Modern I: Semiclassical Mechanics

The basics of quantum mechanics can be found in chapters 46 and 47 of Halliday and Resnick, and are covered more thoroughly in chapters 3 through 6 in Krane. Chapter 10 of Krane covers quantum statistical mechanics as used in the final section. For a complete, but advanced treatment of the WKB approximation, see chapter 9 of Griffiths' *Introduction to Quantum Mechanics* (3rd edition). For some nice conceptual discussion, see chapters I-37 and I-38 of the Feynman lectures, or if you're ambitious, essentially all of volume III. There is a total of **80** points.

1 The WKB Approximation

A proper introduction to quantum mechanics would take a whole book. Luckily, there is a "semiclassical" regime of quantum mechanics which can be handled with much less machinery. Historically, this regime was discovered first, by scientists like Bohr, and it suffices to explain many quantum effects. To introduce the WKB approximation, we'll start by considering classical standing waves.

Idea 1

A classical wave has a phase ϕ, and its wavenumber and frequency give its rate of change,

$$k = \frac{d\phi}{dx}, \quad \omega = \frac{d\phi}{dt}$$

As covered in **W1**, the group velocity is

$$v = \frac{d\omega}{dk}.$$

A standing wave can form if the wave's phase lines back up with itself after one round trip,

$$\oint k \, dx = 2\pi n, \quad n \in \mathbb{Z}.$$

A simple case is a string of length L with fixed ends, where we have

$$2kL = 2\pi n$$

which gives the wavenumbers $k_n = \pi n/L$ and hence the standing wave frequencies $\omega_n = \pi v n/L$, as we saw in **W1**.

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[1] Problem 1. A slightly more subtle case is the case of a string of length L with one fixed and one free end. Verify that in this case, the standing wave frequencies are

$$\omega_n = \frac{\pi v}{L}(n + 1/2).$$

Solution. Here, we see that the end is free, so it corresponds to an anti-node. Thus, the length of the string is a half integer amount of half wavelengths, so $L = \frac{1}{2}(n + 1/2)\lambda_n$, which means that

$$f_n = v/\lambda_n = \frac{v}{2L}(n + 1/2).$$

Thus, $\omega_n = 2\pi f_n = \frac{\pi v}{L}(n + 1/2)$, as desired.

The reason our principle above doesn't give the right answer is that a wave picks up an extra phase shift π when it reflects off a fixed end, so we really should have written

$$\oint k\,dx = 2\pi(n+1/2)$$

in this case. We didn't run into any problems for two fixed ends, because in that case we get two phase shifts of π, which have no overall effect.

[2] **Problem 2.** Suppose a string of length L is hung from the ceiling. The string has mass density μ, and the bottom of the string is held fixed and pulled down with a force $F \gg gL\mu$. If the string were weightless, then the standing wave frequencies would simply be $\pi v n/L$, where $v = \sqrt{F/\mu}$. However, the weight causes the tension and hence the wave speed to vary throughout the rope.

    (a) Explain why the wave's angular frequency ω is uniform, i.e. why standing wave solutions are proportional to $\cos(\omega t)$.

    (b) Find the frequencies of standing waves, including corrections up to first order in $gL\mu/F$.

This is a more quantitative version of a problem we encountered in **W1**.

Solution.   (a) Recall that the solutions of the wave equation were proportional to $e^{i(kx-\omega t)}$ because the wave equation was linear, and had no explicit dependence on x and t. The wave equation describing waves on this string does have explicit dependence on x, because the tension (and hence the wave velocity) varies along the string. But it still doesn't have any explicit dependence on t, so guessing a solution proportional to $e^{-i\omega t}$ (or equivalently $\cos(\omega t)$ in real variables) still works.

    (b) Let h be the height from the bottom of the string. By Newton's second law, the tension at height h is $T(h) = F + \mu g h$, so the speed is $v(h) = \sqrt{F/\mu + gh}$. Thus, the quantization condition is

$$\oint k\,dx = 2\int_0^L k\,dh = 2\int_0^L \frac{\omega}{v}\,dh = 2\int_0^L \frac{\omega}{\sqrt{F/\mu + gh}}\,dh = 2\pi n.$$

Note that

$$\begin{aligned}
2\int_0^L \frac{\omega}{\sqrt{F/\mu + gh}}\,dh &= \frac{2\omega}{\sqrt{F/\mu}}\int_0^L \frac{dh}{\sqrt{1 + gh\mu/F}} \\
&= 2\omega\sqrt{F/\mu}/g \int_0^{gL\mu/F} \frac{dx}{\sqrt{1+x}} \\
&\approx 2\omega\sqrt{F/\mu}/g \int_0^{gL\mu/F} (1 - x/2)\,dx \\
&= 2\omega\sqrt{F/\mu}/g \left(gL\mu/F - \frac{1}{4}(gL\mu/F)^2\right) \\
&= 2\omega L\sqrt{\mu/F}\left(1 - \frac{1}{4}(gL\mu/F)\right).
\end{aligned}$$

We therefore conclude

$$\omega = \frac{\pi n\sqrt{F/\mu}}{L}\left(1 + \frac{1}{4}(gL\mu/F)\right).$$

In quantum mechanics, the state of a particle is described by a wavefunction $\psi(x,t)$ which obeys the Schrodinger equation. When a particle is confined in a finite volume, there are standing wave solutions analogous to those of classical wave mechanics, which have discrete frequencies.

Idea 2: WKB Approximation

The momentum and energy of a quantum particle obey the de Broglie relations

$$p = \hbar k, \quad E = \hbar \omega$$

where E and p are related just as in classical mechanics,

$$E = \frac{p^2}{2m} + V(x).$$

For a particle with reasonably well-defined momentum, the wavefunction is a wavepacket which travels at the group velocity

$$v_g = \frac{d\omega}{dk} = \frac{dE}{dp}.$$

This corresponds to the classical velocity of the particle in the classical limit. (For example, you should check that the above equations imply $p = mv_g$, or $p = \gamma m v_g$ when the relativistic momentum and energy are used.)

Just as for a classical standing wave, ω is the same everywhere for quantum standing waves. Since energy is related to frequency, these standing waves are also states of definite energy. In the semiclassical limit, the standing waves must satisfy

$$\oint p\, dx = (2\pi n + \alpha)\hbar = \left(n + \frac{\alpha}{2\pi}\right) h$$

where the extra phase α depends on the boundaries. We get a phase shift of π for a "hard wall", where the potential suddenly jumps from below E to above E, and a phase shift of $\pi/2$ if the potential slowly increases from below E to above E.

Remark

The left-hand side of the quantization condition above is precisely the adiabatic invariant from **M4**, which stays the same if we change the system parameters slowly. This ensures the quantization condition is preserved over time, as it must be for self-consistency. If you instead change the system parameters quickly, the integral is not preserved, but that's because the change causes transitions from one energy level to another (i.e. to waves with different n).

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[2] **Problem 3.** Consider a one-dimensional box of length L, with hard walls.

(a) Find the energy levels of a particle of mass m.

(b) Now suppose the particle is replaced with a photon, with $E = pc$. Find the allowed energies.

The frequencies you found in part (b) corresponds to the standing wave frequencies for electromagnetic waves in a box with appropriate boundary conditions. (What are they?)

Solution. (a) The quantization condition is that

$$2pL = 2\pi n\hbar \implies p = \pi n\hbar/L.$$

Thus, $E = p^2/2m = \frac{\pi^2 n^2 \hbar^2}{2mL^2}$. Note that this solution only makes sense for $n \geq 1$.

(b) We see that p is the same, and $E = pc = \pi n\hbar c/L$.
Note that this matches the standing wave frequencies for electromagnetic waves in a box with reflecting (i.e. perfectly conducting) walls.

[2] **Problem 4.** Show that the energy levels of a particle of mass m on a one-dimensional spring of spring constant k are

$$E_n = \hbar\omega_0 \left(n + \frac{1}{2}\right), \quad \omega_0 = \sqrt{\frac{k}{m}}.$$

This system is called the quantum harmonic oscillator, and remarkably, this is the exact answer, even though we used an approximation to get it. This result will be used in several problems below.

Solution. Let $\omega = \sqrt{k/m}$. Here we have the quantization condition

$$2 \int_{-L}^{L} m\omega \sqrt{L^2 - x^2}\, dx = 2\pi\hbar(n + 1/2).$$

Note that the integral is just the area of a half-ellipse, so

$$\pi L^2 m\omega = 2\pi\hbar(n + 1/2),$$

so

$$E = \frac{1}{2}m\omega^2 L^2 = \hbar\sqrt{k/m}(n + 1/2) = \hbar\omega_0(n + 1/2)$$

as desired. Note that this solution makes sense for $n \geq 0$.

