Stability of Matter, part 2.

3. Hydrogen atom
4. Uncertainty principle

3. Hydrogen atom

Let us now discuss the most basic example: the hydrogen atom:

$$\mathcal{E}(\psi) = \int_{\mathbb{R}^3} \left(\frac{\hbar^2}{2m} |\nabla\psi|^2 - \frac{Ze^2}{|x|} |\psi(x)|^2 \right) dx$$

change of units

$$\boxed{\mathcal{E}(\psi) = \int_{\mathbb{R}^3} \left(\frac{1}{2} |\nabla\psi|^2 - \frac{Z\alpha}{|x|} |\psi(x)|^2 \right) dx}$$

$\alpha = \frac{e^2}{\hbar c} \cong \frac{1}{137{,}04}$ fine-structure constant.

Two standard ways stability of hydrogen is addressed in QM course.

•) <u>direct computation</u>
→ computation of all eigenvalues by separation of variables. It is merely mentioned why the computed e.v. are giving the whole discrete spectrum.

→ easier direct way of showing stability: finding <u>one</u> special solution to the e.v. problem

$$\varphi(x) = C \exp(-Z_\alpha |x|) \quad , \quad C > 0.$$

Then

- $\varphi(x) > 0$
- $$\left(-\frac{\Delta}{2} - \frac{Z_\alpha}{|x|}\right)\varphi(x) = -\frac{(Z_\alpha)^2}{2}\varphi(x)$$

Since $\varphi(x)$ is an eigenfunction that is positive, it corresponds to the lowest eigenvalue !

This last statement is a Theorem [Lieb-Loss, Analysis, Thm. 11.9] which is based on the fact that

$$|\nabla f| \geq |\nabla |f|| \quad \text{for} \quad f \in H^1(\mathbb{R}^3)$$

complex valued.

- <u>using Heisenberg's uncertainty principle</u> $\boxed{\text{WRONG!}}$

$$\langle \varphi, x^2 \varphi \rangle \langle \varphi, -\Delta \varphi \rangle \geq \frac{\hbar^2 d^2}{4} \underset{\hbar=1,\, d=3}{=} \frac{9}{4}$$

$$\Downarrow$$

$$\left(\int_{\mathbb{R}^3} |\nabla \varphi|^2 dx\right)\left(\int_{\mathbb{R}^3} x^2 |\varphi(x)|^2 dx\right) \geq \frac{9}{4}$$

This implies $\quad \mathcal{E}(\varphi) = T_\varphi - \left\langle \frac{Z}{|x|} \right\rangle_\varphi \geq \frac{c_1}{\langle x^2 \rangle_\varphi} - \frac{Z}{\langle |x| \rangle_\varphi}$

One then often makes the assumption that

$$\frac{1}{\langle x^2\rangle_\varphi} \approx \left\langle \frac{1}{|x|}\right\rangle_\varphi^2$$

$$\Rightarrow \quad \mathcal{E}(\varphi) \geq c_1 \left\langle \frac{1}{|x|}\right\rangle_\varphi^2 - c_2 \left\langle \frac{1}{|x|}\right\rangle_\varphi \geq -C$$

This argument is false!
To see this it is enough to consider

$\varphi = \varphi_1 + \varphi_2$ orthogonal to each other

$\rightsquigarrow$ density distributions $\rho(x) = \frac{1}{2}\left(\rho_1(x) + \rho_2(x)\right)$

$$\left\langle \frac{1}{|x|}\right\rangle_\rho = \frac{1}{2}\left[\left\langle \frac{1}{|x|}\right\rangle_{\rho_1} + \left\langle \frac{1}{|x|}\right\rangle_{\rho_2}\right]$$

$$\frac{1}{\langle x^2\rangle_\rho} = \frac{2}{\langle x^2\rangle_{\rho_1} + \langle x^2\rangle_{\rho_2}}$$

localized close to origin

now choose $\left\langle \frac{1}{|x|}\right\rangle_{\rho_1} \to \alpha \qquad \langle x^2\rangle_{\rho_1} \to 0$

