Quantum Statistical Mechanics and Condensed Matter Physics

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Contents

1	Rev	iew of quantum mechanics	1
	1.1	Basic concepts of quantum mechanics	1
	1.2	Spin $1/2$	4
	1.3	Heisenberg, Ising and the almighty Kron	12
	1.4	The quantum harmonic oscillator	18
	1.5	Coherent states	22
	1.6	The Schrödinger Lagrangian	27
2	Den	sity matrix theory	33
	2.1	Trace and partial trace	33
	2.2	The density matrix	38
	2.3	Reduced density matrices and entanglement	44
	2.4	Entropies and mutual information	50
3	The	Gibbs formalism	58
	3.1	Introduction	58
	3.2	The Gibbs state minimizes the free energy	67
	3.3	The quantum harmonic oscillator	71
	3.4	Spin $1/2$ paramagnetism and non-interacting systems	78
	3.5	The Heat capacity	86

Chapter 1

Review of quantum mechanics

1.1 Basic concepts of quantum mechanics

Quantum mechanics is all about *operators* and *kets*. When an operator acts on a ket it produces a new ket. For instance, Schrödinger's equation reads:¹

$$\partial_t |\psi(t)\rangle = -iH|\psi(t)\rangle \tag{1.1}$$

If we discretize the time derivative as a finite difference with time step Δt , then we may write this equation approximately as

$$|\psi(t + \Delta t)\rangle = (1 - i\Delta tH)|\psi(t)\rangle \tag{1.2}$$

When the operator $(1 - i\Delta tH)$ acts on the state of the system at time t, it evolves the system to time $t + \Delta t$. This defines the role of the Hamiltonian in quantum mechanics as being that operator which propagates a system through time. We say H is the generator of time evolutions.

The state $|\psi\rangle$ is usually expressed in terms of a set of basis vectors $|i\rangle$. These vectors are always chosen so as to be orthonormal:

$$\langle i|j\rangle = \delta_{i,j} \tag{1.3}$$

Orthonormality of any set of basis vectors always implies the *completeness relation*:

$$1 = \sum_{i} |i\rangle\langle i| \tag{1.4}$$

In this formula 1 is actually the identity operator. But since the identity operator satisfies all properties of the number one, we use the same symbol for both (that's how cool people do it).

¹In this course we set $\hbar = 1$.

We may use completeness to decompose any state $|\psi\rangle$ into a linear combination of basis vectors. To do that we insert 1 in a convenient place:

$$|\psi\rangle = 1|\psi\rangle = \sum_{i} |i\rangle\langle i|\psi\rangle = \sum_{i} \psi_{i}|i\rangle$$
(1.5)

where

$$\psi_i = \langle i | \psi \rangle \tag{1.6}$$

is a complex number. The normalization condition $\langle \psi | \psi \rangle = 1$ implies, using the orthogonality (1.3) that

$$\langle \psi | \psi \rangle = \sum_{i} |\psi_i|^2 = 1 \tag{1.7}$$

A particularly important set of basis vectors is the position basis $|x\rangle$. In this case we write Eq. (1.6) a little differently, as

$$\psi(x) = \langle x | \psi \rangle \tag{1.8}$$

We usually call $\psi(x)$ the wave-function, but it is simply the component of the state $|\psi\rangle$ in the basis element $|x\rangle$.²

Back to Eq. (1.1), we now multiply it by $\langle i |$ on the left of both sides and again insert a convenient 1:

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle i|\psi\rangle = -i\langle i|H(1)|\psi\rangle = -i\sum_{j}\langle i|H|j\rangle\langle j|\psi\rangle$$

We then define the matrix elements of H as

$$H_{i,j} = \langle i|H|j\rangle \tag{1.9}$$

This allows us to write Schödinger's equation as a linear vector equation

$$\frac{\mathrm{d}}{\mathrm{d}t} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \vdots \end{pmatrix} = -i \begin{pmatrix} H_{1,1} & H_{1,2} & \dots \\ H_{2,1} & H_{2,2} & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \\ \vdots \end{pmatrix}$$
(1.10)

This is the same as (1.1), but written in terms of components in a specific basis. Since the basis is not unique, we prefer to use Eq. (1.1) which is more general.

A particularly important basis set is that of the eigenvectors of H. They are defined by the equation

$$H|n\rangle = E_n|n\rangle \tag{1.11}$$

$$\langle x|x'\rangle = \delta(x-x'), \qquad 1 = \int \mathrm{d}x \; |x\rangle\langle x|$$

 $^{^2{\}rm This}$ basis is a bit different in that the x are allowed to vary continuously. Thus, orthonormality and completeness now become

where E_n are the eigen-energies of the system. In this basis the Hamiltonian is diagonal:

$$\langle n|H|m\rangle = \delta_{n,m} E_n \tag{1.12}$$

We may also use completeness twice to write

$$H = (1)H(1) = \sum_{n,m} |n\rangle \langle n|H|m\rangle \langle m| = \sum_{n,m} |n\rangle \delta_{n,m} E_n \langle m|$$

Thus, we see that in this basis the Hamiltonian becomes

$$H = \sum_{n} E_n |n\rangle \langle n| \tag{1.13}$$

Returning now to Eq. (1.10) we may choose as a basis set the energy eigenkets $|n\rangle$. Since *H* is diagonal in this basis, the equations become completely decoupled:

$$\frac{\mathrm{d}\psi_n}{\mathrm{d}t} = -iE_n\psi_n \qquad \rightarrow \qquad \psi_n(t) = c_n e^{-iE_nt} \tag{1.14}$$

where $c_n = \langle n | \psi(0) \rangle$ is a constant determined from the initial condition. The complete ket is then reconstructed from Eq. (1.5) as

$$|\psi(t)\rangle = \sum_{n} c_n e^{-iE_n t} |n\rangle \tag{1.15}$$

We can also write the solution of Schrödinger's Eq. (1.1) in a basis-independent way as

$$|\psi(t)\rangle = U(t)|\psi(0)\rangle, \qquad U(t) = e^{-iHt}$$
(1.16)

The operator U is called the time-evolution operator, or the *propagator* (because it propagates the state of the system, from time t = 0 to time t). For small times we may expand the exponential and write $U(t) \simeq 1 - iH\Delta t$, which is the operator in Eq. (1.2). Computing the exponential of an operator, as in e^{-iHt} , can be quite difficult. But if you happen to know all eigenenergies and eigenvectors, then you can always find it, at least in theory. Start with Eq. (1.13) and compute H^2 . You will find that

$$H^2 = \sum_n E_n^2 \; |n\rangle \langle n|$$

This also holds true for higher powers, such as H^3 and etc. It therefore follows that, for any function f(H) that is expressible in a Taylor series, we will have

$$f(H) = \sum_{n} f(E_n) |n\rangle \langle n|$$
(1.17)

Consequently the propagator may always be written as

$$e^{-iHt} = \sum_{n} e^{-iE_{n}t} |n\rangle\langle n|$$
(1.18)

This gives you the propagator as a sum of outer products. Incidentally, we have also shown that the eigenvectors of e^{-iHt} are also $|n\rangle$, with eigenvalues e^{-iE_nt} . Whenever an operator is a function of another, the eigenvectors are the same and the eigenvalues are modified just like the function. For instance, consider the operator $G = (E_0 - H)^{-1}$. This is called a Green's function. The eigenvectors of G are still $|n\rangle$ and the eigenvalues are $(E_0 - E_n)^{-1}$.

Once we have a ket, what do we do with it? We compute expectation values of operators: for an arbitrary operator A, its expectation value in a state $|\psi\rangle$ will be

$$\langle A \rangle = \langle \psi | A | \psi \rangle \tag{1.19}$$

If $|\psi\rangle = |n\rangle$ then $\langle H \rangle = E_n$. Otherwise, we decompose $|\psi\rangle = \sum_n \psi_n |n\rangle$ to get

$$\langle H \rangle = \sum_{n} E_{n} |\psi_{n}|^{2} \tag{1.20}$$

The quantity $|\psi_n|^2$ is the probability of finding the system at $|n\rangle$ given that it is at $|\psi\rangle$. Thus, Eq. (1.20) has the form of a weighted average of the energies with probabilities $|\psi_n|^2$.

For a time-dependent state, $|\psi(t)\rangle = e^{-iHt}|\psi(0)\rangle$. Thus, the expectation value (1.19) becomes

$$\langle A \rangle = \langle \psi(t) | A | \psi(t) \rangle = \langle \psi(0) | e^{iHt} A e^{-iHt} | \psi(0) \rangle$$

This motivates the definition of the Heisenberg picture operator

$$A_H(t) = e^{iHt} A e^{-iHt} \tag{1.21}$$

In the Heisenberg picture the state is fixed at its initial value and it is the operator which evolves with time. The equation governing the time-evolution of the operator is found directly by differentiating (1.21) and reads

$$\frac{\mathrm{d}A_H}{\mathrm{d}t} = i[H, A_H] \tag{1.22}$$

This is called the *Heisenberg equation*. It is an equation for the operator, which admittedly can be a bit abstract. If you want you can convert it to an equation for numbers by taking the average:

$$\frac{\mathrm{d}\langle A\rangle}{\mathrm{d}t} = i\langle [H, A]\rangle \tag{1.23}$$

Here I wrote A instead of A_H since, when we take the average, both coincide.

1.2 Spin 1/2

Spin is angular momentum and must therefore be described by three operators: S_x , S_y and S_z . The orientation of the axes are arbitrary, but you need three of them. The fundamental postulate of angular momentum is that these operators should satisfy the algebra:

$$[S_x, S_y] = iS_z \qquad [S_z, S_x] = iS_y \qquad [S_y, S_z] = iS_x \tag{1.24}$$

If you are ever wondering in the forest and you see 3 operators satisfying these commutation relations then I guarantee you: they are angular momentum operators. You can literally take this as the definition of angular momentum. And every property follows from these simple commutation relations.

In any book on quantum mechanics you learn how to derive all eigenvectors and eigenvalues of the angular momentum operators. What you learn is that the operator $S^2 = S_x^2 + S_y^2 + S_z^2$ will have eigenvalues

eigs
$$(S^2) = S(S+1), \qquad S = \frac{1}{2}, 1, \frac{3}{2}, 2, \dots$$
 (1.25)

We use S to define the spin. So when we say spin 1/2 (like an electron), we mean a system where the eigenvalue of S^2 is $\frac{1}{2}(\frac{1}{2}+1) = \frac{3}{4}$. The other thing we learn is that each operator S_i will have 2S + 1 eigenvalues which go from S to -S in unit steps:

$$eigs(S_i) = S, S - 1, \dots, -S + 1, -S$$
 (1.26)

For spin 1/2 we will therefore have a total of 2S + 1 = 2 states with eigenvalues +1/2 and -1/2. As for the eigenvectors, we usually choose those vectors which diagonalize S_z and then express everything in terms of them. For pedagogical purposes, we will focus in this section on the case of spin 1/2. The case of more general spins will be discussed later.

For spin 1/2 we label the eigenvectors as $|+\rangle$ and $|-\rangle$. They satisfy

$$S_z|+\rangle = \frac{1}{2}|+\rangle, \qquad S_z|-\rangle = -\frac{1}{2}|-\rangle$$

The 1/2's that appear everywhere are annoying, so we like to get rid of them by defining a new set of operators σ_x , σ_y and σ_z , called the **Pauli matrices**, as

$$S_i = \frac{1}{2}\sigma_i \tag{1.27}$$

The algebra of the Pauli matrices is similar to Eq. (1.24), but now there is a factor of 2:

$$[\sigma_x, \sigma_y] = 2i\sigma_z \qquad [\sigma_z, \sigma_x] = 2i\sigma_y \qquad [\sigma_y, \sigma_z] = 2i\sigma_x \tag{1.28}$$

The eigen-equation for σ_z also changes to

$$\sigma_z |+\rangle = |+\rangle, \qquad \sigma_z |-\rangle = -|-\rangle$$
 (1.29)

We can write things even more compactly by defining a variable σ which takes on the values ± 1 :

$$\sigma := \operatorname{eigs}(\sigma_z) = \pm 1 \tag{1.30}$$

$$\sigma_z |\sigma\rangle = \sigma |\sigma\rangle \tag{1.31}$$

We will use this notation throughout the entire text: σ_z is an operator and $\sigma = \pm 1$ is a number representing the eigenvalues of σ_z .

We may write the eigenvectors $|\sigma\rangle$ as two-component vectors

$$|+\rangle = \begin{pmatrix} 1\\0 \end{pmatrix}, \qquad |-\rangle = \begin{pmatrix} 0\\1 \end{pmatrix}$$
 (1.32)

The operators σ_x , σ_y and σ_z , when written in the basis $|\sigma\rangle$, then become

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$
(1.33)

Note that the operator σ_z is diagonal in this basis, as of course is expected. When the operator σ_x acts on $|\sigma\rangle$ it flips the spin:

$$\sigma_x |+\rangle = |-\rangle, \qquad \sigma_x |-\rangle = |+\rangle$$
(1.34)

Something similar happens to $\sigma_y,$ but it leaves out a phase factor:

$$\sigma_y|+\rangle = i|-\rangle, \qquad \sigma_y|-\rangle = -i|+\rangle$$
 (1.35)

Another set of operators that are commonly used are the **spin lowering** and raising operators:

$$\sigma_{+} = \begin{pmatrix} 0 & 1\\ 0 & 0 \end{pmatrix} \quad \text{and} \quad \sigma_{-} = \begin{pmatrix} 0 & 0\\ 0 & 1 \end{pmatrix} \quad (1.36)$$

They are related to $\sigma_{x,y}$ according to

$$\sigma_x = \sigma_+ + \sigma_-$$
 and $\sigma_y = -i(\sigma_+ - \sigma_-)$ (1.37)

or

$$\sigma_{\pm} = \frac{\sigma_x \pm i\sigma_y}{2} \tag{1.38}$$

As their name implies, σ_+ raises the spin value, whereas σ_- lowers it:

$$\sigma_{+}|-\rangle = |+\rangle, \quad \text{and} \quad \sigma_{-}|+\rangle = |-\rangle$$
 (1.39)

If you try to raise a $|+\rangle$ state or lower a $|-\rangle$ state, you get zero:

$$\sigma_{+}|+\rangle = \sigma_{-}|-\rangle = 0 \tag{1.40}$$

Then



Figure 1.1: The most general ket for a spin 1/2 particle can be viewed as a point in a 3-dimensional sphere (know as Bloch's sphere).

General spin 1/2 states

The most general spin state may be written as a *superposition* of the up and down states:

$$|g\rangle = a|+\rangle + b|-\rangle = \begin{pmatrix} a\\b \end{pmatrix}$$
(1.41)

where a and b are complex numbers. Normalization implies that $|a|^2 + |b|^2 = 1$. For this reason, it is convenient to parametrize this state as

$$|g_{\boldsymbol{n}}\rangle = e^{-i\phi/2}\cos\frac{\theta}{2}|+\rangle + e^{i\phi/2}\sin\frac{\theta}{2}|-\rangle = \begin{pmatrix} e^{-i\phi/2}\cos\frac{\theta}{2}\\ e^{i\phi/2}\sin\frac{\theta}{2} \end{pmatrix}$$
(1.42)

I know this sounds weird, but there is actually a cool reason behind it: this state represents a point in a 3-dimensional unit sphere called the **Bloch sphere** (see Fig. 1.1):

$$\boldsymbol{n} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta) \tag{1.43}$$

We can get a glimpse of why this is so if we compute expectation values of the σ operators in the state $|g_n\rangle$. We find:

$$\langle \sigma_x \rangle = \sin \theta \cos \phi, \qquad \langle \sigma_y \rangle = \sin \theta \sin \phi, \qquad \langle \sigma_z \rangle = \cos \theta$$
(1.44)

Thus, the average of σ_{μ} is simply the μ -th component of \boldsymbol{n} . People in quantum information love these ideas. For them $|+\rangle = |0\rangle$ and $|-\rangle = |1\rangle$ are the bits of

a quantum computer. But unlike classical bits, which take on only two values, qubits can take on a continuous set of values given precisely by the vector $|g_n\rangle$. The vector (1.42) is also sometimes called a *spin coherent state*.

In order to have a fuller understanding of the connection between a sphere in 3D and our two-dimensional Hilbert space, we need to think about rotations. If you start at the north pole (0, 0, 1) on a sphere and you want to get to an arbitrary point \boldsymbol{n} as in Eq. (1.43), you need to do two rotations. First you rotate by an angle θ around the y axis and then you rotate by an angle ϕ around the z axis (take a second to imagine this in your head).

In the spin Hilbert space, these rotations are performed by the rotation operators $e^{-i\phi\sigma_z/2}$ and $e^{-i\theta\sigma_y/2}$. Let us try to learn how to deal with them. Consider for now the operator $e^{i\alpha\sigma_z}$. We can find a neat formula for it by noting that $\sigma_z^2 = 1$ (the identity operator). If we then expand the exponential in a Taylor series we get

$$e^{i\alpha\sigma_z} = 1 + i\alpha\sigma_z + \frac{i^2}{2!}\alpha^2\sigma_z^2 + \dots$$

Since $\sigma_z^2 = 1$ the terms in the expansion will be either proportional to σ_z or proportional to 1. We can therefore group terms proportional to the identity and terms proportional to σ_z , which then yields

$$e^{i\alpha\sigma_z} = \cos\alpha + i\sigma_z \sin\alpha \tag{1.45}$$

We showed this formula for σ_z , but it is actually true for any operator that satisfies $A^2 = 1$, since that is all we really used. Now that we have this formula, it is an easy task (which I leave for you to have fun with) to verify that we can obtain the state (1.42) by starting from $|+\rangle$ and then applying the two rotations sequentially:

$$|g_{\boldsymbol{n}}\rangle = e^{-i\phi\sigma_z/2}e^{-i\theta\sigma_y/2}|+\rangle \tag{1.46}$$

Note that the order of the operators is essential since they do not commute.

Another way of understanding the state $|g_n\rangle$ in Eq. (1.42) is to note that it is the eigenstate of the operator $n \cdot \sigma$ with eigenvalue +1. This operator represents the spin component in the direction n. The other eigenstate is

$$|g_{n}'\rangle = \begin{pmatrix} -e^{-i\phi/2}\sin\frac{\theta}{2}\\ e^{i\phi/2}\cos\frac{\theta}{2} \end{pmatrix}$$
(1.47)

and it has eigenvalue -1. That the eigenvalues are ± 1 is, of course, as it must be. After all, the direction of the spin operator is arbitrary. You may also check that $|g_n\rangle$ and $|g'_n\rangle$ are orthogonal. More importantly, these two states are actually the components of the rotation matrix appearing in Eq. (1.46). If you compute the two matrix exponentials you find

$$G := e^{-i\phi\sigma_z/2}e^{-i\theta\sigma_y/2} = \begin{pmatrix} e^{-i\phi/2}\cos\frac{\theta}{2} & -e^{-i\phi/2}\sin\frac{\theta}{2} \\ e^{i\phi/2}\sin\frac{\theta}{2} & e^{i\phi/2}\cos\frac{\theta}{2} \end{pmatrix}$$
(1.48)



Figure 1.2: Illustration of the electronic levels of an atom.

The columns of G are precisely the eigenvectors $|g_n\rangle$ and $|g'_n\rangle$. It then follows that

$$\boldsymbol{n} \cdot \boldsymbol{\sigma} = G \sigma_z G^{\dagger} \tag{1.49}$$

So G is the rotation matrix that takes the spin operator from z to n.

Two-state systems

The framework for spin 1/2 may be conveniently used when studying any system with only two states. In practice, such two-state systems appear often as an approximation to atomic systems. The electronic energy levels of an atom may look something like Fig. 1.2. But in certain applications, the probability of occupying highly excited states is negligible, so we may focus only on the first two states. Then, effectively, the electronic levels may be considered as having only two states, the *ground-state* $|g\rangle$ and the *excited state* $|e\rangle$. If we identify

$$|g\rangle = |-\rangle, \quad \text{and} \quad |e\rangle = |+\rangle \quad (1.50)$$

then we may use the entire framework of spin 1/2 systems to describe any twolevel system (Please note that sometimes people make the correspondence the other way around; it is simply a matter of convenience). The spin lowering and raising operators σ_{\pm} then acquire a simple physical meaning. Since σ_{+} raises the spin, we have $\sigma_{+}|g\rangle = |e\rangle$, so σ_{+} is the operator that *excites* the electron.

Eq. (1.49) can also be used as a very convenient trick to diagonalize arbitrary 2×2 matrices, which do not need to have anything to do with spin or with physics, actually. The convenience is related to the way you write down the eigenvectors. Finding the eigenvalues of a 2×2 matrix is trivial, but the eigenvectors are sometimes clumsy to write down. With this trick, you can relate the eigenvectors with points in the Bloch sphere. Here is how it goes. Let A be a 2×2 matrix. Since it has only four entries, it may be written as

$$A = a_0 + \boldsymbol{a} \cdot \boldsymbol{\sigma} \tag{1.51}$$

for a certain set of four numbers a_0 , a_x , a_y and a_z . Next define a = |a| and n = a/a. That is, write your matrix A as

$$A = a_0 + a(\boldsymbol{n} \cdot \boldsymbol{\sigma}) \tag{1.52}$$

The eigenvalues and eigenvectors of A can now be related to those of $n \cdot \sigma$. First, since the eigenvalues of $n \cdot \sigma$ are ± 1 , the eigenvalues of A will be

$$\lambda_{\pm} = a_0 \pm a \tag{1.53}$$

Moreover, since A is simply the identity plus $\mathbf{n} \cdot \boldsymbol{\sigma}$, both will share the same eigenvectors. These are precisely the vectors $|g_n\rangle$ and $|g'_n\rangle$ in Eqs. (1.42) and (1.47) respectively, but with \mathbf{n} determined as $\mathbf{n} = \mathbf{a}/a$. That is

$$A|g_{\boldsymbol{n}}\rangle = \lambda_{+}|g_{\boldsymbol{n}}\rangle, \quad \text{and} \quad A|g_{\boldsymbol{n}}'\rangle = \lambda_{-}|g_{\boldsymbol{n}}\rangle \quad (1.54)$$

You can also write down the diagonal decomposition of A in matrix form. Namely,

$$A = G \begin{pmatrix} a_0 + a & 0\\ 0 & a_0 - a \end{pmatrix} G^{\dagger}$$
(1.55)

Interaction with a magnetic field

When a spin 1/2 particle is subject to a magnetic field B in the z direction, the interaction Hamiltonian is

$$H = -\mu B\sigma_z = -h\sigma_z \tag{1.56}$$

where μ is the magnetic moment of the particle (it is a constant that depends on the type of particle you have; for electrons it is called the Bohr magneton). It is easier to just work with $h = \mu B$. You may think of h as a field in energy units.

The Hamiltonian (1.56) is already diagonal in the $|\sigma\rangle$ basis since σ_z is diagonal (of course, we are very smart physicists, so we conveniently choose the field in the z direction precisely for this reason). Thus, the energy eigenvalues will be

$$E_{\sigma} = -h\sigma \tag{1.57}$$

Or, more explicitly,

$$E_+ = -h, \qquad E_- = +h$$

We will learn as we go along that we should always keep an eye at the **ground-state**; i.e., the state of lowest energy. If h > 0 the ground state is E_+ , corresponding to the quantum number $\sigma = +1$. Physically this means that the energy is smaller when the spin points parallel to the field.

We may compute the propagator $U(t) = e^{-iHt}$ quite easily in this case, using Eq. (1.18):

$$e^{-iHt} = e^{-iE_{+}t} |+\rangle\langle+| + e^{-iE_{-}t} |-\rangle\langle-| = \begin{pmatrix} e^{-iE_{+}t} & 0\\ 0 & e^{-iE_{-}t} \end{pmatrix}$$
(1.58)

Suppose now that the system started at $|\psi(0)\rangle = (\cos\frac{\theta}{2}, \sin\frac{\theta}{2})$, which is like our $|g_n\rangle$ in Eq. (1.42), but with $\phi = 0$. Applying the time-evolution operator then



Figure 1.3: Illustration of a spin precessing around a magnetic field. Left: the prediction from unitary dynamics, Eq. (1.59). The spin just keeps on precessing indefinitely. Right: what happens in real systems. There is a damping which causes the spin to slowly align itself with the magnetic field.

gives us the state at time t:

$$|\psi(t)\rangle = U(t)|\psi(0)\rangle = \begin{pmatrix} e^{iht}\cos\frac{\theta}{2}\\ e^{-iht}\sin\frac{\theta}{2} \end{pmatrix}$$

This is just like the state $|g_n\rangle$, but with a time-dependent angle $\phi = -ht$. Thus, our operators will evolve in time according to

$$\langle \sigma_x \rangle = \sin \theta \cos(ht), \qquad \langle \sigma_y \rangle = -\sin \theta \sin(ht), \qquad \langle \sigma_z \rangle = \cos \theta \qquad (1.59)$$

This is the phenomenon of **spin precession**. The spin just keeps circling around the magnetic field, as illustrated on the left image of Fig. 1.3. In practice, however, we know there are losses in the system, which cause the spin to eventually align itself in the same direction as the field. This damping is due to the contact of the spin with an external environment and is illustrated by the image on the right. It cannot be described by Hamiltonian dynamics. We need something else.

We can also analyze our problem in terms of Heisenberg's equation (1.23). Using the commutation relation of the Pauli matrices, Eq. (1.28), we get

$$\frac{\mathrm{d}\langle\sigma_x\rangle}{\mathrm{d}t} = 2h\langle\sigma_y\rangle \tag{1.60}$$

$$\frac{\mathrm{d}\langle \sigma_y \rangle}{\mathrm{d}t} = -2h\langle \sigma_x \rangle \tag{1.61}$$

$$\frac{\mathrm{d}\langle \sigma_z \rangle}{\mathrm{d}t} = 0 \tag{1.62}$$

You may verify that Eq. (1.59) is indeed a solution of these equations. These formulas become more transparent if we consider a more general magnetic field

h pointing in an arbitrary dimension. Then they may be written simply as

$$\frac{\mathrm{d}\langle \boldsymbol{\sigma} \rangle}{\mathrm{d}t} = 2\langle \boldsymbol{\sigma} \rangle \times \boldsymbol{h} \tag{1.63}$$

where $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$. This is just like Euler's equation for a symmetric top, which makes sense since spin is angular momentum.