[3] **Problem 5.** 🕐 USAPhO 2015, problem A1.

[5] **Problem 6.** 🕗 IPhO 2006, problem 1. This is a neat problem which illustrates the effect of a gravitational field on quantum particles, as well as the basics of interferometry, a subject developed further in **W2**. Give this a try even if it looks tough; only the ideas introduced above are needed!

Idea 3: Bohr Quantization

In general, $p\,dx$ may be replaced by any generalized momentum/position pair. For example,

$$\oint L\,d\theta = nh.$$

When angular momentum is conserved, the left-hand side is simply $2\pi L$, immediately giving

$$L = n\hbar$$

which is Bohr's quantization condition. Note that unlike the other n's above, this n can be

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positive or negative, representing a particle going clockwise or counterclockwise. In a system of particles rotating together, L stands for the total angular momentum of the system.

Example 1

Find the energy levels and orbit radii of the electron in the hydrogen atom using Bohr quantization.

Solution

We postulate a circular orbit, and quantize the angular momentum. We have

$$\frac{mv^2}{r} = \frac{e^2}{4\pi\epsilon_0 r^2}, \quad L = mvr = n\hbar.$$

Solving the second equation for v and plugging into the first gives

$$r = \frac{4\pi\epsilon_0 \hbar^2}{me^2} n^2 = a_0 n^2$$

where $a_0 = 5.3 \times 10^{-11}$ m is called the Bohr radius; these are the allowed orbit radii. To get the energies, we use the standard result for circular motion with an inverse square force that the total energy is half the potential energy, so

$$E = -\frac{e^2}{8\pi\epsilon_0 r} = -\frac{me^4}{2(4\pi\epsilon_0)^2\hbar^2} \frac{1}{n^2}.$$

Evidently, they get more and more closely spaced together as n increases. The big constant in front is called the Rydberg, and is equal to 13.6 eV.

[1] **Problem 7.** Find the energy levels of positronium, a bound state of a positron and electron.

Solution. You can do this through an explicit analysis very similar to the example. On the other hand, we can also use the idea of reduced mass introduced in **M6**. The reduced mass of positronium is $m/2$, so replacing m with $m/2$ in the example's answer gives

$$E = -\frac{me^4}{4(4\pi\epsilon_0)^2\hbar^2} \frac{1}{n^2}.$$

[2] **Problem 8** (USAPhO 2004). Electrons are accelerated from rest through a potential V into a cloud of cold atomic hydrogen. A series of plates with aligned holes select a beam of scattered electrons moving perpendicular to the plates. Immediately beyond the final plate, the electrons enter a uniform magnetic field B perpendicular to the beam; they curve and strike a piece of film mounted on the final plate.
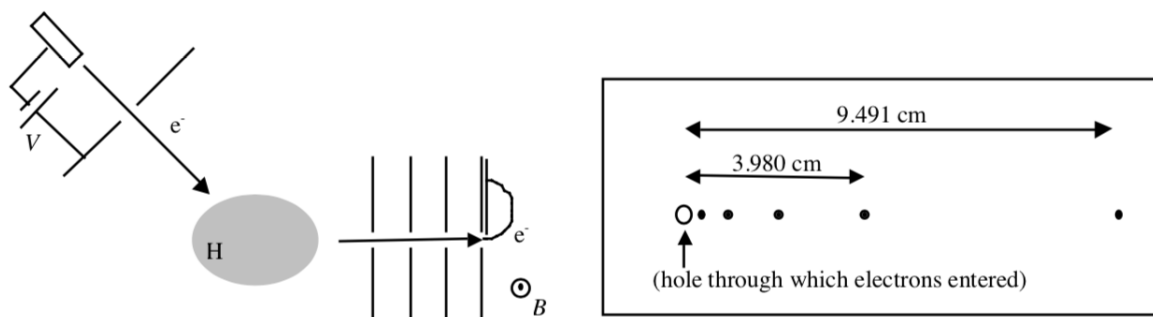
When the film is developed, a series of spots is observed. The distances between the hole and the two most distant spots are measured. You may assume that the film is large enough to have intercepted all of the electrons, i.e. that there are no spots farther from the hole than those shown. The number of spots shown is not necessarily accurate.

Make the approximation that the mass of the hydrogen atom is much larger than the mass of the electron. Assume that each electron scatters off only one atom, which is initially in the ground state (lowest energy state) and has negligible thermal velocity. Determine B, V, and the total number of spots on the film.

Solution. This is USAPhO 2004, problem B1, and you can check its official solutions.

[**2**] **Problem 9.** A rotor consists of two particles of mass m connected by a rigid rod of length L.

(a) Find the energy levels if the particles are not identical.

(b) Find the energy levels if the particles are identical. (Hint: recall that the closed loop integrals in the previous ideas are over paths that take the system back to its original state.)

You might find it disturbing that the result is so different if the particles are or aren't completely identical, but it's a well-verified fact about molecular rotational energy levels. Without the effect of part (b), many predictions of quantum mechanics would come out totally wrong!

Solution.   (a) We see that the angular momentum L_z is constant, so the quantization condition says $L_z \cdot 2\pi = nh$, or $L_z = n\hbar$. Then, $E = \frac{1}{2I}L_z^2 = \frac{n^2\hbar^2}{mL^2}$.

(b) The point here is that after just a π rotation, the system is back in its original state, because the particles are identical. Thus, $L_z \cdot \pi = nh$, or $L_z = 2n\hbar$, or $E = \frac{4n^2\hbar^2}{mL^2}$.

[**3**] **Problem 10.** ⟳ INPhO 2020, problem 3.

Solution. See the official solutions here.

[**3**] **Problem 11.** INPhO 2016, problem 6. Unfortunately, this question automatically comes with the solutions, but it's still useful to work through.

Remark

In popular science, people sometimes speak of "quantizing" a system as similar to making everything discrete. But as you've seen above, it's more complicated than that. For instance, position never becomes discrete; instead, we integrate over it.

The general rule in quantum mechanics is that confinement to a finite "size" causes the conjugate variable to become discrete. For example, above you looked at several examples of particles bound to potentials. These are confined in space, and hence have discrete orbits in phase space by idea 2, and thus discrete energies. But a free particle not bound to a potential can have any energy, because $E = p^2/2m$ and there is no condition at all on p. On the other hand, angles are always confined to the finite range $[0, 2\pi]$, which is why the angular momentum of any system is quantized.

2   Higher Dimensions

Idea 4

For a system with more than one degree of freedom, the WKB quantization condition holds for each individually,

$$\oint p_i \, dx_i = n_i h.$$

In this case, there can be multiple quantum states with a given energy, in which case we say that energy level is degenerate; the number of states with that energy is called the degeneracy.

[2] **Problem 12.** Consider a particle of mass m in a two-dimensional box of width and length L, with hard walls. This is the two-dimensional analogue of problem 3.

(a) Write down the energy of the state corresponding to n_1 and n_2.

(b) What is the lowest energy level with a degeneracy of greater than 2?

Solution.   (a) In each dimension, we have $p_x = \pi n_x \hbar / L$ and $p_y = \pi n_y \hbar / L$ as before. So the energy is

$$E = \frac{\pi^2 \hbar^2}{2mL^2}(n_x^2 + n_y^2)$$

where again, $n_x, n_y \geq 1$.

(b) The first number that can be written as the sum of two squares in two nontrivial ways is

$$50 = 7^2 + 1^2 = 5^2 + 5^2$$

so the first degenerate energy level is $\frac{25\pi^2\hbar^2}{mL^2}$.

[4] **Problem 13.** Consider a particle of mass m in the potential $V(x, y) = kr^2/2$. This is the two-dimensional analogue of problem 4. It is also the potential experienced by an electron in the obsolete "plum pudding" model of the atom, where they are embedded in a ball of uniform charge density.

(a) By working in Cartesian coordinates, find all of the energy levels, as well as the number of states within each energy level, called the degeneracy.

(b) **[A]** Now repeat the exercise in polar coordinates. In this case the integrals

$$\oint p_r \, dr, \quad \oint L \, d\theta$$

are quantized. Find the energy levels and their degeneracies. Note that for the radial motion, you will have to use the effective potential, as covered in **M6**. You will run into a difficult integral, so you may use the fact that

$$\int_{C-\sqrt{C^2-D^2}}^{C+\sqrt{C^2-D^2}} dx \sqrt{\frac{2C}{x} - \frac{D^2}{x^2} - 1} = (C - |D|)\pi$$

valid for $|D| \leq C$. How does your answer compare to that of part (a)?

