Introduction

1. **Particle–wave duality.** Semiclassical analysis is the study of particle–wave duality, the first and most accessible instance of which is light.

Light. Everyday phenomena such as shadows, and reflections in a mirror, are explained simply by light as particles. Many more complicated phenomena, such as refraction and mirages, require only adding an appropriate dependence of the speed of those particles on the medium. To see wave-like behavior, one must work harder, for example examine the splitting of white light into the colors of a rainbow. A clean modern demonstration can be made by shining monochromatic light (such as from a laser pointer) through a small slit: the light will diffract from the slit and create an interference pattern as in Figure 1, which comes from `this book`. The key effect is *destructive interference*: if we add a sinusoid with the same thing shifted by half a period, we get zero:

$$\sin(x) + \sin(x - \pi) = 0.$$

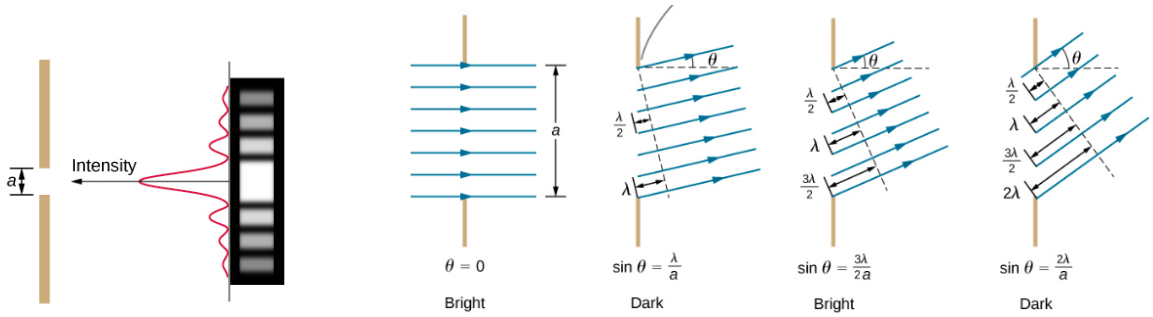

FIGURE 1. Light waves from the slit may interfere constructively or destructively depending on the angle θ. The first dark patch occurs when light from the far edge of the slit (the bottom) travels precisely one wavelength further than light from the near edge of the slit (the top). To do this calculation we place identical sinusoids of wavelength λ on each blue line, starting off in phase at the slit, and then compute how far out of phase they are after they pass the black dashed line.

Thus we have examples of both particle-like and wave-like behavior of light. What is light really? It is a wave, but a wave which behaves like particles in many situations, including most everyday ones. The regime in which particle-like behavior emerges is the *semiclassical* regime. It is the regime of phenomena which take place on a scale much larger than the scale of wavelengths of light. To probe the wavelike nature, we must involve much smaller scales, as in the example of the laser through a slit.

The Schrödinger equation. In this course we will study particle–wave duality in quantum mechanics. In quantum mechanics with every piece of matter we associate a *wave function*, $u(x,t)$, which is a complex-valued function, called an *amplitude*, at position x and time t. The basic example is the sinusoid

$$u(x,t) = e^{i(k\cdot x - \omega t)} = e^{ik\cdot(x - k\omega t/|k|^2)}.$$

Kiril Datchev, September 3, 2026.

The factorization on the right shows that the wave is traveling in the direction of the *wave vector* k, and so the momentum of such a sinusoid should be proportional to k. Meanwhile the energy is proportional to ω. The *quantization relations* give the constant of proportionality in both cases as *Planck's constant* $\hbar = h/2\pi \approx 1.05 \cdot 10^{-34}\,\mathrm{kg}\cdot\mathrm{m}^2\cdot\mathrm{s}^{-1}$ in SI (metric) units.[1] In other words

$$E = \hbar\omega, \qquad \text{and} \qquad \xi = \hbar k. \tag{1.1}$$

Thus we get

$$u(x,t) = e^{i(\xi\cdot x - Et)/\hbar}. \tag{1.2}$$

To get a differential equation we bring in the classical energy formula

$$E = \frac{1}{2m}|\xi|^2, \tag{1.3}$$

where m is mass. Observe that if u is given by (1.2), then

$$Eu = i\hbar\partial_t u, \qquad \text{and} \qquad |\xi|^2 u = -\hbar^2\Delta u. \tag{1.4}$$

Multiplying (1.3) by u and substituting (1.4) leads to

$$i\hbar\partial_t u = -\frac{\hbar^2}{2m}\Delta u,$$

Schrödinger's equation for a free particle. The point is that we have used (1.4) to eliminate E and ξ from the equation, which depend on the particular state the particle is in, and left only the constants $\hbar$ and m which are independent of the state. When the particle is acted on by a force, we add a $V(x)$ term for the potential energy and obtain *Schrödinger's time-dependent equation*:

$$i\hbar\partial_t u = -\frac{\hbar^2}{2m}\Delta u + V(x)u. \tag{1.5}$$

In the special case that the particle has definite energy we have

$$u(x,t) = e^{-iEt/\hbar}\psi(x),$$

and then (1.5) yields *Schrödinger's stationary equation*

$$-\frac{\hbar^2}{2m}\Delta\psi + V(x)\psi = E\psi. \tag{1.6}$$

We also sometimes put $H = -\frac{\hbar^2}{2m}\Delta + V$. The H is the Hamiltonian operator, and (1.5), (1.6) become

$$i\hbar\partial_t u = Hu, \qquad H\psi = E\psi.$$

When $\psi \in L^2(\mathbb{R}^d)$, the probability that the particle is in a region $U \subset \mathbb{R}^d$ is

$$\int_U |\psi|^2 \Big/ \int_{\mathbb{R}^d} |\psi|^2.$$

More generally, if $\psi \in L^2(W)$ for some region $W \subset \mathbb{R}^d$, and if $U \subset W$, then

$$\int_{U\cap W} |\psi|^2 \Big/ \int_W |\psi|^2,$$

[1] The quantization relation $E = \hbar\omega$ in (1.1) comes from Planck's analysis of black body radiation in 1900 and Einstein's analysis of the photoelectric effect in 1905. In 1922 Compton used it and the corresponding relation $\xi = \hbar k$ to explain the increase in X ray wavelength caused by scattering with substances with low atomic numbers. In 1924 de Broglie proposed that the same relations must hold for massive matter, specifically electrons, and in 1926 Schrödinger used these relations to derive his famous equation. The here is based on the one in Section 1.2 of Martinez's *Introduction to Semiclassical and Microlocal Analysis*; for a more detailed discussion, see Hameka's *Quantum Mechanics: A Conceptual Approach*, especially Sections 1.II, 1.VI, 4.II, and 4.III, or Section 1.3 of Weinberg's *Lectures on Quantum Mechanics*.

computes the conditional probability that the particle is in U, given that it is in W.

