Expectation values I

- Imagine having a die (singular of dice): what's the average number you get? Well, it's $(1+2+3+4+5+6)/6 = 21/6 = 3.5$, which sort of makes sense. We can also get this result by constructing a table:

Die value x	1	2	3	4	5	6
Relative probability	1	1	1	1	1	1
Normalized probability $P(x)$	1/6	1/6	1/6	1/6	1/6	1/6

- Maybe if we multiply the thing we are trying to measure, which is x, by the probability $P(x)$ of each value we might get, we can calculate the average value? Let's call the average $\langle x \rangle$:

$$\langle x \rangle = 1 \cdot \frac{1}{6} + 2 \cdot \frac{1}{6} + 3 \cdot \frac{1}{6} + 4 \cdot \frac{1}{6} + 5 \cdot \frac{1}{6} + 6 \cdot \frac{1}{6} = (1+2+3+4+5+6)\frac{1}{6} = \frac{21}{6} = 3.5$$

Expectation values II

- So it looks like $\langle x \rangle = \int_{-\infty}^{\infty} x\, P(x)\, dx$ is a procedure that makes sense for getting averages (see Serway Eq. 6.31).
- Let's try a slightly less trivial situation, like a loaded die such that it comes up on the number 4 twice as often. What's the average number you get? Well, if we double-count the 4 we have seven possibilities:

Die value x	1	2	3	4	5	6
Relative probability	1	1	1	2	1	1
Normalized probability $P(x)$	1/7	1/7	1/7	2/7	1/7	1/7

- In this case we have

$$\langle x \rangle = 1 \cdot \frac{1}{7} + 2 \cdot \frac{1}{7} + 3 \cdot \frac{1}{7} + 4 \cdot \frac{2}{7} + 5 \cdot \frac{1}{7} + 6 \cdot \frac{1}{7} = (1+2+3+8+5+6)\frac{1}{7} = 3.57$$

which sounds plausible.

Expectation values III

What if we want to measure the average value of x^2? Well, we could just multiply each of the possible values of x^2 by their relative probabilities, which would look like

Die value squared x^2	1	4	9	16	25	36
Relative probability	1	1	1	2	1	1
Normalized probability $P(x)$	1/7	1/7	1/7	2/7	1/7	1/7

It looks like we could generalize the procedure for any function of x like $f(x)$—which is x^2 in the above example—to have a rule (see Serway Eq. 6.32)

$$\langle f \rangle = \int_{-\infty}^{\infty} f(x)\, P(x)\, dx \tag{1}$$

Expectation values IV

- Now let's think about some uses for these expectation values. Obviously $\langle x \rangle$ tells us the average value, which we usually like to know.
- But averages don't always tell us the whole story! We could take a lot of precision ball bearings and determine their average diameter, and a collection of pumpkins from a field and determine *their* average diameter. But we know we're missing something in this simple calculation: the degree of uniformity around that average.
- So let's consider the standard deviation σ, which is the square root of the variance σ^2:

(2) $$\sigma = \sqrt{\sigma^2} = \sqrt{\frac{\sum_{i=1}^{N}(x_i - \bar{x})^2}{N}} = \sqrt{\frac{\sum(x_i - \langle x \rangle)^2}{N}}$$

- Why look at the square of the difference of each particular measurement x_i from the average $\bar{x}$? Because the average of the differences without squaring is zero; it's how we determine the average in the first place!

(3) $$\bar{x} = \langle x \rangle = \frac{\sum x_i}{N}$$

Expectation values IV

- By the way, we're supposed to have $N-1$ in the denominator of Eq. 2 because it's only with $N=2$ measurements that we can see some variance...
- Let's expand out the calculation of the variance σ^2 using Eqs. 2 and 3:

$$\begin{aligned} \frac{\sum(x_i - \langle x \rangle)^2}{N} &= \frac{\sum(x_i)^2}{N} - 2(\langle x \rangle)\frac{\sum(x_i)}{N} + (\langle x \rangle)^2 \sum \frac{1}{N} \\ &= \langle x^2 \rangle - 2(\langle x \rangle)(\langle x \rangle) + (\langle x \rangle)^2 = \langle x^2 \rangle - (\langle x \rangle)^2 \end{aligned} \tag{4}$$

so that the standard deviation is (Serway Eq. 6.34)

$$\sigma = \sqrt{\sigma^2} = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} \tag{5}$$

- What has this given us? A way to measure not only the average position of a particle in a particular quantum state, but also the width of its distribution.