$\left\langle \frac{1}{|x|}\right\rangle_{\rho_2} = \frac{1}{L} \qquad \langle x^2\rangle_{\rho_2} = L^2$

localized at narrow shell

$\left(\rho_1 \sim c_1 e^{-\alpha r}_{\alpha\to\infty},\ \rho_2 \sim c_2 e^{-\beta r}\right)$

then $\mathcal{E}(\varphi) \to -\infty$

$\lightning$

4. Uncertainty principle

$$\boxed{\text{uncertainty principle} \equiv \text{domination of potential energy by kinetic energy}}$$

we have already seen one example: Heisenberg's.
Also from the explicit solution of the hydrogen atom we can deduce the so called

Coulomb uncertainty principle

$$\int_{\mathbb{R}^3} |\nabla\psi(x)|^2 dx \int_{\mathbb{R}^3} |\psi(x)|^2 dx \geq \left[\int_{\mathbb{R}^3} \frac{|\psi(x)|^2}{|x|} dx \right]^2$$

[take $Z\alpha = \left(\int |\psi|^2\right)^{-1} \int \frac{|\psi|^2}{x}$ in hydrogen lower bound]

But what about more general potentials?
To this end let us introduce the

Sobolev space

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

$s \geq 0$ (not necessarily integer)

$$\langle u, v \rangle_{H^s} = \int_{\mathbb{R}^d} \overline{\hat{u}(k)}\, \hat{v}(k) \left(1 + |2\pi k|^{2s}\right) dk$$

On $H^s(\mathbb{R}^d)$, weak derivatives can be defined via FT:

$$\widehat{D^\alpha u}(k) = (2\pi i k)^\alpha \hat{u}(k) \in L^2(\mathbb{R}^d)$$

for any $\alpha = (\alpha_1, \alpha_2, \dots, \alpha_d) \in \{0, 1, \dots\}^d$
with $|\alpha| = \alpha_1 + \dots + \alpha_d \leq s$

In particular

$$\langle u, (-\Delta)^s u \rangle_{L^2(\mathbb{R}^d)} = \| (-\Delta)^{s/2} u \|^2_{L^2(\mathbb{R}^d)} =$$

$$= \int_{\mathbb{R}^d} |2\pi k|^{2s} \, |\hat{u}(k)|^2 \, dk$$

$\forall u \in H^s(\mathbb{R}^d)$

fractional Laplacian

Theorem (Sobolev inequality)

If $d > 2s \geq 0$, then $\forall f \in H^s(\mathbb{R}^d)$

$$\boxed{\| f \|_{L^{\frac{2d}{d-2s}}(\mathbb{R}^d)} \leq C_{d,s} \, \| (-\Delta)^{s/2} f \|_{L^2(\mathbb{R}^d)}}$$

Proof:

- we use the "layer cake representation":

for $f \geq 0$:

$$f(x) = \int_0^\infty 1\!\!1_{L(f,t)}(x) \, dt \qquad (*)$$

where $L(f,t) = \{ y \in \Omega \mid f(y) \geq t \}$.

Indeed, $(*)$ follows from the observation that
$1\!\!1_{L(f,t)}(x) = 1\!\!1_{[0, f(x)]}(t) \Rightarrow f(x) = \int_0^{f(x)} dt$

•) important consequence of (*) is

$$\int_\Omega f(x)\, d\mu(x) = \int_0^\infty \mu(\{x \in \Omega \mid f(x) > t\})\, dt$$

and

$$\int_\Omega |f(x)|^p\, d\mu(x) = p \int_0^\infty s^{p-1} \mu(\{x : |f(x)| > s\})\, ds$$

