5. The Schrödinger equation and the direct method in the calculus of variations

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5.1. Introduction

In this section we discuss our first application of the techniques we have developed so far to the calculus of variations. Our object of study will be the time-independent Schrödinger equation that we introduce in the next subsection.

Let us give a basic example why it is necessary to prove the existence of a maximizer/minimizer of a variational problem. In the following we start with a wrong claim about the existence of a maximizer, which allows us to deduce an obviously wrong conclusion:

"Let N be the largest natural number. Since $N^2 \geq N$

and N is the largest natural number, $N^2 = N$ and hence $N = 1$."

The technique we are going to use to prove the existence of minimizers for our variational problems is called **the direct method in the calculus of variations.**

The general strategy is best explained by the example of minimizing a continuous function $f: \Omega \to \mathbb{R}$, where $\Omega \subset \mathbb{R}^n$ is a compact set. To prove the existence of a point $x \in \Omega$ s.t. $f(x) = \inf_{y \in \Omega} f(y)$, we argue as follows: (a) We start by noting that f is bounded.
(b) Next we pick a sequence $\{x_j\}_{j=1}^{\infty}$ with $x_j \in \Omega$ for all $j \in \mathbb{N}$ s.t. $\lim_{j \to \infty} f(x_j) = \inf_{y \in \Omega} f(y)$, which exists by the definition of the infimum. The sequence x_j has a convergent subsequence $x_{j_k} \to x \in \Omega$ because Ω is compact. Using the continuity of f, we thus find

$$\inf_{y\in\Omega} f(y) = \lim_{k\to\infty} f(x_{j_k}) = f(x), \qquad (1)$$

and the existence of a minimizer is proved.

Let us replace $\mathbb{R}^n$ in the above example by $L^2(\mathbb{R}^3)$ and let $\mathcal{F} : L^2(\mathbb{R}^n) \to \mathbb{R}$ be some functional. In many examples $\mathcal{F}$ is strongly continuous, i.e. $\mathcal{F}(\psi_j) \to \mathcal{F}(\psi)$ as $j \to \infty$ whenever $\|\psi_j - \psi\|_2 \to 0$ as $j \to \infty$. Suppose we wish to show that the infimum of $\mathcal{F}$ is attained on the set

$$K = \{ \psi \in L^2(\mathbb{R}^n) \mid \|\psi\|_2 \leq 1 \}. \qquad (2)$$

This set is certainly closed and bounded in the norm topology of $L^2(\mathbb{R}^n)$, but for a bounded sequence $\psi_j \in K$ there need not be a strongly convergent subsequence.

To get around this problem one can relax the strength of convergence. Indeed, if we use the notion of weak convergence instead of strong convergence, then every sequence in K has a weakly convergent subsequence (see Section 4). In this way, the set of convergent subsequences has been enlarged – but a new problem arises. The functional $\mathcal{F}$ need not be weakly continuous and it in practice rarely is. To summarize: The more sequences exist that have convergent subsequences the less likely it is that $\mathcal{F}$ is continuous along these sequences.

The way out of this dilemma is that in many examples the functional turns out to be weakly lower semi-continuous, i.e.,

$$\liminf_{j\to\infty} \mathcal{F}(\psi_j) \geq \mathcal{F}(\psi) \quad \text{if} \quad \psi_j \rightharpoonup \psi. \tag{3}$$

Thus, if ψ_j is a minimizing sequence, i.e., if

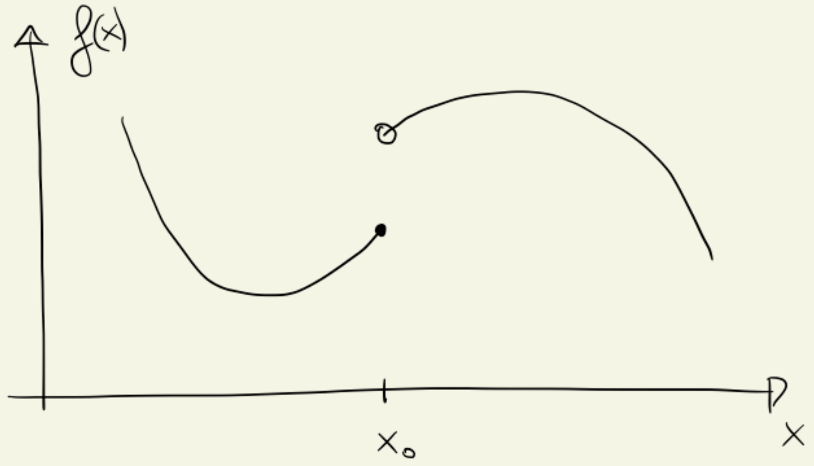
$$\mathcal{F}(\psi_j) \longrightarrow \inf_{\psi\in K} \mathcal{F}(\psi) = \lambda, \tag{4}$$

then there exist a subsequence Ψ_{j_k} and Ψ with $\Psi_{j_k} \rightharpoonup \Psi$ weakly, and hence

$$\lambda = \lim_{j\to\infty} \mathcal{F}(\Psi_j) \geq \mathcal{F}(\Psi) \geq \lambda. \tag{5}$$

Therefore, $\mathcal{F}(\Psi) = \lambda$, and our goal is achieved.

A function $f : \mathbb{R}^n \to \mathbb{R}$ is called lower-continuous if it satisfies $\liminf_{j\to\infty} f(x_j) \geq f(x)$ whenever $x_j \to x$. Here is an example of such a function:



5.2. The Schrödinger equation

In quantum mechanics, a particle moving in $\mathbb{R}^n$ is described by a complex-valued wave function $\psi \in L^2(\mathbb{R}^n)$ with $\int_{\mathbb{R}^n} |\psi(x)|^2 dx = 1$. From a physics point of view, $|\psi(x)|^2$ is a probability density, that is, $\int_{\Omega} |\psi(x)|^2 dx$ equals the probability to find the particle in the measurable set Ω. To every physical observable we can associate a self-adjoint operator (think of a hermitian matrix if you don't know what that is) A on $L^2(\mathbb{R}^n)$, so that its expectation in the wave function ψ is given by the L^2-inner product $\langle \psi, A\psi \rangle$. For example, the position is associated with the map $\psi(x) \mapsto x\psi(x)$, the momentum (or velocity) with the map $\psi \mapsto -i\nabla\psi(x)$, and the energy by the map $\psi \mapsto h\psi$ with

$$h = -\Delta + V(x), \tag{6}$$

where $V(x)$ is a real-valued potential, that acts as multiplication by $V(x)$, that is, $\psi(x) \mapsto V(x)\psi(x)$.

The time-evolution of the particle is determined by the **time-dependent Schrödinger equation**

$$i\partial_t \psi_t(x) = h\psi_t(x) = -\Delta\psi_t(x) + V(x)\psi_t(x). \tag{7}$$

Of particular importance are stationary solutions of this equation of the form $\psi_t(x) = e^{-iet}\psi(x)$ with $e \in \mathbb{R}$. They are constants up to an irrelevant time-dependent phase, which vanishes when expectation values are computed, that is, we have

$$\langle \psi_t, A\psi_t \rangle = \langle \psi_0, A\psi_0 \rangle \tag{8}$$

for all $t > 0$. When we insert $\psi_t(x) = e^{-iet}\psi(x)$ into (7) we see that $\psi(x)$ satisfies the **time-independent Schrödinger equation**

$$\left(-\Delta+V(x)\right)\Psi(x) = e\,\Psi(x). \tag{9}$$

In general this equation has no solutions. The selected values e for which a solution exists are called the eigenvalues of $h=-\Delta+V(x)$ and the solutions Ψ are called the corresponding eigenvectors. It is therefore a natural question to ask whether such eigenvalues and eigenvectors exist. The lowest eigenvalue and the corresponding eigenvector are of particular importance. They are called the ground state energy and the ground state, respectively.