The Schrödinger perscription (again)

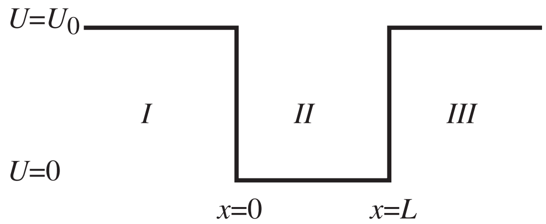
- Find the potential U. Think of boundary conditions.
- Try a guess of the wave function ψ, by taking its second derivative and seeing if it satisfies

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}\right)+U\psi=E\psi.$$

- This will often give you the energies of the solutions.
- Enforcing $\int \psi^*\psi = 1$ will give you the normalization.
- Then ψ gives you the probability amplitude, and $|\psi^*\psi|$ gives you the probability.
- Problems we have solved:
  - → Infinite square well in 1D and in 2D
  - → Harmonic oscillator

Finite square well (Serway 6.5)

- We've done a particle in a restoring force potential (the harmonic oscillator), and also in an infinite square well. Let's now consider a square well:



  Based on our solution to the harmonic oscillator, we expect that a particle should be confined but that it might extend out past its classical limit.

- Outside the well (regions *I* and *II*), Schrödinger's equation for a particle traveling in a constant finite potential is

$$
\begin{aligned}
-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U_0\psi &= E\psi \\
\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} &= (U_0 - E)\psi \\
\frac{d^2\psi}{dx^2} &= \alpha^2\psi \qquad \text{with} \qquad \alpha^2 \equiv \frac{2m(U_0 - E)}{\hbar^2}
\end{aligned}
$$

Finite square well II

- Again, for outside the finite square well (regions I and III) we had

$$\frac{d^2\psi}{dx^2} = \alpha^2\psi \qquad \text{with} \qquad \alpha^2 \equiv \frac{2m(U_0 - E)}{\hbar^2}$$

  Now in the case where $E > U_0$ we have a particle which happily travels along with a different net energy and thus a different de Broglie wavelength, and the particle will never be bound inside the finite square well. So let's consider only the cases where $E < U_0$. In this case, α^2 is always a positive number, and two possible solutions for the wave function are $\psi = Ae^{+\alpha x}$ and $\psi = Ae^{-\alpha x}$.

- Consider region *I*. If we were to have $\psi = Ae^{-\alpha x}$ then the wave function would grow exponentially as we went to increasing $-x$ values farther away from the confining potential. This would not make sense! The converse holds for region III. The solutions that *do* make sense for regions I and III are

$$\psi_I(x) = Ae^{+\alpha x} \qquad \text{and} \qquad \psi_{III}(x) = De^{-\alpha x}$$

Finite square well III

- What we have seen is that in region *III* for example we have a wavefunction which is a decaying exponential:

$$\psi_{III}(x) = Ae^{-\alpha x} \qquad \text{with} \qquad \alpha \equiv \frac{\sqrt{2m(U_0 - E)}}{\hbar}$$

That is, the wavefunction $\psi_{III}(x)$ dies off to $1/e$ of its amplitude in a distance δ of $1/\alpha$, or

$$\delta = \frac{1}{\alpha} = \frac{\hbar}{\sqrt{2m(U_0 - E)}} \tag{6}$$

- The probability $\propto \psi^2$ will be attenuated by $\exp[-1] = \exp[-1/2]^2 = e^{-(\frac{1}{2})^2} = 0.37$ when we have traveled a tunneling distance x_t of $\delta/2$.