An excellent basic reference is Griffiths' *Introduction to Quantum Mechanics* (any edition).

The hydrogen atom. The specific physical example to keep in mind is the electron. In fact, one of the foundational experiments of quantum mechanics is electron diffraction through a slit, just in the manner of the light discussed above. More commonly, electrons are found in hydrogen atoms, which consist of just a proton surrounded by an electron.

On the scale of the atom, the proton is a point, and the electron is distributed in a wave called an *electron cloud*. In its *ground state* (the lowest energy state, and the one it settles down into when left alone) the wave is given by $\psi(r) = e^{-r/a}/\sqrt{\pi a^3}$, (we have included, as is customary, a normalizing factor so that $\int_{\mathbb{R}^3} \psi^2 = 1$) and the corresponding radial probability density is $4\pi r^2 \psi(r) = 4r^2 e^{-2r/a}/a^3$, where a is the Bohr radius, $5.3 \cdot 10^{-11}$ meters. Thus the probability that the electron is to be found at a distance between R_1 and R_2 away from the proton is

$$\frac{4}{a^3} \int_{R_1}^{R_2} r^2 e^{-2r/a}\, dr = 4 \int_{R_1/a}^{R_2/a} r^2 e^{-2r}\, dr,$$

and the probability density is maximal at the Bohr radius $r = a$. See Figure 2, and also Figure 3, which comes from `Wikipedia`. The proton is also smeared out in an analogous way, but its radius is closer to 10^{-15} meters, while its mass is 1836 times greater, so this effect is negligible.

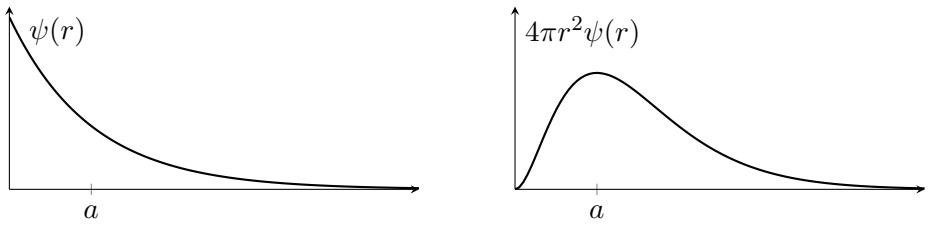

FIGURE 2. The wave function of the electron in hydrogen in its ground state, and the corresponding radial probability density. In this state the wave function is radial, and all angular positions are equally likely.

In terms of the stationary Schrödinger equation (1.6), the potential energy function $V(x)$ of the electron in the hydrogen atom is a constant divided by r, the distance to the proton. In atomic units (i.e. Planck's constant $\hbar$, the mass of the electron, the constant in this V, and the Bohr radius a are all set to one) we have

$$-\frac{1}{2}\Delta\psi - \frac{1}{r}\psi = E\psi.$$

The above ground state is the first eigenvector (i.e. the one with least eigenvalue) of the Hamiltonian operator

$$-\frac{1}{2}\Delta - \frac{1}{r} \tag{1.7}$$

on $\mathbb{R}^3$, (more precisely, the operator acts on $L^2(\mathbb{R}^3)$ with domain $\{\psi \in L^2 \colon \Delta\psi \in L^2\}$) and the eigenvalue is $E_1 = -1/2$ hartrees. This has the meaning of being the amount of energy needed to ionize the atom, i.e. to fully separate the proton and electron. This quantity is more famously known as 13.6 electron volts, an electron volt being the energy needed to move an electron across one volt. More precisely, the true value of this ionization energy is 0.4997 hartrees: the discrepancy is due to

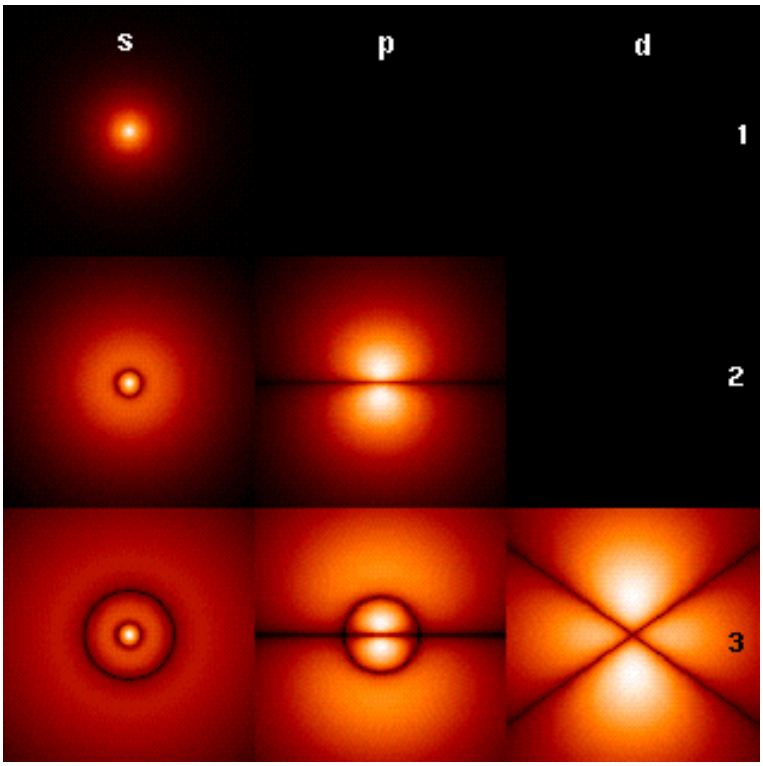

FIGURE 3. Orbitals, or wave functions, of the electron in hydrogen. More precisely, ψ^2 is plotted, with brightness corresponding to magnitude. The ground state is 1s. More generally, the numbers n correspond to the energy levels $-13.6/n^2$eV, and the letters s, p, d index orbitals having the same energy but different angular dependence.

the fact that we are ignoring relativistic effects and spin, but note how well the simple Hamiltonian (1.7) does.

