Quantum mechanics in a nutshell

The state of a classical particle moving in three space is determined by its position and momentum, i.e., six coordinates. In quantum mechanics the state of a particle is given by a complex valued function $\psi(x)$, the wave function. The amount of information, however, is restricted; since Born we interpret $|\psi(x)|^2$ as the probability density of finding a particle at the point $x$. Accordingly we have to require the normalization condition

$$\int_{R^3} |\psi(x)|^2 dx = 1.$$ (1)

The kinetic energy for a classical particle is determined by its momentum and is given by

$$\frac{p^2}{2m},$$ (2)

where $m$ is the mass of the particle. In quantum mechanics the kinetic energy must be determined by the state $\psi$ and is given by

$$T_\psi = \frac{\hbar^2}{2m} \int_{R^3} |(\nabla \psi)(x)|^2 dx.$$ (3)

Any external potential $V(x)$, i.e., $-\nabla V(x)$ is the force acting on the particle at the point $x$, has the quantum mechanical analog

$$V_\psi = \int_{R^3} V(x)|\psi(x)|^2 dx.$$ (4)

Formula (4) can be interpreted as the expectation value of the potential $V$ with respect to the probability distribution $|\psi(x)|^2 dx$. Likewise the kinetic energy can also be interpreted as an expectation value but that is a bit trickier.

Recall that the Fourier transform is defined by

$$\hat{\psi}(k) = \int_{R^3} e^{-2\pi i k \cdot x} \psi(x) dx,$$

and its inverse is given by

$$\psi(x) = \int_{R^3} e^{2\pi i k \cdot x} \hat{\psi}(k) dk.$$

Also recall Plancherel’s theorem which says that

$$\|\hat{\psi}\|_2^2 = \|\psi\|_2^2.$$

A simple calculation leads to

$$\int_{R^3} |(\nabla \psi)(x)|^2 dx = 4\pi^2 \int_{R^3} |k|^2 |\hat{\psi}(k)|^2 dk.$$
and hence
\[ T_\psi = \frac{\hbar^2}{2m} 4\pi^2 \int \mathbb{R}^3 |k|^2 |\hat{\psi}(k)|^2 dk = \frac{\hbar^2}{2m} \int \mathbb{R}^3 |k|^2 |\hat{\psi}(k)|^2 dk, \]
since \( \bar{\hbar} = \hbar/2\pi \). Thus \( T_\psi \) can be interpreted as the expectation value of the quantity \( \frac{\hbar^2}{2m} |k|^2 \) with respect to the probability distribution \( |\hat{\psi}(k)|^2 \), the probability density for the particle to have momentum \( p = \hbar k \). Note our conventions for the Fourier transform differ somewhat from the one usually used.

Classically the total energy of the particle is given by
\[ \frac{p^2}{2m} + V(x) \] (5)
and its quantum analog is then
\[ E_\psi = T_\psi + V_\psi. \] (6)
While the potential \( V(x) \) can be fairly general, let us for the moment consider the case where
\[ V(x) = -\frac{Ze^2}{|x|} \]
which is the Coulomb potential of an electron of charge \( -e \) moving in the field of an infinitely heavy nucleus of charge \( Ze \). Note that classically the kinetic energy (5) associated with this force law can have any value between \( -\infty \) and \( \infty \). If we move the particle towards the origin, the Coulomb potential drowns the potential energy and makes the total energy as large negative as we please.

This is not the case with the quantum mechanical analog given by (6) as we now prove. First let us choose our units. If we replace the wavefunction \( \psi(x) \) by \( \psi_\lambda(x) = \lambda^{3/2} \psi(\lambda x) \) we see that the normalization is preserved. A simple calculation, changing variables leads to
\[ E_{\psi_\lambda} = \lambda^2 \frac{\hbar^2}{2m} \int \mathbb{R}^3 |(\nabla \psi)(x)|^2 dx - \lambda e^2 \int \mathbb{R}^3 |\psi(x)|^2 dx . \]
Pick \( \lambda \) so that
\[ \lambda^2 \frac{\hbar^2}{2m} = \lambda e^2 \]
which leads to
\[ \lambda = \frac{2me^2}{\hbar^2} \]
and hence
\[ E_{\psi_\lambda} = \frac{2me^4}{\hbar^2} \left[ \int \mathbb{R}^3 |(\nabla \psi)(x)|^2 dx - \int \mathbb{R}^3 |\psi(x)|^2 dx \right] . \]
Note that the constant \( \lambda \) has the dimension of an inverse length.

