Lecture 2

Harmonic oscillators

1 Mathematical structure of a single oscillator

The simplest and most important explicitly solvable quantum mechanics problem is the simple harmonic oscilator. The mathematical structure serves as a model for other spectral problems. Moreover, most extended systems, ranging from a lattice of atoms in a crystal to an electromagnetic field in a cavity (black body) to matter fields of elementary particle physics, are usually understood as systems of oscillators (in as much as they can be understood at all).

To start, suppose that the classical system is a particle of mass one moving in one dimension (back and forth on a line) with a force equal to the (negative of the) distance from the origin. The classical equation of motion is

$$\ddot{x} = -x \; .$$

The potential is $x^2/2$, since $-\partial_x x^2/2 = -x =$ the force. Continuing to ignore dimensional constants, $\hbar$ in this case, the hamiltonian operator is

$$H = \frac{1}{2}\left(p^2 + x^2\right) = \frac{1}{2}\left(x^2 - \partial_x^2\right) \; . \tag{1}$$

Finding the possible energy levels for the quantum oscillator means finding the eigenvalues (energy levels) and eigenfunctions (states) of the harmonic oscillator hamiltonian (1).

We do not seek the solution of the time dependent Schrödinger equation directly. Rather we seek the eigenvalues and eigenfunctions of the hamiltonian operator. Of course, the solution of the initial value problem may written using this information: $\psi(x,t) = \sum_n a_n exp(-i\lambda_n t)\phi_n(x)$. The importance of the eigenvalues (energy levels) and eigenfunctions (states) goes geyond their use in the initial value problem. This will become clearer as we proceed, but is still mysterious to me.

The method of raising and lowering operators solves this problem and is ubiquitous in advanced quantum theory. Classically, we could factor the Hamiltonian function (actually, $2H$) as

$$\begin{aligned} x^2 - p^2 &= (x - ip)(x + ip) = (x + ip)(x - ip) \qquad (2) \\ &= -(p + ix)(p - ix) = -(p - ix)(p + ix) \; . \end{aligned}$$

Quantum mechanically, with $p = -i\partial_x$ (and $\hbar = 1$ still), the expressions in the right are not equal and do not equal the left side. To see what happens, define the "lowering" operator

$$a = x + i\widehat{p} = x + \partial_x \; .$$

The other operator, $x - i\widehat{p}$, happens to be the adjoint of a in the sense that if we define the inner product

$$< f \mid g >= \int_{-\infty}^{\infty} \overline{f(x)} g(x) dx \; ,$$

then

$$< f \mid ag >=< a^* f \mid g > \ .$$

To see this, note that the operator x is self adjoint:

$$< f \mid xg >= \int \overline{f(x)} x g(x) dx = \int \overline{x f(x)} g(x) dx =< xf \mid g > \ .$$

Clearly this works for any multiplication operator as long as it is real. Next, since $i\widehat{p} = \partial_x$, we may integrate by parts (ignoring boundary terms as usual):

$$< f \mid i\widehat{p} g >= \int \overline{f(x)} \partial_x g(x) dx = - \int \partial_x \overline{f(x)} g(x) dx =< \partial_x f \mid g > \ .$$

Actually, this calculation shows that the operator $\widehat{p}$ is also self adjoint.

Now for the quantum anologue of $(x - ip)(x + ip)$, which is $a^* a$. The calculation is different because *operators do not commute.* In fact:

$$x\widehat{p} - \widehat{p}x \overset{\text{def}}{=} [x, \widehat{p}] \equiv i \ . \tag{3}$$

This is so basic that you will eventually just know it, but it can be checked by looking at the action of the "commutator" $[x, \widehat{p}]$ on a function, f:

$$x\widehat{p} f(x) - \widehat{p} x f(x) = \frac{1}{i} x \partial_x f - \frac{1}{i} \partial_x (xf) = \frac{1}{i}(-f(x)) = if(x) \ .$$

With this we can do the first fundamental calculation:

$$a^* a = (x - i\widehat{p})(x + i\widehat{p}) = x^2 + \widehat{p}^2 + i(x\widehat{p} - \widehat{p}x) = x^2 + \widehat{p}^2 - 1 \ .$$

This gives an expression for the harmonic oscillator hamiltonian (1):

$$H = \frac{1}{2}(x^2 + \widehat{p}^2) = \frac{1}{2} a^* a + \frac{1}{2} \ . \tag{4}$$

The difference between the classical calculation (2) and the quantum counterpart (4) is the (non)commutation relation (3) which is one of the most basic facts of quantum mechanics.