This relates to the uncertainty principle!

- The particle is no longer confined to being purely inside the box, even though classically it would be! The particle can "leak" some distance out of the box. Consider an electron with $(U_0 - E) = 1$ eV:

$$x_t = \frac{\delta}{2} = \frac{\hbar}{2\sqrt{2m(U_0 - E)}} = \frac{hc}{4\pi\sqrt{2mc^2(U_0 - E)}} = \frac{1240\text{ eV}\cdot\text{nm}}{4\pi\sqrt{2\cdot 511\times 10^3\cdot 1}} = 0.09\text{ nm}.$$

  or about the radius of one atom.

- We can compare this leakage distance with the de Broglie wavelength for a particle with an energy $E_\lambda = (U_0 - E)$:

$$\lambda = \frac{h}{p} = \frac{2\pi\hbar}{\sqrt{2mE_\lambda}} \qquad \text{leading to} \qquad x_t = \frac{\lambda}{4\pi}.$$

  This helps us (in a hand-waving way) to understand why the Heisenberg uncertainty principle is $(\Delta x)\cdot(\Delta p) = \hbar/2$ rather than h.

From infinite to finite quantum well

- Recall that for quantum well of width L with infinite sides, we found that the energies of allowed states were given by

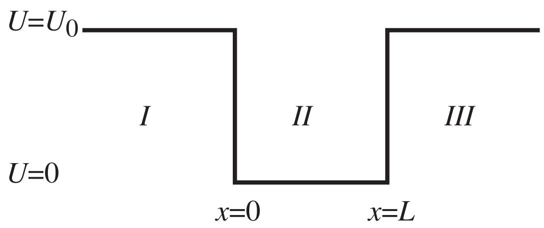
$$E_n = \frac{n^2\pi^2 h^2}{2mL^2} \qquad \text{for} \qquad n = 1, 2, \ldots$$

- We can get a first order approximation of the energies of states in the *finite* quantum well by increasing the width of an infinite box by δ on each side:

$$E_n \simeq \frac{n^2\pi^2 h^2}{2m(L+2\delta)^2} \qquad \text{for} \qquad n = 1, 2, \ldots \tag{7}$$

Finite square well IV

- Let's return to the wave function characteristics. We found $\psi_I = Ae^{+\alpha x}$ and $\psi_{III} = De^{-\alpha x}$, with $\alpha = \sqrt{2m(U_0 - E)}/\hbar$. What about inside the potential, in region *II*?



- Well, here we have a free particle in zero potential which can travel either direction, which we could write as $\psi_{II}(x) = Be^{-ikx} + Ce^{+ikx}$ but since $e^{ikx} = \sin kx + i\cos kx$ we can also write this as

$$\psi_{II}(x) = B\sin(kx) + C\cos(kx) \qquad \text{with} \qquad k = \frac{2\pi}{\lambda} = \frac{2\pi p}{h} = \frac{\sqrt{2mE}}{\hbar}. \tag{8}$$

- Now that we have forms for the wave function in each region, we require the wave function to be continuous and un-kinked.

Boundary conditions in general, and at $x = 0$

- We want the wavefunction to be continuous. We have the wave functions; to get them to be unkinked we need their derivatives:

$$\frac{d\psi_I}{dx} = \frac{d}{dx} Ae^{+\alpha x} = A\alpha e^{+\alpha x} \tag{9}$$

$$\frac{d\psi_{II}}{dx} = \frac{d}{dx}\left(B\sin(kx) + C\cos(kx)\right) = Bk\cos(kx) - Ck\sin(kx) \tag{10}$$

$$\frac{d\psi_{III}}{dx} = \frac{d}{dx} De^{-\alpha x} = -D\alpha e^{-\alpha x} \tag{11}$$

- Now let's consider $x = 0$ which is the boundary between regions I and II. We want to satisfy

$$Ae^{+\alpha\cdot 0} = B\sin(k\cdot 0) + C\cos(k\cdot 0) \quad \Rightarrow \quad A = C$$

$$\text{and} \quad A\alpha e^{+\alpha\cdot 0} = Bk\cos(k\cdot 0) - Ck\sin(k\cdot 0) \quad \Rightarrow \quad A\alpha = Bk$$

which gives $A = C = Bk/\alpha$.