The constant \( \frac{2me^2}{\hbar^2} \) can be written as
\[ \frac{2mc e^2}{\hbar \hbar c} = \frac{2mc}{\hbar} \alpha \]

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where
\[ \alpha = \frac{e^2}{ch} \approx \frac{1}{137.03599911(46)} \]
is a dimensionless number, the **fine structure constant**. In other words the unit of length in which we measure an atom is given by
\[ \frac{1}{2 \alpha} = \frac{\hbar}{2mc} \]
where
\[ \frac{\hbar}{mc} = 386.1592678(26) \times 10^{-15} \text{ m} \]
is the Compton wavelength divided by \( 2\pi \). Hence our atomic length scale is
\[ 2 \times 0.5291772108 \times 10^{-10} \text{ m}, \]
which is twice the Bohr radius. Likewise \( \frac{2mc^4}{\hbar^2} \) can be written as
\[ \frac{2mc^2}{c^2} \frac{e^4}{\hbar^2} = 2mc^2 \alpha^2 \]
The energy
\[ 2mc^2 \alpha^2 = 4 \text{ Ry} \]
where 1 Ry = 13.6 eV. \( mc^2 \) is, of course the rest energy of the electron which is approximately 0.5 MeV. From now on we take as our unit of energy 4 Ry and our unit of length twice the Bohr radius. In this units the functional \( E_\psi \) becomes
\[ E_\psi = \int_{R^3} |(\nabla \psi)(x)|^2 dx - Z \int \frac{1}{|x|} |\psi(x)|^2 dx. \]
We shall often use the abbreviation
\[ \| \nabla \psi \|_2 = \int_{R^3} |(\nabla \psi)(x)|^2 dx. \]
Recall again the main issue, that in contrast to the classical case, \( E_\psi \) cannot be too negative. At the root of this fact is an uncertainty principle. Quite generally, an uncertainty principle says that one cannot localize a state in \( x \) space and Fourier space, i.e., \( p \) space simultaneously. There is a host of those, the most famous being Heisenberg’s uncertainty principle. Here we state another one, namely

**Theorem 1: Coulomb uncertainty principle** Let \( \psi \) be a square integrable function and assume that its gradient is also square integrable. Then
\[ \int_{R^3} \frac{1}{|x|} |\psi(x)|^2 dx \leq \| \nabla \psi \|_2 \| \psi \|_2, \]
where equality holds only if $\psi$ is of the form
\[ \text{const. } e^{-c|x|} \, . \]

where $c > 0$ is a constant.

PROOF: It is a standard fact of analysis that the smooth compactly supported functions are dense in the set of all functions with $\int |\nabla \psi|^2 dx < \infty$. A proof can be found in many text books.

We shall use the abbreviation
\[ (f, g) = \int_{\mathbb{R}^3} f(x) g(x) dx . \]

Using integration by parts it follows that
\[
2(\psi, \frac{1}{|x|}\psi) = \sum_j (\psi, [\partial_{x_j}, \frac{x_j}{|x|}]\psi) = -\sum_j \left[ (\partial_{x_j} \psi, \frac{x_j}{|x|}\psi) + \left( \frac{x_j}{|x|} \psi, \partial_{x_j} \psi \right) \right] \\
= -2\Re \sum_j (\partial_{x_j} \psi, \frac{x_j}{|x|}\psi) \leq 2 \left| (\partial_{x_j} \psi, \frac{x_j}{|x|}\psi) \right| .
\]

Now, using Schwarz’ inequality
\[
| (\partial_{x_j} \psi, \frac{x_j}{|x|}\psi) | \leq \| \partial_{x_j} \psi \|_2 \| \frac{x_j}{|x|}\psi \|_2
\]
with equality only if
\[ \partial_{x_j} \psi = c_j \frac{x_j}{|x|}\psi . \]

Using Schwarz’ inequality once more but this time for sums we get
\[
\sum_j (\partial_{x_j} \psi, \frac{x_j}{|x|}\psi) \leq \| \nabla \psi \|_2 \| \psi \|_2
\]
with equality only if
\[ \nabla \psi = c \frac{\vec{x}}{|x|}\psi . \quad (7) \]

This proves the uncertainty principle (6). Since only the real part is involved the constant $c$ must be real in order to have equality. Further (7) implies that
\[ \psi(x) = \text{const. } e^{c|x|} \]
and hence $c < 0$ for otherwise $\psi$ would not be square integrable.

We use now the uncertainty principle to deal with the ground state energy of the hydrogenic atom.
Theorem 2: Ground state energy for the hydrogenic atom

Consider the minimization problem

$$E_0 := \inf \left\{ E_\psi : \int_{R^3} |(\nabla \psi)(x)|^2 dx < \infty, \int \frac{1}{|x|} |\psi(x)|^2 dx < \infty, \int_{R^3} |\psi(x)|^2 dx = 1 \right\}.$$  

Then $E_0 = -Z^2/4$ and the function

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

is the unique minimizer, i.e.,

$$E_{\psi_0} = -Z^2/4.$$  

REMARK: Note that instead of talking about the constraint $\|\psi\|^2 = 1$ we may instead consider the minimization problem

$$\inf \left\{ E_\psi / \|\psi\|^2 : \int_{R^3} |(\nabla \psi)(x)|^2 dx < \infty, \int \frac{1}{|x|} |\psi(x)|^2 dx < \infty \right\},$$

which leads to the same answer as the one stated in theorem. (Why?)

