WiSe 2015/16 – LMU Mathematics

# Mathematical Quantum Mechanics

Part 1 S. Bachmann

- Hilbert spaces, linear operators, self-adjointness
- The spectral theorem & Stone's theorem,
- Quantum dynamics, Kato-Rellich & the Fourier transform.
- N-body Hamiltonians
- Stability of matter:
  - i) of the first kind
  - ii) of the second kind: a) fermions
    - b) Lieb-Thirring inequality
    - c) electrostatics.
  - iii) instability for bosons
- On the calculus of variations.

References:
- Mathematical Methods in QM, G. Teschl, in Graduate Studies in Mathematics, 157, AMS.
- Analysis, E.H. Lieb & M. Loss in G.S.M, 14, AMS
- The Stability of Matter in QM, E.H. Lieb & R. Seiringer, Cambridge University Press.

# MQM I

## 1. Mathematical physics:

- physics: problems & models directly motivated by physics
- mathematics: it consists of theorems based on mathematical definitions.

a) Classical mechanics: differential and integral calculus, PDE
b) Stat. mechanics: probability, PDE
c) General relativity: differential geometry, PDE
d) Fluid mechanics: non-linear PDE
e) Quantum mechanics: functional analysis, PDE, calc. of variations.
f) QFT: functional analysis, probability, algebra.

some mathematical successes:

* Schrödinger operators: spectral theory, properties of eigenfunctions, H-atom.
* → Dynamics: functional calculus and PDE
* Semi-classics: $\hbar \to 0$.
* N-body QM: quantum chemistry, molecules
* Approximate theories, density functional theory
* Scattering theory ($t \to \pm\infty$).
* → Stability of matter
* Approximate dynamics (non-linear PDE's)
* (Magnetic) phase transitions
* Random Schrödinger operator

...

# 3. Introduction to QM

- Classical mechanics of one particle. $(x, p) \in \mathbb{R}^6$

$$\dot{x} = \frac{\partial H}{\partial p} \quad , \quad \dot{p} = -\frac{\partial H}{\partial x}$$

$H = H(x,p)$ is Hamilton's function

For a particle under force $F(x) = -\nabla V(x)$ :

$$H = \frac{p^2}{2m} + V(x)$$

and Hamilton's eq. yield Newton's eq $m\ddot{x} = F(x)$.

- Magnetic field: Lorentz force $-\frac{e}{c} v \wedge B(x)$ is implemented by the "minimal coupling":

$$p \mapsto p + \frac{e}{c} A(x) \quad , \quad \text{curl } A = B$$

i.e. $$H = \frac{1}{2m}\left(p + \frac{e}{c} A(x)\right)^2 + V(x)$$

- N-body systems $(x_1, \dots x_N, p_1, \dots, p_N) \in \mathbb{R}^{6N}$

or molecules: N-electrons, M-nuclei, Coulomb interaction
$(x_1, \dots, x_N)$ $(R_1, \dots, R_M)$

$$V(\underline{x}, \underline{R}) = \left(W(\underline{x}, \underline{R}) + I(\underline{x}) + U(\underline{R})\right) e^2$$

$$W(\underline{x}, \underline{R}) = -\sum_{i=1}^{N} \sum_{j=1}^{M} \frac{Z_j}{|x_i - R_j|}$$ $Z_j$: nuclear charge, attraction

$$I(\underline{x}) = \sum_{1 \le i < j \le N} \frac{1}{|x_i - x_j|}$$ — repulsive

$$U(\underline{R}) = \sum_{1 \le i < j \le M} \frac{Z_i Z_j}{|R_i - R_j|}$$ — repulsive.

"Potential energy"

and "kinetic energy"

$$T(p) = \sum_{i=1}^{N} \frac{p_i^2}{2m} \qquad \text{(nuclei are fixed because heavy)}.$$

$\rightsquigarrow$ full microscopic model.
magnetic fields can be added.

- Note: the range of $H$ is the full $\mathbb{R}$: arbitrary negative energies can be reached
  $\rightsquigarrow$ the electrons would collapse onto the nuclei, releasing an infinite amount of energy. :-(

Quantum mechanics solves that problem. We will study that in details.
"Stability of matter".

- QM of one-particle. The (pure) state of CM, namely a point in $\mathbb{R}^6$ must be replaced by a function $x \mapsto \Psi(x) \in \mathbb{C}$, with $|\Psi(x)|^2$ a probability density, and hence:

$$\int_{\mathbb{R}^3} |\Psi(x)|^2 dx = 1 \qquad \text{"}L^2\text{-normalization"}.$$

The classical energy is replaced by an energy functional

$$E(\Psi) = T(\Psi) + V(\Psi).$$

$$T(\Psi) = \frac{\hbar^2}{2m} \int_{\mathbb{R}^3} |\nabla \Psi(x)|^2 dx$$

$$V(\Psi) = \int_{\mathbb{R}^3} V(x) |\Psi(x)|^2 dx.$$

In other words: the classical $p \in \mathbb{R}^3$ is "replaced by" the operator $-i\hbar\nabla$ acting on the function $\psi$.

$\rightsquigarrow$ free Hamiltonian: $H_0 = -\frac{\hbar^2}{2m}\Delta$

Hamiltonian $H = H_0 + V$ acting as

$$(H\psi)(x) = -\frac{\hbar^2}{2m}(\Delta\psi)(x) + V(x)\psi(x).$$

Notes. * derivatives to be taken in distributional sense ($H$ meant to act on $L^2(\mathbb{R}^3)$)

* $E(\psi) = \langle \psi, H\psi \rangle_{L^2(\mathbb{R}^3)}$.

where $\langle f, g\rangle_{L^2(\mathbb{R})} := \int_{\mathbb{R}^3} \overline{f(x)} g(x)\, dx$.

- Dynamics: just as in C.M., the energy (Hamiltonian) is also the generator of the dynamics (time-evolution):

$$\psi \mapsto \psi_t$$

is the unique solution of the PDE

$$i\partial_t \psi_t = H\psi_t \quad , \quad \psi_0 = \psi.$$

"Schrödinger equation".

We write $\psi_t = U(t)\psi$ and have:

* $\|U(t)\psi\|_{L^2(\mathbb{R}^3)} = \|\psi\|$ unitarity
* $U(0) = \mathbb{1}$ ; $U(t+s) = U(t)U(s)$ one-parameter group
* $\lim_{t\to t_0} U(t)\psi = U(t_0)\psi$ strong continuity
* $-iH\psi = \lim_{t\to 0} \frac{1}{t}(U(t)\psi - \psi)$ strong differentiability.

# 4. Stability of the first kind – an idea

- Question: Is

$$E_0 = \inf \left\{ E(\Psi) : \int_{\mathbb{R}^3} |\Psi(x)|^2 dx = 1 \right\}$$

finite ? — "stability of the first kind".
What is (an estimate of) its value?
Is the inf a minimum : $\exists! \ \Psi_0 : E_0 = E(\Psi_0)$
"Ground state energy"

Calculus of variations!

- Classically: $E(\Psi) = T(\Psi) + V(\Psi)$ with $V(\Psi)$ not lower bounded and "independent" of $T(\Psi)$ $\leadsto$ instability.

In QM: Uncertainty principles save the day.

1) Heisenberg : $\Psi \in H^1(\mathbb{R}^3)$, $\|\Psi\|_2 = 1$, then

$$\langle \Psi, P^2 \Psi \rangle \geq \frac{9}{4} \langle \Psi, X^2 \Psi \rangle^{-1}.$$

which follows from $P \cdot X - X \cdot P = d \, \mathbb{1}$ in $\mathbb{R}^d$.
... will not be very useful.

2) Sobolev's inequality. $d \geq 3$ $\quad q = \frac{2d}{d-2}$ :
If $\star$ $\Psi$ vanishes at infinity : $|\{x : |\Psi(x)| > a\}| < \infty$ $\quad \forall a > 0$

$\star$ $D\Psi \in L^2(\mathbb{R}^d)$

Then $\Psi \in L^q(\mathbb{R}^d)$ and

$$\|D\Psi\|_2^2 \geq S_d \|\Psi\|_q^2$$

$$S_d = \frac{1}{4} d(d-2) |S^d|^{2/d}$$ area of sphere

$d=3$: $$\underbrace{\int_{\mathbb{R}^3} |\nabla \psi(x)|^2 dx}_{=2T(\psi)} \geq \frac{3}{4}(4\pi^2)^{2/3} \underbrace{\left( \int |\psi(x)|^6 dx \right)^{1/3}}_{\text{relate to } V(\psi)}.$$

We have Hölder's inequality : $f \in L^p$, $g \in L^q$ with $1 \leq p \leq \infty$, $\frac{1}{p} + \frac{1}{q} = 1$, then

$$\int \overline{f(x)}\, g(x)\, dx \leq \|f\|_p \|g\|_q$$

So if $V \in L^{3/2}(\mathbb{R}^3)$ : $V$ real-valued

$$|V(\psi)| \leq \int |\psi(x)|^2 |V(x)| dx \leq \underbrace{\| |\psi|^2 \|_3}_{= \left( \int |\psi(x)|^6 dx \right)^{1/3}} \|V\|_{\frac{3}{2}}$$

Hence $2T(\psi) \geq \frac{3}{4}(4\pi^2)^{2/3} \langle \psi, |V| \psi \rangle \|V\|_{\frac{3}{2}}^{-1}$, and

$$T(\psi) + V(\psi) \geq \left( \frac{3}{8}(4\pi^2)^{2/3} \|V\|_{\frac{3}{2}}^{-1} - 1 \right) |V(\psi)|$$

and $\underline{E(\psi) \geq 0}$ if $\|V\|_{\frac{3}{2}} \leq \frac{3}{8}(4\pi^2)^{2/3}$

↳ stability of the first kind!

- finally, adding a bounded part to the potential does not change the qualitative result that $E(\psi)$ is uniformly bounded below.

$$V \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3) \Rightarrow E_0 > -\infty.$$

which applies for $V(x) = \frac{-\alpha}{|x|}$, the Coulomb potential

i.e. the Hydrogen atom is stable.

- Note: In the case of the Hydrogen atom:

$$-\Delta + \left(\frac{-\alpha}{|x|}\right)$$

the Hamiltonian can in fact be diagonalized completely. The ground state is

$$\psi_0(x) = C\exp\left(-\frac{|x|}{a}\right), \quad C, a > 0,$$

and the ground state energy

$$E(\psi_0) = -\frac{\alpha^2}{4}$$

It is however a very lucky and rare event that a Hamiltonian can be solved like this. Otherwise, estimates are needed, which are a lot more robust.

# 5. Some quantum mechanics : general structure.

- State space: Hilbert space $\mathcal{H}$, a complete inner product space; Notation:

$$\langle f, g\rangle \quad \text{and} \quad \|f\|^2 = \langle f, f\rangle .$$

examples: • $\mathcal{H} = L^2(\Pi, d\mu)$, $\langle f, g\rangle = \int_\Pi f^*(x)\, g(x)\, d\mu(x)$

• $\mathcal{H} = \ell^2(\mathbb{N})$, $\langle f, g\rangle = \sum_{i\in\mathbb{N}} f_i^* g_i$

Dirac notation: $f \in \mathcal{H}$ also denoted $|f\rangle$, and $|f\rangle\langle f|$ is the orthogonal projection on $f$:

$$\big(|f\rangle\langle f|\big)|g\rangle = \langle f, g\rangle f .$$

Lemma (polarization identity)

$$\langle f, g\rangle = \frac{1}{4}\left(\|f+g\|^2 - \|f-g\|^2 + i\|f-ig\|^2 - i\|f+ig\|^2\right)$$

i.e. : the scalar product is completely determined by the norm in a complex $\mathcal{H}$.

- In this course: all $\mathcal{H}$ are separable : there exists a countable orthonormal basis, and every ON basis is countable.
- For any $f \in \mathcal{H}$: $\|f\| = 1$, the map

$$\ell_f : \mathcal{H} \to \mathbb{C} \quad : \quad g \mapsto \langle f, g\rangle$$

is linear and bounded (since $|\langle f, g\rangle| \le \|f\|\|g\| = \|g\|$)

reciprocally:

Theorem (Riesz) : Let $\ell$ be a bdd linear functional on $\mathcal{H}$. Then $\exists$ a unique $f_\ell \in \mathcal{H}$ s.t.

$$\ell(g) = \langle f_\ell, g\rangle \quad \forall g \in \mathcal{H}.$$

Proof: $\mathcal{N} := \{ g \in \mathcal{H} : \ell(g) = 0 \}$ is closed by the continuity of $\ell$.

If $\mathcal{N} = \mathcal{H}$, we choose $f_\ell = 0$.

Otherwise, $\exists\ f \in \mathcal{N}^\perp$, $\|f\| = 1$. For any $g \in \mathcal{H}$:

$$\ell [ \underbrace{\ell(g) f - \ell(f) g}_{\in \mathcal{N}} ] = 0$$

i.e.

$$\Rightarrow \quad 0 = \langle f, (\ell(g) f - \ell(f) g) \rangle$$

$$\Rightarrow \quad \langle f, g \rangle = \frac{1}{\ell(f)} \ell(g)$$

Hence, $f_\ell := \overline{\ell(f)} f$ has the right properties

Uniqueness follows from

$$\langle f_\ell' - f_\ell, g \rangle = \ell(g) - \ell(g) = 0 \quad \forall g \in \mathcal{H}$$

$$\rightarrow \quad f_\ell' - f_\ell \in \mathcal{H}^\perp = \{0\}.$$

□

- Set of observables consists of all self-adjoint operators on $\mathcal{H}$.

The expectation value of $A \in \mathcal{A}$ in the state $\psi \in \mathcal{H}$ is

$$\langle \psi, A \psi \rangle$$

which is real.

- A little bit more on this.

Consider a linear operator $A : \underset{\sim}{\mathcal{D}(A)} \to \mathcal{H}$

domain, always assumed dense.

is called bounded if

$$\|A\| = \sup_{\substack{\psi \in \mathcal{H} \\ \|\psi\| = 1}} \|A\psi\| < \infty .$$

Canonically associated quadratic form

$$Q_A : \mathcal{D}(A) \to \mathbb{C} : \quad Q_A(\psi) = \langle \psi, A \psi \rangle$$

A is called symmetric if

$$\langle f, Ag \rangle = \langle Af, g \rangle \quad , \quad f, g \in \mathcal{D}(A),$$

and A is symmetric iff $Q_A$ is real-valued (by polarization)

<u>Important remark:</u> This is not sufficient for QM, observables are self-adjoint. (At least) two reasons:

* Spectral thm holds for s.-a. ops

  In particular, it associates to any observable A and state $\psi$ a well-defined probability measure $\mu_\psi^{(A)}$ over the reals. For every Borel $M \subset \mathbb{R}$, $\mu_\psi^{(A)}(M)$ is the probability that the result of the measurement of A belongs to M when the ~~state~~ system was in the state $\psi$.

* Stone's thm:

  associates a unitary group $U(t) := e^{itA}$ to any s.a. op. A (and in fact reciprocally).

  $\rightsquigarrow$ dynamics / symmetries (charges).

(* Also: s.a. ops are "maximal": they cannot be extended ).

• On self-adjoint operators: $A^*: \mathcal{D}(A^*) \to \mathcal{H}$,

$$\mathcal{D}(A^*) = \{ f \in \mathcal{H} : \exists h \in \mathcal{H} \text{ s.t. } \langle f, Ag \rangle = \langle h, g \rangle \text{ for all } g \in \mathcal{D}(A) \}.$$

$$A^* f := h \quad \text{(definition of the adjoint)}$$

If A is symmetric, then $\mathcal{D}(A) \subseteq \mathcal{D}(A^*)$ and

$$A^* f = Af \quad \text{for all } f \in \mathcal{D}(A)$$

Hence, $A$ symmetric $\Rightarrow$ $A \subseteq A^*$
($A^*$ is an <u>extension</u> of $A$).

$A$ is <u>self-adjoint</u> if $A = A^*$ (i.e. $\mathcal{D}(A^*) = \mathcal{D}(A)$).

Basic criteria for self-adjointness.

<u>Theorem</u>: Let $A$ be a symmetric operator on $\mathcal{H}$. Tfae:

i) $A$ is self-adjoint

[ ii) $A$ is closed and $\mathrm{Ker}(A^* \mp i\lambda) = \{0\}$ ] $\Big\}$ $\lambda \in \mathbb{R}$.

iii) $\mathrm{Ran}(A \pm i\lambda) = \mathcal{H}$

very useful.

Proof: see your T.A. course.

<u>Remarks</u>: • These subtleties arise only for unbounded operators:

If $A$ is symmetric and $\mathcal{D}(A) = \mathcal{H}$, then $A$ is bounded (Hellinger–Toeplitz)

• In the theorem, we could add

iv) $\mathrm{Spec}(A) \subset \mathbb{R}$, see later.

• If $A$ is symmetric, then $A \subseteq A^{**}$ so that $A^{**}$ is an extension of $A$.

$A^{**}$ is called the closure of $A$

$A$ is called <u>essentially self-adjoint</u> iff $A^{**}$ is self-adjoint.

• A long example: the momentum operator $P$ on $\mathcal{H} = L^2([0,1])$.

• The derivative of $\psi \in L^2([0,1])$ is understood "in the sense of distributions" (cf integration by parts).

$$\frac{d\psi}{dx} : C_0^\infty(0,1) \longrightarrow \mathbb{C}$$

$$v \longmapsto \frac{d\psi}{dx}[v] = -\int_0^1 \psi(x) \frac{dv}{dx}\, dx$$

Lemma (in one dimension!)

If $\frac{d\psi}{dx} \in L^2([0,1])$, then $\psi$ is continuous.