Solution.   (a) Let $\omega = \sqrt{k/m}$. As always, each direction contributes energy $\hbar\omega(n + 1/2)$, so the total energy is $\hbar\omega(n_x + n_y + 1)$. The number of states with energy $\hbar\omega n$ is the number of solutions to $n_x + n_y = n - 1$, which is simply n.

(b) By conservation of energy and angular momentum, we have

$$E = \frac{1}{2}kr^2 + \frac{1}{2}m(\dot{r}^2 + v_\theta^2) = \frac{1}{2}kr^2 + \frac{L^2}{2mr^2} + \frac{p_r^2}{2m}.$$

Quantizing the angular motion gives

$$\oint L \, d\theta = 2\pi L = n_\theta h$$

which means $L = n_\theta \hbar$ as usual. Let $a \leq r \leq b$ where $\dot{r} = 0$ at $r = a$ or $r = b$. Then quantizing the radial motion (accounting for two soft walls) gives

$$(n_r + 1/2)h = 2\int_a^b dr \sqrt{2mE - \frac{n_\theta^2 \hbar^2}{r^2} - \omega^2 m^2 r^2}.$$

To clean this up a bit, let's set $\hbar = k = m = 1$ for now and put them back by dimensional analysis at the end. Then the equation reduces to

$$2\pi(n_r + 1/2) = 2\int_a^b dr \sqrt{2E - \frac{n_\theta^2}{r^2} - r^2}.$$

By substituting $u = 1/r^2$ we find

$$2\pi(n_r + 1/2) = 2\int_{a'}^{b'} \frac{du}{2\sqrt{u}} \sqrt{2E - \frac{n_\theta^2}{u} - u} = \int_{a'}^{b'} du \sqrt{\frac{2E}{u} - \frac{n_\theta^2}{u^2} - 1}$$

where a' and b' are the zeroes of the quantity inside the square root,

$$a' = E - \sqrt{E^2 - n_\theta^2}, \quad b' = E + \sqrt{E^2 - n_\theta^2}.$$

This incidentally shows that we need $|n_\theta| \leq E$ for the result to make sense. Using the provided integral, we find

$$2\pi(n_r + 1/2) = (E - |n_\theta|)\pi.$$

The constraint $|n_\theta| \leq E$ then translates to $n_r \geq 0$, which makes sense. Solving for E gives the final result,

$$E = 2n_r + n_\theta + 1.$$

By dimensional analysis, the right-hand side needs a factor of $\hbar\omega$ to become an energy, so

$$E = \hbar\omega(2n_r + |n_\theta| + 1).$$

The result is identical to that of part (a). The lowest energy level is $E = \hbar\omega$, corresponding to $(n_r, n_\theta) = (0,0)$. The next is $E = 2\hbar\omega$, corresponding to $(n_r, n_\theta) = (0, \pm 1)$. The next is $E = 23\hbar\omega$, corresponding to $(n_r, n_\theta) = (1,0)$ or $(0, \pm 2)$, and so on.

Remark

Sommerfeld applied an analysis like that of part (b) of problem 13 to the Bohr model, yielding the semiclassical orbits which are ellipses with the nucleus at the focus. (In fact, if you're so inclined, you can do this too, using the same provided integral.) This accounted for the quantum numbers n and ℓ in hydrogen. The quantum number m comes from additionally quantizing L_z, which implies that the elliptical orbits can only occur in certain planes, an idea known as "space quantization". Sommerfeld even managed to compute the first relativistic corrections to the energy levels, explaining their so-called "fine structure".

With all this included, the Bohr theory provides a complete description of the energy levels of hydrogen, except that (1) the $\ell = 0$ orbitals are missing, since they would have to go straight through the nucleus, (2) space quantization seems artificial and breaks rotational symmetry, and (3) the number of states isn't quite right, a deficiency that would later be fixed by including spin. Many complicated attempts were made to patch these problems, or to extend the theory to multi-electron atoms, but they were forgotten after the modern theory of quantum mechanics (in terms of the Schrodinger equation) appeared.

However, what you've learned above is not completely irrelevant today. The correspondence principle is the idea that quantum results should yield smoothly transition to classical ones in the limit $\hbar \to 0$, which in this context means sending the quantum numbers to infinity. And that's exactly what happens. For high quantum numbers, you can superpose atomic orbitals of nearby energy to create a sharply peaked wavefunction, just like how we could create wavepackets from plane waves in **W1**. These peaks act like localized classical particles, following the Bohr model's orbits. Thus, the Bohr model is still useful for studying Rydberg atoms, which are hydrogen-like atoms excited to very high energy levels.

[**3**] **Problem 14** (Cahn). A crude model of an electron bound to an atom is a particle of mass m attached to a one-dimensional spring, with spring constant k and hence frequency $\omega = \sqrt{k/m}$. Consider two such atoms.

(a) Write down the energy levels of the system, assuming the atoms are completely independent. How many states correspond to each energy?

(b) Let the electrons have positions x_i relative to their respective equilibrium positions. Now suppose the atoms are brought close together, causing the electrons to repel. For simplicity,

we represent this in terms of an extra potential energy term $k'x_1x_2$, where k' is small. Find the new energy levels of the system exactly. (Hint: this can be done with a clever change of variables. However, you have to be careful because changing to new coordinates x_i' also requires changing the momenta; after all, if we didn't, then the quantization condition of idea 2 would change, leading to different energy levels! If K is the kinetic energy, and you are using momentum variables x_i, then the momenta should be defined as $p_i = \partial K/\partial \dot{x}_i$.)

(c) Your answer should not make sense for large k'. Physically, what is going on?

Part (b) gives a simple example of how energy levels "split" in the presence of interactions.

Solution.   (a) This is just two copies of an ordinary harmonic oscillator, so $E_{n,m} = \hbar\omega(n+m+1)$ for $n, m \geq 0$. The lowest energy has one corresponding state $(n = m = 0)$, the next one has two $((n, m) = (1, 0)$ or $(0, 1))$, the next has three, and so on.

(b) The energy of the system has the form

$$E = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \frac{1}{2}kx_1^2 + \frac{1}{2}kx_2^2 + k'x_1x_2.$$

This can be brought into a simplified form by expanding in normal modes, just as you saw in **M4**. Specifically, we define

$$y_1 = \frac{x_1 + x_2}{\sqrt{2}}, \quad y_2 = \frac{x_1 - x_2}{\sqrt{2}}.$$

The corresponding momenta, defined as suggested in the hint, are

$$p_1' = \frac{p_1 + p_2}{\sqrt{2}}, \quad p_2' = \frac{p_1 - p_2}{\sqrt{2}}.$$

In terms of these new variables, we have

$$E = \frac{p_1'^2}{2m} + \frac{p_2'^2}{2m} + \frac{1}{2}(k + k')y_1^2 + \frac{1}{2}(k - k')y_2^2.$$

But this is just the form of two independent harmonic oscillators, with resonant frequencies $\sqrt{(k \pm k')/m}$. So the energy levels are

$$E_{n,m} = \frac{\hbar}{\sqrt{m}}\left((n + 1/2)\sqrt{k + k'} + (m + 1/2)\sqrt{k - k'}\right).$$

This can be written a bit more simply by Taylor expanding, which gives

$$E_{n,m} \approx \hbar\omega\left(n\left(1 + \frac{k'}{2k}\right) + m\left(1 - \frac{k'}{2k}\right) + 1\right) = \hbar\omega\left((n + m + 1) + (n - m)\frac{k'}{2k}\right).$$

In other words, an energy level that contains N states splits into N separate, closely spaced energy levels. This behavior is ubiquitous in quantum mechanics. This trick of turning everything into a bunch of independent quantum harmonic oscillators by using normal modes is also very important; it'll basically be the bedrock of many graduate physics courses.

(c) For $k' > k$, the energy becomes an imaginary number. When k' is this big, the repulsion between the electrons is so strong that they both just shoot off to infinity in opposite directions. That is, the energy is not bounded below; the energy can be lowered to negative infinity by increasing the separation. That means the electrons are not bound at all, so there aren't discrete energy levels.

Example 2

A nonrelativistic particle of mass m is in a cubical box with side length L and hard walls. Find the approximate number of quantum states with energy at most E_0, where E_0 is large.

