9.3 Applications

We can use the uncertainty relation to estimate the ground state energy and the position uncertainty in the ground state. As an example consider the hydrogen atom. Assuming the proton is infinitely massive, so it doesn't move and we can ignore its kinetic energy, the Hamiltonian for the electron is

$$\mathcal{H}(\vec{x},\vec{p}) = \frac{p^2}{2m} - \frac{e^2}{r} \qquad \text{(in appropriate "Gaussian" units)}$$

$$\Rightarrow \quad \hat{H} = \frac{\hat{P}_x^2 + \hat{P}_y^2 + \hat{P}_z^2}{2m} - \frac{e^2}{(\hat{X}^2+\hat{Y}^2+\hat{Z}^2)^{1/2}}$$

The expectation value of the energy in a normalized state $|\psi\rangle$ is

$$\langle \hat{H} \rangle = \frac{\langle \hat{P}_x^2 + \hat{P}_y^2 + \hat{P}_z^2 \rangle}{2m} - e^2 \left\langle \frac{1}{(\hat{X}^2+\hat{Y}^2+\hat{Z}^2)^{1/2}} \right\rangle$$

The ground state minimizes $\langle \hat{H} \rangle$. Since

$$\langle \hat{P}_x^2 \rangle = (\Delta P_x)^2 + \langle \hat{P}_x \rangle^2 \geq (\Delta P_x)^2 \qquad \text{etc.}$$

the energy can be minimized only by states that have

$$\langle \hat{P}_x \rangle = \langle \hat{P}_y \rangle = \langle \hat{P}_z \rangle = 0$$

For such states

$$\langle \hat{H} \rangle = \frac{(\Delta P_x)^2 + (\Delta P_y)^2 + (\Delta P_z)^2}{2m} - e^2 \left\langle \frac{1}{\sqrt{\hat{X}^2+\hat{Y}^2+\hat{Z}^2}} \right\rangle$$

Different from the Harmonic oscillator, this is not expressible directly as a function of only ΔX, ΔY, ΔZ etc. (because of the square root). So we cannot use the uncertainty relation to establish a strict lower bound for $\langle \hat{H} \rangle$. We can, however, get a feeling for the approximate magnitude of $\langle \hat{H} \rangle_{min}$ by making the approximation

$$\left\langle \frac{1}{\sqrt{\hat{X}^2+\hat{Y}^2+\hat{Z}^2}} \right\rangle \simeq \frac{1}{\langle \sqrt{\hat{X}^2+\hat{Y}^2+\hat{Z}^2} \rangle} \simeq \frac{1}{\sqrt{\langle \hat{X}^2 \rangle + \langle \hat{Y} \rangle^2 + \langle \hat{Z}^2 \rangle}}$$

where $\simeq$ means "of the same order of magnitude"

So we get

$$\langle \hat{H} \rangle = \frac{\langle \hat{P}_x^2 + \hat{P}_y^2 + \hat{P}_z^2 \rangle}{2m} - e^2 \left\langle \frac{1}{\sqrt{\hat{X}^2+\hat{Y}^2+\hat{Z}^2}} \right\rangle$$

$$\geq \frac{(\Delta P_x)^2 + (\Delta P_y)^2 + (\Delta P_z)^2}{2m} - e^2 \left\langle \frac{1}{\sqrt{\hat{X}^2+\hat{Y}^2+\hat{Z}^2}} \right\rangle$$

$$\gtrsim \frac{\Delta P_x^2 + \Delta P_y^2 + \Delta P_z^2}{2m} - e^2 \frac{1}{\sqrt{(\Delta X)^2 + \langle \hat{X} \rangle^2 + (\Delta Y)^2 + \langle \hat{Y} \rangle^2 + (\Delta Z)^2 + \langle \hat{Z} \rangle^2}}$$

$$\gtrsim \frac{(\Delta P_x)^2 + (\Delta P_y)^2 + (\Delta P_z)^2}{2m} - e^2 \frac{1}{\sqrt{(\Delta X)^2 + (\Delta Y)^2 + (\Delta Z)^2}}$$

Clearly, because of the spherical symmetry of the potential, the configuration of least energy should have spherical symmetry, too (otherwise we would encounter something called "spontaneous breaking of rotational symmetry" in the ground state):

$$\Rightarrow (\Delta X)^2 = (\Delta Y)^2 = (\Delta Z)^2 \text{ and } (\Delta P_x)^2 = (\Delta P_y)^2 = (\Delta P_z)^2$$

in the ground state $|\psi_0\rangle$.