Moreover, for any $\varphi \in L^2([0,1])$ s.t. $\frac{d\varphi}{dx} \in L^2([0,1])$:

$$\int_0^1 \left( \frac{d\psi}{dx}\varphi + \psi \frac{d\varphi}{dx} \right) dx = \psi(x)\varphi(x)\Big|_0^1 .$$

Proof (sketch)

Let $\tilde{\psi}(x) := \int_0^x \frac{d\psi}{dx'} dx'$. It is well-defined since

$$\int_0^x \left| \frac{d\psi}{dx'} \right| dx' \underset{C\text{-}S}{\leq} \left( \int_0^x \left| \frac{d\psi}{dx'} \right|^2 dx' \right)^{1/2} \left( \int_0^x 1\, dx' \right)^{1/2},$$

and continuous (as the integral of an integrable function)

and $\frac{d\tilde{\psi}}{dx} = \frac{d\psi}{dx}$. Indeed:

$$\frac{d\tilde{\psi}}{dx}[v] = -\int_0^1 \frac{dv}{dx}\tilde{\psi}(x)\, dx = -\int_0^1 \frac{dv}{dx'}\left( \int_0^x \frac{d\psi}{dy} dy \right) dx'$$

$$= -\int_0^1 \left( \int_y^1 \frac{dv}{dx'} \frac{d\psi}{dy}\, dx' \right) dy$$

$$= -\int_0^1 \frac{d\psi}{dy} v(x')\Big|_y^1 dy = \int_0^1 \frac{d\psi}{dy} v(y)\, dy = \frac{d\psi}{dy}[v].$$

$$\Rightarrow \frac{d}{dx}(\tilde{\psi} - \psi) = 0 \quad \text{a.e.} \quad \Rightarrow \tilde{\psi} = \psi + \text{constant}$$

Since $(\psi\varphi)' = \psi'\varphi + \psi\varphi'$ a similar reasoning yields the second part. □

- Now define two differential operators $\tilde{P}, P_0$ on $\mathcal{H}$:

$D(\tilde{P}) := \{ \psi \in \mathcal{H} : \frac{d\psi}{dx} \in L^2([0,1]) \}$ $\quad \tilde{P}\psi = -i\frac{d\psi}{dx}$

$D(P_0) := \{ \psi \in D(\tilde{P}) : \psi(0) = \psi(1) = 0 \}$, $\quad \tilde{P}\psi = P_0\psi$.

which are well-defined by the lemma.

Also: $P_0 \subsetneq \tilde{P}$.

* Claim $\tilde{P}^* = P_0$. Indeed:

$\varphi \in D(\tilde{P}^*)$ if $\exists\, \xi \in \mathcal{H}$: $\langle \tilde{P}\psi, \varphi \rangle = \langle \psi, \xi \rangle$

in particular $|\langle \tilde{P}\psi, \varphi\rangle| \leq C\|\psi\| \quad \forall \psi \in D(\tilde{P})$

and further $\left|\frac{d\varphi}{dx}[\bar{v}]\right| \leq C\|v\| \quad \forall v \in C_0^\infty(0,1)$.

in other words: $\frac{d\varphi}{dx}$ defines a bounded quadratic form so that $\exists\, \frac{d\varphi}{dx} \in L^2([0,1])$ by Riesz's theorem.

Hence: $D(\tilde{P}^*) \subseteq D(\tilde{P})$. Now for any $\psi \in D(\tilde{P})$:

$$\langle \tilde{P}\psi, \varphi\rangle - \langle \psi, \tilde{P}\varphi\rangle = i\int_0^1 \left(\frac{d\bar{\psi}}{dx}\varphi - \bar{\psi}\frac{d\varphi}{dx}\right)dx$$

$$= \bar{\psi}(1)\varphi(1) - \bar{\psi}(0)\varphi(0) \qquad (*)$$

by the lemma.

$|\langle \psi, \tilde{P}\varphi\rangle| \leq C\|\psi\|$ (where $C = \|\tilde{P}\varphi\|$)

but the r.h.s of $(*)$ cannot be bounded by $\|\psi\|$.

Hence $\langle \tilde{P}\psi, \varphi\rangle \leq C\|\psi\|$

iff $\varphi(0) = \varphi(1) = 0$, namely $\varphi \in D(P_0)$.

Finally, the last formula of the lemma yields that $P_0$ is symmetric.

(and also abstractly: $P_0 \subset \tilde{P} = \tilde{P}^{**} = P_0^*$ where the first equality follows because $\tilde{P}$ is a closed operator)

* $\alpha \in \mathbb{C}$, $|\alpha| = 1$. Define $P_\alpha$:

$D(P_\alpha) = \{\psi \in D(\tilde{P}) : \psi(1) = \alpha\psi(0)\}$, $P_\alpha\psi = \tilde{P}\psi$.

$P_0 \subset P_\alpha \subset \tilde{P}$.

Claim: $P_\alpha = P_\alpha^*$.

Again as above $D(P_\alpha^*) \subset D(\tilde{P})$ and
$$\langle P_\alpha^* \psi, \varphi \rangle - \langle \psi, \tilde{P}\varphi \rangle = \bar{\psi}(0)\left(\bar{\alpha}\varphi(1) - \varphi(0)\right)$$
whenever $\psi \in D(P_\alpha)$.

Hence: $\langle P_\alpha \psi, \varphi \rangle = \langle \psi, \tilde{P}\varphi \rangle + \bar{\alpha}\bar{\psi}(0)\left(\varphi(1) - \alpha\varphi(0)\right)$

so that $\varphi \in D(P_\alpha^*)$ iff $\varphi \in D(P_\alpha)$

and $P_\alpha^* \varphi = \tilde{P}\varphi = P_\alpha \varphi$

* Finally, since $A \subset B \Rightarrow B^* \subset A^*$, we have
$$P_0^* \subsetneq P_\alpha = P_\alpha^* \subsetneq P_0^*$$

* Summarizing:

All above $P$'s act as $-i\frac{d}{dx}$.

With Dirichlet B.C., $P_0$, is symmetric, not self-adjoint.

With periodic B.C., $P_\alpha$, is self-adjoint.

i.e. $\{P_\alpha ; \alpha \in \mathbb{C}, |\alpha| = 1\}$ is a one-parameter family of self-adjoint extensions of $P_0$

* Note: $P_0$ & $P_\alpha$ differ non-trivially, despite agreeing on a dense set $D(P_0)$. For example:

$P_0$ has no eigenvectors, while $P_\alpha$ has a basis of eigenvectors, the plane waves ~~$e^{\dots}$~~ $\exp(-i(\theta + 2\pi n)x)$ $n \in \mathbb{Z}$.

* Given a symmetric operator, when does it have self-adjoint extensions? The full answer involves the deficiency indices but there is one physically relevant case: if $A$ is semi-bounded there is a canonical self-adjoint extension called the Friedrichs extension

Additional remarks on eigenvectors

An eigenvector $\psi \in \mathcal{H}$ is a non-zero solution of

$$T\psi = \lambda\psi, \qquad \text{with eigenvalue } \lambda \in \mathbb{C}$$

i.e. here (formally)

$$i\psi' = \lambda\psi$$

As a differential equation the equation has a unique solution

$$\psi_0^\lambda(x) = e^{-i\lambda x} \cdot \text{Const.}$$

i) if $T = P_0$, $\psi_0(0) = \psi_0(1) = 0 \Rightarrow \psi_0(x) = 0$
there is no eigenvector at all (for any $\lambda \in \mathbb{C}$)

ii) if $T = P_\alpha$, $\psi_0(1) = \alpha\psi_0(0) \Rightarrow e^{-i\lambda} = \alpha$
which has solutions $\lambda_n := \theta + 2\pi n$, $n \in \mathbb{Z}$.
where $\alpha := e^{-i\theta}$, $\psi_0^n(x) = C\exp(-i(\theta + 2\pi n)x)$.

iii) if $T = \tilde{P}$, for any $\lambda \in \mathbb{C}$ $\psi_0^\lambda \in L^2$
and differentiable, so any $\lambda \in \mathbb{C}$ is an eigenvalue.

- Theorem: Let $A: \mathcal{D}(A) \to \mathcal{H}$ be a symmetric operator s.t.
$$\langle \psi, A\psi \rangle \geq \gamma \|\psi\|^2 \quad \forall \psi \in \mathcal{D}(A)$$
Then there exists a self-adjoint extension $\tilde{A}$ of $A$ s.t. $\tilde{A} \geq \gamma$

- Remarks: * $\mathcal{D}(\tilde{A})$ can be described explicitly
  * The condition $\langle \psi, A\psi \rangle \geq \gamma \|\psi\|^2$ implies in prt. that the quadratic form $Q_A$ is real-valued. As noted earlier, this implies that $A$ is symmetric.
  * In practice, it often suffices to define a Hamiltonian on a dense set s.t. $C_0^\infty$, on which one proves that $E(\psi) \geq \gamma > -\infty$ and then use the theorem to obtain an abstract self-adjoint operator (which induces a well-defined quantum dynamics as we shall see).

## 6. Around the spectral theorem (all sketchy, see FA II).

- For matrices, there are at least two important aspects of the spectral thm for self-adjoint maps:
  i) Diagonalization:
$$M = \sum_i \lambda_i P_i$$
eigenprojections, eigenvalues

  ii) Functional calculus: Define $f(M)$ for a large class of functions $f$:
$$f(M) = \sum_i f(\lambda_i) P_i$$

they in both cases are the projections $P_i$.

⇝ in general: projection-valued measure:

i) $P : \mathcal{B}(\mathbb{R}) \to \mathcal{L}(\mathcal{H})$

Borel σ-algebra generated by intervals.

• $P_\Omega = P_\Omega^2 = P_\Omega^*$ $\quad \forall\, \Omega \in \mathcal{B}(\mathbb{R})$

• $P_{\mathbb{R}} = \mathbb{1}$

• σ-additivity: $\Omega = \bigcup_n \Omega_n$ , $\Omega_n \cap \Omega_{n'} = \phi$ $(n \neq n')$:

$$\sum_n P_{\Omega_n} \psi = P_\Omega \psi .$$

ii) $P_\lambda := P((-\infty, \lambda])$ satisfies

• $P_\lambda = P_\lambda^2 = P_\lambda^*$

• $P_\lambda \leq P_{\lambda'}$ if $\lambda \leq \lambda'$

• $\operatorname*{s-lim}_{\lambda_n \downarrow \lambda} \; P_{\lambda_n} = P_\lambda$ ,

with $\operatorname*{s-lim}_{\lambda \to -\infty} P_\lambda = 0$ , $\operatorname*{s-lim}_{\lambda \to +\infty} P_\lambda = \mathbb{1}$.

iii) Given a $P$ and $\psi \in \mathcal{H}$,

$$\mu_\psi(\Omega) := \langle \psi, P_\Omega \psi \rangle$$

is a finite Borel measure $\left( \mu_\psi(\mathbb{R}) = \|\psi\|^2 \right)$,

with distribution function

$$\mu_\psi(\lambda) = \langle \psi, P_\lambda \psi \rangle$$

⇝ Borel-measurable functions can be integrated:

$$\int_{\mathbb{R}} f(\lambda) \, d\mu_\psi(\lambda) =: \langle \psi, P(f) \psi \rangle$$

- from (ii):
  - $P_\emptyset = 0$, $P_{\mathbb{R}\setminus M} = \mathbb{1} - P_M$
  - $P_{M_1} P_{M_2} = P_{M_1 \cap M_2}$
  - $P_{M_1 \cup M_2} = P_{M_1} + P_{M_2} - P_{M_1 \cap M_2}$
  - $M_1 \subset M_2 \Rightarrow \underline{P_{M_1} \leq P_{M_2}}$.

    i.e. $\langle \psi, (P_{M_2} - P_{M_1})\psi \rangle \geq 0$.

- $$\begin{aligned}
\|f(A)\psi\|^2 &= \langle f(A)\psi, f(A)\psi \rangle \\
&= \int_{-\infty}^{+\infty} \overline{f(\lambda)}\, d_\lambda \langle P_\lambda \psi, f(A)\psi \rangle \\
&= \int_{-\infty}^{+\infty} \overline{f(\lambda)}\, d_\lambda \left( \int_{-\infty}^{+\infty} f(\mu)\, d\langle P_\lambda \psi, P_\mu \psi \rangle \right) \\
&= \int_{-\infty}^{+\infty} \overline{f(\lambda)}\, d_\lambda \int_{-\infty}^{\lambda} f(\mu)\, d\langle \psi, P_\mu \psi \rangle \\
&= \int_{-\infty}^{+\infty} |f(\lambda)|^2\, d\langle \psi, P_\lambda \psi \rangle = \int_{-\infty}^{+\infty} |f(\lambda)|^2\, d\mu_\psi(\lambda)
\end{aligned}$$

This defines for any bounded measurable function $f$ a bounded operator $P(f)$:

- polarization:

$$4\langle \varphi, P(f)\psi\rangle = \langle P(f)\rangle_{\varphi+\psi} - \langle P(f)\rangle_{\varphi-\psi} + i\langle P(f)\rangle_{\varphi-i\psi} - i\langle P(f)\rangle_{\varphi+i\psi}$$

- $\|P(f)\psi\|^2 = \int_{\mathbb{R}} |f(\lambda)|^2 d\mu_\psi(\lambda) < \infty.$

i.e. $\|P(f)\| \leq \|f\|_\infty$.

In other words: Theorem: Let $P$ be a proj.-valued meas. Then the map

$$P : \mathcal{B}(\mathbb{R}) \to \mathcal{L}(\mathcal{H})$$
$$f \longmapsto \int f(\lambda)\, dP_\lambda = P(f)$$

is a $*$ homomorphism (of norm 1 if $\mathcal{B}(\mathbb{R})$ is equipped with $\|\cdot\|_\infty$)

<u>Notes</u>:
- $f_n \to f$ pointwise and $\|f_n\|_\infty$ is bounded, then $P(f_n) \to P(f)$ in the strong topology of $\mathcal{L}(\mathcal{H})$ (by dominated convergence)
- in particular: $P(\bar{f}) = P(f)^*$
- Simple case: $\mathcal{H} = \mathbb{C}^n$, $A = A^*$ is a matrix with $\lambda_1, \dots, \lambda_n$ its eigenvalues
  $P_1, \dots, P_n$ its eigenprojectors.

$$P^A_\Omega := \sum_{j : \lambda_j \in \Omega} P_j \quad \text{is a proj-valued meas,}$$

and $P^A(f) = \sum_{j=1}^n f(\lambda_j) P_j$, $\quad (P^A(\lambda) = A)$

and $d\mu_\psi(\lambda) = \sum_{j=1}^n \|P_j\psi\|^2 \delta(\lambda - \lambda_j)$.

iv) This can be extended to unbounded Borel functions with the addition that $P(f)$ may be unbounded, in which case.

$$\mathcal{D}(P(f)) = \{\psi \in \mathcal{H} : \int_{\mathbb{R}} |f(\lambda)|^2 d\mu_\psi(\lambda) < \infty\}.$$

If $f$ is a real function: $P(f) = P(\bar{f}) = P(f)^*$
i.e. $P(f)$ is self-adjoint.

$\Rightarrow$ For every $P$, there is a natural self-adjoint operator $A = P(id)$ $\quad (id : \lambda \mapsto \lambda)$.
and $P(f)$ is usually written $f(A)$
$\leadsto$ "<u>functional calculus</u>"

v) <u>Theorem</u> (spectral theorem, usually the converse of the above)

If $A = A^+$, there exists a unique $P$ s.t.

$$A = \int_{\mathbb{R}} \lambda \, dP_\lambda = P(id)$$

<u>Roughly</u>: this is all the same as in the finite dim. case, up to domain issues, with the difference that the spectral projectors $P_i$ associated to <u>points</u> $\lambda_i \in \mathbb{R}$ have been extended to $P_\Omega$ associated to <u>intervals</u>.

vi) We also have: the spectrum of $A$ is exactly given by the support of $P$:

$\lambda \in \operatorname{supp} P \Leftrightarrow P_M \neq 0 \;\; \forall$ open $M \ni \lambda$

Note: it can well be that $P_{\{\lambda\}} = 0$ while $\lambda \in \sigma(A)$

- for any P.V.M. $P_\Omega$, $\Omega \in \mathcal{B}(\mathbb{R})$

$$f \mapsto P(f)$$

is a $*$-homomorphism from the bounded Borel function to the bounded operators of $\mathcal{H}$.

$$P(\alpha f + g) = \alpha P(f) + P(g)$$
$$P(fg) = P(f)P(g)$$
$$P(f)^* = P(\bar{f}).$$

Reciprocally, if one has such a map, then

$$P_\Omega := P(\chi_\Omega)$$

characteristic function of the set $\Omega \in \mathcal{B}(\mathbb{R})$.

is a P.V.M.

- Having a $P_\Omega$, there is an associated self-adjoint operator

$$A := P(\mathrm{id}) = \int \lambda \, dP_\lambda .$$

The spectral theorem gives the reverse: for any $A = A^*$, there is a unique P.V.M. $P_\Omega^A$. How to prove this?

i) if $A$ is bounded and $f$ is a polynomial $f(x) = \sum_{n=1}^{h} a_n x^n$, this is easy: $P^A(f) = \sum_{n=1}^{h} a_n A^n$ is well-defined.

ii) polynomials are dense in the continuous functions (Weierstrass's theorem) we extend $P^A$ to the continuous functions

iii) extend to $\mathcal{B}(\mathbb{R})$ by $f_n(x) \to f(x)$ and $\|f_n\| < M$ ($\mathcal{B}(\mathbb{R})$ is the smallest algebra closed under these limits and containing the continuous functions) by $P^A(f_n) \xrightarrow{s} P^A(f)$, strongly

iv) extend this to unbounded Borel functions.

v) Notes: • all above applies for normal operators: $AA^* = A^*A$.
• the P.V.M. $P^A$ is the same for any function of $A$.

→ if $A$ is unbounded and self-adjoint, then
$\mathrm{Ran}(A \pm i) = \mathcal{H}$ and
$(A \pm i)^{-1}$ is bounded, and normal

→ apply (iii) to obtain a P.V.M., namely that of $A$.

(finally, one would recover $A$ using iv)

• Support of $P_\Omega$:

$\lambda \in \mathrm{supp}(P) \iff P_\Omega \neq 0 \quad \forall$ open set $\Omega \ni \lambda$

Physically: the $\lambda \in \mathrm{supp}(P)$ are the values that can be obtained in measurements, since $\lambda \in \mathrm{supp}(P)$ implies that there is a $\psi_M$:

$$\langle \psi_M, P_\Omega \psi_M \rangle \neq 0$$

i.e. there is a non-vanishing probability to observe values in $\Omega \ni \lambda$.

Remark: the measure $d\mu_\psi$ is exactly the physically relevant probability measure (if $\|\psi\|=1$) associated to the measurement of the observable A in the state $\psi$.

# 7. Quantum dynamics

- A state is a vector $\psi \in \mathcal{H}$, with $\|\psi\| = 1$.

The dynamics maps states to states, so if we write it as

$$\psi(t) = U(t)\psi(0)$$

we must have $\|U(t)\psi\| = \|\psi\| \quad \forall \psi \in \mathcal{H}$, i.e. $U(t)$ is unitary for all $t$.

We must also have $U(0) = \mathbb{1}$ and we assume that

$$U(t+s) = U(t)U(s)$$

$\Rightarrow$ $U: t \mapsto U(t)$ is a one-parameter unitary group.

Finally, we assume strong continuity:

$$\operatorname*{s-lim}_{t\to 0} U(t) = \mathbb{1}.$$

Define: The generator $H$ of $U$ is given by

$$D(H) := \{\psi : +i \lim_{t\to 0} \tfrac{1}{t}(U(t)-\mathbb{1})\psi \text{ exists}\}$$

$$H\psi = +i \lim_{t\to 0} \tfrac{1}{t}(U(t)-\mathbb{1})\psi \quad , \psi \in D(H)$$

(equivalently: $H\psi = +i \frac{d}{dt} U(t)\psi \big|_{t=0}$).