Solution

Using the same reasoning as in previous problems, we apply "hard wall" boundary conditions, requiring the wavefunction to go to zero at the boundary. Thus, the wavefunction is

$$\psi \propto \sin(k_x x) \sin(k_y y) \sin(k_z z)$$

where

$$k_i = \frac{\pi}{L} n_i, \quad n_i \text{ positive integer}$$

and the energy is

$$E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}.$$

The simplest way to proceed is to think in terms of "momentum space", an abstract space whose axes are p_x, p_y, and p_z. The allowed states form a grid in the first octant of momentum space, with a volume of $(\pi\hbar/L)^3$ for each state. The surface $E = E_0$ corresponds to a sphere of radius $\sqrt{2mE_0}$. Therefore the number of states with energy at most E_0 is approximately

$$N = \frac{1}{8} \left(\frac{4}{3}\pi (2mE_0)^{3/2} \right) \left(\frac{\pi\hbar}{L} \right)^{-3}.$$

Now let's solve the problem a slightly different way: suppose the box has *periodic* boundary conditions, so that the right side is identified with the left side, and so on. In this case, the wavefunctions can all be written in the form

$$\psi \propto \exp(i(k_x x + k_y y + k_z z))$$

but now the allowed values of the wavenumbers are

$$k_i = \frac{2\pi}{L} n_i, \quad n_i \text{ integer}.$$

The allowed states form a grid in all of momentum space, not just the first octant, with a volume of $(2\pi\hbar/L)^3$ for each state. That is, while the volume around each state is eight times as large, the states now occupy eight octants instead of one. Then the overall density of states is still the same, and the number of states with energy at most E_0 is approximately

$$N = \left(\frac{4}{3}\pi (2mE_0)^{3/2} \right) \left(\frac{2\pi\hbar}{L} \right)^{-3}$$

which matches the result for hard walls. The point of this computation is to show that when we care about the statistical properties of many states, the boundary conditions won't matter. In practice, you'll see both kinds of boundary conditions quite often.

If you find the differences between the two boundary conditions confusing, you're not alone. In his original derivation of blackbody radiation, Lord Rayleigh used "hard wall" boundary conditions but allowed negative n_i, leading to a factor of 8 error. Jeans corrected it, which is why the result is now called the Rayleigh–Jeans law.

[4] **Problem 15.** ⏲ Do the following JPhO problem. This pedagogical problem introduces the WKB approximation and phase space, reviewing everything covered above, and applies it to "clusters" of atoms. You can skip sections I and III, which are covered elsewhere on this problem set.

Solution. See the official solutions here.

> **Remark**
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> Because matter has wave properties, particles such as electrons can exhibit interference effects, like those covered in **W2**. For example, you can run a double-slit experiment firing individual electrons at a time and seeing where they hit the screen, which will gradually build up an interference pattern. You'll see an example of this in the next problem.

[4] **Problem 16.** ⏲ IPhO 1993, problem 3. (Hint: to do the final part of this problem, you should *not* try to compare the total path lengths traversed by the electrons. That would be very hard, and worse, it won't give the right answer, because the potential from the wire also affects the electrons' phases. Instead, you should use the facts about wavefronts mentioned in **W2**. That is, waves always propagate perpendicular to wavefronts, and all points on a wavefront have the same phase.)

3   The Uncertainty Principle

> **Idea 5: Heisenberg Uncertainty**
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> So far we have treated a quantum particle as having a well-defined position and momentum, but in reality the uncertainties in the position and momentum obey
>
> $$\Delta x \, \Delta p \geq \frac{\hbar}{2}$$
>
> where, as in **P2**, the uncertainties may be interpreted as standard deviations. The "semi-classical limit" used in the rest of this problem set simply corresponds to the case where the required uncertainty is relatively small, which is reached for energy levels $n \gg 1$. Occasionally, Olympiad questions will ask you to use the Heisenberg uncertainty principle to make a very rough estimate. In these cases, the constant factors will not matter.

> **Idea 6: Energy-Time Uncertainty**
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> There are two commonly used versions of the energy-time uncertainty principle. If the energy of a system is only measured for a finite time Δt, it must have a finite uncertainty ΔE in its energy. In addition, if a system significantly changes its state in time Δt, then its energy must have been uncertain by a finite amount ΔE. In both cases, we have
>
> $$\Delta E \, \Delta t \geq \frac{\hbar}{2}.$$
>
> A third common statement of the energy-time uncertainty principle is "for a short time Δt, a system can violate energy conservation by an amount ΔE". This is wrong, because quantum systems always conserve energy; systems that naively seem to violate energy conservation

simply didn't have a well-defined energy in their initial state to begin with. However, thinking this way will usually get you the right answers, essentially because of dimensional analysis.

Example 3

Consider once again a particle of mass m attached to a one-dimensional spring, with natural frequency ω. Use the uncertainty principle to estimate the minimum possible energy of the particle, and compare it with the result of problem 4.

Solution

Suppose the uncertainties in position and momentum are Δx and Δp. Then the potential energy is of order $k(\Delta x)^2/2$ and the kinetic energy is of order $(\Delta p)^2/2m$. Dropping constants,

$$E \sim k(\Delta x)^2 + \frac{(\Delta p)^2}{m} \gtrsim k(\Delta x)^2 + \frac{\hbar^2}{(\Delta x)^2 m}$$

where we applied the uncertainty principle. The ground state minimizes the energy, which is achieved when $(\Delta x)^2 \sim \hbar/\sqrt{km}$. In this case, the energy is of order $k\hbar/\sqrt{km} \sim \hbar\sqrt{k/m} \sim \hbar\omega$, which is just what we found earlier. (A similar derivation can be used to derive the energy of the ground state of hydrogen, along with the Bohr radius; try it!)

Remark

We can also "solve" the above problem with the energy-time uncertainty principle incorrectly. The only timescale in the problem is $1/\omega$, so

$$\Delta E \gtrsim \frac{\hbar}{\Delta t} \sim \hbar\omega$$

so $E \gtrsim \hbar\omega$. However, in reality the ground state has *no* energy uncertainty; its energy is simply the ground state energy. Another way of saying this is that a particle can hang out in the ground state forever, so Δt is infinite and hence ΔE is zero. This incorrect derivation gives the right answer just because it's the only possible answer by dimensional analysis. Thus, a sloppy problem might ask you to do it.

Example 4

Consider a single slit diffraction experiment, where photons of wavelength λ pass through a slit of width a. If the screen is a large distance D away, roughly how wide is the resulting diffraction pattern on the screen?

Solution

The photon has a momentum $p_x = \hbar k = h/\lambda$, and passing through the slit necessarily gives

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it a transverse momentum uncertainty of

$$\Delta p_y \sim \frac{h}{a}$$

where we dropped order one constants, which means an angle uncertainty of

$$\Delta \theta \sim \frac{\Delta p_y}{p_x} \sim \frac{\lambda}{a}.$$

Therefore, using basic geometry, the size of the pattern on the screen is

$$\Delta y \sim D \Delta \theta \sim \frac{D\lambda}{a}.$$

This is the approximate width of the central maximum for single slit diffraction, as we found in **W2**. The reason the result is the same is that light acts like a wave both classically and quantum mechanically; the quantum version of the derivation is just the same as the classical version, but with "everything multiplied by h". What's new about this derivation is that it also applies for matter particles, which have $\lambda = h/p$.

Example 5

The Higgs boson has a mass of $125\,\text{GeV}$ and a lifetime of about $\tau = 1.6 \times 10^{-22}\,\text{s}$. About what percentage uncertainty must a measurement of a Higgs boson's mass have?

Solution

Decay is a significant change in the particle's state, and this change happens over a time τ, which means the energy uncertainty is

$$\Delta E \sim \frac{\hbar}{\tau} = 7 \times 10^{-13}\,\text{J} = 0.004\,\text{GeV}.$$

When we measure the Higgs boson's mass, we really measure the $E = mc^2$ energy released when it decays, so the unavoidable uncertainty of the mass is $\Delta E/E \sim 0.003\%$. (But the actual measured uncertainties are much higher, due to a variety of other effects.)

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[1] **Problem 17** (Krane 4.39). An apparatus is used to prepare an atomic beam by heating a collection of atoms to a temperature T and allowing the beam to emerge through a hole of diameter d in one side of the oven. Show that the uncertainty principle causes the diameter of the beam, after traveling a length L, to be larger than d by an amount of order $L\hbar/d\sqrt{mk_BT}$, where m is the mass of an atom.

Solution. The energy of the particles is on order k_BT, so $v \sim \sqrt{k_BT/m}$. Thus, the time taken to travel the length L is $t \sim L/v \sim L\sqrt{m/k_BT}$. Now, the uncertainty in the vertical direction is d, so the momentum in the vertical direction is on order $\hbar/d$, so vertical speed on order $\hbar/md$. Thus, in the time t, we get a spread of order

$$\frac{t\hbar}{md} = \frac{L\hbar}{d\sqrt{m\,k_BT}},$$

as desired.

[2] Problem 18 (Insight 8.26)**.** When helium is cooled to extremely cold temperatures, it becomes a superfluid, an exotic type of liquid that can flow with zero dissipation. These strange properties occur because quantum mechanical effects are large, making the quantum uncertainty in the position of each helium atom on the same order as the separation between atoms.

