11.2. Harmonic oscillator

Consider arbitrary $d \geq 1$ and the potential $V(x) := \frac{\omega^2}{2} x^2$ with $\omega > 0$. Since $V \geq 0$ and $|V(x)| \leq \frac{\omega^2}{2} R^2$ for $|x| \leq R$, we can apply Theorem 10.5. to define a self-adjoint operator H on $L^2(\mathbb{R}^d)$: $H = "(H_0 + V)_{dist}"$.

Suppose then that $\lambda_j \in \mathbb{C}$ and $\psi_j \in C^{(2)}(\mathbb{R})$, $j = 1, \dots, d$, each solve the differential equation

$$-\frac{1}{2}\psi_j''(y) + \frac{\omega^2}{2} y^2 \psi_j(y) = \lambda_j \psi_j(y) \quad \forall y \in \mathbb{R}, \; j = 1, \dots, d.$$

Define $\psi(x) := \prod_{j=1}^{d} \psi_j(x_j)$

$$\Rightarrow -\frac{1}{2}\nabla^2 \psi(x) = -\frac{1}{2} \sum_{i=1}^{d} \partial_{x_i}^2 \Big(\prod_{j=1}^{d} \psi_j(x_j) \Big)$$

$$= \sum_{i=1}^{d} \prod_{j \neq i} \psi_j(x_j) \cdot \underbrace{\Big(-\frac{1}{2}\psi_i''(x_i)\Big)}_{= (\lambda_i - \frac{\omega^2}{2} x_i^2)\psi_i(x_i)}$$

$$= \sum_{i=1}^{d} \Big(\lambda_i - \frac{\omega^2}{2} x_i^2\Big) \psi(x) = \sum_{i=1}^{d} \lambda_i \cdot \psi(x) - \frac{\omega^2}{2} x^2 \psi(x)$$

$$\Rightarrow -\frac{1}{2}\nabla^2 \psi(x) + \frac{\omega^2}{2} x^2 \psi(x) = \lambda \psi(x) \quad \forall x \in \mathbb{R}^d$$

where $\lambda := \sum_{i=1}^{d} \lambda_i$. If, in addition, each $\psi_j \in L^2(\mathbb{R})$ with $\|\psi_j\| = 1$, then $\int_{\mathbb{R}^d} dx \, |\psi(x)|^2 = \prod_{j=1}^{d} \Big(\int dy \, |\psi_j(y)|^2 \Big) = 1 \Rightarrow \psi \in L^2(\mathbb{R}^d)$ and $\|\psi\| = 1$. Moreover,

$\psi \in C(\mathbb{R}^d)$ and thus $V\psi \in L^1_{loc}$ and, if $f \in \mathcal{D}(\mathbb{R}^d)$ with support contained in the box $|x_j| \leq R \; \forall j = 1, \dots, d$,

$$\Rightarrow (\nabla^2 f, \psi) = \sum_{j=1}^{d} \int_{[-R,R]^d} dx \, \big(\partial_{x_j}^2 f|_x\big)^* \psi(x) \overset{\text{Fubini \& partial integration}}{=} \sum_{j=1}^{d} \int_{[-R,R]^{d-1}} d\hat{x}$$

$$\times \Big[\underbrace{\int_{-R}^{R} \partial_{x_j} f|_x^* \, \psi(x)}_{=0} - \int_{-R}^{R} dx_j \, \partial_{x_j} f|_x^* \, \partial_{x_j} \psi(x) \Big]\Big|_{x = \hat{x} + x_j \hat{e}_j}$$

$$= \int_{[-R,R]^d} dx \, f(x)^* \nabla^2 \psi(x) = (f, \nabla^2 \psi)$$

$$\Rightarrow (-\tfrac{1}{2}\Delta f, \psi) = (f, -\tfrac{1}{2}\Delta\psi) = \int dx\, f(x)^* \left(\lambda\psi(x) - (V\psi)(x)\right)$$
$$= (f, \lambda\psi) - \int dx\, f(x)^* (V\psi)(x)$$
$$\psi \in L^2$$

Hence by Thm 10.5. then $\psi \in D(H)$ and $H_0\psi = \lambda\psi$.
$\Rightarrow \psi$ is an eigenvector of H with eigenvalue λ.

Proposition: The solutions to equation

$$-\tfrac{1}{2}\psi''(x) + \tfrac{1}{2}\omega^2 x^2 \psi(x) = \lambda\psi(x), \quad x \in \mathbb{R}$$

with $\lambda \in \mathbb{C}$ and $\psi \in C^{(2)}(\mathbb{R}) \cap L^2(\mathbb{R})$ are given by $\lambda = \lambda_n$, $\psi = C\psi_n$, $n = 0, 1, 2, \ldots$, $C \in \mathbb{C}$, where

$$\lambda_n := \omega\left(n + \tfrac{1}{2}\right) > 0 \quad \text{and}$$

$$\psi_n(x) := \frac{1}{\sqrt{n!\, 2^n}} \left(\frac{\omega}{\pi}\right)^{\frac{1}{4}} e^{-\frac{\omega}{2}x^2} H_n(\omega^{\frac{1}{2}} x), \quad x \in \mathbb{R},$$

and H_n denotes the n:th Hermite polynomial satisfying

$$H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n} e^{-x^2}.$$

In addition, $\|\psi_n\|_{L^2} = 1$, and $(\psi_n)_{n \in \mathbb{N}_0}$ forms an ONB for $L^2(\mathbb{R})$.