As in the case of a hermitian matrix, this eigenvalue has the following variational characterisation:

$$e_0 = \inf_{\|\Psi\|_2=1} \langle \Psi, (-\Delta+V(x))\Psi\rangle = \inf_{\|\Psi\|_2=1} \mathcal{E}(\Psi), \tag{10}$$

where

$$\mathcal{E}(\Psi) = \int_{\mathbb{R}^n} |\nabla\Psi(x)|^2\,dx + \int_{\mathbb{R}^n} V(x)\,|\Psi(x)|^2\,dx. \tag{11}$$

To show that the ground state exists, we will first prove the existence of a minimizer for this minimization problem. Afterwards, we will show that this minimizer indeed solves the Schrödinger equation in (9).

After having established the existence of the ground state we will, if time permits, construct solutions to (9) with energies $e > e_0$ and discuss some of their properties.

5.3 Domination of the potential energy by the kinetic energy

The first question we have to ask is whether the energy $\mathcal{E}$ is bounded from below. This property will depend on our choice of V. Before presenting a positive result, let us discuss one choice of V, for which $\inf_{\|\psi\|=1} \mathcal{E}(\psi) = -\infty$ holds. In this case one cannot expect a minimizer to exist.

We choose $V(x) = \frac{-1}{|x|^{5/2}}$ for $x \in \mathbb{R}^n$ with $n \geq 3$. In this case $\mathcal{E}$ reads

$$\mathcal{E}(\psi) = \int_{\mathbb{R}^n} |\nabla \psi(x)|^2 dx - \int_{\mathbb{R}^n} \frac{|\psi(x)|^2}{|x|^{5/2}} dx. \tag{12}$$

Next we let $\psi \in C_c^\infty(\mathbb{R}^n)$ with $\int_{\mathbb{R}^n} |\psi(x)|^2 dx = 1$ and define $\psi_\ell(x) = \ell^{n/2} \psi(\ell x)$ for $\ell > 0$. We have

$$\mathcal{E}(\psi_\ell) = \ell^2 \int_{\mathbb{R}^n} |\nabla\psi(x)|^2 dx - \ell^{5/2} \int_{\mathbb{R}^n} \frac{|\psi(x)|^2}{|x|^{5/2}} dx. \tag{13}$$

By letting $\ell \to \infty$ we conclude that

$$\inf_{\|\psi\|_2 = 1} \mathcal{E}(\psi) = -\infty. \tag{14}$$

In the next theorem we give conditions on V that guarantee the existence of a finite lower bound for $\mathcal{E}$.

<u>**Theorem 5.3.1.**</u> *Let $n \in \mathbb{N}$ and assume that $V \in L^\infty(\mathbb{R}^n) + L^{n/2}(\mathbb{R}^n)$ if $n \geq 3$, that $V \in L^\infty(\mathbb{R}^2) + L^{1+\varepsilon}(\mathbb{R}^2)$ for arbitrary $\varepsilon > 0$ in two dimensions, or that $V \in L^\infty(\mathbb{R}) + L^{1+\varepsilon}(\mathbb{R})$ in dimention one. For $\psi \in H^1(\mathbb{R}^n)$ we then have*

$$\mathcal{E}(\psi) \geq \frac{1}{2} \int_{\mathbb{R}^n} |\nabla\psi(x)|^2 dx - C\, \|\psi\|_2^2 \tag{15}$$

for some $C > 0$ that depends on V.

Proof: We only consider the case $n \geq 3$. The cases $n = 1,2$ are left for the exercises. Our assumptions guarantee the existence of a decomposition of the form

$$V(x) = V_1(x) + V_2(x) \tag{16}$$

with $V_1 \in L^\infty(\mathbb{R}^n)$ and $V_2 \in L^{n/2}(\mathbb{R}^n)$. W.l.o.g. we can assume that V_1 and V_2 are negative, because a positive part would only raise the energy. It is also possible to assume that $\| V_2 \|_{n/2} \leq \delta$ for given $\delta > 0$. To see this we decompose $V_2(x)$ for given $\mu > 0$ as

$$V_2(x) = \mathbb{1}\left(-V_2(x) \leq \mu\right) V_2(x) + \mathbb{1}\left(-V_2(x) > \mu\right) V_2(x), \tag{17}$$

where $\mathbb{1}(-V_2(x) \leq \mu)$ denotes the characteristic function of the set $\{ x \in \mathbb{R}^n \mid -V_2(x) \leq \mu \}$. The first summand on the r.h.s. of (17) is a function in $L^\infty(\mathbb{R}^n)$. The second summand satisfies

$$|V_2(x)| \, \mathbb{1}\left(-V_2(x) > \mu\right) \leq |V_2(x)|, \tag{18}$$

and dominated convergence therefore implies

$$\lim_{\mu\to\infty} \int_{\mathbb{R}^n} |V_2(x)|^{n/2} \mathbb{1}\big(-V_2(x)>\mu\big)\, dx = 0. \tag{19}$$

Choosing μ large enough we can assume that the $L^{n/2}(\mathbb{R}^n)$-norm of $V_2(x)\,\mathbb{1}(-V_2(x)>\mu)$ is smaller than any $\delta>0$. This proves the above claim concerning the decomposition of V_2.

Using the decomposition $V = V_1 + V_2$, we construct a lower bound for $\mathcal{E}$ as follows:

$$\mathcal{E}(\psi) = \int_{\mathbb{R}^n} |\nabla\psi(x)|^2 + \underbrace{\int_{\mathbb{R}^n} V_1(x)\, |\psi(x)|^2 dx}_{\geq -\underbrace{\|V_1\|_\infty}_{\leq C_\delta} \|\psi\|_2^2} + \underbrace{\int_{\mathbb{R}^n} V_2(x)\, |\psi(x)|^2 dx}_{\substack{\geq -\|V_2\|_{n/2}\, \| |\psi|^2 \|_{\frac{n}{n-2}} \\ \geq -\delta\, \underbrace{\|\psi\|^2_{\frac{2n}{n-2}}}_{\leq C_d \|\nabla\psi\|_2^2}}} \tag{20}$$

Theorem 3.10 (Sobolev inequality)

Choosing $\delta = \frac{1}{2C_d}$ in (20) proves

$$\mathcal{E}(\psi) \geq \frac{1}{2} \|\nabla\psi\|_2^2 - C\|\psi\|_2^2 \tag{21}$$

for some $C>0$, and therewith the claim. $\blacksquare$

Remark 5.3.1. If $U(x) \geq -C$ for some constant $C>0$ then $\mathcal{E}$ is bounded from below by $-C$. The point of the theorem above is that if U is not bounded from below then $\mathcal{E}$ can still be bounded from below. An important example with great physical relevance is the Coulomb potential $\frac{-1}{|x|}$ with $x \in \mathbb{R}^3$. The Hamiltonian $-\Delta - \frac{1}{|x|}$ describes the electron in the hydrogen atom. In classical physics the hydrogen atom is unstable because the energy $E(p,x) = p^2 - \frac{1}{|x|}$ is unbounded from below. As a charged particle, the electron in classical physics looses energy due to emitted radiation and would spiral into the nucleus. The quantum energy $\mathcal{E}$ is bounded from below because $\frac{1}{|x|} \in L^{3/2}(\mathbb{R}^3) + L^{\infty}(\mathbb{R}^3)$. That is, even if the electron is coupled to a radiation field and looses energy, it does not fall into the nucleus. This insight was one of the early successes of quantum mechanics.