The expression (4) is the basis for a complete algebraic treatment of the harmonic oscilator problem. A first illustration of this is the demonstration that if λ is an eigenvalue of H then $\lambda \geq \frac{1}{2}$. The same calculation shows (if you haven't seen this already in linear algebra) that because H is self adjoint, λ must be real. So, suppose that $a^* a \phi = \mu \phi$, and, after a possible normalization, that $< \phi \mid \phi >= 1$. To see that $\mu \geq 0$, do the calculation

$$\mu =< \phi \mid \mu \phi >=< \phi \mid a^* a \phi >=< a\phi \mid a\phi >= \|a\phi\|^2 \geq 0$$

as claimed. The fact used here was that, if a^* is the adjoint of a, then a is the adjoint of a^*.

The operator a is called the lowering operator [1] because it lowers the eigenvalue by one. That is, if $a^*a\phi = \mu\phi$ and $\psi = a\phi$ then $a^*a\psi = (\mu - 2)\psi$. If we use the definition of the harmonic oscillator hamiltonian in terms of a, we see that a lowers the eigenvalue by one. The basis for this is the fundamental calculation

$$[a^*, a] = -2 \ , \tag{5}$$

which is equivalent to the $x, \widehat{p}$ commuation relation (3), given the definition $a = x + i\widehat{p}$. For many purposes, (5) is the more useful form of this fact. Now, the final(!) fundamental calculation is:

$$\begin{aligned}
a^*a\psi &= (a^*a)a\phi \\
&= aa^*a\phi + (a^*a - aa^*)a\phi \\
&= a\mu\phi - 2a\phi \qquad \text{(This is (5) in action.)} \\
&= (\mu - 2)a\phi \\
&= (\mu - 2)\psi \ ,
\end{aligned}$$

as claimed.

These facts allow us to find the eigenvalues and eigenfunctions for the harmonic oscillator in closed form. To start, suppose that ψ is any eigenfunction of H with eigenvalue λ. If we apply the lowering operator to ψ, we either get zero or another eigenfunction with eigenvalue $\lambda - 1$. This lowering process cannot continue indefinitely because every eigenvalue of H is positive. For that reason, we eventually find a ϕ_0 with $a\phi_0 = 0$. This ϕ_0 is the "ground state" of H, the eigenfunction with smallest eigenvalue. Actually, in the abstract setup with only the definition (4) and the commutation relation (5) we are not sure "the" ground state is unique. However, for our particular $a = x + i\widehat{p}$, we have

$$a\phi_0 = 0 \implies (x + \partial_x)\phi_0(x) = 0 \implies \phi_0(x) = \mathit{const} \cdot e^{-x^2/2} \ .$$

If we normalize so that $< \phi_0 \mid \phi_0 >= 1$, we get the ground state eigenfunction for the simple harmonic oscilator:

$$\phi_0(x) = \pi^{-1/4} e^{-x^2/2} \ . \tag{6}$$

The ground state energy is the eigenvalue is $e_0 = 1/2$, which follows from $a\phi_0 = 0$ and $H = \frac{1}{2}a^*a + \frac{1}{2}$.

The eigenfunctions corresponding to higher energies are called excited states because in a physical system they would find a way to give off their extra energy and go to the ground state. All the excited states can be constructed by applying the "raising operator", a^* repeatedly to ϕ_0. First, it is easy to check using the commutation relations that if $H\phi = \lambda\phi$ then $Ha^*\phi = (\lambda + 1)a^*\phi$. Moreover, exercise 3 below shows that $a^*\phi$ cannot be zero. In this way we construct a family of energy states $\phi_1 = \mathit{const} \cdot a^*\phi_0$, $\phi_2 = \mathit{const} \cdot a^*\phi_1$ and so

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[1] In quantum field theory, a is called the anihilation operator because is reduces the number of particles by one. This interpretation is explained later.

on. Exercise 3 below explains how to compute the normalization constants so that $< \phi_n \mid \phi_n >= 1$. In our case with $a^* = x - \partial_x$ and 6), we have successively, ignoring normalizing constants:

$$\begin{aligned}
\phi_1(x) &= xe^{-x^2/2} , \\
\phi_2(x) &= \left(2x^2 - 1\right) e^{-x^2/2} , \\
\phi_3(x) &= \left(2x^3 - 3x\right) e^{-x^2/2} , \\
&\cdots \\
\phi_n(x) &= H_n(x)e^{-x^2/2} .
\end{aligned}$$

The corresponding energy levels are:

$$H\phi_n = \left(n + \frac{1}{2}\right) \phi_n . \tag{7}$$

Here $H_n(x)$ is a polynomial of degree n. These are often called Hermite polynomials.