1.3 Heisenberg, Ising and the almighty Kron

Now I want to show you how to work with systems composed of many particles. And to do that, I will use as an example the two most important spin interactions, named after Heisenberg and Ising. These interactions form the basis for our understanding of ferromagnetism and we will come back to them several times again.

For simplicity we start assuming that we have two spin 1/2 particles. We attribute a set of spin operators to each particle. Thus, particle number one will be described by the operators σ_1^x , σ_1^y and σ_1^z , whereas particle 2 will be described by the operators σ_2^x , σ_2^y and σ_2^z . The algebra of operators concerning the same particle is the same as before. For instance, just like in Eq. (1.28), we continue to have $[\sigma_1^x, \sigma_1^y] = 2i\sigma_1^z$. But, in addition, we now also make the assumption that **operators pertaining to different particles commute**. Thus,

$$[\sigma_1^i, \sigma_2^j] = 0, \qquad i, j = x, y, z \tag{1.64}$$

Stuff related to particle 1 always commute with stuff related to particle 2.

Now let's talk about states. In total, there must be four possible configurations: (\uparrow,\uparrow) , (\uparrow,\downarrow) , (\downarrow,\uparrow) , (\downarrow,\downarrow) . We may therefore label these states as $|\sigma_1,\sigma_2\rangle$ where $\sigma_i = \pm 1$. These states are constructed to be eigenstates of σ_1^z and σ_2^z :

$$\sigma_1^z |\sigma_1, \sigma_2\rangle = \sigma_1 |\sigma_1, \sigma_2\rangle, \qquad \sigma_2^z |\sigma_1, \sigma_2\rangle = \sigma_2 |\sigma_1, \sigma_2\rangle \tag{1.65}$$

When determining the action of other operators on these states, all you need to remember is that "1" operators only act on the first component of $|\sigma_1, \sigma_2\rangle$ and "2" operators only act on the second component. For instance, we learned above that σ_x flips the sign of a spin. Thus,

$$\sigma_1^x |++\rangle = |-+\rangle$$

$$\sigma_2^x |-+\rangle = |--\rangle$$

and so on.

The Heisenberg interaction

The Heisenberg exchange interaction between two spins is given by

$$H = -J\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 = -J(\sigma_1^x \sigma_2^x + \sigma_1^y \sigma_2^y + \sigma_1^z \sigma_2^z)$$
(1.66)

where J is called the *exchange constant*. What is interesting about it is that it is *isotropic*: since it is the scalar product of two "vectors", it does not depend on any particular reference frame. We can determine the matrix elements of this interaction using the above rules for operating with two-particle states. This is one of those things that have to be done slowly. We start with:

$$\sigma_1^x \sigma_2^x | ++\rangle = |--\rangle$$

$$\sigma_1^x \sigma_2^x | +-\rangle = |-+\rangle$$

$$\sigma_1^x \sigma_2^x | -+\rangle = |+-\rangle$$

$$\sigma_1^x \sigma_2^x | --\rangle = |++\rangle$$

Now we take the product with all possible bras $\langle \sigma_1, \sigma_2 |$. This will give us all 16 matrix elements. Hopefully most of them are zero. What we get in the end is

$$\sigma_1^x \sigma_2^x = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}$$
(1.67)

When we write matrix elements like this, we always order the states as $|++\rangle$, $|+-\rangle$, $|-+\rangle$ and $|--\rangle$. Then we associate with each of these elements the vectors

$$|++\rangle = \begin{pmatrix} 1\\0\\0\\0 \end{pmatrix} \qquad |+-\rangle = \begin{pmatrix} 0\\1\\0\\0 \end{pmatrix} \qquad |-+\rangle = \begin{pmatrix} 0\\0\\1\\0 \end{pmatrix} \qquad |--\rangle = \begin{pmatrix} 0\\0\\0\\1 \end{pmatrix} (1.68)$$

This is called *lexicographic order*: for each value of the first, you run through all values of the second. If we had 3 particles, we would fix each value of the first two and then run over all values of the third. The order would then be

$$|+++\rangle, |++-\rangle, |+-+\rangle, |+--\rangle, |-++\rangle, |-+-\rangle, |--+\rangle, |---\rangle$$

I will leave for you as an exercise to find the matrix elements of $\sigma_1^y \sigma_2^y$ and $\sigma_1^z \sigma_2^z$ (you can also just keep on reading. In a few paragraphs I will teach you a much easier way to do this). The final result is that the Hamiltonian (1.66) becomes

$$H = -J\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 = -J \begin{pmatrix} 1 & 0 & 0 & 0\\ 0 & -1 & 2 & 0\\ 0 & 2 & -1 & 0\\ 0 & 0 & 0 & 1 \end{pmatrix}$$
(1.69)

Now let us see if we can figure out the eigenvalues and eigenvectors of this Hamiltonian. Lucky for us, two eigenvectors are already starring at our face: they are represented by the two lonely 1's in the first and last entries, which mean that

$$H|++\rangle = -J|++\rangle, \qquad H|--\rangle = -J|--\rangle$$

Thus the first two eigenvectors are $|1\rangle = |++\rangle$ and $|2\rangle = |--\rangle$, with eigenvalues $E_1 = E_2 = -J$.

Now we need to look for the remaining two. If we look at the matrix (1.69) we see that these remaining two eigenvectors will be related to the block in the middle. So all we need to do is diagonalize a 2×2 matrix. Whenever I need to do that, I always like to write it in terms of Pauli matrices:

$$\begin{pmatrix} -1 & 2\\ 2 & -1 \end{pmatrix} = -1 + 2\sigma_x$$

For some reason I memorized that the eigenvectors of σ_x are $\frac{1}{\sqrt{2}}(1,1)$ and $\frac{1}{\sqrt{2}}(1,-1)$, with eigenvalues 1 and -1. The eigenvectors of $-1 + 2\sigma_x$ will be the same as those of σ_x :

$$|3\rangle = \frac{|+-\rangle + |-+\rangle}{\sqrt{2}}, \qquad |4\rangle = \frac{|+-\rangle - |-+\rangle}{\sqrt{2}},$$

Moreover, the eigenvalues will be $-1 + 2(\pm 1)$. Multiplying by -J then gives us the corresponding energies: $E_3 = -J[-1 + 2(1)] = -J$ and $E_4 = -J[-1 + 2(-1)] = 3J$. We see that, out of the four states, three are degenerate with energy -J and the other has energy 3J.

It is customary to relabel these eigenvectors and eigenvalues a little differently:

$$|1,1\rangle = |++\rangle$$

$$|1,0\rangle = \frac{|+-\rangle + |-+\rangle}{\sqrt{2}}, \qquad E_1 = -J$$

$$|1,-1\rangle = |--\rangle \qquad (1.70)$$

$$|0,0\rangle = \frac{|+-\rangle - |-+\rangle}{\sqrt{2}}, \qquad E_0 = 3J$$

You may have seen these states before in quantum mechanics. The first 3 are called the triplet states and the last one is the singlet. The reason behind this change in notation is the following. Define two operators:

$$S_z = \frac{1}{2}(\sigma_1^z + \sigma_2^z) \tag{1.71}$$

$$\boldsymbol{S}^{2} = \frac{1}{4} (\boldsymbol{\sigma}_{1} + \boldsymbol{\sigma}_{2})^{2} = \frac{1}{2} (1 + \boldsymbol{\sigma}_{1} \cdot \boldsymbol{\sigma}_{2})$$
(1.72)

where, in the last line, I used the fact that $\sigma_i^2 = 1$. These are the total spin component in the z direction and the total spin operator of the composite system.

The eigenvectors of H are the same as those of $\sigma_1 \cdot \sigma_2$. We therefore see that these will also diagonalize S^2 . The first numbers 1 and 0 in Eq. (1.70) are related to the allowed eigenvalues of S^2 which, from Eq. (1.25), are of the

form S(S + 1), with S being 1 or 0. Thus, in the states $|1, m\rangle$ the total spin of the system is 1 and in the state $|0, 0\rangle$ it is zero. The second set of numbers in Eq. (1.70) are the eigenvalues of S_z , the total z component of the spin. For S = 1 the S_z component may have eigenvalues m = 1, 0, -1 corresponding to the three states $|1, 1\rangle$, $|1, 0\rangle$ and $|1, -1\rangle$. For S = 0, the only eigenvalue of S_z will be 0, which gives $|0, 0\rangle$. The state $|1, 0\rangle$ is perhaps the weirdest of them all: it has spins pointing in opposite directions, one up and one down. Yet, it still has a total spin S = 1. This illustrates the difference between S^2 and S_z .

Let us analyze the physics of Eq. (1.70). Suppose first that J > 0. In this case the state of smallest energy will be $E_1 = -J$. This corresponds to a state of spin 1, which we associate with the spins being aligned in the same direction, either both up or both down (plus the weirdo $|1,0\rangle$). We will learn later in life that J > 0 corresponds to the *ferromagnetic* case, where the spins tend to align with each other. On the other hand, when J < 0 the ground-state will be $E_0 = 3J$. It is a state of spin 0 corresponding to the spins anti-parallel to each other. It will later give rise to *antiferromagnetism*.

Behold, the kron

With what we have discussed above, you have essentially all ingredients to write down matrix elements of many-particle systems. But before we move on, I want to show you another way of working with these states. I will introduce the idea of a **Kronecker product**, or tensor product, or **kron** for the intimate. The Kronecker product between two objects A and B is written as $A \otimes B$. It is defined such that it satisfies the fundamental property

$$(A \otimes B)(C \otimes D) = (AC) \otimes (BD) \tag{1.73}$$

The kron separates two universes. Everything that is to the left of \otimes only interacts with stuff that is on the left and everything to the right only interacts with stuff on the right. With the kron in hand, we may now rewrite our spin operators as

$$\sigma_1^{\mu} = \sigma_{\mu} \otimes 1, \qquad \sigma_2^{\mu} = 1 \otimes \sigma_{\mu} \tag{1.74}$$

Particle 1 stays on the left and particle 2 stays on the right. An operator like $\sigma_1^x \sigma_2^x$ is now written as

$$\sigma_1^x \sigma_2^x = (\sigma_x \otimes 1)(1 \otimes \sigma_x) = \sigma_x \otimes \sigma_x \tag{1.75}$$

We do the exact same thing for states:

$$\sigma_1, \sigma_2 \rangle = |\sigma_1\rangle \otimes |\sigma_2\rangle \tag{1.76}$$

Then the action of $\sigma_1^x \sigma_2^x$ onto $|\sigma_1, \sigma_2\rangle$ becomes

$$\sigma_1^x \sigma_2^x |\sigma_1, \sigma_2\rangle = (\sigma_x \otimes \sigma_x)(|\sigma_1\rangle \otimes |\sigma_2\rangle) = (\sigma_x |\sigma_1\rangle) \otimes (\sigma_x |\sigma_2\rangle)$$
(1.77)

The final result is the operator σ_x (just a 2×2 matrix) acting on a single-particle state.

In a sense, there is nothing fundamentally new about the kron. It does make things a bit more formal, specially if you like linear algebra [Then what we are doing is essentially constructing the many-particle Hilbert space as a direct product of single-particle states.] But, to be honest, from a conceptional point of view what the kron does most is that it introduces a new notation where you can separate more clearly stuff from one side and the other. The biggest advantage of the kron is actually computational: it gives an automated way to construct many-particle matrices.

If A and B are two matrices, then in order to satisfy Eq. (1.73), the components of the Kronecker product must be given by

$$A \otimes B = \begin{pmatrix} a_{1,1}B & \dots & a_{1,N}B \\ \vdots & \ddots & \vdots \\ a_{M,1}B & \dots & a_{M,N}B \end{pmatrix}$$
(1.78)

This is one of those things that you sort of just have to convince yourself that is true. At each entry $a_{i,j}$ you introduce the full matrix B (and then get rid of the parenthesis lying around). For instance

$$\sigma_x \otimes \sigma_x = \begin{pmatrix} 0 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} & 1 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\ 1 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} & 0 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}$$
(1.79)

This is exactly Eq. (1.67) and, you must admit, the calculation was much easier. We can also do the same for vectors:

$$|+-\rangle = |+\rangle \otimes |-\rangle = \begin{pmatrix} 1 \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}$$
(1.80)

This is the second vector in Eq. (1.68). You can proceed similarly to find the others. Note also how the kron naturally uses lexicographic order.

Also have in mind that the Kronecker product is implemented in all numerical libraries. So there are really no excuse for finding these matrix elements: just let the electrons in your computer do the work for you!

Ising vs. Heisenberg

Now that we are pros at dealing with two particles, we can easily generalize to a system of N particles. The operators will be labeled σ_i^{μ} where $\mu = x, y, z$ and i = 1, ..., N. The states will have the form $|\sigma_1, ..., \sigma_N\rangle$, which gives a total of 2^N different states. The size of the Hilbert space grows exponentially with the number of particles, which is why working with many-body systems is so difficult. The general Heisenberg Hamiltonian can be written as

$$H = -\sum_{i,j} J_{i,j} \boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j \tag{1.81}$$

where $J_{i,j}$ is the interaction between spin *i* and spin *j*. Usually we choose the $J_{i,j}$ so that only nearest neighbors interact, but at this stage it is best to leave things general. Surprising as it may sound, in general we do *not* know what are the eigenvalues and eigenvectors of (1.81). The only exception is a onedimensional chain with nearest-neighbor interactions (where this problem can be diagonalized using something called the Bethe ansatz). Otherwise, in general we do not know (or maybe it is not possible) to diagonalize it exactly. There are, though, several approximation schemes to get some rough properties out of this model. We will go through some of them later on. My favorite one is the Holstein-Primakkoff approximation, which will lead us to the idea of magnons.³

Another very popular model is the **Ising model**:

$$H = -\sum_{i,j} J_{i,j} \sigma_i^z \sigma_j^z \tag{1.82}$$

It looks similar to Eq. (1.81), but it has one fundamental difference: we already know *all* its eigenvalues and eigenvectors. The Ising Hamiltonian is written only in terms of σ^z operators and these are all diagonal in the basis $|\sigma_1, \ldots, \sigma_N\rangle$. Thus, this basis diagonalizes H. The eigenvalues are then simply

$$E = -\sum_{i,j} J_{i,j} \sigma_i \sigma_j \tag{1.83}$$

There are in total 2^N eigenvectors and eigenvalues. The funny thing is that, even though we know all eigenvalues and eigenvectors, that still does not help us much since we still have to deal with 2^N of everything. So even though we know how to *diagonalize* the Ising model, that does not mean we know how to extract the *physics* out of it. That is the real challenge of statistical mechanics and many-body physics: diagonalization is just the first step. Even if we diagonalize a model, we still need to learn what to do with it. And, indeed, the physics of the Ising model is extremely rich.

Lastly, I want to compare the Ising model with a longitudinal field,

$$H = -\sum_{i,j} J_{i,j} \sigma_i^z \sigma_j^z - h \sum_i \sigma_i^z$$
(1.84)

with the Ising model in a transverse field:

$$H = -\sum_{i,j} J_{i,j} \sigma_i^z \sigma_j^z - h \sum_i \sigma_i^x$$
(1.85)

 $^{^3}$ You must admit, physicists are a wesome at naming things. I mean, $magnon,\ kron...$ These all sound like the name of villa ins in a Transformers movie.

At first they seem similar. But they are not. Oh boy they are not. Eq. (1.84) only contains σ_z 's so we know how to diagonalize it (the eigenvectors continue to be the $|\sigma_1, \ldots, \sigma_N\rangle$). But Eq. (1.85) contains σ_x 's, which means that $|\sigma_1, \ldots, \sigma_N\rangle$ will no longer be an eigenvector. In fact, the physics of the transverse field Ising model is quite rich since the field term will *compete* with the Ising term. One makes the spin point in the *x* direction and the other in the *z* direction. This competition will, as we will learn one day, lead to a **quantum phase transition**, which is similar to a phase transition, but occurs at zero temperature. But before we can get to all these exciting models, we still have a lot of fundamental concepts to cover. So hang on.

1.4 The quantum harmonic oscillator

The Hamiltonian of the quantum harmonic oscillator is given by

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$$
(1.86)

where x and p are operators satisfying

$$[x,p] = i\hbar \tag{1.87}$$

I will plug \hbar back for now but soon I will throw it away again. I know this is going to sound dramatic but I assure you: this is *by far* the most important example in all of quantum mechanics. The reason for this will only become clear later when we learn about **second quantization**. But trust me on this: what you will learn in this section you will carry with you for the rest of your life. Thus, even though you have probably seen this before, I will redo all the calculations anyway, simply because they are so important.

The characteristic scales of position and momentum are given by

$$x_0 = \sqrt{\frac{\hbar}{m\omega}}, \qquad p_0 = \frac{\hbar}{x_0} = \sqrt{\hbar m\omega}$$
 (1.88)

Apart from numerical factors, theses are the only quantities with dimension of position and momentum that we can construct with \hbar , m and ω . To diagonalize Eq. (1.86) we define a non-Hermitian operator a and its adjoint a^{\dagger} as

you may verify that Eq. (1.87) implies

$$[a, a^{\dagger}] = 1 \tag{1.90}$$

Moreover, the Hamiltonian (1.86) becomes

$$H = \hbar\omega (a^{\dagger}a + 1/2) \tag{1.91}$$

If you have never worked out the steps leading to these last two results, then *please* do it. This is one of those things that you need to do once in your life.

An algebraic problem

Looking at Eqs. (1.90) and (1.91), we see that we have essentially reduced the problem to the diagonalization of the operator $a^{\dagger}a$. We can frame the problem as follows:

What are the eigenthings of
$$a^{\dagger}a$$
 given that $[a, a^{\dagger}] = 1$ (1.92)

Note that $a^{\dagger}a$ is Hermitian, even though a is not. Thus, its eigenvalues must be real and its eigenvectors can be chosen to form an orthonormal basis. Let us write them as

$$a^{\dagger}a|n\rangle = n|n\rangle$$
 (1.93)

My goal is to show you that the eigenvalues n can be all natural numbers (non-negative integers):

$$eigs(a^{\dagger}a) = n \in \{0, 1, 2, 3, ...\}$$
 (1.94)

One thing we can say out front: n cannot be negative because $a^{\dagger}a$ is a *positive semi-definite operator*. What this means is the following: start with Eq. (1.93) and multiply on both sides by $\langle n|$. We get

$$\langle n|a^{\dagger}a|n\rangle = n$$

But the left-hand side is the absolute value of the ket $a|n\rangle$, which is always non-negative. Consequently we must have $n \ge 0.4$

To prove Eq. (1.94) we first work out some commutators. The following formulas are useful to remember:

$$[A, BC] = B[A, C] + [A, B]C$$

$$[AB, C] = A[B, C] + [A, C]B$$
(1.95)

⁴If you want to be rigorous: an operator is said to be positive definite when its eigenvalues are strictly positive and positive semi-definite when they are either zero or positive. Many people don't care about this subtlety and call both types "positive definite". So watch out.

There is an easy way to remember them. For instance, in [A, BC] you first take B out to the left and then C out to the right. Now let's use this to compute:

$$[a^{\dagger}a, a] = a^{\dagger}[a, a] + [a^{\dagger}, a]a = -a$$

where I used Eq. (1.90). We can obtain a similar result for a^{\dagger} , either using the same procedure or by taking the dagger of this result. In any case, let me summarize the results as

$$[a^{\dagger}a, a] = -a, \qquad [a^{\dagger}a, a^{\dagger}] = a$$
 (1.96)

This type of result also appears in other situations and it immediately implies that the eigenvalues will form a ladder of equally spaced values.

To see why, we use this result to compute

$$(a^{\dagger}a)a|n\rangle = [a(a^{\dagger}a) - a]|n\rangle = a(a^{\dagger}a - 1)|n\rangle = (n - 1)a|n\rangle$$

From this we conclude that if $|n\rangle$ is an eigenvector with eigenvalue n, then $a|n\rangle$ is also an eigenvector, but with eigenvalue (n-1) [read this sentence again; it is very important]. However, I wouldn't call this $|n-1\rangle$ just yet because $a|n\rangle$ is not normalized. Thus we need to write

$$|n-1\rangle = \alpha a |n\rangle$$

where α is a normalization constant. To find it we simply write

$$\langle n-1|n-1\rangle = |\alpha|^2 \langle n|a^{\dagger}a|n\rangle = |\alpha|^2 n$$

Thus $|\alpha|^2| = 1/n$. The actual sign of α is arbitrary so we choose it for simplicity as being real and positive. We then get

$$|n-1\rangle = \frac{a}{\sqrt{n}}|n\rangle$$

From this analysis we conclude that a reduces the eigenvalues by unity:

$$a|n\rangle = \sqrt{n}|n-1\rangle$$

We can do a similar analysis with a^{\dagger} . We again use Eq. (1.96) to compute

$$(a^{\dagger}a)a^{\dagger}|n\rangle = (n+1)a^{\dagger}|n\rangle$$

Thus a^{\dagger} raises the eigenvalue by unity. Its normalization factor is found by a similar procedure: we write $|n + 1\rangle = \beta a^{\dagger} |n\rangle$, for some constant β , and then compute

$$\langle n+1|n+1\rangle = |\beta|^2 \langle n|aa^{\dagger}|n\rangle = |\beta|^2 \langle n|(1+a^{\dagger}a)|n\rangle = |\beta|^2 (n+1)$$

Thus

$$a^{\dagger}|n\rangle = \sqrt{n+1}|n+1\rangle$$

These results are important, so let me summarize them in a boxed equation:

$$a|n\rangle = \sqrt{n}|n-1\rangle, \qquad a^{\dagger}|n\rangle = \sqrt{n+1}|n+1\rangle$$
(1.97)

Now start with some state $|n\rangle$ and keep on applying *a* a bunch of times. At each application you will lower the eigenvalue by one tick:

$$a^{\ell}|n\rangle = \sqrt{n(n-1)\dots(n-\ell+1)}|n-\ell\rangle$$

But this party cannot continue forever because, as we have just discussed, the eigenvalues of $a^{\dagger}a$ cannot be negative. They can, at most, be zero. The only way for this to happen is if there exists a certain integer ℓ for which $a^{\ell}|n\rangle \neq 0$ but $a^{\ell+1}|n\rangle = 0$. And this can only happen if $\ell = n$ because, then

$$a^{\ell+1}|n\rangle = \sqrt{n(n-1)\dots(n-\ell+1)(n-\ell)}|n-\ell-1\rangle = 0$$

Since ℓ is an integer, we therefore conclude that n must also be an integer. This analysis also serves to define the state with n = 0, which we call the **vacuum**, $|0\rangle$. It is defined by

$$a|0\rangle = 0 \tag{1.98}$$

We therefore emerge from this analysis with the conclusion that, as anticipated in Eq. (1.94), the eigenvalues of $a^{\dagger}a$ can be all non-negative integers. The operator a is the **annihilation operator** and a^{\dagger} is the **creation operator**. Moreover, $a^{\dagger}a$ is the **number operator** because it counts the number of quanta in the system. What this analysis taught us is that, if you want to count how many people are there in a room, you first need to annihilate them and then create fresh new humans. Quantum mechanics is indeed strange.

We can build all states starting from the vacuum and applying a^{\dagger} successively:

$$|n\rangle = \frac{(a^{\dagger})^n}{\sqrt{n!}}|0\rangle \tag{1.99}$$

Using this and the algebra of a and a^{\dagger} it then follows that the states $|n\rangle$ form an orthonormal basis, as expected:

$$\langle n|m\rangle = \delta_{n,m} \tag{1.100}$$

Back to the Hamiltonian

Since H in Eq. (1.91) is a function of $a^{\dagger}a$, it will share the same eigenvectors. We therefore get

$$H|n\rangle = E_n|n\rangle, \qquad E_n = \hbar\omega(n+1/2)$$
 (1.101)

The energies of the harmonic oscillator are equally spaced, $\Delta E = \hbar \omega$. This is a signature of harmonic motion. It is found, for instance, in the vibrational spectra of molecules.

We can also look at wavefunctions, which are defined as

$$\psi_n(x) = \langle x | n \rangle \tag{1.102}$$

But wavefunctions are boring, so we will not look at them.

1.5 Coherent states

For the harmonic oscillator, there is a very special set of states which appear frequently in condensed matter, quantum field theory and quantum optics.⁵ They are called coherent states. We begin by defining the **displacement op**erator

$$D(\alpha) = e^{\alpha a^{\dagger} - \alpha^* a} \tag{1.103}$$

where α is an arbitrary complex number and α^* is its complex conjugate. The reason why it is called a "displacement" operator will become clear soon. A coherent state is defined as the action of $D(\alpha)$ into the vacuum state:

$$|\alpha\rangle = D(\alpha)|0\rangle \tag{1.104}$$

We sometimes say that "a coherent state is a displaced vacuum". This sounds like a typical Star Trek sentence: "Oh no! He displaced the vacuum. Now the entire planet will be annihilated!"

$D(\alpha)$ displaces a and a^{\dagger}

Let us first try to understand why $D(\alpha)$ is a displacement operator. First, one may verify directly from Eq. (1.103) that

$$D^{\dagger}(\alpha)D(\alpha) = D(\alpha)D^{\dagger}(\alpha) = 1$$
 (it is unitary) (1.105)

$$D^{\dagger}(\alpha) = D(-\alpha) \tag{1.106}$$

This means that if you displace by a given α and then displace back by $-\alpha$, you return to where you started. Next I want to compute $D^{\dagger}(\alpha)aD(\alpha)$. To do that

⁵ If you ever need more advanced properties of coherent states, the best source is the paper by K. Cahill and R. Glauber entitled "Ordered expansions in boson amplitude operators" *Phys. Rev.* **177**, 1857-1881 (1969). Another comprehensive source is chapter 4 of the book by Gardiner and Zoller called "Quantum Noise".

we use the BCH formula⁶

$$e^{A}Be^{-A} = B + [A, B] + \frac{1}{2!}[A, [A, B]] + \frac{1}{3!}[A, [A, [A, B]]] + \dots$$
 (1.107)

with B = a and $A = \alpha^* a - \alpha a^{\dagger}$. Using Eq. (1.90) we get

$$[\alpha^* a - \alpha a^\dagger, a] = \alpha$$

This is a c-number so that all higher order commutators are zero. We therefore conclude that

$$D^{\dagger}(\alpha)aD(\alpha) = a + \alpha \tag{1.108}$$

This is why we call D the displacement operator: it displacements the operator by an amount α . Since $D^{\dagger}(\alpha) = D(-\alpha)$ it follows that

$$D(\alpha)aD^{\dagger}(\alpha) = a - \alpha \tag{1.109}$$

The action on a^{\dagger} is similar: you just need to take the adjoint: For instance

$$D^{\dagger}(\alpha)a^{\dagger}D(\alpha) = a^{\dagger} + \alpha^{*} \tag{1.110}$$

The coherent state is an eigenstate of a

What I want to do now is apply a to the coherent state $|\alpha\rangle$ in Eq. (1.104). Start with Eq. (1.108) and multiply by D on the left. Since D is unitary we get $aD = D(a + \alpha)$. Thus

$$a|\alpha\rangle = aD|0\rangle = D(a+\alpha)|0\rangle = D(\alpha)|0\rangle = \alpha|\alpha\rangle$$

where I used the fact that $a|0\rangle = 0$. Hence we conclude that the coherent state is the eigenvector of the annihilation operator:

$$a|\alpha\rangle = \alpha|\alpha\rangle$$
 (1.111)

The annihilation operator is not Hermitian so its eigenvalues do not have to be real. In fact, this equation shows that the eigenvalues of a are all complex numbers.