Proof: Parts of it can be found in any QM textbook. For mathematical details see e.g. Teschl Sec. 9.2. Completeness of $(H_n)_n$ is outlined e.g. on p. 121, problem 7, of Reed & Simon II. $\square$

* Since (ψ_n) forms an ONB for $L^2(\mathbb{R})$, by the Proposition on p. 24, the functions $\psi_{\bar{n}} := \prod_{i=1}^{d} \psi_{n_i}(x_i)$, $\bar{n} \in \mathbb{N}_0^d$, form an ONB for $\bigotimes_{i=1}^{d} L^2_i(\mathbb{R}) \cong L^2(\mathbb{R}^d)$. Defining $\lambda_{\bar{n}} := \sum_{i=1}^{d} \lambda_{n_i} = \omega\left(\frac{d}{2} + \sum_{i=1}^{d} n_i\right) \in \mathbb{R}$, one can rely on uniqueness of the spectral representation to conclude that $\sigma(H) = \bigcup_{n \in \mathbb{N}_0^d} \{\lambda_{\bar{n}}\}$, and $\inf \sigma(H) = \frac{\omega d}{2} > 0$, non-degenerate eigenv.

11,3, Example : Hydrogen atom

Consider $d=3$ and $V(x) = -\frac{\gamma}{|x|}$, for $\gamma > 0$.

(For a specific choice of constants this corresponds to movement of electron around the proton in a hydrogen atom. The proton is assumed to be at $x=0$, which is also an approximation: proton is treated classically, and we are in the "comoving" coordinate system. ($x = \underline{x}_{\text{electron}} - \underline{x}_{\text{proton}}$, $\underline{x} \in \mathbb{R}^3$ denoting positions in the "laboratory frame".) Then $\gamma = \alpha_{\text{fine}} \approx 7{,}3 \cdot 10^{-3}$.)

Here $V = V_{\leq} + V_{>}$ with $V_{\leq}(x) := -\frac{\gamma}{|x|} \mathbb{1}(|x| \leq 1)$

and $V_{>}(x) := -\frac{\gamma}{|x|} \mathbb{1}(|x| > 1)$. Now $|V_{>}(x)| \leq \gamma < \infty$

and $\int_{\mathbb{R}^3} dx\, |V_{\leq}(x)|^2 = \int_0^\infty dr\, r^2 \frac{\gamma^2}{r^2} \mathbb{1}(r \leq 1) \cdot 4\pi$

$= 4\pi\gamma^2 \int_0^1 dr < \infty. \Rightarrow V_{>} \in L^\infty$, $V_{\leq} \in L^2$.

Thus by Kato-Rellich theorem $H_c = H_0 + V$ is self-adjoint on $D(H_0)$.

The following results are computed in most QM textbooks and mathematically derived in Teschl's book, chapter 10. (Thm. 10.9.)

* $\sigma(H_c) = \sigma_p \cup \sigma_0$, were σ_p collects all eigenvalues of H which have a finite eigenspace and $\sigma_0 := \sigma(H_c) \setminus \sigma_p$

Here $\sigma_0 = [0, \infty)$ and $\sigma_p = \bigcup_{n=0}^{\infty} \{+E_n\}$

where $E_n := -\left(\frac{\gamma}{n+1}\right)^2$, $n = 0, 1, \ldots$

$\Rightarrow E_0 < E_1 < \cdots < E_n < \cdots < 0$ and $E_n \not\to 0$ as $n \to \infty$.
The eigenspace is parametrized by spherical harmonics Y_ℓ^m, $|m| \leq \ell \leq n$ $\Rightarrow$ has $\dim = (n+1)^2$.

11.4. Kato's theorem and Molecular Hamiltonians

Consider a system of N electrons (treated quantum mechanically) moving between M nuclei (at static positions). The charge of any one electron is $-q_e$, $q_e > 0$, and the nucleus with label j is assumed to be at position $\bar{R}_j \in \mathbb{R}^3$ with a charge $+Z_j q_e$, $Z_j \in \mathbb{Z}$, and mass $M_j \times m_e > 0$. (m_e denotes the mass of electron, which in our units is scaled to $m_e = 1$.)

This approximation makes sense for crystalline solids for which the nuclei are always close to their "equilibrium positions" in the crystal structure. Since $M_j \gg 1$ (even for the lightest nucleus, Hydrogen, $M \approx 2000$), typically $\bar{R}_j$ are considered fixed.

The classical electromagnetic interaction potential of such a system is (in our units) $\alpha_{\text{fine}} V_C$ where

$$V_c(x; R) := W(x; R) + I(x) + U(R), \quad \begin{matrix} x \in (\mathbb{R}^3)^N, \\ R \in (\mathbb{R}^3)^M, \end{matrix}$$

with

$W(x;R)$ = electron-nucleus interaction potential

$$:= -\sum_{i=1}^{N} \sum_{j=1}^{M} \frac{Z_j}{|\bar{x}_i - \bar{R}_j|}$$

$I(x)$ = electron-electron interaction potential

$$:= \sum_{\substack{i',i=1 \\ i'<i}}^{N} \frac{1}{|\bar{x}_{i'} - \bar{x}_i|} \quad (= \text{sum over all e-e pairs})$$

$U(R)$ = nucleus-nucleus potential

$$:= \sum_{\substack{j',j=1 \\ j'<j}}^{M} \frac{Z_{j'} Z_j}{|\bar{R}_{j'} - \bar{R}_j|}$$