Another common definition of hermite polynomials gives slightly different polynomials, here called $\tilde{H}_n$. The $\tilde{H}_n$ are defined by the properties that $\tilde{H}_n$ is a polynomial of degree n and the orthogonality conditions,

$$\int \tilde{H}_n(x)\tilde{H}_m(x)e^{-x^2/2}dx = 0 \qquad \text{for } n \neq m,$$

are satisfiled. The first disagreement is H_2 which we say is $x^2 - 2$ while $\tilde{H}_2 = x^2 - 1$. For H_3, the choices are $2x^3 - 3x$ and $x^3 - 3x$. The orthogonality relation for our Hermite polynomials is that

$$0 = \int \phi_n(x)\phi_m(x)dx = \int H_n(x)H_m(x)e^{-x^2}dx \qquad \text{for } n \neq m.$$

Clearly $\tilde{H}_n(x) = H_n(x/\sqrt{2})$.

Perhaps the most striking feature of the energy levels is that the spacing between them is uniform. To go from level n to level $n+1$ you have to add exactly one "quantum" of energy. We often speak of the n^{th} excited state as having n quanta of energy. In quantum field theory, these quanta are associated with elementary particles. The level n would represent the number of particles occupying a particular oscillator mode.

Looking back, you can see that the solution of this eigenvalue problem was almost entirely algebraic, resting only on the commutation relation and the definition of the Hamiltonian. If you add the additional axiom that the ground state is simple, the entire structure follows. You can see that we had to prove that the ground state was simple in our case by using the first order ODE $(x + \partial_x)\phi_0 = 0$. The ϕ_n are a complete set (they span the Hilbert space) because[2] they are all the eigenfunctions of the self adjoint operator a^*a.

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[2] This course, and this discussion in particular, are not absolutely rigorous mathematically. Someone who had taken a course on Hilbert space that included unbounded self adjoint operators and spectral theory could easily complete the proof at this point.

2 Physics and scales

We just finished the mathematics of the simple harmonic oscillator. The only physics left out concerns units. Suppose a particle with mass m moves in one dimension subject to a linear restoring force $F = -kx$. The the kinetic energy is $\widehat{p}^2/2m$, the potential energy is $kx^2/2$, and the eigenvalue problem is

$$e\phi = H\phi = \left(\frac{1}{2m}\widehat{p}^2 + kx^2/2\right)\phi = \left(\frac{k}{2}x^2 - \frac{\hbar^2}{2m}\partial_x^2\right)\phi \ . \tag{8}$$

This differs from the "cannonical" operator (1) only by the dimensional coefficients $\hbar^2/2m$ and $k/2$.

Nondimensionalization is a process that at the same time identifies important scales, here length scale and energy scale, and puts the problem in a simple cannonical form. The technique is to measure problem variables, not in dimensional terms, but in multiples of a single well chosen dimensional scale. For example, we let L be a "length scale" with units of length and write x as a multiple of L,

$$x = L \cdot \xi \ , \tag{9}$$

where ξ is our new "nondimensional" measure of length. Substituting (9) into (8) gives

$$H\phi = \left(\frac{L^2k}{2}\xi^2 - \frac{\hbar^2}{2L^2m}\partial_\xi^2\right)\phi \ .$$

We get the cannonical problem if the coefficients of ξ^2 and ∂_ξ^2 are equal:

$$L^2k = \frac{\hbar^2}{L^2m} \ ,$$

which gives the famous formula

$$L = \left(\frac{\hbar^2}{mk}\right)^{1/4} \ . \tag{10}$$

In terms of this length, we can write the eigenvalue problem as

$$e\phi = e_0\lambda H_c\psi \ , \tag{11}$$

where

$$e_0 = \hbar\omega \quad , \quad \omega = \sqrt{\frac{k}{m}} \ , \tag{12}$$

and the cannonical harmonic oscilator hamiltonian is

$$H_c = \frac{1}{2}\left(\xi^2 - \partial_\xi^2\right) \ .$$

The formula (12) is line (10) in that it expresses the dimensional variable e as a dimensional constant e_0 times a dimensionless factor λ.