Alternative way of writing D

It is possible to express D in a different way, which may be more convenient for some computations. To do that we use another BCH formula: if it happens that [A, B] commute with both A and B, then

$$e^{A+B} = e^A e^B e^{-\frac{1}{2}[A,B]} \tag{1.112}$$

 $^{^{6}}$ There is no magic behind this formula: you simply need to expand the exponentials in a Taylor series and organize the multiple terms.

Since $[a, a^{\dagger}] = 1$, we may write

$$D(\alpha) = e^{-|\alpha|^2/2} e^{\alpha a^{\dagger}} e^{-\alpha^* a} = e^{|\alpha|^2/2} e^{-\alpha^* a} e^{\alpha a^{\dagger}}$$
(1.113)

This result is useful because now the exponentials of a and a^{\dagger} are completely separated.

From this result it follows that

$$D(\alpha)D(\beta) = e^{(\beta^*\alpha - \alpha^*\beta)/2}D(\alpha + \beta)$$
(1.114)

This means that if you do two displacements in a sequence, it is almost the same as doing just a single displacement; the only thing you get is a phase factor (the quantity in the exponential is purely imaginary).

Poisson statistics

Let us use Eq. (1.113) to write the coherent state a little differently. Since $a|0\rangle = 0$ it follows that $e^{-\alpha a}|0\rangle = |0\rangle$. Hence we may also write Eq. (1.104) as

$$|\alpha\rangle = e^{-|\alpha|^2/2} e^{\alpha a^{\dagger}} |0\rangle \tag{1.115}$$

Now we may expand the exponential and use Eq. (1.99) to write $(a^{\dagger})^n |0\rangle$ in terms of the number states. We get

$$|\alpha\rangle = e^{-|\alpha|^2/2} \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} |n\rangle$$
(1.116)

Thus we find that

$$\langle n | \alpha \rangle = e^{-|\alpha|^2/2} \frac{\alpha^n}{\sqrt{n!}} \tag{1.117}$$

The probability of finding it in a given state $|n\rangle$, given that it is in a coherent state, is therefore

$$|\langle n|\alpha\rangle|^2 = e^{-|\alpha|^2} \frac{(|\alpha|^2)^n}{n!}$$
 (1.118)

This is a Poisson distribution with parameter $\lambda = |\alpha|^2$. The photons in a laser are usually in a coherent state and the Poisson statistics of photon counts can be measured experimentally. If you measure this statistics for thermal light you will find that it is not Poisson (usually it follows a geometric distribution). Hence, Poisson statistics is a signature of coherent states.

Orthogonality

Coherent states are not orthogonal. To figure out the overlap between two coherent states $|\alpha\rangle$ and $|\beta\rangle$ we use Eq. (1.115):

$$\langle \beta | \alpha \rangle = e^{-|\beta|^2/2} e^{-|\alpha|^2/2} \langle 0 | e^{\beta^* a} e^{\alpha a^\dagger} | 0 \rangle$$

We need to exchange the two operators because we know how a acts on $|0\rangle$ and how a^{\dagger} acts on $\langle 0|$. To do that we use Eq. (1.112):

$$e^{\beta^* a} e^{\alpha a^{\dagger}} = e^{\alpha a^{\dagger}} e^{\beta^* a} e^{\beta^* \alpha} \tag{1.119}$$

We therefore conclude that

$$\langle \beta | \alpha \rangle = \exp\left\{ \beta^* \alpha - \frac{|\beta|^2}{2} - \frac{|\alpha|^2}{2} \right\}$$
(1.120)

The overlap of the two states, squared, can be simplified to read:

$$|\langle \beta | \alpha \rangle|^2 = \exp\left\{-|\alpha - \beta|^2\right\}$$
(1.121)

If $\beta = \alpha$ then

$$\langle \alpha | \alpha \rangle = 1 \tag{1.122}$$

which we already knew from Eq. (1.104) and the fact that D is unitary.

We therefore conclude that, in general, two coherent states are not orthogonal. However, they become roughly orthogonal when both α and β are very big (because then the exponential overlap becomes very small). Coherent states therefore do *not* form an orthonormal basis. In fact, they form an overcomplete basis in the sense that there is more states than actually needed.

Completeness

Even though the coherent states do not form an orthonormal basis, we can still write down a completeness relation for them. However, it looks a little different:

$$\int \frac{\mathrm{d}^2 \alpha}{\pi} |\alpha\rangle \langle \alpha| = 1 \tag{1.123}$$

where integral is over the entire complex plane and $d^2\alpha = d\alpha_R d\alpha_I$. The proof of Eq. (1.123) is a little bit cumbersome, so you may skip it if you want.

It goes as follows. Consider an arbitrary state $|\psi\rangle$ and expand it in the number basis $|n\rangle$:

$$|\psi\rangle = \sum_{n} \psi_n |n\rangle$$

Now write

$$\int \frac{\mathrm{d}^2 \alpha}{\pi} |\alpha\rangle \langle \alpha |\psi\rangle = \sum_n \psi_n \int \frac{\mathrm{d}^2 \alpha}{\pi} |\alpha\rangle \langle \alpha |n\rangle$$

To compute the integral we use Eq. (1.117) to write $\langle \alpha | n \rangle$ and Eq. (1.116) to expand $|\alpha\rangle$. We then get, in addition to the α -integral, a double sum over the number states:

$$\int \frac{\mathrm{d}^2 \alpha}{\pi} |\alpha\rangle \langle \alpha |\psi\rangle = \sum_{n,m} \frac{\psi_n}{\sqrt{n!m!}} |m\rangle \int \frac{\mathrm{d}^2 \alpha}{\pi} e^{-|\alpha|^2} \alpha^m (\alpha^*)^m \tag{1.124}$$

To compute the integral we change variables to polar coordinates:

$$\alpha = r e^{i\theta}, \qquad \mathrm{d}^2 \alpha = r \, \mathrm{d} r \, \mathrm{d} \theta$$

The integral over θ will give us a $\delta_{n,m}$:

$$\int \frac{\mathrm{d}^2 \alpha}{\pi} e^{-|\alpha|^2} \alpha^m (\alpha^*)^m = \int \frac{r \,\mathrm{d}r \,\mathrm{d}\theta}{\pi} r^{m+n} e^{i\theta(m-n)} e^{-r^2}$$
$$= 2\delta_{n,m} \int_0^\infty \mathrm{d}r \ r^{2n+1} e^{-r^2}$$
$$= \delta_{n,m} n!$$

Substituting this back into Eq. (1.124) finally gives

$$\int \frac{\mathrm{d}^2 \alpha}{\pi} |\alpha\rangle \langle \alpha |\psi\rangle = \sum_n \psi_n |n\rangle = |\psi\rangle$$

This shows that Eq. (1.123) is indeed true.

Expectation values of normal-ordered operators

We say an operator is **normal ordered** when we have arranged all creation operators to the left. For instance $(a + a^{\dagger})^2$ is not normal ordered because

$$(a+a^{\dagger})^2 = aa + a^{\dagger}a^{\dagger} + a^{\dagger}a + aa^{\dagger}$$

In the last term we have a dagger on the right. To normal order this operator, we use the commutation relation (1.90) to write $aa^{\dagger} = a^{\dagger}a + 1$. Thus, if we express this as

$$(a+a^{\dagger})^{2} = aa + a^{\dagger}a^{\dagger} + 2a^{\dagger}a + 1$$
(1.125)

then this operator is normal ordered.

The reason why normal ordering is useful is because, if we compute the expectation value in any coherent states, we know how a acts on $|\alpha\rangle$ and we know how a^{\dagger} acts on $\langle \alpha |$. Thus, for instance,

$$\langle \alpha | (a+a^{\dagger})^2 | \alpha \rangle = \alpha^2 + \alpha^{*2} + 2\alpha^* \alpha + 1 \tag{1.126}$$

This looks identical to Eq. (1.125), except that the operators a and a^{\dagger} are replaced by the numbers α and α^* . Coherent states are the basis for several approximate techniques that we will learn later. And, in this sense, it is useful to remember the following rule: let $H(a^{\dagger}, a)$ be some operator (usually a Hamiltonian, but it can be other operators as well) which are written in normal order. It then follows that

$$\langle \alpha | H(a^{\dagger}, a) | \alpha \rangle = H(\alpha^*, \alpha)$$
 (1.127)

1.6 The Schrödinger Lagrangian

It is possible to cast the Schrödinger equation as a consequence of the **principle of least action**, similar to what we do in classical mechanics. This method has several advantages. First, it will introduce us to ideas of field theory. Second, it is the starting point for a **variational principle** that can be used to study approximations to the *dynamics* of a system.

Do you remember the usual variational principle? It says that if $|\psi\rangle$ is an arbitrary wave-function then

$$E_{\rm gs} \le \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \tag{1.128}$$

In words it says that the energy of the ground-state $E_{\rm gs}$ is always a *lower bound* to the sandwich of the Hamiltonian H. In practice, we use the variational principle by choosing a trial state $|\psi\rangle$ which has some free parameters. We then try to minimize the sandwich in the right-hand side of Eq. (1.128) with respect to these parameters, which will give us an estimate of the ground-state energy. The larger is the number of free parameters the better the estimate is (and the more complicated the calculation becomes). The Schrödinger Lagrangian does exactly this, but for the dynamics. Unlike the previous sections, this theory is likely new to you and perhaps a little bit more advanced for this level. Notwithstanding, I think it is really cute. So here it goes.⁷

The principle of least action in classical mechanics

Before we start with the quantum stuff, we need a brief review of classical mechanics. Consider a system described by a set of generalized coordinates q_i and characterized by a Lagrangian $L(q_i, \partial_t q_i)$. Also, define the action as

$$S = \int_{t_1}^{t_2} L(q_i, \partial_t q_i) \,\mathrm{d}t$$
 (1.129)

The motion of the system is then generated by the principle of least action; ie, by requiring that the actual path should be an extremum of S. We can

 $^{^7 \}rm Since this is the last section in the chapter, you should interpret it as a boss fight. It is definitely harder, but the loot is also better.$

find the equations of motion (the Euler-Lagrange equations) by performing a tiny variation in S and requiring that $\delta S = 0$ (which is the condition on any extremum point; maximum or minimum). To do that we write $q_i \rightarrow q_i + \eta_i$, where $\eta_i(t)$ is supposed to be an infinitesimal distortion of the original trajectory. We then compute

$$\begin{split} \delta S &= S[q_i(t) + \eta_i(t)] - S[q_i(t)] \\ &= \int_{t_1}^{t_2} \mathrm{d}t \sum_i \left\{ \frac{\partial L}{\partial q_i} \eta_i + \frac{\partial L}{\partial (\partial_t q_i)} \partial_t \eta_i \right\} \\ &= \int_{t_1}^{t_2} \mathrm{d}t \sum_i \left\{ \frac{\partial L}{\partial q_i} - \partial_t \left(\frac{\partial L}{\partial (\partial_t q_i)} \right) \right\} \eta_i \end{split}$$

where, in the last line, I integrated by parts the second term. Setting each term proportional to η_i to zero then gives us the **Euler-Lagrange equations**

$$\frac{\partial L}{\partial q_i} - \partial_t \left(\frac{\partial L}{\partial (\partial_t q_i)} \right) = 0 \tag{1.130}$$

The example you are probably mostly familiar with is the case when

$$L = \frac{1}{2}m(\partial_t q)^2 - V(q)$$
 (1.131)

with V(q) being some potential. In this case Eq. (1.130) gives Newton's law

$$m\partial_t^2 q = -\frac{\partial V}{\partial q} \tag{1.132}$$

Another example, which you may not have seen before, but which will be interesting for us, is the case when we write L as a function of coordinates q and momenta p; , ie $L(q, \partial_t q, p, \partial_t p)$. For instance,

$$L = p\partial_t q - H(q, p) \tag{1.133}$$

where H is the Hamiltonian function. In this case there will be two Euler-Lagrange equations:

$$\frac{\partial L}{\partial q} - \partial_t \left(\frac{\partial L}{\partial (\partial_t q)} \right) = -\frac{\partial H}{\partial q} - \partial_t p = 0$$
$$\frac{\partial L}{\partial p} - \partial_t \left(\frac{\partial L}{\partial (\partial_t p)} \right) = \partial_t q - \frac{\partial H}{\partial p} = 0$$

Rearranging, this gives us Hamilton's equations

$$\partial_t p = -\frac{\partial H}{\partial q}, \qquad \partial_t q = \frac{\partial H}{\partial p}$$
 (1.134)

Another thing we will need is the **conjugated momentum** π_i associated to a generalized coordinate q_i . It is always defined as

$$\pi_i = \frac{\partial L}{\partial(\partial_t q_i)} \tag{1.135}$$

For the Lagrangian (1.131) we get $\pi = m\partial_t q$. For the Lagrangian (1.133) we have two variables, $q_1 = q$ and $q_2 = p$. The corresponding conjugated momenta are $\pi(q) = p$ and $\pi(p) = 0$ (there is no momentum associated with the momentum!). Once we have the momentum we may construct the Hamiltonian from the Lagrangian using the Legendre transform:

$$H = \sum_{i} p_i \partial_t q_i - L \tag{1.136}$$

For the Lagrangian (1.131) we get

$$H = \frac{p^2}{2m} + V(q)$$

whereas for the Lagrangian (1.133) we get

$$H = \pi(q)\partial_t q + \pi(p)\partial_t p - L = p\partial_t q + 0 - p\partial_t q + H = H$$

as of course expected.

The principle of least action for Schrödinger's equation

Now consider the Schrödinger equation (1.1)

$$i\partial_t |\psi(t)\rangle = H|\psi(t)\rangle \tag{1.137}$$

and let us write it in terms of the components ψ_n in some basis, as in Eq. (1.10):

$$i\partial_t \psi_n = \sum_m H_{n,m} \psi_m \tag{1.138}$$

We now ask the following question: can we cook up a Lagrangian and an action such that the corresponding Euler-Lagrange equations give Eq. (1.138)? The answer, of course, is yes.⁸ The "variables" in this case are all components ψ_n . But since they are complex variables, we actually have ψ_n and ψ_n^* as an independent set. That is, $L = L(\psi_n, \partial_t \psi_n, \psi_n^*, \partial_t \psi_n^*)$. and the action is

$$S[\psi_n^*, \psi_n] = \int_{t_1}^{t_2} L(\psi_n, \partial_t \psi_n, \psi_n^*, \partial_t \psi_n^*) \,\mathrm{d}t \tag{1.139}$$

 $^{^{8}}$ If the answer was no, I would be a completely crazy person, because I just spent more than one page describing Lagrangian mechanics, which would have all been for nothing.

I will now tell you what is the correct Lagrangian we should use and then we will verify that it indeed works. The correct Lagrangian is:

$$L = \sum_{n} i \psi_n^* \partial_t \psi_n - \sum_{n,m} H_{n,m} \psi_n^* \psi_m \tag{1.140}$$

where ψ_n and ψ_n^* are to be interpreted as independent variables. Please take notice of the similarity with Eq. (1.133): ψ_n plays the role of q and ψ_n^* plays the role of p. To check that this works we use the Euler-Lagrange equations with $q_1 = \psi_n^*$ and $q_2 = \psi_n$:

$$\frac{\partial L}{\partial \psi_n^*} - \partial_t \left(\frac{\partial L}{\partial (\partial_t \psi_n^*)} \right) = 0$$

The second term is zero since $\partial_t \psi_n^*$ does not appear in Eq. (1.140). The first term then gives

$$\frac{\partial L}{\partial \psi_n^*} = i\partial_t \psi_n - \sum_m H_{n,m} \psi_m = 0$$

which is precisely Eq. (1.138). Thus, we have just cast Schrödinger's equation as a principle of least action for a weird action that depends on the quantum state $|\psi\rangle$. I will leave to you as an exercise to compute the Euler-Lagrange equation for ψ_n ; you will simply find the complex conjugate of Eq. (1.138).

Eq. (1.140) is written in terms of the components ψ_n of a certain basis. We can also write it in a basis independent way, as

$$L = \langle \psi | (i\partial_t - H) | \psi \rangle \tag{1.141}$$

This is what I call the Schrödinger Lagrangian. Isn't it beautiful? If this abstract version ever confuse you, simply refer back to Eq. (1.140).

Let us now ask what is the conjugated momentum associated with the variable ψ_n for the Lagrangian (1.140). Using Eq. (1.135) we get, as you may have anticipated,

$$\pi(\psi_n) = \frac{\partial L}{\partial(\partial_t \psi_n)} = i\psi_n^*, \qquad \pi(\psi_n^*) = 0$$
(1.142)

This means that ψ_n and $i\psi_n^*$ are conjugated variables. As a sanity check, we can now find the Hamiltonian using the definition (1.136):

$$H = \sum_{n} i\psi_n^* \partial_t \psi_n - L \tag{1.143}$$

which is, of course, just the actual Hamiltonian H.

The idea of using Eq. (1.141) [or Eq. (1.140)] is as follows. Suppose, just for the sake of argument, that the dimension of your Hilbert space is d. This means that there are in total d coefficients ψ_n which will completely describe your quantum state. If you extremize the action with respect to all these coefficients your Euler-Lagrange equations will be the exact Schrödinger equation. But in some problems that may be a complicated task. Instead, we may use only a smaller set d' < d of parameters. This will still give you some equation of motion, but this equation will be approximate because we are focusing only on a sub-space of the full Hilbert space. This is how we implement a variational principle for the dynamics. The larger is the number of parameters d', the better will the approximation be, until d' = d, in which case the calculation becomes exact.

Position representation

Things get even naughtier if we look at the position representation. Assume that

$$H = \frac{\boldsymbol{p}^2}{2m} + V(\boldsymbol{x}) \tag{1.144}$$

Then we know that, in the position representation,

$$\langle \psi | H | \psi \rangle = \int d^3 \boldsymbol{x} \, \psi^* \left[-\frac{\nabla^2}{2m} + V(\boldsymbol{x}) \right] \psi$$
 (1.145)

The Schrödinger Lagrangian (1.141) then becomes

$$L = \int d^3 \boldsymbol{x} \, \psi^*(\boldsymbol{x}, t) \left[i\partial_t + \frac{\nabla^2}{2m} + V(\boldsymbol{x}) \right] \psi(\boldsymbol{x}, t)$$
(1.146)

We may also define a Lagrangian density \mathcal{L} as

$$L = \int \mathrm{d}^3 \boldsymbol{x} \, \mathcal{L} \tag{1.147}$$

Then

$$\mathcal{L} = \psi^*(\boldsymbol{x}, t) \left[i\partial_t + \frac{\nabla^2}{2m} + V(\boldsymbol{x}) \right] \psi(\boldsymbol{x}, t)$$
(1.148)

This is interesting because now we can write the action not as an integral in time, but as an integral over space-time:

$$S = \int dt L = \int d^4x \mathcal{L}$$
 (1.149)

where $d^4x = dt d^3x$. Before S and L depended on a set of variables $\psi_n(t)$ and $\psi_n^*(t)$. Now they depend on a set of continuous variables $\psi(x, t)$ and $\psi^*(x, t)$.

This is perhaps your first encounter of a **field theory**. We have just shown that a quantum system is described by a field $\psi(\boldsymbol{x},t)$ (which is just the wave-function of course). The system is governed by an action/Lagrangian and Schrödinger's equation is simply the corresponding Euler-Lagrange equation. This is very similar to electromagnetism, which is also characterized by a field and by a Lagrangian (you will learn about the electromagnetic Lagrangian in

field theory courses). The Euler-Lagrange equations for the electromagnetic Lagrangian are Maxwell's equations. In this sense Schrödinger's equation is therefore a *classical field theory*. I know this sounds weird, but it is classical in the sense that the field (in this case ψ) is a classical object; ie a complex number. To obtain a *quantum field theory* we must promote the fields themselves to operators, a procedure called **second quantization**. In electromagnetism, quantization leads to the idea of photons as the elementary excitations. We may also think about quantizing the Schrödinger Lagrangian and this will lead to a similar idea, with the actual particles interpreted as excitations out of the field. We will learn how to do this on later chapters.

The momentum conjugated to $\psi(\mathbf{x}, t)$ is again $i\psi^*(\mathbf{x}, t)$ (which is also a field). From the Lagrangian density we then obtain the Hamiltonian density

$$\mathcal{H} = i\psi^*\partial_t\psi - \mathcal{L} = \psi^* \left[-\frac{\nabla^2}{2m} + V(\boldsymbol{x}) \right] \psi$$
(1.150)

The total energy is then the integral of this quantity over all space

$$H = \int d^3 \boldsymbol{x} \, \mathcal{H} = \int d^3 \boldsymbol{x} \, \psi^* \left[-\frac{\nabla^2}{2m} + V(\boldsymbol{x}) \right] \psi \qquad (1.151)$$

As expected, this is nothing but Eq. (1.145).

In the position representation \mathcal{L} will depend not only on ψ and $\partial_t \psi$, but also on $\partial_i \psi$. Thus, when constructing the equations of motion, we need to consider the dependence on these derivatives as well. Actually, the Lagrangian (1.148) also depends on $\partial_i^2 \psi$, which is a bit messy. But we can get rid of that by integrating by parts and transferring one of the ∇ 's to act on ψ^* (two Lagrangians differing only by an integration by parts are physically equivalent since boundary terms always vanish). We then get

$$\mathcal{L} = \psi^* i \partial_t \psi - \frac{1}{2m} (\nabla \psi^*) \cdot (\nabla \psi) + V(\boldsymbol{x}) \psi^* \psi \qquad (1.152)$$

This is absolutely equivalent to Eq. (1.148), but it is more convenient to work with.

The general structure of the Euler-Lagrange equations is almost identical to Eq. (1.130); you just need to sum the derivatives with respect to the position coordinates.⁹ That is, they become

$$\frac{\partial \mathcal{L}}{\partial \psi} - \partial_t \left(\frac{\partial \mathcal{L}}{\partial (\partial_t \psi)} \right) - \sum_{i=1}^3 \partial_i \left(\frac{\partial \mathcal{L}}{\partial (\partial_i \psi)} \right) = 0 \tag{1.153}$$

And similarly for ψ^* . As before, the Euler-Lagrange equation for ψ^* will give an equation of motion for ψ and vice-versa.

⁹This can be demonstrated exactly as in Eq. (1.130), by adding to the field $\psi(\boldsymbol{x}, t)$ a small perturbative field $\eta(\boldsymbol{x}, t)$ and analyzing the corresponding variation in the action.

Chapter 2

Density matrix theory

2.1 Trace and partial trace

The concept of a *trace* will be used extensively in this course, starting in the next section. So I want to take a second to explain it in detail. The trace of an operator is defined as the sum of its diagonal entries:

$$\operatorname{tr}(A) = \sum_{i} \langle i | A | i \rangle \tag{2.1}$$

It does not matter which basis you use: it turns out that the trace is always the same. You can see that using completeness: for instance, if $|a\rangle$ is some other basis then

$$\sum_{i} \langle i|A|i\rangle = \sum_{i} \sum_{a} \langle i|a\rangle \langle a|A|i\rangle = \sum_{i} \sum_{a} \langle a|A|i\rangle \langle i|a\rangle = \sum_{a} \langle a|A|a\rangle$$

Thus, we conclude that

$$\operatorname{tr}(A) = \sum_{i} \langle i | A | i \rangle = \sum_{a} \langle a | A | a \rangle \tag{2.2}$$

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The trace is a property of the operator, not of the basis you choose.

Since it does not matter which basis you use, let us choose the basis which diagonalizes the operator A. If $|a\rangle$ happens to be that basis, then $\langle a|A|a\rangle = \lambda_a$ will be an eigenvalue of A. Thus, we also see that

$$\operatorname{tr}(A) = \sum_{a} \lambda_{a} = \operatorname{sum of all eigenvalues of } A$$
 (2.3)

For instance, $\operatorname{tr}(H) = \sum_{n} E_{n}$ is the sum of all energies. Or we can also look at the operator e^{-iHt} . We have seen before that the eigenvalues of this operator

are e^{-iE_nt} . Thus, we conclude that

$$\operatorname{tr}(e^{-iHt}) = \sum_{n} e^{-iE_{n}t}$$
(2.4)

Perhaps the most useful property of the trace is that it is *cyclic*:

$$\operatorname{tr}(AB) = \operatorname{tr}(BA) \tag{2.5}$$

I will leave it for you to demonstrate this. You can do it, as with all demonstrations in quantum mechanics, by inserting a convenient completeness relation in the middle of AB. Using the cyclic property (2.5) you can also move around an arbitrary number of operators, but only in cyclic permutations. For instance:

$$tr(ABC) = tr(CAB) = tr(BCA)$$
(2.6)

Note how I am moving them around in a specific order: $tr(ABC) \neq tr(BAC)$. An example that appears often is a trace of the form $tr(UAU^{\dagger})$, where U is a unitary operator; i.e., $UU^{\dagger} = U^{\dagger}U = 1$. In this case, it follows from the cyclic property that

$$\operatorname{tr}(UAU^{\dagger}) = \operatorname{tr}(AU^{\dagger}U) = \operatorname{tr}(A)$$

Finally, let $|\psi\rangle$ and $|\phi\rangle$ be arbitrary kets and let us compute the trace of the outer product $|\psi\rangle\langle\phi|$:

$$\mathrm{tr}(|\psi\rangle\langle\phi|) = \sum_{i} \langle i|\psi\rangle\langle\phi|i\rangle = \sum_{i} \langle\phi|i\rangle\langle i|\psi\rangle$$

The sum over $|i\rangle$ becomes a 1 due to completeness and we conclude that

$$\operatorname{tr}(|\psi\rangle\langle\phi|) = \langle\phi|\psi\rangle \tag{2.7}$$

Notice how this follows the same logic as Eq. (2.5), so you can pretend you just used the cyclic property. As an example, consider the coherent states of the harmonic oscillator discussed in Sec. 1.5. Using the completeness relation (1.123) together with Eq. (2.7) we may write the trace of any operator as

$$\operatorname{tr} \mathcal{O} = \operatorname{tr} \int \frac{\mathrm{d}^2 \alpha}{\pi} |\alpha\rangle \langle \alpha | \mathcal{O} = \int \frac{\mathrm{d}^2 \alpha}{\pi} \langle \alpha | \mathcal{O} | \alpha \rangle$$
(2.8)

This is similar to a sum over the diagonal entries, except that now we are using an overcomplete basis.