Remark 5.3.2. The difference between the potential $-\frac{1}{|x|^{5/2}}$ for $n \geq 3$ and the potentials in the above theorem is that the former has a more severe singularity at $x=0$ as is allowed for the latter. Choosing $v(x) = -\frac{1}{|x|^{\alpha}}$ and Ψ_ℓ as in the example we see that

$$\mathcal{E}(\Psi_\ell) = \ell^2 \int_{\mathbb{R}^n} |\nabla \Psi(x)|^2 dx - \ell^{\alpha} \int_{\mathbb{R}^n} \frac{|\Psi(x)|^2}{|x|^{\alpha}} dx. \tag{22}$$

The mass of the function Ψ_ℓ is localized more and more close to the origin for $\ell \to \infty$. In this limit both, its kinetic energy (1st term in (22)) and its potential energy (2nd term in (22)) diverge. Which one wins is decided by the scaling of the two terms in l. The critical potential is therefore $-\frac{1}{|x|^2}$.

5.4. Weak continuity of the potential energy

As we noted in Section 5.1., the weak lower semi-continuity of a functional plays an important role in the proof of the existence of minimizers. In this section we show that the potential energy is weakly continuous on $H^1(\mathbb{R}^n)$.

Theorem 5.4.1. Assume that $V \in L^\infty(\mathbb{R}^n) + L^{n/2}(\mathbb{R}^n)$ if $n \geq 3$, that $V \in L^\infty(\mathbb{R}^2) + L^{1+\varepsilon}(\mathbb{R}^2)$ in two dimensions for arbitrary $\varepsilon > 0$, or that $V \in L^\infty(\mathbb{R}) + L^1(\mathbb{R})$ in the one-dimensional case. Assume additionally that V vanishes at infinity in the sense that

$|\{x\in\mathbb{R}^n \mid |V(x)|\geq \alpha\}| < +\infty$ holds for all $\alpha>0$. Then the map $\psi \mapsto \int_{\mathbb{R}^n} V(x)|\psi(x)|^2 dx$ is weakly continuous on $H^1(\mathbb{R}^n)$.
That is, $\psi_j \rightharpoonup \psi$ in $H^1(\mathbb{R}^n)$ implies

$$\int_{\mathbb{R}^n} V(x)|\psi_j(x)|^2 dx \xrightarrow{j\to\infty} \int_{\mathbb{R}^n} V(x)|\psi(x)|^2 dx. \tag{23}$$

Remark 5.4.1. It should be highlighted that weak continuity is a stronger property than strong continuity since convergence needs to hold along more sequences.

Proof: We again consider the case $n\geq 3$ and leave the cases $n=1,2$ as an exercise. To keep formulas short, we introduce the notation $V(\psi) = \int_{\mathbb{R}^n} V(x)|\psi(x)|^2 dx$ and we write

$$V(x) = V_1(x) + V_2(x) \quad \text{with } V_1\in L^\infty(\mathbb{R}^n) \text{ and } V_2\in L^{n/2}(\mathbb{R}^n). \tag{24}$$

We assume that $\psi_j \rightharpoonup \psi$ weakly in $H^1(\mathbb{R}^n)$, which, by the uniform boundedness principle, also implies $\|\Psi_j\|_{H^1} \leq C$ for some $C>0$ and all $j \in \mathbb{N}$. We need to show that $V(\Psi_j) \to V(\Psi)$ as $j \to \infty$. To prove this claim we show that we can replace v by a bounded potential.

For $\delta > 0$ we define

$$v_\delta(x) = \begin{cases} v(x) & \text{if } |v(x)| \leq 1/\delta, \\ 0 & \text{instead}. \end{cases} \qquad (25)$$

We have $v_\delta(x) \to v(x)$ a.e. for $\delta \to 0$ as well as

$$\begin{aligned} |v(x) - v_\delta(x)| &= |v(x)| \, \mathbb{1}\left(|v(x)| > 1/\delta\right) \\ &\leq |v_1(x)| \, \mathbb{1}\left(|v(x)| > 1/\delta\right) + |v_2(x)| \, \mathbb{1}\left(|v(x)| > 1/\delta\right) \\ &\leq \|v_1\|_\infty \, \mathbb{1}\left(|v(x)| > 1/\delta\right) + |v_2(x)| \end{aligned} \qquad (27)$$

for $0 < \delta < 1$ and a.e. $x \in \mathbb{R}^n$. By assumption, $v_2 \in L^{n/2}(\mathbb{R}^{n/2})$ and $|\{x \in \mathbb{R}^n \mid |v(x)| > 1\}| < +\infty$. It follows that the r.h.s. of (27) is in $L^{n/2}(\mathbb{R}^n)$. An application of dominated convergence thus shows

$$\| V - V_\delta \|_{n/2}^{n/2} = \int_{\mathbb{R}^n} |V(x) - V_\delta(x)|^{n/2} \, dx \xrightarrow{\delta \to 0} 0 , \tag{28}$$

which implies

$$\begin{aligned} \int_{\mathbb{R}^n} |V(x) - V_\delta(x)| \, |\psi_j(x)|^2 \, dx &\leq \| V - V_\delta \|_{n/2} \, \| \psi_j \|^2_{\frac{2n}{n-2}} \\ &\leq \text{const.} \, \| V - V_\delta \|_{n/2} \underbrace{\| \psi_j \|^2_{H^1}}_{\leq \text{const.}} \leq \text{const.} \, \| V - V_\delta \|_{n/2} \\ &\xrightarrow{\delta \to 0} 0 . \end{aligned} \tag{29}$$

uniformly in j

The above bound allows us to reduce the problem to the case of a bounded potential. Next, we restrict the integral to a domain with finite measure.

For $\sigma > 0$ we define $A_\sigma = \{ x \in \mathbb{R}^n \mid |V_\delta(x)| > \sigma \}$. By assumption we have $|A_\sigma| < +\infty$. We write

$$\int_{\mathbb{R}^n} V_\delta(x) \, |\psi_j(x)|^2 \, dx = \int_{A_\sigma} V_\delta(x) \, |\psi_j(x)|^2 \, dx + \int_{A_\sigma^c} V_\delta(x) \, |\psi_j(x)|^2 \, dx . \tag{30}$$

For the second term in (30) we have the bound

$$\int_{A_\sigma^c} V_\delta(x)\, |\psi_j(x)|^2\, dx \leq \sigma \, \|\psi_j\|_2^2 \leq \text{const.}\, \sigma\,, \tag{31}$$

which allows us to restrict the problem to a finite volume.

To close the argument, we need to show that

$$\lim_{j\to\infty} \int_{A_\sigma} V_\delta(x)\, |\psi_j(x)|^2 dx = \int_{A_\sigma} V_\delta(x)\, |\psi(x)|^2 dx \tag{32}$$

holds for fixed $\sigma, \delta > 0$. From Chapter 4 we know that if $\psi_j \to \psi$ in $H^1(\mathbb{R}^n)$, then $\chi_{A_\sigma} \psi_j \to \chi_{A_\sigma} \psi$ strongly in $L^p(\mathbb{R}^n)$ for all $1 \leq p < \frac{2n}{n-2}$ $(n \geq 3)$. We use this statement with $p = 2$ to show that

$$\int_{A_\sigma} V_\delta(x) \left|\, |\psi_j(x)|^2 - |\psi(x)|^2 \right| dx$$

$$\leq \| \chi_{A_\sigma} V_\delta \|_\infty \, \| \chi_{A_\sigma} \left| \, |\psi_j|^2 - |\psi|^2 \right| \|_1$$

$$\leq \underbrace{\| \chi_{A_6} V_\delta \|_\infty}_{\leq C_\delta} \underbrace{\| \chi_{A_6} (|\psi_j| - |\psi|) \|_2}_{\leq \| \chi_{A_6} (\psi_j - \psi) \|_2} \underbrace{\left(\|\psi_j\|_2 + \|\psi\|_2 \right)}_{\leq \text{const.}}. \tag{33}$$

$$\xrightarrow[j \to \infty]{} 0 .$$

We combine (29), (32), and (33), and find

$$\left| \int_{\mathbb{R}^n} V(x) \, |\psi_j(x)|^2 \, dx - \int_{\mathbb{R}^n} V(x) \, |\psi(x)|^2 \, dx \right|$$

$$\leq C \left(\| V_\delta - V \|_{n/2} + 6 + C_\delta \, \| \chi_{A_6} (\psi_j - \psi) \|_2 \right). \tag{34}$$

Let $\varepsilon > 0$ be given. When we choose δ s.t. $\| V_\delta - V \|_{n/2} \leq \frac{\varepsilon}{3C}$, $6 = \frac{\varepsilon}{3C}$, and $j \geq j_0(\varepsilon)$ s.t. $C C_\delta \| \chi_{A_6} (\psi_j - \psi) \|_2 \leq \varepsilon/3$, we see that the r.h.s. is bounded by ε. This proves the claim.

