Problems:
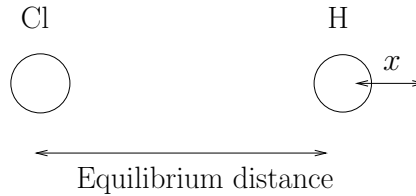
1. Stationary States:

   (a) Take the stationary states of the a particle in the box $\Psi_n(x,t) = \Psi_n(x)e^{-iE_n t/\hbar}$. Show that that $\overline{\mathbb{E}} = E_n$, $\overline{\mathbb{E}^2} = E_n^2$, and $\Delta E = 0$

2. **Graded** Consider a (pretty good!) model of the vibrations of HCl made up of hydrogen and clorine atoms in an ionic bond shown below.

Cl   H

Equilibrium distance

In general the hydrogen nucleus (i.e. the proton) vibrates around its equilibrium position since it can never be exactly at one spot. Make a model of these vibrations by considering the chlorine nucleus to be very heavy and therefore fixed in space (it is 35 times heavier than the hydrogen atom.) When discussing the vibrations of the hydrogen nucleus neglect any effects due to the motion of the electrons (electrons are very light compared to nucleus – e.g. when two trucks collide the motion of the mirror is irrelevant. The electrons move much more quickly than the nuclei too as we will see below.) For small displacements of the hydrogen nucleus from its equilibrium position, the force will be proportional to the displacemnet $F = -Cx$ (I use C instead of k because thats what the book uses). This means that the potential energy is like a spirng $\frac{1}{2}Cx^2$. We recall that the classical oscillation frequency is

$$\omega_o = 2\pi f = \sqrt{\frac{C}{m}}$$

where m is the mass of the hydrogen nucleus. Classically the hydrogen nucleus would arrive at the bottom of the potential well and have no displacement from equilibrium. Quanum mechanically the potential tries to squish the wave function of the proton to the very bottom of the well. But this is balanced by the kinetic energy associated with the uncertainty principle, i.e. if a wave is small in size its typical momentum is very large. We will describe the wave function of the proton

   (a) Estimate the size of the ground state wave function by balancing the kinetic and potential energies. (Answer : size $\sim \left(\frac{\hbar^2}{mC}\right)^{1/4} \sim \left(\frac{\hbar}{m\omega_o}\right)^{1/2}$)

   (b) Estimate the average kinetic, potential, and total energies in terms of ω_o using the uncertainty principle. (Answer, should be very simple)

   (c) The normalized ground state wave function of the harmonic oscillator is

$$\Psi_0(x) = \left(\frac{1}{\sqrt{\pi}L}\right)^{1/2} e^{-\frac{x^2}{2L^2}} \tag{1}$$

   where

$$L = \left(\frac{\hbar^2}{mC}\right)^{1/4} = \left(\frac{\hbar}{m\omega_o}\right)^{1/2}.$$

   This is the wave function of the proton Show that this wave function is a solution to the time independent Schrödinger equation and determine the energy associated with this state.

   (d) Determine $\bar{x}$, $\overline{x^2}$, $\bar{p}$, $\overline{p^2}$. (Answers: simple, $L^2/2$, simple, $(\hbar/L)^2/2$)

   (e) Show that the ground state of the harmonic oscillator saturates the uncertainty principle:

$$\Delta x \Delta p = \frac{\hbar}{2}$$

(f) Determine the average kinetic, potential and total energies using the results of part (d) and compare to your estimate of part 2.

(g) Measured spring constants are typically $C = 29.6 \, \text{eV}/\text{Å}^2$. Substitute numbers into parts (a), (b) and compare your results to the Bohr radius and a typical atomic-electronic energy $\sim 2 \, \text{eV}$. You should find that the energies associated with molecular vibrations are about 1/20th of electronic excitation energies.

(h) Finally determine the root-mean-square velocity of the hydrogen nulceus

$$v_{\text{rms}} \equiv \sqrt{\frac{\overline{p^2}}{m^2}} \, ,$$

and compare your velocity to the velocity of an electron in the lowest Borh orbit. You should find $v \sim 3600 m/s$ or about 1/1000th of the bohr orbital velocity.

(i) You may find the following integrals useful.

$$\int_{-\infty}^{\infty} du \, e^{-u^2} = \sqrt{\pi} \qquad \int_{-\infty}^{\infty} du \, u^2 e^{-u^2} = \frac{\sqrt{\pi}}{2} \tag{2}$$

Wavefunctions

1. The electron wave function squared $|\Psi(x,t)|^2 = \text{P}(x,t)$ is *a probability per unit length* to find the particle at time t. Thus the probability $\text{d}\mathscr{P}$ to find a particle between x and $x + dx$ at time t

$$\text{d}\mathscr{P} = \text{P}(x,t)dx = |\Psi(x,t)|^2 dx \tag{3}$$

2. The electron must be somewhere so

$$\int_{-\infty}^{\infty} dx \, |\Psi(x,t)|^2 = 1 \tag{4}$$

3. The average position at time t

$$\overline{x} = \int dx \, x \, |\Psi(x,t)|^2 \tag{5}$$

4. The average position squared at time t is

$$\overline{x^2} = \int dx \, x^2 \, |\Psi(x,t)|^2 \tag{6}$$

5. The uncertainty squared in position $(\Delta x)^2$ (or standard deviation squared) is defined to be

$$(\Delta x)^2 \equiv \overline{x^2} - \overline{x}^2 = \overline{(x - \overline{x})^2} \tag{7}$$

If the average position is zero $\overline{x} = 0$ then $(\Delta x) \equiv \sqrt{\overline{x^2}}$ is the "root mean square" position. This gives a measure of how spread out is the wave function