Boundary conditions at $x = L$

Now let's look at the right boundary. From continuity of the wavefunctions and $C = Bk/\alpha$ we get

$$B\sin(kL) + C\cos(kL) = B\sin(kL) + B\frac{k}{\alpha}\cos(kL) = De^{-\alpha L} \tag{12}$$

while from the continuity of the derivative we get

$$Bk\cos(kL) - Ck\sin(kL) = Bk\cos(kL) - B\frac{k^2}{\alpha}\sin(kL) = -D\alpha e^{-\alpha L}. \tag{13}$$

The ratio of these two expressions is

$$\frac{\sin(kL) + \frac{k}{\alpha}\cos(kL)}{\cos(kL) - \frac{k}{\alpha}\sin(kL)} = -\frac{k}{\alpha}. \tag{14}$$

While this is nothing that is easily simplified, we can still gain some insight into the solution.

What have we learned from the boundary conditions?

- We have found that the boundary conditions let us relate $A = C = Bk/\alpha$ and once we know a particular energy solution (and thus $k = \sqrt{2mE}/\hbar$) we can get a relationship to coefficient D from Eq. 12.
- More importantly, we have arrived at the relationship of Eq. 13 of

$$\frac{\sin(kL) + \frac{k}{\alpha}\cos(kL)}{\cos(kL) - \frac{k}{\alpha}\sin(kL)} = -\frac{k}{\alpha}.$$

where $k = \sqrt{2mE}/\hbar$ and $\alpha = \sqrt{2m(U_0 - E)}/\hbar$, or

$$\frac{\sin(\sqrt{2mE}\frac{L}{\hbar}) + \sqrt{\frac{E}{U_0-E}}\cos(\sqrt{2mE}\frac{L}{\hbar})}{\cos(\sqrt{2mE}\frac{L}{\hbar}) - \sqrt{\frac{E}{U_0-E}}\sin(\sqrt{2mE}\frac{L}{\hbar})} = -\sqrt{\frac{E}{U_0 - E}}. \tag{15}$$

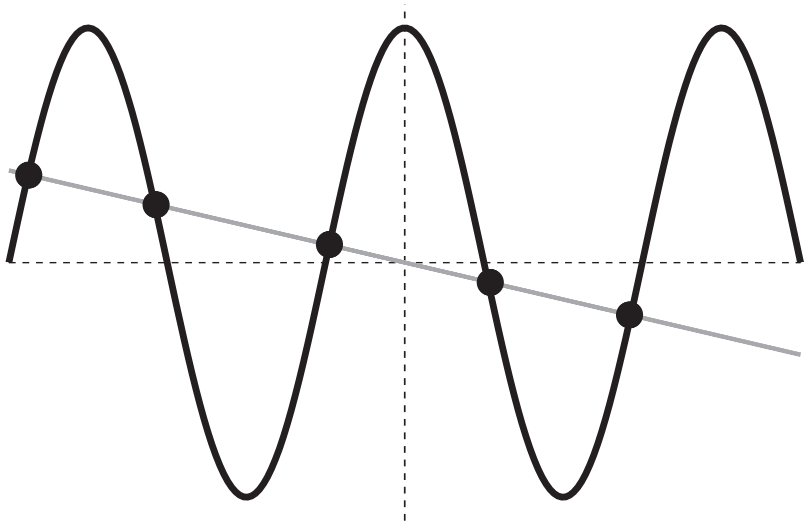
So what can we do with this?

What does this tell us?