The partial trace

The trace is an operation which starts with an operator and spits out a number. It is also possible to do a *partial trace*, which eliminates only part of a Hilbert space. Why this is useful will only become clear in Sec. 2.3, but the mathematical procedure can be outlined here.
Suppose you have a system composed of two parts, A and B. They may be, for instance, two particles. Or each part may be a set of particles. It does not matter. When a system is divided in two, we call it a **bipartite system**. Suppose system A has a certain basis set $|a\rangle$ spanning a Hilbert space \mathscr{H}_A , whereas B has a basis $|b\rangle$ for the Hilbert space \mathscr{H}_B . As we learned in Sec. 1.3, when we work with the two systems combined, we can use as basis kets the Kronecker product

$$|a,b\rangle = |a\rangle \otimes |b\rangle \tag{2.9}$$

This is just like the $|\sigma_1, \sigma_2\rangle$ in Sec. 1.3, only a bit more general. The state $|a, b\rangle$ lives in the product space $\mathscr{H}_{AB} = \mathscr{H}_A \otimes \mathscr{H}_B$.

Now let us study the trace of operators that act on \mathscr{H}_{AB} . The most general such operator may always be written as

$$\mathcal{O} = \sum_{\alpha} A_{\alpha} \otimes B_{\alpha} \tag{2.10}$$

for some index α and some set of operators A_{α} and B_{α} . For instance, in Sec. 1.3 we saw the operator $\sigma_A \cdot \sigma_B$, which had exactly this form. In order not to complicate things, we start with an operator of the form $\mathcal{O} = A \otimes B$. To find its trace, we may use the $|a, b\rangle$ basis:

$$\operatorname{tr}(\mathcal{O}) = \sum_{a,b} \langle a, b | \mathcal{O} | a, b \rangle$$
(2.11)

Expanding out the krons we get

$$\operatorname{tr}(\mathcal{O}) = \sum_{a,b} (\langle a | \otimes \langle b |)(A \otimes B)(|a\rangle \otimes |b\rangle)$$
$$= \sum_{a,b} \langle a | A | a \rangle \otimes \langle b | B | b \rangle$$
$$= \sum_{a} \langle a | A | a \rangle \sum_{b} \langle b | B | b \rangle$$

I got rid of the \otimes in the last line because the kron of two numbers is a number. The two terms in this formula are simply the trace of the operators A and B in their respective Hilbert spaces. Whence, we conclude that

$$\operatorname{tr}(A \otimes B) = \operatorname{tr}(A)\operatorname{tr}(B)$$
(2.12)

Now we can imagine an operation where we only trace over a part of the system. This is what we call the **partial trace**. It is defined as

$$\operatorname{tr}_A(A \otimes B) = \operatorname{tr}(A)B, \qquad \operatorname{tr}_B(A \otimes B) = A\operatorname{tr}(B)$$
 (2.13)

When you "trace over A", you eliminate the variables pertaining to A and what you get left is an operator acting only on \mathscr{H}_B . This is something we often forget, so please pay attention: the result of a partial trace is still an operator. More generally, for an arbitrary operator \mathcal{O} as defined in Eq. (2.10), we have

$$\operatorname{tr}_{A} \mathcal{O} = \sum_{\alpha} \operatorname{tr}(A_{\alpha}) B_{\alpha} \qquad \operatorname{tr}_{B} \mathcal{O} = \sum_{\alpha} A_{\alpha} \operatorname{tr}(B_{\alpha})$$
(2.14)

As an example, suppose we have two spins, with Pauli operators σ_A^i and σ_B^i . Then we would have, for instance,

$$\operatorname{tr}_A(\sigma_A^x \sigma_B^x) = \operatorname{tr}(\sigma_x) \sigma_B^x$$

Note how in the right-hand side I write σ_x instead of σ_B^x . The partial trace acts only on the single-spin subspace, so it does not matter which notation I use. Of course, this example I just gave is a bit silly because $\operatorname{tr}(\sigma_x) = 0$. But still, you get the idea. As another example, consider the partial trace of $\sigma_A \cdot \sigma_B$. To compute it we need to use the linearity of the trace:

$$\operatorname{tr}_A(\boldsymbol{\sigma}_A \cdot \boldsymbol{\sigma}_B) = \operatorname{tr}(\sigma_x)\sigma_B^x + \operatorname{tr}(\sigma_y)\sigma_B^y + \operatorname{tr}(\sigma_z)\sigma_B^z$$

Again, all terms are zero in the end. In principle every operator may be written in the form (2.10) so linearity solves all problems. However, that does not mean that writing down such an expansion is easy. For instance, suppose you want to compute the partial trace of $e^{\sigma_A \cdot \sigma_B}$. This turns out to be a quite clumsy calculation. For two spin 1/2 particles the matrices will be 4×4 , so albeit clumsy, this is something a computer can readily do. For N spin 1/2 particles things become more difficult.

We can also write down the partial trace in terms of components. For instance, the partial trace over B reads:

$$\operatorname{tr}_{B} \mathcal{O} = \sum_{b} \langle b | \mathcal{O} | b \rangle \tag{2.15}$$

This notation may be a bit confusing at first. Actually, when we write $|b\rangle$ here, what we really mean is $1 \otimes |b\rangle$. So the full formula would be

$$\operatorname{tr}_{B} \mathcal{O} = \sum_{b} (1 \otimes \langle b |) \mathcal{O}(1 \otimes |b\rangle)$$
(2.16)

We can check that this works using $\mathcal{O} = A \otimes B$. We then get

$$\operatorname{tr}_{B} \mathcal{O} = \sum_{b} (1 \otimes \langle b |) (A \otimes B) (1 \otimes |b\rangle)$$
$$= \sum_{b} (1A1) \otimes (\langle b | B | b\rangle)$$
$$= A \sum_{b} \langle b | B | b\rangle$$
$$= A \operatorname{tr}(B)$$

Eq. (2.15) with $1 \otimes |b\rangle$ is a convenient way to implement the partial trace in a computer.

Finally we could also write down a general formula for the partial trace in terms of the components of \mathcal{O} in a basis. To do that, note that we may always insert two identities to decompose \mathcal{O} as

$$\mathcal{O} = \sum_{a,b,a',b'} |a,b\rangle \langle a,b|\mathcal{O}|a',b'\rangle \langle a',b'|$$
(2.17)

To perform the partial trace over B, for instance, we sum over the diagonal entries of the B part (b' = b):

$$\operatorname{tr}_{B} \mathcal{O} = \sum_{a,b,a'} |a\rangle \langle a, b| \mathcal{O} |a', b\rangle \langle a'|$$
(2.18)

The result is an operator acting on \mathscr{H}_A , which we can see from the fact that this is a sum of outer products of the form $|a\rangle\langle a'|$. To make that more transparent, we can factor the sum over b and write

$$\operatorname{tr}_{B} \mathcal{O} = \sum_{a,a'} \left[\sum_{b} \langle a, b | \mathcal{O} | a', b \rangle \right] |a\rangle \langle a'|$$
(2.19)

An example that is often encountered is the partial trace of some outer product, such as $|a,b\rangle\langle a',b'|$. To take the partial trace, remember that this can be written as

$$|a,b\rangle\langle a',b'| = |a\rangle\langle a'|\otimes |b\rangle\langle b'|$$

The partial trace over B, for instance, will simply go right through the first part and act only on the second part; i.e.,

$$\operatorname{tr}_{B}|a,b\rangle\langle a',b'| = |a\rangle\langle a'|\operatorname{tr}\left\{|b\rangle\langle b'|\right\}$$
$$= |a\rangle\langle a'|\left\{\langle b'|b\rangle\right\}$$

Thus, we conclude that

$$\operatorname{tr}_{A}|a,b\rangle\langle a',b'| = \delta_{a,a'}|b\rangle\langle b'|, \qquad \operatorname{tr}_{B}|a,b\rangle\langle a',b'| = |a\rangle\langle a'|\delta_{b,b'}$$
(2.20)

2.2 The density matrix

A ket $|\psi\rangle$ is actually not the most general way of defining a quantum state. To motivate this, consider the state $|g_n\rangle$ in Eq. (1.42) and the corresponding expectation values computed in Eq. (1.44). The spin in this state always points somewhere: it points at the direction n of the Bloch sphere. It is never possible to find a quantum ket $|\psi\rangle$ where all spin components are zero on average; ie, where the spin is isotropic. That sounds strange since, if we put the spin in a high temperature oven without any magnetic fields, then we certainly expect that it will never have a preferred magnetization direction. The solution to this paradox is that, when we put a spin in an oven, we are actually adding a classical uncertainty to the problem, whereas kets are only able to encompass quantum uncertainty.

The most general representation of a quantum system is written in terms of an operator ρ called the *density operator*, or *density matrix*. It is built in such a way that it naturally encompasses both quantum and classical probabilities. This is very important for quantum statistical mechanics since finite temperature states mix both. The need for a density operator is also closely related to the notion of **entanglement**, as will be discussed below.

The density matrix from classical probabilities

Suppose we have an apparatus which prepares quantum systems in certain states. For instance, this could be an oven producing spin 1/2 particles, or a quantum optics setup producing photons. But suppose that this apparatus is imperfect, so it does not always produces the same state. That is, suppose that it produces a state $|\psi_1\rangle$ with a certain probability q_1 or a state $|\psi_2\rangle$ with a certain probability q_2 and so on. Notice how we are introducing here a *classical uncertainty*. We can have as many q's as we want. All we assume is that they behave like classical probabilities:

$$q_i \in [0, 1],$$
 and $\sum_i q_i = 1$ (2.21)

Now let A be an observable. If the state is $|\psi_1\rangle$, then the expectation value of A will be $\langle \psi_1 | A | \psi_1 \rangle$. But if it is $|\psi_2\rangle$ then it will be $\langle \psi_2 | A | \psi_2 \rangle$. To compute the actual expectation value of A we must therefore perform an average of quantum averages:

$$\langle A \rangle = \sum_{i} q_i \langle \psi_i | A | \psi_i \rangle \tag{2.22}$$

What is important to realize is that this type of average *cannot* be writen as $\langle \phi | A | \phi \rangle$ for some ket $| \phi \rangle$. If we want to attribute a "state" to our system, then we must generalize the idea of ket. To do that, we use Eq. (2.7) to write

$$\langle \psi_i | A | \psi_i \rangle = \mathrm{tr} \left[A | \psi_i \rangle \langle \psi_i | \right]$$

Then Eq. (2.22) may be written as

$$\langle A \rangle = \sum_{i} q_{i} \operatorname{tr} \left[A |\psi_{i}\rangle \langle \psi_{i}| \right] = \operatorname{tr} \left\{ A \sum_{i} q_{i} |\psi_{i}\rangle \langle \psi_{i}| \right\}$$

This motivates us to define the **density matrix** as

$$\rho = \sum_{i} q_i |\psi_i\rangle \langle \psi_i| \tag{2.23}$$

Then we may finally write Eq. (2.22) as

$$\langle A \rangle = \operatorname{tr}(A\rho)$$
 (2.24)

which, by the way, is the same as $tr(\rho A)$ since the trace is cyclic [Eq. (2.5)].

Instead of working with kets, we may now start to work only with density matrices. In fact, the density matrix is the actual general quantum state. Whenever a density matrix can be writte as $\rho = |\psi\rangle\langle\psi|$, we say we have a **pure state**. In this case Eq. (2.24) reduces to the usual result: $\langle A \rangle = \langle \psi | A | \psi \rangle$. A state which is not pure is usually called a **mixed state**.

The density matrix and entanglement

We will discuss entanglement in more detail in the next section. For now, a short introduction will suffice. Suppose we have a bipartite system and, for simplicity, assume that the two parts are identical. Let $|i\rangle$ denote a basis for any such part and assume that the composite system is in a state of the form

$$|\psi\rangle = \sum_{i} c_{i} |i\rangle \otimes |i\rangle \tag{2.25}$$

for certain coefficients c_i .¹ If $c_1 = 1$ and all other $c_i = 0$ then $|\psi\rangle = |i\rangle \otimes |i\rangle$ becomes a **product state**. When more than one c_i is non-zero, then the state can never be written as a product. Whenever a state of a bipartite system cannot be written as a product state, we say it is **entangled**.

 $^{^{1}}$ At first this may seem like a restrictive choice. However, as we will discuss in the next section, it turns out that any state of the composite system can always be written in this way.

The expectation value of some operator A that acts only on the first system is, by definition,

$$\langle A \rangle = \langle \psi | (A \otimes 1) | \psi \rangle \tag{2.26}$$

where, just for caution, I wrote $A \otimes 1$ to emphasize that $|\psi\rangle$ is actually a state in \mathscr{H}_{AB} . Carrying out the calculation we get:

$$egin{aligned} &\langle A
angle &= \sum_{i,j} c_i^* c_j \langle i,i | (A \otimes 1) | j,j
angle \ &= \sum_{i,j} c_i^* c_j \langle i | A | j
angle \langle i | j
angle \ &= \sum_i |c_i|^2 \langle i | A | i
angle \end{aligned}$$

This result is quite remarkable. Note how it has *exactly* the same form as Eq. (2.22), even though we have *no* classical probabilities at play here (we started with a pure state). We could then define a density matrix, exactly as before:

$$\rho = \sum_{i} |c_i|^2 |i\rangle \langle i| \tag{2.27}$$

In general, therefore, we find that the reduced state of a bipartite system will be a mixed state. The only exception is when the state is a product state; ie, when the two systems are not entangled. In this case $\rho = |i\rangle\langle i|$. We thus reach the following important conclusion: when a bipartite system is entangled, the reduced states of each sub-systems will be mixed states.

Examples

Consider again spin 1/2 systems. Suppose that the system is in a pure state characterized by the ket $|x_+\rangle = \frac{1}{\sqrt{2}}(1,1)$, which is the eigenvector of σ_x with eigenvalue +1. The corresponding density matrix will be

$$\rho = |x_+\rangle\langle x_+| = \frac{1}{2} \begin{pmatrix} 1\\1 \end{pmatrix} \begin{pmatrix} 1 & 1 \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 & 1\\1 & 1 \end{pmatrix}$$

We may now use Eq. (2.24) to compute some expectation values (of course, in this case, we could also use $\langle x_+ | \mathcal{O} | x_+ \rangle$). We will find that $\operatorname{tr}(\sigma_x \rho) = 1$ and $\operatorname{tr}(\sigma_{y,z}\rho) = 0$, which makes sense. Similarly, if we consider the state $|x_-\rangle = \frac{1}{\sqrt{2}}(1,-1)$, which is the eigenstate of σ_x with eigenvalue -1, then the corresponding density matrix will be

$$\rho = |x_{-}\rangle\langle x_{-}| = \frac{1}{2} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \begin{pmatrix} 1 & -1 \end{pmatrix} = \frac{1}{2} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}$$

In this state we have $\langle \sigma_x \rangle = -1$.

Now consider a 50-50 mixture of these two states:

$$\rho = \frac{1}{2} |x_+\rangle \langle x_+| + \frac{1}{2} |x_-\rangle \langle x_-| = \frac{1}{2} \begin{pmatrix} 1 & 0\\ 0 & 1 \end{pmatrix}$$

This state has $\langle \sigma_x \rangle = \langle \sigma_y \rangle = \langle \sigma_z \rangle = 0$. It is fully isotropic, with no preferred spin direction. We may also reach the same state if we consider a 50-50 mixture of $|+\rangle$ and $|-\rangle$ (the σ_z eigenstates):

$$\rho = \frac{1}{2} |+\rangle \langle +| + \frac{1}{2} |-\rangle \langle -| = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Even though the states we started with are different, the final density matrix is the same: a 50-50 mixture of $|x_{\pm}\rangle$ gives the same *quantum state* as a 50-50 mixture of $|\pm\rangle$. This example shows us that there is more than one way to decompose a certain ρ in the form (2.23) (actually, there are an infinite number of ways).

Properties of the density matrix

The density matrix satisfies a bunch of very special properties. We can figure them out using only the definition (2.23) and recalling that $q_i \in [0, 1]$ and $\sum_i q_i = 1$ [Eq. (2.21)]. First, the density matrix is a Hermitian operator:

$$\rho^{\dagger} = \rho \tag{2.28}$$

Second,

$$\operatorname{tr}(\rho) = \sum_{i} q_{i} \operatorname{tr}(|\psi_{i}\rangle\langle\psi_{i}|) = \sum_{i} q_{i}\langle\psi_{i}|\psi_{i}\rangle = \sum_{i} q_{i} = 1$$
(2.29)

This is the *normalization* condition of the density matrix. You can also see this directly from Eq. (2.24) by choosing A = 1 (the identity operator). Then, since $\langle 1 \rangle = 1$ we get again $\operatorname{tr}(\rho) = 1$. Third, ρ is **positive semi-definite**. What this means is that the sandwich of ρ in any quantum state is always non-negative. In symbols, if $|\phi\rangle$ is an arbitrary quantum state then

$$\langle \phi | \rho | \phi \rangle = \sum_{i} q_{i} |\langle \phi | \psi_{i} \rangle|^{2} \ge 0$$
(2.30)

These are the two defining properties of a density operator: it normalizes to one and is positive semi-definite. We usually write the latter symbolically as $\rho \ge 0$. Thus:

Defining properties of a density matrix:
$$\operatorname{tr}(\rho) = 1$$
 and $\rho \ge 0$

$$(2.31)$$

We also see from Eq. (2.30) that $\langle \phi | \rho | \phi \rangle$ is a sum of quantum probabilities $|\langle \phi | \psi_i \rangle|^2$ averaged by classical probabilities q_i . This entails the following interpretation: for an arbitrary state $|\phi\rangle$,

 $\langle \phi | \rho | \phi \rangle = {\rm Prob.}$ of finding the system at state $| \phi \rangle$ given that it's state is ρ

(2.32)

Now let's talk about eigenvalues and eigenvectors. In Eq. (2.23) it already looks as if ρ is in diagonal form [cf. Eq. (1.13)]. However, we need to be a bit careful because the $|\psi_i\rangle$ are arbitrary states and do not necessarily form a basis. Thus, in general, the diagonal structure of ρ will be different. Notwithstanding, ρ is Hermitian and may therefore be diagonalized by some orthonormal basis $|k\rangle$ as

$$\rho = \sum_{k} p_k |k\rangle \langle k| \tag{2.33}$$

for certain eigenvalues p_k . Since Eq. (2.30) must be true for any state $|\phi\rangle$ we may choose, in particular, $|\phi\rangle = |k\rangle$, which gives

$$p_k = \langle k | \rho | k \rangle \ge 0$$

This is another way of stating that an operator is positive semi-definite: its eigenvalues are non-negative. In addition to this, we also have that $tr(\rho) = 1$, which implies that $\sum_k p_k = 1$. Thus we conclude that the eigenvalues of ρ behave like probabilities:

$$p_k \in [0,1], \qquad \sum_k p_k = 1$$
 (2.34)

Next let us look at ρ^2 . The eigenvalues of this matrix are p_k^2 so

$$\operatorname{tr}(\rho^2) = \sum_k p_k^2 \le 1$$
 (2.35)

The only case when $\operatorname{tr}(\rho^2) = 1$ is when ρ is a pure state. In that case it can be written as $\rho = |\psi\rangle\langle\psi|$ so it will have one eigenvalue $p_1 = 1$ and all other eigenvalues equal to zero. Hence, the quantity $\operatorname{tr}(\rho^2)$ represents the **purity** of the quantum state. When it is 1 the state is pure. Otherwise, it will be smaller than 1:

$$Purity := tr(\rho^2) \le 1 \tag{2.36}$$

There are three absolutely equivalent ways of determining whether a state is pure: (i) $\rho = |\psi\rangle\langle\psi|$; (ii) $\rho^2 = \rho$ (which is a direct consequence of (i)) and (iii) $\operatorname{tr}(\rho^2) = 1$. The last one is, perhaps, the most practical one.

As a side note, when the dimension of the Hilbert space d is finite, it also follows that $tr(\rho^2)$ will have a lower bound:

$$\frac{1}{d} \le \operatorname{tr}(\rho^2) \le 1 \tag{2.37}$$

This lower bound occurs when ρ is the maximally disordered state

$$\rho = \frac{\mathbb{I}_d}{d} \tag{2.38}$$

where \mathbb{I}_d is the identity matrix of dimension d.

Two-state systems

For a spin 1/2 or two-state system, the most general density matrix may be written as

$$\rho = \frac{1}{2}(1 + \boldsymbol{s} \cdot \boldsymbol{\sigma}) = \frac{1}{2} \begin{pmatrix} 1 + s_z & s_x - is_y \\ s_x + is_y & 1 - s_z \end{pmatrix}$$
(2.39)

where $\mathbf{s} = (s_x, s_y, s_z)$ is a vector. The physical interpration of \mathbf{s} becomes evident from the following relation, which I leave for you to check:

$$s_i = \operatorname{tr}(\sigma_i \rho) \tag{2.40}$$

Looking at Eq. (2.39) we can see that $tr(\rho) = 1$ since we just need to sum the diagonal entries. Moreover, a straightforward calculation shows that

$$\operatorname{tr}(\rho^2) = \frac{1}{2}(1+s^2) \tag{2.41}$$

Thus, due to Eq. (2.35), it also follows that

$$s^2 = s_x^2 + s_y^2 + s_z^2 \le 1 \tag{2.42}$$

When $s^2 = 1$ we are in a pure state. In this case the vector s lays on the surface of the Bloch sphere. For mixed states $s^2 < 1$ and the vector is inside the Bloch sphere. The maximally disordered state occurs when s = 0.

The von Neumann equation

The time evolution of any ket $|\psi\rangle$ under unitary dynamics is given by Eq. (1.16): $|\psi(t)\rangle = e^{-iHt}|\psi(0)\rangle$. Any density operator may be written in the form (2.23) so its time evolution will be

$$\rho(t) = \sum_{i} q_i e^{-iHt} |\psi_i(0)\rangle \langle \psi_i(0)| e^{iHt} = e^{-iHt} \rho(0) e^{iHt}$$

Differentiating with respect to t we then get

$$\frac{d\rho}{dt} = (-iH)e^{-iHt}\rho(0)e^{iHt} + e^{-iHt}\rho(0)e^{iHt}(iH) = -iH\rho(t) + i\rho(t)H$$

Thus, we reach von Neumann's equation:

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = -i[H,\rho], \qquad \rho(t) = e^{-iHt}\rho(0)e^{iHt}$$
(2.43)

This is somewhat similar to Heisenberg's equation (1.22), except for a minus sign.

We can still define the Heisenberg picture for density matrices. For instance, the expectation value of an operator is $\langle A \rangle_t = \operatorname{tr}(A\rho(t))$. Using the cyclic property of the trace we may write this in two ways:

$$\langle A \rangle_t = \operatorname{tr} \left\{ A e^{-iHt} \rho(0) e^{iHt} \right\} = \operatorname{tr} \left\{ e^{iHt} A e^{-iHt} \rho(0) \right\}$$
(2.44)

The first way is $A\rho(t)$ and the second is $A_H(t)\rho(0)$.

2.3 Reduced density matrices and entanglement

Consider again a bipartite system AB with a certain density matrix ρ (which can be either pure or mixed). If we want, we can *trace out* one of the sub-systems to obtain a *reduced density matrix* for the other system. To do that, we simply take the partial trace (Sec. 2.1) over the system we don't want anymore:

$$\rho_A = \operatorname{tr}_B \rho, \qquad \rho_B = \operatorname{tr}_A \rho$$
(2.45)

To see where this may come in, let A be an operator acting only on \mathscr{H}_A . Its expectation value in the state ρ is, by definition $\langle A \rangle = \operatorname{tr}(A\rho)$. But this is a trace over the full Hilbert space \mathscr{H}_{AB} . Using the reduced density matrix, on the other hand, we can write down the expectation value as a trace only over \mathscr{H}_A :

$$\langle A \rangle = \operatorname{tr}(A\rho) = \operatorname{tr}_A(A\rho_A)$$
 (2.46)

The reduction operation in Eq. (2.45) can always be performed and, when dealing with operators that act only on \mathscr{H}_A or \mathscr{H}_B , it is always possible to use the reduced density matrices to compute expectation values, as in Eq. (2.46). However, please bear in mind that in general $\rho_A \otimes \rho_B \neq \rho$, so when computing expectation values of operators in \mathscr{H}_{AB} (such as, e.g., $A \otimes B$), we must use the full density matrix ρ . The test of whether $\rho_A \otimes \rho_B \neq \rho$ is also what we use to define the **correlation** between two systems:

If
$$\rho_A \otimes \rho_B = \rho$$
 then A and B are uncorrelated (2.47)

This follows a logic similar to classical probability theory. However, unlike classical probability theory, correlation for quantum systems may be either of classical or quantum origin. Quantum correlations is what we call *entanglement*. Below we will learn how to distinguish the two. Another thing that you should bear in mind is that taking the partial trace is, in general, an *irreversible* operation in the sense that in general you cannot reconstruct ρ from ρ_A and ρ_B . Putting it differently, *information is generally lost* when taking the partial trace.