In other words: if $\psi(0) \in D(H)$, then $\psi(t)$ satisfies Schrödinger's equation.

Firstly: $H$ is symmetric: $\varphi, \psi \in \mathcal{D}(H)$:

$$0 = i \frac{d}{dt} \langle U(t)\varphi, U(t)\psi \rangle \Big|_{t=0} = -\langle H\varphi, \psi \rangle + \langle \varphi, H\psi \rangle .$$

More is true:

<u>Theorem</u>: i) (Stone) The generator $H$ of a strongly continuous one-parameter unitary group is self-adjoint and $U(t) = \exp(-itH)$

ii) For any $H = H^*$, $U(t) = \exp(-itH)$ is a strongly continuous one-parameter unitary group and $H$ is its generator.

Moreover,

$$U(t)\mathcal{D}(H) = \mathcal{D}(H), \quad HU(t) = U(t)H .$$

<u>Proof</u>. ad (i): * $\mathcal{D}(H)$ is dense

* $H$ is essentially self-adjoint:

Let $\varphi$ be s.t. $(A^* + i)\varphi = 0$, $\varphi \in \mathcal{D}(A^*)$.

Then, for each $\psi \in \mathcal{D}(A)$:

$$\frac{d}{dt} \langle U(t)\psi, \varphi \rangle = i \langle H U(t)\psi, \varphi \rangle$$
$$= \langle U(t)\psi, iH^*\varphi \rangle$$
$$= \langle U(t)\psi, \varphi \rangle$$

Hence $\langle U(t)\psi, \varphi \rangle = e^t \langle \psi, \varphi \rangle$

The l.h.s. is uniformly bounded by $\|\psi\|\|\varphi\|$, while the r.h.s is not, so that

$$\langle \psi, \varphi \rangle = 0 , \text{ implying } \varphi = 0$$
since $\mathcal{D}(H)$ is dense.

$$\Rightarrow \ker(H^* \pm i) = \{0\} .$$

* that $U(t) = e^{-itH}$ follows from the fact that they satisfy the same diff.-equation.

ad (ii). * strong continuity follows from the continuity property of the functional calculus and that of the function $t \mapsto e^{it\lambda}$.

* if $\psi \in D(A)$, then

$$\lim_{t\to 0} \| \tfrac{1}{t}(e^{-itH}\psi - \psi) + iH\psi\|^2$$
$$= \lim_{t\to 0} \int \left| \tfrac{1}{t} \left[ (e^{-it\lambda} - 1) \right] + i\lambda \right|^2 d\mu_\psi(\lambda) = 0$$

so that $\lim \frac{1}{t}(U(t)-1)\psi$ exists and $= -iH\psi$

hence $D(A) \subseteq D(\tilde{A})$ where $\tilde{A}$ is the generator of $U(t)$

as pointed out: $\tilde{A}$ is symmetric, hence it is a symmetric extension of $A = A^*$, hence $A = \tilde{A}$.

* the same argument with $U(t')\psi$ instead of $\psi$ yields the last statement □

In particular, if $\psi(0) \in D(H)$ and $\psi(t) := U(t)\psi(0)$, then $\psi(t) \in D(H)$ and $\psi(t)$ is the unique solution of

$$i \frac{d}{dt} \psi(t) = H\psi(t)$$

<u>Summary</u>: * One-to-one correspondence between unitary group (time evolution!) and self-adjoint operators (the Hamiltonian!)

* Self-adjoint operators have a spectral representation $A = \int_{\mathbb{R}} \lambda \, dP_\lambda$, which yields the physical probabilities

- Back to the atomic Hamiltonian: $H = H_0 + V$

where $H_0 = H_0(P)$ and $V = V(X)$.

in particular, they do not commute. Still, we would like to express $\exp(-itH)$ in terms of $\exp(-itH_0)$ (which can be computed explicitly by Fourier transformation) and $\exp(-itV(x))$ (which adds a time-dep. phase to $\psi(x)$).

<u>Theorem</u> (Trotter). Let $A, B$ be self-adjoint on $D(A)$, resp. $D(B)$ and such that $A+B$ is self adjoint on $D(A+B) = D(A) \cap D(B)$.

$$\exp(it(A+B)) = \underset{n\to\infty}{s\text{-}\lim} \left[\exp\left(i\tfrac{t}{n}A\right)\exp\left(i\tfrac{t}{n}B\right)\right]^n \quad t\in\mathbb{R}.$$

<u>Note</u>: * very useful for concrete computations and at the heart of the path integral formulation of Q.M.

* also holds "in imaginary time" if $A, B$ & $A+B$ are semi-bounded below $\rightarrow \exp(-t(A+B))$.
* needs a priori self-adjointness of $A+B$ ...

<u>Proof</u>: Denote $S_n = \exp\left(i\frac{t}{n}(A+B)\right)$

$$T_n = \exp\left(i\tfrac{t}{n}A\right)\exp\left(i\tfrac{t}{n}B\right)$$

Then we have the telescopic sum

$$T_n^n - S_n^n = \sum_{j=0}^{n-1} T_n^{n-1-j}(T_n - S_n)S_n^j$$

Since $S_n^j = \exp\left(i\frac{j}{n}t(A+B)\right)$

$$\|(T_n^n - \exp(it(A+B)))\psi\| \le |t| \max_{|s|\le|t|} F_{t/n}(s)$$

where $F_{t/n}(s) = \left\| \frac{n}{t}\left(T_n - S_n\right)\exp\left(is(A+B)\right)\psi \right\|$

Now if $\psi \in D(A) \cap D(B)$ :

* $\frac{1}{\tau}\left(e^{i\tau A}e^{i\tau B} - \mathbb{1}\right)\psi = \frac{1}{\tau}\left(e^{i\tau A} - \mathbb{1}\right)\psi$

$$+ \frac{1}{\tau} e^{i\tau A}\left(e^{i\tau B} - \mathbb{1}\right)\psi \longrightarrow iA\psi + iB\psi.$$

* $\frac{1}{\tau}\left(e^{i\tau(A+B)} - \mathbb{1}\right)\psi \longrightarrow i(A+B)\psi.$

so that $\lim_{n\to\infty} F_{\frac{t}{n}}(s) = 0$ for any fixed $s$ (and $t$).

The fact that this convergence is uniform in $s$ requires a bit more work (and the use of the uniform boundedness principle) $\square$

- Now: what about establishing self-adjointness of operators of the form $A+B$ ?

  $\leadsto$ series of perturbative results, namely when $B$ is small compared to $A$

<u>Def</u>: $A, B$ densely defined s.t. $\mathcal{D}(A) \subseteq \mathcal{D}(B)$. $B$ is <u>relatively bounded</u> w.r.t. $A$ if $\exists\ a, b \geq 0$ :

$$\|B\psi\| \leq a\|A\psi\| + b\|\psi\| \qquad \psi \in \mathcal{D}(A)$$

infimum over all possible $a$'s (at the cost of increasing $b$, in general) is called the $A$-bound of $B$.

<u>Thm</u> (Kato-Rellich) If $A$ is self-adjoint on $\mathcal{D}(A)$ and $B$ is symmetric with $A$-bounded with $A$-bound strictly less than $1$, then

$A+B$ is self-adjoint on $\mathcal{D}(A+B) = \mathcal{D}(A) \cap \mathcal{D}(B) = \mathcal{D}(A)$.

<u>Proof</u>: Since $A = A^*$, $R_{\pm\lambda} := (A \pm \lambda\mathbb{1})^{-1} \in \mathcal{L}(\mathcal{H})$ $\forall \lambda \in i\mathbb{R}$,

and $\operatorname{Ran}(R_\lambda) = \mathcal{D}(A) \subseteq \mathcal{D}(B)$

Hence we can write

$$(\mathbb{1} + BR_{\pm\lambda})(A \pm \lambda\mathbb{1}) = A + B \pm \lambda\mathbb{1}$$

on $\mathcal{D}(A)$. Since $A = A^*$, $\mathrm{Ran}(A \pm \lambda\mathbb{1}) = \mathcal{H}$ $\forall \lambda \in i\mathbb{R}$

so in order to prove that $\mathrm{Ran}(A+B \pm \lambda\mathbb{1}) = \mathcal{H}$, it suffices to prove that $\mathbb{1} + BR_{\pm\lambda}$ is invertible (because then, in particular, it is onto). This is true if $\|BR_{\pm\lambda}\| < 1$, since then the Neumann series is norm convergent

$$\sum_{n=0}^{\infty} (-BR_{\pm\lambda})^n = (\mathbb{1} + BR_{\pm\lambda})^{-1}.$$

Let $\psi \in \mathcal{D}(A)$, and $\psi = R_{\pm\lambda}\varphi$, i.e. $\varphi = (A \pm \lambda\mathbb{1})\psi$.

$$\|(A \pm \lambda\mathbb{1})\psi\|^2 = \|A\psi\|^2 + |\lambda|^2 \|\psi\|^2$$

since $A = A^*$ and $\bar{\lambda} = -\lambda$. Hence

$$\|\varphi\|^2 = \|AR_{\pm\lambda}\varphi\|^2 + |\lambda|^2 \|R_{\pm\lambda}\varphi\|^2$$

so that

$$\|AR_{\pm\lambda}\varphi\| \le \|\varphi\| \quad \text{and} \quad \|R_{\pm\lambda}\varphi\| \le \frac{1}{|\lambda|}\|\varphi\|$$

Finally, the $A$-bound of $B$ yields, for any $\varphi \in \mathcal{H}$

$$\|BR_{\pm\lambda}\varphi\| \le a\|AR_{\pm\lambda}\varphi\| + b\|R_{\pm\lambda}\varphi\| \le \left(a + \frac{b}{|\lambda|}\right)\|\varphi\|$$

$$< 1\,\|\varphi\| \quad \text{for } |\lambda| \text{ large enough.}$$

$\square$

- Suppose further that $A \geq m\mathbb{1}$. Then $-t < m$, $(A+t)^{-1} \in \mathcal{L}(\mathcal{H})$, so that the argument above yields

$$A + B \geq m - \max\left\{\frac{b}{1-a}, \, a|m| + b\right\}$$

See exercises

# 8. The Fourier transform

- For us: it is a nice tool to transform differential operators such as $-\Delta = P^2$ or $\sqrt{-\Delta + m^2} = \sqrt{P^2 + m^2}$ into multiplication operators.
  All integrals are over $\mathbb{R}^d$.

**Def**: $f \in L^1(\mathbb{R}^d)$. Its Fourier transform is

$$\hat{f}(k) := \int_{\mathbb{R}^d} e^{-ikx} f(x) \frac{dx}{(2\pi)^{d/2}} \qquad (*)$$

Note: Notation $\hat{f} \equiv \mathcal{F}(f)$.

$\mathcal{F} : L^1(\mathbb{R}^d) \to L^\infty(\mathbb{R}^d)$ since $\|\hat{f}\|_\infty \leq (2\pi)^{-d/2} \|f\|_1$

**Proposition**: (i): $f, g \in L^1(\mathbb{R}^d)$

convolution: $(f * g)(x) = \int_{\mathbb{R}^d} f(x-y) g(y)\, dy$

and $\widehat{f * g} = (2\pi)^{d/2} \hat{f} \cdot \hat{g}$

(ii): translation: $\widehat{f(\cdot - y)}(k) = e^{-iky} \hat{f}(k)$

(iii): scaling: $\widehat{f(\cdot/\lambda)}(k) = \lambda^d \hat{f}(\lambda k)$

- Now: we would like to extend $\mathcal{F}$ to $L^2(\mathbb{R}^d)$, where $(*)$ doesnot make sense (apart from on $L^2 \cap L^1$, of course)

**Theorem**: Let $f \in L^1(\mathbb{R}^d) \cap L^2(\mathbb{R}^d)$. Then

(i) $\hat{f} \in L^2(\mathbb{R}^d)$ and

$$\|f\|_2 = \|\hat{f}\|_2 \qquad \text{(Plancherel)}$$

(ii) $\mathcal{F}$ can be extended to bounded map on all of $L^2(\mathbb{R}^d)$

(iii) $f, g \in L^2(\mathbb{R}^d)$: $\langle f, g \rangle_{L^2(\mathbb{R}^d, dx)} = \langle \hat{f}, \hat{g} \rangle_{L^2(\mathbb{R}^d, dk)}$

in particular, $\mathcal{F}$ is an isometry $L^2 \to L^2$.

Proof (i) Since $\hat{f} \in L^\infty(\mathbb{R}^d)$, $\int |\hat{f}(h)|^2 e^{-\varepsilon h^2} dh < \infty \quad \forall \varepsilon > 0$.

Now:

$$\int |\hat{f}(h)|^2 e^{-\varepsilon h^2} dh = (2\pi)^{-d} \int \left( \int \bar{f}(x) e^{ihx} dx \right) \left( \int f(y) e^{-ihy} dy \right) e^{-\varepsilon h^2} dh$$
$$= (2\pi)^{-d} \int \bar{f}(x) f(y) \int e^{ih(x-y)} e^{-\varepsilon h^2} dh dx dy$$

by Fubini.

By an explicit computation:

$$j_\varepsilon(x-y) := \int e^{ih(x-y)} e^{-\varepsilon h^2} dh = (4\varepsilon\pi)^{-d/2} e^{-\frac{(x-y)^2}{4\varepsilon}}$$

so that

$$\int |\hat{f}(h)|^2 e^{-\varepsilon h^2} dh = \langle f, f * j_\varepsilon \rangle_{L^2(\mathbb{R}^d, dx)}$$

We have: $f * j_\varepsilon \xrightarrow{L^2} f \quad (\varepsilon \to 0)$ so that

$$\lim_{\varepsilon \downarrow 0} |\langle f, f * j_\varepsilon \rangle| \leq \lim_{\varepsilon \downarrow 0} \|f\|_2 \|f * j_\varepsilon\|_2 = \|f\|_2^2$$

hence: $\hat{f}(h) e^{-\frac{\varepsilon}{2} h^2}$ is a convergent sequence in $L^2(\mathbb{R}^d, dh)$ and it has a limit since $L^2$ is complete. Since $\hat{f}(h) e^{-\frac{\varepsilon}{2} h^2} \to \hat{f}(h)$ pointwise,

$$\lim_{\varepsilon \downarrow 0} \int |\hat{f}(h)|^2 e^{-\varepsilon h^2} dh = \|\hat{f}(h)\|_2^2$$

(ii) Let $f \in L^2(\mathbb{R}^d)$ and $f_n(x) = f(x) e^{-\frac{x^2}{n^2}} \to f(x)$ in $L^2$

Then, by (i):

$$\|\hat{f}_n - \hat{f}_m\|_2 = \|f_n - f_m\|_2$$

so again $\hat{f}_n$ is Cauchy and has a limit $\hat{f} \in L^2$.

(iii) $\|f\|_2 = \|\hat{f}\|_2$ implies $\langle f, g \rangle = \langle \hat{f}, \hat{g} \rangle$ by polarization $\square$

Note: (ii) gives a formula for $\hat{f}$ whenever $f \in L^2$:

$$\hat{f}(k) = \lim_{L\to\infty} \int e^{-ikx} e^{-\frac{x^2}{L^2}} f(x) \frac{dx}{(2\pi)^{d/2}}$$

in $L^2$-sense!

- Finally: we prove that $\mathcal{F}\ L^2(\mathbb{R}^d) \to L^2(\mathbb{R}^d)$ is in fact unitary.

If $g \in L^2(\mathbb{R}^d)$, let

$$\check{g}(x) := \hat{g}(-x) = \int e^{ikx} g(k) \frac{dk}{(2\pi)^{d/2}}$$

Then: $(\hat{f})^\vee = f$.

i.e. the Fourier transform is invertible, ~~since~~

Note this is what physicists write as

$$\frac{1}{2\pi} \int e^{ikx} \int e^{-iky} f(y)\, dy\, dk = f(x)$$

namely $\frac{1}{2\pi} \int e^{ik(x-y)}\, dk = \delta(x-y)$

- Remark: $\mathcal{F}$ is therefore, in particular, a bounded map $L^2 \to L^2$.

It turns out that more is true (Hausdorff-Young):

$$\|\hat{f}\|_{L^q(\mathbb{R}^d)} \leq C(d)\, \|f\|_{L^p(\mathbb{R}^d)}$$

$$1 \leq p \leq 2, \quad \frac{1}{p} + \frac{1}{q} = 1$$

- Def. Sobolev space $\forall r \geq 0$

$$H^r(\mathbb{R}^d) := \{ f \in L^2(\mathbb{R}^d) : |k|^r \hat{f}(k) \in L^2(\mathbb{R}^d) \}$$

Note: * $H^r(\mathbb{R}^d)$ is a Hilbert space:

$$\langle f, g \rangle_{H^r} := \int \hat{f}(k)\, \hat{g}(k)\, (1+|k|^2)^r\, dk$$

* In particular: if $f \in H^r(\mathbb{R}^d)$: 

$$\|f\|^2_{H^r(\mathbb{R}^d)} = \int |\hat{f}(k)|^2 (1+|k|^2)^r dk$$
$$= \|\hat{f}\|^2_{L^2(\mathbb{R}^d, (1+|k|^2)^r dk)}$$

and $\mathcal{F}$ maps $H^r(\mathbb{R}^d)$ unitarily onto $L^2(\mathbb{R}^d, (1+|k|^2)^r dk)$.

- If $f \in C^r(\mathbb{R}^d) \cap H^r(\mathbb{R}^d)$

$$\widehat{D^r f}(k) = (ik)^r \hat{f}(k)$$

by integration by parts.

In particular:

$$-\widehat{\Delta f}(k) = k^2 \hat{f}(k).$$

and so $H^r(\mathbb{R}^d)$ can also be defined as the space of functions have weak partial derivatives of order $|\alpha| \leq r$, all of which are in $L^2(\mathbb{R}^d)$.

- We can now define the <u>free Hamiltonian $H_0$</u> on $L^2(\mathbb{R}^d)$.