More generally, the bound energy levels are $E_n = E_1/n^2$, n a positive integer, with 0 energy corresponding to being just barely ionized, $n = 1$ being the ground state, the lowest energy state, and $n \geq 2$ the excited states. The bound states are *quantized*, meaning values other than E_n, are impossible, whence the name *quantum mechanics*. Examples of excited states are shown in Figures 3 and 4, and the energy levels are plotted in Figure 5.

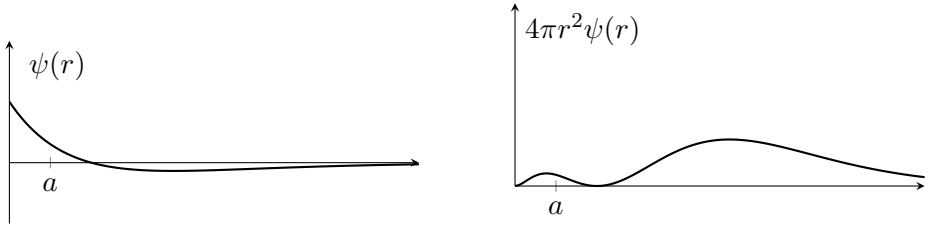

FIGURE 4. The wave function and radial probability density of the electron in hydrogen in its first radially excited state. This is the 2s state: see Figure 3.

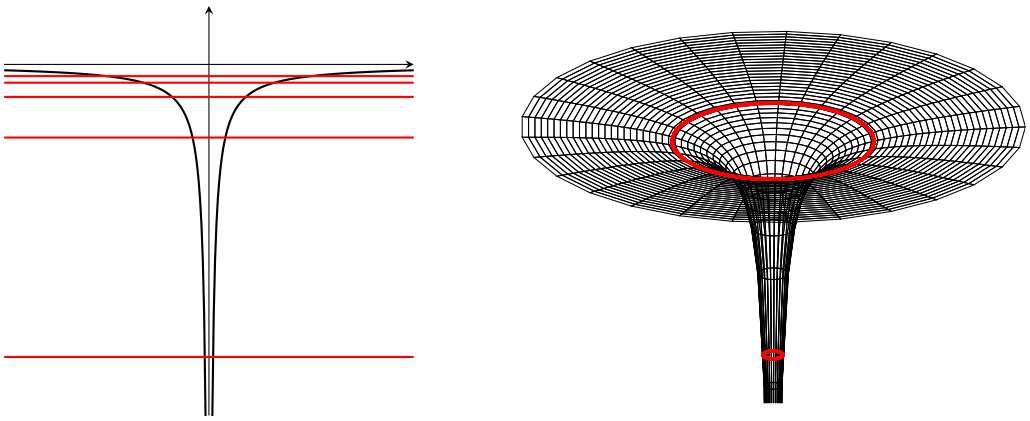

FIGURE 5. On the left, black is the Coulomb potential function $-1/r$, and red are the first energy levels $E_n = -1/2n^2$ for $n = 1, 2, 3, 4, 5$. On the right, the same thing but with $n = 1, 2$. The classical analog is a curved race track given by $-1/r$, with cars zipping around at the different energy levels, faster at the higher levels and slower at the lower ones. To ionize is to go so fast as to escape the track.

To go from a state of lower energy E_n to one of higher energy E_m, an atom can absorb a photon with the energy difference, with the wavelength given by

$$\lambda_{n,m} = \frac{hc}{E_m - E_n} = \frac{hcm^2n^2}{(n^2 - m^2)E_1} = \frac{2 \cdot 2\pi \cdot 137m^2n^2}{m^2 - n^2} \text{ bohr radii.}$$

Light from stars, including the sun, has holes in its spectrum corresponding to these values, which are called absorption spectrum values. If $n = 1$ then $\lambda_{n,m}$ is ultraviolet, and most of the rest of the $\lambda_{n,m}$ are infrared or longer, but $\lambda_{2,m}$ is visible for $m = 3, 4, 5, 6$, with $\lambda_{n,m}$ being deep red and the most visible. The element helium was discovered, and named, when a new bright yellow wavelength was observed in the spectrum of the sun.

Ammonia. All the electron states we have examined so far are highly wave-like, while the protons are highly particle-like. While higher energy electron states do become more particle-like, ammonia provides the simplest and best illustration of the intermediate regime.

To understand ammonia, it is helpful to start with water. Water, H_2O, has its distincive shape because the eight valence electrons form pairs which are roughly equidistributed on the surface of the sphere. Two of those pairs are the H–O bonds, and this explains the shape of water to leading order. The ammonia molecule works the same way, except now H_2O is replaced by NH_3, and so we have an extra hydrogen and the oxygen is replaced by nitrogen: see Figure 6.

EXERCISE 1.8. Find what the H–O–H angle in water would be if the electron pairs lay on an exact regular tetrahedron, and compute the percent error relative to 104.45°, the true value.[2] Then do the same thing for the H–N–H angle in ammonia, where the true value is 106.67°.

Thus ammonia has the structure of a squat pyramid, and there is a natural ambiguity about which way the pyramid is oriented, relative to the plane of the hydrogens. To be more precise, let x be the

[2] *Hint:* It may be helpful to consider a tetrahedron with vertices at $(\pm 1, 0, a)$ and $(0, \pm 1, -a)$ for suitable a. Or you may find a more efficient way.