Example

As an example suppose that we have two spin 1/2 particles in a singlet state

$$|\psi\rangle = \frac{|+-\rangle - |-+\rangle}{\sqrt{2}} \tag{2.48}$$

In this state we have $\langle \sigma_{\alpha}^i \rangle = 0$ for $\alpha \in \{A, B\}$ and $i \in \{x, y, z\}$. However, one may verify that, for instance, $\langle \sigma_A^z \sigma_B^z \rangle = -1$. This immediately means that the two particles are correlated. For, if they were not, we would have $\langle \sigma_A^z \sigma_B^z \rangle = \langle \sigma_A^z \rangle \langle \sigma_B^z \rangle$. Since the state (2.48) is a pure state, all correlation must be of quantum origin; ie, entanglement.

Let us compute the reduced density of system A. To do that we first write the full density matrix

$$\rho = |\psi\rangle\langle\psi| = \frac{1}{2} \bigg\{ |+-\rangle\langle+-|+|-+\rangle\langle-+|-|+-\rangle\langle-+|-|-+\rangle\langle+-|\bigg\}$$

Now we use Eq. (2.20) to get

$$\rho_A = \operatorname{tr}_B \rho = \frac{1}{2} \left\{ |+\rangle \langle +|+|-\rangle \langle -| \right\} = \frac{\mathbb{I}_2}{2}$$
(2.49)

By symmetry, ρ_B will be exactly the same. We can therefore readily see that $\rho_A \otimes \rho_B$ will be a diagonal operator, whereas ρ is clearly not diagonal. Whence, $\rho_A \otimes \rho_B \neq \rho$, as expected. Also note that, if we use $\rho_A \otimes \rho_B$ to compute $\langle \sigma_A^z \sigma_B^z \rangle$ we will get zero, even though the actual result is -1.

Entanglement

The most general pure state of a bipartite system may be written as

$$|\psi\rangle = \sum_{a,b} C_{a,b} |a\rangle \otimes |b\rangle \tag{2.50}$$

for certain coefficients $C_{a,b}$. A particular case of this state is when the coefficients $C_{a,b}$ can be written as a product: $C_{a,b} = f_a g_b$. In this case the state $|\psi\rangle$ will factor as

$$|\psi\rangle = \left[\sum_{a} f_{a}|a\rangle\right] \otimes \left[\sum_{b} g_{b}|b\rangle\right] := |\psi_{a}\rangle \otimes |\psi_{b}\rangle$$
(2.51)

which is a **product state**. It is what you expect to happen when sub-system 1 is in Tokyo and sub-system 2 is in Aruba (specially if they are on vacation). When a state cannot be written as a product state (ie, when $C_{a,b}$ cannot be factored as a product) we say the two sub-systems are **entangled**. This is how we define entanglement for pure states. The definition for mixed states will be discussed below.

Now let us compute the reduced density matrix of system A:

$$\rho_{A} = \operatorname{tr}_{B}(|\psi\rangle\langle\psi|)$$

$$= \operatorname{tr}_{B}\sum_{a,b}\sum_{a',b'}C_{a,b}^{*}C_{a',b'}\left[|a\rangle\otimes|b\rangle\right]\left[\langle a'|\otimes\langle b'|\right]$$

$$=\sum_{a,b}\sum_{a',b'}C_{a,b}^{*}C_{a',b'}\left[|a\rangle\langle a'|\right]\otimes\underbrace{\left[\operatorname{tr}_{B}|b\rangle\langle b'|\right]}_{\delta_{b,b'}}$$

$$=\sum_{a,a'}\left[\sum_{b}C_{a,b}^{*}C_{a',b}\right]|a\rangle\langle a'| \qquad (2.52)$$

This is in general a mixed state. The only exception is again when $C_{a,b} = f_a g_b$. Due to normalization we must have $\sum_b |g_b|^2 = 1$ so, in this case, ρ_A becomes

$$\rho_A = \sum_{a,a'} f_a^* f_{a'} |a\rangle \langle a'| = \left[\sum_a f_a^* |a\rangle\right] \left[\sum_{a'} f_{a'} \langle a'|\right] = |\psi_a\rangle \langle \psi_a|$$

Thus, entanglement means that the reduced density matrices will be in mixed states. We of course already seen this from the previous section. This is just a different way to do the same calculation.

The Schmidt decomposition

The Schmidt decomposition is a way of writing the general state (2.50) in a cleaner way, which will make the physics of entanglement more transparent [the final result will have the form (2.25)]. The basic idea is to note that the coefficients $C_{a,b}$ may be interpreted as forming a matrix (which will be rectangular if \mathscr{H}_A and \mathscr{H}_B are of different dimensions). Any rectangular matrix may be decomposed in the so-called **Singular Value Decomposition (SVD)**:

$$C = U\Sigma V^{\dagger} \tag{2.53}$$

where U and V are unitary matrices and

$$\Sigma = \operatorname{diag}(\sigma_1, \sigma_2, \dots, \sigma_r, 0, 0, \dots)$$

The quantities σ_i are called the singular values of the matrix and they are always non-negative: $\sigma_i > 0.^2$ The number of non-zero σ_i , which I denoted by r, is called the *Schmidt rank*. I will not discuss here how to compute the SVD in practice. It is an operation that is seldom done analytically, but it is implemented in any linear algebra library you can imagine.

Inserting the SVD (2.53) into Eq. (2.50) we get

$$|\psi\rangle = \sum_{a,b} \sum_{i} (U_{a,i}\sigma_i V_{b,i}^*) |a\rangle \otimes |b\rangle$$

Now define

$$|i_A\rangle = \sum_a U_{a,i} |a\rangle, \qquad \quad |i_B\rangle = \sum_b V_{b,i}^* |b\rangle$$

Moreover (just for convenience) define the *Schmidt coefficients* $\lambda_i = \sigma_i^2$. Then we may finally write the state (2.50) as

$$|\psi\rangle = \sum_{i=1}^{r} \sqrt{\lambda_i} |i_A\rangle \otimes |i_B\rangle \tag{2.54}$$

The vectors $|i_A\rangle$ and $|i_B\rangle$ are orthonormal due to the unitarity of U and V. Moreover, since the state $|\psi\rangle$ must be normalized, it follows that

$$\sum_{i} \lambda_i = 1 \tag{2.55}$$

If the Schmidt rank is r = 1 (i.e., if there is only one non-zero λ_i) then the state is a product state (no entanglement). Otherwise, the two systems are entangled. The Schmidt rank therefore characterizes entanglement. We used this in the previous section in the context of Eq. (2.25).

Now let us compute the reduced density matrix of sub-systems A and B. Following the exact same procedure as above, we get

$$\rho_A = \operatorname{tr}_B |\psi\rangle\langle\psi| = \sum_i \lambda_i |i_A\rangle\langle i_A| \qquad (2.56)$$

$$\rho_B = \operatorname{tr}_A |\psi\rangle\langle\psi| = \sum_i \lambda_i |i_B\rangle\langle i_B| \qquad (2.57)$$

We see that the Schmidt coefficients play the role of the probabilities for the two reduced density matrices. Moreover, the purity of these reduced density

²In general the singular value decomposition has no relation whatsoever with the eigendecomposition of a matrix. The only exception is for Hermitian positive semi-definite matrices (like density matrices) for which the two coincide.

matrices turn out to be equal and have the value:

purity = tr
$$\rho_A^2$$
 = tr ρ_B^2 = $\sum_i \lambda_i^2$ (2.58)

They therefore serve as a way to characterize the degree of entanglement: if the two systems are not entangled then $\lambda_1 = 1$ and all other $\lambda_i = 0$. In this case the purity is 1. The distance from 1 therefore quantifies the degree of entanglement. Highly entangled states lead to highly impure reduced density matrices. The maximally entangled state is obtained by making the purity as small as possible. For simplicity assume both systems have dimension d. Then the maximally entangled state will occur when r = d and $\lambda_i = 1/d$. In this case the purity will be 1/d. The state (2.48) is an example of a maximally entangled state.

The purity is not the only measure of entanglement. Usually, entanglement is quantified using *entropies*, as we will discuss in the next section. But it turns out that the purity is related to the so-called Rényi-2 entropy so in essence, characterizing the entanglement by the purity is the same as characterizing by an entropy.

State purification

The Schmidt decomposition is also closely related to the idea of *state purification*. Consider a physical system A described by a general mixed state ρ_A with diagonal form

$$\rho = \sum_{a} p_{a} |a\rangle \langle a|$$

Purification is a method to write this mixed state as a pure state in a larger Hilbert space. That is, we expand the Hilbert space and in this larger space we have more room to work with, so we can write a mixed state as a pure state. There is more than one way of purifying a state. The simplest is to introduce an auxiliary system R which is an exact copy of A. We then define the pure state

$$|\psi\rangle = \sum_{a} \sqrt{p_a} |a\rangle \otimes |a\rangle \tag{2.59}$$

Then, tracing over R we get

$$\operatorname{tr}_{R}|\psi\rangle\langle\psi|=\rho\tag{2.60}$$

Thus, $|\psi\rangle$ is a purified version of ρ , which lives in a doubled Hilbert space. Notice how the probabilities p_a appear naturally here as the Schmidt coefficients.

As an example, consider the general two-state density matrix in Eq. (2.39). Let |s| = s and write s = sn, where n is a unit vector. Recall that $s \leq 1$, with s = 1 for a pure state. As we have seen in Eq. (1.49), the matrix $n \cdot \sigma$ can be diagonalized by the matrix G defined in Eq. (1.48). Thus we may write Eq. (2.39) as

$$\rho = G\left(\frac{1+s\sigma_z}{2}\right)G^{\dagger} \tag{2.61}$$

This shows that the eigenvalues of ρ are $p_1 = (1+s)/2$ and $p_2 = (1-s)/2$, with eigenvectors $|g_n\rangle$ and $|g'_n\rangle$, as defined in Eqs. (1.42) and (1.47). That is

$$\rho = \frac{(1+s)}{2} |g_{\boldsymbol{n}}\rangle \langle g_{\boldsymbol{n}}| + \frac{(1-s)}{2} |g_{\boldsymbol{n}}'\rangle \langle g_{\boldsymbol{n}}'|$$
(2.62)

When s = 1 the state becomes pure and $\rho = |g_n\rangle\langle g_n|$. Otherwise, the state is mixed. This density matrix is already in Schmidt form, so the corresponding purified state is readily found to be

$$|\psi\rangle = \sqrt{\frac{1+s}{2}} |g_{\boldsymbol{n}}\rangle \otimes |g_{\boldsymbol{n}}\rangle + \sqrt{\frac{1-s}{2}} |g_{\boldsymbol{n}}'\rangle \otimes |g_{\boldsymbol{n}}'\rangle$$
(2.63)

Classical correlations

We have just learned that there is a concrete recipe for quantifying the entanglement between two systems when they are in a pure state. Things become much more difficult if their state is mixed. For, in that case, they may also have some degree of classical correlation and separating the classical and quantum contributions is usually very difficult.³ The total degree of correlation (irrespective of whether it is quantum or classical) can be quantified by something called the **quantum mutual information**, that will be introduced in Sec. 2.4. But separating the two is not at all trivial.

A density matrix is termed **separable** if it can be written as

$$\rho = \sum_{k} p_{k} |\phi_{k}\rangle \langle \phi_{k}| \otimes |\psi_{k}\rangle \langle \psi_{k}|$$
(2.64)

for certain probabilities p_k adding up to 1. A separable density matrix is a linear combination of product states and hence is not entangled. Putting it differently, for a separable density matrix, all correlation is classical. We have therefore seen two particular cases of a general density matrix: when it is a pure state, all the correlation is quantum (entanglement). When it is separable, all the correlation is classical. In between there will be a messy mixture of the two. Quantifying the degree of entanglement of a bipartite system in a mixed state is not at all trivial. Different criteria are used in different contexts and the calculations are usually quite difficult. We will not discuss this further here.

 $^{^{3}}$ In quantum information processing, there is a discussion that even for pure state only half of the correlations are quantum, with the other half being classical. Here I will not make this distinction and simply call "quantum correlations" the entanglement of pure states.

2.4 Entropies and mutual information

A quantity which appears throughout all of statistical mechanics and quantum information is the von Neumann entropy, defined as

$$S = -\operatorname{tr}(\rho \ln \rho) \tag{2.65}$$

It is a little bit awkward to work with the log of an operator. The best way to operate with it is by working in a basis where ρ is diagonal. Recall that if $f(\rho)$ is an arbitrary function of ρ and if p_k are the eigenvalues of ρ , then the eigenvalues of $f(\rho)$ will be $f(p_k)$. Thus, using the basis $|k\rangle$ to take the trace in (2.65) gives

$$S = -\sum_{k} p_k \ln(p_k) \tag{2.66}$$

In information theory this is also called the **Shannon entropy** (they usually use the log in base 2, but the idea is the same).

The entropy is seen to be a sum of functions of the form $-p\ln(p)$, where $p \in [0, 1]$. The behavior of this function is shown in Fig. 2.1. It tends to zero both when $p \to 0$ and $p \to 1$, and it has a maximum at p = 1/e. Hence, any state which has $p_k = 0$ or $p_k = 1$ will not contribute to the entropy. The entropy does not like certainty. It feeds on randomness.

Since each $-p\ln(p)$ is always non-negative, the same must be true for S:

$$S \ge 0 \tag{2.67}$$

Moreover, if the system is in a pure state $(\rho = |\psi\rangle\langle\psi|)$ then it will have one eigenvalue $p_1 = 1$ and all others zero. Consequently, in a pure state the entropy will be zero:

In information theory the quantity $-\ln(p_k)$ is sometimes called the *surprise*. When an "event" is rare $(p_k \sim 0)$ this quantity is big and when an event is common $(p_k \sim 1)$ this quantity is small. The entropy is then interpreted as the *average surprise* of the system. I think this is funny. But maybe I am just immature.

As we have just seen, the entropy is bounded below from 0. Now we will show that when the dimension d of the Hilbert space is finite, the entropy will also be bounded above by $\ln(d)$. To show this we need to maximize Eq. (2.66) with respect to the p_k . But that must be done carefully since the maximization must always be subject to the constraint $\sum_k p_k = 1$. Thus, we should introduce



Figure 2.1: The function $-p \ln(p)$, corresponding to each term in the von Neumann entropy (2.66).

a Lagrange multiplier and redefine

$$S' = -\sum_{k} p_k \ln(p_k) + \alpha \left(1 - \sum_{k} p_k\right)$$

Then the condition $\partial S'/\partial \alpha = 0$ guarantees that $\sum_k p_k = 1$. As for the other derivatives, we get

$$\frac{\partial S'}{\partial p_k} = -\ln(p_k) - 1 - \alpha = 0$$

This shows that all p_k must be equal to a constant. By normalization, this constant must be 1/d; that is we will have all $p_k = 1/d$. The corresponding entropy will then be

$$S = -\frac{1}{d}\ln(1/d)\sum_{k}(1) = \ln(d)$$

Thus, we conclude that

$$\max(S) = \ln(d).$$
 Occurs when $p_k = \frac{1}{d}$ (2.69)

The entropy is maximum for the maximally disordered state. Whence, we conclude that the entropy varies between 0 for pure states and $\ln(d)$ for maximally disordered states. It therefore serves as a measure of how disordered (mixed) is a state.

Another special property of the von Neumann entropy is that it is invariant under unitary transformations $\rho \to U\rho U^{\dagger}$. To see this note that, since $UU^{\dagger} = 1$, it follows that $U\rho^2 U^{\dagger} = (U\rho U^{\dagger})(U\rho U^{\dagger})$ and similarly for higher powers of ρ . This means that, for any function that can be written as a power series in ρ , we will have $f(U\rho U^{\dagger}) = Uf(\rho)U^{\dagger}$. Thus, using also the cyclic property of the trace, we get

$$\operatorname{tr}\left[U\rho U^{\dagger}\ln(U\rho U^{\dagger})\right] = \operatorname{tr}\left[U\rho U^{\dagger}U(\ln\rho)U^{\dagger}\right] = \operatorname{tr}(\rho\ln\rho)$$

which shows that

$$S(U\rho U^{\dagger}) = S(\rho) \tag{2.70}$$

The most important such transformation is unitary time-evolution with $U = e^{-iHt}$ [Eq. (2.43)]. Our result then shows that in any closed system, the entropy is a constant of the motion. This may sound weird to you at first, because you probably heard that the entropy of a closed system can only increase. We will get to that in the next chapter.

Quantum relative entropy

Given two density matrices ρ and σ , we define their *relative entropy* or **Kullback-Leibler divergence** as

$$S(\rho||\sigma) = \operatorname{tr}\left\{\rho \ln \rho - \rho \ln \sigma\right\}$$
(2.71)

Even though it is called a relative entropy, we will learn in the next chapter that in quantum statistical mechanics this quantity is related to the relative **free energy**. The relative entropy is always non-negative and is zero only when $\rho = \sigma$:

$$S(\rho||\sigma) \ge 0, \qquad S(\rho||\sigma) = 0 \text{ iff } \rho = \sigma$$
 (2.72)

The proof of this inequality is really boring. I will give it in the end of this section but you can skip it if you want (or you can look it up on Wikipedia). This property of the relative entropy gives us the idea that we could use the relative entropy as a measure of the distance between two density matrices. But that is not actually true since the relative entropy does not satisfy the triangle inequality, something a true measure of distance must always satisfy.

Quantum mutual information

Consider again a bipartite system AB. Let ρ_{AB} be the total density matrix and ρ_A and ρ_B the reduced density matrices of each sub-systems. We have seen in the previous section that, in general $\rho_A \otimes \rho_B \neq \rho_{AB}$. In fact, when there is an equality we say the two systems are uncorrelated. The question I want to answer now is how to quantify the degree of correlation between two systems. This is done using the **quantum mutual information**. The starting point is the so-called **subadditivity condition** of the von Neumann entropy, which states that

$$S(\rho_{AB}) \le S(\rho_A) + S(\rho_B) \tag{2.73}$$

with the equality holding only when $\rho_{AB} = \rho_A \otimes \rho_B$. Saying it differently, if the two systems are independent ($\rho_{AB} = \rho_A \otimes \rho_B$) the entropy will be additive: $S(\rho_{AB}) = S(\rho_A) + S(\rho_B)$. But when they have some correlation, $S(\rho_A) + S(\rho_B) \geq S(\rho_{AB})$. We can also write this as $S(\rho_A \otimes \rho_B) \geq S(\rho_{AB})$, which has a clear physical interpretation: when we take the partial trace we *loose* information, hence increasing the entropy.

Another related result, which is straightforward to check, is that

$$S(\rho_{AB}||\rho_A \otimes \rho_B) = S(\rho_A) + S(\rho_B) - S(\rho_{AB})$$
(2.74)

This quantity therefore measures the relative information lost when taking the partial trace. The quantum mutual information is defined precisely as this quantity:

$$I(A:B) := S(\rho||\rho_A \otimes \rho_B) = S(\rho_A) + S(\rho_B) - S(\rho_{AB})$$
(2.75)

Since it is simply a relative entropy, it follows from Eq. (2.72) that

$$I(A:B) \ge 0 \tag{2.76}$$

with the equality holding only when the two sub-systems are uncorrelated $(\rho_{AB} = \rho_A \otimes \rho_B)$. The mutual information therefore measures the degree of correlation between two systems, be it of quantum or classical origin.

Rényi entropy

A generalization of the von Neumann entropy that is being used more and more each day is the so-called Rényi entropy, defined as

$$S_{\alpha}(\rho) = \frac{1}{1-\alpha} \ln \operatorname{tr} \rho^{\alpha}$$
(2.77)

where α is a tunable parameter in the range $[0, \infty)$. I particularly like $\alpha = 2$, which is simply minus the logarithm of the purity:

$$S_2(\rho) = -\ln \operatorname{tr} \rho^2 \tag{2.78}$$



Figure 2.2: The Rényi entropies for a 2-state system, computed using Eq. (2.80) for different values of α .

But, by far, the most important case is $\alpha = 1$, where we recover the von Neumann entropy. To see this, what I like to do is expand x^{α} in a Taylor series in α around $\alpha = 1$. We have the following result from introductory calculus:

$$\frac{\mathrm{d}}{\mathrm{d}\alpha}x^{\alpha} = x^{\alpha}\ln(x)$$

Thus, expanding x^{α} around $\alpha = 1$ we get:

$$x^{\alpha} \simeq x^1 + x^1 \ln(x)(\alpha - 1)$$

Now we substitute this into Eq. (2.77) to get

$$S_{\alpha}(\rho) \simeq \frac{1}{1-\alpha} \ln \left\{ \operatorname{tr} \rho + (\alpha - 1) \operatorname{tr}(\rho \ln \rho) \right\}$$
$$= \frac{1}{1-\alpha} \ln \left\{ 1 + (\alpha - 1) \operatorname{tr}(\rho \ln \rho) \right\}$$

Since we want the limit $\alpha \to 1$, we my expand the logarithm above using the formula $\ln(1+x) \simeq x$. The terms $\alpha - 1$ will then cancel out, leaving us with

$$\lim_{\alpha \to 1} S_{\alpha}(\rho) = -\operatorname{tr}(\rho \ln \rho) \tag{2.79}$$

which is the von Neumann entropy. The Rényi entropy therefore forms a family of entropies which contains the von Neumann entropy as a particular case.

To get a feeling of what we are dealing with, suppose we have a 2-state system. Since the eigenvalues of a density matrix must behave like probabilities, we may parametrize them by $p_1 = p$ and $p_2 = 1 - p$, where $p \in [0, 1]$. We then get $\operatorname{tr}(\rho^{\alpha}) = p^{\alpha} + (1 - p)^{\alpha}$ so that Eq. (2.77) becomes

$$S_{\alpha}(\rho) = \frac{1}{1-\alpha} \ln \left\{ p^{\alpha} + (1-p)^{\alpha} \right\}$$
 (2.80)

This result is plotted in Fig. 2.2 for several values of α . As can be seen, except for $\alpha \to 0$, which is crazy, the behavior of all curves is qualitatively similar.

In Eq. (2.58) we saw how to use the purity of the reduced density matrix as a measure of the entanglement of a bipartite system. But in practice, most researchers quantify entanglement using the entropy of the reduced state. The most common choice is the von Neumann entropy but, based on Fig. 2.2 we can anticipate that most Rényi entropies will give similar measures of entanglement. I like to use the Rényi-2 entropy since it is directly related to the purity and hence is very easy to calculate.

Proof that $S(\rho || \sigma) \ge 0$

Now let me prove Eq. (2.72) to you. This proof is really boring so please try not to fall asleep. We will need two inequalities. The first is very easy:

$$\ln(x) \ge 1 - \frac{1}{x} \tag{2.81}$$

This follows from the fact that $y \ge \ln y$, by making $y = \frac{1}{x} - 1$.

The second inequality is due to Jensen. Let f(x) be a convex function.⁴ It the follows that if $\lambda \in [0, 1]$,

$$f((1-\lambda)x_1 + \lambda x_2) \le (1-\lambda)f(x_1) + \lambda f(x_2) \tag{2.82}$$

The usual way of understanding this result is through a figure like Fig. 2.3. Changing λ from 0 to 1 takes $(1 - \lambda)x_1 + \lambda x_2$ linearly from x_1 to x_2 . The right-hand side of Eq. (2.83) is therefore the straight dashed line in the figure, whereas the left-hand side is the function itself. Since f(x) is convex, the line is always above the real curve. Conversely, if g(x) is a concave function, the picture is reversed and we obtain:

$$g((1-\lambda)x_1 + \lambda x_2) \ge (1-\lambda)g(x_1) + \lambda g(x_2)$$
(2.83)

Eq. (2.83) can be generalized to combinations of the form $\lambda_1 x_1 + \lambda_2 x_2 + \lambda_3 x_3 + \ldots$, provided that $\sum_n \lambda_n = 1$ and each $\lambda_n \in [0, 1]$. That is, for a convex function f(x),

$$f\left(\sum_{n}\lambda_{n}x_{n}\right) \leq \sum_{n}\lambda_{n}f(x_{n})$$
(2.84)

which is Jensen's inequality. For a concave function

$$g\left(\sum_{n}\lambda_{n}x_{n}\right) \geq \sum_{n}\lambda_{n}g(x_{n})$$
(2.85)

This formula has many uses, an important one being in probability theory. For instance, it states that

$$f(\langle \mathcal{O} \rangle) \le \langle f(\mathcal{O}) \rangle \tag{2.86}$$

⁴ Prof. Mario José de Oliveira taught me a neat mnemonic to remember the difference between convex and concave. You just need to remember that e^x is conve^x.



Figure 2.3: The graphical motivation for Jensen's inequality.