Domain? Formally:

$$(-\Delta\psi)(x) = \left(k^2 \hat{\psi}(k)\right)^\vee (x)$$

The operator $\hat{\psi} \mapsto k^2 \hat{\psi}(k)$ is self-adjoint in the domain $\{\hat{\psi} : \int k^4 |\hat{\psi}(k)|^2 dk < \infty\}$ (see spectral theorem)

But functions $\psi \in L^2(\mathbb{R}^d)$: $\int k^4 |\hat{\psi}(k)|^2 dk < \infty$ are exactly those in $H^2(\mathbb{R}^d)$. In other words:

$$H_0 \psi = -\Delta \psi, \quad \mathcal{D}(H_0) = H^2(\mathbb{R}^d)$$

is self-adjoint,

and unitarily equivalent to

$$((\mathcal{F}\circ H_0\circ \mathcal{F}^{-1})\varphi)(k) = k^2\varphi(k)$$

$$\mathcal{D}(k^2) := \{\varphi\in L^2(\mathbb{R}^d) : k^2\varphi(k)\in L^2(\mathbb{R}^d)\}$$

- The dynamics $\psi(t) = U(t)\psi(0) = \exp(-itH_0)\psi(0)$ can therefore be expressed as

$$e^{-itH_0}\psi(0,x) = \mathcal{F}^{-1}\left(e^{-itk^2}\hat{\psi}(0,k)\right)$$

The $\mathcal{F}^{-1}$ cannot be computed immediately since $e^{-itk^2}\notin L^1$.
Consider $j_\varepsilon(k^2) := e^{-(it+\varepsilon)k^2}$, $\varepsilon>0$, which is a Schwartz function and $j_\varepsilon(k)\to e^{-itk^2}$ pointwise; so by the spectral thm:

$$j_\varepsilon(H_0)\psi \longrightarrow e^{-itH_0}\psi \qquad \forall\psi\in\mathcal{D}(H_0).$$

Now:

$$\mathcal{F}^{-1}\left(j_\varepsilon(k^2)\hat{\psi}(k)\right) = \mathcal{F}^{-1}\left(\widehat{\check{j}_\varepsilon * \psi}(k)\right) = (\check{j}_\varepsilon * \psi)(k).$$

so that (by a Gaussian integration)

$$j_\varepsilon(H_0)\psi(x) = \frac{1}{(4\pi(it+\varepsilon))^{d/2}}\int_{\mathbb{R}^d} e^{-\frac{|x-y|^2}{4(it+\varepsilon)}}\psi(y)\,dy$$

and

$$e^{-itH_0}\psi(x) = \lim_{\varepsilon\downarrow 0}\frac{1}{(4\pi(it+\varepsilon))^{d/2}}\int_{\mathbb{R}^d} e^{-\frac{|x-y|^2}{4(it+\varepsilon)}}\psi(y)\,dy$$

It follows, e.g. (see exercise): if $\psi\in L^1(\mathbb{R}^d)\cap L^2(\mathbb{R}^d)$, then $\psi(t)\in L^\infty(\mathbb{R}^d)$ and

$$\|\psi(t)\|_\infty \leq \frac{1}{|4\pi t|^{d/2}}\|\psi(0)\|_1 \qquad \text{"diffusive spreading".}$$

- let $\psi \in L^2(\mathbb{R}^d)$. Recall: the weak derivatives of $\psi$ are defined as

$$\partial_j \psi [\varphi] := - \int (\partial_j \varphi)(x) \psi(x) \, dx .$$

and we say that $\partial_j \psi \in L^2(\mathbb{R}^d)$ if $\exists\, g_j \in L^2(\mathbb{R}^d)$ s.t.

$$- \int (\partial_j \varphi)(x) \psi(x) \, dx = \int \varphi(x) g_j(x) \, dx$$

↳ <u>Theorem</u>: Let $\psi \in L^2(\mathbb{R}^d)$. Then $\psi \in H^1(\mathbb{R}^d)$ if and only if $D\psi \in L^2(\mathbb{R}^d)$ (understood in the weak sense).

which gives an equivalent characterisation of the Sobolev spaces: all derivatives of order $|\alpha| \leq r$ belong to $L^2(\mathbb{R}^d)$.

We prove here: if $(i\cdot)^\alpha \hat{f} \in L^2$, for $\alpha = (\alpha_1, \dots, \alpha_d)$, $|\alpha| \leq r$, then $f$ has a weak derivative $D_\alpha f \in L^2$. Indeed

- $\langle \hat{\varphi}, (ik)^\alpha \hat{f} \rangle = (-1)^{|\alpha|} \langle (ik)^\alpha \hat{\varphi}, \hat{f} \rangle$

$$= (-1)^{|\alpha|} \langle \widehat{D_\alpha \varphi}, \hat{f} \rangle = (-1)^{|\alpha|} \int \overline{D_\alpha \varphi} \, f$$

- $(i\cdot)^\alpha \hat{f} \in L^2 \Rightarrow \mathcal{F}^{-1}\left( (i\cdot)^\alpha \hat{f} \right) \in L^2$, call that $g_\alpha$.

$$\langle \hat{\varphi}, (i\cdot)^\alpha \hat{f} \rangle = \langle \varphi, g_\alpha \rangle = \int \overline{\varphi} \, g_\alpha .$$

i.e. $\forall \overline{\varphi} \in C_c^\infty$: $(-1)^{|\alpha|} \int D_\alpha \overline{\varphi}(x) f(x) \, dx = \int \overline{\varphi}(x) g_\alpha(x) \, dx$

- An often useful fact is the density of $C_c^\infty(\mathbb{R}^d)$ in $H^r$ in the $H^r$ norm:

<u>Theorem</u>: $H^r(\mathbb{R}^d) = \overline{C_c^\infty(\mathbb{R}^d)}^{\|\cdot\|_{H^r(\mathbb{R}^d)}}$

i.e. any $f \in H^1$ can be approximated by $f_n \in C_c^\infty$, s.t.

$$f_n \to f \quad \text{and} \quad Df_n \to Df \quad \text{in } L^2$$

# 9. Atomic Hamiltonians

- We have everything at hand to prove self-adjointness of atomic Hamiltonians with Coulomb interaction in $\mathbb{R}^3$.
- <u>Lemma</u>: Let $\psi \in H^2(\mathbb{R}^3)$. Then for any $a>0$, $\exists\, b$, independent of $\psi$, s.t.

$$\|\psi\|_\infty \leq a\|-\Delta\psi\|_2 + b\|\psi\|_2$$

in other words: functions in the domain of $-\Delta$ are bounded.

<u>Proof</u>: If $\psi \in H^2(\mathbb{R}^3)$, then $(1+k^2)\hat{\psi}(\cdot) \in L^2(\mathbb{R}^3)$. Since $(1+k^2)^{-1} \in L^2(\mathbb{R}^3)$, Cauchy-Schwarz yields that $\hat{\psi} \in L^1(\mathbb{R}^3)$ and

$$\begin{aligned}\|\hat{\psi}\|_1 &= \int (1+k^2)|\hat{\psi}(k)|\,(1+k^2)^{-1}\,dk \\ &\leq c\|(1+k^2)\hat{\psi}\|_2, \qquad c = \|(1+k^2)^{-1}\|_2 \text{ indep of } \psi. \\ &\leq c\left(\|\hat{\psi}\|_2 + \|k^2\hat{\psi}\|_2\right).\end{aligned}$$

For $\lambda>0$, the scaling $\hat{\psi}_\lambda(k) := \lambda^3\hat{\psi}(\lambda k)$ satisfies

- $\|\hat{\psi}_\lambda\|_1 = \|\hat{\psi}\|_1$
- $\|\hat{\psi}_\lambda\|_2 = \lambda^{3/2}\|\hat{\psi}\|_2$
- $\|k^2\hat{\psi}_\lambda\|_2 = \lambda^{-1/2}\|k^2\hat{\psi}\|_2$, so that

$$\|\hat{\psi}\|_1 \leq c\lambda^{3/2}\underbrace{\|\hat{\psi}\|_2}_{=\|\psi\|_2} + c\lambda^{-1/2}\underbrace{\|k^2\hat{\psi}\|_2}_{=\|-\Delta\psi\|_2} \quad \text{for any } \lambda>0.$$

Finally,

$$\|\psi\|_\infty = \sup_x\left|\int e^{ikx}\hat{\psi}(k)\frac{dk}{(2\pi)^{3/2}}\right| \leq \frac{\|\hat{\psi}\|_1}{(2\pi)^{3/2}}$$ concludes the proof $\square$

- Theorem: Let $V = V_1 + V_2$, where $V_1 \in L^2(\mathbb{R}^3_x)$
$V_2 \in L^\infty(\mathbb{R}^3_x)$

Then $H = -\Delta + V$ is self-adjoint on $\mathcal{D}(H) = H^2(\mathbb{R}^3_x)$

Proof: Since $V$ is real-valued, the operator of multiplication by $V$ is self-adjoint on

$$\mathcal{D}(V) := \{\psi : \psi \in L^2(\mathbb{R}^3_x),\ V(x)\psi(x) \in L^2(\mathbb{R}^3_x)\}.$$

Moreover, if $\psi \in \mathcal{D}(-\Delta)$, then $\psi \in L^\infty(\mathbb{R}^3_x) \cap L^2(\mathbb{R}^3_x)$.

$$\|V\psi\|_2 \leq \|V_1\psi\|_2 + \|V_2\psi\|_2 \leq \|V_1\|_2 \|\psi\|_\infty + \|V_2\|_\infty \|\psi\|_2$$

and $\mathcal{D}(V) \supset \mathcal{D}(-\Delta)$. Furthermore, by the lemma:

$$\|V\psi\|_2 \leq a\|V_1\|_2 \|-\Delta\psi\|_2 + (b + \|V_2\|_\infty)\|\psi\|_2$$

for any $a > 0$.

Hence $V$ is $-\Delta$-bounded with $-\Delta$-bound $a = 0$ and the theorem follows from Kato-Rellich. $\square$

- The Hamiltonian of the hydrogenic atom, with Coulomb potential

$$V(x) = -\frac{\alpha}{|x|}$$

is self-adjoint on $H^2(\mathbb{R}^3)$. Indeed:

$$V = V_1 + V_2 := \underbrace{\chi_{\{|x| \leq 1\}}(x) V(x)}_{\text{local square integrable singularity}} + \underbrace{(1 - \chi_{\{|x| \leq 1\}}(x))}_{\text{bounded potential at infinity}} (V(x))$$

- Corollary (see exercises).

$$H_N = -\sum_{i=1}^N \Delta_i - \sum_{i=1}^N \sum_{j=1}^M \frac{\alpha Z_j}{|x_i - R_j|} + \sum_{1 \leq i < j \leq N} \frac{\alpha}{|x_i - x_j|}$$ is s.-a. on $H^2$

- Remarks: * true for any $Z_j$'s and any value of $\alpha$.
  * there are other classes of potentials for which $-\Delta + V$ can be realized as a self-adjoint operator, e.g.
    - $V \in L^\infty_{loc}$ and $V(x) \geq C$ (harmonic oscillator)
    - "$V = \delta$"
    - $V \in L^2_{loc}$ and $V \geq 0$.
    - ...
  * Since $-\Delta \geq 0$, Kato-Rellich also yields that the atomic / molecular Hamiltonians are bounded below ⇝ stability of the first kind.

# 10. Many-body Q.M. & stability of the second kind.

- State of $N$ spinless particles

$$\Psi : \mathbb{R}^{3N} \to \mathbb{C}, \quad \int_{\mathbb{R}^{3N}} |\Psi(x_1, \dots, x_N)|^2 dx = 1$$

i.e. Hilbert space:

$$L^2(\mathbb{R}^{3N}) \cong \bigotimes_{i=1}^{N} L^2(\mathbb{R}^3).$$

Note: one function of $N$ variables and not $N$ functions of one variable ⇝ "entanglement".

Interpretation: $|\Psi(x_1, \dots x_N)|^2$ is the proba density to find part. 1 at $x_1$, …, part. $N$ at $x_N$.

↳ marginals: (P to find $i^{th}$ particle at $x$)

$$\rho_\Psi^i(x) = \int_{\mathbb{R}^{3(N-1)}} |\Psi(x_1 \dots x_{i-1}, x, x_{i+1} \dots x_N)|^2 dx_1 \dots \cancel{dx_i} \dots dx_N.$$

and $$\rho_\Psi(x) = \sum_{i=1}^{N} \rho_\Psi^i(x)$$ "one-particle density"

with $$\int_{\mathbb{R}^3} \rho_\Psi(x)\, dx = N$$

- Kinetic energy:

$$T(\Psi) = \sum_{i=1}^{N} T^i(\Psi) = \sum_{i=1}^{N} \frac{1}{2} \int_{\mathbb{R}^{3N}} |\nabla_i \Psi|^2$$

Potential energy

$$V(\Psi) = \int_{\mathbb{R}^{3N}} V(x_1 \dots x_N)\, |\Psi(x_1, \dots x_N)|^2$$

- Bosons & fermions.

  * Bosons: $\Psi$ of $N$ identical particles is totally symmetric under exchange of particles:

$$\Psi(x_1 \ldots, x_i \ldots x_j \ldots x_N) = \Psi(x_1 \ldots, x_j \ldots, x_i \ldots x_N)$$

  * Fermions: — " — is totally antisymmetric

$$\Psi(x_1 \ldots, x_i, \ldots x_j \ldots x_N) = -\Psi(x_1 \ldots x_j \ldots x_i, \ldots x_N).$$

electrons, protons, neutrons are all fermions

example of a fermionic wave function: the Slater determinant: Let $f_1, \ldots, f_N \in L^2(\mathbb{R}^3)$ be s.t. $\langle f_i, f_j \rangle = 0$ if $i \neq j$ and $\|f_i\| = 1$; the $N$-part. wavefunction

$$\Psi(x_1 \ldots, x_N) = \frac{1}{\sqrt{N!}} \det \left( (f_i(x_j))_{i,j=1}^{N} \right) \qquad (*)$$

is antisymmetric and normalized.

Note: if $\{f_i\}_i$ is an ONB of $L^2(\mathbb{R}^3)$, then all Slaters $(*)$ for a basis of the antisymmetric wavefunctions, denoted

$$\Lambda^N L^2(\mathbb{R}^3)$$

"antisymmetric tensor product" space.

- $H$ of an atom with $N$ electrons therefore acts on $\Lambda^N L^2(\mathbb{R}^3)$

A system with $N$ electrons and $\Pi$ nuclei satisfies stability of the second kind if $\exists$ $C$, independent of $N, \Pi$, s.t.

$$E(\Psi) \geq -C(N + \Pi) \qquad \forall \Psi$$

How does that work? Three ingredients:

i) Uncertainty principles: Potential energy bounded by kinetic energy

ii) Electrostatic screening

iii) Pauli-principle.

(i) already seen: stability of the first kind.

(ii) effective cancellations of negative and positive charge in the potential felt "far away".

$\rightsquigarrow$ Baxter's inequality

(iii) the electronic wave function is antisymmetric

$\rightsquigarrow$ Lieb-Thirring's inequality.

Heuristics: * N electrons on a single nucleus

$$H = \sum_{i=1}^{N} \left( -\Delta_i - \frac{Z}{|x_i|} \right)$$

Ground state $\psi_0(x) = Ce^{-\frac{Z|x|}{2}}$ for one electron with $E(\psi_0) = -Z^2/4$. Without interaction,

$\psi(x_1, \dots, x_N) = \psi_0(x_1) \dots \psi_0(x_N)$

is a symmetric state with energy $-\frac{Z^2}{4} N$

* all nuclei on top of each other:

$$E(\psi) \geq -\frac{1}{4}(Z_1 + \dots + Z_M)^2 N \geq -\frac{1}{4} Z^2 M^2 N$$

with $Z = \max_k Z_k$. i.e. $E(\psi) \geq -C(M+N)^3$

by the geometric-arithmetic mean inequality:

$$(a_1 \dots a_k)^{1/k} \leq \frac{1}{k}(a_1 + \dots + a_k) \quad (\text{with } k=3)$$

* taking into account electrostatic (repulsion among nuclei in particular): $-C(M+N)^{5/3}$

i.e. a $\frac{4}{3}$ gain.

* Pauli principle: The lowest energy antisymmetric state of $-\Delta - \frac{Z}{|X|}$ is obtained by filling the tub from below. Recall: $-\Delta - \frac{Z}{|X|}$ has eigenvalues $\{E_j\}_{j\in\mathbb{N}}$

$$E_j = -C\frac{Z^2}{j^2}$$

with degeneracy $j^2$.

For $\Psi = \psi_1 \wedge \dots \wedge \psi_N$, we have

$$\langle \Psi, H\Psi\rangle = E_1 + \dots + E_N.$$

For $N$ large, the "orbitals" are filled up to the $k$th one, with

$$N = \sum_{k=1}^{k} k^2 \sim k^3$$

for a total energy

$$\sum_{j=1}^{k} \underbrace{j^2}_{\text{degeneracy}} \cdot \underbrace{\frac{1}{j^2}}_{E_j} = \sum_{j=1}^{N^{1/3}} 1 \sim N^{1/3}$$

⇝ all in all: Pauli principle alone yields

$$E(N) \geq -CZ^2M^2N^{1/3} \geq -CZ^2\left(6\Pi^{1/3} + N^{1/3}\right)^7$$

$$\geq -CZ^2(\Pi + N)^{7/3}$$

hence a $\frac{2}{3}$ gain.

⇝ electrostatics + Pauli give a $\frac{4}{3} + \frac{2}{3}$ gain i.e.

$$3 - \frac{6}{3} = 1$$

☺

## 11. Recap: stability of the hydrogenic atom

- We have already seen that the inf

$$E_0 := \inf \left\{ \frac{1}{2} \int |\nabla\psi|^2 + \int V\psi \;:\; \int |\psi|^2 = 1 \right\}$$

is $> -\infty$ for $V \in L^{3/2} + L^\infty$, using Sobolev's inequality. Here, we reconsider this for the special case of the Coulomb potential

$$V(x) = -\frac{Z}{|x|},$$

using the following Lemma:

Let $\psi \in H^1(\mathbb{R}^3)$. Then

$$\int \frac{|\psi(x)|^2}{|x|} dx \leq \|\nabla\psi\|_2 \|\psi\|_2$$

with equality iff $\psi_0(x) = Ce^{-c|x|}$, $c > 0$.

Proof: $\psi \in C_0^\infty(\mathbb{R}^3)$ and conclude by density.

We have $\frac{1}{|x|} = \frac{1}{2} \sum_{j=1}^{3} [\partial_j, \frac{x_j}{|x|}]$, so that

$$2\langle \psi, \frac{1}{|x|}\psi \rangle = \sum_{j=1}^{3} \left[ \langle \psi, \partial_j \frac{x_j}{|x|}\psi \rangle - \langle \psi, \frac{x_j}{|x|}\partial_j \psi \rangle \right]$$

$$\overset{\text{i.b.p.}}{=} -\sum_{j=1}^{3} \left[ \langle \partial_j \psi, \frac{x_j}{|x|}\psi \rangle + \langle \frac{x_j}{|x|}\psi, \partial_j \psi \rangle \right]$$

$$\leq 2 \sum_{j=1}^{3} \underbrace{\left| \langle \partial_j \psi, \frac{x_j}{|x|}\psi \rangle \right|}$$

$$\leq \|\partial_j \psi\|_2 \|\frac{x_j}{|x|}\psi\|_2 \quad \text{(C.S.)}$$

$$\leq 2 \|\nabla\psi\|_2 \|\psi\|_2$$

On $\mathbb{R}^3 \setminus \{0\}$ : $\frac{2}{|x|} = \sum_{j=1}^{3} \left[ \partial_j , \frac{x_j}{|x|} \right]$ $(*)$

Note: $\langle \psi, \frac{1}{|x|} \psi \rangle = \left( \int_{B_\varepsilon(0)} + \int_{B_\varepsilon(0)^c} \right) \left( \frac{|\psi(x)|^2}{|x|} \right) dx$

Let $\psi \in C_0^\infty(\mathbb{R}^3)$.