Again, by matching boundary conditions we have found the requirement of Eq. 15:

$$\frac{\sin(\sqrt{2mE}\frac{L}{\hbar}) + \sqrt{\frac{E}{U_0-E}}\cos(\sqrt{2mE}\frac{L}{\hbar})}{\cos(\sqrt{2mE}\frac{L}{\hbar}) - \sqrt{\frac{E}{U_0-E}}\sin(\sqrt{2mE}\frac{L}{\hbar})} = -\sqrt{\frac{E}{U_0 - E}}.$$

This is of course not straightforward to solve! However, if we know L, m, and U_0, we can at least plot the left hand side versus E, and we can also plot the right hand side versus E. This allows us to find a discrete set of solutions! Let's say the left hand side was a simple cosine function, and the right hand side was a simple linear slope; we'd then find particular energy solutions graphically as follows:



Finite square well: the picture

OK, so you get the idea. The wavefunction solutions ψ at the discrete energy states look like this (Serway Fig. 6.16):

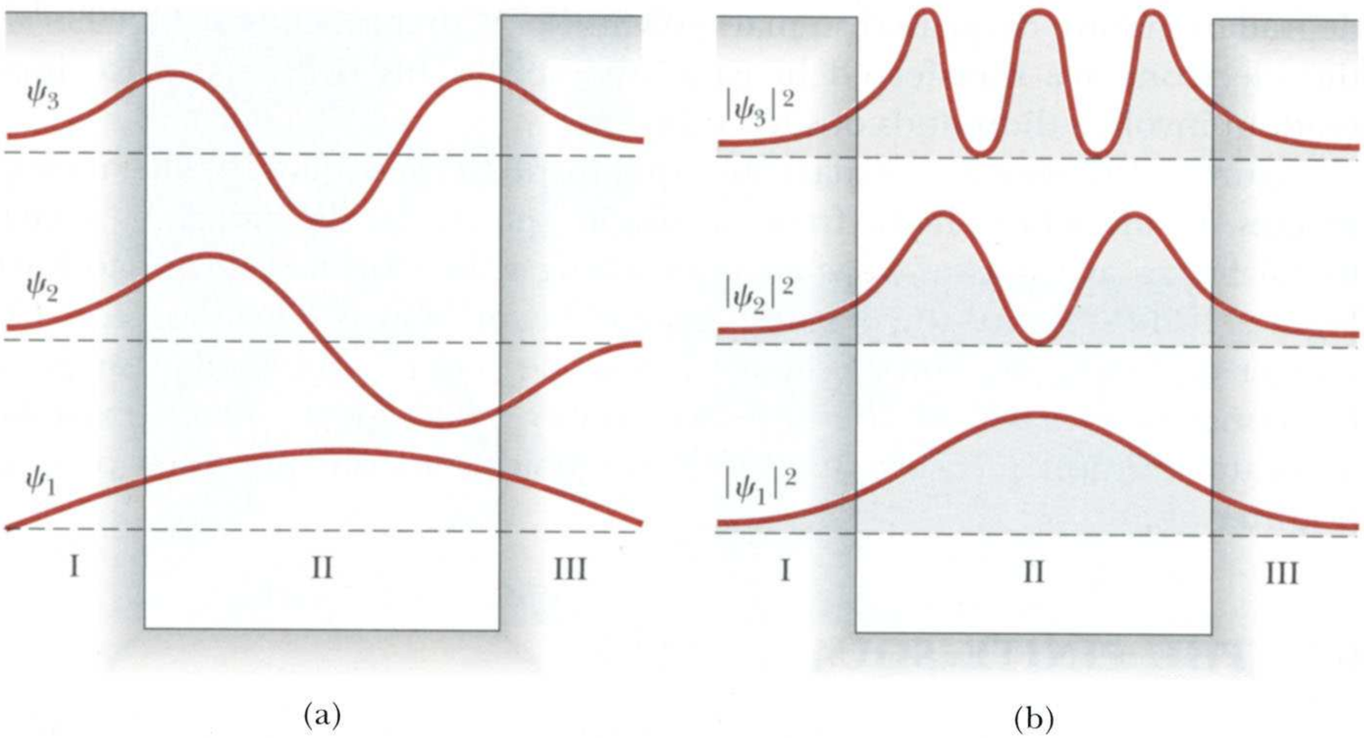
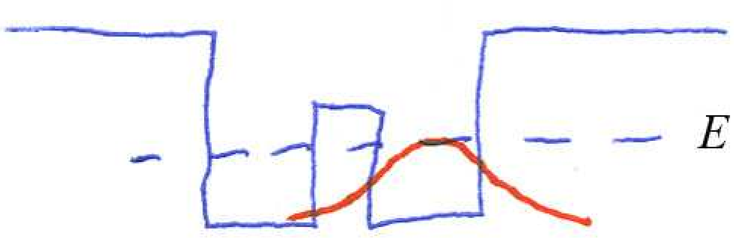


