L)^2}}{(2k+1)^3} \sin\left[\frac{(2k+1)\pi x}{L}\right]$$

Its first time-derivative is however given by

$$\partial_t \Psi(x,t) \sim \sum_{k=0}^{\infty} \frac{e^{-i\pi^2(2k+1)^2 t/(2L)^2}}{2k+1} \sin\left[\frac{(2k+1)\pi x}{L}\right]$$

which is the Weierstrass-type function of before.

$\partial_t^2 \Psi(x,t)$ does not exist almost anywhere..

Regularity of the time-dependent Schrödinger equation

Hamiltonian

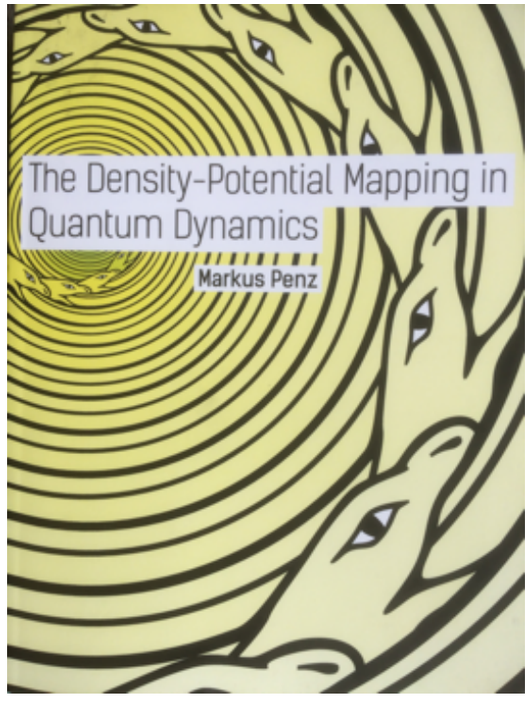
$$\hat{H}(t) = \hat{T} + \hat{V}(t) + \hat{W}$$

Schrödinger equation

$$i\partial_t |\Psi[v](t)\rangle = \hat{H}(t)|\Psi[v](t)\rangle \qquad |\Psi[v](t_0)\rangle = |\Psi_0\rangle$$

For which class of external potentials and initial states has the initial value problem of the time-dependent Schrödinger equation a solution ?

Which class of potentials preserves regularity of the initial state?



Self-adjoint domain of the Laplacian

Let us now go to the many-particle 3D case and ask whether

$$i\partial_t \Psi(t) = \hat{T}\Psi(t) \qquad \hat{T} = \sum_{j=1}^{N} -\frac{1}{2}\nabla_j^2$$

has a solution. Stone's theorem tells us that this is possible if the kinetic energy operator is defined on a self-adjoint domain

This domain is the set of wave functions for which the norm

$$\|\Psi\|_{H^2} = \|\Psi\| + \|\hat{T}\Psi\|$$

is finite

$$\Psi(0) \in H^2(\mathbb{R}^{3N}) \qquad \Psi(t) \in H^2(\mathbb{R}^{3N}) = D(\hat{T})$$

Now we add some interactions

$$\hat{H}_0 = \hat{T} + \hat{W}$$

$$(\hat{H}_0\Psi)(\underline{r}) = \left[\sum_{j=1}^{N}\left(-\frac{1}{2}\nabla_j^2\right) + \frac{1}{2}\sum_{i\neq j}^{N} w(\mathbf{r}_i - \mathbf{r}_j)\right]\Psi(\underline{r})$$

We want to choose the interactions such that this Hamiltonian remains self-adjoint on the domain of the kinetic energy. This problem was solved by Kato

$$w = w_1 + w_2 \qquad w_1 \in L^2(\mathbb{R}^3) \qquad w_2 \in L^\infty(\mathbb{R}^3)$$

$$\frac{1}{|\mathbf{r}|} = \underbrace{\frac{\theta(1-|\mathbf{r}|)}{|\mathbf{r}|}}_{L^2} + \underbrace{\frac{\theta(|\mathbf{r}|-1)}{|\mathbf{r}|}}_{L^\infty}$$

Finally we add external potentials

$$\hat{H}_0 + \hat{V}(t) \qquad \hat{V}(t) = \sum_{j=1}^{N} v(\mathbf{r}_j, t)$$

The same Kato theory applies again. The full Hamiltonian is self-adjoint on the same domain if the external potentials are again in the class of Kato perturbations

$$\mathcal{K} = L^\infty(\mathbb{R}^3) + L^2(\mathbb{R}^3)$$

Now finally we can make a rigorous statement on the solvability of the TDSE

The TDSE initial value problem is solvable for the class of time-dependent potentials

$$\mathcal{V} = C^1([0,T],\mathcal{K})$$

$$\|v(t+\Delta t) - v(t)\| \to 0 \quad (\Delta t \to 0)$$
$$\|\partial_t v(t+\Delta t) - \partial_t v(t)\| \to 0 \quad (\Delta t \to 0)$$

i.e, the one times differentiable mappings to the Kato class of potentials

If the initial state is in $\mathcal{D}(\hat{T}) = H^2(\mathbb{R}^{3N})$ and the interaction is in the Kato class

then there is a classical solution to the TDSE :

$$\Psi \in C^1([0,T], L^2(\mathbb{R}^{3N}))$$

$$\|\Psi(t+\Delta t) - \Psi(t)\| \to 0 \quad (\Delta t \to 0)$$
$$\|\partial_t \Psi(t+\Delta t) - \partial_t \Psi(t)\| \to 0 \quad (\Delta t \to 0)$$

For such a solution the expectation values of the kinetic and potential energies are finite.