(i) Since $\psi$ is bounded:

$$\int_{B_\varepsilon(0)} \frac{|\psi(x)|^2}{|x|} dx \leq C \sup |\psi(x)|^2 \cdot \int_0^\varepsilon r\, dr \longrightarrow 0 \quad (\varepsilon \downarrow 0).$$

(ii) By $(*)$ :

$$\langle \psi, \frac{2}{|x|} \psi \rangle = \int_{B_\varepsilon(0)^c} \Big[ \Big( \operatorname{div} \big( \overline{\psi(x)} \tfrac{x}{|x|} \psi(x) \big) - \overline{D\psi(x)} \cdot \tfrac{x}{|x|} \psi(x) \Big) - \overline{\psi(x)} \tfrac{x}{|x|} \cdot D\psi(x) \Big] dx$$

By the divergence theorem: (and the boundedness of $\psi$).

$$\left| \int_{B_\varepsilon(0)^c} \operatorname{div} \left( \overline{\psi} \frac{x}{|x|} \psi \right) \right| = \left| \int_{\partial B_\varepsilon(0)} |\psi(x)|^2 d\sigma \right| \longrightarrow 0 \; (\varepsilon \downarrow 0)$$

(iii) Hence, taking the $\varepsilon \downarrow 0$ limit:

$$\begin{aligned} 2 \langle \psi, \tfrac{1}{|x|} \psi \rangle &= - \sum_{j=1}^{3} \left[ \langle \partial_j \psi, \tfrac{x_j}{|x|} \psi \rangle + \langle \tfrac{x_j}{|x|} \psi, \partial_j \psi \rangle \right] \\ &\leq 2 \sum_{j=1} \left| \langle \partial_j \psi, \tfrac{x_j}{|x|} \psi \rangle \right| \\ &\leq 2 \sum_{j=1}^{3} \| \partial_j \psi \|_2 \, \| \tfrac{x_j}{|x|} \psi \|_2 \qquad (\text{C-S in } L^2) \\ &\leq 2 \| D\psi \|_2 \, \| \psi \|_2 \qquad (\text{C.-S. in } \mathbb{C}^3). \end{aligned}$$

where we used C-S for the sum $\square$

- <u>Proposition</u>. Let $Z > 0$ and

$$E_0 := \inf \left\{ \int |\nabla\psi|^2 - \int \frac{Z}{|x|}|\psi|^2 \ : \ \psi \in H^1(\mathbb{R}^3),\ \|\psi\|_2 = 1 \right\}.$$

Then $E_0$ is finite and

$$E_0 = -\frac{Z^2}{4}$$

and $E_0 = E(\psi_0)$ where

$$\psi_0 = \frac{Z^{3/2}}{\sqrt{8\pi}} e^{-\frac{Z|x|}{2}}$$

<u>Proof</u>: By the Lemma:

$$\int |\nabla\psi|^2 - Z\int \frac{|\psi|^2}{|x|} \geq \|\nabla\psi\|_2^2 - Z\|\nabla\psi\|_2$$

$$= \left( \|\nabla\psi\|_2 - \frac{Z}{2} \right)^2 - \frac{Z^2}{4}$$

$$\geq -\frac{Z^2}{4}.$$

with "=" in the first iff $\psi_0 = C e^{-c|x|}$ (by the Lemma)
and in the second iff $\|\nabla\psi\|_2 = \frac{Z}{2}$ i.e. $c = \frac{Z}{2}$
The constant arises from $\|\psi_0\|_2 = 1$ $\square$

- <u>Theorem</u> (stability of the first kind for atoms & molecules).
Let $Z_1, \dots, Z_M > 0$ and

$$E(\psi) := \sum_{j=1}^{N} \int |\nabla_j\psi|^2 + \int V_c(x, R)|\psi|^2$$

for $\psi \in H^1(\mathbb{R}^{3N})$.

Then: $E_0(R) := \inf \{ E(\Psi) : \Psi \in H^1(\mathbb{R}^{3N}),\ \|\Psi\|_2 = 1 \}$

is finite for any $R \in \mathbb{R}^{3M}$ and

$$E_0 = \inf_R E_0(R) > -\infty .$$

Note: The nuclei at $R_1, \dots, R_M$ are considered static here. Including their kinetic energy would only help as these are non-negative terms.

Proof: We neglect the positive (nucleus - nucleus / electron - electron) interaction, looking for a minimizer of

$$\sum_{j=1}^{N} \int_{\mathbb{R}^{3N}} |\nabla_j \Psi(x)|^2 - \sum_{i=1}^{M} \sum_{j=1}^{N} \int_{\mathbb{R}^{3N}} \frac{Z_i |\Psi(x)|^2}{|x_j - R_i|} \qquad (1)$$

$Z = \max_i Z_i$. We need to prove that for any fixed $i, j$:

$$\underbrace{\frac{1}{M} \int |\nabla_j \Psi|^2 - \int \frac{Z |\Psi|^2}{|x_j - R_i|}}_{=: \frac{1}{M} \int dx_1 \dots \cancel{dx_j} \dots dx_N \, H_j(x_1 \dots \cancel{x_j} \dots x_N)} \geq - C \|\Psi\|_2^2 \qquad (2)$$

where $H_j = \int dx_j \underbrace{\left( |\nabla \Psi|^2 - \frac{MZ}{|x_j - R_i|} |\Psi|^2 \right)}$

see as a function of one variable $x_j$, with parameters $x_1 \dots \cancel{x_j} \dots x_N$

$$g_j : x_j \to \Psi(x_1 \dots x_j \dots x_N)$$

$$(\dots) = |\nabla g_j(x_j)|^2 - \frac{MZ}{|x_j - R_i|} |g_j(x_j)|^2$$

By the theorem:

$$H_j \geq - \frac{(MZ)^2}{4} \|g\|_2^2$$

Note that

$$\int \|g_j\|_2^2 \, dx_1 \cdots \cancel{dx_j} \cdots dx_N = \int \left( \int dx_j \, |\psi|^2 \right) dx_1 \cdots \cancel{dx_j} \cdots dx_N = 1$$

hence, (2) holds with $C = \frac{1}{4} M Z^2$ and (1) is bounded below by

$$-\frac{1}{4} M^2 Z^2 N$$

uniformly in $R_1 \dots R_M$ $\square$

We recovered the cubic dependence : $M^2 N \leq \frac{8}{27}(M+N)^3$.

Indeed: no electrostatic repulsion was taken into account, and the minimizer is over all of $L^2(\mathbb{R}^{3N})$, not its antisymmetric subspace.

In fact: it can be shown (quite generally) that absolute minimizer must belong to the symmetric subspace, which is, here, unphysical.

# 12 Stability of the second kind

$$H = \sum_{j=1}^{N} -\frac{1}{2}\Delta_j + \alpha V_c(x, R)$$

$$V_c(x,R) = \sum_{1\le i<j\le N} \frac{1}{|x_i - x_j|} - \sum_{i=1}^{N}\sum_{j=1}^{M} \frac{z_j}{|x_i - R_j|} + \sum_{1\le k<l\le M} \frac{z_k z_l}{|R_k - R_l|}$$

with $z_j > 0$

Note: magnetic fields can be introduced as well, through "minimal coupling"

$$\Delta_j \rightsquigarrow (-i\nabla_j + \sqrt{\alpha}A(x_j))^2$$

see later (diamagnetic inequality).

Theorem: Let $Z = \max_j z_j$. For any $\Psi \in \Lambda^N H^1(\mathbb{R}^3)$, $\|\Psi\| = 1$,

$$\langle \Psi, H\Psi \rangle \geq -C((2Z+1)\alpha)^2(M+N)$$

for a $C > 0$

The proof has two important technical ingredients: the Lieb-Thirring inequality and Baxter's electrostatic inequality, which we prove later. Let $V = V_+ - V_-$ be a real-valued function on $\mathbb{R}^d$.

Theorem (LT inequality) Let $\gamma \geq 0$ and $V_- \in L^{\gamma + \frac{d}{2}}(\mathbb{R}^d)$.
Let $E_0 \le E_1 \le \dots$ be the non-positive eigenvalues of $-\Delta + V$ in $L^2(\mathbb{R}^d)$. Then, $\exists\, L_{\gamma,d} > 0$ s.t.

$$\sum_{j\geq 0} |E_j|^\gamma \le L_{\gamma,d} \int_{\mathbb{R}^d} V_-(x)^{\gamma+\frac{d}{2}}\,dx$$

with the condition:

$\gamma \geq \frac{1}{2}$ if $d=1$

$\gamma > 0$ if $d=2$

$\gamma \geq 0$ if $d \geq 3$

- Remarks:
  - this is a "one-body" estimate
  - explicit upper bounds are known for $L_{\gamma,d}$, for any $\gamma, d$. The sharp values not in all cases. It is conjectured that
$$L_{1,3} = \frac{1}{(2\pi)^3} \int_{|p| \leq 1} (1-p^2)\,dp = \frac{1}{(4\pi)^{3/2}} \frac{\Gamma(2)}{\Gamma(\frac{7}{2})} \sim 0.0068$$
  - the case $\gamma=0$ corresponds to the number of eigenvalues ("CLR bound")
  - Again, magnetic fields can be included.

- Theorem (Baxter's inequality) Let $V_c(x,R)$ be as above with $Z_j = Z$ $\forall j=1,\dots,M$. Then:
$$V_c(x,R) \geq -(2Z+1)\sum_{i=1}^{N} \frac{1}{D(x_i)} + \frac{Z^2}{8}\sum_{j=1}^{M} \frac{1}{D_j}$$
where:
  - $D(x_i)$ denotes the distance to the nearest $R$
$$D(x_i) = \min \{ |x_i - R_j| : j=1,\dots,M \}.$$
  - $D_j$ is half the nearest neighbour distance:
$$D_j := \frac{1}{2} \min_{i \neq j} |R_i - R_j|$$

- Remarks
  - For a lower bound, the electrostatic interaction effectively cancels out, except for the interaction with the nearest nucleus

* There are order $(N+M)^2$ terms in $V_c$, while the lower bound has only $N$ ⇝ non-interacting!

- Finally, we shall use the antisymmetry as follows:

<u>Lemma</u>: Let $H_0 = \sum_{i=1}^{N} h_i$ acting on $\Lambda^N L^2(\mathbb{R}^d)$, where $h_i$ acts only on the $i^{th}$ factor and

$$h_i = -\Delta + V, \quad V \in L^{d/2} + L^\infty$$

Let $E_0(N) = \inf \langle \Psi, H\Psi \rangle$. Then

$$\inf_N E_0(N) = \sum_{i:\, E_i < 0} E_i$$

In other words, the ground state energy is lower bounded by "filling in" all negative energy levels of the one-body Hamiltonian $h_i$ for such <u>non-interacting</u> electrons

- <u>Proof of stability</u>

By the electrostatic inequality:

$$H \geq \sum_{j=1}^{N} \left( -\tfrac{1}{2}\Delta_j - (2Z+1)\alpha \frac{1}{D(x_j)} \right) = \sum_{j=1}^{N} h_j$$

where we dropped the positive term for a lower bound.
We would like to apply the lemma and LT inequalities, but $D(x)^{-1} \notin L^{5/2}$. However, for any $b>0$:

$$-D(x)^{-1} = -\left( D(x)^{-1} - b \right) - b$$

and $\left( D(x)^{-1} - b \right)_+ \in L^{5/2}$ (since the local Coulomb singularity is so: $|x|^{-5/2}$ is integrable in $d=3$).

$$H \geq \sum_{j=1}^{N} \left( -\tfrac{1}{2}\Delta_j - (2Z+1)\alpha \left( D(x_j)^{-1} - b \right) \right) - bN(2Z+1)\alpha .$$

Applying the lemma and LT-inequality:

$$\langle \Psi, H\Psi \rangle \geq - L_{1,3}\, 2^{3/2} \left[(2Z+1)\alpha\right]^{5/2} \int \left( D(x)^{-1} - b \right)_+^{5/2} dx$$

(rescaling $x_i \to y_i = 2^{1/2} x_i$ to account for $-\frac{1}{2}\Delta$)

Now

$$\left( D(x)^{-1} - b \right)_+^{5/2} = \max_{1 \le k \le M} \left( |x - R_k|^{-1} - b \right)_+^{5/2} \le \sum_{k=1}^{M} \left( |x - R_k|^{-1} - b \right)_+^{5/2} ,$$

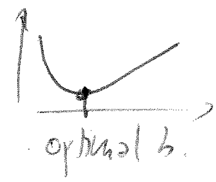
so that

$$\int_{\mathbb{R}^3} \left( D(x)^{-1} - b \right)_+^{5/2} \le M \int_{\mathbb{R}^3} \left( |x|^{-1} - b \right)_+^{5/2} dx = M \int_{|x| \le \frac{1}{b}} \left( |x|^{-1} - b \right)^{5/2} dx$$

$$\le \frac{5\pi^2}{4} M b^{-1/2}$$

i.e.

$$\langle \Psi, H\Psi \rangle \geq - \left[ C_1 \left[(2Z+1)\alpha\right]^{5/2} M b^{-1/2} + \left[(2Z+1)\alpha\right] N b \right]$$

as a function of $b$: 


the optimal $b$ reads $C_2 (2Z+1)\alpha \left(\frac{M}{N}\right)^{2/3}$, yielding:

$$\langle \Psi, H\Psi \rangle \geq - C \left[(2Z+1)\alpha\right]^2 M^{\frac{2}{3}} N^{\frac{1}{3}}$$

and the theorem follows from $M^{\frac{2}{3}} N^{\frac{1}{3}} \le \frac{2}{3}(M+N)$ □

## B. Lieb-Thirring inequalities

- We now prove the LT-inequalities on the negative eigenvalues of $-\Delta+V$ on $L^2(\mathbb{R}^3)$.

Recall: $V=V_+-V_-$ ; $V_+(x):=\max\{V(x),0\}$, $V_-(x)=-\min\{V(x),0\}$.

so that $\langle\psi,V\psi\rangle=\int V_+|\psi|^2-\int V_-|\psi|^2\geq-\langle\psi,V_-\psi\rangle$

i.e. $-\Delta+V\geq-\Delta-V_-$

so for a lower bound, we may assume that $V$ is negative.

- Let $-e$, $e>0$, be a negative eigenvalue of $-\Delta-V_-$ :

$$(-\Delta+e)\psi=V_-\psi \qquad , \quad \psi\in H^1,\ \|\psi\|_{L^2}=1$$

(this should be understood as an equation between two vectors in $H^{-1}(\mathbb{R}^3)$ )

Define $\varphi(x):=\sqrt{V_-(x)}\,\psi(x)$, and we claim

$$\varphi\in L^2(\mathbb{R}^3) \qquad (\text{Claim } 1)$$

Since $-\Delta\geq0$, $-\Delta+e$ is invertible so that

$$(-\Delta+e)\psi=\sqrt{V_-}\,\varphi \implies \psi=(-\Delta+e)^{-1}\sqrt{V_-}\,\varphi$$

(again $\varphi\in L^2\Rightarrow\sqrt{V_-}\,\varphi\in H^{-1}$ and $(-\Delta+e)^{-1}$ extends to a bounded map from $H^{-1}$ to $H^1$, which is consistent with $\psi\in H^1$)

In other words:

$$\varphi=K_e\varphi \quad , \quad K_e=\sqrt{V_-}(-\Delta+e)^{-1}\sqrt{V_-}$$

the Birman-Schwinger operator.

(as an equation on $L^2$ now)

Note: $\varphi\neq0$ since otherwise $-\Delta\psi=-e\psi$ which is a contradiction with $-\Delta\geq0$.

<u>Hence</u>: if $-e$ is an eigenvalue of $-\Delta-V_-$, then $1$ is an

eigenvalue of $K_e$.

Furthermore: Reciprocally, for any $\varphi \in L^2$ s.t. $\varphi = K_e \varphi$, there is a $\psi \in H^1$ : $(-\Delta - V_-)\psi = -e\psi$ (Claim 2)

i.e. one-to-one correspondence $\varphi \leftrightarrow \psi$.

Finally: Birman-Schwinger principle:

$$N_e = B_e \qquad \text{(Claim 3)}$$

$N_e$: # eigenvalues of $-\Delta + V$ that are $\leq -e$

$B_e$: # eigenvalues of $K_e$ that are $\geq 1$

* Proof of Claim 1: if $\psi \in H^1$, then $\Pi_{\sqrt{V_-}} \psi \in L^2$

i.e. $\Pi_{\sqrt{V_-}}$ is a bounded map $H^1 \to L^2$.

$$\int |\sqrt{V_-(x)}\,\psi(x)|^2 dx = \int V_- |\psi|^2 = \int (V_1 + V_2)|\psi|^2, \quad V_1 \in L^{3/2}, V_2 \in L^\infty$$

$$\underset{\substack{\text{Hölder on}\\ V_1}}{\leq} \|V_1\|_{3/2} \underbrace{\||\psi|^2\|_3}_{= \|\psi\|_6^2 \leq C\|\nabla\psi\|_2^2 \text{ by Sobolev's ineq.}} + \|V_2\|_\infty \|\psi\|_2^2$$

$< \infty$ by the assumptions.

i.e. if $\varphi = \Pi_{\sqrt{V_-}}\psi$ : $\|\varphi\|_2^2 \leq C(V)\|\psi\|_{H^1}^2$ $\square$

* Claim B: $K_e$ is a bounded, non-negative self-adjoint operator on $L^2$

Proof: Let $B_e := \sqrt{V_-}(-\Delta + e)^{-1/2}$. First of all, $\xi \in L^2$

$$\|(-\Delta+e)^{-1/2}\xi\|_{H^1}^2 = \int (1+|k|^2)\left|\frac{1}{\sqrt{|k|^2+e}}\hat{\xi}(k)\right|^2 \leq C\|\xi\|_2^2$$

since $\dfrac{1+|k|^2}{e+|k|^2} \leq \max\{1, \frac{1}{e}\}$,

so that $(-\Delta+e)^{-1/2}$ is bounded from $L^2$ to $H^1$. But by Claim 1, $\Pi_{\sqrt{V_-}}$ is bounded from $H^1$ to $L^2$, whence $B_e$ is a bounded operator from $L^2$ to $L^2$.