Since the eigenvalues of H_c are $\lambda_n = n + \frac{1}{2}$, equation (11) tells us what the energy levels for a quantum oscillator are, in terms of the classical oscilator frequency, ω. The lowest level is $\hbar\omega/2$. The other energy levels differ from this by adding an integer number of quanta of energy, each quantum having energy $e = \hbar\omega$. Max Planck began the development of quantum mechanics with the suggestion that a harmonic oscillator cannot have an arbitrary amount of energy, but that the energy must be an integer multiple of $\hbar\omega$. He did not suggest a physical mechanism for this restriction but he did show that if the parameter $\hbar$ is chosen properly then it is possible to fit experimentally observed black body radiation curves. As far as we know, there is no way to tell the difference between $e_n = n\hbar\omega$ (Planck's formula) and $e_n = (n + \frac{1}{2})\hbar\omega$ (our harmonic oscillator formula). The physical meaning of the "zero point energy" $\hbar\omega/2$ for electromagnetic vibration modes is unclear. However, the zero point energy for vibrations in a crystal lattice can be measured and has important physical implications.

There is a less formal argument physicists often use to justify the basic length and energy scales (10) and (12). We just suppose the ground state wave function ϕ_0 is basically a blob whose size is about L. In terms of L we can estimate the kinetic and potential energy. We then choose L to minimize the total energy. The potential energy is $p^2/2m$ and $p \sim \hbar k$ with $k \sim 1/L$, so kinetic energy is $\sim \hbar^2/mL^2$. The kinetic energy increases as L decreases because a more confined wave function needs to have larger gradients. The potential energy is $\sim kL^2$. This decreases with decreasing L because it takes energy to pull the particle away from its equilibrium point. The total energy is $E \sim \hbar^2/mL^2 + kL^2$. Minimizing this with respect to L gives the length scale (10) and energy scale (12).

3 Stastical mechanics for one oscillator

3.1 Introduction to statistical mechanics

Statistical mechanics is the study of large interacting systems as though they were random. The randomness arises from the chaos of complex behavior of most large systems. The main modeling assumption we use is the Gibbs–Boltzmann postulate that

$$\text{Prob[state]} = \frac{1}{Z} e^{-E/kT} \ , \tag{13}$$

where E is the energy of the state. Here T is the temperature and k is a physical constant, Boltzmann's constant, having units of energy per unit temperature (e.g. $k = .861 \cdot 10^{-4} ev/\text{deg}K$). Note how (13) depends on the energy, E, and temperature. States with more energy are always less likely than states with less energy. This weighting of low energy states is stronger at low temperature than at high temperature. The normalization factor Z, which is called the "partition function" ensures that the right side of (13) is a probability (or probability density). In specific problems, once we have calculated Z, we are often able to compute the quantities of physical interest easily.

For a classical system, the state is given by, say, specifying the positions and momenta of all the particles in the system. In quantum mechanics, the state is a wave function. We use energy eigenfunctions because they have a definite value of E to use in (13).

It is remarkable that a generic hypothesis of randomness can be refined to a probability distribution as specific as (13). The basic argument is that we have a grand completely isolated system that consists of our system weakly coupled to a much larger completely chaotic system called the "heat bath". Our system coupled to the heat bath so weakly that it basically acts as it would in complete isolation. However, the coupling allows it to exchange energy with the heat bath in a way that the total energy is conserved. The formula (13) arises from the fact that the volume in phase space of the heat bath depends exponentially on the energy of the heat bath, becoming larger with increasing energy. Since total energy is conserved, this makes low high energy states for the heat bath, and thus low energy states of our little system, more likely. If you really want to understand this cryptic argument, look in the Feynmann Lectures on Physics Volume 1 chapter 40, or chapter 4 of Thermal Physics by Charles Kittel. I should add that the argument sketched here and presented in detail in the references argues for the classical Gibbs-Boltzmann distribution. I do not know an argument, even a heuristic one, that directly gives the quantum Gibbs-Boltzmann distribution. The study of spectral properties of quantum systems for which the classical counterpart is chaotic is called "quantum chaos".