•) back to Sobolev. By layer cake:

$$|2\pi k|^s = \int_0^\infty 1\!\!1(|2\pi k|^s > E)\, dE$$

Take $u \in H^s(\mathbb{R}^d)$. We write:

$$K := \|(-\Delta)^{s/2} u\|^2_{L^2(\mathbb{R}^d)} = \int_{\mathbb{R}^3} |2\pi k|^{2s} |\hat{u}(k)|^2\, dk$$

$$= \int_{\mathbb{R}^3} \left(\int_0^\infty 1\!\!1(|2\pi k|^{2s} > E)\, |\hat{u}(k)|^2\, dE \right) dk$$

$$= \int_0^\infty \left(\int_{\mathbb{R}^3} 1\!\!1(|2\pi k|^{2s} > E)\, |\hat{u}(k)|^2\, dk \right) dE$$

$$= \int_0^\infty \left(\int_{\mathbb{R}^3} |\hat{u}^{E_+}(k)|^2\, dk \right) dE = \int_0^\infty \left(\int_{\mathbb{R}^3} |u^{E_+}(x)|^2\, dx \right) dE$$

$$= \int_{\mathbb{R}^3} \left(\int_0^\infty |u^{E_+}(x)|^2\, dE \right) dx \qquad (*)$$

where the function u^{E_+} is defined via FT

$$\hat{u}^{E_+}(k) = 1\!\!1(|2\pi k|^{2s} > E)\, \hat{u}(k).$$

We estimate:

$$|u(x) - u^{E_+}(x)| = \left|\int_{\mathbb{R}^d} e^{2\pi i k\cdot x} \left(\hat{u}(k) - \hat{u}^{E_+}(k)\right) dk\right|$$

$$= \left|\int_{\mathbb{R}^d} e^{2\pi i k\cdot x} \frac{\cdot|2\pi k|^s}{|2\pi k|^s} \mathbb{1}\left(|2\pi k|^{2s} \le E\right) \hat{u}(k)\, dk\right|$$

$$\overset{CS}{\le} \Big(\underbrace{\int_{\mathbb{R}^d} |2\pi k|^{2s} |\hat{u}(k)|^2 dk}_{K}\Big)^{1/2} \left(\int_{\mathbb{R}^d} \frac{\mathbb{1}(|2\pi k|^{2s} \le E)}{|2\pi k|^{2s}} dk\right)^{\frac{1}{2}}$$

$$= C\sqrt{K}\, E^{(d-2s)/4s}$$

when $d > 2s$, $C = C(d,s)$

By triangle inequality

$$|u^{E_+}(x)| \ge \Big|\,|u(x)| - |u(x) - u^{E_+}(x)|\,\Big| \ge$$

$$\ge \left[|u(x)| - C\sqrt{K}\, E^{\frac{d-2s}{4s}}\right]_+$$

where $t_+ = \max\{t, 0\}$ is the positive part of t.

Integrating over E we get

$$\int_0^\infty |u^{E_+}(x)|^2 dE \ge \int_0^\infty \underbrace{\left[|u(x)| - C\sqrt{K}\, E^{\frac{d-2s}{4s}}\right]_+^2}\, dE$$

$$\Rightarrow C E^{\frac{d-2s}{4s}} \sqrt{K} \le |u(x)|$$

$$\Rightarrow E \le c\,|u(x)|^{\frac{4s}{d-2s}} K^{\frac{-2s}{d-2s}}$$

$$\ge \int_0^{c|u(x)|^{\frac{4s}{d-2s}} K^{\frac{-2s}{d-2s}}} |u(x)|^2 dE = C\, |u(x)|^{\frac{2d}{d-2s}} K^{\frac{-2s}{d-2s}}$$

$$\overset{(*)}{\Longrightarrow} K \ge C K^{\frac{-2s}{d-2s}} \int_{\mathbb{R}^d} |u(x)|^{\frac{2d}{d-2s}} dx \Longrightarrow \text{tada} \quad \blacksquare$$

We will now prove another inequality that will be used later. We do it now since the method of proof is analogous.