(a) Given that superfluid helium has density ρ and a helium atom has mass m, estimate the temperature T at which helium becomes a superfluid. This is closely related to, but not quite the same thing as Bose–Einstein condensation, a phase transition that bosons undergo at low temperatures.

(b) Numerically evaluate T, given that $\rho \sim 100 \, \text{kg/m}^3$ and $m \sim 7 \times 10^{-27} \, \text{kg}$.

Solution.   (a) The energy is of order $k_B T$, so the momentum is of order $p \sim \sqrt{2mE} \sim \sqrt{mk_B T}$. This leads to a spread in position by the uncertainty principle of

$$\Delta x \sim \frac{\hbar}{p} \sim \frac{\hbar}{\sqrt{m \, k_B T}}.$$

The volume per helium atom is m/ρ, giving a typical separation of $(m/\rho)^{1/3}$. Setting this equal to Δx and solving for T gives

$$T \sim \frac{\rho^{2/3} \hbar^2}{k_B m^{5/3}}.$$

(b) Plugging in the numbers gives $T \sim 0.7 \, \text{K}$. The actual answer is $2.172 \, \text{K}$, so this isn't bad for such a rough estimate!

[4] Problem 19. A neutron is inside a small cubical box of side length d. Ignore gravity.

(a) Estimate the minimum possible pressure on the walls using the uncertainty principle, dropping all numeric factors. In the next two parts, we'll calculate the pressure more carefully.

(b) Calculate the average pressure on the walls by treating the neutron as a classical particle bouncing back and forth, with the same momentum as expected for the ground state in the WKB approximation.

(c) Calculate the average pressure on the walls by finding the energy E of the ground state using the WKB approximation, and the definition of pressure, $P = -\partial E / \partial V$. (This actually gives the exact answer. Of course, by dimensional analysis, taking $P \sim E/V$ would also produce the right answer, up to a constant factor.)

(d) Now suppose that $N \gg 1$ neutrons are inside the box. Neutrons are fermions, as explained in the next section, and hence no two can share the same quantum state. Neglecting any interactions between the neutrons, estimate the minimum possible pressure on the walls, using either the method of part (b) or (c). How does it scale with the number density $n = N/V$?

The large pressure you will find in part (d) is known as degeneracy pressure. It supports compact objects such as white dwarfs and neutron stars, as you'll investigate in **X3**.

Solution.   (a) The uncertainty of position in each dimension is around $d/2$, and for momentum, p_i (factors of 2 can be ignored). Consider the pressure on the faces in the yz-plane. The time between every collision is $t \sim d/v_x = md/p_x$, and the impulse is $\sim p_x$. Thus the force is $\sim p_x^2/md$, giving a pressure of around p_x^2/md^3. Thus Heisenberg's uncertainty principle gives

$$P_{\text{min}} \sim \frac{\hbar^2}{md^5}$$

(b) Earlier, we found that $p_i = \frac{\pi}{d} n_i \hbar$. The time between collisions is $t = 2md/p_i$ and the impulse is $2p_i$, giving a pressure of p_i^2/md^3. Note that this is a directional pressure, i.e. if the p_i were different, the pressures on each wall would be different.

The pressure on the wall perpendicular to the i direction is

$$P_i = \frac{\pi^2 \hbar^2}{md^5} n_i^2.$$

For the ground state, the n_i are all equal to one, so we have a uniform pressure,

$$P = \frac{\pi^2 \hbar^2}{md^5}$$

which is the same order of magnitude as in part (a).

(c) Earlier, we found that for a two-dimensional box,

$$E = \frac{\pi^2 \hbar^2}{2md^2}(n_x^2 + n_y^2).$$

This generalizes straightforwardly to a three-dimensional box. In the ground state, $n_x = n_y = n_z = 1$, giving

$$E = \frac{\pi^2 \hbar^2}{2md^2}(1 + 1 + 1) = \frac{3\pi^2}{2}\frac{\hbar^2}{mV^{2/3}}.$$

Carrying out the derivative,

$$P = \frac{3\pi^2}{2}\frac{2}{3}\frac{\hbar^2}{mV^{5/3}} = \frac{\pi^2 \hbar^2}{md^5}.$$

As expected, this coincides with the answer to (b), since both ultimately originate from the same approximation.

(d) In this case, it's clearest to use the method of part (c), even though it's rougher. We don't want to keep track of the different pressures on each wall from part (b), because we know that once we average over many particles, it's going to average out to a uniform pressure anyway.

If we keep track of the n_i dependence, we have

$$E_{\mathbf{n}} = \frac{\pi^2}{2}\frac{\hbar^2}{mV^{2/3}}n^2, \quad n^2 = n_x^2 + n_y^2 + n_z^2$$

where we're treating the n_i like the components of a vector. This contributes a pressure

$$P_{\mathbf{n}} = \frac{\pi^2}{3}\frac{\hbar^2}{mV^{5/3}}n^2.$$

Just as in example 2, an eighth of a sphere of $\mathbf{n}$ values is filled, where for N particles in total, the radius $n_{\max}$ of the sphere obeys

$$N = \frac{1}{8}\left(\frac{4}{3}\pi n_{\max}^3\right)$$

which tells us that

$$n_{\max} = \sqrt[3]{\frac{6N}{\pi}}.$$

The total pressure can be found by summing over all the lattice points within this eighth of a sphere. Since N is large, this sum can be approximated as an integral,

$$P = \int_0^{n_{\max}} \frac{4\pi n^2\,dn}{8}P_{\mathbf{n}} = \frac{\pi^3\hbar^2}{6mV^{5/3}}\int_0^{n_{\max}} n^4\,dn = \frac{\pi^3\hbar^2}{30md^5}\left(\frac{6N}{\pi}\right)^{5/3} \propto \frac{\hbar^2 n^{5/3}}{m}.$$

Thus, the degeneracy pressure scales as $n^{5/3}$. (If you solved this problem instead using part (b), or using periodic boundary conditions from example 2, you should get the exact same answer.)

[3] **Problem 20.** ⊙ USAPhO 2018, problem B2.

[3] **Problem 21.** Classically, an electron orbiting a proton with frequency ω_o emits radiation with frequency $\omega_c = \omega_o$, as covered in **E7**. On the other hand, quantum mechanically the energy levels are discrete, and using the de Broglie relation $\Delta E = \hbar\omega$ indicates the frequencies of radiation emitted when the electron drops between energy levels are discrete as well. The classical and quantum models thus seem to be radically different, but in the limit $n \to \infty$ where quantum effects become negligible, the two should match.

(a) Suppose that the electron can orbit the proton in circular orbits with discrete radii r_n. For the nth orbit, compute the frequency ω_c of the emitted radiation according to classical mechanics.

(b) Now suppose the electron drops from the nth energy level to the $(n-1)^{\text{th}}$ energy level. Compute the frequency ω_q of the emitted radiation according to quantum mechanics, assuming the orbits have radii r_n.

(c) In the limit $n \to \infty$, the results of parts (a) and (b) should coincide. Therefore, by equating these results, infer how r_n depends on n, and thus how L depends on n. If all goes well, you should recover the result of Bohr quantization.

The reasoning here is exactly how Bohr came up with Bohr quantization in the first place. (The de Broglie relation we had to use was motivated earlier through Planck's law, as we showed in **T2**.)

Solution.   (a) Classically, we need to balance the centripetal force with the Coulomb force,

$$m\omega_0^2 r = \frac{e^2}{4\pi\epsilon_0 r^2}.$$

Since $\omega_c = \omega_0$, we get

$$\omega_c = \sqrt{\frac{e^2}{4\pi\epsilon_0 r_n^3 m}}.$$

(b) The de Broglie relation tells us that $\hbar\omega_q = E_n - E_{n-1}$, so using standard results for circular orbits in an inverse square potential,

$$\omega_q = \frac{e^2}{4\pi\hbar\epsilon_0}\frac{1}{2}\left(\frac{1}{r_{n-1}} - \frac{1}{r_n}\right).$$

(c) Thinking of n as a large number, we can approximate

$$\left(\frac{1}{r_{n-1}} - \frac{1}{r_n}\right) = \frac{r_n - r_{n-1}}{r_{n-1}r_n} \approx \frac{r_n - r_{n-1}}{r_n^2} \approx \frac{1}{r_n^2}\frac{dr_n}{dn}.$$

Plugging this into the equation $\omega_c = \omega_q$ and simplifying, we get

$$2\hbar\sqrt{\frac{4\pi\epsilon_0}{e^2m}} = \frac{1}{\sqrt{r_n}}\frac{dr_n}{dn}.$$

Separating and integrating, we have

$$r_n = \frac{4\pi\epsilon_0\hbar^2}{e^2m}n^2.$$

There could be a constant of integration, but for large n, it's negligible, and we can conclude that for large n, $r_n \propto n^2$. On the other hand, we have

$$L_n = mv_nr_n = m\omega_cr_n^2 \propto r_n^{1/2}$$

which means that for high n, $L_n \propto n$.