It is often convenient to use the "inverse temperature", $\beta = 1/kT$ as the parameter. If ξ is a typical state of the system and $E(\xi)$ the corresponding energy, the requirement that

$$1 = \frac{1}{Z}\sum_{\xi} e^{-\beta E(\xi)}$$

leads to

$$Z(\beta) = \sum_{\xi} e^{-\beta E(\xi)} \; .$$

The expected energy, then, is

$$\begin{aligned}\langle E\rangle &= \sum_{\xi} E(\xi)\mathrm{Prob}(\xi) \\ &= \frac{1}{Z}\sum_{\xi} E(\xi) e^{-\beta E(\xi)} \; .\end{aligned}$$

The trick is to notice that

$$\frac{\partial Z}{\partial \beta} = -\sum_{\xi} E(\xi) e^{-\beta E(\xi)} \; ,$$

so

$$\langle E \rangle = -\partial_\beta \log\left(Z(\beta)\right) \ . \tag{14}$$

As we said above, the physical quantity $\langle E \rangle$ is easily calculated from the partition function.

An example of this formalism in action is the treatment of a single classical harmonic oscillator moving in one dimension. The state is given by the position and momentum: $\xi = (x, p)$. The probability density is given by the Gibbs-Boltzmann formula

$$f(x,p) = \frac{1}{Z} e^{-\beta\left(kx^2/2 + p^2/2m\right)} \ .$$

First we calulate the partition function function:

$$\begin{aligned} Z &= \int\int e^{-\beta\left(kx^2/2+p^2/2m\right)} dx dp \\ &= \int e^{-\beta k x^2/2} dx \cdot \int e^{-\beta p^2/2m} dp \\ &= \sqrt{\frac{2\pi}{\beta k}} \cdot \sqrt{\frac{2\pi m}{\beta}} \\ &= 2\pi \sqrt{\frac{m}{k}} \frac{1}{\beta} \ . \end{aligned}$$

Then $\log(Z) = \log(2\pi\sqrt{\frac{m}{k}}) - \log(\beta)$, so

$$\langle E \rangle = -\partial_\beta \left(const - \log(\beta)\right) = \frac{1}{\beta} = kT \ .$$

This is the famous result that an oscillator at temperature T has thermal energy kT, independent of the physical parameters of the oscillator k and m. If there were n oscillators, the total mean thermal energy would be nkT, one unit of thermal energy per mode.

3.2 A single thermal quantum oscilator.

One feature of the energy scale (12) is that the amount of energy needed to excite an oscillator increases with the classical oscillator frequency. Thus, a system at temperature T or might not have enough energy to excite an oscillator of frequency ω. In particular, if ω is very large, then the oscillator is unlikely to be excited. Now consider the electromagnetic vibration modes inside a perfectly conducting and closed metal can. It is natural to suppose that these modes are independent oscillators each weakly coupled to the walls of the can but coupled just strongly enough so that thermal energy in the walls can excite the modes. According to classical ideas above, there would be "equipartition" of energy: each mode would have the same kT of energy. Since there are infinitely many modes, equipartition implies an infinite total energy. Even without this infinite energy paradox, it is possible to measure the energy spectrum of thermally excited electromagnetic radiation (black body radiation) inside a can, and above a certain frequency modes stop being excited. This section discusses how the Gibbs Boltzmann thermodynamic formalism leads to this Planck high frequency cutoff for a single oscilator. The following section applies this to systems with many modes like the inside of a can.

The theory of quantum equilibrium statistical mechanics uses the energy states ϕ_n and energies e_n. The Gibbs Boltzmann hypothesis (13) for this system is that the probability for the system to be in state ϕ_n is

$$\Pr\left(\text{state } n\right) = \frac{1}{Z} e^{-e_n/kT} \; . \tag{15}$$

The partition function, Z, is determined by the requirement that the sum of all probabilities should equal one:

$$Z = Z(T) = \sum_n e^{-e_n/kT} \; , \tag{16}$$

where the sum is over all states of the system.

I emphasize that these are probabilities, not quantum amplitudes. For example, suppose we want to know the probability that $0 < x < 1$. We compute this by summing over all possible states and then computing the probability given that the system is in that state:

$$\Pr\left(0 < x < 1\right) = \frac{1}{Z} \sum_n \int_0^1 \left|\phi_n^2(x)\right| dx \; .$$

Observe how the Gibbs expression (15) depends on the temperature. For any temperature, the probability of a given state decreases with temperature. At lower temperatures, low energy states are more strongly preferred than at higher temperatures. Of course, kT must have units of energy so that the exponent will be dimensionless. Essentially, Boltzmann's constant is a conversion between units of temperatore, say degrees Kelvin, to units of energy, say, electron volts.

