5.2 Stability of matter

The Hilbert space for the electron is $\mathcal{H} = L^2(\mathbb{R}^3)$ and the Hamiltonian is

$$H = -\frac{\hbar^2}{2m}\Delta - \frac{e^2}{\|x\|}.$$

That is, the proton is located at the origin and the interaction between proton and electron is Coulomb.

The first question is why H should be bounded below? That is, $(\Psi, H\Psi)$ cannot be arbitrarily negative. This is the simplest question of the more general problem of stability of matter. There are several ways to prove a lower bound for H, and we consider two of them. One is an operator inequality for $-\Delta$. The other is a Sobolev inequality.

Proposition 5.1 Let $\mathcal{H} = L^2(\mathbb{R}^d)$ with $d \geq 3$. Then

$$-\Delta \geq \frac{(d-2)^2}{4\|x\|^2}.$$

In other words, we have $\int_{\mathbb{R}^d} \|\nabla f\|^2 \geq \frac{(d-2)^2}{4}\int_{\mathbb{R}^d} \frac{1}{\|x\|^2}|f(x)|^2 dx$ for all f in a dense subspace of $L^2(\mathbb{R}^d)$. Here, the notation means

$$\|\nabla f\|^2 = \sum_{j=1}^d \left|\frac{\partial f}{\partial x_j}(x)\right|^2.$$

Proof: Recall that $P_j = -i\frac{\partial}{\partial x_j}$ and that it is self-adjoint. Using $\frac{\partial}{\partial x_j}\frac{1}{\|x\|} = -\frac{x_j}{\|x\|^3}$, one can check that

$$\frac{1}{\|x\|^2} = \frac{i}{d}\sum_{j=1}^d \left[\frac{1}{\|x\|}P_j\frac{1}{\|x\|}, X_j\right].$$

It follows that

$$\left(f, \frac{1}{\|x\|^2}f\right) = -\frac{2}{d}\sum_{j=1}^d \operatorname{Im}\left(\frac{1}{\|x\|}P_j\frac{1}{\|x\|}f, X_j f\right).$$

Next, consider the identity

$$P_j\frac{1}{\|x\|} = \frac{1}{\|x\|}P_j + \left[P_j, \frac{1}{\|x\|}\right] = \frac{1}{\|x\|}P_j + i\frac{x_j}{\|x\|^3}.$$

~~A few calculations show that~~ Then

$$\left(\frac{1}{\|x\|}P_j\frac{1}{\|x\|}f, X_j f\right) = \left(P_j f, \frac{x_j}{\|x\|^2}f\right) - i\left(f, \frac{x_j^2}{\|x\|^4}f\right).$$

Summing over $j=1,\dots,d$, we get

$$(d-2)\left(f, \frac{1}{\|x\|^2}f\right) = -2\operatorname{Im}\sum_{j=1}^d\left(P_j f, \frac{x_j}{\|x\|^2}f\right).$$

Then

$$\begin{aligned}
\frac{(d-2)^2}{4}\left|\left(f, \frac{1}{\|x\|^2}f\right)\right|^2 &= \left|\operatorname{Im}\sum_{j=1}^d\left(P_j f, \frac{x_j}{\|x\|^2}f\right)\right|^2 \\
&\leq \left|\sum_{j=1}^d\left(P_j f, \frac{x_j}{\|x\|^2}f\right)\right|^2 \\
&\overset{\text{Cauchy-Schwarz}}{\leq} \left(\sum_{j=1}^d (P_j f, P_j f)\right)\left(\sum_{j=1}^d\left(\frac{x_j}{\|x\|^2}f, \frac{x_j}{\|x\|^2}f\right)\right) \\
&= \Big(f, \underbrace{\sum_{j=1}^d P_j^2}_{-\Delta} f\Big)\left(f, \sum_{j=1}^d\frac{x_j^2}{\|x\|^4}f\right) \\
&= (f, -\Delta f)\left(f, \frac{1}{\|x\|^2}f\right).
\end{aligned}$$

$\square$

From Proposition 5.1 we immediately obtain a lower bound for H:

$$(\psi, H\psi) \geq \Big(\psi, \underbrace{\Big(\frac{\hbar^2}{8m}\frac{1}{\|x\|^2} - \frac{e^2}{\|x\|}\Big)}_{\geq -\frac{2me^4}{\hbar^2}} \psi\Big) \geq -\frac{2me^4}{\hbar^2}.$$

This lower bound is ~~four~~ eight times too negative.

The second method uses a variational principle.

__Exercise 11.__ Consider the functional

$$\mathcal{E}(\psi) = \int_{\mathbb{R}^d} \left(\|\nabla\psi\|^2 + V|\psi|^2 \right) dx$$

Assume that $\mathcal{E}(\psi)$ has a unique minimiser in $\{\psi \in H^1 : \|\psi\| = 1\}$ and that it belongs to $H^2(\mathbb{R}^d)$. Show that it is eigenvector of the Hamiltonian $H = -\Delta + V$ with the lowest eigenvalue.

Hint: $\frac{d}{d\eta}\mathcal{E}(f+\eta h)\Big|_{\eta=0} = 2\,\mathrm{Re}\int(-\Delta f + Vf)\bar{h}$, and this is zero $\forall\, h \perp f$, if f is the minimiser.

It is clear that, if $H = -\Delta + V$, we have $(\psi, H\psi) = \mathcal{E}(\psi)$. We therefore seek a lower bound for $\mathcal{E}(\psi)$. We use a Sobolev inequality.

__Theorem 5.2__ (Sobolev inequality for gradients)
Let $d \geq 3$, and let $q = \frac{2d}{d-2}$. Then any $f \in L^q(\mathbb{R}^d)$ such that ∇f exists and is in $L^2(\mathbb{R}^d)$ satisfies

$$\|\nabla f\|_2^2 \geq S_d \|f\|_q^2$$

where $S_d = \frac{d(d-2)}{4}|S^d|^{\frac{2}{d}} = \frac{d(d-2)}{4}\, 2^{\frac{2}{d}}\, \pi^{1+\frac{1}{d}}\, \Gamma\!\left(\frac{d+1}{2}\right)^{-\frac{2}{d}}$.

For the proof, see [Lieb-Loss, Analysis, Theorem 8.3]. Notice that when $d=3$, we have $q=6$ and $S_3 = 3\left(\frac{\pi}{2}\right)^{\frac{4}{3}}$.

For the hydrogen atom, we get from Theorem 5.2 that

$$\mathcal{E}(\psi) = \int_{\mathbb{R}^3}\left(\|\nabla\psi\|^2 - \frac{1}{\|x\|}|\psi|^2\right) \geq 3\left(\frac{\pi}{2}\right)^{\frac{4}{3}}\|\psi\|_6^2 - \int_{\mathbb{R}^3}\frac{1}{\|x\|}|\psi(x)|^2\,dx.$$

Let $\rho(x) = |\psi(x)|^2$. Then

$$\mathcal{E}(\psi) \geq \inf_{\rho\geq 0,\ \int\rho = 1}\left[3\left(\frac{\pi}{2}\right)^{\frac{4}{3}}\|\rho\|_3 - \int_{\mathbb{R}^3}\frac{1}{\|x\|}\rho(x)\,dx\right].$$

The minimisation problem "is an easy exercise" [Lieb "The Stability of Matter: From Atoms to Stars", 1989 Gibbs Lecture] and one finds $\mathcal{E}(\psi) \geq -\frac{1}{3}$. This is very good since the infimum of $(\psi, H\psi) = \mathcal{E}(\psi)$ is $-\frac{1}{4}$.