PROOF: Using the Coulomb uncertainty principle we obtain the lower bound

$$\|\nabla \psi\|^2 - Z\|\nabla \psi\|$$

which is a quadratic function in the ‘variable’ $\|\nabla \psi\|$ which has its minimal value precisely at $Z/2$ and its value is $Z^2/4$. Using what we know about the cases of equality yields the result.

Some elementary facts about $L^p$-spaces

Fix $1 \leq p < \infty$. The set of complex valued functions $f$ on $R^n$ whose $p$-th power is summable, i.e.,

$$\int_{R^n} |f(x)|^p dx < \infty,$$

is denoted by $L^p(R^n)$ and we denote

$$\|f\|_p = \left( \int_{R^n} |f(x)|^p dx \right)^{1/p}.$$  

The integral is the Lebesgue integral. Further we denote by $L^\infty(R^n)$ the space of functions whose essential supremum is finite, i.e., there exists a positive number $K$ so that

$$\{x \in R^n : |f(x)| > K\}$$
has measure zero. The infimum among all such numbers is denoted by
\[ \|f\|_\infty. \]
The two important inequalities are Hölder’s inequality and Minkowsi’s inequality. Hölder’s says that
\[ |\int f(x)g(x)dx| \leq \|f\|_p\|g\|_q \]
provided \(1 \leq p, q \leq \infty\) and \(1/p + 1/q = 1\). Minkowski’s is essentially the triangle inequality
\[ \|f + g\|_p \leq \|f\|_p + \|g\|_p \]
provided \(1 \leq p \leq \infty\). Thus, \(L^p(R^n)\) is a normed linear space with norm \(\|f\|_p\).

**Exercises:**
1) Prove Hölder’s and Minkowski’s inequality.
2) Show that for \(f \in \bigcap_{p \geq p_0} L^p(R^n)\)
\[ \lim_{p \to \infty} \|f\|_p = \|f\|_\infty. \]

One of the key points about \(L^p\) spaces is that they are examples of **Banach spaces**, i.e., **complete normed linear spaces**. Concretely this means that for any Cauchy sequence \(f_n \in L^p(R^n)\) there exists \(f \in L^p(R^n)\) such that \(\|f_n - f\| \to 0\) as \(n \to \infty\).

Let us finally remark that one can define \(L^p\) spaces over any measure space \((\Omega, \Sigma, \mu)\) where \(\Omega\) is a set, \(\Sigma\) is a sigma algebra and \(\mu\) is a measure.

It is clear from the discussion that the space \(L^2(R^n)\) plays a special role because it carries an inner product
\[ (f, g) := \int_{R^n} \overline{f(x)}g(x)dx, \]
and hence its norm can be expressed as
\[ \|f\|_2 = \sqrt{(f, f)}. \]
We say that two function \(f, g\) are **orthogonal** to each other if \((f, g) = 0\).

**Exercises:** 1) Prove the parallelogram identity
\[ \|f - g\|_2^2 + \|f + g\|_2^2 = 2\|f\|_2^2 + 2\|g\|_2^2. \]
2) Prove Schwarz’ inequality in the following strong from
\[ |(f, g)| \leq \|f\|_2\|g\|_2 \]
with equality if and only if \(f\) and \(g\) are proportional.
3) Why is the notion of completeness useful?

4) Show Heisenberg’s uncertainty principle in $\mathbb{R}^n$ which says that

$$n\|\psi\| \leq \|\nabla\psi\|_2 \|\vec{x}\psi\|_2,$$

and deduce from it the ground state energy for the minimization problem

$$H_\psi = \int_{\mathbb{R}^3} |(\nabla\psi)(x)|^2 dx + \int |x|^2 |\psi(x)|^2 dx$$

as well as the normalized minimizer.

**The Schrödinger equation for the hydrogenic atom**

It is now a simple exercise to verify that the function $\psi_0$ satisfies the partial differential equation

$$-\Delta \psi_0 - \frac{Z}{|x|} \psi_0 = -\frac{Z^2}{4} \psi_0 .$$

Thus the value $E_0 = Z^2/4$ appears as an eigenvalue which is no coincidence since by a perturbing $\psi_0$ by a smooth and compactly supported function $f$ one obtains that

$$F(\varepsilon) := \frac{E_{\psi_0 + \varepsilon f}}{\|\psi_0 + \varepsilon f\|_2^2} \geq \frac{E_{\psi_0}}{\|\psi\|_2^2} .$$

Since the derivative of $F(\varepsilon)$ at $\varepsilon = 0$ with respect to $\varepsilon$ vanishes we get that

$$\int_{\mathbb{R}^3} (\nabla\psi)(x) \cdot (\nabla f)(x) dx - Z \int \frac{1}{|x|} \overline{\psi(x)} f(x) dx = E_{\psi_0} \int \overline{\psi(x)} f(x) dx = 0 ,$$

for all $f$ smooth and with compact support. Note that from this one cannot conclude that equation (8) holds everywhere on $\mathbb{R}^3$ directly. It is, however, possible starting from (9) and in particular not knowing what the explicit solution is, to show that the solution is in fact smooth and decays fast enough so that the equations make sense. This is known as the ‘regularity theory’ for partial differential equations.