This is as far as we can go, "rigorously". The amazing thing is that this derivation is based on $\omega_c = \omega_q$, which only holds at large n, along with approximations that only work at large n, and also involves an unknown constant of integration. But if we just set the constant of integration to zero, and assume the derivation works for all n, then you can check that we recover $L = n\hbar$, which happens to be exactly true in the real world!

[4] **Problem 22.** ⏲ IPhO 2005, problem 3. You may skip part 4, since it's quite similar to another problem on this problem set.

4   Bosons and Fermions

So far, we've only solved for the energy levels of individual particles. Now we'll consider what happens when we put many of these particles together. We will assume the particles do not interact, which means their energy levels are just the same as the energy levels for individual particles. If the particles are fermions, they obey the Pauli exclusion principle, which means no two can occupy the same energy level. If they are bosons, there is no such restriction; we'll consider bosons first.

[3] **Problem 23.** This problem is a modification and clarification of USAPhO 2011 A4. (In fact, the answers differ, so don't compare against the USAPhO solution!) Consider a simplified model of the electromagnetic radiation inside a cubical box of side length L at temperature T. In this model, modes of the electric field have spatial dependence

$$E(x, y, z) = E_0 \sin(k_x x)\sin(k_y y)\sin(k_z z)$$

where one corner of the box lies at the origin and the box is aligned with the x, y, and z axes. For simplicity, we will treat the electric field as a *scalar*.

(a) The electric field must be zero everywhere at the sides of the box. What condition does this impose on the k_i?

(b) Each permitted value of the triple (k_x, k_y, k_z) corresponds to a mode, which can be occupied by any number of photons. Each photon has an energy $E = \hbar\omega$, where $\omega = ck$ is the frequency of the mode. How many modes have an energy per photon of at most $k_B T$?

(c) As a crude approximation, suppose that in thermal equilibrium, each mode with energy per photon at most $k_B T$ contains exactly one photon, while all other modes contain no photons. Compute the total energy of the photons in the box. (Answer: $(k_B T)^4 L^3 / 8\pi^2 \hbar^3 c^3$.)

Note that the procedure here is different from what we did above. Before, we started with particles and quantized $\oint p\,dx$ to get the allowed quantum states. Here, we're treating a situation with many particles (photons), which are excitations of an underlying field (the electromagnetic field). In this case, we found the (normal) modes of the classical field, then quantized by saying that photons could occupy these modes. This is the methodology of quantum field theory.

Solution. (a) We see that $k_x L = n_x \pi$, $k_y L = n_y \pi$, and $k_z L = n_z \pi$.

(b) Define the vector $\mathbf{n} = (n_x, n_y, n_z)$. For each mode, the energy per photon is

$$E = \hbar\omega = \hbar ck = \frac{\pi \hbar c}{L}\sqrt{n_x^2 + n_y^2 + n_z^2}.$$

Moreover, the values of the n_i are positive integers. Therefore, the quantum states we are looking for form an eighth of a sphere in phase space, bounded by states with

$$n_{\max} = \frac{E_{\max} L}{\pi \hbar c}.$$

The number of modes (i.e. the number of values of $\mathbf{n}$) with an energy per photon of at most $E_{\max}$ is thus

$$N(E_{\max}) = \frac{1}{8}\left(\frac{4}{3}\pi n_{\max}^3\right) = \frac{1}{6\pi^2}\left(\frac{EL}{\hbar c}\right)^3.$$

In this case, the requested answer is

$$N(k_B T) = \frac{1}{6\pi^2}\left(\frac{k_B T L}{\hbar c}\right)^3.$$

Note that this is different from the official USAPhO solution, because they also allowed negative values for the n_i. This is incorrect, because flipping the sign of one of the n_i gives you exactly the same mode, up to an irrelevant -1 factor.

(c) We sum over the modes. For each occupied mode, we assume the energy stored is E, so

$$U = \int E\,dN = \int E \frac{dN}{dE}\,dE = \frac{1}{6\pi^2}\left(\frac{L}{\hbar c}\right)^3 \int_0^{k_B T} E(3E^2)\,dE = \frac{1}{8\pi^2}\frac{(k_B T)^4 L^3}{\hbar^3 c^3}.$$

[4] **Problem 24.** The final result of the problem above is correct dimensionally, but has incorrect numerical factors because of the crude approximations made. In this problem we'll do a more careful analysis to get the right result. This question is self-contained, but background from **T1** and **T2** will be helpful.

(a) Consider a quantum mode that can support photons of energy E. The mode can be occupied by any whole number of photons. Thus, using the Boltzmann distribution, the probability of having n photons is

$$p_n \propto e^{-nE/k_BT}.$$

Show that the expected number of photons in the mode is

$$\langle n \rangle = \frac{1}{e^{E/k_BT} - 1}.$$

This is the Bose–Einstein distribution.

(b) Sketch $\langle n \rangle$ as a function of E. How does it behave at high and low E, and do those results make physical sense?

(c) Using the Bose–Einstein distribution, show that the total energy is

$$U = \frac{L^3 \hbar}{\pi^2 c^3} \int_0^\infty d\omega \, \frac{\omega^3}{e^{\hbar\omega/k_BT} - 1}$$

where ω is the frequency. You'll have to multiply by a factor of two, because there are two independent photon polarizations for each mode we found above. (Note that if we open the box, the photons will fly out, and the frequency distribution of the emitted light will be given by the integrand; this yields Planck's law for blackbody radiation.)

(d) [A] Using an appropriate substitution, show that U is a dimensionful constant times the dimensionless integral

$$\int_0^\infty dx \, \frac{x^3}{e^x - 1}.$$

To evaluate this integral, expand the denominator as a power series, integrate each term individually, and use the fact that the Riemann zeta function obeys

$$\zeta(s) = \sum_{n=1}^\infty \frac{1}{n^s}, \quad \zeta(4) = \frac{\pi^4}{90}.$$

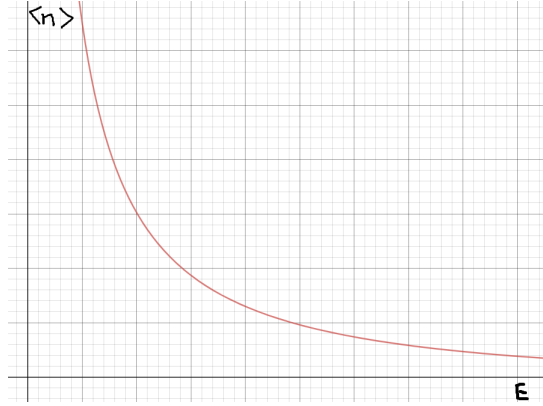When the smoke clears, you should find that

$$U = \frac{\pi^2}{15} \frac{(k_BT)^4 L^3}{(\hbar c)^3}.$$

Solution. (a) We see that

$$\langle n \rangle = \frac{\sum_n n e^{-nE/k_BT}}{\sum_n e^{-nE/k_BT}} = \frac{\left(\frac{1}{e^{E/k_BT}-1}\right)^2}{\frac{1}{e^{E/k_BT}-1}} = \frac{1}{e^{E/k_BT} - 1},$$

as desired.

(b) $\langle n \rangle$ as a function of E looks like this:

For modes with low E, we have $\langle n \rangle \approx k_B T / E \ll 1$. This means the energy stored in this mode is approximately $\langle n \rangle E \approx k_B T$. That makes physical sense: in this limit where there are lots of photons, their discreteness doesn't matter, so the mode can be treated classically, getting energy $k_B T$ by the equipartition theorem.

For modes with high E, we have $\langle n \rangle \approx e^{-E/k_B T} \ll 1$. This also makes sense, because in this limit there isn't enough thermal energy to significantly excite the modes.

(c) The logic is exactly the same as part (c) of the previous problem, but instead of saying that some modes have 1 photon and others have 0 photons, we just assign the proper $\langle n \rangle$ photons to every mode. Then

$$U = \int \langle n \rangle E \, dN = \frac{1}{2\pi^2} \left(\frac{L}{\hbar c} \right)^3 \int_0^\infty \langle n \rangle E^3 \, dE.$$

As stated, we multiply by a factor of 2 to account for the two polarizations per mode. We also change variables from E to ω using $E = \hbar \omega$. This gives

$$U = \frac{L^3 \hbar}{\pi^2 c^3} \int_0^\infty d\omega \, \frac{\omega^3}{e^{\hbar \omega / k_B T} - 1}$$

just as desired.