$\blacksquare$

5.5. Existence of a unique minimizer for the energy and the Schrödinger equation

We are now prepared to prove the existence of minimizers for e_0. The statement we are going to prove is captured in the following theorem.

Theorem 5.5.1. Suppose that $V \in L^\infty(\mathbb{R}^n) + L^{n/2}(\mathbb{R}^n)$ if $n \geq 3$, that $V \in L^\infty(\mathbb{R}^2) + L^{1+\varepsilon}(\mathbb{R}^2)$ for some $\varepsilon > 0$ if $n = 2$, or that $V \in L^\infty(\mathbb{R}) + L^1(\mathbb{R})$ if $n = 1$. Assume additionally that V vanishes at infinity in the sense that $|\{x \in \mathbb{R}^n \mid |V(x)| > \alpha\}| < +\infty$ for all $\alpha > 0$. Finally, we assume that

$$e_0 := \inf \{ \mathcal{E}(\psi) \mid \psi \in H^1(\mathbb{R}^n),\ \|\psi\|_2 = 1 \} < 0. \qquad (35)$$

Then there exists $\psi_0 \in H^1(\mathbb{R}^n)$ with $\|\psi_0\|_2 = 1$ and $\mathcal{E}(\psi_0) = e_0$. Moreover, any minimizer $\psi \in H^1(\mathbb{R}^3)$ with $\|\psi\|_2 = 1$ of $\mathcal{E}$

satisfies the Schrödinger equation

$$-\Delta\Psi(x) + V(x)\Psi(x) = e_0\Psi(x) \tag{36}$$

in the sense of distributions.

Remark 5.5.1. The assumption $e_0 < 0$ is crucial. Consider for example the case $V=0$, where

$$\mathcal{E}(\Psi) = \int_{\mathbb{R}^3} |\nabla\Psi(x)|^2 dx \geq 0. \tag{37}$$

The value 0 is attained by constant functions, which are not in $L^2(\mathbb{R}^n)$, except for $\Psi(x) \equiv 0$. But the $L^2(\mathbb{R}^n)$-norm of this function does not equal 1. This is also reflected by the fact that the minimizing sequence

$$\Psi_j(x) = \exp\left(-\frac{x^2}{2j}\right)\left(\frac{1}{\pi j}\right)^{n/2}; \quad j \in \mathbb{N} \tag{38}$$

of $\mathcal{E}$ converges weakly to zero in $H^1(\mathbb{R}^n)$. It therefore cannot have a convergent subsequence with $\Psi_{j_k} \xrightarrow{\text{in } L^2} \Psi$ s.t. $\|\Psi\|_2 = 1$.

Proof: Let $\{\Psi_j\}_{j=1}^{\infty}$ be a sequence in $H^1(\mathbb{R}^n)$ with $\|\Psi_j\|_2 = 1$ for all $j \in \mathbb{N}$ and s.t. $\mathcal{E}(\Psi_j) \to e_0$ for $j \to \infty$.
From Theorem 5.3.1 we know that

$$\mathcal{E}(\Psi_j) \geq \frac{1}{2} \int_{\mathbb{R}^n} |\nabla \Psi_j(x)|^2 dx - C \|\Psi_j\|_2^2 \qquad (39)$$

holds for some $C > 0$. Hence, the $H^1(\mathbb{R}^n)$-norm of Ψ_j is uniformly bounded. The Banach-Alaoglu theorem therefore implies that Ψ_j has a subsequence that converges weakly in $H^1(\mathbb{R}^n)$ to some function $\Psi_0 \in H^1(\mathbb{R}^n)$. By a slight abuse of notation we continue to denote this subsequence by Ψ_j. In Chapter 4 we have shown that

$$\liminf_{j \to \infty} \int_{\mathbb{R}^n} |\Psi_j(x)|^2 dx \geq \int_{\mathbb{R}^n} |\Psi_0(x)|^2 dx,$$

$$\liminf_{j \to \infty} \int_{\mathbb{R}^n} |\nabla \Psi_j(x)|^2 dx \geq \int_{\mathbb{R}^n} |\nabla \Psi_0(x)|^2 dx \qquad (40)$$

hold. The first inequality tells us that $\|\psi_0\|_2 \leq 1$, and in combination with Theorem 5.4.1, the second implies the weak lower semi-continuity of $\mathcal{E}$, i.e.,

$$\liminf_{j\to\infty} \mathcal{E}(\psi_j) \geq \mathcal{E}(\psi_0). \tag{41}$$

We conclude that

$$0 > e_0 = \liminf_{j\to\infty} \mathcal{E}(\psi_j) \geq \mathcal{E}(\psi_0) \geq e_0 \|\psi_0\|_2^2. \tag{42}$$

Here we use $\mathcal{E}\left(\frac{\psi_0}{\|\psi_0\|}\right) \geq e_0$.

From $0 > \mathcal{E}(\psi_0)$ we see that $\|\psi_0\|_2 \neq 0$. Using $0 > e_0 \geq e_0 \|\psi\|_2^2$ we see that $\|\psi_0\|_2 = 1$. We conclude that $\mathcal{E}(\psi_0) = e_0$ and the first claim of the theorem is proved.

It remains to show that ψ_0 solves the Schrödinger equation in the sense of distributions. To that end, we choose $f \in C_c^\infty(\mathbb{R}^n)$ and define $\psi_t(x) = \psi_0 + tf$. We consider

$$R(t) = \frac{\mathcal{E}(\Psi_t)}{\|\Psi_t\|^2} \tag{43}$$

and note that

$$\mathcal{E}(\Psi_t) = \mathcal{E}(\Psi_0) + t \int_{\mathbb{R}^n} \{ \overline{\nabla \Psi_0(x)}\, \nabla f(x) + \nabla \Psi_0(x)\, \overline{\nabla f(x)} \} dx$$
$$+ t \int_{\mathbb{R}^n} v(x) \{ \overline{\Psi_0(x)}\, f(x) + \Psi_0(x)\, \overline{f(x)} \} dx$$
$$+ t^2 \int_{\mathbb{R}^n} \{ |\nabla f(x)|^2 + v(x)\, |f(x)|^2 \} dx$$

$$= e_0 + 2t \operatorname{Re} \langle -\Delta f + v f, \Psi_0 \rangle + t^2 \mathcal{E}(f). \tag{44}$$

Integration by parts

We also have

$$\|\Psi_t\|_2^2 = \underbrace{\|\Psi_0\|_2^2}_{=1} + 2t \operatorname{Re} \langle f, \Psi_0 \rangle + t^2 \|f\|_2^2. \tag{45}$$

As a rational function in t, $R(t)$ is differentiable at $t=0$.

Its minimum occurs by assumption at $t=0$, and hence $\left.\frac{dR(t)}{dt}\right|_{t=0}=0$.