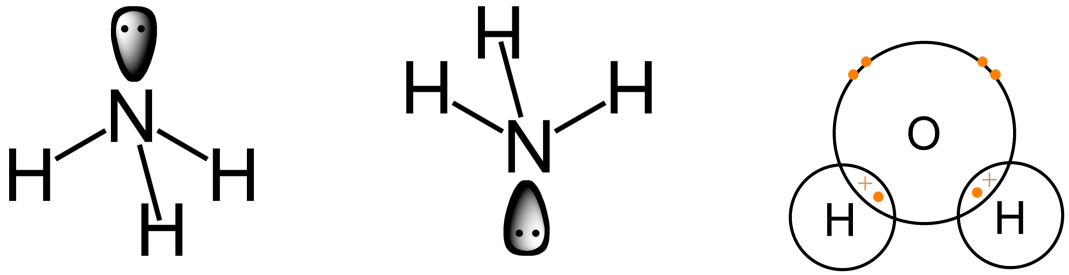

FIGURE 6. Two configurations of ammonia, one with nitrogen on one side of the hydrogens and one with nitrogen on the other. At equilibrium, the equilateral triangle of H nuclei has side length about three bohr radii, while the distance from the N to the plane of that triangle is about one fourth of that. The configuration is a higher dimensional version of that of water. In each case, the large nucleus (N or O) is approximately at the center of a regular tetrahedron, with the pairs of electrons occupying the vertices.

displacement between the nitrogen nucleus and the plane of the hydrogens, and let $V(x)$ be the energy of the molecule if the hydrogens are placed at their equilibrium position and then the electrons take their equilibrium state: see Figure 7.

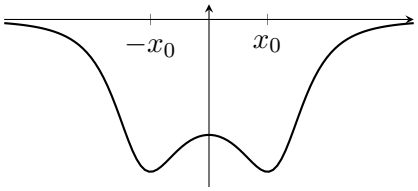

FIGURE 7. A schematic of the potential energy $V(x)$ of the ammonia molecule as a function of x, the displacement between the nitrogen and the plane of the hydrogens. The minima occur at $x = \pm x_0$, where x_0 is .7 Bohr radii. Being closer to planar, or completely planar, is disfavored, but not nearly as strongly as separation is.

If the nuclei behaved just like classical particles the configuration would end up either at x_0 or at $-x_0$ at equilibrium. Since they are quantum particles they arrange themselves like waves, and we will see later that the most energetically favored situation is a symmetric one, balanced between the two sides. A slightly higher energy state is an antisymmetric variant of this. Having most of the probability on one side or the other only arises as a superposition of such states: see Figure 8.

Taking the results of Figure 8 for granted for now, suppose we arrange the system into the state $\psi = (\psi_a + \psi_s)/\sqrt{2}$, i.e. concentrated in the left well, and let it evolve freely. By the time-dependent Schrödinger equation (1.5), we have

$$u(x,t) = \frac{e^{itE_s}\psi_s + e^{itE_a}\psi_a}{\sqrt{2}} = \frac{e^{itE_s}}{\sqrt{2}}(\psi_s + e^{it(E_a - E_s)}\psi_a).$$

The factorization makes it easy to see that the wave function will be proportional to $\psi_s - \psi_a$, concentrated in the right well, precisely when $e^{it(E_a-E_s)} = -1$, i.e. the first time is when $t = \pi/(E_a - E_s)$, on the order of 10^{-10} seconds.

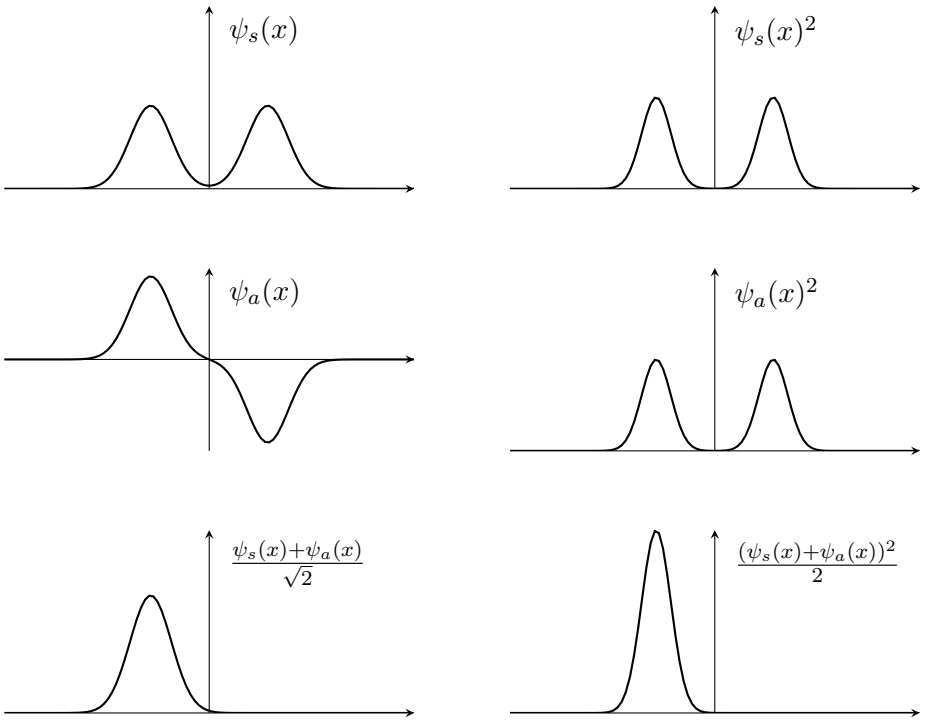

FIGURE 8. The horizontal coordinate is the displacement between the nitrogen nucleus and the plane of the hydrogen nuclei. The ground state wave function is ψ_s and is symmetric (even), and the first excited state is ψ_a and is antisymmetric (odd): the corresponding densities are nearly identical, but the ground state has no zeroes while the first excited state has one (compare hydrogen above). The combination $\frac{\psi_s(x)+\psi_a(x)}{\sqrt{2}}$, which favors one side over the other, is not an energy state, and the molecule cannot stay in such a state unless some outside force keeps it there.

More generally, any Hamiltonian with an even potential V has even and odd eigenstates. Still more generally, if another operator S commutes with H, then S and H can be simultaneously diagonalized, although various technicalities arise when the operators are unbounded and/or have essential spectrum. Let us focus on the case of discrete spectrum of a one-dimensional Schrödinger operator, such as in the present example of ammonia. Then the operator $S\colon L^2(\mathbb{R}) \to L^2(\mathbb{R})$ is reflection of the x variable, i.e.

$$(S\psi)(x) = \psi(-x).$$

The eigenspaces of S are the spaces of even and odd functions, with eigenvalue 1 and -1 respectively. Call these eigenspaces W_s and W_a. Then $L^2(\mathbb{R}) = W_s \oplus W_a$, i.e, every vector in the original Hilbert space $L^2(\mathbb{R})$ can be written uniquely as a sum of a vector from W_s and a vector from W_a.