As for the classical oscilator, the thermal energy in a quantum oscilator is the expected energy in the Gibbs state:

$$\langle E \rangle = \sum_n E_n \Pr\left(\text{energy level n}\right) = \frac{1}{Z} \sum_n E_n e^{-\beta E_n} = -\partial_\beta \log(Z(\beta)) \; .$$

The calculation is generally done not for the energy, but for what might be called the excitation energy, $\epsilon = E - \hbar\omega/2$. Subtracting the zero point energy simplifies the computation a little. If you really want $\langle E \rangle$, you can add back the zero point energy at the end. Anyway, with $\epsilon_n = n\hbar\omega$, we calculate

$$Z = \sum_{n=0}^{\infty} e^{-\beta n \hbar\omega} = \sum_{n=0}^{\infty} \alpha^n = \frac{1}{1-\alpha} \quad , \qquad \text{where } \alpha = e^{-\beta\hbar\omega}.$$

From this,

$$\langle \epsilon \rangle = -\partial_\beta \log \frac{1}{1 - e^{-\beta\hbar\omega}} == \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} \; . \tag{17}$$

This formula has the features we expect by now. For low temperature, the energy is essentially the ground state energy $\hbar\omega/2$. For high temperature, the energy is roughly proportional to the temperature, agreeing with the classical formula. The transition from quantum freezing to classical kT equipartition depends on the relation between the thermal energy, kT, and the oscilator energy $\hbar\omega$. In discussing quantum systems at a certain temperature, people often measure the excitation energy ($\hbar\omega$ in the present case) in multiples of the thermal energy, kT. If an oscilator energy is several kT, it is essentially "frozen" in it's ground state. If the excitation energy is much less than kT, it is essentially classical and holds kT energy.

4 Systems of oscillators

The dynamic electromagnetic field inside a cavity and the vibrations of a block of metal are two examples of linear dynsmical systems. In general, we understand the dynamics of linear systems using eigenvalues and eigenvectors. Classically, this diagonalization represents the system as a collection of independent oscilators. The same is true quantum mechanically, as we explain below. The quantum thermal energy in a linear system is the sum of the energies in each mode, with each mode treated as above. For example, we understand black body ratiation in a cavity by finding the classical modes and applying Einstein's formula (17) to each. The conclusion is essentially that modes with $\hbar\omega > kT$ have kT thermal energy while modes with $\hbar\omega < kT$ are frozen.

Einstein and Debye used this freezing to explain the specific heat of metals, assuming that the atoms are arranged in a lattice connected by linear springs. Experimentally, one can see that the specific heat decreases as the temperature decreases, indicating that a cold metal is less able to absorb energy. The explination is that at low temperatures, few modes can be excited. Debye's version of this argument gives reasonable agreement with some experiments.

4.1 Independent systems, the classical and quantum view

This section is a belaboring of the obvious fact that the energy of two independent systems is the sum of the individual energies. First we give the definition; two systems are independent if the total energy (hamiltonian function for classical systems, hamiltonian operator for quantum systems) is a sum of individual energies. Then we show taht the thermal energy of the total system in the Gibbs Boltzmann distribution is the sum of the thermal energies of the somponent systems. Presumably there is a sense in which Gibbs Boltzmann is the uniqe distribution with this property.

I want to treat a system of interacting particles of various masses. Suppose there are k particles and that particle j has mass m_j, position $x_j \in R^3$, and momentum $p_j \in R^3$. The "configuration" of the systemis given by a vector $x \in R^{3k}$ made of all the positions, x_j. The first three components of x are the components of x_1, and so on. It will be convenient to use a diagonal "mass matrix", m, whose entries are the masses of the particles, each mass being repeated three times. In this notation, the kinetic energy is

$$\frac{1}{2}\left(p, m^{-1}p\right) = \frac{1}{2}\sum_{l=1}^{3k} m_l^{-1}p_l^2 .$$

I use round braces $(\cdot,\cdot)$ to represent inner product in a finite dimensional space that is not the quantum mechanical $\langle\cdot\mid\cdot\rangle$. The total energy including potential energy is

$$H(x,p) = \frac{1}{2}\left(p, m^{-1}p\right) + V(x) \ ,$$

and the force is $-\bigtriangledown V$.