We have

$$0 = \left.\frac{dR(t)}{dt}\right|_{t=0} = \left[\frac{\frac{d}{dt}\mathcal{E}(\Psi_t)}{\|\Psi_t\|_2^2} - \frac{\mathcal{E}(\Psi_t)}{\|\Psi_t\|_2^4}\frac{d}{dt}\|\Psi_t\|_2^2\right]_{t=0}$$

$$= 2\,\mathrm{Re}\langle -\Delta f + Vf, \Psi_0\rangle - e_0\, 2\,\mathrm{Re}\langle f, \Psi_0\rangle$$

$$= 2\,\mathrm{Re}\langle (-\Delta + V - e_0) f, \Psi_0\rangle. \tag{46}$$

Replacing f by if, we conclude that

$$0 = 2\,\mathrm{Im}\langle (-\Delta + V - e_0) f, \Psi_0\rangle. \tag{47}$$

Hence,

$$(-\Delta + V)\Psi_0 = e_0 \Psi_0 \tag{48}$$

holds in the sense of distributions and the claim is proved.

$\blacksquare$

As we will show in the next theorem, minimizers of e_0 are unique up to multiplication with a complex number z with $|z|=1$ and can be chosen nonnegative. For the sake of simplicity we assume $n \leq 3$. It should also be noted that the assumptions on V can be relaxed quite a lot.

Theorem 5.5.2. (Uniqueness of minimizers)

Let $n \in \mathbb{N}$, $n \leq 3$ $V \in L^2(\mathbb{R}^n)$ and assume additionally that there exists a constant $C > 0$ s.t. $V(x) \leq C \quad \forall\, x \in \mathbb{R}^n$ holds. Then there exists a minimizer $\varphi_0 \in H^2(\mathbb{R}^n)$ of e_0, which is strictly positive (functions in $H^2(\mathbb{R}^n)$ are continuous for $n \leq 3$, so this makes sense). Moreover, every other minimizer $\tilde{\varphi}_0$ of e_0 is of the form $\tilde{\varphi}_0(x) = z\varphi_0(x)$ with $z \in \mathbb{C}$, $|z| = 1$.

Before we prove Theorem 5.5.2., we state and prove three lemmas, which are of independent interest.

Lemma 5.5.1. Let $\Psi \in H^2(\mathbb{R}^n)$, $\phi \in L^2(\mathbb{R}^n)$, $\mu > 0$, and assume that

$$(-\Delta + \mu^2)\Psi(x) = \phi(x) \tag{49}$$

holds. Then

$$\Psi(x) = \int_{\mathbb{R}^n} G_\mu(x-y)\,\phi(y)\,dy \tag{50}$$

with

$$G_\mu(x) = \int_0^\infty \left(\frac{1}{4\pi t}\right)^{n/2} \exp\left(-\frac{|x|^2}{2t} - \mu^2 t\right) dt. \tag{51}$$

Remark 5.5.2. The function $G_\mu(x)$ is called the Yukawa potential. It is the Greens function of $-\Delta+\mu^2$, that is, it satisfies $(-\Delta+\mu^2)G_\mu = \delta_0$ in the sense of distributions. We have

$$G_\mu(x) = \frac{1}{2\mu}\exp\left(-\mu|x|\right) \qquad \text{if} \quad n=1,$$

$$G_\mu(x) = \frac{1}{4\pi|x|}\exp\left(-\mu|x|\right) \qquad \text{if} \quad n=3. \tag{52}$$

Proof: When written in Fourier space, eq. (49) reads

$$\left(2\pi p^2+\mu^2\right)\hat{\varphi}(p) = \hat{\phi}(p)$$

$$\Leftrightarrow \quad \hat{\varphi}(p) = \left(2\pi p^2+\mu^2\right)^{-1}\hat{\phi}(p). \tag{53}$$

Next, we use

$$x^{-1} = \int_0^\infty e^{-tx}\,dt \tag{54}$$

to see that

$$\frac{1}{2\pi p^2+\mu^2} = \int_0^\infty e^{-2\pi p^2 t}\,e^{-\mu^2 t}\,dt. \tag{55}$$

Assume that $\tilde{\phi} \in S(\mathbb{R}^n)$. We have

$$\int_{\mathbb{R}^n} e^{2\pi i p\cdot x} \frac{1}{(2\pi p^2)+\mu^2} \hat{\tilde{\phi}}(p)\, dp$$

$$\underset{\text{Fubini}}{=} \int_0^\infty e^{-\mu^2 t} \underbrace{\int_{\mathbb{R}^n} e^{2\pi i p\cdot x} e^{-2\pi p^2 t} \hat{\tilde{\phi}}(p)\, dp}\, dt$$

$$= \int_{\mathbb{R}^n} \left(\frac{1}{4\pi t}\right)^{n/2} \exp\left(-\frac{|x-y|^2}{4t}\right) \tilde{\phi}(y)\, dy$$

FT of a product and FT of a gaussian

$$\underset{\text{Fubini}}{=} \int_{\mathbb{R}^n} G_\mu(x-y) \tilde{\phi}(y)\, dy . \tag{56}$$

To prove the same equality for $\phi \in L^2(\mathbb{R}^n)$, we first note that

$$\|G_\mu\|_1 = \int_0^\infty e^{-\mu^2 t} \underbrace{\int_{\mathbb{R}^n} \left(\frac{1}{4\pi t}\right)^{-n/2} \exp\left(-\frac{|x|^2}{4t}\right) dx}_{=1}\, dt \qquad (57)$$

$$= \frac{1}{\mu^2}.$$

For given $\varepsilon > 0$, we choose $\tilde{\phi} \in \mathcal{S}(\mathbb{R}^n)$ s.t.

$$\|\phi - \tilde{\phi}\|_2 \leq \eta(\varepsilon) \leftarrow \text{to be chosen later} \qquad (58)$$

holds. Let us also denote the l.h.s. of (56) by $F(\tilde{\phi})$ and the r.h.s. by $G(\tilde{\phi})$. We have

$$\|F(\phi) - G(\phi)\|_2 \leq \underbrace{\|F(\phi) - F(\tilde{\phi})\|_2}_{\text{Plancherel}} + \|G(\phi) - G(\tilde{\phi})\|_2 + \underbrace{\|F(\tilde{\phi}) - G(\tilde{\phi})\|_2}_{=0 \ \leftarrow (56)}$$

$$= \left\| \frac{1}{|\cdot|^2 + \mu^2} (\hat{\phi} - \hat{\tilde{\phi}}) \right\|_2$$

Young's inequality (next page)

$$\leq \frac{1}{\mu^2} \|\phi - \tilde{\phi}\|_2$$

$$\leq \frac{1}{\mu^2} \|\phi - \tilde{\phi}\|_2 + C \underbrace{\|G_\mu\|_1}_{\frac{1}{\mu^2}} \|\phi - \tilde{\phi}\|_2 \qquad (59)$$

for some $C>0$.

Young's inequality: Let $p,q,r \geq 1$ with $\frac{1}{r} = \frac{1}{p} + \frac{1}{q}$ and let $f \in L^p(\mathbb{R}^n)$, $g \in L^q(\mathbb{R}^n)$. Then there exists a constant $C>0$ only depending on q,r,p, and n s.t.

$$\|f*g\|_r \leq C \|f\|_p \|g\|_q .$$

When we choose $\eta(\varepsilon)$ as

$$\eta(\varepsilon) = \frac{\mu^2}{1+C} \varepsilon , \tag{60}$$

we thus have

$$\| F(\phi) - G(\phi) \|_2 \leq \varepsilon . \tag{61}$$

Since $\varepsilon > 0$ was arbitrary, this proves (56) with $\tilde{\phi}$ replaced by $\phi \in L^2(\mathbb{R}^n)$. In particular, (50) holds. $\blacksquare$

Lemma 5.5.2. (A simple maximum principle)

Let $w \in L^1_{loc}(\mathbb{R}^n)$ be s.t. $w \leq C$ for a constant $C > 0$.