An example which appears in quantum thermodynamics is that of $\langle e^{\alpha H} \rangle$. Since $e^{\alpha E_n}$ is a convex function we must have

$$\langle e^{\alpha H} \rangle \le e^{\alpha \langle H \rangle}$$

To prove Eq. (2.72) we must be a bit careful since we have to work with the logarithm of a matrix. Let us then introduce the eigendecomposition of the two density matrices:

$$\label{eq:rho} \begin{split} \rho &= \sum_n p_n |n\rangle \langle n| \\ \sigma &= \sum_\ell q_\ell |\ell\rangle \langle \ell| \end{split}$$

The states $|n\rangle$ and $|\ell\rangle$ form two different set of basis states, with no relation whatsoever to one another. With this decomposition we may write

$$\ln \rho = \sum_{n} \ln(p_n) |n\rangle \langle n|$$
$$\ln \sigma = \sum_{\ell} \ln(q_\ell) |\ell\rangle \langle \ell|$$

which gives

$$\begin{aligned} \operatorname{tr}(\rho \ln \rho) &= \sum_{n} p_{n} \ln p_{n} \\ \operatorname{tr}(\rho \ln \sigma) &= \sum_{n} p_{n} \langle n | \ln \sigma | n \rangle = \sum_{n,\ell} p_{n} |\langle n | \ell \rangle|^{2} \ln q_{\ell} \end{aligned}$$

The relative entropy may therefore be written in components as

$$S(\rho||\sigma) = \sum_{n} p_n \left\{ \ln p_n - \sum_{\ell} |\langle n|\ell\rangle|^2 \ln q_n \right\}$$
(2.87)

The quantity $|\langle n|\ell\rangle|^2$ satisfies

$$\sum_{\ell} |\langle n|\ell\rangle|^2 = \sum_{\ell} \langle n|\ell\rangle \langle \ell|n\rangle = \langle n|n\rangle = 1$$

Hence, it has the same properties as the λ 's in Jensen's inequality (2.85). Since $\ln(x)$ is a concave function we must then have

$$\sum_{\ell} |\langle n|\ell\rangle|^2 \ln q_\ell \leq \ln \left(\sum_{\ell} |\langle n|\ell\rangle|^2 q_\ell\right)$$

Consequently,

$$S(\rho||\sigma) \ge \sum_{n} p_n \left\{ \ln p_n - \ln \left(\sum_{\ell} |\langle n|\ell \rangle|^2 q_\ell \right) \right\}$$

Let us call this sum over ℓ inside the parenthesis as $a_n = \sum_{\ell} |\langle n|\ell \rangle|^2 q_{\ell}$. It follows that $\sum_n a_n = 1$ so we may write

$$S(\rho||\sigma) \ge \sum_{n} p_n \ln\left(\frac{p_n}{a_n}\right)$$

Using Eq. (2.81) gives

$$\sum_{n} p_n \ln\left(\frac{p_n}{a_n}\right) \ge \sum_{n} p_n \left(1 - \frac{p_n}{a_n}\right) = 0$$

This is zero because both p_n and a_n add up to 1. Combining this with our previous inequality finally shows that

 $S(\rho||\sigma) \ge 0$

which is what we wanted to show in the first place. That S = 0 only when $\rho = \sigma$ follows from Eq. (2.87). The right-hand side will only be zero if $|\ell\rangle$ and $|n\rangle$ form an orthonormal basis and if $q_{\ell} = p_{\ell}$. These two requirements are tantamount to saying that $\sigma = \rho$. I just spent 3 pages on a really boring proof that can be found on Wikipedia. Should I really have done that?

Chapter 3

The Gibbs formalism

3.1 Introduction

Here is the most important result in all of equilibrium statistical mechanics: if a system with Hamiltonian H is in thermal equilibrium with a heat bath at a certain temperature T, then its density matrix will be

$$\rho = \frac{e^{-\beta H}}{Z}, \qquad Z = \operatorname{tr}(e^{-\beta H}), \qquad \beta = \frac{1}{k_B T}$$
(3.1)

This is called the **Gibbs formula** or the **canonical ensemble**. When I say it is the most important result, trust me: I am not exaggerating. The quantity Z is called the **partition function**:¹

$$Z = \operatorname{tr}(e^{-\beta H}) = \sum_{n} e^{-\beta E_{n}}$$
(3.2)

and

$$k_B = 8.6173324 \times 10^{-5} \text{ eV/K}$$
 (3.3)
= $1.38 \times 10^{-23} \text{ J/K}$

is **Boltzmann's constant**. Pieces of these results were already contemplated by Maxwell and Boltzmann, but it was Josiah Willard Gibbs, a professor at Yale, around 1902, who really saw its enormous potential and scope.² This chapter and the next contains the essential ingredients for dealing with and understanding these **thermal states**. We will go back and forth between applications and

 $^{^1}$ The use of the letter Z stems from the German word for it, "Zustandssumme", which literally means "Sum over states".

²If you want, you can read his results straight from the source: J. W. Gibbs, *Elementary Principles in Statistical Mechanics*. This book was republished by Dover so you can purchase it cheaply.

formal results which will help us justify the correctness of Eq. (3.1). Please make sure you thoroughly understand the contents of these two chapters. They will be the basis for much that follows.

The state (3.1) is the state a system will relax to when it is weakly coupled to a very large heat bath. It contains no information about *how* the system relaxes toward the thermal state (3.1), which is a much more difficult question. Moreover, the size of the system is not important (it can even be a single electron), but the bath is always a macroscopic body. If the system itself is macroscopically large then it does not really need a heat bath: you can just divide it in multiple parts and one part will play the role of the heat bath for the other part. In either case, T always represent the temperature of the bath, not the system. The system may be a single electron and you cannot define temperature for a single electron.

Eq. (3.1) holds quites generally but, of course, there are situations where it fails. Most notably, it requires the system to be *weakly coupled* to the bath. This means that the typical interaction energies be much smaller than the energies of the system. A typical example where we may run into trouble is systems with long-range interactions, like gravitational systems. The validity of Eq. (3.1) also relies on the assumption that the bath is a macroscopically large and highly complex body. This is true if your bath is a bucket of water. Sometimes, when very special baths are used, the system may relax to a so-called **Generalized Gibbs State**, which are the subject of intensive theoretical research nowadays. We won't be discussing these anytime soon.

Another comment I must make right from the start is this: Boltzmann's constant simply converts temperature units (Kelvin) into energy units (Joules or eV). If you set $k_B = 1$ you are simply measuring temperature in energy units. For instance T = 300K is the same as T = 0.026 eV. Throughout these notes we will adopt this convention and set $k_B = 1$:

In these notes
$$k_B = 1$$

I guarantee that doing this will never lead to any confusion. All you need to remember is that T is measured in eV. If you ever want to get k_B back, simply replace T by $k_B T$ everywhere:

Since ρ in Eq. (3.1) is an exponential of H, both are diagonalized by the same basis. That is, if

$$H|n\rangle = E_n|n\rangle \tag{3.4}$$

then

$$e^{-\beta H}|n\rangle = e^{-\beta E_n}|n\rangle$$

Whence, we may write

$$\rho = \sum_{n} P_n |n\rangle \langle n|, \qquad P_n = \frac{e^{-\beta E_n}}{Z}$$
(3.5)

The quantities $P_n = \langle n | \rho | n \rangle$ are the eigenvalues of ρ and represent the probabilities of finding the system in the energy eigenstates $|n\rangle$.

Expectation values of operators are written as usual, with Eq. (2.24):

$$\langle \mathcal{O} \rangle = \operatorname{tr}(\mathcal{O}\rho) = \frac{\operatorname{tr}(\mathcal{O}e^{-\beta H})}{\operatorname{tr}(e^{-\beta H})} = \sum_{n} \langle n|\mathcal{O}|n\rangle P_n$$
 (3.6)

The most important expectation value is that of the energy. For historical reasons it is called the **internal energy** and receives the special symbol U:

$$U = \langle H \rangle = \operatorname{tr}(H\rho) = \sum_{n} E_{n} P_{n}$$
(3.7)

It is possible to relate the internal energy to the partition function Z in Eq. (3.2) as

$$U = -\frac{\partial}{\partial\beta}\ln(Z) = T^2 \frac{\partial}{\partial T}\ln(Z)$$
(3.8)

which I leave for you as an exercise. This formula is very useful, specially in more sophisticated problems. Finding Z can already be a terribly difficult task and to find U would require the computation of an even more difficult sum. With this formula we avoid that entirely and obtain U from a simple differentiation. It also shows that Z is more than simply a "normalization constant". You will be amazed by how much information is hidden inside it.

Another important quantity that will appear often, starting on the next section, is the **von Neumann entropy**:

$$S = -\operatorname{tr}(\rho \ln \rho) \tag{3.9}$$

It measures the degree of disorder of the distribution. If you work with $k_B \neq 1$, then the entropy is usually defined to have units of k_B ; ie, $S = -k_B \operatorname{tr}(\rho \ln \rho)$. Since the thermal density matrix is already diagonal in the energy basis, we may also write

$$S = -\sum_{n} P_n \ln P_n \tag{3.10}$$

The physics behind entropy will be discussed in more detail on the next section.

Example: 2-state system

To practice, let us consider the simplest example: a two-state system with eigenstates $|0\rangle$ and $|1\rangle$. Since energy is only defined up to a constant we may

parametrize the energy eigenvalues as $E_0 = 0$ and $E_1 = \epsilon$. The Hamiltonian may then be written as

$$H = \epsilon |1\rangle \langle 1| = \begin{pmatrix} 0 & 0\\ 0 & \epsilon \end{pmatrix}$$
(3.11)

The state of this system when it is in thermal equilibrium will be given by the Gibbs formula (3.1). To compute the exponential of an operator that is already diagonal, we simply exponentiate its diagonal entries:

$$e^{-\beta H} = |0\rangle\langle 0| + e^{-\beta\epsilon}|1\rangle\langle 1| = \begin{pmatrix} 1 & 0\\ 0 & e^{-\beta\epsilon} \end{pmatrix}$$
(3.12)

The $|0\rangle\langle 0|$ term sometimes confuses people. But it is there since $e^0 = 1$.

The partition function is the trace of $e^{-\beta H}$ and hence reads

$$Z = 1 + e^{-\beta\epsilon} \tag{3.13}$$

If you are feeling a little insecure, you can also do it step by step:

$$Z = \operatorname{tr}(e^{-\beta H})$$
$$= \langle 0|e^{-\beta H}|0\rangle + \langle 1|e^{-\beta H}|1\rangle$$
$$= e^{-\beta E_0} + e^{-\beta E_1}$$

which is the same as (3.13). The density matrix will then be

$$\rho = P_0 |0\rangle \langle 0| + P_1 |1\rangle \langle 1| = \begin{pmatrix} P_0 & 0\\ 0 & P_1 \end{pmatrix}$$
(3.14)

where

$$P_0 = \frac{1}{1 + e^{-\beta\epsilon}} \tag{3.15}$$

$$P_1 = \frac{e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}} = \frac{1}{e^{\beta\epsilon} + 1}$$
(3.16)

These results are plotted in Fig. 3.1(a) as a function of T/ϵ . As the temperature goes to zero we see that $P_0 \rightarrow 1$, so the density matrix tends to the pure state

$$\lim_{T \to 0} \rho = |0\rangle \langle 0| \tag{3.17}$$

Thus, in the limit $T \rightarrow 0$ the system tends to occupy predominantly the ground state. On the other hand, as the temperature increases both probabilities grad-ually tend to 1/2, leading to the maximally disordered density matrix:

$$\lim_{T \to \infty} \rho = \frac{\mathbb{I}_2}{2} = \frac{1}{2} \begin{pmatrix} 1 & 0\\ 0 & 1 \end{pmatrix}$$
(3.18)

This means that at high temperatures you are equally likely to find the system in any of the two states, Note, however, that P_0 is always larger than P_1 so it is



Figure 3.1: (a) The probabilities P_0 and P_1 of a 2-state system, Eqs. (3.15) and (3.16). (b) The entropy of a 2-state system, computed using Eq. (3.20).

always more likely to find the system in the ground state. In thermal states you will never find a *population inversion*, where the excited state is more populated. As we will learn soon, these properties are actually general features of thermal states.

The probability P_1 physically means the probability of finding the system in the excited state.³ When $T/\epsilon \sim 1$, this probability is around 0.2, but when $T/\epsilon \sim 0.1$, this already falls to approximately 10^{-5} . This means that excited states will only be significantly occupied when the temperature has the same order of magnitude as the energy gap between the two states. This is a good thing to remember: always try to compare energy gaps with the thermal energy T (or $k_B T$ if you want k_B back). If $T \ll \epsilon$ then the excited states will be practically unoccupied.

The internal energy can be computed using Eq. (3.7):

$$U = E_0 P_0 + E_1 P_1 = \epsilon P_1 = \frac{\epsilon}{e^{\beta\epsilon} + 1}$$
(3.19)

Thus, a graph of U/ϵ will be exactly the curve P_1 in Fig. 3.1. At T = 0 the internal energy is zero, which is the same energy as the ground state. And then U increases monotonically with T until it reaches the value $(E_0 + E_1)/2 = \epsilon/2$ at $T = \infty$. The entropy, on the other hand, is computed from Eq. (3.10) and

³We will find an identical formula later on under the name of **Fermi-Dirac distribution**.

reads

$$S = -P_0 \ln P_0 - P_1 \ln P_1$$

= $\frac{\beta \epsilon}{e^{\beta \epsilon} + 1} + \ln(1 + e^{-\beta \epsilon})$ (3.20)

This result is shown in Fig. 3.1(b). When $T \to 0$ the entropy tends to zero and when $T \to \infty$ it tends to $\ln(2)$. The meaning of $\ln(2)$ was already discussed in Eq. (2.69): it represents the maximum value possible for S, which occurs in the maximally disordered state (3.18).

Making sense of $e^{-\beta H}$

The first thing to note about the Gibbs state is that ρ is a function only of the system Hamiltonian: $\rho = \rho(H)$. Putting it differently, since $P_n = e^{-\beta E_n}/Z$, two states which have the same energy will be equally likely. This puts energy on a pedestal. It says that, somehow, the consequence of the interaction between the system and the bath will produce a state which is a functional only of the system Hamiltonian. It could, in principle, depend on other observables, which are precisely the **generalized Gibbs states** mentioned earlier. But they only appear when your bath has a very special structure. Whenever your bath is something ordinary like a bucket of water, the state will be the Gibbs state.

Now suppose our system is actually composed of two *non-interacting* parts, meaning that the Hamiltonian H has the form:

$$H = H_A + H_B = H_A \otimes 1 + 1 \otimes H_B$$

[I am writing the formulas with and without the kron notation, just so you can practice with it.] The corresponding Gibbs state will then be

$$e^{-\beta H} = e^{-\beta H_A} e^{-\beta H_B} = e^{-\beta H_A} \otimes e^{-\beta H_B}$$

which means that the density matrix will factor as a product:

$$\rho = \rho_A \rho_B = \rho_A \otimes \rho_B \tag{3.21}$$

In Sec. 2.3 we saw that whenever the density matrix of a bipartite system could be factored in this way, the two systems were completely uncorrelated. Whence we conclude that when two non-interacting systems are placed in the same thermal bath, there will be no correlation between them.

In principle, however, one could expect the bath to serve as an interacting medium between systems A and B. That is to say, even though A and B do not interact directly, if you wiggle system A this excitation could propagate through the bath and eventually tickle system B. However, according to the above result, that does not happen. The reason for this is actually related to the underlying assumption that the bath is macroscopically large and highly complex, which means that excitations within it do not propagate efficiently. This is, of course, an idealization. But it turns out that it is not such a bad one after all. We could now reverse the question. Assume that the density matrix is some function of the system Hamiltonian, $\rho = \rho(H)$. What is the only function which is such that $H = H_A + H_B$ implies $\rho = \rho_A \rho_B$. Answer: an exponential. In fact, the most general function must have exactly the form $\rho = e^{-\beta H}/Z$, for some yet unknown functions β and Z. The function Z is readily determined from normalization (tr $\rho = 1$), so all we are left with is figuring out what β should be. Quite remarkably, all information about the bath is contained within β . This shows that $e^{-\beta H}$ is a **universal result**; it is the *only* functional form which satisfies: (i) $\rho = \rho(H)$ and (ii) $H = H_A + H_B$ implies $\rho = \rho_A \rho_B$.

Now suppose we didn't know what β was. What can we say about it based only on reasonable physical arguments? Well, one thing we can say upfront: we must have $\beta > 0$. The reason is that, from Eq. (3.5) we have $P_n = e^{-\beta E_n}/Z$. Now consider two states with energies E_n and E_m and assume that $E_n < E_m$. The ratio of the probabilities will then be

$$\frac{P_n}{P_m} = \frac{e^{-\beta E_n}}{e^{-\beta E_m}} = e^{-\beta (E_n - E_m)}$$
(3.22)

If $\beta < 0$ then the condition $E_n < E_m$ would imply $P_m > P_n$. This means that it would be more likely to find the system in an excited state, which is absolutely nonsensical. If that were true, we would always find the system in higher and higher energy levels. For instance, if our system were a hydrogen atom, this would say that it is more likely to find the electron ionized than it is to find it bounded to the proton. Matter would be unstable and we would all die. Since we are all alive we must conclude that $\beta > 0$. We therefore reach the conclusion that *lower energy states are always more likely*.

This is essentially a statement on **thermodynamic stability**. Of course, in general, there is nothing wrong with having a system whose excited states are more populated than the ground state (that is what happens in a Laser, for instance). But that is just not thermal equilibrium. In thermal equilibrium things must be stable and the only way for things to be stable is by having most particles in the lower energy states. That said, it is worth mentioning that in certain situations it is possible to produce states which have **negative temperature**; ie, states of the form $e^{|\beta|H}$. But this type of state is unstable and can only exist for a small period of time. Hence, it is not an equilibrium state.

Finally, suppose we didn't know that $\beta = 1/T$. Could we infer this from some smart reasoning? In the 2-state system example the energy U in Eq. (3.19) was a decreasing function of β . This is actually a general result for thermal states, which will be proved in Sec. 3.5. On the other hand, from our intuition we expect that high temperatures imply high energies, giving us an idea that β should somehow be inversely proportional to T. However, is it 1/T or is it $1/T^2$ or something even weirder? That we cannot say. And for a very simple reason: the definition of temperature is something we, humans, created. We defined the quantity T centuries ago analyzing the properties of gases and liquids. Maybe aliens did the same thing but used T^2 as temperature. So this final piece of the puzzle actually requires *experimental input*. We must compare the predictions of the Gibbs theory with experiment and from that fix the relation between β and T. Lucky for us, we only need to do that for a single system because, since both are universal, once you fix that for a specific experiment, it is fixed for all of them. Historically, the ideal gas was used to do this since it is both exactly soluble and experimentally realizable.

To summarize, the calculations we just did touched upon the three most important properties of the thermal state:

- 1. States with the same energy are equally likely.
- 2. When the energy is a sum, the state is a product (no correlation).
- 3. Lower energy states always have higher probabilities (thermodynamic stability).

The zero-temperature limit

Suppose the energy levels are labeled in ascending order, with E_0 representing the ground-state of the system:

$$E_{\rm gs} = E_0 \le E_1 \le E_2 \le \dots$$

For any excited state $E_n > E_0$, the Gibbs formula (3.5) gives, when T is small (large β):

$$\frac{P_0}{P_n} = e^{-\beta(E_0 - E_n)} \gg 1$$

This shows that

When
$$T \to 0$$
 the system always tends to the ground state

If the ground-state is non-degenerate then $P_0 \rightarrow 1$. Otherwise, if the groundstate has degeneracy g, we may label the states as $|0, i\rangle$, with $i = 1, \ldots, g$. Since thermal probabilities depend only on their corresponding energies, all groundstates will be equally likely. To preserve normalization we should then have

$$\lim_{T \to 0} P_{0,i} = \frac{1}{g} \tag{3.23}$$

Moreover, irrespective of whether there is degeneracy or not, the average energy tends to the ground-state energy:

$$\lim_{T \to 0} U = E_{\rm gs} \tag{3.24}$$

As for the entropy, using Eq. (3.10) we get

$$S = -\sum_{i=1}^{g} \frac{1}{g} \ln(1/g) = \frac{g}{g} \ln(g)$$

Thus, we conclude that

$$\lim_{T \to 0} S = \ln g = \ln(\text{degeneracy of the ground-state})$$
(3.25)

Suppose now that our system actually has N particles, where N is a large number. Most of the times the degeneracy is a finite number, like g = 42, or something. In this case the *entropy per particle* S/N will tend to zero in the ground state, even though it is degenerate. Conversely, there are more unusual cases (the most famous of which are the so-called **spin glasses**) where the ground-state degeneracy is of the form g^N , for some g. In these cases the entropy per particle will remain finite at zero temperatures. These results are known as the **third law of thermodynamics or Nernst's postulate**:

3rd law: the entropy tends to a constant when
$$T \to 0$$
 (3.26)

The meaning of "low temperature" depends on the energy gap between the ground state and the first excited state, $\Delta E = E_1 - E_0$. If this gap is 1 eV and we are at room temperature (T = 0.026 eV), then

$$\frac{P_1}{P_0} \simeq e^{-1/0.026} \sim 10^{-18}$$

So for a 1 eV gap, room temperature is still a very very low temperature: it is overwhelmingly more likely to find the system in the ground state. This is why, when we construct the atomic orbitals, we place the electrons sequentially in lower energy states. The excited states will start to become populated when $\Delta E \sim T$. So for room temperature, gaps of the order of 0.02 eV already lead to a reasonable population of the first excited state.

Very high temperatures; finite Hilbert space

Now let us study the opposite limit of extremely high temperatures and let us suppose that our system has a finite number of states (as, for instance, in the spin 1/2 case). We denote by d the total number of states. For one spin 1/2 particle d = 2. For N spin 1/2 particles $d = 2^N$ and so on. When β is very small $e^{-\beta(E_n - E_m)} \sim 1$ so all probabilities become roughly equal. In the limit of $T \to \infty$ we then find

$$P_n \to \frac{1}{d}$$

The density operator will therefore tend to the maximally disordered state

$$\lim_{T \to \infty} \rho = \frac{\mathbb{I}_d}{d} \tag{3.27}$$

Consequently, the internal energy will tend to the arithmetic average of all energies:

$$\lim_{T \to \infty} U = \frac{E_0 + E_1 + \ldots + E_{d-1}}{d}$$
(3.28)

and the entropy will tend to

$$\lim_{T \to \infty} S = \ln d = \ln(\text{dimension of the entire Hilbert space})$$
(3.29)

3.2 The Gibbs state minimizes the free energy

There is a beautiful way of interpreting the Gibbs state (3.1), which I really think is worth remembering. We saw in the previous section that at T = 0 the system tends to the ground state. This can be stated as a variational principle: at T = 0 the system will tend to that state which minimizes the energy U of the system. At finite temperatures that is no longer true since the system will have a tendency to occupy also some of the excited states. What I want to show you in this section is that, at finite temperatures, instead of minimizing the energy, the state of the system will be that which minimizes the **free energy**:

$$F = U - TS \tag{3.30}$$

where U is given in Eq. (3.7) and S is the von Neumann entropy given in Eq. (3.9). When temperature is present there is a competition between the energy U and the disorder -TS. The state which minimizes these two competing quantities is the Gibbs state (3.1).

But let's start from the beginning. We defined the free energy as in Eq. (3.30), which is a general definition since U and S can be defined for any density matrix ρ . However, when ρ is a Gibbs state there is a much more convenient way to write it. To do that we massage the entropy a bit. As we have seen, since ρ is diagonal in the energy basis we may write it as [Eq. (3.10)]:

$$S = -\sum_{n} P_n \ln P_n$$

Now substitute $P_n = e^{-\beta E_n}/Z$ only in the logarithm, leaving the other P_n untouched:

$$S = -\sum_{n} P_n \bigg\{ -\beta E_n - \ln Z \bigg\}$$

The first term is $-\beta U$ since $U = \sum_n E_n P_n$. In the second term the quantity $\ln Z$ goes outside of the sum and we are left with $\sum_n P_n = 1$. Thus we conclude that

$$S = -\beta U - \ln Z \tag{3.31}$$

Substituting this in Eq. (3.30) then gives

$$F = -T \ln Z$$
 or $Z = e^{-\beta F}$ (3.32)

This clarifies the physical meaning of Z, as being directly related to the free energy. In the limit $T \to 0$ we have seen that $U \to E_{\rm gs}$ and S tends to a constant. Whence, F = U - TS will also tend to the ground-state energy:

$$\lim_{T \to 0} F = E_{\rm gs} \tag{3.33}$$

When dealing with equilibrium problems, specially the more difficult ones, I always compute Z then F then U then S. This order is nice because F and U are very easily found from Z using Eqs. (3.8) and (3.32). Then from U and F we can find S by inverting Eq. (3.30) and writing:

$$S = \frac{U - F}{T} \tag{3.34}$$

This is usually much easier to use than Eq. (3.9). But, of course, it only holds for the Gibbs state, whereas (3.9) is absolutely general.

Minimizing the free energy using the relative entropy

We are now ready to prove our main claim: namely that the Gibbs state is the state which minimizes the free energy. This is a calculation I really like. I hope you enjoy it too. Suppose that we have a system with some arbitrary density matrix ρ , which does not need to be the Gibbs state. We continue to define a free energy for this system using Eq. (3.30), whether or not the system is in equilibrium. Now consider the relative entropy (or Kullback-Leibler divergence) defined in Eq. (2.71) between the state of the system ρ and the Gibbs state $\rho_{\rm eq} = e^{-\beta H}/Z$ [Eq. (3.1)]:

$$S(\rho||\rho_{\rm eq}) = \operatorname{tr}\left\{\rho \ln \rho - \rho \ln \rho_{\rm eq}\right\}$$
(3.35)

The first term is $-S(\rho)$. In the second term we substitute $\rho_{eq} = e^{-\beta H}/Z$ to get

$$S(\rho||\rho_{\rm eq}) = -S(\rho) + \beta U(\rho) + \ln Z$$
(3.36)

Multiplying both sides by T we see, on the right-hand side, the quantities $U - TS := F(\rho)$ and $T \ln Z = -F(\rho_{eq})$ (the equilibrium free energy). Thus, we conclude that

$$F(\rho) = F(\rho_{\rm eq}) + TS(\rho||\rho_{\rm eq})$$
(3.37)

Even though $S(\rho||\rho_{eq})$ is called the relative entropy, in this case it is really a relative free energy.

We set out to show that the state which minimizes the free energy is the Gibbs state ρ_{eq} . By expressing $F(\rho)$ in terms of the relative entropy, we just did precisely that. For, as discussed in Sec. 2.4 the relative entropy $S(\rho||\rho_{eq})$ is always non-negative and it is zero if and only if $\rho = \rho_{eq}$:

$$S(\rho||\rho_{\rm eq}) \ge 0, \qquad S(\rho||\rho_{\rm eq}) = 0 \text{ iff } \rho = \rho_{\rm eq}$$

$$(3.38)$$

Eq. (3.37) therefore shows that $F(\rho) \geq F(\rho_{\rm eq})$, which means that the state ρ which minimizes $F(\rho)$ is precisely $\rho = \rho_{\rm eq}$. I really like this proof since it is a fully operator-based demonstration: nowhere did we have to assume that ρ is diagonal in the energy eigenbasis.