EXERCISE 1.9. Derive the formula which writes a function on $\mathbb{R}$ as a sum of an even function and an odd function, and prove this decomposition is unique. It may help to review how one writes a complex number as a sum of a real number and an imaginary number, and proves this is unique. The lively student can do this in a general way, which unifies both of these decompositions and also includes other similar ones.

The vector spaces W_s and W_a are both Hilbert spaces (they are subspaces, and they are closed because they are each the inverse image of a point under a continuous function). The original Hamiltonian H acts on $L^2(\mathbb{R})$ with domain $\mathcal{D}$ which is the Sobolev space $H^2(\mathbb{R})$. It is a self-adjoint (aka Hermitian) operator.

Definition. Let $k \in \mathbb{N}$, and let I be a closed interval. The Sobolev space $H^k(I)$ is the set of $u \in C^{k-1}(I)$ for which there exist $v \in L^2(I)$, a point a in I, and a constant c such that $u^{(k-1)}(x) = c + \int_a^x v$. We also put $H^0(I) = L^2(I)$.

EXERCISE 1.10. Let γ be a real number, $u(x) = |x|^\gamma$. For which k is $u \in H^k((-1,1))$?

Since H commutes with S, H is also self-adjoint as an operator $\mathcal{D} \cap W_s \to W_s$ and $\mathcal{D} \cap W_a \to W_a$. Thus by the spectral theorem it can be diagonalized over each of W_s and W_a, and in particular all eigenvectors can be taken from W_s and W_a. We will see later that very general one dimensional Schrödinger operators have simple eigenvalues, and hence that ψ_s and ψ_a have different eigenvalues. The fact that ψ_s has the lower energy will follow from the fact that the ground state is positive, which we will also establish.

The states ψ_s and ψ_a from Figure 8 have an energy difference of just a few microhartees, which corresponds to absorption or emission of a microwave photon. Controlling this process led to the development of the ammonia maser, which was the first laser, and from there to all modern lasers, including the laser pointer from the demo at the beginning. For more about ammonia, and the ammonia maser, a good source is Chapters III.8–9 from the `Feynman lectures`.

Many particles and the high-energy limit. How do we analyze a molecule like ammonia, and compute its energies, as in the function V above? The direct approach is to minimize the N body Schrödinger equation,

$$H\Psi = E\Psi, \qquad H = -\frac{1}{2}\Delta + V, \qquad \Psi \colon \mathbb{R}^{Nd} \to \mathbb{R}, \qquad E \in \mathbb{R}, \qquad E = \min_{\Psi} \frac{\int (H\Psi)\Psi}{\int \Psi^2},$$

d is 1, 2, or 3, and N is the number of electrons, where Ψ ranges over an appropriate domain in $L^2(\mathbb{R}^{Nd})$. For the hydrogen atom, $d = 3$, $N = 1$, and $H = -\frac{1}{2}\Delta - \frac{1}{r}$ as in (1.7). But for more complicated systems the dimensionality rapidly gets out of hand: even for a single molecule of ammonia this is $\mathbb{R}^{Nd} = \mathbb{R}^{30}$, which is at the limit of what can be brute-forced by a powerful computer.[3]

To make the problem more manageable, *density functional theory* introduces the *electron density* $n \colon \mathbb{R}^d \to [0, \infty)$, which is defined by the property that for any measurable $U \in \mathbb{R}^d$, we have

$$\int_U n = \text{the expected number of electrons in } U.$$

When $N = 1$, $n = \psi^2$, and we will give more general formulas for n later.

For a typical 3d problem,

$$\int_{\mathbb{R}^{3N}} (H\Psi)\Psi = \frac{1}{2}\int_{\mathbb{R}^{3N}} |\nabla\Psi|^2 + \sum_{1 \le j < k \le N} \int_{\mathbb{R}^{3N}} \frac{\Psi(x)^2}{|x_j - x_k|} + \int_{\mathbb{R}^3} V_{ext} n. \tag{1.11}$$

[3]Afterwards, to get the full energy, one must add the energies of the nuclei. But this can be done to good accuracy by treating them as classical point particles: this is called the Born–Oppenheimer approximation, and as mentioned above already for hydrogen the relative error involved is less than 10^{-3}, and for heavier nuclei the accuracy is better: see Jensen's *Introduction to Computational Chemistry*, especially Section 1.6.2.

Here $\frac{1}{2}\int |\nabla\Psi|^2$ is the kinetic energy term, $\sum\int \frac{\Psi(x)^2}{|x_j-x_k|}$ is the repulsive Coulomb potential energy between the electrons, and $\int_{\mathbb{R}^3} V_{ext} n$ is the potential energy due to external forces: for the hydrogen atom it is $\int_{\mathbb{R}^3} \psi^2/r$, and more generally it is the attractive Coulomb potential energy between the electrons and the nuclei. For example, for an atom with Z protons, it is $V_{ext} = Z/r$.

The term $\int_{\mathbb{R}^d} V_{ext} n$ depends on the system but is explicit and has simple dependence on n. The other terms of (1.11) are more complicated but universal. People study them in simple systems and then bring the results to more complicated systems. For a more detailed introduction and references, see Appendix B of `this book`.

Semiclassical analysis becomes relevant for large N, as the electrons occupy higher energy states (analogous to the larger values of n in Figure 3). In this limit, beautiful and simple universal behaviors emerge. The central fact is that *states equidistribute in phase space*. This has various precise formulations in different settings, and we begin with the simplest one dimensional example.

2. **Particles in a box.** The first system we will analyze in detail is that of an electron, or electrons, in a one-dimensional box. We look at

$$-\frac{1}{2}\psi'' + V(x)\psi = E\psi, \qquad V(x) = \begin{cases} 0, & 0 < x < L \\ +\infty, & \text{otherwise} \end{cases}$$

or in other words

$$-\frac{1}{2}\psi''(x) = E\psi(x) \text{ for } x \in (0, L), \quad \psi(0) = \psi(L) = 0. \tag{2.1}$$

or in other words find the spectrum of $H = -\frac{1}{2}\frac{d^2}{dx^2}$ on $L^2(I)$, $I = [0, L]$ with domain $\mathcal{D} = \{u \in H^2(I)$ such that $u(0) = u(L) = 0\}$.