Let $\Psi \in H^2(\mathbb{R}^n)$, $\Psi \not\equiv 0$ and assume $\Psi(x) \geq 0$ for a.e. $x \in \mathbb{R}^n$

as well as

$$-\Delta\Psi(x) + w(x)\Psi(x) \geq 0 \quad \text{for a.e. } x \in \mathbb{R}^n. \qquad (62)$$

Then
$$\Psi(x) > 0 \quad \text{a.e.} \qquad (63)$$

Proof: We choose $k > 0$ s.t. $k^2 > \max\{0, C\}$, where $w \leq C$.

In combination with (62), this implies

$$(-\Delta + k^2)\Psi(x) \geq -(\underbrace{w(x)}_{\leq C} - k^2)\underbrace{\Psi(x)}_{\geq 0} \geq (\underbrace{k^2 - C}_{>0})\underbrace{\Psi(x)}_{\in L^2(\mathbb{R}^n)}. \qquad (64)$$

That is, there exists a function $g \in L^2(\mathbb{R}^n)$ with $g(x) \geq (k^2 - C)\Psi(x)$

s.t.

$$(-\Delta + k^2)\Psi(x) = g(x). \qquad (65)$$

In particular, $g \geq 0$ and $g \not\equiv 0$. In this step we used $\Psi \in H^2(\mathbb{R}^n)$.

An application of Lemma 5.5.1 thus implies

$$\Psi(x) = \int_{\mathbb{R}^n} G_k(x-y)\, g(y)\, dy. \qquad (66)$$

That Ψ is strictly positive a.e. is an immediate consequence of the properties of G_μ and g. This proves the claim.

$\blacksquare$

The last Lemma shows that any solution to the Schrödinger equation is in $H^2(\mathbb{R}^n)$ provided $V \in L^2(\mathbb{R}^n)$ and $n \in \{1,2,3\}$.

Lemma 5.5.3 (H^2-regularity of solutions): Let $n \in \{1,2,3\}$, let $V \in L^2(\mathbb{R}^n)$ and assume that $\Psi \in H^1(\mathbb{R}^n)$ is a solution to the Schrödinger equation

$$-\Delta\Psi(x) + V(x)\Psi(x) = e\,\Psi(x) \qquad (67)$$

in the sense of distributions. Then $\Psi \in H^2(\mathbb{R}^n)$.

Proof: We spell out the proof only for $n=3$. The cases $n=1,2$ are straightforward extensions and are left to the reader. From (67) we know that the distribution $T_{\Delta\Psi}$ equals the distribution $T_{(V-e)\Psi}$. Accordingly, $\Delta\Psi$ is a function and its L^2-norm is bounded by

$$\|\Delta\Psi\|_2 = \|(V-e)\Psi\|_2 \leq |e| \, \|\Psi\|_2 + \|V\|_2 \, \|\Psi\|_\infty . \tag{68}$$

To obtain a bound for $\|\Psi\|_\infty$ we write the Schrödinger equation in Fourier space with some $c>0$ as

$$(p^2+c)\,\hat{\Psi}(p) + \hat{V} * \hat{\Psi}(p) = (e+c)\,\hat{\Psi}(p)$$

$$\Leftrightarrow \quad \hat{\Psi}(p) = \frac{1}{p^2+c}\Big[(e+c)\,\hat{\Psi}(p) - \hat{V} * \hat{\Psi}(p)\Big]$$

$$= \hat{\Phi}_1(p) - \hat{\Phi}_2(p), \tag{69}$$

where $\hat{\Phi}_1(p) = \frac{e+c}{p^2+c}\hat{\Psi}(p)$ and $\hat{\Phi}_2(p) = \frac{1}{p^2+c}\,\hat{V} * \hat{\Psi}(p)$.

The function Φ_1 is in $H^2(\mathbb{R}^3) \subset L^\infty(\mathbb{R}^3)$ because $\hat{\Psi} \in L^2(\mathbb{R}^3)$, and hence $\|\phi_1\|_\infty \overset{\text{Hausdorff-Young inequality}}{\leq} C\|\hat{\phi}_1\|_1 \underset{\text{Hölder}}{\leq} C(|e|+c)\,\| \frac{1}{(\cdot)^2+c} \|_2 \, \|\hat{\psi}\|_2$.

It therefore remains to check that $\phi_2 \in L^\infty(\mathbb{R}^3)$. We have

$$\Big\| \frac{1}{(\cdot)^2+c}\, \hat{V} * \hat{\psi} \Big\|_r \leq \Big\| \frac{1}{(\cdot)^2+c} \Big\|_p \, \| \hat{V} * \hat{\psi} \|_q . \tag{70}$$

We know that $V\psi \in L^1(\mathbb{R}^3) \cap L^{3/2}(\mathbb{R}^3)$ because $V \in L^2(\mathbb{R}^3)$ and $\psi \in H^1(\mathbb{R}^3) \Rightarrow \psi \in L^2(\mathbb{R}^3) \cap L^6(\mathbb{R}^3)$, and hence $\widehat{V\psi} = \hat{V} * \hat{\psi} \in L^3(\mathbb{R}^3) \cap L^\infty(\mathbb{R}^3)$. As long as $p > 3/2$, the first factor on the r.h.s. of (70) is finite. This implies

$$\frac{1}{(\cdot)^2+c}\, \hat{V} * \hat{\psi} \in L^r(\mathbb{R}^3) \quad \text{for} \quad r \in (1,\infty]. \tag{71}$$

In combination with (69) we conclude that $\psi \in L^p(\mathbb{R}^3)$ with $p \in [2,\infty)$. Using this information we can argue as above to see that $V\psi \in L^p(\mathbb{R}^3)$ with $p \in [1,2)$, and hence $\hat{V} * \hat{\psi} \in L^q(\mathbb{R}^3)$ with $q \in (2,\infty]$. Accordingly,

$$\frac{1}{(\cdot)^2+c}\, \hat{V} * \hat{\psi} \in L^r(\mathbb{R}^3) \quad \text{for} \quad r \in [1,\infty], \tag{72}$$

and using (69) again we conclude that $\psi \in L^\infty(\mathbb{R}^3)$. In combination with (68) this proves $\Delta\psi \in L^2(\mathbb{R}^3)$. It is straightforward to check that this implies $\psi \in H^2(\mathbb{R}^3)$ and proves the claim. $\blacksquare$

We are now prepared to give a proof of Theorem 5.5.2.

<u>**Proof of Theorem 5.5.2.:**</u> The first step in our proof is to show that if $\psi \in H^1(\mathbb{R}^n)$ is a solution to the Schrödinger equation $-\Delta\psi(x) + V(x)\psi(x) = e_0\psi(x)$ in the sense of distributions, then ψ is a minimizer of e_0. We chose a sequence $\{\varphi_n\}_{n=1}^\infty$ with $\varphi_n \in C_c^\infty(\mathbb{R}^n)$ and $\varphi_n \to \psi$ in $H^1(\mathbb{R}^n)$ and note that

$$e_0 \int_{\mathbb{R}^n} \overline{\varphi_n(x)}\,\Psi(x)\,dx \xrightarrow{n\to\infty} e_0 \underbrace{\int_{\mathbb{R}^n} |\Psi(x)|^2 dx}_{=1} = e_0 \qquad (73)$$

$$\|$$

$$\int_{\mathbb{R}^n} \overline{(-\Delta + v(x))\,\varphi_n(x)}\,\Psi(x)\,dx = \int_{\mathbb{R}^n} \left\{ \overline{\nabla\varphi_n(x)}\,\nabla\Psi(x) + v(x)\,\overline{\varphi_n(x)}\,\Psi(x) \right\} dx.$$

$$\downarrow n\to\infty$$

$$\mathcal{E}(\Psi)$$

Accordingly, Ψ satisfies $\mathcal{E}(\Psi) = e_0$, and therefore is a minimizer of e_0.