If we have two systems $(x^{(1)}, p^{(1)}, m^{(1)}, V^{(1)}(x^{(1)}))$, and $(x^{(2)}, p^{(2)}, m^{(2)}, V^{(2)}(x(2)))$, we can combine them to form a single system, $x = (x^{(1)}, x^{(2)})$, $p = (p^{(1)}, p^{(2)})$, $m = \text{diag}(m^{(1)}, m^{(2)})$, and, most importantly, $H(x,p) = H^{(1)}(x^{(1)}, p^{(1)}) + H^{(2)}(x^{(2)}, p^{(2)})$. The forces in the $x^{(1)}$ system are independent of $x^{(2)}$ and $p^{(2)}$ because $\partial_{x^{(1)}}V(x) = \partial_{x^{(1)}}V^{(1)}(x^{(1)})$.

The point of this subsection is to verify that the thermal energies in the Gibbs Boltzmann distribution also add. In the classical case, the partition function is a product:

$$\begin{aligned}
Z &= \int\int e^{-\beta H(x,p)}dxdp \\
&= \int\int\int\int \exp\left(-\beta\left(H^{(1)}(x^{(1)},p^{(1)}) + H^{(2)}(x^{(2)},p^{(2)})\right)\right)dx^{(1)}dp^{(1)}dx^{(2)}dp^{(2)} \\
&= \int\int e^{-\beta H^{(1)}(x^{(1)},p^{(1)})}dx^{(1)}dp^{(1)} \cdot \int\int e^{-\beta H^{(2)}(x^{(2)},p^{(2)})}dx^{(2)}dp^{(2)} \\
&= Z^{(1)} \cdot Z^{(2)}
\end{aligned}$$

Therefore,

$$\begin{aligned}
\langle E\rangle &= -\partial_\beta \log(Z(\beta)) \\
&= -\partial_\beta\left(\log(Z^{(1)}(\beta)) + \log(Z^{(2)}(\beta))\right) \\
&= \left\langle E^{(1)}\right\rangle + \left\langle E^{(2)}\right\rangle \ ,
\end{aligned}$$

as claimed.

The quantum analogue is essentially the separation of variables construction of eigenfunctions. We have a hamiltonian operator,

$$H = \frac{1}{2}\left(\widehat{p}, m^{-1}\widehat{p}\right) + V((x^{(1)}, (x^{(2)})) \ ,$$

that is a sum $H = H^{(1)}(x^{(1)}) + H^{(2)}(x^{(1)})$ in the analogous way. Let $\phi_j^{(1)}(x^{(1)})$ and $\phi_k^{(1)}(x^{(2)})$ be the energy states for $H^{(1)}(x^{(1)})$ and $H^{(2)}(x^{(2)})$ respectively, then we may form product eigenfunctions for H of the form

$$\psi_{jk}(x) = \phi_j^{(1)}(x^{(1)}) \cdot \phi_j^{(2)}(x^{(2)}) \ ,$$

which have eigenvalues $E_{jk} = E_j^{(1)} + E_k^{(2)}$, as you can check. If the $\phi_1^{(1)}$ and $\phi_k^{(2)}$ are complete, the products ψ_{jk} also form a complete set. You could say "duh" here too: additive energy on the operator level implies additive energy on the eigenvalue level. But remember that not every classical property holds in quantum mechanics, and given the differences in formalism (ODE vs. PDE), it is surprising how much they have in common.

In fact, the possibility of forming products $\phi_j^{(1)}(x^{(1)}) \cdot \phi_j^{(2)}(x^{(2)})$ depends on $x^{(1)}$ and $x^{(2)}$ representing distinguishable systems. Otherwise Bose or Fermi symmetry would forbid simple products. This is a new quantum phenomenon that is as important as energy quantization and the uncertainty principle: *identical particles interact even when there is no force between them.* Only distinguishable particles can be truly independent of each other.

For distinguishable systems, the partition function again is a product and therefore the thermal energy is again additive. This is because

$$\begin{aligned} Z &= \sum_{jk} e^{-\beta E_{jk}} \\ &= \sum_{jk} e^{-\beta\left(E_j^{(1)}+E_k^{(2)}\right)} \\ &= \sum_j e^{-\beta E_j^{(1)}} \cdot \sum_k e^{-\beta E_k^{(2)}} \\ &= Z^{(1)} \cdot Z^{(2)} \ . \end{aligned}$$