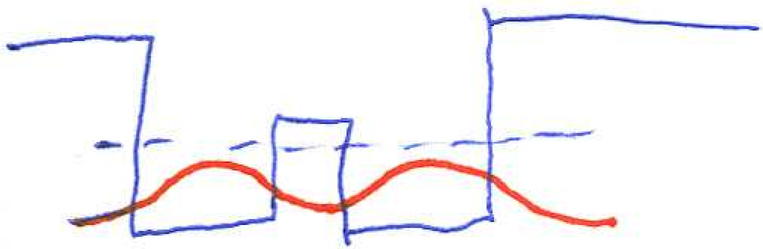
Figure 6.16 (a) Wavefunctions for the lowest three energy states for a particle in a potential well of finite height. (b) Probability densities for the lowest three energy states for a particle in a potential well of finite height.

You can see how this works out a bit more explicitly when you solve problem 6.23!

Leaking/sloshing states

- Consider two finite wells with a reduced barrier between them. If we put a classical particle in one well, with less energy than the height of the barrier, it's stuck in that well forever.
- Not so with quantum mechanics! The particle can "leak" out of one well and into the other! Particles can slosh back and forth between these two wells, and end up distributed between them:





- Which well is the particle in? Both! This is a better situation to visualize than Schrödinger's cat being both alive and dead.

Walking through walls

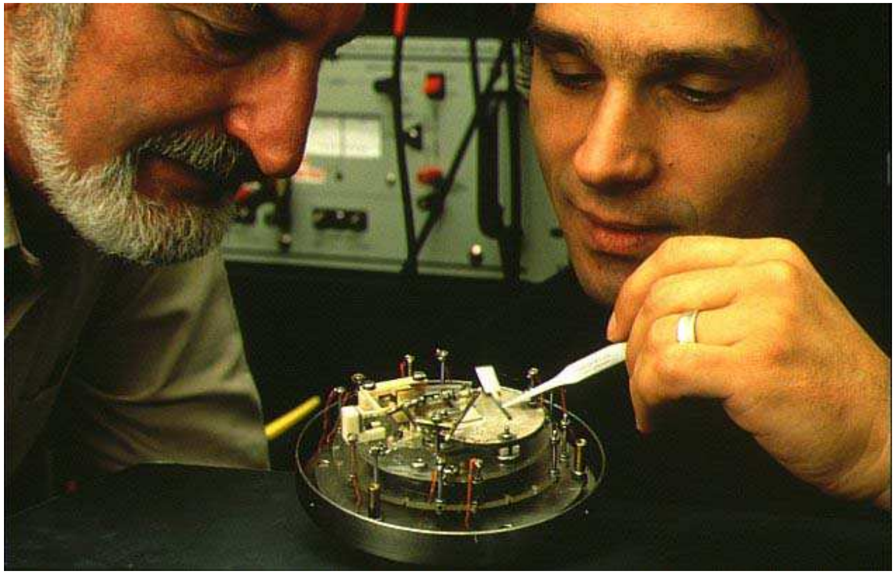
- Can we walk through a wall? Not very likely. . .
- But perhaps nucleons can escape from the nucleus by tunneling! George Gamow, 1936: explanation for radioactivity. We'll get to this. . .
- Tunnelling of an electron over a 5 eV gap:

$$x_t = \frac{\hbar}{2\sqrt{2m(V-E)}} = \frac{1}{2\pi}\frac{hc}{2\sqrt{2mc^2(V-E)}}$$
$$= \frac{1}{2\pi}\frac{1240\text{ eV}\cdot\text{nm}}{2\sqrt{2\cdot 511\times 10^3\text{ eV}\cdot 5\text{ eV}}} = 0.044\text{ nm}$$