Assume now that $\Psi_0 = f + ig$ with two real-valued functions $f, g \in H^1(\mathbb{R}^n)$ is a minimizer for e_0. We have

$$\underbrace{-\Delta\Psi_0 + v(x)\,\Psi_0}_{-\Delta f(x) + v(x) f(x) + i\left(-\Delta g(x) + v(x) g(x)\right).} = e_0\Psi_0 = e_0 f(x) + i e_0 g(x). \qquad (74)$$

We must have equality for both, the real and the imaginary part, and therefore conclude that

$$\left(-\Delta+V(x)\right)f(x)=e_0 f(x) \quad \text{as well as} \quad \left(-\Delta+V(x)\right)g(x)=e_0 g(x) \tag{75}$$

hold. In particular, both, f and g, are minimizers for e_0. Since f,g are real-valued, we have

$$\int_{\mathbb{R}^n}|\nabla f(x)|^2 dx = \int_{\mathbb{R}^n}|\nabla|f(x)||^2 dx \tag{76}$$

See formula for gradient of absolute value.

and the same for g. Hence $\mathcal{E}(f)=\mathcal{E}(|f|)$, $\mathcal{E}(g)=\mathcal{E}(|g|)$ and we conclude that $|f|$ and $|g|$ are minimizers. We check that the function $\phi_0(x) = f(x) + i|g(x)|$ is a solution to the Schrödinger equation on the top of p. 36 because f and $|g|$ are solutions. Hence, also ϕ_0 is a minimizer. From the convexity inequality for gradients we know that $\int_{\mathbb{R}^n}|\nabla\phi_0(x)|^2dx \geq \int_{\mathbb{R}^n}|\nabla|\phi_0(x)||^2dx$, which implies

$$\inf_{\substack{\varphi \in H^1 \\ \|\varphi\|_2 = 1}} \mathcal{E}(\varphi) = e_0 = \mathcal{E}(\phi_0) \geq \mathcal{E}(|\phi_0|). \tag{77}$$

Accordingly, the inequality must be an equality. In particular, equality must hold in the convexity inequality for the gradient above (72). From Theorem 3.7 we know that if we have

$$\int_{\mathbb{R}^d} \left| \nabla \sqrt{\tilde{f}^2 + \tilde{g}^2} \right|^2 dx = \int_{\mathbb{R}^d} \left\{ |\nabla \tilde{f}|^2 + |\nabla \tilde{g}|^2 \right\} dx \tag{78}$$

for two real-valued functions $\tilde{f}, \tilde{g}$ with $\tilde{g} > 0$ a.e. then there exists a constant $c \in \mathbb{R}$ s.t. $\tilde{f}(x) = c\,\tilde{g}(x)$ a.e..

In our case $\tilde{f}(x) = f(x)$ and $\tilde{g}(x) = |g(x)|$. To show that $|g(x)| > 0$ a.e. we note that

$$-\Delta |g(x)| + (V(x) - e_0)\,|g(x)| \geq 0. \tag{79}$$

An application of Lemma 5.5.3 shows that $|g(x)| \in H^2(\mathbb{R}^4)$, and Lemma 5.5.2 therefore implies $|g(x)|>0$ a.e.. We conclude that $f(x) = c|g(x)|$ for some $c \in \mathbb{R}_+$. By considering the functions $|f(x)| + ig(x)$ and $|f(x)| + i|g(x)|$ we also conclude that $g(x) = c_1 |f(x)|$ and $|f(x)| = c_2 |g(x)|$, and hence $f(x) = cg(x)$ for some real constant c.

The function Ψ_0 can thus be written as

$$\Psi_0(x) = (1+ci) f(x), \tag{80}$$

which proves the existence of a strictly positive minimizer (just multiply (74) by $\frac{1-ci}{|1-ci|}$).

It remains to show that any other minimizer ϕ_0 of e_0 is of the form $\phi_0(x) = z\Psi_0(x)$ with $z \in \mathbb{C}$, $|z| = 1$. From (79) we know that there exists a phase $z \in \mathbb{C}$, $|z|=1$ s.t. $z\phi_0(x)$ is strictly positive. The uniqueness claim follows when we investigate the function $\Psi_0 + iz\phi_0$ as above. This proves the claim. ∎

Corollary 5.5.4. (Uniqueness of positive solutions): Let

the assumptions of Theorem 5.5.2. hold and assume that $\psi \in H^2(\mathbb{R}^n)$, $\psi \not\equiv 0$ be a nonnegative solution to the Schrödinger equation

$$\left(-\Delta + V(x)\right)\psi(x) = e\psi(x) \tag{81}$$

in the sense of distributions. Then $e = e_0 = \inf_{\|\psi\|_2 = 1} \mathcal{E}(\psi)$ and ψ is the unique minimizer of e_0.

Proof: With an approximation argument as the one on p.39 we show that

$$\mathcal{E}(\psi) = e\,\|\psi\|_2^2 \tag{82}$$

holds for the solution to (81). If we can prove that $e = e_0$, then the statement for ψ therefore follows from Theorem 5.5.2. To prove $e = e_0$, we prove that $e \neq e_0$ implies the orthogonality relation $\int_{\mathbb{R}^n} \Psi(x)\Psi_0(x)\,dx = 0$, where Ψ_0 denotes the unique minimizer of e_0. Since Ψ_0 is strictly positive and Ψ is nonnegative, this orthogonality is impossible.

To prove orthogonality when $e \neq e_0$ we first integrate (81) against Ψ_0 and find

$$\int_{\mathbb{R}^n} \left[\nabla\Psi_0(x)\,\nabla\Psi(x) + V(x)\,\Psi_0(x)\Psi(x)\right] dx = e \int_{\mathbb{R}^n} \Psi_0(x)\Psi(x)\,dx. \quad (83)$$

Note that the integration by parts can be justified when we approximate Ψ and Ψ_0 by functions in $C_c^\infty(\mathbb{R}^n)$. Next, we integrate the equation $(-\Delta + V(x))\Psi_0(x) = e_0\Psi_0(x)$ against Ψ and obtain

$$\int_{\mathbb{R}^n} \left[\nabla\Psi(x)\,\nabla\Psi_0(x) + V(x)\,\Psi(x)\Psi_0(x)\right] dx = e_0 \int_{\mathbb{R}^n} \Psi(x)\Psi_0(x)\,dx. \quad (84)$$

In combination, (83) and (84) show

$$(e-e_0)\int_{\mathbb{R}^n} \Psi(x)\Psi_0(x)\,dx = 0. \tag{85}$$

With $e \neq e_0$ we conclude $\int_{\mathbb{R}^n} \Psi(x)\Psi_0(x)\,dx = 0$, which proves the claim. ∎

As a final topic concerning the Schrödinger equation we discuss higher eigenvalues and eigenfunctions. Let $e_0 < 0$ denote the minimum of $\mathcal{E}$ and let Ψ_0 be the unique minimizer. Let us define the first eigenvalue e_1 by

$$e_1 = \inf_{\substack{\Psi \in H^1(\mathbb{R}^n),\ \|\Psi\|_2 = 1 \\ \int_{\mathbb{R}^n} \overline{\Psi(x)}\,\Psi_0(x)\,dx = 0}} \mathcal{E}(\Psi). \tag{86}$$

If the infimum is attained we call the corresponding minimizer, Ψ_1, the first excited state or the second eigenfunction. Similarly, we define the $(k+1)^{\text{th}}$ eigenvalue recursively (under the assumption that the first k eigenfunctions $\Psi_0, \dots, \Psi_{k-1}$ exist)

$$e_k = \inf \left\{ \mathcal{E}(\psi) \;\middle|\; \psi \in H^1(\mathbb{R}^n),\ \|\psi\|_2 = 1,\ (\psi, \psi_i) = 0,\ i = 0, \dots, k-1 \right\}. \tag{87}$$

In the physical context these eigenvalues have the important meaning that their differences determine the possible frequencies of light emitted by a quantum mechanical system.