Solving (2.1) yields

$$\psi_j(x) = \sqrt{\frac{2}{L}} \sin\Big(\frac{\pi j x}{L}\Big), \qquad E_j = \frac{\pi^2 j^2}{2L^2}, \quad \text{for } j = 1, 2, 3 \ldots. \tag{2.2}$$

See Figure 9. It is easy to check that these are eigenvectors and eigenvalues of H: the hard part is checking that they span $L^2(I)$, a.k.a. checking completeness, i.e. checking that we haven't missed anything.

FIGURE 9. Above, the first four eigenfunctions $\psi_j(x)$ of the 1d particle in a box problem. They are the same as modes of a vibrating string. Below, the corresponding probability densities $\psi_j(x)^2$.

This check reduces to a fundamental fact about Fourier series. We focus on the case $L = \pi$ for simplicity, as the general case follows from this one by change of variables. We must check that

$$\int_0^\pi f(x) \sin(jx)\, dx = 0, \qquad \text{for } j = 1,\ 2,\ 3, \ldots \tag{2.3}$$

implies that f is zero. For this, extend f to be odd, so that (2.3) can be rewritten

$$\int_{-\pi}^{\pi} f(x)\sin(jx)\,dx = 0, \qquad \text{for } j = 1,\, 2,\, 3, \ldots. \tag{2.4}$$

Next, (2.4) can be rewritten

$$\int_{-\pi}^{\pi} f(x)e^{ijx}\,dx = 0, \qquad \text{for } j \in \mathbb{Z}, \tag{2.5}$$

since f is odd. The aforementioned fundamental fact about Fourier series is that (2.5) implies that f is zero: see for example Theorem 1-2 of Seeley's *Introduction to Fourier Series and Integrals* for a beautiful classic Fourier analytic proof. A second proof proceeds by invoking the Stone–Weierstrass theorem, which says that the span of $\{e^{ijx},\ j \in \mathbb{Z}\}$ is dense in continuous functions on $[-\pi, \pi]$, and hence in $L^2(-\pi, \pi)$. A third proof uses the spectral theorem directly, and involves establishing that the resolvent of H is compact: see Theorem 2 in `these notes`. Whichever proof we use, some serious real analysis is needed, and this is so for any thorough computation of the spectrum of a differential operator.

Exercise 2.6. Fill in details of the above approach (or use another one) to show that if $g \in L^2([0, L])$, then there are unique numbers c_1, c_2, ... such that

$$g(x) = \sum_{j=1}^{\infty} c_j \sin\Big(\frac{\pi j x}{L}\Big).$$

In the semiclassical limit, i.e. the high-energy limit, i.e. the limit as $j \to \infty$, the eigensates (2.2) *equidistribute*, in the sense that for any interval $[a, b] \subset [0, L]$, we have

$$\int_a^b \psi_j(x)^2\,dx = \frac{2}{L}\int_a^b \sin^2\Big(\frac{\pi j x}{L}\Big)\,dx \to \frac{b-a}{L}. \tag{2.7}$$

Exercise 2.8. Give the details of the limit (2.7)

The same problem can be solved for higher dimensional boxes, more or less explicitly depending on the shape. The most similar case is a product of intervals. For simplicity we consider $d = 2$, but any d works in the same way. Look at

$$\Big(-\frac{1}{2}\partial_x^2 - \frac{1}{2}\partial_y^2 + V(x,y)\Big)\psi(x,y) = E\psi(x,y), \qquad V(x,y) = \begin{cases} 0, & 0 < x < a \text{ and } 0 < y < b, \\ +\infty, & \text{otherwise} \end{cases} \tag{2.9}$$

Looking for solutions of the form $\psi(x, y) = f(x)g(y)$ leads to

$$\Big(-\frac{1}{2}\partial_x^2 - \frac{1}{2}\partial_y^2 + V(x,y)\Big)\psi_{m,n}(x,y) = E_{m,n}\psi_{m,n}(x,y),$$

$$\psi_{m,n}(x,y) = \frac{2}{\sqrt{ab}}\sin\Big(\frac{\pi m x}{a}\Big)\sin\Big(\frac{\pi n x}{b}\Big), \qquad E_{m,n} = \frac{\pi^2}{2}\Big(\frac{m^2}{a^2} + \frac{n^2}{b^2}\Big).$$

The formula for the eigenvectors and eigenvalues is not much more complicated in two dimensions than in one dimension, but putting them in order is. For example, if $a = b = \pi$, then

$$E_1 = E_{1,1} = 1, \quad E_2 = E_3 = E_{1,2} = E_{2,1} = 2.5, \quad E_4 = E_{2,2} = 4, \quad E_5 = E_6 = E_{1,3} = E_{3,1} = 5. \tag{2.10}$$

See Figure 10.