Theorem (Lieb - Thirring kinetic inequality)

Let $d > 2\kappa \geq 0$ and $s \geq 0$ (κ, s are not necessarily integers). For any $N \geq 1$, let $\{(-\Delta)^{\kappa/2} u_n\}_{n=1}^{N}$ be orthonormal functions in $L^2(\mathbb{R}^d)$ and denote $\rho(x) = \sum_{n=1}^{\infty} |u_n(x)|^2$.

Then

$$\boxed{\sum_{n=1}^{N} \|(-\Delta)^{s/2} u_n\|^2_{L^2(\mathbb{R}^d)} \geq K_{d,s,\kappa} \int_{\mathbb{R}^d} \rho(x)^{1+\frac{2s}{d-2\kappa}} dx.}$$

The constant $K_{d,s,\kappa}$ is independent of N and $\{u_n\}$.

Proof Exactly as in the previous proof (*) we have

$$\sum_{n=1}^{N} \|(-\Delta)^{s/2} u_n\|^2_{L^2(\mathbb{R}^d)} = \int_{\mathbb{R}^d} \left(\int_0^{\infty} \sum_{n=1}^{N} |u_n^{E+}(x)|^2 dE \right) dx$$

where

$$\hat{u}_n^{E+}(k) = \mathbb{1}(|2\pi k|^{2s} > E)\, \hat{u}_n(k).$$

Now we use that $\{(-\Delta)^{\kappa/2} u_n\}_{n=1}^{N}$ are orthonormal. This implies

$$\{|2\pi k|^{\kappa} \hat{u}_n(k)\}_{n=1}^{N} \text{ are orthonormal in } L^2(\mathbb{R}^d, dk).$$

Hence, by Bessel's inequality $\left(\sum_k |\langle x, e_k \rangle|^2 \le \|x\|^2\right)$

$$\sum_{n=1}^{\infty} |u_n(x) - u_n^{E+}(x)|^2 = \sum_{n=1}^{\infty} \left| \int_{\mathbb{R}^d} e^{2\pi i k x} \mathbb{1}(|2\pi k|^{2s} \le E)\, \hat{u}_n(k)\, dk \right|^2$$

$$= \sum_{n=1}^{N} \left| \int_{\mathbb{R}^d} e^{2\pi i k x} \frac{\mathbb{1}(|2\pi k|^{2s} \le E)}{|2\pi k|^k} |2\pi k|^k \hat{u}_n(k)\, dk \right|^2$$

$$\le \left\| e^{2\pi i k x} \frac{\mathbb{1}(|2\pi k|^{2s} \le E)}{|2\pi k|^k} \right\|^2_{L^2(\mathbb{R}^d, dk)} = C E^{\frac{d-2k}{2s}}.$$

Here $C = C(d,k) \ge 0$ is finite when $d > 2k$

Next, by triangle inequality for $\mathbb{C}^N$ vectors

$$\left(\sum_{n=1}^{N} |u_n^{E+}(x)|^2\right)^{1/2} \ge \left(\sum_{n=1}^{N} |u_n(x)|^2\right)^{1/2} - \left(\sum_{n=1}^{N} |u_n(x) - u_n^{E+}(x)|^2\right)^{1/2} \ge$$

$$\ge \left[\sqrt{\rho(x)} - C E^{\frac{d-2k}{4s}}\right]_+.$$

Consequently,

$$\int_0^{\infty} \sum_{n=1}^{N} |u_n^{E+}(x)|^2\, dE \ge \int_0^{\infty} \left(\left[\sqrt{\rho(x)} - C E^{\frac{d-2k}{4s}}\right]_+ \right)^2 dE$$

$$\ge C \rho(x)^{1 + \frac{2s}{d-2k}}$$

$\blacksquare$