(d) Now we make the substitution $x = \hbar \omega / k_B T$, where $dx = \hbar d\omega / k_B T$.

$$U = \frac{L^3 \hbar}{\pi^2 c^3} \int_0^\infty \left(\frac{k_B T}{\hbar} dx \right) \frac{(k_B T x / \hbar)^3}{e^x - 1} = \frac{(k_B T)^4 L^3}{\pi^2 c^3 \hbar^3} \int_0^\infty dx \, \frac{x^3}{e^x - 1}.$$

We can rearrange the integral into

$$I = \int_0^\infty dx \, \frac{x^3}{e^x - 1} = \int_0^\infty e^{-x} x^3 \frac{1}{1 - e^{-x}} dx.$$

Recognizing $1/(1 - e^{-x})$ as a geometric series $\sum_{n=0}^\infty (e^{-x})^n$, we can represent the integral as

$$I = \int_0^\infty \sum_{n=0}^\infty x^3 e^{-(n+1)x} dx.$$

We can reindex this since the only instance of n is $n + 1$, so we can start the summation at $n = 1$. Since we can integrate this term by term, we can change the order of the integral and

summation, then integrate by parts to get

$$I = \sum_{n=1}^{\infty} \int_0^{\infty} x^3 e^{-nx} dx = \sum_{n=0}^{\infty} \int_0^{\infty} (3x^2 dx) \left(\frac{e^{-nx}}{n} \right) = \sum_{n=0}^{\infty} \int_0^{\infty} (6x dx) \left(\frac{e^{-nx}}{n^2} \right)$$

$$= \sum_{n=0}^{\infty} \int_0^{\infty} (6 dx) \left(\frac{e^{-nx}}{n^3} \right) = \sum_{n=0}^{\infty} \frac{6}{n^4} = 6\zeta(4).$$

Putting this into our original expression gets

$$U = \frac{\pi^2 k_B^4}{15 c^3 \hbar^3} L^3 T^4.$$

[5] **Problem 25.** ⏲ APhO 2002, problem 1. This useful problem covers the other common example of a quantized bosonic field. In the above problems, we quantized the electromagnetic field to get photons. Here, we quantize a displacement field to get phonons.

Idea 7

In problems 23 and 24, we handled a system of bosons (specifically photons) by considering the modes the photons could occupy, then calculating how many photons were in each mode. This was the easiest route. If we had instead fixed the number of photons, then counted the ways they could be distributed among the mode, the combinatorics would have been a complete nightmare, because multiple photons can occupy the same mode.

Fermions, which obey the Pauli exclusion principle, are simpler, because no two can be in the same state. For instance, if there are n noninteracting fermions in a system, then the lowest energy state of the whole system consists of having one fermion occupy the lowest energy state, the second occupy the second-lowest energy state, and so on. (Accounting for interactions makes the problem much more complicated, because it means the energy of a state depends on whether other states are occupied. However, you can explain a surprising amount while completely neglecting interactions.)

Example 6: Tremaine–Gunn Bound

Suppose all of the dark matter in the galaxy is composed of a single kind of fermionic particle, of mass m. The escape velocity of the galaxy is of order $v_{\text{esc}} \sim 10^{-3} c$, and the dark matter density near Earth is $\rho \sim 0.3 \, \text{GeV}/(c^2 \, \text{cm}^3)$. What's the minimum possible value of m?

Solution

The reason there's a minimum possible value of m is that, as m gets smaller, we need more dark matter particles. But the Pauli exclusion principle tells us that if we want to add more particles, they need to have higher and higher energy, and at some point the particles will have so much energy they won't be bound to the galaxy at all.

To get a rough estimate, let's suppose the galaxy has length scale L, so that we need at least $N \sim \rho L^3/m$ dark matter particles. They need to have energy less than $E_0 \sim m_0 v_{\text{esc}}^2$. Plugging this into the final result of example 2 and dropping all numeric factors gives

$$\frac{\rho L^3}{m} \gtrsim \frac{m^3 v_{\text{esc}}^3 L^3}{\hbar^3}$$

which yields the bound

$$m \lesssim \left(\frac{\rho\, \hbar^3}{v_{\text{esc}}^3}\right)^{1/4} \sim 10\,\text{eV}/c^2.$$

A few decades ago, neutrinos were leading dark matter candidates, since they are light fermionic particles that interact very weakly with ordinary matter. But we now know that the neutrino mass is well below this bound, so that nice idea doesn't work. On the other hand, dark matter could still be composed of bosonic particles of much lighter mass.

[2] **Problem 26.** Consider a system with many noninteracting fermions, and many quantum states. Each quantum state can be either empty or occupied by a fermion. We want to find the probability that a given quantum state, of energy E, is occupied.

(a) To put a fermion in this state, we need to remove a fermion from some other state. Suppose the energy released by doing this, suitably averaged, is μ. (This is the chemical potential, and it depends on the temperature, the number of fermions, and the number of states and their energies.) Using the Boltzmann distribution, show that the probability of occupancy is

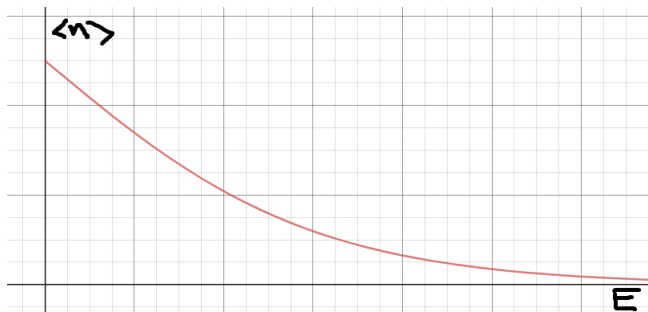$$\langle n \rangle = \frac{1}{e^{(E-\mu)/k_B T} + 1}.$$

This is the Fermi–Dirac distribution.

(b) Sketch $\langle n \rangle$ as a function of E for small but nonzero temperature, as well as the limit attained for zero temperature.
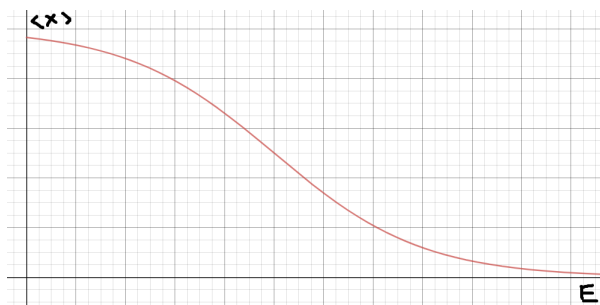
Solution.   (a) The two possibilities are being occupied and not occupied, and the latter comes with a Boltzmann factor of $e^{-(E-\mu)/k_B T}$. Thus,

$$\langle n \rangle = \frac{e^{-(E-\mu)/k_B T}}{1 + e^{-(E-\mu)/k_B T}} = \frac{1}{1 + e^{(E-\mu)/k_B T}}.$$

(b) The graph looks like this for $\mu = 0$:

For a nonzero value of μ, the graph should look like this:

As $T \to 0$, the form of $\langle n \rangle$ will start to look like a step function, $\theta(\mu - E)$. This simply means that the fermions fill up the lowest energy states first, to minimize their total energy. The chemical potential is set by how many fermions there are in total.

[3] **Problem 27.** In this problem we'll consider the energy of the conducting electrons in a solid at low temperatures. Model a solid as a cubical box of side length L with periodic boundary conditions.

(a) Find the number of quantum states with energy at most E_F, making sure to account for the two spin states of the electron.

(b) Suppose there are N electrons in total. They will fill all of the energy levels up to $\mu = E_F$, where E_F is called the Fermi energy. Show that

$$E_F = \frac{h^2}{2m} \left(\frac{3N}{8\pi V} \right)^{2/3}.$$

(c) A sodium crystal has one conduction electron per atom. The density and molar mass are

$$\rho = 0.971 \times 10^3 \, \text{kg/m}^3, \quad M = 0.023 \, \text{kg/mol}.$$

Find N/V and E_F, and use this to evaluate the typical speed v of an electron.