Momentum Averages

1. We use a notation for "Operators"

$$\overline{x} = \int_{-\infty}^{+\infty} dx \, \Psi^*(x)\mathbb{X}\Psi(x) \tag{8}$$

$$= \int_{-\infty}^{+\infty} dx \, \Psi^*(x)x\Psi(x) \tag{9}$$

Here $\mathbb{X}$ is an simply an "operator" which takes the function $\Psi(x)$ and spits out the new function $x\Psi(x)$. It just gives a notation to things that we alaready understand, for example $\mathbb{X}^2\Psi(x) = \mathbb{X}\,x\Psi(x) = x^2\Psi(x)$

2. The average momentum is

$$\bar{p} = \int_{-\infty}^{+\infty} dx \, \Psi^*(x) \mathbb{P} \Psi(x) \tag{10}$$

$$= \int_{-\infty}^{+\infty} dx \, \Psi^*(x) \left(-i\hbar \frac{d}{dx} \right) \Psi(x) \tag{11}$$

$$= \int_{-\infty}^{+\infty} dx \, \Psi^*(x) \left(-i\hbar \frac{d\Psi}{dx} \right) \tag{12}$$

Here the momentum operator is

$$\mathbb{P} = -i\hbar \frac{d}{dx}$$

takes the function $\Psi(x)$ and spits out the derivative $-i\hbar \frac{d\Psi}{dx}$.

3. The average momentum squared is

$$\overline{p^2} = \int_{-\infty}^{+\infty} \Psi^*(x) \mathbb{P}^2 \Psi(x) \tag{13}$$

$$= \int_{-\infty}^{+\infty} \Psi^*(x) \left(-\hbar^2 \frac{d^2}{dx^2} \right) \Psi(x) \tag{14}$$

4. The uncertainty squared in momentum (or standard deviation squared) is defined like for $(\Delta x)^2$

$$(\Delta p)^2 \equiv \overline{p^2} - \bar{p}^2 \tag{15}$$

Again if $\bar{p}$ is zero then $\Delta p \equiv \sqrt{\overline{p^2}}$ is the "root mean square" momentum.

5. The average kinetic energy is

$$\overline{KE} = \int_{-\infty}^{+\infty} \Psi^*(x) \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right] \Psi(x) \tag{16}$$

6. The formal statement of the uncertainty principle is

$$(\Delta x)(\Delta p) \geq \frac{\hbar}{2} \tag{17}$$

where the standard deviation in position Δx and momentum Δp are defined as above. (You can see why its a good thing that we know how to use it before we can state it precisely)

Quantum Mechanics

1. As with momentum, the average energy of a particle

$$\overline{E} = \int \Psi^*(x,t) \mathbb{E} \Psi(x,t) \tag{18}$$

$$= \int_{-\infty}^{\infty} dx \Psi^*(x,t) \left[+i\hbar \frac{\partial}{\partial t} \right] \Psi(x,t) \tag{19}$$

and the energy operator

$$\mathbb{E} = +i\hbar \frac{\partial}{\partial t} \tag{20}$$

Note the difference in sign between this and the momentum operator $\mathbb{P}$ which ultimately is a reflection of the fact that waves are written $e^{+i(kx-\omega t)}$ with opposite signs for k and ω

2. The Schrödinger equation can be written

$$\left[\frac{\mathbb{P}^2}{2M} + V(\mathbb{X})\right]\Psi(x,t) = \mathbb{E}\Psi(x,t) \tag{21}$$

$$\left[-\frac{\hbar^2}{2M}\frac{d^2}{dx^2} + V(x)\right]\Psi(x,t) = +i\hbar\frac{\partial\Psi}{\partial t} \tag{22}$$

where V(x) is the potential energy (think $V = 1/2\,kx^2$)

3. The stationary wave functions (or eigenfunctions, or standing wave patterns) have the following form

$$\Psi(x,t) = e^{-i\frac{E_n t}{\hbar}}\Psi_n(x) \tag{23}$$

These are called stationary because the square does not depend on time

$$|\Psi(x,t)|^2 = \left|e^{-i\frac{E_n t}{\hbar}}\right|^2 |\Psi_n(x)|^2 \tag{24}$$

$$= |\Psi_n(x)|^2 \tag{25}$$

Since the wave funcion does not depend on time, we can take a long time to determine the energy. So stationay wave functions have functions exactly one energy, $E = E_n$, and ΔE is zero. $\Delta E^2 = \overline{\mathbb{E}^2} - \overline{\mathbb{E}}^2$

4. Stationary wave functions (also known as eigenfunctions) obey the time independent Schrödinger equation.

$$\left[-\frac{\hbar^2}{2M}\frac{d^2}{dx^2} + V(x)\right]\Psi_n(x) = E_n\Psi_n(x) \tag{26}$$

Here the E_n are the energy levels (as in the $E_n = -13.6eV/n^2$ in the Bohr Model) and Ψ_n are the stationary wave functions

Particle in the Box

1. For an electron bouncing around in a box of size a the stationary wave functions (eigen-functions) are

$$\Psi_n(x) = \begin{cases} \sqrt{\frac{2}{a}}\cos\left(\frac{n\pi x}{a}\right) & n = 1, 3, 5, \ldots \\ \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right) & n = 2, 4, 6, \ldots \end{cases} \tag{27}$$

while the stationary energies are

$$E_n = \frac{\hbar^2 k_n^2}{2M} = \frac{\hbar^2\pi^2}{2Ma^2}n^2 \qquad n = 1, 2, 3, 4, 5, \ldots \tag{28}$$