Minimizing the free energy by hand

However, if you prefer, we can also do a more "by hand" demonstration, assuming that ρ is diagonal in the basis $|n\rangle$. In this case the free energy becomes

$$F = \sum_{n} E_n P_n + T \sum_{n} P_n \ln P_n \tag{3.39}$$

The idea is to minimize F with respect to each P_n and show that the minimum condition implies that we must have $P_n = e^{-\beta E_n}/Z$. However, to carry out this minimization, we need to be a bit careful since it is subject to the constraint $\sum_n P_n = 1$. To enforce this we introduce a Lagrange multiplier and redefine

$$F' = \sum_{n} (E_n + T \ln P_n) P_n + \alpha \left(1 - \sum_{n} P_n\right)$$
(3.40)

Then $\partial F'/\partial \alpha = 0$ imposes the condition $\sum_{n} P_n = 1$. We now have,

$$\frac{\partial F'}{\partial P_n} = E_n + T \ln P_n + T - \alpha = 0$$

This shows that indeed $P_n = Ce^{-\beta E_n}$, where $C = e^{(\alpha - T)/T}$. The value of α (or C) is then fixed to ensure normalization.

In some books the Gibbs ensemble is derived from the argument that it is the distribution which maximizes the entropy, subject to the constraint that the average energy is fixed. That is to say, we maximize

$$S' = -\sum_{n} P_n \ln P_n + \beta \left(U - \sum_{n} E_n P_n \right) + \alpha \left(1 - \sum_{n} P_n \right)$$

where β is to be interpreted as a Lagrange multiplier. Maximizing S' is exactly the same thing as minimizing F' in Eq. (3.40) since, except for a constant here and there, $S' = -\beta F'$. This therefore gives two complementary interpretations of the Gibbs state: it is the state which minimizes the free energy *and* it is the state which maximizes the entropy, subject to the constraint that the average energy is fixed. I personally prefer the former, since thinking in terms of energy is easier. But that is simply a matter of taste.

The Bogolyubov variational formula

Eq. (3.37) can also be used as the basis for an approximation method due to Bogolyubov, that is frequently used in diverse problems.⁴ I will not give any applications of this method here, but I feel an obligation to write down the result since it is almost starring at our face. If you are a bit tired of formal results and want to look at some applications, then I suggest you skip this section for now.

Recall the variational principle of quantum mechanics: If H is a Hamiltonian with ground-state energy $E_{\rm gs}$, then for any state $|\psi\rangle$ we have

$$E_{\rm gs} \le E(\psi) = \langle \psi | H | \psi \rangle$$
 (3.41)

The trick is to use a $|\psi\rangle$ with some free parameters and then minimize the functional $E(\psi)$. The better is your choice of $|\psi\rangle$ (and the larger is the number of free parameters) the closer you will get to the ground-state energy.

With Eq. (3.37) we can do the exact same thing for thermal states. Suppose the system has thermal state $\rho_{\rm eq} = e^{-\beta H}/Z$ and we don't really know how to find the corresponding free energy $F(\rho_{\rm eq})$ exactly. Since $S(\rho||\rho_{\rm eq}) \ge 0$, from Eq. (3.37) we get that, given an arbitrary density matrix ρ

$$F(\rho_{\rm eq}) \le F(\rho) = U(\rho) - TS(\rho)$$
(3.42)

Thus, if you choose an arbitrary ρ with a bunch of free parameters and minimize the quantity $U(\rho) - TS(\rho)$ you will get an approximation to the real free energy which becomes better the larger is the number of parameters being used.

A natural choice is to use a trial density matrix ρ which is itself a Gibbs state, but with some other *trial Hamiltonian* H_0 that we know how to deal with. That is, we can choose

$$\rho = \rho_0 = e^{-\beta H_0} / Z_0$$

where $Z_0 = \operatorname{tr}(e^{-\beta H_0})$. The free parameters are then encoded inside the trial Hamiltonian H_0 . To evaluate U - TS we need to be a bit careful not to mix the real Hamiltonian H with the trial Hamiltonian H_0 . This is specially so for the internal energy which is defined in terms of the actual Hamiltonian H:

$$U(\rho_0) = \operatorname{tr}(H\rho_0) := \langle H \rangle_0$$

Here I also introduced the notation $\langle \mathcal{O} \rangle_0 := \operatorname{tr}(\mathcal{O}\rho_0)$. On the other hand, for the entropy we get

$$S(\rho_0) = -\operatorname{tr}(\rho_0 \ln \rho_0) = \beta \operatorname{tr}(\rho_0 H_0) + \ln Z_0$$

⁴ See N. N. Bogolyubov, *Physica* **32** (1966) 933-944.
Thus,

$$-TS(\rho_0) = -\langle H_0 \rangle_0 + F_0$$

where $F_0 = -T \ln Z_0$ (the confusing part is that $F_0 \neq F(\rho_0)$ because $F(\rho_0)$ is defined for the Hamiltonian H not H_0). Substituting all this in Eq. (3.42) we then finally get

$$F(\rho_{\rm eq}) \le F_0 + \langle H - H_0 \rangle_0 \tag{3.43}$$

This is the Bogolyubov variational formula. All quantities in the right-hand side are computed from the trial state $\rho_0 = e^{-\beta H_0}/Z_0$. By minimizing parameters contained in the trial Hamiltonian H_0 we can get closer and closer to the true free energy. In the limit $T \to 0$ the free energy tends to the ground-state energy and we recover the usual variational principle of quantum mechanics.

3.3 The quantum harmonic oscillator

A simple, yet fundamental example, is the quantum harmonic oscillator discussed in Sec. 1.4. The Hamiltonian is given by Eq. (1.86) or (1.91):

$$H = \omega(a^{\dagger}a + 1/2) \tag{3.44}$$

and the eigenvalues are

$$E_n = \omega(n+1/2), \qquad n \in \mathbb{N}$$
(3.45)

The ground state corresponds to n = 0 and has energy $\omega/2$. As usual I will set $\hbar = 1$. To get it back simply replace $\omega \to \hbar \omega$ everywhere.

We begin by computing the partition function:

$$Z = \operatorname{tr}(e^{-\beta H}) = \sum_{n=0}^{\infty} \langle n | e^{-\beta H} | n \rangle = \sum_{n=0}^{\infty} e^{-\beta E_n}$$

We can also write it as

$$Z = e^{-\beta\omega/2} \sum_{n=0}^{\infty} (e^{-\beta\omega})^n$$

Since $\beta \omega > 0$ it follows that $e^{-\beta \omega} < 1$ so the resulting sum is nothing but a geometric series:

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$$
(3.46)

where $x = e^{-\beta \omega}$. Hence,

$$Z = \frac{e^{-\beta\omega/2}}{1 - e^{-\beta\omega}} \tag{3.47}$$

The free energy is then readily found from Eq. (3.32):

$$F = -T\ln Z = \frac{\omega}{2} + T\ln(1 - e^{-\beta\omega})$$
(3.48)

The first term is the constant shift $\omega/2$ in the energy eigenvalues. When $T \to 0$ this is the only term that survives. We can also see that from the fact that F = U - TS so that, at T = 0, we get $F = U = E_{\rm gs} = \omega/2$.

Armed with Z, we now have the complete set of probabilities P_n from Eq. (3.5):

$$P_n = \frac{1 - e^{-\beta\omega}}{e^{-\beta\omega/2}} e^{-\beta\omega(n+1/2)}$$

Note how the factor $e^{-\beta\omega/2}$ cancels, to give only:⁵

$$P_n = (1 - e^{-\beta\omega})e^{-\beta\omega n}$$
(3.49)

This cancelation is actually reassuring: the factor $e^{-\beta\omega/2}$ traces back to the constant energy shift $\omega/2$ in Eq. (3.45). A constant energy shift of all energy levels should not affect the probabilities since energy is only defined up to a constant. The density matrix is

$$\rho = (1 - e^{-\beta\omega})e^{-\beta\omega a^{\dagger}a}$$
(3.50)

We cannot write it as a matrix since the matrix would be infinite. Thus, we just leave it in this abstract form. If you ever need to work with it, it is simpler to write it as a sum of outer products:

$$\rho = (1 - e^{-\beta\omega}) \sum_{n=0}^{\infty} e^{-\beta\omega n} |n\rangle \langle n|$$
(3.51)

Let us first analyze P_0 , the probability of finding the oscillator in the ground state:

$$P_0 = 1 - e^{-\omega/T} \tag{3.52}$$

The convenient dimensionless temperature here is T/ω (or $k_B T/\hbar\omega$ if you are feeling saudade of k_B and \hbar). This result is shown in Fig. 3.2. As $T \to 0$ P_0 tends to 1 so the system tends to the ground state. Conversely, when the temperature increases, higher energy states begin to become populated causing P_0 to gradually fall to zero.

 $^{^{5}}$ In probability theory this result is known as the Geometric distribution.



Figure 3.2: Probability P_0 of finding the harmonic oscillator in the ground state, computed from Eq. (3.52) as a function of the dimensionless temperature T/ω .

The function P_n is plotted in Fig. 3.3 for two different values of T/ω , representing low and high temperatures. At low temperatures we see that the system concentrates around the ground state, with only a small probability of begin found in the first few excited states. Conversely, at high temperatures the probabilities are homogeneously distributed through several excited states. Notwithstanding, note how the P_n are always monotonically decreasing, meaning that lower energy levels are always more likely to be occupied.



Figure 3.3: Probabilities P_n for the quantum harmonic oscillator computed from Eq. (3.49) for two different values of T/ω , as shown in each image.

Now that we have P_n , the next step is to use Eq. (3.6) to find the expectation values of quantum mechanical observables. From Eq. (1.97) we find that $\langle n|a|n\rangle = 0$. Therefore,

$$\langle a \rangle = \langle a^{\dagger} \rangle = 0$$

Due to the definitions (1.89), it then also follows that

$$\langle x \rangle = \langle p \rangle = 0 \tag{3.53}$$

which is expected due to symmetry arguments.

The most important operator for the quantum harmonic oscillator is the occupation number operator $a^{\dagger}a$. Since $\langle n|a^{\dagger}a|n\rangle = n$, we find that

$$\bar{n} := \langle a^{\dagger}a \rangle = \sum_{n} nP_n \tag{3.54}$$

The notation \bar{n} is simply introduced for convenience and will be used extensively later on. Note that if you want, you can also interpret $\langle a^{\dagger}a \rangle$ as the average of the quantum number n. This is a sort of "not-so-quantum" way of looking at the quantum harmonic oscillator, but is mostly a matter of taste. We are allowed to think like this because the eigenvalues of $a^{\dagger}a$ are diagonal in the Hamiltonian basis. To compute the sum (3.54) we use Eq. (3.49) and again let $x = e^{-\beta\omega}$. We then have

$$\bar{n} = (1-x)\sum_{n=0}^{\infty} nx^n$$

There is a lovely trick to carry out this sum. Start with the geometric series in Eq. (3.46) and differentiate both sides with respect to x. We then get:

$$\sum_{n=0}^{\infty} nx^{n-1} = \frac{1}{(1-x)^2}$$

The left-hand side is almost what we want. It is just missing an x. So we multiply both sides by x and obtain

$$\sum_{n=0}^{\infty} nx^n = \frac{x}{(1-x)^2}$$

Using this result, we obtain for the average occupation number

$$\bar{n} = \frac{e^{-\beta\omega}}{1 - e^{-\beta\omega}}$$

which we can write more neatly as:

$$\bar{n} = \langle a^{\dagger} a \rangle = \frac{1}{e^{\beta \omega} - 1} \tag{3.55}$$

This is called the **Bose-Einstein distribution**. You will find it many times during your journey through statistical mechanics. It is illustrated in Fig. 3.4. For low temperatures it is flat near zero, but then it bends and eventually becomes linear for high T. The reason why we call it a "distribution" will only become clear later on, when we discuss quantum gases in more detail.

From \bar{n} we may compute the internal energy with zero effort starting with the Hamiltonian (3.44) and using the fact that the operation $\langle \rangle$ is linear. We



Figure 3.4: Bose-Einstein distribution \bar{n} vs. T/ω , computed from Eq. (3.55).

then find

$$U = \langle H \rangle = \omega(\bar{n} + 1/2) = \frac{\omega}{2} \coth\left(\frac{\omega}{2T}\right)$$
(3.56)

In the last equality I simply rearranged the exponentials to write it as the hyperbolic cotangent. Alternatively, we can also find U from Z using Eq. (3.8). Let us analyze the limits of this equation. When $T \to 0$ the occupation number tends to zero so

$$\lim_{T \to 0} U(T) = E_0 = \frac{\omega}{2}$$

At zero temperature the system tends to the ground state, something we knew already. Conversely, when T is large we may use the series expansion $\coth(x) \sim 1/x$. We then get

or

$$U \simeq \frac{\omega}{2} \frac{21}{\omega}$$

$$U \simeq T$$
(3.57)

Thus, at high temperatures, the energy becomes linearly proportional to T. Whenever a system has an infinite number of states, the high temperature results usually match their classical analog. In these notes we will not discuss the classical formulation of statistical mechanics, as that is done in practically any textbook on the subject. But if you do the calculations for the classical harmonic oscillator, you find precisely U = T. We therefore customarily say that high temperatures correspond to the **classical limit**. The idea is that when T is large all states are significantly populated so the discreteness of quantum states is washed away.

The uncertainty principle

According to Heisenberg's uncertainty principle, we should always have

$$\Delta x \Delta p \geq \frac{1}{2}$$

Let us then verify what is the uncertainty product $\Delta x \Delta p$ for a thermal state. We have already seen that $\langle x \rangle = \langle p \rangle = 0$. So $\Delta x = \sqrt{\langle x^2 \rangle}$ and $\Delta p = \sqrt{\langle p^2 \rangle}$. From Eq. (1.89) we have, for instance,

$$x^{2} = \frac{x_{0}^{2}}{2} \left\{ (a^{\dagger})^{2} + a^{2} + 2a^{\dagger}a + 1 \right\}$$

where I already used Eq. (1.87) to write $aa^{\dagger} = a^{\dagger}a + 1$. The terms $(a^{\dagger})^2$ and a^2 will average to zero because $\langle n|a^2|n\rangle = 0$. Moreover, the average of $a^{\dagger}a$ is given in Eq. (3.55) Thus:

$$\langle x^2 \rangle = x_0^2 (\bar{n} + 1/2) \tag{3.58}$$

$$\langle p^2 \rangle = p_0^2 (\bar{n} + 1/2)$$
 (3.59)

Consequently,

$$\Delta x \Delta p = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} \sqrt{\langle p^2 \rangle - \langle p \rangle^2}$$
$$= x_0 p_0 (\bar{n} + 1/2)$$

But from Eq. (1.88), $x_0 p_0 = \hbar = 1$, so we conclude that

$$\Delta x \Delta p = (\bar{n} + 1/2) \tag{3.60}$$

When $T \rightarrow 0$ the average occupation number tends to zero and we obtain the uncertainty limit 1/2 (this is the ground state). As the temperature increases the uncertainty product increases and therefore we leave the quantum realm. This is another way of interpreting the classical limit.

The Husimi Q function

The expectation value of the harmonic oscillator density operator in a coherent state (Sec. 1.5) is called the Husimi Q function:

$$Q(\alpha^*, \alpha) = \langle \alpha | \rho | \alpha \rangle \tag{3.61}$$

Here α and α^* are to be interpreted as independent variables. The Husimi Q function is extensively used in quantum optics because, as we will see, it functions as a sort of quasi-probability distribution in the complex plane. It therefore

gives a semi-classical interpretation of the quantum harmonic oscillator.⁶ Using Eq. (2.8) for the trace in the coherent state basis, we get

$$1 = \operatorname{tr} \rho = \int \frac{\mathrm{d}^2 \alpha}{\pi} \langle \alpha | \rho | \alpha \rangle$$

Thus, we conclude that the Husimi Q function is normalized as

$$\int \frac{\mathrm{d}^2 \alpha}{\pi} Q(\alpha^*, \alpha) = 1 \tag{3.62}$$

which resembles the normalization of a probability distribution.

As a simple example, suppose that the system is itself in a coherent state $|\mu\rangle$ so that $\rho = |\mu\rangle\langle\mu|$. Then, using Eq. (1.121) we get

$$Q(\alpha^*, \alpha) = \langle \alpha | \mu \rangle \langle \mu | \alpha \rangle = \exp\left\{ - |\alpha - \mu|^2 \right\}$$
(3.63)

This is a *Gaussian distribution in the complex plane*, centered around μ and with unit variance. The ground-state of the harmonic oscillator is also a unit-variance Gaussian, but centered at zero. The coherent state has the same shape as the ground-state, but centered in a different position.

As a second example consider the thermal Gibbs state. In this case we have

$$Q(\alpha^*, \alpha) = \sum_{n=0}^{\infty} \frac{e^{-\beta E_n}}{Z} \langle \alpha | n \rangle \langle n | \alpha \rangle$$

This is a straightforward and fun calculation, which I will leave for you as an exercise. All you need is the overlap Eq. (1.117). The result is

$$Q(\alpha^*, \alpha) = \frac{1}{\bar{n}+1} \exp\left\{-\frac{|\alpha|^2}{\bar{n}+1}\right\}$$
(3.64)

Thus, we see that the thermal state is also a Gaussian distribution, centered at zero but with a variance proportional to $\bar{n} + 1$. At T = 0 ($\bar{n} = 0$) we get the sharpest possible Gaussian, which is the ground-state $\rho = |0\rangle\langle 0|$. The width of the Gaussian distribution can be taken as a measure of the fluctuations in the system. At high temperatures \bar{n} becomes large and so does the fluctuations. But even at T = 0 there is still a finite width, which is a consequence of quantum fluctuations.

The two examples above motivate us to consider a **displaced thermal** state. It is defined in terms of the displacement operator (1.103) as

$$\rho = D(\mu) \frac{e^{-\beta H}}{Z} D^{\dagger}(\mu) \tag{3.65}$$

⁶ The Q function is not the only quasi-probability distribution. Most notably, there are also the P function and the Wigner functions. Each has its own weaknesses and strengths. For a thorough account of these functions, I recommend the book "Quantum Noise" by Gardiner and Zoller, more specifically chapter 4.

The corresponding Q function, as you can probably expect, is

$$Q(\alpha^*, \alpha) = \frac{1}{\bar{n} + 1} \exp\left\{-\frac{|\alpha - \mu|^2}{\bar{n} + 1}\right\}$$
(3.66)

which is sort of a mixture of Eqs. (3.63) and (3.64): it represents a thermal state displaced in the complex plane by an amount μ .

If we know Q we can also use it to compute the expectation value of operators. But for things to come out organized, we should always take expectation values of *anti-normally ordered* operators. This means that we use the commutation relations to push the a^{\dagger} always to the right. A anti-normally ordered operator therefore has the form $a^k(a^{\dagger})^{\ell}$. Any operator which is a combination of a's and a^{\dagger} 's can always be put in this form. Using the cyclic property of the trace we then have

$$\langle a^k (a^\dagger)^\ell \rangle = \operatorname{tr}\left\{ \rho a^k (a^\dagger)^\ell \right\} = \operatorname{tr}\left\{ (a^\dagger)^\ell \rho a^k \right\}$$

Now we use Eq. (2.8) to get

$$\langle a^k(a^{\dagger})^\ell \rangle = \int \frac{\mathrm{d}^2 \alpha}{\pi} \langle \alpha | (a^{\dagger})^\ell \rho a^k | \alpha \rangle$$

But we know that $a|\alpha\rangle = \alpha |\alpha\rangle$ and $\langle \alpha | a^{\dagger} = \alpha^* \langle \alpha |$ so

$$\langle a^k (a^{\dagger})^{\ell} \rangle = \int \frac{\mathrm{d}^2 \alpha}{\pi} \alpha^k (\alpha^*)^{\ell} Q(\alpha^*, \alpha)$$
(3.67)

which is the desired formula.

3.4 Spin 1/2 paramagnetism and non-interacting systems

So far we have considered examples where our system is composed of a single body (a two-state system or a quantum harmonic oscillator). The purpose of this section is to teach you how to work with systems composed of several particles. The primary message that you should take is that, when the different particles do not interact, things are very easy to deal with: the density operator factors as a product and most expectation values become a sum of independent terms. But when there is interaction, things become exponentially more difficult (there is no free lunch). We of course love interactions since they are the ones responsible for most of the interesting phenomena in condensed matter physics. We love them so much that most of the remaining of these notes will be dedicated to interacting systems.

However, in this section we must first learn how to deal with systems of *non-interacting particles*. To have a contrete example in mind, we will consider spin 1/2 paramagnetism, which is the effect whereby a magnetic moment aligns

in the direction of an externally applied field. Non-interacting spin systems appear, for instance, in the so-called **paramagnetic salts**, like $\text{KCr}(\text{SO}_4)_2$. In these salts only a few of the atoms are paramagnetic (in the above case the Cr atoms) and due to the crystal structure they are kept far apart from each other so that any interaction between them may be neglected. Another example is doped **graphene**. In 2012 the group of Andre Geim, who won the 2010 Nobel prize "for groundbreaking experiments regarding the two-dimensional material graphene", showed that fluorine defects in graphene induce a paramagnetic response which perfectly matches the spin 1/2 paramagnetism.⁷

Paramagnetism response of a single spin

If we have a single spin 1/2 particle the Hamiltonian of interaction between the spin and an external magnetic field may be written using the notations of Sec. 1.2, more specifically Eq. (1.56):

$$H = -\mu B\sigma_z = -h\sigma_z = \begin{pmatrix} -h & 0\\ 0 & h \end{pmatrix}$$
(3.68)

At T = 0 the system will tend to the ground state. This corresponds to the spin fully aligned in the direction of the magnetic field, which will be the $|+\rangle$ state if h > 0. However, when $T \neq 0$ thermal fluctuations will impede the system from fully aligning with the field. The degree of alignment can be quantified by the magnetization $m = \langle \sigma_z \rangle$. To find it, we follow the usual recipe.

First, we compute

$$e^{-\beta H} = \begin{pmatrix} e^{\beta h} & 0\\ 0 & e^{-\beta h} \end{pmatrix}$$
(3.69)

The partition function will be the trace of this matrix:

$$Z = e^{\beta h} + e^{-\beta h} = 2\cosh\left(\frac{h}{T}\right)$$
(3.70)

so that the free energy will be

$$F = -T \ln\left\{2\cosh\left(\frac{h}{T}\right)\right\}$$
(3.71)

Combining these results we then get the density operator:

$$\rho = \frac{1}{Z} \begin{pmatrix} e^{\beta h} & 0\\ 0 & e^{-\beta h} \end{pmatrix}$$
(3.72)

⁷ See R. R. Nair, et. al., in Nature 8 (2012) 1-4

We can also write it as $\rho = \sum_{\sigma} P_{\sigma} |\sigma\rangle \langle \sigma |$ where

$$P_{\sigma} = \frac{e^{\beta h \sigma}}{2 \cosh(\beta h)} \tag{3.73}$$

Sanity check: if h > 0, $P_+ > P_-$ so the ground-state always has a higher probability.

The expectation value of $\langle \sigma_z \rangle$ is now readily found to be

$$\langle \sigma_z \rangle = \operatorname{tr}(\sigma_z \rho) = \tanh\left(\frac{h}{T}\right)$$
(3.74)

This is the famous paramagnetic response of a spin 1/2 particle. As for the other Pauli matrices, we find $\langle \sigma_x \rangle = \langle \sigma_y \rangle = 0$, which is of course expected from symmetry reasons. Since $\sigma_a^2 = 1$, there aren't any more spin operators to worry about. In Fig. 3.5 we plot $\langle \sigma_z \rangle$ vs. h/T. For small values of h/T the response is linear. But for large fields it bends and then saturates at ± 1 . These asymptotic values are simply the eigenvalues ± 1 of σ_z . Thus, this result shows that under extremely large fields or extremely low temperatures, the spin tends to be completely polarized in the direction of the field. This is something we already knew since when $T \to 0$ the system should tend to the ground-state.



Figure 3.5: Average spin response $\langle \sigma_z \rangle$ vs. h/T for the spin 1/2 particle, plotted using Eq. (3.74). The dotted line has slope 1.

We may also plug back all dimensional quantities in Eq. (3.74). We then get

$$\langle \sigma_z \rangle = \tanh\left(\frac{\mu B}{k_B T}\right)$$
(3.75)

When the quantity $\mu B/k_BT$ is small we may expand

 $\tanh(x) \simeq x$

to write Eq. (3.75) as

$$\langle \sigma_z \rangle \simeq \frac{\mu B}{k_B T}$$
 (3.76)

We should also ask under what conditions this approximation is reasonable. For an electron μ is the Bohr magneton,

$$\mu_B = \frac{e}{2m_e} = 5.788 \times 10^{-5} \text{ eV/T} = 9.274 \times 10^{-24} \text{ J/T}$$
(3.77)

Together with Eq. (3.3) this then gives

$$\frac{\mu_B}{k_B} \simeq 0.672 \ \mathrm{T/K}$$

In Fig. 3.5 we see a significant deviation from a straight line when $h/T \sim 1$. At room temperature, T = 300 K so to see a deviation would require fields of the order of $B \sim 100$ T. A field of 1 T is already huge. With superconducting coils we can reach around 10 T and with pulsed fields (which last only for nano-seconds), maybe 30 or 50 T. Conclusion: at room temperature, the response is *always* a straight line. For this reason, many people automatically associate paramagnetism with a linear response (this is done in almost every electromagnetism course). Conversely, at T = 1 K, some deviations from the linear behavior can already be observed for fields of around 1 T.

N spin 1/2 particles

Now let us consider a system of N non-interacting spin 1/2 particles. To each spin we attribute a spin operator σ_i^z . The Hamiltonian will then be

$$H = -h \sum_{i=1}^{N} \sigma_i^z \tag{3.78}$$

which is a sum of operators each living in its own Hilbert space. Our first task is now to compute the partition function and the density operator. But before we do that, I want to make a tiny change to the problem. Imagine that perhaps the external field is not homogeneous so that the field h changes from spin to spin. In this case the Hamiltonian will be

$$H = -\sum_{i=1}^{N} h_i \sigma_i^z \tag{3.79}$$

where h_i is the field acting on spin *i*. I am introducing this simply for bookkeeping purposes. In the end we can take $h_i = h$.