(proof M.Penz generalisation of a proof by B. Simon….strictly speaking the proof by Markus is softened to Lipshitz continuous mappings…but this is less pedagogical for this presentation)

Regularity stability theorem for the TDSE

Let the initial state $\Psi_0 \in H^{2m}$ i.e. $D^\alpha \Psi_0 \in L^2 \qquad |\alpha| \leq 2m$

The static two-body interaction is a Kato perturbation (for example Coulomb).
Then if the set of time-dependent external potentials is given by

$$v \in \mathrm{Lip}([0,T], W^{2(m-1),\Sigma})$$

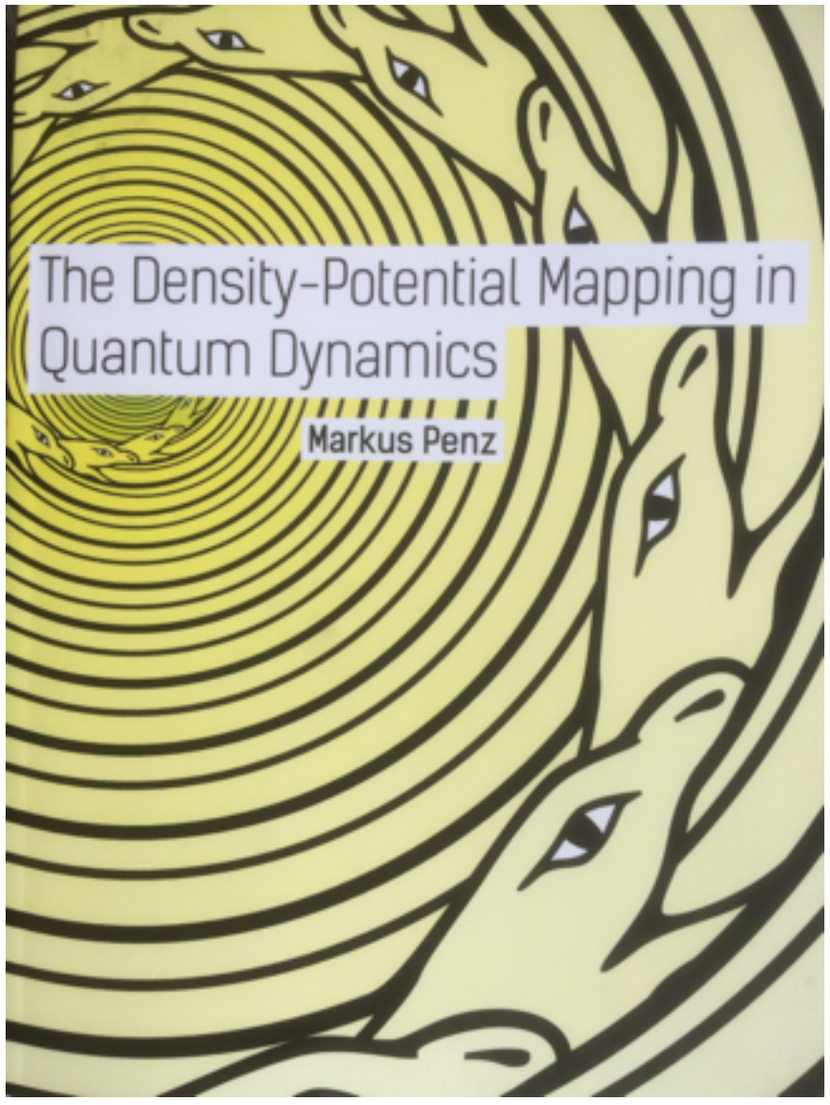
$$W^{m,\Sigma} = \{v | D^\alpha v \in \Sigma(L^2 + L^\infty), |\alpha| \leq m\}$$

Then the TDSE is solvable and the time-evolved state $\Psi(t) \in H^{2m}$

In other words for a well-defined set of external potentials its differentiability properties are preserved

To make the local force equation well-defined we need $\Psi_0 \in H^4$

For many more discussions on this and other issues I refer to…



Summary

The density-potential mapping of TDDFT forces us to ask about the class of external potentials for which the TDSE can be solved

Solvability is closely related to the self-adjointness of the Hamiltonian

The self-adjointness can be established for the Kato class of interactions and external potentials

If the initial state is in the self-adjoint domain then a proper time-evolution can be defined

It the initial state is outside a time-evolution can still be defined but requires a generalisation of TDSE (mild solutions)

A regularity theorem can be proven for the TDSE

…….work is in progress on the density potential mapping ….