This allows us to write

$$\langle \hat{H} \rangle_0 \gtrsim \frac{3(\Delta P_x)^2}{2m} - \frac{e^2}{\sqrt{3}\,\Delta X}$$

Now we use the uncertainty relation $\Delta P_x \cdot \Delta X \geq \frac{\hbar}{2}$ to find

$$\langle \hat{H} \rangle_0 \gtrsim \frac{3\hbar^2}{8m(\Delta X)^2} - \frac{e^2}{\sqrt{3}\,\Delta X}$$

Minimizing w.r.t. ΔX gives

$$-\frac{6\hbar^2}{8m(\Delta X)^3} + \frac{e^2}{\sqrt{3}(\Delta X)^2} = 0 \quad \Rightarrow \Delta X = 3\sqrt{3}\,\frac{\hbar^2}{4me^2} \approx 1.3\,\frac{\hbar^2}{me^2}$$

which, when inserted into $\langle \hat{H} \rangle_0$, yields

$$\boxed{\langle \hat{H} \rangle_0 \gtrsim -\frac{2me^4}{9\hbar^2}}$$

This estimate gives us the order of magnitude of the ground state energy ($E_0 \simeq -\frac{2}{9}\frac{me^4}{\hbar^2}$ — we can't trust the factor $\frac{2}{9}$, though, to better than a factor 2, say) and of the spread of the ground state wave function ($(\Delta X)_0 \simeq 1.3\,\frac{\hbar^2}{me^2}$, again without warranty for the factor 1.3).

The exact results are (see Chapter 13)

$$E_0 = -\frac{me^4}{2\hbar^2} \quad \text{and} \quad (\Delta X)_0 = a_0 \equiv \frac{\hbar^2}{me^2} \quad \text{(Bohr radius)}$$

They agree with our estimate within the expected (in)accuracy.

The wave function $\psi_0(\vec{r})$ is not a Gaussian, but

$$\psi_0(\vec{r}) = c\, e^{-r/a_0} \quad \text{where } r = \sqrt{x^2+y^2+z^2} .$$

So we see that the uncertainty relation allows us to determine the natural energy and length scales for the problem and estimate the ground state energy and spread of the ground state wave function in terms of these length scales. Only in special cases such as the harmonic oscillator these estimates become exact.

9.4 The energy-time uncertainty relation

There exists an uncertainty relation

$$\Delta E \cdot \Delta t \geq \hbar/2 \qquad (\Delta)$$

which does not follow from the inequality at the bottom of p. 2. Instead, it is a consequence of the Schrödinger equation for the time evolution of the state $|\psi(t)\rangle$, combined with the $\hat{X}$-$\hat{P}$-uncertainty relation.

The meaning of the relation (Δ) is that, if the system has been in existence (or has been allowed to settle down) only for a finite time Δt, its energy expectation value is uncertain by an amount $\Delta E \geq \frac{\hbar}{2\Delta t}$.
Energy conservation can be violated by an amount $\Delta E \sim \frac{1}{\Delta t}$ that vanishes in the limit $\Delta t \to \infty$.

To see how this comes about, recall that eigenstates of energy (i.e. states with $\Delta E = 0$) have time dependence $e^{-iEt/\hbar}$, i.e. correspond to states with definite frequency $\omega = \frac{E}{\hbar}$.
Only a wave train that is infinitely long in time (i.e. only a system that has been in existence for an infinite time), has definite frequency $\omega = E/\hbar$. All finite-time states, when Fourier-analyzed, are a superposition of states with different frequencies.

To illustrate this, look at two examples:

(1) Consider a 1-dimensional Gaussian wavepacket of spatial width ΔX and momentum uncertainty $\Delta P = \frac{\hbar}{\Delta X}$, moving with average momentum $\langle \hat{P} \rangle = p_0$.

Its (kinetic) energy is $\langle \hat{H} \rangle = \frac{\langle \hat{p}^2 \rangle}{2m}$. One can show that the energy uncertainty

$$\Delta E = \sqrt{\langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2} = \frac{p_0}{m} \Delta P = v_0 \Delta P$$

A monitor located at fixed position sees the wave packet sweeping through its position. Due to the width of the wavepacket, the determination of the time at which the particle passes the monitor is uncertain by the amount

$$\Delta t = \frac{\Delta X}{v_0} \geq \frac{\hbar/2}{v_0 \Delta P} = \frac{\hbar/2}{\Delta E} \Longrightarrow \Delta t \cdot \Delta E \geq \hbar/2$$

(2) At time $t = 0$ we turn on light of frequency ω and shine it on an ensemble of hydrogen atoms in their ground state. Since the light consists of photons of energy $\hbar\omega$, we expect it to excite only states with energy $\hbar\omega$ above the ground state (if such states exist). However, if we switch off the light after time Δt, we will observe hydrogen atoms that have been excited to different levels not obeying this constraint (just wait until they

de-excite and measure the frequency of the emitted light).

However, as Δt increases, the deviation ΔE from the expected final state energy will decrease like $\Delta E \sim \frac{\hbar}{2\Delta t}$. The reason is that a light source of finite duration Δt has time structure $e^{-i\omega t}\theta(t)\,\theta(\Delta t - t)$ whose Fourier transform is not a δ-function at frequency ω — only for $\Delta t \to \infty$ does it become infinitesimally narrowly peaked at ω.

Similarly, if excited atoms with mean lifetime Δt deexcite by emitting a photon, the energy of the photon is spread around $E_{if} = E_i - E_f$ with a width $\Delta E = \frac{\hbar}{2\Delta t}$. This explains the line-shapes of atomic emission and absorption spectra.

We will return to this example in Section 18.5.