Claim B follows from $K_e = B_e B_e^*$ $\square$

* Proof of Claim 2: Let $\varphi \in L^2$ be an eigenfunction of $K_e$ for the eigenvalue 1. We show:

$$\psi := (-\Delta+e)^{-1}\sqrt{V_-}\,\varphi \in H^1 \quad \text{and} \quad (-\Delta - V_-)\psi = -e\psi.$$

Indeed: $\psi = (-\Delta+e)^{-1/2} B_e^* \varphi$

Since $B_e^*\varphi \in L^2$, the first step of the proof of Claim B yields that $(-\Delta+e)^{-1/2} B_e^*\varphi \in H^1$

Finally:

$$(-\Delta+e)\psi = \sqrt{V_-}\,\varphi \overset{\text{assumption}}{=} \sqrt{V_-}\,K_e\varphi = V_-(-\Delta+e)^{-1}\sqrt{V_-}\,\varphi$$
$$= V_-\psi \quad \text{, by definition of } \psi. \qquad \square$$

* In fact, $K_e$ is even a compact operator (because it is given by an integral kernel which is in $L^2(\mathbb{R}^3\times\mathbb{R}^3)$)

Hence its eigenvalues can be enumerated in decreasing order:

$$\lambda_0(e) \geq \lambda_1(e) \geq \lambda_2(e) \geq \dots \geq \lambda_n(e) \geq \dots \geq 0.$$

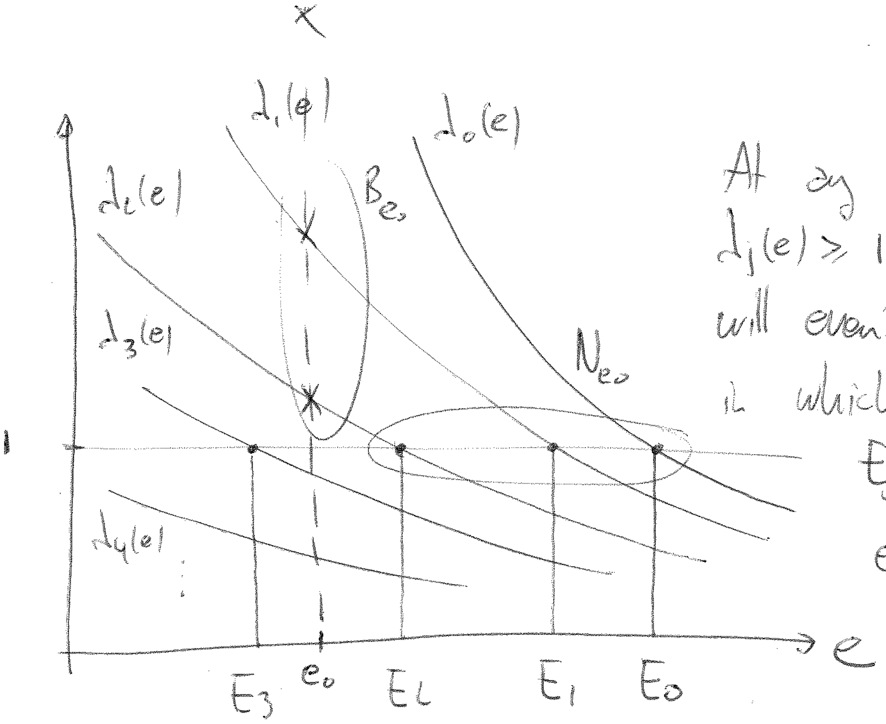
(they may accumulate at 0).

By Fourier transform again

$$(-\Delta+e')^{-1} \leq (-\Delta+e)^{-1} \quad \text{if} \quad e < e'$$

so that $K_e$ is "monotone decreasing" in $e$ and in particular, its eigenvalues $\lambda_j(e)$ are monotone decreasing functions of $e$ (and they are continuous by perturbation theory)

Since $K_e \to 0$ (by explicitly considering its kernel again), the following picture proves Claim 3:




At any fixed $e_0$, all eigenvalues $\lambda_j(e) \geq 1$ (counting towards $B_{e_0}$) will eventually cross the value 1, in which case the corresponding $E_j : \lambda_j(E_j) = 1$ is an eigenvalue of the Schrödinger operator.

- Proof of LT-inequalities ($\gamma > 0$, $d = 3$)

The function $e \mapsto N_e$ is piecewise constant with $N_e = 0$ for $e$ large enough. Hence,

$$\int_0^\infty e^{\gamma-1} N_e \, de = -\sum_j \frac{1}{\gamma} \left. e^\gamma \right|_{|E_j|}^{|E_{j+1}|} = \frac{1}{\gamma} \sum_j |E_j|^\gamma$$

i.e. $$\sum_j |E_j|^\gamma = \gamma \int_0^\infty e^{\gamma-1} N_e \, de \underset{B-S}{=} \gamma \int_0^\infty e^{\gamma-1} B_e \, de .$$

Now: all eigenvalues counted in $B_e$ are such that $\lambda_j(e) \geq 1$, so that

$$B_e \leq \sum_{\lambda_j \geq 1} \lambda_j^2 \leq \mathrm{Tr}(K_e^2)$$

and we note (see exercises) that

$$(K_e \varphi)(x) = \int K_e(x,y) \varphi(y) \, dy \quad \text{with}$$

$$K_e(x,y) = \sqrt{V_-(x)} \frac{1}{4\pi |x-y|} e^{-\sqrt{e}|x-y|} \sqrt{V_-(y)}$$

Hence,

$$\operatorname{Tr} K_e^2 = \iint V_-(x) \frac{1}{16\pi^2 |x-y|^2} e^{-2\sqrt{e}|x-y|} V_-(y)\,dx\,dy$$
$$\leq \dots \leq \frac{C}{\sqrt{e}} \int V_-^2$$

if $V_- \in L^2(\mathbb{R}^3)$.

Now of course $|x|^{-1} \notin L^2$ at infinity so we consider again

$$W_e := \left(V(x) + \frac{e}{2}\right)_- \geq V_-(x) - \frac{e}{2}$$

and claim:

$$N_e(-V_-) = N_{\frac{e}{2}}(-V_- + e/2) \leq N_{e/2}(-W_e)$$

since $-W_e \leq -V_- + \frac{e}{2}$. Hence:

$$\sum_j |E_j|^\gamma \leq C \int_0^\infty de\, e^{\gamma - 1 - \frac{1}{2}} \int_{\mathbb{R}^3} W_e^2\, dx$$
$$\overset{(*)}{=} C \int_{\mathbb{R}^3} dx \int_0^{2V_-(x)} de\, e^{\gamma - \frac{3}{2}} \left(V_-(x) - \frac{e}{2}\right)^2$$
$$= C \int_{\mathbb{R}^3} dx \int_0^1 du\, V_-(x)^{\gamma - \frac{3}{2} + 2 + 1} u^{\gamma - \frac{3}{2}} (1-u)^2\, du$$

with $e = 2V_-(x) u$

$$= C \int_{\mathbb{R}^3} V_-(x)^{\gamma + \frac{3}{2}}\, dx$$

since the $u$ integral is convergent at 0. $\square$

---

(*) $\left(V(x) + \frac{e}{2}\right)_-^2 = \left(V(x) + \frac{e}{2}\right)^2 \chi_{\{e:\, V(x) + \frac{e}{2} \leq 0\}} = \left(V(x) + \frac{e}{2}\right)^2 \chi_{\{e:\, e \leq -2V(x)\}}$

Since $e > 0$, on the set $e: e \leq -2V(x)$, $V(x) < 0$ i.e. $V(x) = -V_-(x)$ and $\left(V(x) + \frac{e}{2}\right)^2 \chi_{\{e:\, e \leq -2V(x)\}} = \left(-V(x) + \frac{e}{2}\right)^2 \chi_{\{e:\, e \leq 2V_-(x)\}}$

**Scaling arguments for Lieb-Thirring inequalities**

Let $V \leq 0$ and $E_0 \leq E_1 \leq \cdots \leq 0$ be the negative eigenvalues of $-\Delta + V$. We look for the only possible power $\alpha$ for which a bound of the type

$$\sum_j |E_j|^\gamma \leq L_{\gamma,d} \int V(x)^\alpha dx \tag{1}$$

holds uniformly for all $V$.

Let $\lambda > 0$. We note that if $\psi$ is an eigenvector $((-\Delta + M_V)\psi)(x) = E\psi(x)$, then under the scaling $x \mapsto y = \lambda x$, the function $\tilde{\psi}(y) = \psi(\lambda x)$ solves

$$((-\Delta_y + M_{\tilde{V}})\tilde{\psi})(y) = \tilde{E}\tilde{\psi}(y), \qquad \tilde{E} = \lambda^{-2}E,$$

where $\tilde{V}(y) = \lambda^{-2}V(\lambda x)$. Indeed,

$$\lambda^2(-\Delta_y\tilde{\psi})(y) = (-\Delta_x\psi)(\lambda x) = (-M_V\psi)(\lambda x) + E\psi(\lambda x)$$

and the claim follows from

$$\lambda^{-2}(M_V\psi)(\lambda x) = \lambda^{-2}V(\lambda x)\psi(\lambda x) = \tilde{V}(y)\tilde{\psi}(y) = (M_{\tilde{V}}\tilde{\psi})(y).$$

On the other hand, (1) must hold for $\tilde{E}, \tilde{V}$ with the same constant. Hence

$$\lambda^{-2\gamma}\sum_j |E_j|^\gamma = \sum_j |\tilde{E}_j|^\gamma \leq L_{\gamma,d}\int \tilde{V}(y)^\alpha dy = \lambda^{-2\alpha+d}L_{\gamma,d}\int V(x)^\alpha dx$$

which implies that $-2\gamma = -2\alpha + d$, namely

$$\alpha = \gamma + \frac{d}{2}.$$

Instead of scaling the variables (the 'passive' transformation), one could also scale the wavefunction (the 'active' transformation), namely consider $\psi_\lambda(x) := \psi(\lambda x)$, in which case the choice $V_\lambda(x) := \lambda^2 V(\lambda x)$ yields

$$\begin{aligned}((-\Delta_x + M_{V_\lambda})\psi_\lambda)(x) &= -\lambda^2(\Delta_x\psi)(\lambda x) + V_\lambda(x)\psi_\lambda(x) = \lambda^2((-\Delta_x + M_V)\psi)(\lambda x)\\ &= \lambda^2 E\psi(\lambda x) = \lambda^2 E\psi_\lambda(x),\end{aligned}$$

namely $(-\Delta_x + M_{V_\lambda})\psi_\lambda = E_\lambda\psi_\lambda$ with $E_\lambda = \lambda^2 E$. This yields again

$$\lambda^{2\gamma}\sum_j |E_j|^\gamma = \sum_j |(E_\lambda)_j|^\gamma \leq L_{\gamma,d}\int V_\lambda(x)^\alpha dx = L_{\gamma,d}\lambda^{2\alpha-d}\int V(y)^\alpha dy$$

with the same conclusion.

Sven Bachmann

## 14. Electrostatics

- Coulomb potential in $\mathbb{R}^3$. For a charge distribution given by a Borel measure $\rho$:

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

Coulomb energy of $\rho$:

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

Notes: * This is well-defined if $\rho = \sigma - \tau$, with $\sigma, \tau$ are positive measures s.t. $\nu := \sigma + \tau$ satisfies

$$\int \frac{1}{1+|x|} \, d\nu(x) < \infty.$$

* If $\rho$ is absolutely continuous w.r.t. the Lebesgue measure, $d\rho(x) = \rho(x) dx$, then

$$D(\rho,\rho) = \frac{1}{2} \int \frac{\rho(x)\rho(y)}{|x-y|} \, dx \, dy$$

* The interaction energy between $\rho$ & $\sigma$:

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

* There are two issues with the Coulomb potential $|x|^{-1}$:
  i) Singularity at $x = 0$: not too serious because integrable
  ii) Slow decay at $|x| \to \infty$: serious problem.

• Lemma Let $\rho, \sigma$ be two charge distributions. Then:

$$0 \le D(\rho,\rho) < \infty$$

and

$$|D(\rho,\sigma)|^2 \le D(\rho,\rho)\,D(\sigma,\sigma).$$

Formal argument: $-\Delta\Phi_\rho = 4\pi\rho$ (easy check if $\rho$ is a.c. with density in $C_c^\infty(\mathbb{R}^3)$)

implies:

* $D(\rho,\rho) = \frac{1}{2}\int \Phi_\rho \cdot \rho = \frac{1}{8\pi}\int \Phi_\rho(-\Delta\Phi_\rho) = \frac{1}{8\pi}\langle \Phi_\rho, -\Delta\Phi_\rho\rangle \ge 0.$
* $|D(\rho,\sigma)| = \frac{1}{8\pi}\left|\int \Phi_\rho(-\Delta\Phi_\sigma)\right| = \frac{1}{8\pi}\left|\int D\Phi_\rho \cdot D\Phi_\sigma\right|$

$$= \frac{1}{8\pi}|\langle D\Phi_\rho, D\Phi_\sigma\rangle| \le \left(\frac{1}{8\pi}\langle D\Phi_\rho, D\Phi_\rho\rangle\right)^{1/2}\left(\frac{1}{8\pi}\langle D\Phi_\sigma, D\Phi_\sigma\rangle\right)^{1/2}$$

• Fundamental identity to understand screening: Newton's theorem: $\Phi$ outside the charge distribution that is rotationally symmetric looks as if all charge was concentrated at the center:

Theorem: Let $\rho$ be a charge distribution that is rotationally symmetric about the origin:

$$\Phi_\rho(x) = \frac{1}{|x|}\int_{|y|\le|x|} d\rho(y) + \int_{|y|>|x|} \frac{1}{|y|}\,d\rho(y)$$

Consequences: i) if $\rho(\{y : |y| > R\}) = 0$ for some $R > 0$, then

$$\Phi_\rho(x) = \frac{1}{|x|}\underbrace{\rho(\mathbb{R}^3)}_{\text{total charge}}$$

ii) if $\rho(\{y : |y| < R\}) = 0$, then $\Phi(x)$ is constant on $|x| \le R$:

$$\Phi(x) = \int_{|y|>R} \frac{1}{|y|}\,d\rho(y)$$

Proof. $\rho$ rotationally symmetric $\to$ $\Phi(x) = \Phi(y)$ if $|x| = |y|$ and thus

$$\Phi(x) = \int_{S^2} \Phi(|x|\omega)\, d\omega \quad \leftarrow \text{normalized surface measure.}$$

but

$$\int_{S^2} \frac{1}{\big||x|\omega - y\big|}\, d\omega = \min\left(\frac{1}{|x|}, \frac{1}{|y|}\right)$$

i.e.

$$\Phi(x) = \int_{\mathbb{R}^3} \min\left(\frac{1}{|x|}, \frac{1}{|y|}\right) d\rho(y) \qquad \square$$

- Back to the $M$ nuclei at $R_1, \dots, R_M$, all with charge $Z$, assume $R_i \neq R_j$, $i \neq j$.

Voronoi cells: $\Gamma_j \subseteq \mathbb{R}^3$, $j = 1, \dots, M$

$$\Gamma_j = \{x \in \mathbb{R}^3 : |x - R_j| < |x - R_i| \ \forall i \neq j\}$$

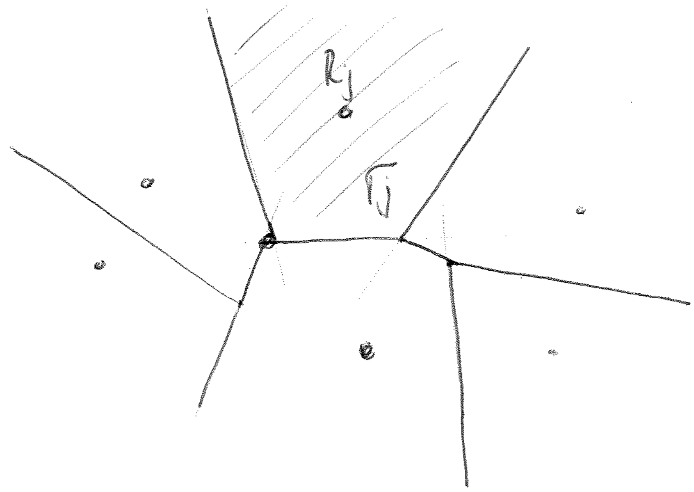
Recall: $D_j := \frac{1}{2} \min_{i \neq j} |R_i - R_j| = \operatorname{dist}(R_j, \partial\Gamma_j)$

$$\mathcal{D}(x) = \min\{|x - R_i| : 1 \le i \le M\}$$

Total Coulomb potential: $W(x) = Z \sum_{j=1}^{M} \frac{1}{|x - R_j|}$

Define $\Phi(x) := W(x) - \frac{Z}{\mathcal{D}(x)}$ is continuous (all $Z$'s equal)

i.e. if $x \in \Gamma_j$ $\quad$ $\Phi(x)$ is the potential of all nuclei outside $\Gamma_j$.



Lemma: For any charge distribution $\rho$ and distinct $R_1, \dots, R_n \in \mathbb{R}^3$.

$$\underbrace{D(\rho,\rho)}_{\text{total } e^- e^- \text{ Coulomb energy}} - \underbrace{\int \Phi(x)\, d\rho(x)}_{\substack{\text{total } e^-\text{-nuclei Coulomb energy, except for the}\\ \text{nucleus in the cell where}\\ \text{the } e^- \text{ finds itself}}} + \underbrace{\sum_{1\le i<j\le n} \frac{z^2}{|R_i - R_j|}}_{\text{total nucl-nucl Coulomb energy}} \geq \frac{1}{8} \sum_{j=1}^{M} \frac{z^2}{D_j}$$

for $\rho \sim$ electronic charge density.

Proof: Step (i) find $\nu$ s.t. $\Phi(x) = \int \frac{1}{|x-y|} d\nu(y)$

it will be a surface charge density on the surfaces of the Voronoi cells $\bigcup_j \partial\Gamma_j$.

Equivalently, $-\Delta\Phi = 4\pi\nu$ i.e. for all $f \in C_c^\infty(\mathbb{R}^3)$:

$$\int \Phi \Delta f = 4\pi \int f\, d\nu$$

$$\int \Phi \Delta f = \sum_j \int_{\Gamma_j} \Phi \Delta f\, dx$$

$$\overset{\text{Green's formula}}{=} \sum_j \int_{\partial\Gamma_j} \Phi \nabla f \cdot \underbrace{n_j}_{\text{exterior normal}}\, dS - \sum_j \int_{\Gamma_j} \nabla\Phi \cdot \nabla f\, dx.$$

$\Phi$ has no singularity within each $\Gamma_j$

all segments appear twice, with opposite signs since $\Phi, \nabla f$ are continuous $\Rightarrow = 0$.