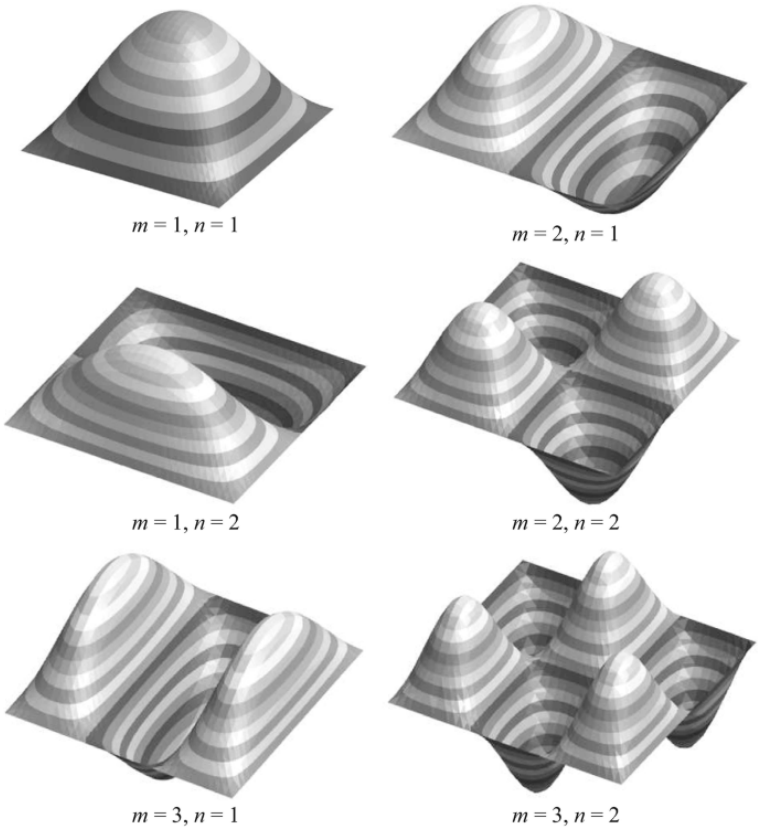

FIGURE 10. Some eigenfunctions for the square box, having the form $\sin(nx)\sin(my)$, from `Figure 6.2` of Garrett's *Understanding Acoustics*.

If $a = \pi$ and $b = \pi/2$, then we have the same list but keeping only the even n indices:

$$E_1 = E_{1,2} = 2.5, \quad E_2 = E_{2,2} = 4, \quad E_3 = E_{3,2} = 6.5, \quad E_4 = E_{1,4} = 8.5.$$

To make sense of the ordering, note that for an arbitrary box B we have

$$E_j = \frac{1}{2} \int_B |\nabla \psi_j|^2 \Big/ \int_B |\psi_j|^2,$$

which is obtained from $-\frac{1}{2}\Delta\psi_j = E_j\psi_j$ by multiplying both sides by ψ_j, integrating, and applying Green's identity $\int_B |\nabla\psi_j|^2 = -\int_B (\Delta\psi_j)\psi_j$. Thus we are arranging the eigenfunctions according to how big the derivatives get (measured by L^2 norm).

EXERCISE 2.11. Do the analogue Exercise 2.6 for $g \in L^2([0, L] \times [0, M])$

A more complicated but also more physically important two-dimensional box is the unit disk. For that we use the polar coordinate formula $-\Delta = -\partial_r^2 - \frac{1}{r}\partial_r - \frac{1}{r}^2\partial_\theta^2$ and writing $\psi(r, \theta) = \sum_{m=-\infty}^{\infty} u_m(r)e^{im\theta}$ to get

$$-u_m'' - \frac{1}{r}u_m' + \frac{m^2}{r^2}u_m = 2Eu_m.$$

To solve this equation we use Bessel functions[4] and obtain

$$\psi_1(r,\theta) = J_0(\sqrt{2E_1}r), \quad E_1 = j_{0,1}^2/2 = 2.9\ldots$$
$$\psi_2(r,\theta) = J_1(\sqrt{2E_2}r)\cos(\theta), \quad \psi_3(r,\theta) = J_1(\sqrt{2E_3}r)\sin(\theta), \quad E_2 = E_3 = j_{1,1}^2/2 = 7.3\ldots$$
$$\psi_4(r,\theta) = J_2(\sqrt{2E_4}r)\cos(2\theta), \quad \psi_5(r,\theta) = J_2(\sqrt{2E_5}r)\sin(2\theta), \quad E_4 = E_5 = j_{2,1}^2/2 = 13.1\ldots$$
$$\psi_6(r,\theta) = J_0(\sqrt{2E_6}r), \quad E_6 = j_{0,2}^2/2 = 15.2\ldots$$
$$\psi_7(r,\theta) = J_3(\sqrt{2E_7}r)\cos(3\theta), \quad \psi_8(r,\theta) = J_3(\sqrt{2E_8}r)\sin(3\theta), \quad E_7 = E_8 = j_{3,1}^2/2 = 20.3\ldots$$

Just as in the 1d case the eigenfunctions were the modes of a vibrating string, so here the eigenfunctions are modes of a vibrating circular drum. See Figure 11. They also show up in quantum corrals: see Figure 12.

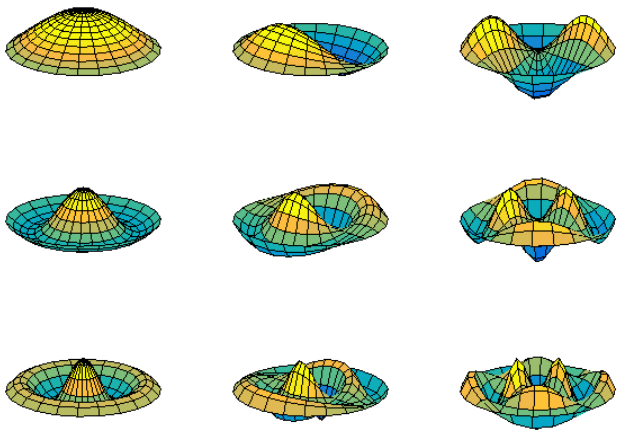

FIGURE 11. Eigenfunctions for a particle in a disk, aka modes of a vibrating drum, from `this site`. Top left is ψ_1, top middle is ψ_2 or ψ_3, top right is ψ_4 or ψ_5, middle left is ψ_6, middle middle is ψ_9 or ψ_{10}, and the others are higher excited states. The first column is states with J_0, the second is J_1, the third is J_2. The chart continues infinitely going right and down: moving to the right, the states gain angular excitation, and moving down they gain radial excitation.

The sequence goes on, but the orders m of the Bessel functions J_m and the corresponding values $j_{m,k}$ of their kth zeroes are delicate to compute. But the *Weyl law* tells us that

$$E_j = \frac{2\pi}{A}j + \frac{P}{A}\sqrt{\frac{\pi}{A}}\sqrt{j} + r_j = 2j + 2\sqrt{j} + r_j, \tag{2.12}$$

where A is the area of the disk and P is its perimeter, and where r_j is a remainder that grows more slowly than $j^{1/2}$ as $j \to \infty$. See Figure 13 for a plot which shows how accurate (2.12) is even for small j. It is more common to write the following more beautiful formula

$$N(\lambda) = \frac{A}{4\pi}\lambda^2 - \frac{P}{4\pi}\lambda + R(\lambda), \tag{2.13}$$

[4]See Chapter 5 of Folland's *Fourier Analysis and its Applications* for an introduction.