Theorem 5.5.5. (Higher eigenvalue and eigenfunctions) Let V be as in Theorem 5.5.1 and assume that the $(k+1)^{th}$ eigenvalue is negative. This includes the assumption that the first k eigenfunctions exist. Then the $(k+1)^{th}$ eigenfunction also exists and satisfies the Schrödinger equation

$$\left(-\Delta + V(x)\right) \psi_{k+1}(x) = e_{k+1} \psi_{k+1}(x) \tag{88}$$

in the sense of distributions. In other words, the recursion described above does not stop until energy zero is reached. Furthermore each e_k can have only finite multiplicity, i.e., each number $e_k < 0$ occurs only finitely many times in the list of eigenvalues. Conversely, every normalized solution to $(-\Delta + V(x))\Psi(x) = e\Psi(x)$ with $e \leq 0$ and $\Psi \in H^1(\mathbb{R}^n)$ is a linear combination of eigenfunctions with eigenvalue e.

Remark 5.5.6. There is no general theorem about the existence of a minimizer if $e_{k+1} = 0$.

Proof: The proof for the existence of a minimizer is basically the same as the one in Theorem 5.5.1. The only additional thing we have to check is that if we have a minimizing sequence $\{\Psi^j\}_{j=1}^{\infty}$ with $\Psi^j \rightharpoonup \Psi_{k+1}$ weakly in $H^1(\mathbb{R}^n)$ and $\langle \Psi^j, \Psi_i \rangle = 0$ for $i = 0, \dots, k$, then $\langle \psi_{k+1}, \psi_i \rangle = 0$ for $i = 0, \dots, k$. This, however, follows immediately because

$$\underbrace{\langle \psi^j, \psi_i \rangle}_{=0 \text{ for all } j \in \mathbb{N}} \xrightarrow{j \to \infty} \langle \psi_{k+1}, \psi_i \rangle. \qquad (89)$$

Next we show (88). We argue as in the proof of Theorem 5.5.1 to see that

$$\left\langle (-\Delta + V - e_{k+1}) f, \psi_{k+1} \right\rangle = 0 \qquad (90)$$

holds for all $f \in C_c^\infty(\mathbb{R}^n)$ with $\langle f, \psi_i \rangle = 0$ for $i = 1 \dots k$. When we approximate the relevant functions in $H^1(\mathbb{R}^n)$ by functions in $C_c^\infty(\mathbb{R}^n)$ we see that (90) implies

$$\int \left[\overline{\nabla g(x)} \nabla \psi_{k+1}(x) + (V(x) - e_{k+1}) \overline{g(x)} \psi_{k+1}(x) \right] dx = 0 \qquad (91)$$

for all $g \in H^1(\mathbb{R}^n)$ with $\langle g, \psi_i \rangle = 0$ for $i = 1 \dots k$. Every function $\varphi \in L^2(\mathbb{R}^n)$ can be written as

$$\varphi(x) = \sum_{i=1}^{k} d_i \,\psi_i(x) + \tilde{\varphi}(x) \tag{S2}$$

with coefficients $d_i \in \mathbb{C}$, $i=1\ldots k$, and $\langle \tilde{\varphi}, \psi_i \rangle = 0$ for $i = 1\ldots k$. Let $g \in H^1(\mathbb{R}^n)$ and write

$$g(x) = \sum_{i=1}^{k} c_i \,\psi_i(x) + \tilde{g}(x). \tag{S3}$$

Since $\psi_i \in H^1(\mathbb{R}^n)$ for $i=1\ldots k$ we know that $\tilde{g} \in H^1(\mathbb{R}^n)$.

We have

$$\int \Big[\overline{\nabla g(x)}\, \nabla \psi_{k+1}(x) + \big(V(x) - e_{k+1}\big) \overline{g(x)}\, \psi_{k+1}(x) \Big] dx$$

$$= \underbrace{\int \Big[\overline{\nabla \tilde{g}(x)}\, \nabla \psi_{k+1}(x) + \big(V(x) - e_{k+1}\big) \overline{\tilde{g}(x)}\, \psi_{k+1}(x) \Big] dx}_{=0 \text{ because of (S1)}}$$

$$+ \sum_{i=1}^{k} \overline{c_i} \underbrace{\int \Big[\overline{\nabla \psi_i(x)}\, \nabla \psi_{k+1}(x) + \big(V(x) - e_{k+1}\big) \overline{\psi_i(x)}\, \psi_{k+1}(x) \Big] dx}$$

ψ_i solves SE in sense of distr., and therefore also in sense of (S1)

$$= (e_i - e_{k+1}) \underbrace{\int_{\mathbb{R}^n} \overline{\psi_i(x)}\, \psi_{k+1}(x) dx}_{=0 \ (\text{orthogonality in } L^2(\mathbb{R}^n))}. \tag{S4}$$

This proves (88).

To prove that e_k has finite multiplicity, we assume the contrary, that is, $e_k = e_{k+1} = e_{k+2} = \dots$. Our previous considerations show there is an orthonormal (in L^2) sequence $\Psi_k, \Psi_{k+1} \dots$ satisfying (88). We claim that this sequence converges weakly to zero in $L^2(\mathbb{R}^n)$: Indeed, for given $\varphi \in L^2(\mathbb{R}^n)$ we can write $\varphi = \sum_{i=k}^{\infty} c_k \Psi_k + \tilde{\varphi}$ with $\langle \tilde{\varphi}, \Psi_i \rangle = 0 \;\; \forall\, i \geq k$ and $\sum\limits_{i=k}^{\infty} |c_k|^2 < +\infty$. Hence,

$$\langle \varphi, \Psi_j \rangle = \overline{c_j} \xrightarrow{j\to\infty} 0 \quad \text{because of} \; . \tag{95}$$

By Theorem 5.3.1 we know that

$$e_i = \mathcal{E}(\Psi_i) \geq \frac{1}{2} \int_{\mathbb{R}^n} |\nabla \Psi_i(x)|^2 dx - C$$

$$\Leftrightarrow \int_{\mathbb{R}^n} |\nabla \Psi_i(x)|^2 \leq 2\big(\underbrace{e_i + C}_{\text{independent of } i}\big) = 2(e_k + C). \tag{96}$$

Hence the sequence $\{\psi_j\}_{j=k}^{\infty}$ has a weakly convergent subsequence in $H^1(\mathbb{R}^n)$, which we continue to denote by the same symbol. The weak limit equals 0 because $\psi_j \to 0$ in $L^2(\mathbb{R}^n)$. With Theorem 5.4.1 we can therefore conclude that $V(\psi_j) \xrightarrow{j\to\infty} 0$, and hence

$$0 > e_k = \mathcal{E}(\psi_k) = \lim_{j\to\infty} \underbrace{\mathcal{E}(\psi_j)}_{\underbrace{\int_{\mathbb{R}^n} |\nabla \psi_j(x)|^2 dx}_{\geqslant 0} + \underbrace{V(\psi_j)}_{\downarrow\, j\to\infty \atop 0}} \geq 0, \qquad (97)$$

which is a contradiction. We conclude that each e_k has only finite multiplicity.

The fact that any solution ψ to the Schrödinger equation

$$\left(-\Delta + v(x)\right)\psi(x) = e\,\psi(x) \qquad (98)$$

can be written as

$$\psi(x) = \sum_{i=1}^{n} c_i \psi_i(x) , \tag{99}$$

where ψ_i , $i=1 \dots n$, are eigenfunctions to the EV e, can be proved with similar arguments as above and is left to the reader.

$\blacksquare$