Solution. (a) In a cubical box with period boundary conditions, the wavenumbers satisfy $k_i = \frac{2\pi}{L} n_i$ where n_i can also be a negative integer. As seen in the example, the number of states is $\frac{4}{3}\pi(\sqrt{2mE_F})^3 (2\pi\hbar/L)^{-3}$, but we multiply that by 2 due to the two spin states of the electron.

$$N = \frac{8}{3}\pi(2mE_F)^{3/2} \left(\frac{2\pi\hbar}{L} \right)^{-3}.$$

(b) In a cube, $V = L^3$. Rearranging the above equation gets

$$E_F = \frac{h^2}{2m} \left(\frac{3N}{8\pi V} \right)^{2/3}.$$

(c) If N_A is Avogadro's number, then the mass of each atom is $m = M/N_A$, which gives an atom density of ρ/m. Since there's one conduction atom per atom, we have $N/V = \rho/m = N_A\rho/M$, which gives us $N/V = 2.54 \times 10^{28} \, \text{m}^{-3}$. Putting this into our previous formula gives $E_F = 5.05 \times 10^{-19}$ J. The typical speed v_F satisfies

$$E_F \sim \frac{1}{2}mv_F^2$$

which gives $v_F \sim 10^6$ m/s, or on the order of 1% of the speed of light! This verifies a statement made in **E4** about electrical conduction in solids.

[3] **Problem 28** (MIT). [A] This is an advanced problem that is only placed here because the final result is neat. An integer N can be *partitioned* by writing it as a sum of positive integers, and the partition function $p(N)$ is the number of unique ways this can be done. For example,

$$4 = 1+1+1+1 = 1+1+2 = 2+2 = 1+3 = 4$$

which implies $p(4) = 5$. Counting the number of partitions of an integer is a very hard combinatorics problem, but we can get an estimate for large N using string theory.

(a) Consider an ideal string with hard boundary conditions and fundamental frequency ω. Show that the number of distinct quantum states with energy $N\hbar\omega$ is $p(N)$.

(b) Now suppose the string is at temperature T, where T is chosen so that the expected energy is $N\hbar\omega$. In the thermodynamic limit $N \gg 1$, find a relation between N and T. You may use the result $\zeta(2) = \pi^2/6$.

(c) By approximating the entropy as $S \approx k_B \log p(N)$, show that

$$\frac{\hbar\omega}{kT} = \frac{d\log p(N)}{dN}.$$

Combine this with your previous result to find an estimate for $p(N)$.

To check your answer, the celebrated Hardy–Ramanujan formula (which is more accurate than the very rough treatment we give above) is

$$p(N) \sim \frac{1}{4\sqrt{3}\,N} \exp\left(\pi\sqrt{\frac{2N}{3}}\right).$$

While we only considered a simple nonrelativistic string here, calculations of this sort show up in the thermodynamics of string theory. For further discussion, see chapter 22 of Zwiebach.

Solution.   (a) The modes of the string have frequencies $m\omega$, which means that upon quantization, each quantum in mode m will have energy $m\hbar\omega$. Thus, putting in quanta to reach total energy $N\hbar\omega$ is the same as building a partition of N out of integers m. For example, $4 = 1+1+1+1$ corresponds to putting 4 quanta in the fundamental mode, while $4 = 4$ corresponds to putting 1 quantum in the fourth harmonic.

(b) By borrowing some results from previous problems, we have

$$N = \sum_m \frac{m}{e^{m\hbar\omega/kT} - 1} \approx \int_0^\infty \frac{m\,dm}{e^{m\hbar\omega/kT} - 1}.$$

We have already done a similar integral in problem 24, and using the same trick of expanding the denominator in a Taylor series and integrating term by term gives

$$N \approx \frac{\pi^2}{6}\left(\frac{kT}{\hbar\omega}\right)^2.$$

(c) Using the definition of temperature,

$$T = \frac{dE}{dS} = \frac{\hbar\omega}{k}\frac{dN}{d\log p(N)}.$$

Rearranging slightly gives the desired result. Eliminating T using the above result,

$$\frac{d\log p}{dN} \approx \frac{\pi}{\sqrt{6N}}.$$

Separating and integrating,

$$\log p(N) \sim \int_0^N \frac{\pi}{\sqrt{6N}}\, dN = \pi\sqrt{\frac{2N}{3}}$$

which agrees with the Hardy–Ramanujan formula. (Of course, this only gets the leading term right, because we made approximations. The most severe approximation we did was taking $S \approx k_B \log p(N)$. In reality, the energy at a given temperature is not fixed, but rather has fluctuations, so we should have instead summed $p(n)$ for a range of n near N.)

Example 7: Casimir Forces

Consider an infinite uniform string, on which waves propagate with speed v. The string is held fixed by pins at two points separated by a distance L. When the string is in its ground state, what is the resulting force between the pins?

Solution

Of course, in classical mechanics the ground state would just be $y(x) = 0$, and the force would just be the tension T. But there is an additional quantum mechanical contribution, which arises because each of the standing waves between the pins, with frequencies $\omega_n = n\pi v/L$, carries a so-called "zero point" energy $\hbar\omega_n$.

As usual, force can be found by differentiating energy, $F = -dE/dx$. By summing up the zero point energy in all of the standing waves, we naively get

$$E = \sum_n \frac{\hbar\omega_n}{2} = \frac{\pi\hbar v}{2L}\sum_{n=1}^{\infty} n = E_0 \sum_{n=1}^{\infty} n = \infty$$

which is rather unhelpful. This result is off for two reasons. First, even when there aren't any pins, the string still has standing waves, and these waves *also* have a naively infinite energy density. When we move the pins a bit, we change both the zero point energy outside the pins and inside, by infinite amounts, but the *net* change is finite, giving a finite force.

Quantitatively, the energy in between the pins due to the standing waves is

$$E_{\text{plate}} = E_0 \sum_{n=1}^{\infty} n = \infty$$

and the energy we would have had there if the pins didn't exist is the "continuous" sum,

$$E_{\text{vac}} = E_0 \int_0^\infty x \, dx = \infty.$$

The difference should be finite, but we can't just subtract infinity with infinity, which brings us to the second problem: none of these quantities are *actually* infinite. Any real string will have a finite maximum oscillation frequency – for instance, the wavelength certainly can't get smaller than the atomic spacing. Alternatively, even if we had an idealized string where E_{vac} was actually infinite, no real pin can perfectly block waves of all frequencies. For sufficiently high frequencies the waves won't be affected by the pins, so that the sum in E_{plate} eventually behaves like the integral in E_{vac}, leaving a finite difference between the two.

In other words, the difference between E_{plate} and E_{vac} in reality comes from only low n and x, Therefore, let's "regulate" the two expressions above so that they're unchanged in this regime, but match each other at high n and x. The simplest way to do this is to take

$$E_{\text{plate}} = E_0 \sum_{n=1}^\infty n e^{-\epsilon n}, \quad E_{\text{vac}} = E_0 \int_0^\infty x e^{-\epsilon x} \, dx = \frac{E_0}{\epsilon^2}$$

for small ϵ. To handle the sum, let $\alpha = e^{-\epsilon}$, so that

$$E_{\text{plate}}/E_0 = \alpha + 2\alpha^2 + 3\alpha^3 + \dots.$$

Now we use the usual trick for arithmetic-geometric series. Note that

$$\alpha E_{\text{plate}}/E_0 = \alpha^2 + 2\alpha^3 + 3\alpha^4 + \dots.$$

Subtracting, we find

$$(1 - \alpha) E_{\text{plate}}/E_0 = \alpha + \alpha^2 + \alpha^3 + \dots = \frac{\alpha}{1 - \alpha}.$$

We thus conclude that

$$E_{\text{plate}} = \frac{e^{-\epsilon}}{(1 - e^{-\epsilon})^2} E_0 = E_{\text{vac}} - \frac{1}{12} E_0 + O(\epsilon)$$

where we used a result from **P1**. Finally, when we take ϵ to zero, the difference is simply

$$E = E_{\text{plate}} - E_{\text{vac}} = -\frac{1}{12} E_0.$$

Differentiating gives the force,

$$F = \frac{\pi \hbar v}{24 L^2}$$

which turns out to be attractive. Not only is this finite, it's right! Experiments have measured this "Casimir force" precisely for light between two conductors, where $v = c$, and confirmed the expected results.

You're probably suspicious about this derivation because it depends on the arbitrary choice of an exponential suppression. What if the sums and integrals were regulated at high n and x in a different way? Shouldn't the answer depend on the details of the string and pin? Remarkably, the answer is no: the regulator doesn't matter. If you try others, such as $e^{-\epsilon n^2}$ or $1/n^\epsilon$, you'll get the same result; you can find a general proof in chapter 15 of Schwartz's *Quantum Field Theory and the Standard Model*. The reason is that the effect comes from physics at low frequencies, so it doesn't matter how you regulate the high frequencies.

It is for precisely this reason that you will sometimes see the mysterious equation

$$1 + 2 + 3 + \ldots = -\frac{1}{12}.$$

It's not really true. Instead, what it physically means is that the difference between the regulated sum and integral is $-1/12$ for any reasonable regulator.