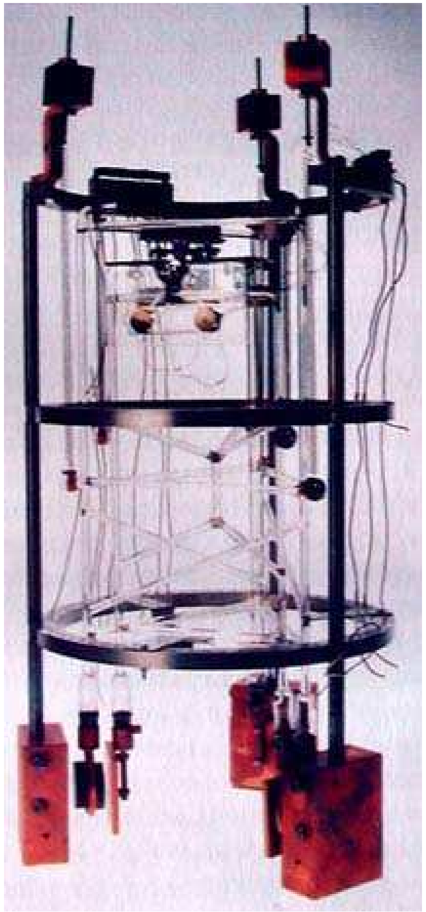
so for every 0.1 nm or 1 Å the current will be reduced by a factor of $\exp[-0.1/0.044] = 0.1$.

The scanning tunneling microscope

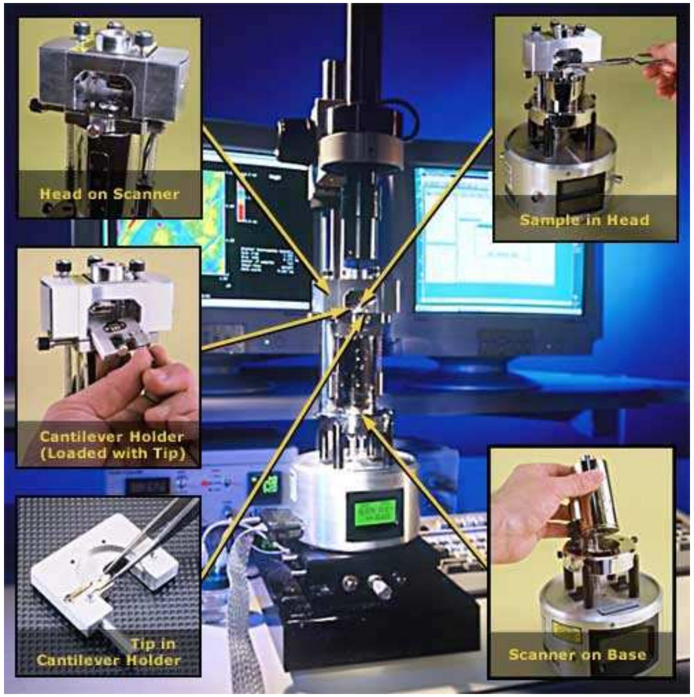
The first STM, with its inventors Heinrich Rohrer (b. 1933) and Gerd Binnig (b. 1947) at the IBM Zurich lab (they won the 1986 Nobel Prize):