Since $-\nabla\Phi \cdot \nabla f = -\mathrm{div}(f\nabla\Phi) + f\underbrace{\Delta\Phi}_{\substack{=0 \text{ in each } \Gamma_j\\ \text{by def.}}}$

By divergence theorem:

$$\int \Phi \Delta f\, dx = -\sum_j \int_{\partial\Gamma_j} f \nabla\Phi \cdot n_j\, dS$$

now: $\nabla\Phi$ is discontinuous across $\partial\Gamma_j$!

because $D(x)$ has a kink there.

In fact: $\nabla \Phi = \nabla W - z \nabla \mathcal{D}^{-1}$
$\uparrow$ is continuous and contribution appears twice with opposite signs.

$$\int \Phi \Delta f \, dx = + \sum_j \int_{\partial \Gamma_j} f \nabla \frac{z}{\mathcal{D}} \cdot n_j \, dS .$$

On any hyperplane between $\Gamma_j$ and $\Gamma_k$, $\nabla \mathcal{D}^{-1}$ on either side of the plane have equal magnitude, but opposite signs, i.e.

$$\nabla \frac{1}{|x-R_j|} \cdot n_j = \nabla \frac{1}{|x-R_k|} \cdot n_k \quad \text{on all such segments.}$$

$$\Rightarrow \int \Phi \Delta f \, dx = 2z \int_{\bigcup_j \partial \Gamma_j} f \, n_j \cdot \nabla \frac{1}{|x-R_j|} \, dS$$

$= -(\text{magnitude of } \nu) \cdot 4\pi .$

<u>Step (ii)</u> Since $\int \Phi \, d\rho = \int \left( \int \frac{1}{|x-y|} d\nu(y) \right) d\rho(x) =$
$= D(\nu, \rho) + D(\rho, \nu)$ :

$$D(\rho,\rho) - \int \Phi \, d\rho + \sum \frac{z^2}{|R_i - R_j|}$$
$$= D(\rho-\nu, \rho-\nu) - D(\nu,\nu) + \sum \frac{z^2}{|R_i - R_j|}$$
$$\geq -D(\nu,\nu) + \sum_{i<j} \frac{z^2}{|R_i - R_j|} \quad \text{by the first lemma.}$$

Note that $W(x) = z \sum_j \int \delta(y - R_j) \frac{1}{|y-x|} dy$

so that $\int W(x) \, d\nu(x) = z \sum_j \Phi(R_j)$

Furthermore: by the very definition of $\Phi$.

$$\frac{1}{2} z \sum_j \Phi(R_j) = z^2 \sum_{i<j} \frac{1}{|R_i - R_j|}$$

so that $\frac{1}{2} \int W d\nu = z^2 \sum 1/|R_i - R_j|$ and

$$D(\nu,\nu) = \frac{1}{2}\int \Phi \, d\nu = \frac{1}{2}\int W\, d\nu - \frac{1}{2}\int \frac{z}{D}\, d\nu$$

$$= \underbrace{\sum_{i<j} \frac{z^2}{|R_i - R_j|}}_{\text{cancels out}} - \frac{1}{2}\int \frac{z}{D(x)}\, d\nu(x)$$

it remains to bound

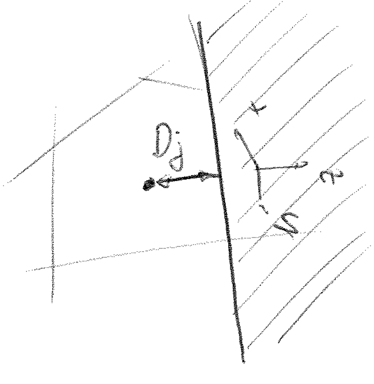
$$\frac{1}{2}\int \frac{z}{D(x)}\, d\nu(x) = -\frac{z^2}{4\pi} \underbrace{\int_{\bigcup_j \partial\Gamma_j}}_{d\nu_0 \,=\, \frac{1}{8\pi}\sum_j \int_{\partial\Gamma_j}} \frac{1}{|x-R_j|}\, n_j \cdot \nabla \frac{1}{|x-R_j|}\, dS$$

$$= -\sum_j \frac{z^2}{16\pi} \int_{\partial\Gamma_j} n_j \cdot \nabla \frac{1}{|x-R_j|^2}\, dS = \sum_j \frac{z^2}{16\pi}\int_{\Gamma_j^c} \Delta \frac{1}{|x-R_j|^2}\, dx$$

to change sign!

for $x \in \Gamma_j^c$: $\Delta |x-R_j|^{-2} = 2|x-R_j|^{-4}$

For a lower bound of the integral. Intergrate over a half-space




$$\frac{z^2}{8\pi}\int_{\Gamma_j^c} \frac{1}{|x-R_j|^4}\, dx \geq$$

$$\frac{z^2}{8\pi}\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{D_j}^{\infty} dz \frac{1}{(x^2+y^2+z^2)^2} = \frac{z^2}{8 D_j} \quad \blacksquare$$

• Applying the lemma to the electronic charge distribution

$$\rho(x) = \sum_{i=1}^{N} \delta(x - x_i)$$

we shall obtain Baxter's inequality.

only issue: $D(\rho,\rho) \underset{\text{formally}}{=} \frac{1}{2}\sum_{i,j} \frac{1}{|x_i - x_j|} = \infty$ ↙ self-energy, $i=j$ term.

• Proof of Baxter's inequality:

Let $d\rho_i(x) := \frac{1}{\pi D(x_i)} \delta\left(|x-x_i| - \tfrac{1}{2}D(x_i)\right)$

i.e. the unit (electronic) charge is smeared out over the sphere of radius $\frac{1}{2}D(x_i)$ around $x_i$: $B_i$.

and $\rho := \sum_i \rho_i$.

By Newton's theorem:

* $D(\rho_i,\rho_i) = \frac{1}{2}\int_{B_i} \Phi_{\rho_i}(y)\,d\rho_i(y) \overset{(NT)}{=} \frac{1}{2}\int_{B_i} \frac{1}{|y-x_i|}\,d\rho_i(y)$

$$= \frac{1}{2}\Phi_{\rho_i}(x_i) \overset{(NT)}{=} \frac{1}{2}\frac{1}{D(x_i)/2} = D(x_i)^{-1}$$

* $D(\rho_i,\rho_j) \le \frac{1}{2}\frac{1}{|x_i-x_j|}$ (equality iff $B_i \cap B_j = \emptyset$).
* Since $|x_i - R_j| \geq D(x_i) > \frac{1}{2}D(x_i)$, $i \neq j$:

$$\frac{1}{|x_i-R_j|} = \int \frac{1}{|x-R_j|}\,d\rho_i(x)$$

Hence,

$$V_C(x) \geq \underbrace{\sum_{1\le i<j\le N} 2D(\rho_i,\rho_j)}_{= D(\rho,\rho) - \sum_{i=1}^{N}\frac{1}{D(x_i)}} - \underbrace{\sum_{j=1}^{M}\int \frac{Z}{|x-R_j|}\,d\rho(x)}_{= \int \Phi\, d\rho + \sum_{i}\int \frac{Z}{D(x)}\,d\rho_i(x)} + \sum_{1\le i<j\le M}\frac{Z^2}{|R_i-R_j|}$$

$$\overset{\text{Lemma}}{\geq} -\sum_{i=1}^{N}\left(\int \frac{Z}{D(x)}\,d\rho_i(x) + \frac{1}{D(x_i)}\right) + \frac{Z^2}{8}\sum_{j=1}^{M}\frac{1}{D_j}$$

on $\operatorname{supp} \rho_i$: $D(x) \geq \frac{D(x_i)}{2}$

since $|x-R_j| \geq \underbrace{|x_i-R_j|}_{\geq D(x_i)} - \underbrace{|x_i-x|}_{= \frac{D(x_i)}{2}}$ for $x \in \operatorname{supp}\rho_i$.

$\square$

- We finally compute the ground state energy for non-interacting fermions with Hamiltonian

$$H^{(N)} = \sum_{i=1}^{N} \left(-\Delta_{x_i} + V(x_i)\right) = \sum_{i=1}^{N} h_i$$

Let $\Psi \in \Lambda^N L^2(\mathbb{R}^3)_1$ and let

$$\gamma_\Psi^{(1)}(x,y) := N \int_{\mathbb{R}^{3(N-1)}} \Psi(x, x_2, \dots x_N)\overline{\Psi(y, x_2 \dots x_N)}\, dx_2 \dots dx_N$$

be the integral kernel of the 1-particle reduced density matrix

$$\left(\gamma_\Psi^{(1)}\varphi\right)(x) = \int \gamma_\Psi^{(1)}(x,y)\varphi(y)\,dy$$

See exercises.

Since $0 \le \gamma_\Psi^{(1)} \le 1$ (and it is a compact operator), its spectral decomposition is

$$\gamma_\Psi^{(1)} = \sum_j \lambda_j P_{\psi_j} \qquad \|\psi_j\| = 1 \qquad \text{with } 0 \le \lambda_j \le 1. \text{ and } \sum_j \lambda_j = N.$$

Using the antisymmetry of $\Psi$

$$E^{(N)}(\Psi) = \langle \Psi, H^{(N)}\Psi\rangle = \int \left(h\, \gamma_\Psi^{(1)}\right)(x,x)\,dx$$

$$= \sum_j \lambda_j \int \left(|D\psi_j|^2 + V|\psi_j|^2\right)$$

Let now $f_0, f_1, \dots$ be eigenfunctions of $-\Delta + V$, $f_i \in H^1$, and

$$\psi_j := \sum_k a_{jk} f_k + \varphi_j \quad , \quad \langle \varphi_j, f_n\rangle = 0$$

i.e. $\varphi_j = \psi_j - \sum_k a_{jk} f_k \in H^1$ as well

also: $\|\psi_j\| = 1 \Rightarrow \|\varphi_j\| + \sum_k |a_{jk}|^2 = 1 \Rightarrow \sum_k |a_{jk}|^2 \le 1$

Now: Since $\varphi_j \perp$ to all states $f_n$ with negative energy:

(1) $E(\varphi_j) = \int (|D\varphi_j|^2 + V|\varphi_j|^2) \geq 0.$

Since the $f_n$'s are $\perp$ to each other and eigenvectors:

(2) $\int \left(\overline{Df_n}\, Df_m + \overline{V f_n} f_m\right) = \delta_{n,m}\, e_n$

Finally: $\langle \varphi_j, (-\Delta + V) f_n \rangle = \langle \varphi_j, f_n\rangle e_n = 0$, i.e.

(3) $\int \left(\overline{D\varphi_j}\, Df_n + \overline{V\varphi_j} f_n\right) = 0$

Altogether:

$$\int (|D\varphi_j|^2 + V|\varphi_j|^2) \geq \sum_k |a_{jk}|^2 e_k$$

i.e. $E(\Psi) \geq \sum_j \lambda_j \sum_k |a_{jk}|^2 e_k = \sum_k \mu_k e_k$

with $\mu_k = \sum_j \lambda_j |a_{jk}|^2$

Note:
* $\mu_k \leq \sum_j |a_{jk}|^2 = \sum_j |\langle \varphi_j, f_k\rangle|^2 = \|f_k\|^2 = 1$
* $\sum_k \mu_k = \sum_{k,j} \lambda_j |a_{jk}|^2 \leq \sum_j \lambda_j = N$

$\Rightarrow E(\Psi) \geq \inf \left\{ \sum_k \mu_k e_k : 0 \leq \mu_k \leq 1, \sum_k \mu_k \leq N \right\}$

with $e_0 \leq e_1 \leq \dots \leq 0$ are the negative eigenvalues of $-\Delta + V$.

solve this minimization problem: $\mu_0, \dots, \mu_N = 1$, $\mu_{N+1}, \dots = 0$

i.e. $E(\Psi) \geq \sum_{k=0}^{N-1} e_k$ if there are at least $N$ negative eigenvalues, otherwise $\sum_k e_k$

In all cases: $\inf_N E(N) \geq \sum_k e_k$

Equality reached either with Slater of the first $N$ eigenfunctions, or all eigenfunctions plus a number of $\varphi_h$'s which have arbitrarily small positive energy:

& very flat : $T(\varphi_h) \sim 0$

& supported far out : $V(\varphi_h) \sim 0$. $\square$

- Note if the one-body Hamiltonian $h$ has an eigenbasis of eigenvectors $\psi_0, \psi_1, \dots$ for the eigenvalues $E_0, E_1, \dots$

This can all be proved easily.

$\Lambda^N \mathcal{H}$ has a basis $\{\psi_{i_1} \wedge \dots \wedge \psi_{i_N}, \ i_1 < i_2 < \dots < i_N\}$

& which

$$\left(\sum_{i=1}^{N} h_i\right) \psi_{i_1} \wedge \dots \wedge \psi_{i_N} = \left(\sum_{i=1}^{N} e_{i_1}\right) (\psi_{i_1} \wedge \dots \wedge \psi_{i_N})$$

so that $\{\psi_{i_1} \wedge \dots \wedge \psi_{i_N}; \ i_1 < \dots < i_N\}$ is an eigenbasis of $\sum_{i=1}^{N} h_i$,

and the lowest eigenvalue is $\sum_{i=0}^{N-1} e_i$ for the eigenvector

$$\psi_0 \wedge \psi_1 \wedge \dots \wedge \psi_N$$

"The orbitals are filled up from below"

- <u>Instability for bosons</u>: For bosons the wavefunction for $N$ particles must be symmetric. In particular, if they are non-interacting, the ground state is simply a product state of the one-particle G.S. and one loses the "power 2/3" gain from the Pauli principle. Indeed:

<u>Theorem</u> Let $Z_i = Z$ for all $1 \le i \le M$. There exists

$$\Psi \in \bigotimes_S^N L^2(\mathbb{R}^3) \quad \text{and a vector } R = (R_1, \dots, R_M)$$

s.t.

$$E(\Psi) \le -C\alpha^2 Z^{4/3} \min\{N, ZM\}^{5/3}$$

in other words: bosons are unstable of the second kind!

The proof of this <u>upper</u> bound is by constructing a suitable trial function for a good choice of $R$.

- <u>Proof</u>: Assume ($M = n^3$, $n \in \mathbb{N}$, and) $N = Z \cdot M$.
Let

$$\Psi(x_1, \dots, x_N) = \prod_{i=1}^N \phi_\lambda(x_i)$$

for a fixed $\phi_\lambda$, where $\phi_\lambda(x) = \lambda^{3/2}\phi(\lambda x)$ and $\|\phi\|_2 = 1$ (hence $\|\phi_\lambda\|_2 = 1$). With this:

$$\begin{aligned}
\langle \Psi, H\Psi \rangle = {} & N \int |D\phi_\lambda|^2 dx \\
& + \alpha \cdot \tfrac{1}{2} N(N-1) \int \frac{|\phi_\lambda(x)|^2 |\phi_\lambda(y)|^2}{|x-y|} dx\,dy \\
& - \alpha Z N \sum_{i=1}^M \int \frac{|\phi_\lambda(x)|^2}{|x - R_i|} dx + U(R) \\
= {} & N\lambda^2 \int |D\phi|^2 dx + \lambda\alpha\, W(N, R)
\end{aligned}$$

where
$$\begin{aligned}
W(N,R) = {} & \tfrac{1}{2} N(N-1) \int \frac{|\phi(x)|^2 |\phi(y)|^2}{|x-y|} dx\,dy \\
& - ZN \sum_{i=1}^M \int \frac{|\phi(x)|^2}{|x - \lambda R_i|} + U(\lambda R)
\end{aligned}$$

and we drop the $\lambda$ in $\lambda R$ since $R_i$ are still not fixed.

Claim: $W(N,R) \leq -C Z^{2/3} N^{4/3}$ and the theorem follows by choosing the optimal

$$\lambda = \frac{1}{2} N^{1/3} Z^{2/3} \frac{C}{\int |\nabla\phi|^2}$$

Choose $\phi \in C_c^\infty(\mathbb{R}^3)$, and let $\Gamma_k$, $1 \leq k \leq n$ be a partition of supp $\phi$ s.t.

$$\int_{\Gamma_k} |\phi(x)|^2 dx = \frac{1}{M}$$

and place one nucleus at $R_k \in \Gamma_k$ $1 \leq k \leq n$.
$M|\phi(x)|^2$ being a probability density in each $\Gamma_k$ the average of $W(N,R)$ is given by

$$\sum_{k=1}^{M} \int_{\Gamma_k} W(N,R)\, M |\phi(R_k)|^2 dR_k = \ldots$$

* electronic-electronic repulsion unchanged.
* $$\sum_{k=1}^{n} \int_{\Gamma_k} \int_{\mathbb{R}^3} M \frac{|\phi(x)|^2 |\phi(R_k)|^2}{|x - R_k|} dx\, dR_k$$
$$= M \int_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{|\phi(x)|^2 |\phi(y)|^2}{|x-y|} dx\, dy.$$

* $$\sum_{1 \leq i < j \leq n} Z_i Z_j \int_{\Gamma_i} \int_{\Gamma_j} n^2 \frac{|\phi(R_i)|^2 |\phi(R_j)|^2}{|R_i - R_j|} dR_i\, dR_j$$
$$= \frac{1}{2} M^2 Z^2 \int_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{|\phi(x)|^2 |\phi(y)|^2}{|x-y|} dx\, dy$$
$$- \sum_{i=1}^{n} n^2 Z^2 \int_{\Gamma_i \times \Gamma_i} \frac{|\phi(x)|^2 |\phi(y)|^2}{|x-y|} dx\, dy$$

all in all: the coefficient in front of the $\int_{\mathbb{R}^3\times\mathbb{R}^3}$-integral reads

$$\frac{1}{2}N(N-1) - ZNM + \frac{1}{2}M^2Z^2 \overset{N=ZM}{=} -\frac{1}{2}N \le 0$$

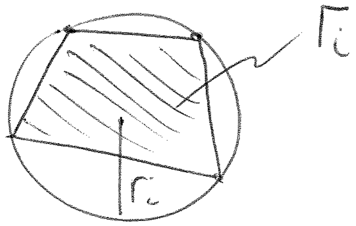
and

$$\min_{\{R_k\in\Gamma_k\}} W(N,R) \le \langle W(N,R)\rangle$$

$$\le -\frac{1}{2}Z^2M^2\sum_{i=1}^{M} \underbrace{\int_{\Gamma_i\times\Gamma_i} \frac{|\phi(x)|^2|\phi(y)|^2}{|x-y|}\,dx\,dy}_{\text{need a lower bound on this self-energy } S_i(\phi)}$$

Now:

$S_i(\phi) \ge$ smallest self-energy of charge distribution in the ball $B_i \supset \Gamma_i$ of smallest radius $r_i$, with total charge $\frac{1}{M}$