The partition function is, by definition, $Z = tr(e^{-\beta H})$. I will compute this in two ways. The first way is to notice that all terms in the Hamiltonian (3.79) commute so that we are allowed to write

$$e^{-\beta H} = e^{\beta h_1 \sigma_1^z} \dots e^{\beta h_N \sigma_N^z}$$
$$= e^{\beta h_1 \sigma^z} \otimes \dots \otimes e^{\beta h_N \sigma^z}$$

The kron notation makes the magic of $e^{-\beta H}$ quite clear: the exponential of a sum of independent terms is the product of the exponentials. Of course, this is only true when the systems do not interact. We may now use Eq. (2.12) to deal with the trace of a kron:

$$Z = \operatorname{tr}(e^{-\beta H}) = \operatorname{tr}(e^{\beta h_1 \sigma_1^z}) \dots \operatorname{tr}(e^{\beta h_N \sigma_N^z})$$
(3.80)

Each of these traces will now be exactly like Eq. (3.70) so we may readily write down

$$Z = \prod_{i=1}^{N} \left[2 \cosh\left(\frac{h_i}{T}\right) \right]$$
(3.81)

If all $h_i = h$ then this simplifies to

$$Z = \left[2\cosh\left(\frac{h}{T}\right)\right]^{N} \tag{3.82}$$

The partition function is therefore simply the product of the individual partition functions of each particle. Since $F = -T \ln Z$, the free energy will be a sum of terms:

$$F = -T\sum_{i} \ln\left[2\cosh\left(\frac{h_i}{T}\right)\right] = -NT\ln\left[2\cosh\left(\frac{h}{T}\right)\right]$$
(3.83)

where, for compactness, I wrote the two versions of the result. The free energy scales proportionally with the number of particles N. Quantities which scale in this way are called **extensive**. The fact that Z is a product of Z_i 's also mean, due to Eq. (3.8) that the internal will also be an extensive quantity:

$$U = -\frac{\partial}{\partial\beta}\ln(Z_1\dots Z_N) = U_1 + \dots + U_N$$
(3.84)

For completeness, let us also compute Z in another way, by brute force. We have a trace to take so we need to choose a basis. The natural choice is the Pauli basis

$$|\boldsymbol{\sigma}\rangle = |\sigma_1, \dots, \sigma_N\rangle = |\sigma_1\rangle \otimes \dots \otimes |\sigma_N\rangle$$
 (3.85)

We then have

$$Z = \sum_{\sigma_1,...,\sigma_N} \langle \pmb{\sigma} | e^{-\beta H} | \pmb{\sigma} \rangle$$

This is a messy sum because each σ_i may take on 2 values giving a total of 2^N terms in the sum. The Hamiltonian is diagonal in this basis:

$$H|\boldsymbol{\sigma}
angle = \left(\sum_{i} h_i \sigma_i\right)|\boldsymbol{\sigma}
angle$$

where $\sigma_i = \pm 1$. Thus the partition function becomes

$$Z = \sum_{\sigma_1, \dots, \sigma_N} e^{\beta \sum_i h_i \sigma_i}$$
(3.86)

Now comes a part which causes a lot of confusion when you see it for the first time: we may factor Z as

$$Z = \left(\sum_{\sigma_1} e^{\beta h_1 \sigma_1}\right) \dots \left(\sum_{\sigma_N} e^{\beta h_N \sigma_N}\right)$$
(3.87)

I think it is funny how this operation is absolutely natural when we do it for integrals,

$$\int dx \, dy \, f(x)g(y) = \int dx \, f(x) \int dy \, g(y)$$

but when we do it for a sum we get insecure,

$$\sum_{n,m} f(n)g(m) = \sum_n f(n)\sum_m g(m)$$

An integral is a sum, so if it is true for one it must be true for the other. This is what we just did above for Z. The sums in Eq. (3.87) are now all identical. They can be computed as

$$\sum_{\sigma_i=\pm 1} e^{\beta h_i \sigma_i} = e^{\beta h_i} + e^{-\beta h_i} = 2\cosh(\beta h_i)$$

We then obtain again Eq. (3.81).

Next let us discuss the density operator $\rho = e^{-\beta H}/Z$. As before, we may factor this as

$$\rho = \prod_{i} \rho_{i} = \prod_{i} \left[\frac{e^{\beta h_{i} \sigma_{i}^{z}}}{Z_{i}} \right] = \frac{e^{\beta h_{1} \sigma_{1}^{z}}}{Z_{1}} \otimes \dots \otimes \frac{e^{\beta h_{N} \sigma_{N}^{z}}}{Z_{N}}$$
(3.88)

The total density operator factors as a tensor product of the individual density operators for each spin. The different spins are therefore completely uncorrelated. For thermal states, non-interacting implies uncorrelated.

Suppose now we want to compute the expectation value of some local operator. For instance, suppose we want σ_k^z for some k. We will then have

$$\langle \sigma_k^z \rangle = \operatorname{tr} \left\{ \frac{e^{\beta h_1 \sigma_1^z}}{Z_1} \otimes \ldots \otimes \sigma_k^z \frac{e^{\beta h_k \sigma_k^z}}{Z_k} \otimes \ldots \otimes \frac{e^{\beta h_N \sigma_N^z}}{Z_N} \right\}$$
$$= \operatorname{tr} \left(\frac{e^{\beta h_1 \sigma_1^z}}{Z_1} \right) \ldots \operatorname{tr} \left(\sigma_k^z \frac{e^{\beta h_k \sigma_k^z}}{Z_k} \right) \ldots \operatorname{tr} \left(\frac{e^{\beta h_N \sigma_N^z}}{Z_N} \right)$$

Each quantity here represents the trace of the density matrix ρ_i for spin i. Hence, all traces except the k-th will give 1 by normalization and we are left with

$$\langle \sigma_k^z \rangle = \operatorname{tr}\left(\sigma_k^z \frac{e^{\beta h_k \sigma_k^z}}{Z_k}\right) = \tanh\left(\frac{h_k}{T}\right)$$

which is simply the response of a single spin 1/2 particle. You are probably starting to notice that I am overcomplicating the problem: the moral of the

story is that if we have a system of non-interacting particles, we can compute stuff related to a single particle as if the other particles weren't even there. We don't even need to know the other spins exist. As a sanity check, suppose we want to compute $\langle \sigma_k^z \sigma_\ell^z \rangle$ for $k \neq \ell$. To do this we follow the same drill:

$$\langle \sigma_k^z \sigma_\ell^z \rangle = \operatorname{tr}(e^{\beta h_1 \sigma_1^z}) \dots \operatorname{tr}(\sigma_k^z e^{\beta h_k \sigma_k^z}) \dots \operatorname{tr}(\sigma_\ell^z e^{\beta h_\ell \sigma_\ell^z}) \dots \operatorname{tr}(e^{\beta h_N \sigma_N^z}) = \langle \sigma_k^z \rangle \langle \sigma_\ell^z \rangle$$

as expected for a non-interacting system.

Magnetization and susceptibility

The magnetization that is measured in the laboratory is proportional to

$$M = \sum_{i} \langle \sigma_i^z \rangle \tag{3.89}$$

which is the sum of the magnetic response of each spin (hence M is clearly extensive). Let us assume that $h_i = h$. Then all $\langle \sigma_i^z \rangle$ will be equal to Eq. (3.74) and we get

$$M = N \tanh\left(\frac{h}{T}\right) \simeq \frac{Nh}{T} \tag{3.90}$$

Another quantity of great experimental importance is the **susceptibility** defined as

$$\chi = \frac{\partial M}{\partial h} \tag{3.91}$$

It measures the *sensitivity* of the magnetization to changes in the external field. Most of the times (although not always) the susceptibility is measured in the limit of zero field. That is, it measures the *initial slope* of the M vs. h curve. Differentiating the last part of Eq. (3.90) we get

$$\chi = \frac{N}{T} \tag{3.92}$$

The susceptibility therefore scales as 1/T, which is known as **Curie's law**. Here we defined everything to be dimensionless so the susceptibility turned out to have a very simple form. In more general paramagnetic systems one usually finds

$$\chi = \frac{NC}{T} \tag{3.93}$$

where C is called the **Curie constant** and depends on the magnetic moment of the system and other basic quantities. A common experimental practice is to plot $1/\chi$ vs. T. For paramagnets the result should be a straight line whose coefficient is proportional to C. In Fig. 3.6 I show illegally extracted data of the magnetization and the susceptibility for fluorine-doped graphene. Eqs. (3.90) and (3.93) are plotted on top of the curves and present a perfect agreement.

It is also possible to relate the magnetization to a derivative of the partition function or, what is nicer, to a derivative of the free energy. I will do here



Figure 3.6: (a) Magnetization vs. H/T and (b) $1/\chi$ vs. T of fluorine-doped graphene for a doping ratio of 0.9. Data extracted with absolutely no authorization from R. R. Nair, *et. al.*, in *Nature* **8** (2012) 1-4.

a slightly more general calculation, so that we can get a more useful formula. Suppose that the Hamiltonian of our system depends on some parameter h. This does not have to be the magnetic field, but can be any scalar parameter appearing in H. We then have the following result:

10---

(---)

$$\left\langle \frac{\partial H}{\partial h} \right\rangle = \frac{1}{Z} \operatorname{tr} \left(\frac{\partial H}{\partial h} e^{-\beta H} \right)$$
$$= -\frac{1}{\beta Z} \frac{\partial}{\partial h} \operatorname{tr} (e^{-\beta H})$$
$$= \frac{\partial}{\partial h} \left[-\frac{1}{\beta} \ln Z \right]$$

Thus we conclude that

$$\left\langle \frac{\partial H}{\partial h} \right\rangle = \frac{\partial F}{\partial h} \tag{3.94}$$

This result is absolutely general and gives another interesting way of looking at the free energy. We will come back to this formula on later chapters when we discuss work.

Now let us specialize Eq. (3.94) to a Hamiltonian of the form

$$H = H_0 - h\mathcal{M} \tag{3.95}$$

where H_0 and \mathcal{M} are operators, whereas h is a number. Again, this structure extends beyond spin systems. But, for concreteness, you may think of \mathcal{M} as the magnetization operator

$$\mathcal{M} = \sum_{i} \sigma_i^z \tag{3.96}$$

whereas H_0 may represent, for instance, some interaction between the spins. In this case $\partial H/\partial h = -\mathcal{M}$ so we conclude that

$$M = \langle \mathcal{M} \rangle = -\frac{\partial F}{\partial h} \tag{3.97}$$

The magnetization is simply the derivative of the free energy with respect to the field. The susceptibility will then be

$$\chi = -\frac{\partial F}{\partial h^2} \tag{3.98}$$

These results are absolutely general. All we assumed was that H had the form (3.95).

3.5 The Heat capacity

Consider a system coupled to a bath at a temperature T. Now suppose you unplug the system from this bath and connect it to another bath at some other temperature T'. The system and the T'-bath will then begin to exchange energy until the system settles down in a new equilibrium state. The difference in internal energy U(T') - U(T) represents the average energy that the system exchanged with the T'-bath in order to equilibrate. We call it the **heat** which entered or left the system:

$$Q = U(T') - U(T)$$
(3.99)

In the particular case where $T' = T + \Delta T$ and ΔT is very small, we may expand Eq. (3.99) and write⁸

$$\delta Q = \frac{\partial U}{\partial T} \Delta T = C(T) \Delta T \tag{3.100}$$

where

$$C(T) = \frac{\partial U}{\partial T} \tag{3.101}$$

is called the **heat capacity** of the system. The heat capacity is the most important observable related to thermal states, which is why it deserves a section named after itself. You can also express it in terms of the free energy F or the entropy S. I will simply quote the result and leave the derivation as an exercise:

$$C(T) = \frac{\partial U}{\partial T} = -T\frac{\partial^2 F}{\partial T^2} = T\frac{\partial S}{\partial T}$$
(3.102)

⁸In many materials C is roughly constant over a large temperature range. When this happens, Eq. (3.100) remains valid even when ΔT is not small.

This gives C several interpretations:

- It represents the *slope* of U(T), meaning it measures how sensitive are the changes in the energy of the system due to changes in temperature.
- C/T represents the slope of S(T).
- -C/T represents the concavity of the free energy.

From the relation between C and S it follows that, since S tends to a constant in the limit $T \to 0$ (Nernst's postulate), then

$$\lim_{T \to 0} C(T) = 0$$
 (3.103)

The heat capacity has units of k_B and is therefore dimensionless when $k_B = 1$. Moreover, since U is extensive, the same must be true for C:

$$C = C_1 + C_2 + \ldots + C_N$$

If you double the system, you double its heat capacity. This property of additivity is also very important from an experimental viewpoint. For instance, the heat capacity of a metal at very low temperatures has one important contribution from the electrons and another from the lattice vibrations. The total heat capacity is therefore simply a sum of these two contributions.

Experimentally, it is more convenient to work with the **specific heat**, which is the heat capacity divided by *something*: the number of particles, the volume, the mass, the number of moles, etc. One therefore speaks about the "molar specific heat", the "volume specific heat" and so on. In theory we usually divide by the number of particles, defining:

$$c = \frac{C}{N} \tag{3.104}$$

Experimentally, on the other hand, it is more common to divide by the number of moles which gives the specific heat in units of J/(mol K) (recall that k_B has units of J/K). To convert theoretical results to these units and vice-versa, simply multiply by the gas constant

$$R = \frac{k_B}{N_A} = 8.314 \text{ J/mol K}$$
(3.105)

So the rule is:

$$c = \frac{C}{N}$$
 (dimensionless; theory) \xrightarrow{R} c (J/mol K) (experiment)
(3.106)

Fluctuations

Now let us relate C with the partition function Z. To do that we start with $U = -\frac{\partial}{\partial\beta} \ln Z$ and then differentiate with respect to β . We then get

$$C = \frac{1}{T^2} \left[\frac{Z''}{Z} - \left(\frac{Z'}{Z} \right)^2 \right]$$

where $Z' = \partial Z / \partial \beta$. But, from the definition of Z we have

$$\frac{Z''}{Z} = \sum_{n} E_n^2 \frac{e^{-\beta E_n}}{Z} = \langle H^2 \rangle$$

Thus, we conclude that

$$C(T) = \frac{1}{T^2} \left[\langle H^2 \rangle - \langle H \rangle^2 \right]$$
(3.107)

The heat capacity is therefore seen to be related to the **variance of the energy**. It measures the **fluctuations** of the energy in thermal equilibrium.

The variance can be equivalently written as

$$\langle H^2 \rangle - \langle H \rangle^2 = \langle (H - U)^2 \rangle$$

which is the average of a positive quantity. Whence, we conclude that

$$C(T) = \frac{\partial U}{\partial T} \ge 0 \tag{3.108}$$

This is a very important result. It shows that U(T) is a **monotonically nondecreasing** function of T: the slope of the function U(T) is never negative. It is either positive or, in a limiting case, zero. Physically it means that if you increase the temperature, you also increase the energy: hotter systems are always more energetic. It also means that U and T are in one-to-one correspondence, so a given temperature uniquely determines the corresponding energy. This is illustrated in Fig. 3.7. Since $C = T \frac{\partial S}{\partial T}$ the exact same conclusion also follows for the entropy: S is a monotonically non-decreasing function of T. From the relation between C and F in Eq. (3.102) we also see that F(T) is a concave function of T:

$$\frac{\partial^2 F}{\partial T^2} \le 0 \tag{3.109}$$

Finally, returning to Eq. (3.100), we see that the positivity of C implies that δQ must have the same sign as ΔT . This is a piece of the second law: **heat always flows from hot to cold**. The full statement will be given when learn how to deal with *work*.



Figure 3.7: Allowed shapes for the function U(T) in thermal equilibrium.

Examples

Let us compare the 2-state system and the quantum harmonic oscillator. The internal energies of both models are quite similar:

(2-state):
$$U = \frac{\epsilon}{e^{\beta\epsilon} + 1}$$
 (3.110)

(QHO):
$$U = \frac{\omega}{e^{\beta\omega} - 1} + \frac{\omega}{2}$$
(3.111)

These results are illustrated again in Fig. 3.8 for comparison. The corresponding heat capacities are:

(2-state):
$$C = (\beta \epsilon)^2 \frac{e^{\beta \epsilon}}{(e^{\beta \epsilon} + 1)^2}$$
 (3.112)

(QHO):
$$C = (\beta \omega)^2 \frac{e^{\beta \omega}}{(e^{\beta \omega} - 1)^2}$$
 (3.113)

which are shown in Fig. 3.9.

By comparing the energies and heat capacities for the two models, we see certain similarities but also certain important differences. Let us try to understand them in some detail. The most important similarity is that U(T)is monotonically increasing in both cases, which means that C is always nonnegative. However, for the 2-state system the energy grows and eventually saturates, whereas for the harmonic oscillator it keeps on growing indefinitely. Consequently, for the 2-state system the heat capacity has a maximum (called a **Schottky anomaly**) and then decays to zero, whereas for the oscillator it tends to a finite constant.

These differences are a consequence of the number of allowed states in each model. For the 2-state system there are only two allowed states, whereas for the oscillator the number of states is infinite. As we increase T things get more and more energetic. But if you have only two states there is nowhere else to put this energy, which is why C for the 2-state system tends to zero as $T \to \infty$. It



Figure 3.8: Internal energies for the 2-state system and the quantum harmonic oscillator, computed from Eqs. (3.110) and (3.111)



Figure 3.9: Internal energies for the 2-state system and the quantum harmonic oscillator, computed from Eqs. (3.112) and (3.113)

basically means that the *capacity* to store thermal energy is depleted. The peak of the Schottky anomaly is therefore a signature of having a finite number of states.⁹ Conversely, for the oscillator, the number of states is infinite so there is always some extra room to store more energy. At high temperatures we have seen in Eq. (3.57) that $U \simeq T$ for the oscillator. Hence, $C \to 1$, as can be seen in Fig. 3.9(b). Note also that at low temperatures both specific heats tend to zero as expected from Nernst's postulate.

The specific heat of metals

Table 3.1 shows the specific heats of some selected metals at room temperature. The first line presents the mass specific heat; i.e., the specific heat *per gram* of material. To understand what these numbers mean, suppose you have

 $^{^{9}\}mathrm{In}$ phase transitions C may diverge at the critical point. This is not related to the Schottky anomaly.

 Table 3.1:
 Room temperature mass specific heat for certain metals.

	Cu	Pb	Ag	Zn	Al
c (J/g K)	0.389	0.130	0.23	0.39	0.90
$c(\mathrm{J/mol}\ \mathrm{K})$	24.5	26.4	25.5	25.4	24.4
c/k_B	2.95	3.18	3.07	3.05	2.93

two samples, one of Pb and the other of Al, both weighting exactly 1 g and both at T = 300 K. We then place each sample separately in two identical big buckets of water at 299 K. Since the buckets are colder than the samples (by 1 degree), each sample will release some heat to its bucket, heating it up. Looking at Table 3.1 we see that the Pb sample will release 0.13 J of energy to the bucket, whereas the Al sample will release 0.9 J of energy. Despite being very basic, this is a very interesting result: two materials with the same mass and temperature will heat up water by different amounts. This therefore provides a method of distinguishing between two materials. It also shows why temperature and energy are two distinct quantities. And what connects them is the heat capacity.¹⁰

In 1819, Pierre Dulong and Alexis Petit decided to look at the specific heat of metals *per mole*, instead of *per mass*. To connect the two you simply multiply by the atomic mass of each element. The results are shown in the second line of Table 3.1. As can be seen, all values are now remarkably similar. Hence, the heat capacity *per atom* is practically independent of the element in question. This is known as the **law of Dulong and Petit**. We can also convert the data in J/(mol K) to dimensionless units, by dividing by the gas constant. As a result we get the data in the third line of Table 3.1, showing that all specific heats are close to 3.

With the advent of cryogenic techniques in the beginning of the twentieth century it became clear that the law of Dulong and Petit was only valid around room temperature. At lower temperatures, one observed instead a behavior such as that shown in Fig. 3.10. This discrepancy was puzzling for researchers for a long time. The first big breakthrough came with Einstein, who noticed the similarity between Fig. 3.10 and the specific heat of a harmonic oscillator, Fig. 3.9(b). For one harmonic oscillator, the heat capacity tends to $c \rightarrow 1$, whereas the results of Dulong and Petit show that the heat capacity per particle tends to 3. Einstein therefore argued that a solid containing N atoms could be described as being a collection of 3N harmonic oscillators, all vibrating independently. The factor of 3 comes from the fact that each atom can vibrate in the x, y and z directions. Based on Eq. (3.113), Einstein therefore proposed

¹⁰From this analysis you know how much energy entered the bucket. To know how much the bucket will heat up you need to know the heat capacity of the water.



Figure 3.10: Typical experimental specific heat curve. At high temperatures the curves tend approximately to the value 3.

the following formula for the specific heat of a solid:

$$C = 3N \left(\frac{\omega}{T}\right)^2 \frac{e^{\omega/T}}{(e^{\omega/T} - 1)^2}$$
(3.114)

where ω represents the typical vibration frequency of an atom. This is the **Einstein model for the solid**.

The Einstein model was very successful and came at a time where the importance of quantum mechanics to the macroscopic world was still in question. It showed that something as bulky as the heat capacity of a solid may notwithstanding also have important quantum contributions. However, this model makes wrong predictions at very low temperatures. Experimentally, it is found that when T is very low, $c \propto T^3$. But Eq. (3.114) predicts an exponential decay. This fix was latter provided by Debye and his now famous **Debye model of the solid**., which will be studied later on.

The specific heat at very low temperatures

The behavior of c vs. T at very low temperatures constitutes one of the most widely used experimental techniques in condensed matter physics. Recall that as $T \to 0$ only the lowest eigenstates remain significantly populated. Hence, this type of measurement can shed light on the structure of the lowest eigenvalues. A typical example, of great historical importance, is the specific heat of a superconductor. Take Niobium, for instance, which becomes a superconductor at the critical temperature $T_c = 9.26$ K. Its specific heat will look something like the drawing in Fig. 3.11. Above T_c the specific heat is linear. But at $T = T_c$ it jumps (this is an actual discontinuity, not a smooth jump) and then it starts to go down exponentially as $e^{-\Delta/T}$. The specific heat therefore not only serves as a signal of the onset of a phase transition, but it also characterizes the behavior of the two phases.



Figure 3.11: Typical behavior of the specific heat for a superconductor. Above T_c it is a straight line, but below T_c it changes exponentially.

The two behaviors in Fig. 3.11 reflect two possible structures of the energy eigenvalues. Whenever the eigenvalues vary continuously, as they do in most many-body systems due to the enormous number of eigenvalues, the specific heat will behave as some power of T; something like $c \sim T^{\alpha}$ for some exponent α . We will show this later on, when we discuss second quantization. On the other hand, if the spectrum has an **energy gap** then the specific heat will behave exponentially. To see this, it suffices to note that at very low temperatures only the first two energy eigenvalues will be populated. Hence, we may approximate the heat capacity by that of a 2-state system, Eq. (3.112),

$$C = (\beta \Delta)^2 \frac{e^{\beta \Delta}}{(e^{\beta \Delta} + 1)^2}$$

where $\Delta = E_1 - E_0$ is the energy difference between the first two energy eigenvalues. At very low temperatures $e^{\beta \Delta} \gg 1$ and C may be approximated further to

$$C \simeq (\beta \Delta)^2 e^{-\beta \Delta} \tag{3.115}$$

The pre-factor $(\beta \Delta)^2$ is irrelevant compared to the exponential. Consequently, we see that at very low temperatures the specific heat behaves as $e^{-\Delta/T}$ where Δ is the energy gap. Scientists are very smart people. When they first noticed that the specific heat of a superconductor below T_c behaved exponentially, they *knew* that an energy gap must have opened. In fact, nowadays we know that many of the properties of a superconductor stem precisely from the appearance of an energy gap.

Susceptibility

The heat capacity is the slope of $\langle H \rangle$ with respect to T. In Sec. 3.4 we also saw another quantity with a similar interpretation: namely, if the Hamiltonian had the form

$$H = H_0 - h\mathcal{M}$$

then the **susceptibility** was defined as the slope of $\langle \mathcal{M} \rangle$ with respect to h:

$$\chi = \frac{\partial \langle \mathcal{M} \rangle}{\partial h}$$

Now I will show that, similarly to Eq. (3.107), χ may be related to the variance of \mathcal{M} . We start with

$$\langle \mathcal{M} \rangle = -\frac{\partial F}{\partial h} = \frac{T}{Z} \frac{\partial Z}{\partial h}$$

The susceptibility then becomes

$$\chi = T \left[\frac{1}{Z} \frac{\partial^2 Z}{\partial h^2} - \frac{1}{Z^2} \left(\frac{\partial Z}{\partial h} \right)^2 \right]$$

In the last term we notice the presence of $\frac{1}{Z} \frac{\partial Z}{\partial h} = \frac{\langle \mathcal{M} \rangle}{T}$. Thus

$$\chi = \frac{T}{Z} \frac{\partial^2 Z}{\partial h^2} - \frac{\langle \mathcal{M} \rangle^2}{T}$$

Now we need to figure out what to do with the first term. Unlike the heat capacity, however, in this case we must distinguish whether H_0 and \mathcal{M} commute or not.

If $[H_0, \mathcal{M}] = 0$ then we may factor $e^{-\beta H} = e^{-\beta H_0} e^{\beta h \mathcal{M}}$, allowing us to write

$$\frac{T}{Z}\frac{\partial^2 Z}{\partial h^2} = \frac{T}{Z}\frac{\partial^2}{\partial h^2}\operatorname{tr}(e^{-\beta H_0}e^{\beta h\mathcal{M}})$$
$$= \frac{1}{TZ}\operatorname{tr}(\mathcal{M}^2 e^{-\beta H_0}e^{\beta h\mathcal{M}})$$
$$= \frac{\langle \mathcal{M}^2 \rangle}{T}$$

Thus, we conclude that

$$\chi = \frac{1}{T} \bigg[\langle \mathcal{M}^2 \rangle - \langle \mathcal{M} \rangle^2 \bigg], \qquad \text{if } [H_0, \mathcal{M}] = 0 \qquad (3.116)$$

which is exactly what we wanted: we have related the response of the system (the susceptibility) to the fluctuations of the \mathcal{M} operator. The case when $[H_0, \mathcal{M}] \neq 0$ is much more difficult and requires thermodynamic perturbation theory. I will simply quote the result:

$$\chi = \int_{0}^{\beta} d\tau \langle \mathcal{M}(\tau) \mathcal{M}(0) \rangle - \frac{\langle \mathcal{M} \rangle^{2}}{T}$$
(3.117)

where $\mathcal{M}(\tau) = e^{\tau H_0} \mathcal{M} e^{-\tau H_0}$. If $[H_0, \mathcal{M}] = 0$ then $\mathcal{M}(\tau) = \mathcal{M}$ and we recover Eq. (3.116).