4.2 Coupled linear systems and oscillator modes.

In classical mechanics, any stable dynamical system with linear forces and no friction is equivalent to a collection of independent linear oscillators. This is also true in quantum mechanics. We now review the classical construction, normal modes, and show that is carries over directly to the quantum case. So far, this has been taken for granted. Let $x = (x_1, \ldots, x_n)$ be a vector representing all the position coordinates of all the particles in a system. The kinetic energy is

$$\mathrm{KE} = \sum_{k=1}^{n} p_k^2/2m_k = \frac{1}{2}\left(p, m^{-1}p\right) \ ,$$

where m is the diagonal matrix with mass m_k in the (k,k) position. If the force is linear, the potential energy is quadratic:

$$\mathrm{PE} = (x, Qx) \ .$$

It will be easy to see, once we have found modes, that the dynamical system is stable (trajectories to not go to infinity as $t \to \infty$) if and only if Q is positive definite. The classical equations of motion may be written in the form

$$m\ddot{x} = -Qx \ , \tag{18}$$

A normal vibrational mode is a generalized eigenvector, v, so that

$$\gamma m v = Q v \ .$$

It is easy to verify the following facts in our case, where m and Q are symmetric and positive definite[3]: (i) There is a complete family of modes $v_1, \ldots, v_n$ and corresponding positive generalized eigenvalues $\gamma_1, \ldots, \gamma_n$. (ii) The v_k can be chosen to be orthonormal with respect to m: $(v_j, m v_k) = \delta_{jk}$, and orthogonal with respect to Q: $(v_j, Q v_k) = 0$ if $j \neq k$, $(v_k, Q v_k) = \gamma_k$. If we write the coordinates in terms of the normal modes:

$$x(t) = \sum_k \xi_k(t) v_k \ ,$$

substitute into the equations of motion, and take the inner product with v_j on both sides, we get

$$\ddot{\xi}_j = -\gamma \ddot{\xi}_j \ .$$

In this way the system is equivalent to a system of independent oscilators, and the generalized eigenvalues are the squares of the frequencies.

This would have been slightly simpler if we had assumed that all the masses were the same. The we would have had an ordinary eigenvalue problem rather than a generalized eigenvalue problem. That assumption would have been fine for simple crystals but not, for example, for salt (sodium chloride) crystals with more than one kind of atom.

The corresponding quantum system is the Schrödinger eigenvalue problem:

$$E\psi = -\hbar^2 \sum_k \frac{1}{2m_k} \partial_{x_k}^2 \psi + \frac{1}{2} Q \psi \ . \qquad (19)$$

The classical normal modes allow us to transform the operator into a sum of independent one variable operators.

5 Exercises

1. Show that the commutator of any two self adjoint operators is skew adjoint. That is, if $A^* = A$ and $B^* = B$ and $C = [A, B]$ then $C^* = -C$. Note that $[x, \widehat{p}] = i$ is consistent with this.

2. Show that there is no alologue of the commutation relation (3) for finite dimensional matrices. If A and B with are matrices, then it is not possible that $[A, B] = \mathit{const} \cdot I$. Hint: use the trace.

3. Suppose $a^* a \phi = \lambda \phi$ and $\psi = a^* \phi$ and $\|\phi\|^2 = < \phi \mid \phi > = 1$. Using only the commutation relations (not the definition of a in terms of x and $\widehat{p}$) compute $< \psi \mid \psi >$. Note, in particular, that we cannot have $\psi = 0$ unless $\phi = 0$, so there no limit to how high we can raise the energy.

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[3] One way to do this is to reduce this to the ordinary eigenvalue problem for the symmetric positive definite matrix $\tilde{Q} = m^{-1/2} Q m^{-1/2}$.

4. Show that the length scale formula (10) indeed has units of length. Show that the energy scale formula (12) has units of energy.

5. The classical factorization,

$$kx^2 - p^2/m = \left(\sqrt{k}x - i\frac{p}{\sqrt{m}}\right)\left(\sqrt{k}x + i\frac{p}{\sqrt{m}}\right) ,$$

has a quantum anologue involving the operator

$$a_\omega = \sqrt{k}x + i\frac{\widehat{p}}{\sqrt{m}} .$$

Check the commutation relation $[a_\omega, a_\omega^*] = 2\omega$ and use it to recover the energy spectrum of the harmonic oscillator.

6. Do the computation leading up to (**??**). Also verify that the thermal mean kinetic energy $\langle KE\rangle = \left\langle p^2/2m\right\rangle$ and potential energy are equal. Find a simple abstract proof of this by nondimensionalizing.

7. Verify that the normal mode variables ξ_j transform the Schrödinger equation into an equation for a collection of independent oscilators. In general, show that "quantization commutes with linear changes of variable". On the other hand, quantization does not commute with nonlinear changes of variables.