$\to$ minimizing distribution: uniform on the boundary:

$$\Rightarrow S_i(\phi) \ge \frac{1}{2}\frac{1}{M^2}\int_{\partial B_{r_i}\times\partial B_{r_i}} \frac{1}{|x-y|}\,d\sigma(x)\,d\sigma(y) = (2r_iM^2)^{-1}$$

and

$$\sum_{i=1}^{M} S_i(\phi) \ge \frac{1}{2M}\left(\frac{1}{M}\sum_{i=1}^{M}\frac{1}{r_i}\right)$$

$$\overset{\text{Jensen's inequality}}{\ge} \frac{1}{2M}\left(\frac{1}{M}\sum_{i=1}^{M} r_i\right)^{-1}$$

Hence: $\min W(N,R) \le -Z^2M\left(\frac{1}{M}\sum_{i=1}^{M} r_i\right)^{-1}$

and we need an upper bound on the mean radius:

$$\frac{1}{M}\sum_{i=1}^{M} r_i \le C\,\frac{1}{M^{1/3}}$$

Summarizing:

$$\min_{\{R_k\}} \langle \Psi, H\Psi \rangle \leq N\lambda^2 \int |\nabla\phi|^2 dx - \lambda C Z^2 \underbrace{\Pi^{4/3}}_{= Z^{2/3} N^{4/3}} \alpha$$

$\square$

## 15. Miscellaneous results on the stability of matter

a) Magnetic fields:

Introduced by replacing $-i\nabla$ by $-i\nabla + A(x)$, where $(\nabla \wedge A)(x) = B(x)$ is the magnetic field felt by the electrons. Without spin, this can be dealt with using the diamagnetic inequality: (for $\psi$ s.t. $(\nabla + iA)\psi \in L^2(\mathbb{R}^d)$):

$$|(\nabla + iA)\psi(x)| \geq |\nabla|\psi|(x)| \qquad \text{[L-L, thm 7.21]}.$$

i.e. removing the magnetic field allows for a decrease of the kinetic energy by the replacement $\psi \to |\psi|$ (which does not change the potential energy)

[note: diamagnets create an induced field, opposite to an applied magnetic field and are repelled by it]

This covers "orbital magnetism". More complicated situation if spin is considered because of cancellations with $\sigma \cdot B$-term, "spin-orbit coupling".

b) Relativistic matter:

Replacement of $-\Delta$ by $\sqrt{-\Delta + m^2} - m$, i.e. morally $P^2$ by $P$ ... "less positive".

we have the relativistic Hardy inequality: $(d=3)$

$$\langle \Psi, |p| \Psi \rangle \geq \frac{2}{\pi} \int \frac{|\Psi(x)|^2}{|x|} dx$$

so that

$$E_{rel}(\Psi) = \langle \Psi, |p| \Psi \rangle - \alpha Z V(\Psi) \geq \left(\frac{2}{\pi} - \alpha Z\right) \int \frac{|\Psi(x)|^2}{|x|} dx$$

can be made arbitrarily negative if $\alpha Z > \frac{2}{\pi}$

$\Rightarrow$ relativistic stability of the first kind holds only if

$$\alpha Z \leq \frac{2}{\pi}$$

(in the non-rel. case: $\int |\nabla \Psi|^2 - (\alpha Z) \int \frac{|\Psi|^2}{|x|} \geq -\frac{(\alpha Z)^2}{4}$ for any $(\alpha Z)$.)

Furthermore: to obtain stability of the second kind, one needs additionally that $\alpha$ is small enough (in which case stability hold for all $Z$ s.t. $\alpha Z \leq \frac{2}{\pi}$ ; for the physical value of $\alpha$: $Z \leq 87$ (Francium))

c) Quantized electromagnetic fields, with or without UV cutoffs, with Schrödinger or Dirac kinetic energy: a zoo of results, see [L.-S, chap. 11.].

d) Thomas-Fermi theory.

We've already seen (see exercises) that

$$T(\Psi) \geq C \int \rho_\Psi(x)^{5/3} dx$$

as a consequence of the Lieb-Thirring inequality

i.e. all info about $\Psi$ that is needed in that bound is the one-particle density $\rho_\Psi(x)$.

the potential energy $V(\psi)$ requires the two-body density matrix but one may wonder how well it can be approximated by the Coulomb interaction of the densities

$\rightsquigarrow$ Lieb-Oxford bound

$$\langle \psi, \sum_{1\le i<j\le N} \frac{1}{|x_i-x_j|} \psi \rangle - \frac{1}{2}\int \frac{\rho_\psi(x)\rho_\psi(y)}{|x-y|} \geq$$

$$\geq C \int \rho_\psi^{4/3}(x)\,dx$$

"direct part" of the Coulomb energy

"exchange-correlation" or "indirect part" of the Coulomb energy. useful for quantum chemistry!

hence: (we neglect the nuclear repulsion)

$$\langle \psi, H\psi \rangle \geq c\int \rho_\psi(x)^{5/3}\,dx - \sum_{i=1}^{M}\int \frac{z_i\,\rho_\psi(x)}{|x-R_i|}\,dx$$

$$+ \frac{1}{2}\int \frac{\rho_\psi(x)\rho_\psi(y)}{|x-y|}\,dx\,dy - 2\int \rho_\psi^{4/3}\,dx.$$

since $\int \rho_\psi^{4/3} \leq \|\rho_\psi^{5/6}\|_2 \, \|\rho_\psi^{1/2}\|_2$

$$\leq C_1\left(\int \rho_\psi^{5/3}\right) + C_2\underbrace{\left(\int \rho_\psi\right)}_{=N}$$

$$\Rightarrow \langle \psi, H\psi \rangle \geq E_{TF}(\rho_\psi) - CN$$

where $E_{TF}(\rho)$ is the Thomas-Fermi functional

$$E_{TF}(\rho) := C_1\int \rho^{5/3} - \sum z_i \int \frac{\rho}{|x-R_i|} + D(\rho,\rho)$$

which can be proved to be bounded below by $-CZ^{7/3}M$ on

$$\{\rho \in L^{5/3} : \rho(x) \geq 0,\ \int \rho(x) = N\}$$

# 16. Remarks on the calculus of variations

- We have established that if $V \in L^{3/2}(\mathbb{R}^3) + L^\infty(\mathbb{R}^3)$ then
  $E_0 := \inf \{ E(\psi) = \int |\nabla \psi|^2 + \int V |\psi|^2 \, : \, \psi \in H^1(\mathbb{R}^3), \|\psi\|_2 = 1 \}$.
  is finite.
  The question is the existence of a $\psi_0 \in H^1(\mathbb{R}^3)$ s.t.
  $$E_0 = E(\psi_0)$$
  "ground state".

- To illustrate the following "direct method", we consider a real function $f : M \to \mathbb{R}$, which is continuous.
  If $M$ is compact, it is known that $f$ reaches its minimum $f_0$.
  i) pick $x_j$, $j \in \mathbb{N}$ s.t. $f(x_j) \to f_0 = \inf_{x \in M} f(x)$ $(j \to \infty)$
  ii) since $M$ is compact, $x_j$ has a convergent subsequence (Bolzano-Weierstrass) $x_{j_k} \to x$, $x \in M$
  iii) by continuity of $f$:
  $$f_0 = \lim_{k \to \infty} f(x_{j_k}) = f(x)$$

This strategy fails if $M$ is not compact, or $f$ is not $C^0$.

- Here: replace $M$ by $\{ \psi \in H^1(\mathbb{R}^3) : \|\psi\|_2 = 1 \}$ (or possibly a larger set) and $f$ by $E = E(\psi)$

  Problem: the unit ball in $L^2$ or $H^1$ is not compact, i.e. if ~~$\psi_j \xrightarrow{L^2} \psi$~~ $\psi_j$ is a bounded sequence there may be no convergent subsequence
  $\leadsto$ relax the topology on $L^2$ to have more convergent sequences
  but: $E(\cdot)$ may not be continuous any more.

what will be true is weak <u>lower semi-continuity</u>.

$$\liminf_{j\to\infty} E(\psi_j) \geq E(\psi) \quad \text{if } \psi_j \rightharpoonup \psi \text{ weakly.}$$

Altogether: i) Let $\psi_j$ be a minimizing sequence:

$$E(\psi_j) \to E_0 \quad \text{as } j \to \infty.$$

ii) By weak compactness, $\psi_j$ has a weakly convergent subsequence $\psi_{j_k} \rightharpoonup \psi_0$

iii) $E_0 = \lim_{k\to\infty} E(\psi_{j_k}) \geq E(\psi_0) \geq E_0$

$\Rightarrow E(\psi_0) = E_0$ goal achieved.

- Some details:

  * Weak convergence. $1 \leq p < \infty$: since $(L^p(\mathbb{R}^3))^* = L^q(\mathbb{R}^3)$,

    $\psi_j \rightharpoonup \psi$ weakly in $L^p$ if

    $$\int \varphi(x)\left(\psi_j(x) - \psi(x)\right)dx \to 0$$

    for all $\varphi \in L^q$, $\frac{1}{p} + \frac{1}{q} = 1$

  * <u>Theorem</u> (Banach-Alaoglu): $1 < p < \infty$. Let $\{\psi_j\}_{j\in\mathbb{N}}$ be a sequence of functions, bounded in $L^p(\mathbb{R}^d)$.

    Then there exists a subsequence $\{\psi_{j_k}\}_{k\in\mathbb{N}}$ and a $\psi \in L^p(\mathbb{R}^d)$ s.t. $\psi_{j_k} \rightharpoonup \psi \quad (k\to\infty)$

    $\leadsto$ weak compactness of $\{\psi \in L^2(\mathbb{R}^3) : \|\psi\|_2 = 1\}$.

  * <u>Lemma</u>: If $V$ is as above and $|\{x : |V(x)| > a\}| < \infty$ for all $a > 0$, then $\psi \mapsto V(\psi)$ is weakly continuous in $H^1(\mathbb{R}^n)$

Key technical lemma!

- **Theorem**: Let $V$ be as in the lemma.
  i) If $E_0 < 0$, there is a $\psi_0 \in H^1(\mathbb{R}^3)$, $\|\psi_0\|_2 = 1$ s.t. $E(\psi_0) = E_0$
  ii) Moreover, $\psi_0$ is unique up to a phase, and can be chosen to be positive
  iii) Furthermore:
  $$(-\Delta + V)\psi_0 = E_0 \psi_0$$
  in the sense of distributions.

i.e. $$\langle(-\Delta+V)\varphi, \psi_0\rangle = E_0 \langle \varphi, \psi_0\rangle \quad \forall \varphi \in C_c^\infty(\mathbb{R}^3).$$

We prove (i) & (iii):

- $\psi_j$ a minimizing sequence : $E(\psi_j) \to E_0 \quad (j \to \infty)$.
- $T(\psi_j)$ is uniformly bounded since (see exercises)
  $$T(\psi) \leq C E(\psi) + D\|\psi\|_2^2$$
  and since $\|\psi\|_2 = 1$, $\psi_j$ is a bounded sequence in $H^1(\mathbb{R}^3)$.
- Since $H^1(\mathbb{R}^3)$ is just $L^2(\mathbb{R}^3; (1+|k|^2)dk)$, Banach-Alaoglu gives a subsequence $\psi_{j_k} \in H^1(\mathbb{R}^3)$ and a $\psi_0 \in H^1(\mathbb{R}^3)$ s.t. $\psi_{j_k} \rightharpoonup \psi_0$
- Also: $\|\psi_0\|_2 = \sup_{\substack{\|\varphi\|=1 \\ \varphi \in L^2}} \left[\langle \varphi, \psi_{j_k}\rangle + \langle \varphi, \psi_0 - \psi_{j_k}\rangle\right] \leq \|\psi_{j_k}\|_2 + \varepsilon$
  so that $\|\psi_0\|_2 \leq 1$
- Finally, $\psi \mapsto V(\psi)$ is weakly lower semi-continuous and $\psi \mapsto T(\psi)$ as well (needs a bit of additional work)
  $\Rightarrow E_0 = \lim_{k\to\infty} E(\psi_{j_k}) \geq E(\psi_0) \geq E_0 \|\psi_0\|^2$

and $\psi_0$ is the minimizer $\sqcap$ $\|\psi_0\| = 1$. But

$$0 > \underset{\text{assumption}}{E_0} \geq \mathcal{E}(\psi_0) \geq E_0 \|\psi_0\|^2$$

$$\text{i.e.} \quad 1 \leq \|\psi_0\|^2 \overset{\text{seen above}}{\leq} 1 \quad \Rightarrow \quad \|\psi_0\|^2 = 1$$

To prove (iii): $\varphi \in C_c^\infty(\mathbb{R}^3)$ and $\psi^\varepsilon := \psi_0 + \varepsilon\varphi$

$$R(\varepsilon) := \frac{\mathcal{E}(\psi^\varepsilon)}{\|\psi^\varepsilon\|^2}$$

is differentiable in $\varepsilon$ (ratio of two polynomials of order 2) and has a minimum at $\varepsilon = 0$, hence $R'(0) = 0$, i.e.

$$\frac{d\mathcal{E}(\psi^\varepsilon)}{d\varepsilon}\bigg|_{\varepsilon=0} - \frac{\mathcal{E}(\psi^\varepsilon)}{\|\psi^\varepsilon\|^2} \, \frac{d(\|\psi^\varepsilon\|^2)}{d\varepsilon}\bigg|_{\varepsilon=0} = 0 \qquad (*)$$

i.e. $*$ $\frac{1}{\varepsilon}\left[\int |\nabla(\psi_0 + \varepsilon\varphi)|^2 + \int V|\psi_0 + \varepsilon\varphi|^2\right]$

$$\to \int \left(\overline{\nabla\varphi}\, \nabla\psi_0 + \overline{\nabla\psi_0}\, \nabla\varphi + V\psi_0\bar{\varphi} + V\bar{\psi}_0\varphi\right)$$

$*$ $\frac{1}{\varepsilon}\langle \psi_0 + \varepsilon\varphi, \psi_0 + \varepsilon\varphi\rangle \to \int \bar{\varphi}\psi_0 + \bar{\psi}_0\varphi$

so that $(*)$ reads

$$\int \left(\overline{\nabla\varphi}\, \nabla\psi_0 + V\bar{\varphi}\psi_0\right) - E_0 \int \bar{\varphi}\psi_0 = 0,$$

namely

$$\langle (-\Delta + V)\varphi, \psi_0\rangle = E_0 \langle \varphi, \psi\rangle$$

$$\forall \varphi \in C_c^\infty(\mathbb{R}^3) \qquad \square$$

- What about "excited states"?
  ↳ they can also be defined by a variational approach.

Assuming $E_0 > -\infty$ and $E_0 = E(\psi_0)$, then we can minimize $E(\psi)$ over all $\psi \in H^1$, $\|\psi\|_2 = 1$ that are orthogonal to the ground state, $\langle \psi, \psi_0 \rangle_{L^2} = 0$. Recursively if the first $k$ eigenfunctions exist $\psi_0, \dots, \psi_{k-1}$, then

$$E_k := \inf \left\{ E(\psi) : \psi \in H^1(\mathbb{R}^3),\ \|\psi\|_2 = 1 \text{ and } \langle \psi, \psi_i \rangle = 0 \quad 0 \le i \le k-1 \right\}$$

and the $(k+1)^{\text{th}}$ eigenstate, if it exists, is $E_k = E(\psi_k)$.

**Theorem**: Let $V \in L^{3/2} + L^\infty$ and

$$|\{x : |V(x)| > a\}| < \infty \quad \forall a > 0$$

Assume that $E_k < 0$. Then $\psi_k$ exists and

$$(-\Delta + V)\psi_k = E_k \psi_k$$

in the sense of distributions.

i.e. $\forall \varphi \in C_c^\infty(\mathbb{R}^3)$:

$$\int \Big( (-\Delta + V(x))\varphi(x) \Big) \psi_k(x)\,dx = E_k \int \varphi(x) \psi_k(x)\,dx.$$

Note: if $E_0 < 0$ (as in the previous theorem), then the recursion does not stop until $E_k$ reaches $0$.
(and there is no general result about the case $E_k = 0$)

Proof: * Existence: As above, with a minimizing sequence $\psi_k^j$, $j \in \mathbb{N}$: $E(\psi_k^j) \to E_k$ $(j \to \infty)$.
and $\langle \psi_k^j, \psi_i \rangle = 0 \quad 0 \le i \le k-1$.
$\leadsto$ convergent subsequence in $H^1$ with weak limit $\psi_k$.

(71)

and similarly $E(\psi_h) = E_h$, $\|\psi_h\|_2 = 1$

By weak convergence and the fact that $H^1(\mathbb{R}^3)$ is its own dual since it is a Hilbert space:

$\langle \varphi, \psi_h^l \rangle \to \langle \varphi, \psi_h \rangle \quad \forall \varphi \in H^1(\mathbb{R}^3)$

so that $\langle \psi_i, \psi_h \rangle = 0 \quad 0 \leq i \leq h-1$.

* Eigenvalue equation. Variation as before, with $\psi^\varepsilon = \psi_h + \varepsilon\varphi$

with $\langle \varphi, \psi_i \rangle = 0 \quad \forall\ 0 \leq i \leq h-1$ and $E(\psi^\varepsilon)|_{\varepsilon=0} = E_h$, yields:

$$\langle (-\Delta + V - E_h)\varphi, \psi_h \rangle = 0$$

for all $\varphi \in C_c^\infty(\mathbb{R}^3)$ s.t. $\langle \varphi, \psi_i \rangle = 0 \quad 0 \leq i \leq h-1$.

Hence, $(-\Delta + V - E_h)\psi_h$, seen as a distribution, must be a linear combination of the $\psi_i$:

$$(-\Delta + V - E_h)\psi_h = \sum_{i=0}^{h-1} a_i \psi_i$$

namely, for a sequence $\psi_j^\alpha$, $\alpha \in \mathbb{N}$: $\psi_j^\alpha \to \psi_j$ in $H^1$:

$$\int \underbrace{(-\Delta + V - E_h)\overline{\psi_j^\alpha}(x)\,\psi_h(x)} = \sum_{i=0}^{h-1} a_i \underbrace{\int \overline{\psi_j^\alpha}(x)\,\psi_i(x)\,dx}$$

$$\to \int \overline{\nabla\psi_j}\,\nabla\psi_h + V\overline{\psi_j}\psi_h - E_j\delta_{jh} \qquad \longrightarrow a_j$$

$= E_j\delta_{jh} - E_j\delta_{jh}$ by the eigenvalue eq for $\psi_j$

Hence $a_j = 0$ for all $0 \leq j \leq h-1$

and $(-\Delta + V - E_h)\psi_h = 0$ as a distribution. $\square$