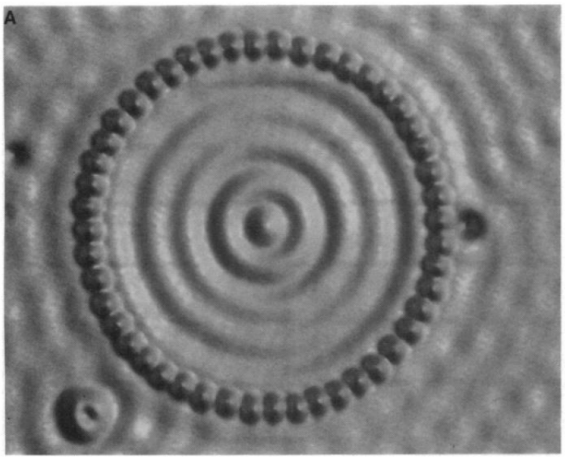

Fig. 2. Spatial image of the eigenstates of a quantum corral. (**A**) 48-atom Fe ring constructed on the Cu(111) surface (V = 0.01 volt, I = 1.0 nA). Average diameter of ring (atom center to atom center) is 142.6 Å.

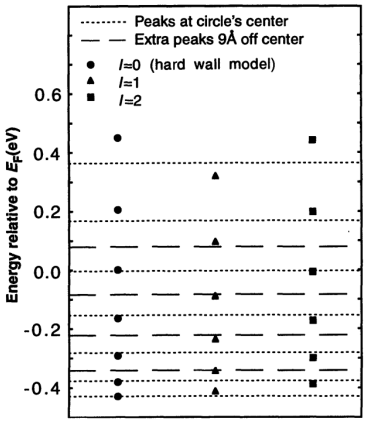

Fig. 4. Theoretical eigenenergies for l = 0, 1, and 2 states of "hard wall" circular box (solid symbols) compared to experimental energies (dashed lines)

FIGURE 12. Left, a quantum corral with an electron enclosed. Right, corresponding energy level measurements. The three columns of theoretical energies $l = 0, 1\,2$, correspond to the three columns in Figure 11. The figures are taken from the paper *Confinement of Electrons to Quantum Corrals on a Metal Surface* by Crommie, Lutz, and Eigler. The • dots are to be compared with the smaller dashed lines: note that the agreement is best at low energies and gets worse as the electrons get more excited. This makes sense because approximating the barrier as infinitely high is more accurate at lower energies. See `this paper` for more recent experimental results and beautiful pictures.

where $N(\lambda)$ is the number of eigenvalues of the Laplacian less than λ^2, and $R(\lambda) = O(\lambda^{2/3})$.[5] Versions of the Weyl law (2.12) and (2.13) holds for much more general domains, and also on manifolds and for other operators: see Section 3.3 of Levitin, Mangoubi, and Polterovich's *Topics in Spectral Geometry*. We will prove a version for Schrödinger operators later in the course.

EXERCISE 2.14. Deduce (2.12) from (2.13).[6]

EXERCISE 2.15. Make a version of Figure 13 for one or more rectangular boxes.

It is also interesting to consider multiple noninteracting particles in a box. We start with two particles in $[0, L]$. The classical energy is $\frac{1}{2m_1}\xi_1^2 + \frac{1}{2m_2}\xi_2^2$ and so the quantum hamiltonian is

$$H = -\frac{1}{2m_1}\partial_{x_1}^2 - \frac{1}{2m_2}\partial_{x_2}^2, \qquad x_1, x_2 \in [0, L].$$

This is precisely the rectangular box problem studied in (2.9), with different notation. If the particles are electrons then $m_1 = m_2 = 1$ because we are in atomic units. If the electrons are in a definite spin state, then their wave function must be antisymmetric by the *spin-statistics theorem*, which we do not

[5]Here $R(\lambda) = O(\lambda^{2/3})$ means there is a constant C such that $|R(\lambda)| \le C\lambda^{2/3}$ for λ sufficiently large. See Section 1.2 of Olver's *Asymptotics and Special Functions* for an introduction to O notation.

[6]*Hint:* Show that $j = \frac{A}{4\pi}E_j - \frac{P}{4\pi}\sqrt{E_j} + \widetilde{R}(E_j)$, where $\widetilde{R}(\widetilde{E}_j)$ grows more slowly than $\sqrt{E_j}$, and solve for E_j. Better yet, make 'grows more slowly than' precise.

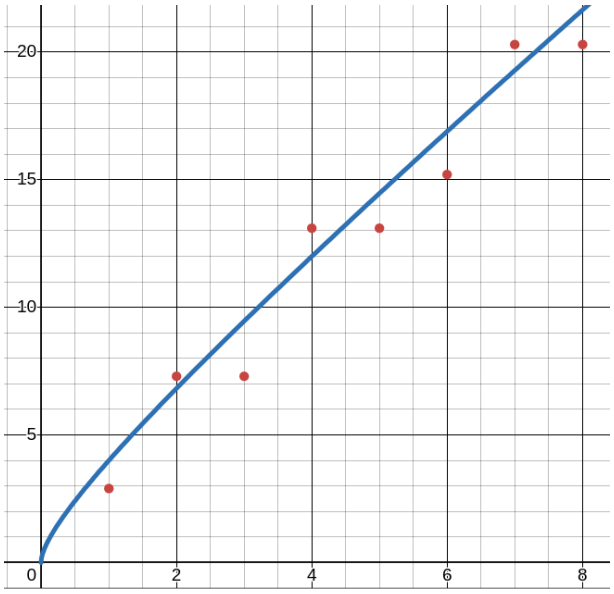

FIGURE 13. The red dots are the values of E_j for the disk of radius 1, and the blue curve is the asymptotic $2x + 2\sqrt{x}$ from (2.12). Here is a Desmos link.

discuss here. Letting $B = [0, L] \times [0, L]$, this means the operator

$$H = -\frac{1}{2}\partial_{x_1}^2 - \frac{1}{2}\partial_{x_2}^2$$

must act on $L_a^2(B) = \{u \in L^2(B) \colon u(x_1, x_2) = -u(x_2, x_1)\}$. But this is the same as solving the particle in a box problem for the triangular box $0 \leq x_1 \leq x_2 \leq L$.