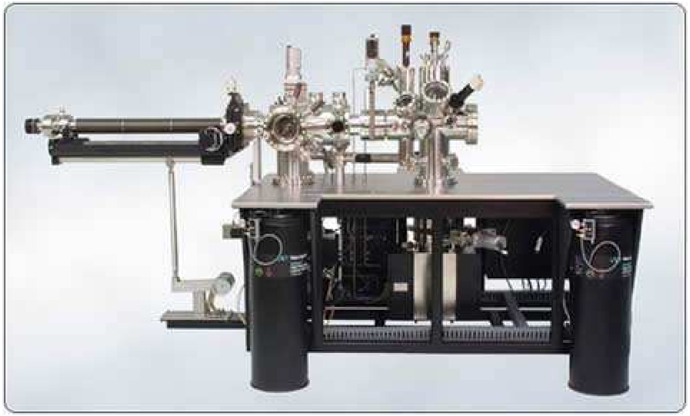
Binning and Rohrer's third STM:



Modern STMs

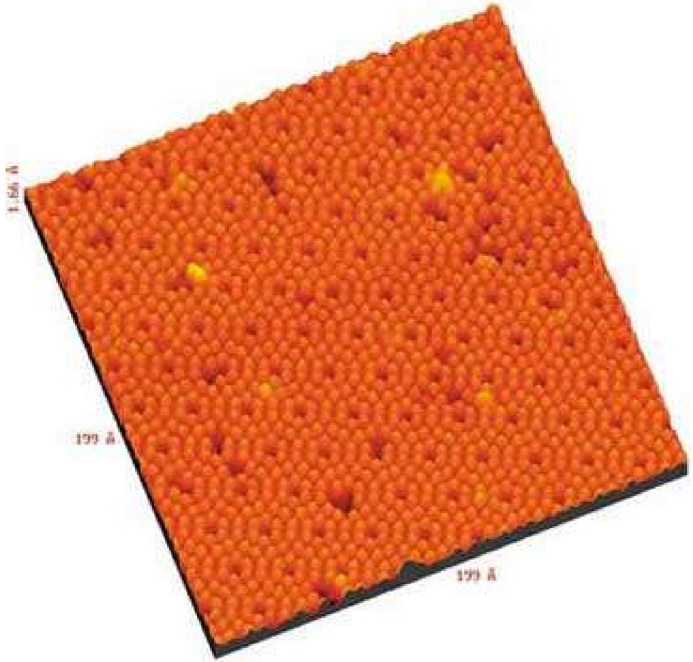


Veeco Instruments: an example of a system that can be run on a desk top.

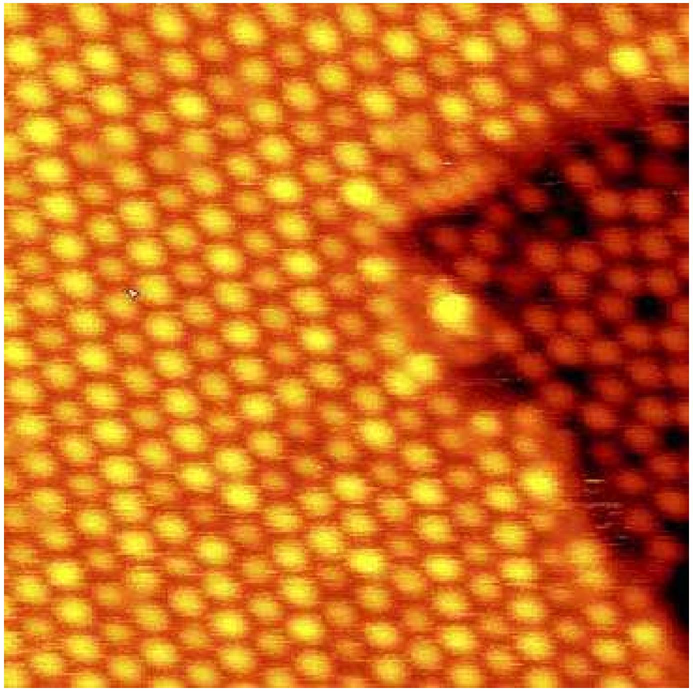


RHK Instruments: an example of an ultra high vacuum system for surface studies.

Example STM images



Silicon (111) surface, 7×7 reconstruction. Courtesy RHK Instruments.



Iron monolayer making FeSi on Si (111). Courtesy RHK instruments.

The Quantum Corral

Don Eigler's quantum corral: